FR-1706

RD/CRG/D/GL/FR

Schedule F

Section 1

Information regarding Project/Project Personnel:

i. Grant Number: RG/2011/NANO/01
Title of the Project: Water based UV-curable polyurethane latex coatings with nano- particles to impart special properties
ii. Principal Investigator: Prof. L.Karunanayake
iii. Co-Investigators: Dr. Shantha Amarasinghe, Prof.Veranja Karunarathna and Dr. Masilamani Koneswaran
iv. Institute(s) where research was being carried out:
SLINTEC/University of Sri Jayewardenepura/University of Moratuwa
v. Date of award: 21/02/2012
vi. Date of completion of Project: 31/08/2015
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viii. Total spent (Rs):2211045.00
ix. Number of Research Students employed: One
x. Post graduate degree completed with dates: PhD thesis submitted
xi. Number of Technical Assistants and/or labourers employed and period of service: 0
xii. Publications/Communications arising from the project during the reporting period: 01

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Section 2

Executive Summary of the Project:

An aqueous polyurethane system was developed and it has been end-capped with ene groups to facilitate UV curing. Stability of the Polyurethane Dispersion (PUD) produced was studied in detail. In addition, the effect of factors such as molar mass of the pre-polymer, PTHF/DMPA ratio etc. on the stability and particle size distribution were studied. It was found that controlling above parameters dispersions with required stability and particle size distributions can be produced. Further, polyurethane films containing iron nano particles were produced. Properties of these composites were studied, too.

During the study it was found that the polyurethanes produced has fluorescent properties that can be used as a special property. A method was developed to make the fluorescent property reversible opening a new avenue to use it as a chemical sensor.

XRD, FTIR, DSC, UV-Vis and fluorescent spectroscopy was used to characterize films prepared. Factors such as crystallinity, H-bonding, thermal properties and optical behavior of films with different morphologies were investigated. A mechanism to explain the behavior of the film under UV irradiation was developed.

It was found that isolated hard-segments emit a fluorescence peak around 356 nm when excited with 293 nm UV radiation. However, continues exposure reduces the emission peak at 356 nm while producing a new emission peak around 423 nm. It was found that the second peak is due to crystalline hard-segments. In addition, it was found that the solvent used in the film preparation affect the reversibility of the fluorescent behavior. Depending on the procedure used to prepare nano-composites fluorescent properties change significantly.

Section 3

INTRODUCTION

Polymers are a remarkable category in the field of material science with the wide range of applications in the day to day life and the industry. Polymers are macro molecules made up by linking small repeating units called as monomers together. Large number of polymer varieties has been prepared in the world by changing the repeating unit. Polyurethane is one of the most interesting polymers in the industry. From the invention of polyurethane by Dr. Otto Bayer in 1937 (1), still the attention to the polyurethane has not been diminished yet due to the numerous applications of it.

Polyurethane

Polyurethane structure

Polyurethane is one of the most versatile polymers in the world. It is a co-polymer consisting of a soft segment domain and a hard segment domain. (2) Polyurethane is formed via a poly-addition reaction (3) by forming urethane linkages (4). Urethane linkage is formed between a hydroxyl group and an isocyanate group. (5) Most of the time hydroxyl group is coming from a long chain polyether polyol or polyester polyol and isocyanate group is from an aliphatic or aromatic diisocyanate. In addition to polyol and diisocyanate, a chain extender is also involved in the polyurethane synthesis. It is a simple organic molecule which has two hydroxyl or amine groups in two terminals. Compared to diisocyanate compound and the chain extender polyol group is very long, so it is more flexible compared to others. Because of this higher flexibility polyol is known as the soft segment and comparatively rigid diisocyanate compound and chain extender altogether is known as hard segment. (6)

Polyurethane applications

Due to the versatile nature of the chemistry of polyurethanes, products developed can be found in various forms of thermoplastics, fibers, soft and hard elastomers, foams, skins, adhesives, binders, coatings and highly cross-linked plastics. (7) Polyurethanes are applied in lacquers, paints, foam mattresses, cushions, floor finishings, medical implants, sealants, in engineering components, in the maritime industry, electrical encapsulations, wide range of rollers from soft printing rollers to hard rollers used in steel industry, in nuclear industry and in the mining industry. (5)

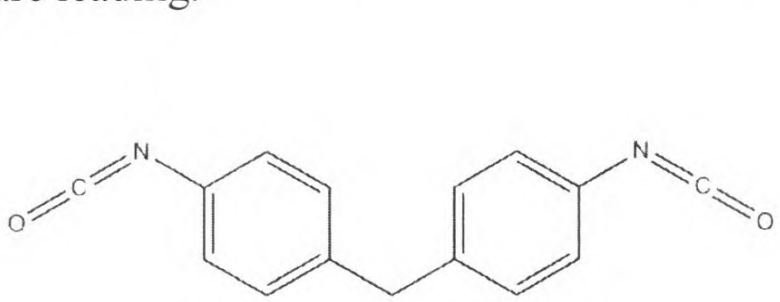
Chemical components for polyurethane synthesis

Polyurethane synthesis is carried out by reacting a polyol and a diisocyanate in the presence of a catalyst under a nitrogen environment in order to reduce the side reactions. In order to control the chain length chain extenders and chain terminators are also involved during the synthesis.

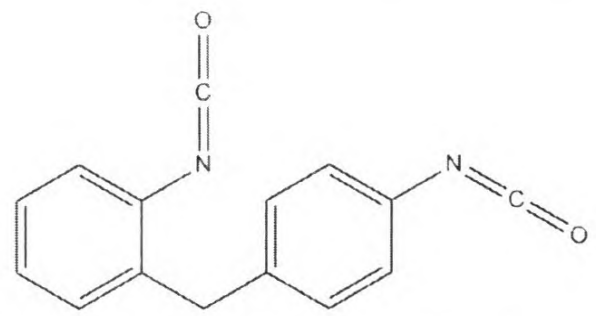
Diisocyanates

Diisocyanate is one of the main two precursors of the polyurethane synthesis process. As everybody knows, in order to form a urethane linkage it is needed an isocyanate group to react with a hydroxyl group. In order to continue the polymerization it is a must to have at least two isocyanate groups within the molecule. So diisocyanates are highly important. Mainly there are two types of isocyanates aliphatic and aromatic. The usage of aromatic isocyanates in the polyurethane industry is very high compared to aliphatics as aromatic isocyanates are more reactive towards hydroxyl groups compared to aliphatics. (8) Toluene diisocyanate (TDI) and methylenebis(phenyl isocyanate) (MDI) are the most frequently used aromatic isocyanates. From their isomeric structures 2,4-TDI and 4,4'-MDI are commonly applied in the industry. In addition to them 1,5-

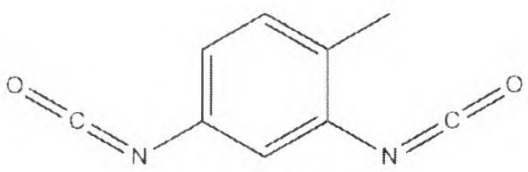
naphthalene diisocyanate (NDI), p-phenylene diisocyanate (PPDI) are also categorized under aromatic isocyanates. Even though aromatic isocyanates are more reactive they are less stable in the presence of light. Because of that, aliphatic isocyanates are utilized during the synthesis of polyurethanes for outside usages. Among them [5-isocyanato-1-(isocyanatomethyl)-1,3,3-trimethylcyclo-hexane] (IPDI; isophorone diisocyanate), hexamethylene diisocyanate (HDI), 4,4'-methylenebis(cyclohexyl isocyanate) (HMDI) are leading.



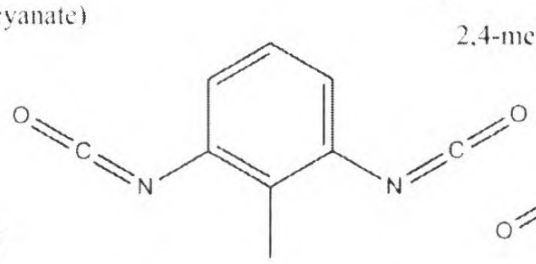
4,4-methylenebis(phenyl isocyanate)



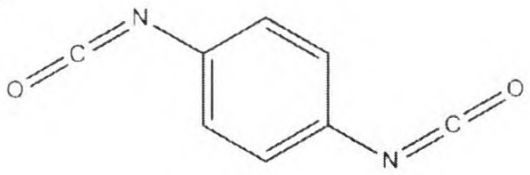
2,4-methylenebis(phenyl isocyanate)



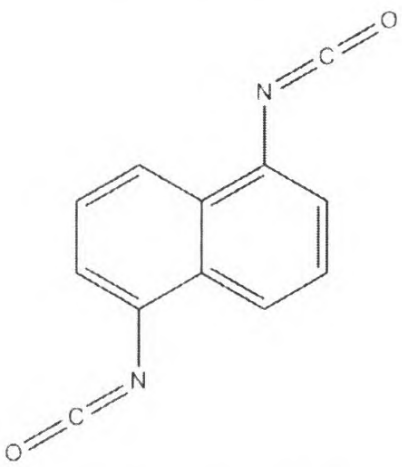
2,4-toluene diisocyanate



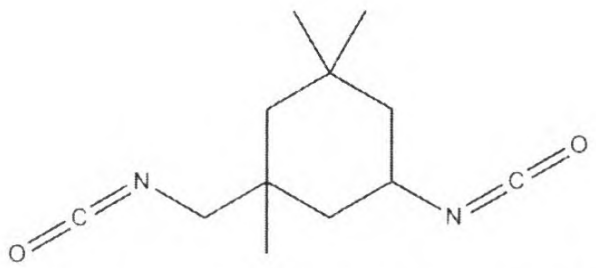
2,6-toluene diisocyanate



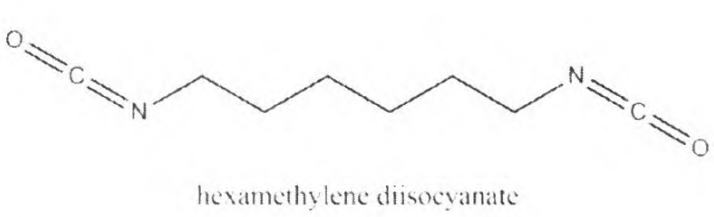
p-phenylene diisocyanate



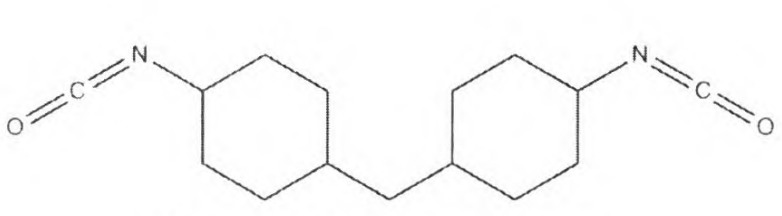
1,5-naphthalene diisocyanate



[5-isocyanato-1-(isocyanatomethyl)-1,3,3-trimethylcyclo-hexane]



hexamethylene diisocyanate



4,4-methylenebis(cyclohexyl isocyanate)

Figure 1: Commonly used diisocyanate compounds

The predominant commercial method for isocyanate production is the Hetschel method which is basically the phosgenation of amines. (8,9)

$$R-NH_2 + COCl_2 \longrightarrow R-N=C=O + 2HCl$$;Phosgenation

Polyols

In order to react with isocyanate, polyols are required during the polyurethane synthesis as the other precursor. Polyols are responsible for the flexibility and some other properties of polyurethanes. The polyurethane properties can be changed widely by varying the polyol chain length and the chemical composition of the polyol. Polyols can

mainly be divided into two categories. Those are polyether polyols and polyester polyols.

Mainly there are two ways to obtain polyether polyols. Ring opening polymerization of cyclic ethers and anionic polymerization of alkylene oxides with di or poly functional alcohol initiators. Later type polyols are known as polyoxyalkylene polyols. Commonly used polyether polyol, polytetramethylene ether glycol is obtained through ring opening. (8) Using the second method functionality and equivalent weight of polyol can be easily varied. For linear polyurethanes via polyether polyols, di-functional polyols or in other words polyether diols are utilized. Polyether polyols have lot of advantages compared to polyester polyols such as possibility to obtain polyols with different functionalities and equivalent weights, lower viscosity, cost effectiveness, higher hydrolytic stability. (8)

Polyester polyol based polyurethanes have lesser hydrolytic stability (9) than polyether polyols but higher oxidation resistance. (8) Polyester polyols can be subdivided into aliphatics and aromatics. Common preparation techniques for aliphatic polyesters are poly-condensation of dibasic acids with glycols and ring opening polymerization of lactones. Trans-esterification of recycled polyethylene terephthalate is the method for aromatic polyester polyols. (8)

In addition to these two types there are polyols in the form of polycarbonate polyols, hydrogenated polyols, polyolefinic polyols and hydantoin-containing polyols. (8)

Chain extenders

Chain extenders are compounds with low molecular weights and having two hydroxyl groups or two amine groups. They are used to bond the polyurethane prepolymers together to obtain the long chain polyurethanes with desired properties. In the case of amines instead of polyurethane links polyurethane-urea links are formed. (9) Commonly used extenders are ethylene glycol, diethylene glycol, 1,4-butanediol, 1,6-hexanediol, 1,2-ethylenediamine 1,6-hexamethylene diamine. (9) In the waterborne polyurethane synthesis proeesses hydrophilicity is achieved by using ionic chain extenders. Anionic extenders have a carboxylic group while cationic chain extenders have an amine group.2,2-bis(hydroxymethyl)propionic acid (DMPA) and N,N.'-bis(2-hydroxyethyl)isonicotinamide are examples for an anionic and cationic extenders respectively. (9)

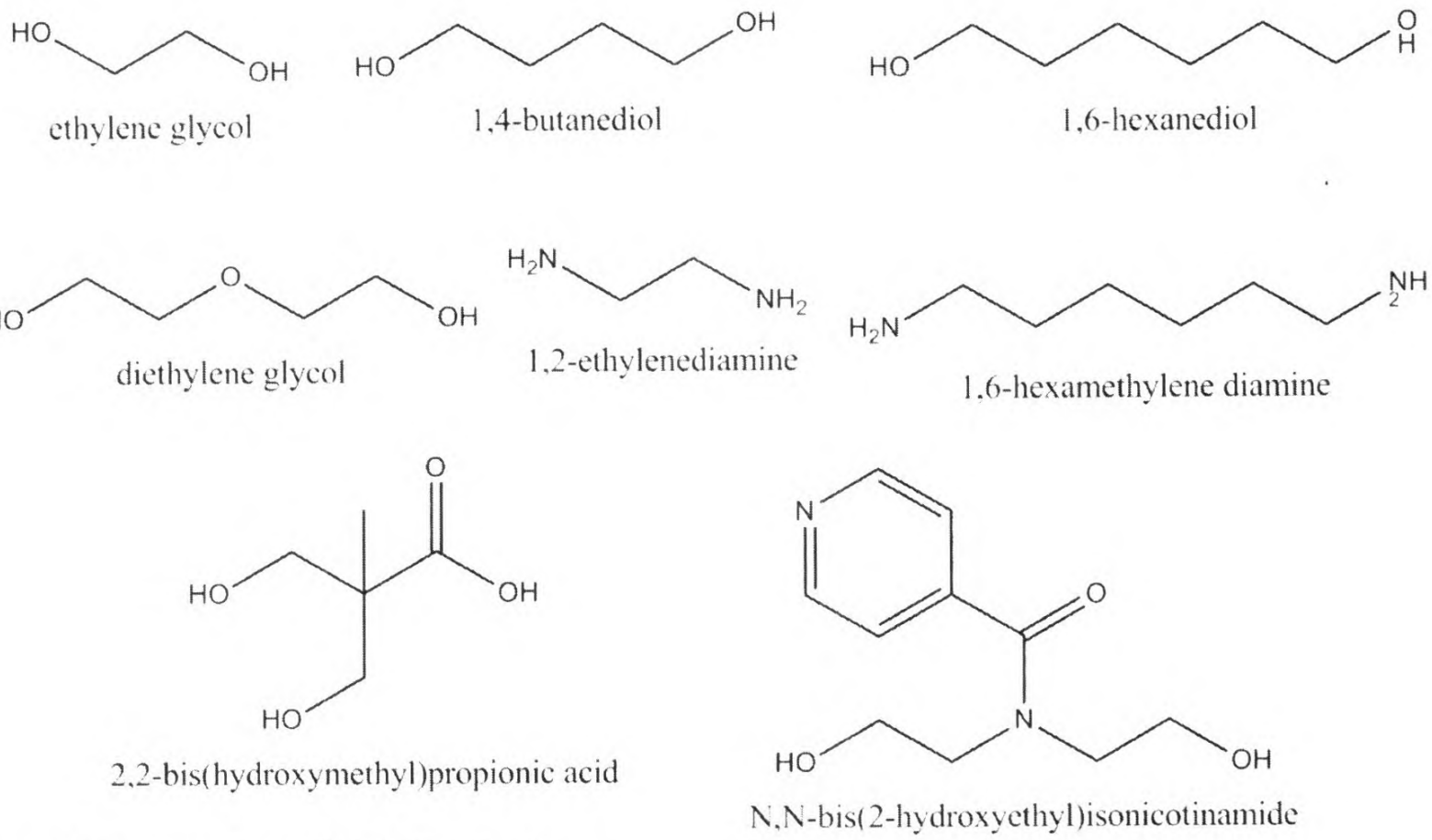


Figure 2: Commonly applied chain extenders

Chain terminators

Polyurethane formation is a step growth polymerization (10,11) which involves two different monomers each having the functionality of 2.In order to terminate this kind of polymerizations; a mono-functional compound having a functional group similar to one of the monomers has to be introduced. (11) This kind of compounds can behave as chain terminators. Simply mono-alcohols are used for polyurethane termination. (12) As more selective chain terminators mono-functional organic molecules containing secondary hydroxyl groups such as 2,6,8-trimethylnonanol-4 and 2,4,8-trimethyl-2,4,8-trichloro-6-nonanol have been introduced to the industry. (12)

Catalysts

The help of catalysts is used during the polyurethane synthesis in order to catalyze the isocyanate and hydroxyl reaction. Generally amines and Lewis acids such as organometallic compounds are employed as catalysts. (13) N,N-dimethylcyclohexylamine, tryethylenediamine, 1,4-diazabicyclo-[2,2,2]-octane, 2,2-bis-(dimethylaminoethylether), N-ethylmorpholine, N,N-dimethylpiperazine are some of the catalysts under amine category while dibutyltindilaurate , dibutyltindioctanoate stannous octoate, zirconium chelates are widely utilized under organometallic catalysts. (14)

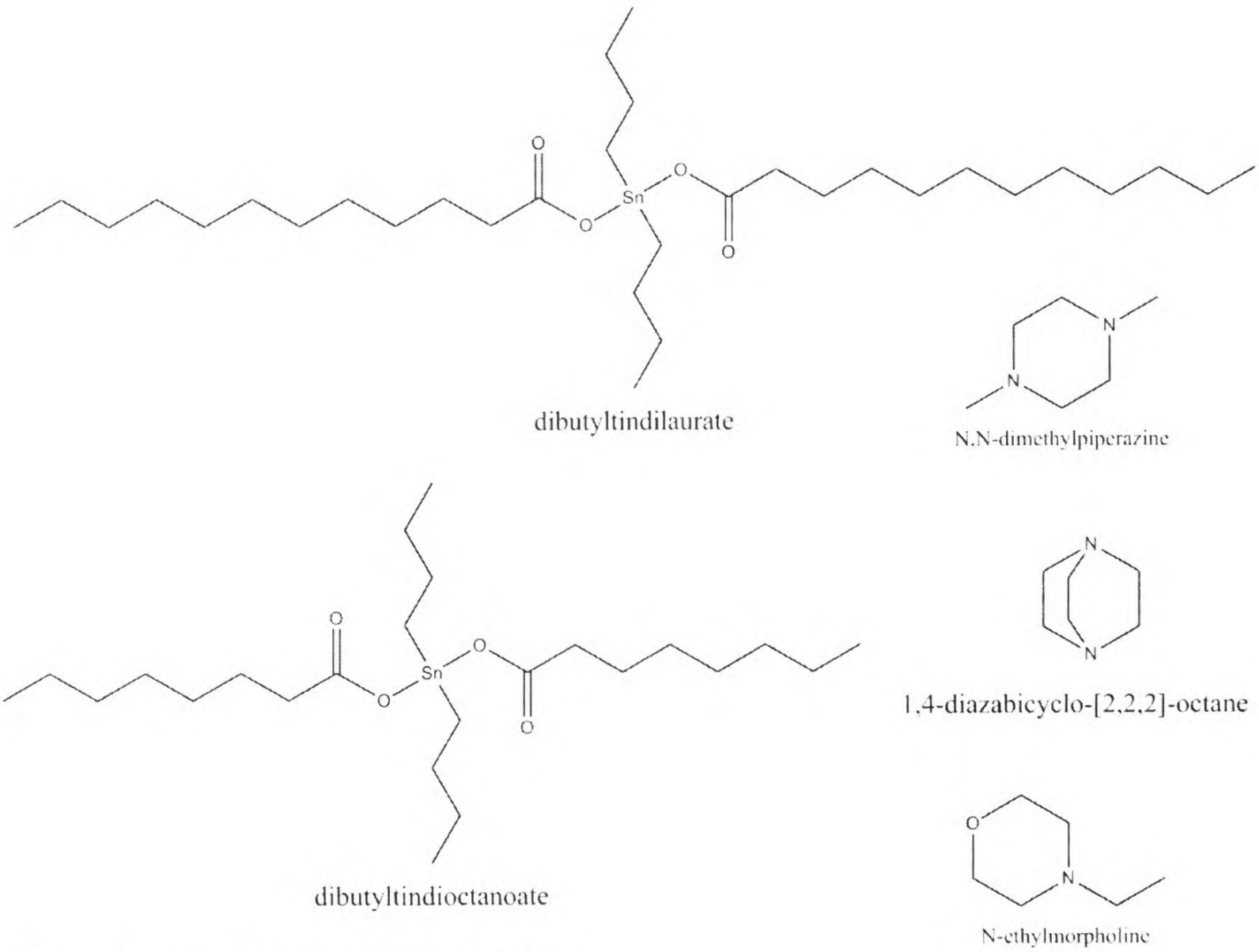


Figure 3: Catalysts used for polyurethane synthesis

Two mechanisms have been proposed for the amine catalysis of polyurethane reaction. (14) According to one mechanism isocyanate forms a complex with tertiary amine and then nucleophilic reagent forms a hydrogen bonded complex with that complex through the tertiary amine and subsequently through a second step, nucleophile attacks to the isocyanate. (14) The other mechanism also involves two steps, in the first step protonation of the catalyst and complex formation via nucleophilic addition of alcohol adduct to the isocyanate is taken place and through the next step proton transfer from protonated catalyst to the complex is occurred. (14)

For the organo-tin catalysts also have two possible paths to explain the catalytic activity. (14)First one proposes an activation of isocyanate via coordination of tin through oxygen or nitrogen in isocyanate group prior to the nucleophilic attack of hydroxyl group. (14) The other path is the opposite of the first one in such a way initially activation of alcohol by the tin catalyst is happen and then complex formation with isocyanate. (14)

Polyurethane chemistry

Polyurethane is a result of a poly-addition reaction between a polyol and a diisocyanate. (8) An addition reaction takes place between the nucleophilic hydroxyl group and the electrophilic isocyanate group in order to form the urethane linkage. The isocyanate group is highly reactive towards nucleophiles. It is due to the high electrophilicity developed on to the C atom on isocyanate group by the cumulative double bond sequence of nitrogen, carbon, and oxygen. (1) High electronegativity of oxygen and nitrogen leads to this pronounced electrophilicity of the C atom on isocyanate group. (1) Reactivity is high in aromatic systems due to resonance effect in such a way the

negative charge delocalized through aromatic ring will increase the electrophilicity of C atom in isocyanate group. (15)

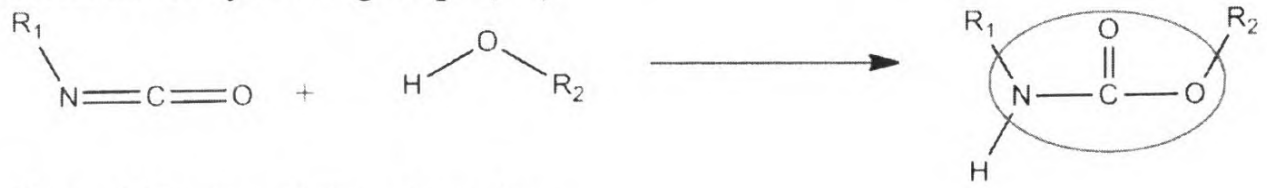


Figure 4: Urethane linkage formation

In order to obtain the linear polyurethane chains diisocyanates and polyols with functionality of 2 have to be reacted. (9) Polyurethane chain formation via poly-addition from polytetrahydrofuran (PTHF) and 4,4'-methylenebis(phenyl isocyanate) (MDI) is shown below.

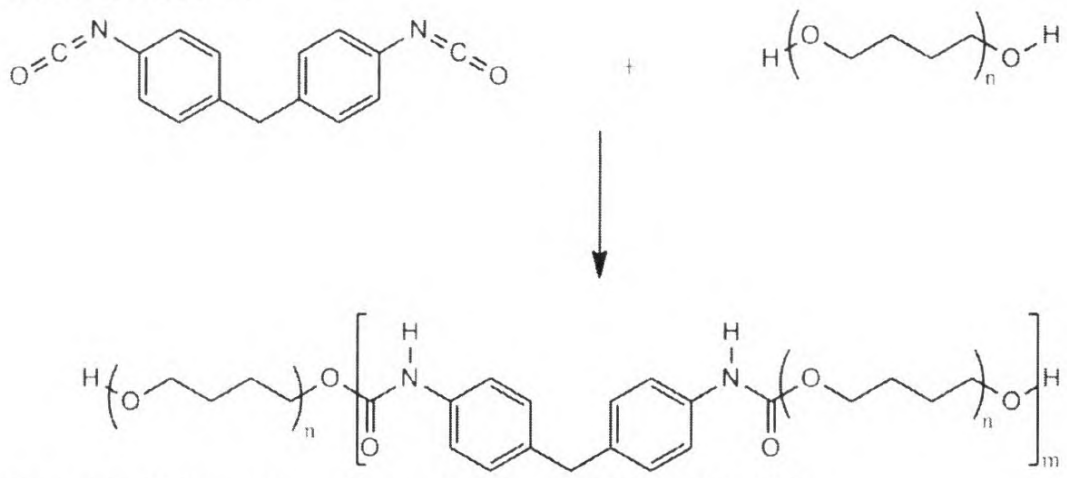


Figure 5: Polyurethane formation from MDI and PTHF

As the isocyanate groups are highly reactive, there are lots of side reactions possible during the polyurethane synthesis. Similar to the urethane linkage formation, isocyanates can give different addition products by reacting with compounds containing any active hydrogen. (8) Hence, in the presence of water isocyanates react with water to give unstable carbamic acid which is readily decompose into an amine and carbon dioxide (Figure 6). (5) As those amines also contain active hydrogen they can react with more isocyanate groups to give substituted urea molecules. (5) Therefore, reaction of isocyanates with water leads to a substituted urea compound while carbon dioxide is evolved. During the polyurethane synthesis, it is advisable to keep the reactants dry and to use a moisture free environment such as nitrogen atmosphere.

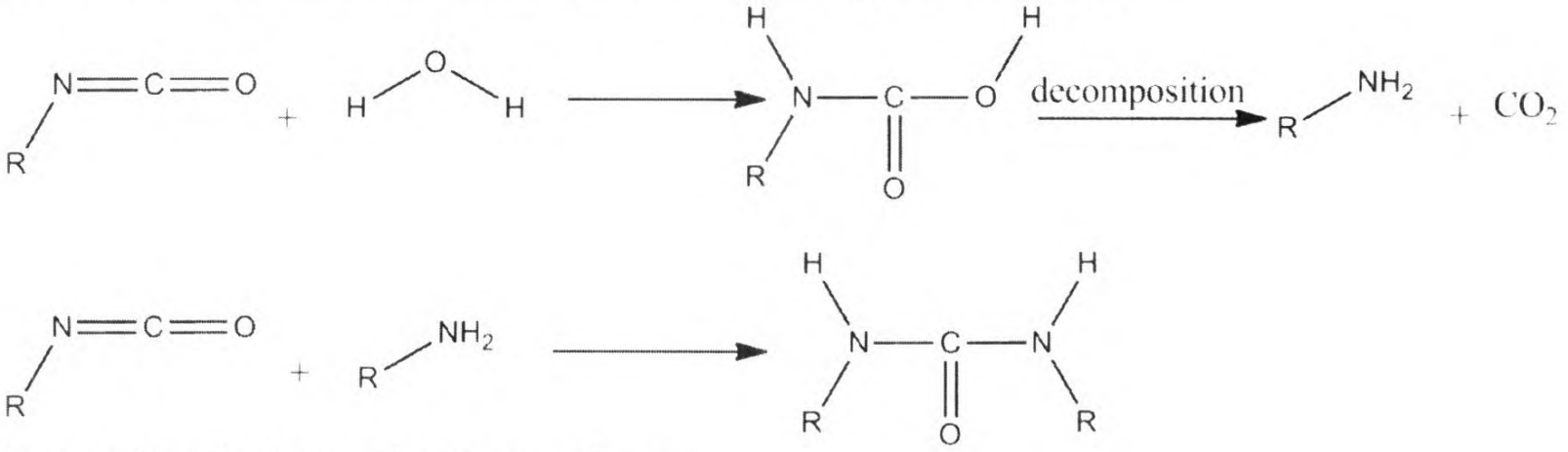


Figure 6: Reaction between isocyanate and water

Highly reactive isocyanate group can reacts with pre-formed urethane group to give allophanate group which can also interfere to polyurethane formation. (8)

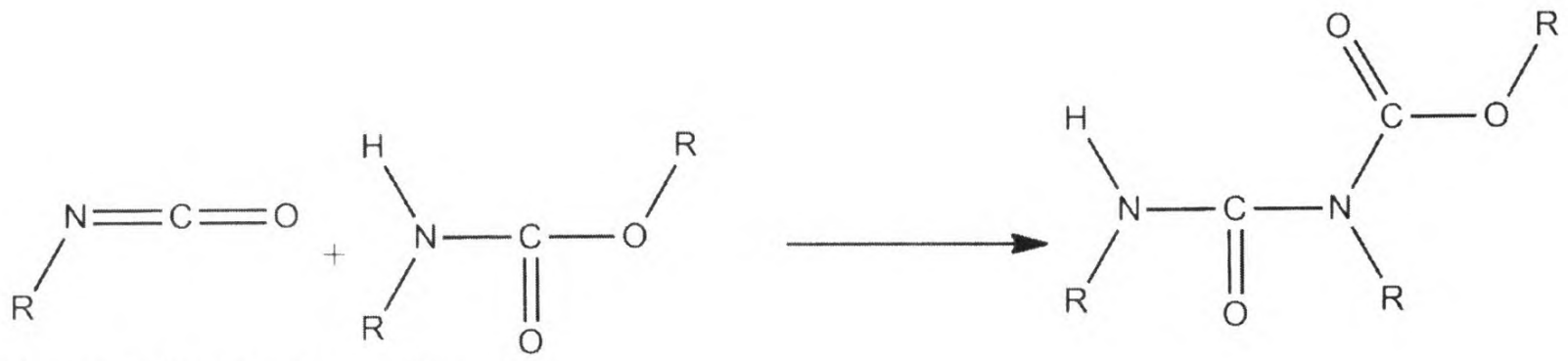


Figure 7: Allophanate group formation

Similarly pre-formed urea group leads to a biuret compound by reacting with isocyanates. (8)

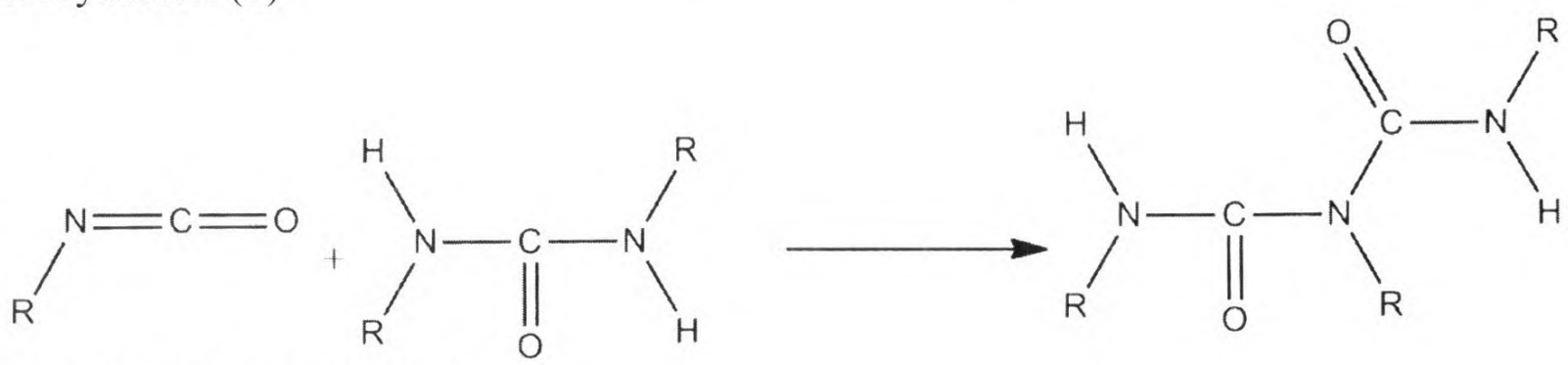


Figure 8: Biuret group formation

In addition to addition reactions there are several side reactions which are possible in the polyurethane reaction medium. Isocyanate dimerization and trimerization lead to form uretidione and isocyanurate structures respectively. (8,9)

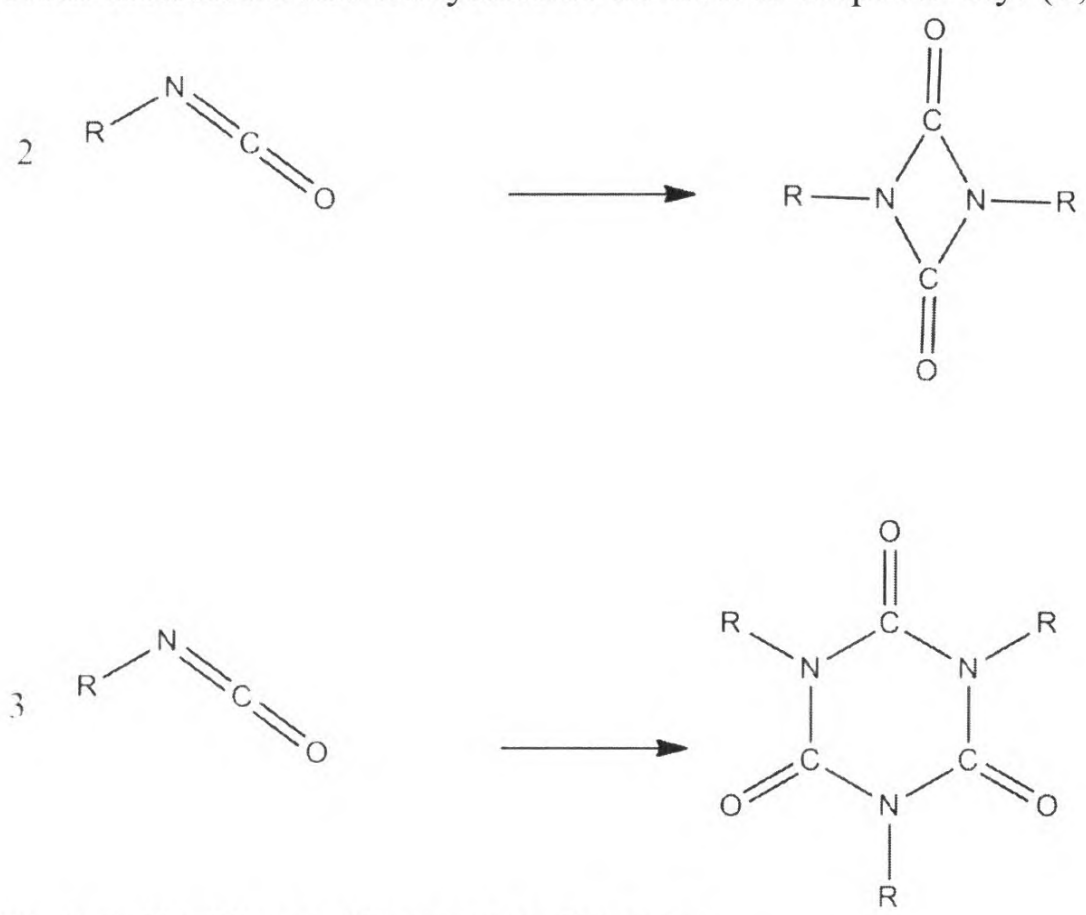


Figure 9: Uretidione and isocyanurate formation

Radical polymerization of isocyanate compound is also possible but need low temperatures and alkaline environment. (8,9)

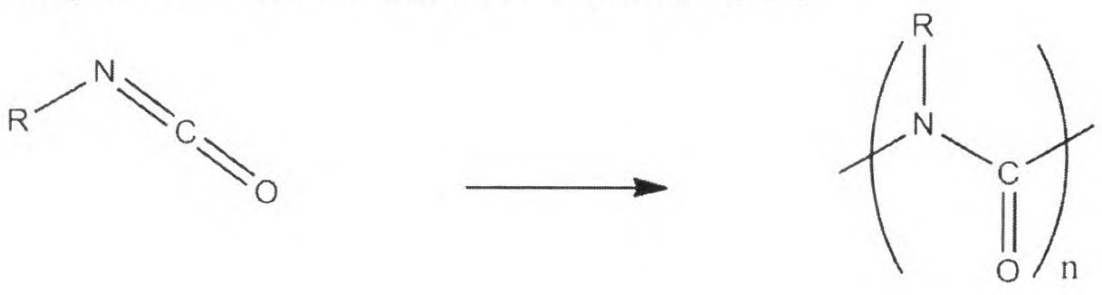


Figure 10: Poly-condensation of isocyanates

Condensation polymerization of isocyanates is also observable some times. Condensation leads to carbodiimide structures. (8,9)

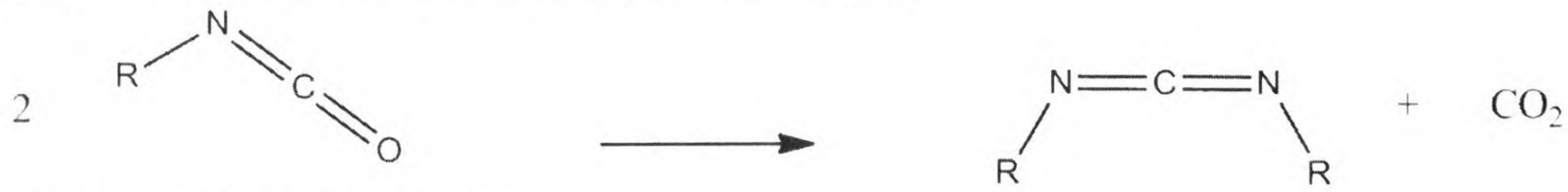


Figure 11: Carbodiimide formation

To promote the required reaction and avoid the possible side reactions, correct monomers and catalysts have to be selected. The reaction conditions such as temperature, time, molar ratio of monomers, method of feeding, amount of catalyst, the reaction environment (eg: under nitrogen environment) also play a major role in this point. (9)

Characterization techniques

During the polyurethane synthesis and after the polyurethane synthesis there are lot of characterization techniques which are applied to study the polyurethane synthesis processes and polyurethane properties.

FT-IR

Infrared spectroscopy is an important analytical technique which can be used in wide variety of research areas in such a way to monitor the reactions, identify the products. It is based on the vibrations of the atoms of a given molecule. It is widely applied because it is a versatile and easy technique. It can be applied with any kind of sample at any stage such as liquids, solutions, pastes, powders, films, fibers, gases and surfaces. (16) However, all the molecules do not show infrared absorption. There is a selection rule for infrared spectroscopy that is "for a molecule to show the infrared absorptions an electric dipole moment of the molecule must change during the vibration". (16)

In this technique the spectrum is obtained by passing the infrared light through the sample and monitoring the fraction of incident light absorbed at certain energy by the sample. To absorb the incoming infrared radiation by a molecule the frequency of that radiation should same as the one of the fundamental modes of vibration of the molecule. (16) Hence, each peak corresponds to the frequency of a vibration of a part of the sample molecule. Molecular vibrations can be divided into two parts stretching and bending which change the bond length and bond angle respectively. Further stretching can be divided as symmetric stretching (in phase) and asymmetric stretching (out of phase) while bending as deformation, rocking, wagging and twisting. (16)

There are two kinds of infrared spectrometers known as dispersive infrared spectrometers and Fourier-transformation infrared (FT-IR) spectrometers albeit the latter is predominantly used. (16) FT-IR spectroscopy is based on interference of radiation between two beams. Here the source radiation is passed through an interferometer to the sample. Then the beam that comes through the sample is pointed to the detector. The detected signal is amplified and converted to digital signal and is subjected to the Fourier-transformation which is a mathematical function used to interconvert distance domains to frequency domains. There are two spectroscopic methods to obtain a spectrum known as transmission and reflectance where reflectance can further divided as attenuated total reflectance (ATR) spectroscopy, diffuse reflectance spectroscopy and specular reflectance spectroscopy. (16)

Interpretation is the most important part of this analytical technique. Lots of the peaks can be interpreted by relating them to a functional group or to a common bond using the group frequencies which are assigned to particular parts of a molecule.
During the polyurethane synthesis polymerization process is monitored basically by the variation in the intensity of the peak corresponding to isocyanate group which is located around 2270 cm^{-1}. (17) It is reduced with the urethane linkage formation as isocyanate is consumed to form urethane during the polymerization.
Chemical changes to the polyurethane structure can also be monitored using FT-IR technique. It is well known that polyurethanes undergo photo-degradation and photo-oxidation in the presence of UV light. Those photo induced effects can be monitored using FT-IR spectroscopy. (18) Conversion of urethane into ortho aromatic amine ester via photo-Fries rearrangement, decomposition of aliphatic ester via Norrish type reaction, oxidation of aromatic structure to quinone products, formation of peroxides via photo-oxidation are such photo induced effects are taken place simultaneously in the presence of UV light which can be monitored via FT-IR. (18) The conversion of polyurethane into photo-induced products has been explained by recording the FT-IR spectra before and after the UV irradiation and interpreting the changes in the spectra. (18)
Hydrogen bonding plays a major role in determining the overall properties of polyurethane. It is important to monitor the hydrogen bonding in polyurethane. It can be carried out using FT-IR. There are frequency shifts in peaks corresponding to N-H and C=O stretching to a lower frequency due to the formation of hydrogen bonding. (19,20) Free N-H stretching at around 3445–3450 cm^{-1} shift down towards the 3260-3290 cm^{-1} range for H bonded N-H while free urethane C=O stretching at around 1730-1740 cm^{-1} shift down towards the 1703-1710 cm^{-1} range for H bonded C=O stretching. (19,21) This is a strong evidence to prove the H bond formation in polyurethanes. Hence, FT-IR can be used as a straight forward technique to monitor H bonding phenomena.
As attention towards UV curable polyurethane has increased, it is essential to monitor the UV curing process. Most of the time to obtain UV curability to polyurethanes, "ene" groups are incorporated at the chain ends. (22,23) With the UV curing they are cross-linked to give improved physical and chemical properties. (22) Therefore, the UV curing can be monitored using FT-IR via the changes in peaks given by "ene" groups such as 1638 cm^{-1} (C=C) 1410 cm^{-1} (=CH_2) and 810 cm^{-1} (=CH). (22,23)

DSC

The differential scanning calorimetry (DSC) is a good analytical technique that can be used to monitor the thermal transitions and reactions which can be occurred in a material. (24) As data obtained can be used in characterizing a material DSC can be defined as a good characterization tool. It is widely used in industries related to semiconductors, batteries, food, explosives, metallurgy, cosmetics, textile, petroleum, coal and polymers. (24)
The instrument has two pans called as reference pan and sample pan and it has designed to heat both the pans in a given constant rate. To do that heat flow supplied to the sample pan is varied relative to the reference pan depending on the thermal transitions occurred in the sample. And instrument records the difference in supplied heat flows to the reference pan and sample pan in other words heat flow to the sample against the temperature. The plot of supplied heat flow to the sample against temperature is known as a thermogram. (24)

DSC can be used to monitor the phase transitions such as solid to liquid (melting), liquid to solid (crystallization), liquid to gas (vaporization), solid to gas (sublimation).Those transitions can be taken place by gaining or releasing the heat. (24) If the transition is happen by gain in the heat by the sample it is known as endothermic transition. (24) During an endothermic transition sample pan need a higher heat flow compared to relative pan. If the transition is happen by releasing the heat by the sample it is known as exothermic transition. (24) During an exothermic transition sample pan need a lower heat flow compared to relative pan. Using the peaks corresponding to those transitions it is possible to obtain the transition temperatures such as melting point, boiling point and also the enthalpies associated with those transitions. In addition to this kind of first order transitions there are second order transitions which can also be monitored by DSC. Glass transition is a good example for this. If a material changes its state from glass (a lower energy state) to rubber (a higher energy state) it is known as glass transition. (24) As during this kind of transition heat capacity of sample molecules increases it is necessary to increase the heat flow of the sample pan. So it can be monitored from the thermogram and the glass transition temperature can be read.

In the polyurethane industry, the DSC technique has been applied for several aspects. It is commonly applied to determine the thermal properties of polyurethanes. (25,26,27,28,29) Murakami and coworkers have used DSC to monitor the influence of the molecule rotaxane on thermal properties of polyurethane and revealed that no influence on glass transition temperature of polyurethane but retards to the re-crystallization of polycaprolactone (PCL) in polyurethane. (25) The effect of aromatic polyamide sulfone (APAS) on the glass transition temperature has been discussed by Mohamed and his team and increase in glass transition temperature with APAS is related to the increase in polymer rigidity. (26) Pan J et al have obtained the thermogram of polyethyleneglycol (PEG) based polyurethane and the melting peak observed around 30-50 ^{0}C has been assigned to melting of PEG moiety and percentage crystallinity has been calculated using melting enthalpy obtained from the thermogram. (27) In addition to thermal properties, to monitor the reaction between isocyanate and hydroxyl group DSC has been applied. (30) In that study they have used data obtained from DSC to fit with a kinetic model for the bulk reaction of isophorone diisocyanate and castor oil. (30)

UV-VIS Spectrophotometry

Absorbance is one of the possibilities that can occur when radiation interacts with matter. (31) It can be monitored using UV-visible spectrometers. UV visible spectroscopy can be applied in both qualitative and quantitative analysis. As UV spectra are consisting of very little number of broad peaks, the use of UV spectroscopy for qualitative analysis is limited.

As energy of UV and visible light can move an electron from lower energy level to higher energy level, electrons in some molecules and atoms can absorb radiation having the energy equals to the energy between two energy levels and move to a higher energy level. (31) Using UV-visible spectroscopy it can be measured the absorbed wavelengths by those atoms or molecules. For atoms very narrow absorbance bands are observed while for molecules broad bands are observed due to the influences of vibrational and rotational bands associated with electronic levels. (31)

As particular wavelengths are absorbed by particular chromophores, UV visible spectroscopy can be applied as a qualitative method. (31) Depending on the absorbance maxima observed, the presence of chromophores can be confirmed in a given molecule.

However, the absorbance maxima can show little shifts with environmental conditions. Confirmation of the presence of certain molecule by comparing the observed spectrum with a reference spectrum is another way to use UV spectroscopy, qualitatively. (31)
According to the Beer's law there is a simple linear relationship between absorbance and concentration. (31) The equation related to Beer's law is shown below. (31)

$$A = -\log T = -\log {}^{I}/_{I_0} = \log {}^{I_0}/_{I} = \varepsilon b c \quad \text{; Equation 1: Beer's law}$$

Here A represents the absorbance while T represents the transmittance. I and I_0 are transmitted intensity and incident intensity, respectively. ε is the molar absorption or extinction coefficient, b is the path length and c is the concentration of the absorbance species.
Due to this linear relationship and easiness of obtaining data using UV visible spectrometer, UV visible spectroscopy has been developed as a good quantitative analytical technique. Using a calibration plot it is able to determine the analyte concentrations using UV-visible spectroscopy. (31)
In polyurethane industry also this technique has been applied in several aspects. In literature UV absorption spectroscopy has been applied to determine the naphthalene content in the polyurethanes using a calibration curve. (32) To monitor the structural changes in polyurethanes modified with stilbene chromophores upon the UV irradiation variation in UV visible spectra of those polyurethanes with irradiation time has been recorded. (33)

Fluorescence

Florescence is a sub category of luminescence where the fluorescence involves a phenomenon of the emission of light from an excited species during the first excited singlet state electrons comes to their ground state. (34) Therefore, it is clear that fluorescence is one of the processes that can be occurred in excited states. The Jablonski diagrams are used to illustrate the possible processes in excited state. (34)

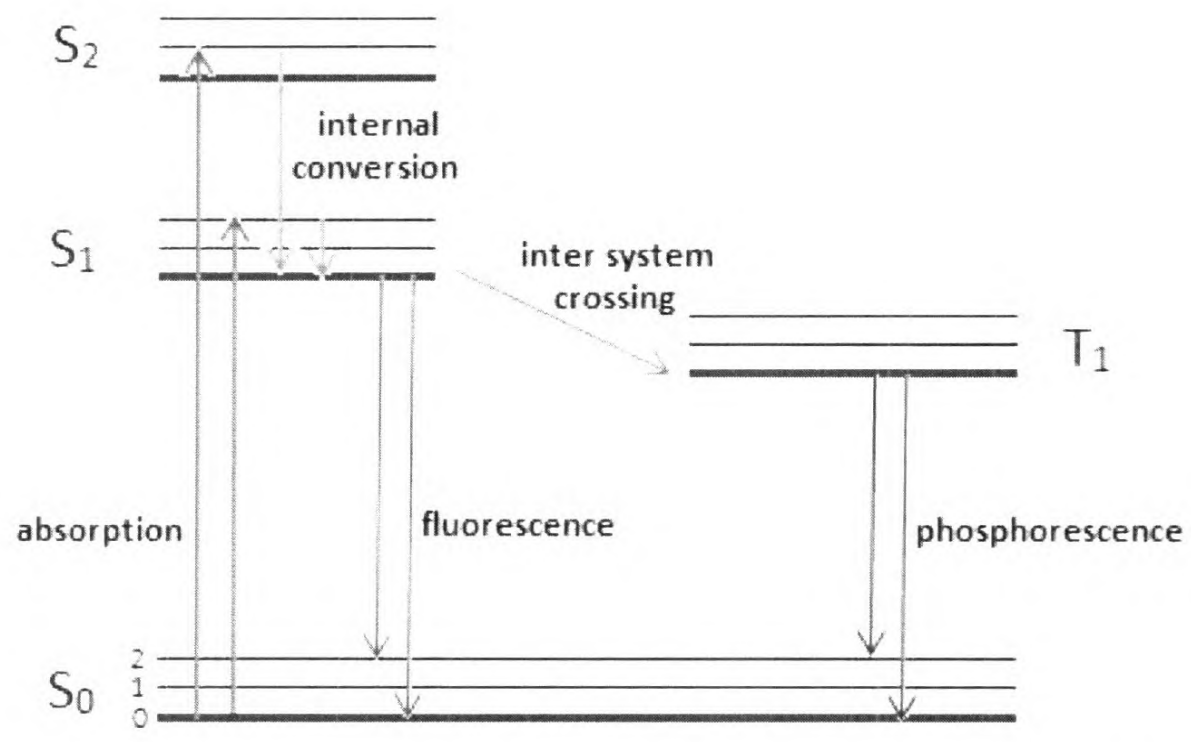


Figure 12: A simple Jablonski diagram to illustrate the processers that can be occurred in excited states

Generally, fluorescence can be observed from aromatic molecules. There are several common fluorophores which are famous as species having the ability of fluorescence. Among them quinine, fluorescein, rhodamine, anthracene, perylene, pyridine are

frequently applied in the field. (34) In addition to aromatic molecules atoms in the lanthanide series are also fluorescent.

To use this fluorescence phenomenon as an analytical technique fluorescence spectroscopy has been developed. Emission spectra are recorded using spectrofluorometer as a plot of fluorescence intensity against the wavelength. Simply emission spectrum gives the idea of wavelength distribution of an emission in the presence of single constant excitation wavelength. (34)

Fluorescence technique can be used to monitor lot of molecular processes such as interactions of solvent molecules with fluorophores, rotational diffusion of bio molecules, conformational changes, and binding interactions. (34)

Fluorescence technology has been applied in the field of polyurethane to achieve different aspects.

Particle size analysis

As many kinds of materials are consisting of particles, it is important to characterize the particles of a given material. Powders, granules, suspensions, emulsions, slurries, aerosols, and sprays are some of the forms of materials which consist of particles. (35) Depending on the form of the material, using different techniques particle properties can be monitored. There are some important parameters required to characterize a particle. Particle size, particle shape, surface properties, mechanical properties, charge properties, and microstructure are dominant parameters. (35) Among them particle size is the most important parameter which is required to discuss. The imperativeness of particle size is arrived due to the direct influence of particle size on the properties of the corresponding material. It is influenced on material properties depending on the form of material such as stability in suspension (for sediments and paints), reactivity or dissolution rate (for catalysts and tablets), efficacy of delivery (asthma inhalers), texture and feel (for food ingredients), appearance (for powder coating and inks), flowing ability and handling (for granules), viscosity (for nasal sprays), packing density and porosity (for ceramics). (35)

As particles are three dimensional it is difficult to fully describe using a one dimension such as radius or diameter. In order to overcome this, normally particle size is given as the diameter of an equivalent sphere having a certain property as the actual particle. That property may be volume, weight, surface area, sedimentation rate, maximum length, minimum length or translational diffusion coefficient. (35) Depending on the selected property to obtain the equivalent sphere, the given particle size for a one particle may be varied.

As particles in a given sample have different sizes it is practicable to give the particle size data as a statistical distribution. A particle size distribution can be represented in different ways such as number weighted distributions (each particle have an equal weight irrespective of its size), intensity weighted distributions (distribution is related to the intensity of light scattered by the particle), and volume weighted distributions (contribution of each particle to the distribution depends on the volume of that particle). (35) The distribution type depends on the technique which is applied to determine the size and it is possible to convert from one distribution to other with several assumptions. Using those distributions the average particle size can also be recorded for a given sample.

Dynamic light scattering is the technique more suitable to determine the particle size in nano range. (35) It can be applied with polymers, proteins, nanoparticles, emulsions, and colloidal dispersions as this technique need samples having particles suspended in a

liquid. (35) It gives the diameter of a hypothetical sphere having a similar translational diffusion coefficient as the particle and produces an intensity based distribution. (35)
Particle size analysis can also be applied in polyurethane industry. It is important to control the particle size of aqueous polyurethanes depending on their applications. Large particles are required to obtain in surface coating with rapid drying while small particles are required to achieve a deep penetration of the dispersion in to a substrate. (36) Particle sizes of grafted polyurethanes which were synthesized using Poly(ethylene glycol monomethyl ether) (PEGMME) as the grafting agent has been studied by Mohaghegh *et al* and they were able to correlate the particle size of polyurethanes and the molecular weights of PEGMME. (36) They have observed that particle size is decreased with the increase of the molecular weight of PEGMME. As the reasons for this decrease they have explained that the increase of hydrophilicity of PEGMME and also the increase in chain flexibility with the increase in molecular weight. (36) To evaluate the effect of the amount of ionic groups on the polyurethane properties this technique has been used. (37) Liminana and coworkers have observed that particle size of polyurethane particles obtained from number distribution has increased with decreasing the amount of dimethylolpropionic acid and have explained that it is due to two reasons namely the decrease in hydrophilicity of the polyurethane ionomer and decrease in electrolytic stability of the dispersion. (37) There is a literature support to explain that there is an effect from the type of the ionic group on the polyurethane particle size. (38) According to that sulphonated polyurethanes have small particle sizes compared to carboxylated polyurethanes due to the dispersion formation efficiency of sulphonate ions. (38) The hard segment content has also been affected on particle size of polyurethanes in such a way that increase in the solid content leads to a decrease in particle size. (39) It has been explained as the increase of solid content leads to decrease in particle mobility subsequently to a reduction in probability of particle-particle interactions. (39) Due to that, large numbers of small particles are formed when solid content is high. (39)

Zeta potential

Zeta potential is also related to particles as it measures the electrostatic or charge repulsion or attraction between particles in a liquid suspension. (35) It is an indication of the stability level of the dispersion. High absolute value of the zeta potential indicates that the amount of the charge on the surface of nanoparticles is high which leads to a higher repulsion between the particles in the dispersion. (40) This repellent interactions lead to a higher stability of the dispersions. (40) Zeta potential is obtained thorough the electrophoretic mobility. Electrophoretic mobility of particles is measured using electrophoretic light scattering technique. (35)
Zeta potential has also been applied in polyurethane study especially waterborne polyurethanes to check the dispersion stability. (40,41,42) The effect of surfactant on polyurethane dispersions have been established and accordingly ionic surfactants lead to a higher stability compared to non-ionic surfactants and stability of dispersions increase as surfactant concentration increases. (40) The effect of the position of ionic groups in the polyurethane chain, the weight percentage of ionic group, and chain flexibility of polyurethane chain on the polyurethane dispersion stability has been measured using the zeta potential values. (41) The position of ionic group has been effected in such a way that when an ionic group is at the chain end, it gives the highest stability while when the ionic group is at the hard segment, it gives the least stability and stability of the ionomers when ionic groups in the soft segment is in between. (41) As ionic content

increases dispersion stability increases due to increase hydrophilicity and increase in chain flexibility leads to a higher stability. (41) To monitor the influence of different ingredients on water based polyurethanes zeta potential measurements has been applied as a strong tool. (42) The influence of lot of factors such as the type of the surfactant, percentage content of acrylic polymerization initiator azobisisobutyronitrile (AIBN), molecular weight of polypropylene oxide, the weight percentage of the ionomer DMPA, the weight percentage of acrylic monomer cross-linker, and polyurethane to acrylate mass ratio on the dispersion stability has been discussed using the zeta potential data. (42)

Focus of this study

Even though vast variety of studies has been carried out on polyurethanes still there are unexplored areas.

In this study attention was paid to MDI based polyurethane systems. The fluorescence behavior of MDI based polyurethanes was studied in detail. It was identified that PU molecule contains an internal fluorophore and the fluorescence behavior can be correlated to the micro-structural arrangements of the polyurethane structure.

As a solution to reduce the volatile organic content (VOC) the highly hydrophobic MDI based polyurethanes were converted to hydrophilic by introducing an ionomer DMPA to the polymer backbone. By reducing the solvent usage, DMF-water mixture was used as solvent and tried to optimize the dispersion properties, crystalline and thermal properties of the films which were obtained from those dispersions through the variation of DMPA/PTHF molar ratio.

The composites of iron-polyurethane components were prepared and the effect of compositing to the fluorescence behavior of the polyurethanes was investigated.

LITERATURE REVIEW

Polyurethane fluorescence

In addition to common techniques such as DSC, TGA, GPC, FT-IR (7,27,28,29) which are applied in the field of polyurethane, fluorescence is an additional technique which can be used as a method to monitor the photo induced changes in polyurethanes such as photo-isomerization (43,33), photo-oxidation (44,45) and photo-degradation (46,47,48). In addition, fluorescence techniques can be used as a way to develop new applications of polyurethanes such as humidity sensors (49), vapor-based chemical sensors (50) , anion sensors (51) and metal ion sensors (52). Using the difference in fluorescence behavior of cis and trans isomers of stilbene chromophores, the photo-isomerization of polyurethanes with stilbene pendants was studied by EC Buruiana and his team. (43,33) Stilbene trans isomer gives fluorescence while conversion to cis isomer leads to a loss of fluorescence. This conversion (cis-trans isomerization) of the pendant stibene can be used to control the chain conformation of the polymer backbone. (33) Photo-oxidation of polyurethanes leads to form peroxides which are liable to easy decomposition to alkoxy and hydroxyl radicals. (44,45) Quenching of the excited states of fluorophores by those photo-oxidation products creates a path to monitor the photo-oxidation of polyurethane via fluorescence. (44,45) The main advantage of fluorescence as a technique to detect the photo-oxidation is its ablility to detect the initial stages of the oxidation. (44) The main disadvantage of aromatic diisocyanate based polyurethane is the discoloration with the exposure to ultra violet light. (46) This discoloration is a consequence of photo-degradation. (46) Two different ways of aromatic diisocyanate based polyurethane photo degradation have explained in literature. (46,47,48) One path leads quinoid products in other word quinone-imide products which are colored while the other leads to aryl amine cleavage type products and photo-Fries rearrangement type products (ortho and para photo-Fries products). (46,47) Photo-Fries products yield colored azo compounds with further photolysis. (47) Hence, both the degradation schemes lead to discoloration. The differences shown in fluorescence spectra before and after photo-degradation, such as emission maxima and intensity variations, are useful to explain the photo-degradation of polyurethanes. (46,47,48)

In order to apply the fluorescence technique in the field of polyurethane it is necessary to incorporate a fluorophore to the polymer system. It may be either extrinsic or intrinsic. In the case of extrinsic, a fluorescent probe is externally introduced to the surrounding environment of the polymer. C Peinado and co-workers have used two extrinsic fluorescent probes p-dimethylamino salicylic acid and 2',7'-difluorfluorescein to monitor the photo-oxidation of polyurethanes. (44) To develop a humidity sensor, P Bosch and co-workers have used several extrinsic fluorophores. (49) They have obtained a homogeneous mixture of polyurethane adhesive and fluorescent probe and then casted on to glass slides to obtain polyurethane films which can be used as humidity sensors. (49) Hydrophilic polyurethanes have been used as a matrix to embed 2,3-di(pyrrole-2yl)quinoxaline(DPQ) based fluorescence sensors which are developed as anion sensors to increase their water compatibility. (51) Increase in water compatibility is very important as water is the natural solvent for most anions. (51) In the case of intrinsic, fluorophore is attached to the polymer chain. It may be in the polymer backbone or it may be attached to polymer backbone as a pendant. If the isocyanate group consists of highly conjugated aromatic system which can produce fluorescence, it can be used as the intrinsic fluorophore which is in the backbone to

study the fluorescence properties of that polyurethane. For example, fluorescence properties of naphthalene diisocyanate based polyurethanes have been studied widely. (32,53) Some fluorescence properties of naphthalene diisocyanate based polyurethanes have been attributed to excimer formation. (53) It has been reported that naphthalene diisocyanate based polyurethane forms solvent dependent intra-molecular excimers between carbamate groups on the same polymer at low concentrations and that the critical concentration required for intermolecular excimer formation is dependent on the compatibility of the solvent to the polymer. (53) It has also been suggested that the excimer formation in polyurethane is enhanced by the hydrogen bonds which are formed between a hydrogen atom connected to the central nitrogen atom of a urethane linkage and the carbonyl of another urethane group. (53) Similarly in MDI based polyurethanes, MDI has been used as the intrinsic fluorophore which is in the backbone to study the photo-degradation behavior of MDI based polyurethanes. (46,47,48) Another possibility for the incorporation of a fluorophore to the backbone is the use of a new monomer having a fluorophore to combine the two conventional prepolymers. Such efforts were made to synthesis a polyurethane containing the fluorescent brightening agent, disodium 4,4'-bis[(4-anilino-6hydroxyethylamino-1,3,5-triazin-2-yl)amino]stilbene-2,2-disulphonate (VBL). (54,55) It was proved that VBL-based polyurethane shows a very stable fluorescence. As another effort to incorporate a fluorophore to the polymer backbone, an aqueous polyurethane emulsion that contains the fluorescent moiety 1,4-diamino-2,3-diphenoxyanthraquinone (DDAQ) has been developed by incorporating DDAQ into the polyurethane chain made using 2,4-tolylenediisocyanate (TDI), poly(propyleneglycol) and 2,2-dimethylolpropionic acid to produce a polyurethane with very stable fluorescence properties. (56) Fluorophore can be attached to polymer backbone as a pendant to the polymer chain as well. It can be easily carried out during the quaternisation step of polyurethane ionomers using a neutralizer which contains the fluorophore. Polyurethane cationomers with anthracene chromophores attached on the quaternary ammonium units have been used as metal ion sensors since they show fluorescence quenching in the presence of different metal ions (UO_2^{2+}, Fe^{3+}, Cu^{2+}). (52) Another study where the incorporation of pendant fluorophores during the quaternisation is the work carried out by EC Buruiana to study the photo-isomerization of stilbene. (43) Pyrene is also an interesting fluorophore which can be incorporated to polyurethane chain as a pendant. There are studies carried out to develop vapor based chemical sensors by incorporating pyrene during the quaternisation of polyurethane ionomers. (50,57,58) Quenching of excited pyrene by nitrobenzene vapour has been applied to develop the sensors. (50,57,58) In addition to at the quaternisation step, pendant fluorophore can be attached to the chain by reacting an active region of polymer chain (eg: urethane linkage) with a suitable compound containing the fluorophore. Stilbene fluorophores have been located on to the urethane nitrogen atoms of the polyurethane chain as a pendant and photo-isomerization of stilbene has been discussed by the same team who incorporated the stilbene to the quaternisation center. (33)

Waterborne Polyurethanes

Volatile organic compounds (VOCs) are a huge problem faced by lot of industries such as paints, inks, and coatings industries. (59) As a solution for this problem world industry has focused on replacing the reaction mediums from organic solvents to the environmental friendly solvents such as water. (59) With this revolution, the attention was paid towards the aqueous polyurethanes (polyurethane dispersions). Basically there

are two main methods for making polyurethane dispersions called as prepolymer mixing process and acetone process. (59) In the prepolymer mixing process medium molecular weight polymer known as prepolymer is synthesized by reacting a polyol and a diisocyanate. In order to disperse the polymer in water internal emulsifier is also added to the reaction mixture to introduce the internal emulsifier to the polymer backbone. A small amount of organic solvent is used to dissolve the emulsifier and reduce the viscosity. After the neutralization of the emulsifier, dispersion in water is carried out. Finally chain extension is carried out using a water soluble chain extender. (59) This prepolymer process leads to a product with least amount of organic solvents. However, the acetone process leads to a product with no organic solvent. In that process also a prepolymer is obtained and emulsifier is introduced then neutralized and chain extended while acetone is used as the solvent in comparatively higher amount. Then disperse in water. Here, after the dispersion in water no further chain extension is proceed. After the dispersion the low boiling acetone is removed from the system to obtain a product with no organic solvent. (59)

Researchers have focused on either prepolymer method (60,37,61,62) or acetone process (63,64,65,66). One of the main differences in prepolymer mixing method and acetone process is the stage where the chain extension step is carried out. In prepolymer mixing method chain extension is carried out after the water addition. Jhon Y and coworkers have studied on the chain extension of polyurethane dispersions and discussed about the degree of chain extension. (60) Lei L and his team have also studied on the chain extension by changing the chain extender. (62) They have used three different chain extenders ethylenediamine (EDA), diethylenetriamine (DETA), and triethylenetetramine (TETA). The effect of the amount of ionic groups on the polyurethane dispersion properties such as particle size, electrolyte stability and film properties such as crystallinity, thermal stability was investigated by the Luminana and coworkers. (37) The NCO/OH ratio is also important parameter in polyurethane field. The effect of NCO/OH ratio on dispersion, film and coating properties has been discussed by Pacios G *et al.* (63) When acetone process is applied there are several factors which can effect on dispersion properties such as initial PU content in acetone, phase-inversion temperature, evaporation conditions, and solvent nature. (65)

AK Nanda and co-workers have tried both the prepolymer mixing process (67) and acetone process (59) to obtain polyurethane dispersions using poly(hexyleneadipate-isophthalate)diol, IPDI, DMPA, triethylamine (TEA) as the neutralizer, hexamethylenediamine (HMDA) as the chain extender. For prepolymer mixing process N-methylpyrrolidinone was used as the organic solvent. (67) They have focused on effect of DMPA concentration, concentration of the polymer, degree of pre/post-neutralization of the carboxylic acids and chain extension on the dispersion properties. (59,67)

When the attention is paid towards polyurethane dispersions, it is important to discuss about emulsifier or the ionomer which is introduced to the polymer backbone to make the polymer water dispersible. Most of the time it is a diol compound with ionic groups. (59) It can be categorized as anionic and cationic. Dimethylol propionic acid (59,67,68,37) is the most commonly used ionomer which is anionic. Dimethylol butanic acid is also used as anionomer. (69) In addition to carboxylate pendants there are some situations where the sulfonate pendants impart the hydrophilicity of polyurethanes in dispersions. (61) Instead of DMPA a compound known as PESS which comprise a long side chain with 23–24 repeat units of ethylene oxide and/or propylene oxide, and end-

capped with a sulfonate group has been applied by Lee HT *et al.* (61) Cationic ionomers are also used during the preparation of polyurethane dispersions. (70,71,72) N-methyldiethanolamine has been used as cationomer by those researchers to achieve a polyurethane dispersion. (70,71,72) In addition to incorporation of diol compound with ionic groups to polymer backbone there are techniques of introducing pendent ionic groups to the polymer chain. In literature, it is explained that 2-acrylamido-2-methylpropanesulphonic acid (ATBS) anionomer has been introduced to the polyurethane chain by graft polymerization of ATBS to the unsaturated polyester polyol before the reaction with diisocyanate. (73) Athawale and his team were able to achieve a PU dispersion with high viscosity compared to DMPA based polyurethane dispersions due to crosslinking ability of the new anionomer and also improved thermal stability and enhancement in mechanical and chemical properties. (73)

After the incorporation of ionomer to the polymer backbone it is a must to neutralize those ionomer groups to achieve the hydrophilicity. If it is an anionomer most of the time a carboxylic acid group is present. In such cases an amine is used to neutralize the carboxylic acid group by converting into carboxylate ion. Triethylamine is the neutralizing agent which is commonly concomitant with the anionomer DMPA. (59,67,68) With the cationomers an amine group is neutralized by a carboxylic acid to give a quaternary ammonium salt. Acetic acid (70,71) and formic acid (72) were used to neutralize the N-methyldiethanolamine.

In literature, there are lot of works carried out which are related to aqueous polyurethane dispersions. Among the studies on aqueous polyurethanes a considerable attention is paid towards the UV curable waterborne polyurethanes due to their excellent mechanical properties. UV curable waterborne polyurethanes have been developed by incorporating different functional groups to the polyurethane chain. In general UV curable waterborne coatings are prepared by capping the isocyanate terminated polyurethane chains with a single hydroxyl acrylate. Hwang HD and coworkers have introduced acrylate groups to the polyurethane chain ends by reacting the isocyanate terminated polyurethane chains with three different capping agents 2-hydroxyethylmethacrylate, 2-hydroxyethylacrylate and pentaerythritoltri-acrylate. (22)

XY Zhang and coworkers have modified the conventional aqueous anionic polyurethane synthesis process to increase the UV curing ability. (23) They have introduced 'ene' groups via the pendent side chains attached to the polyurethane backbone in addition to the 'ene' groups which are present in the chain terminators. In that process the isocyanate terminated anionic polyurethane prepolymer was reacted with 2,2-bis(hydroxymethyl)propane-1,3-diyl diacrylate to incorporate the 'ene' group containing pendent side chains before the chain termination with 2-Hydroxyethyl acrylate. (23) The effect of the amount of 'ene' groups on various film properties has been studied by them.

Z Yang and coworkers have introduced the thiol- 'ene' chemistry to UV curable polyurethane industry to achieve a higher degree of crosslinking. (74,75) They have prepared UV curable polyurethane coatings by mixing multifunctional thiol terminated aqueous polyurethane dispersion and a multifunctional 'ene' terminated aqueous polyurethane dispersion together. 2,2-bis(3-sulfanylpropanoyloxymethyl)butyl-3-sulfanylpropanoate (TriSH), 2,2-bis(prop-2-enoxymethyl)butan-1-ol (DiAE) were the thiol terminator and ene terminator respectively which they have used. (74) They were able to achieve excellent physical properties compared to the conventional UV curable urethane–acrylate based systems.

Polyurethane Composites

Scientists have taken steps to prepare polyurethane-nano particle composites to achieve the polyurethanes with enhanced properties. Several methods to prepare polyurethane-nano particle composites have been explained in literature namely by dispersing the synthesized nano particles in a polymeric solution, by polymerizing the corresponding monomers in the presence of nano particles and by synthesizing nano particles in the presence of polymers. (76) First one is an *ex situ* method while other two can be categorized as *in situ* method. (76) There are different kind of nano particles and different kind of techniques which have been used in preparation of polyurethane nano composites. It has been able to obtain more flexible polyurethane- iron oxide-nano composites using a surface initiated polymerization technique. (76) Moisture absorbed to the iron oxide nano particles has been used as initiators and hydroxyl groups on it has been reacted with isocyanate and through the other end of diisocyanate polymerization has been continued. (76) It has been reported in another article that polyurethane nano composites based on iron oxide nanoparticles has been synthesized using the surface initiated polymerization technique and has been developed as lighter weight microwave absorbers. (77) TiO_2 nano particles have been incorporated to polyurethane matrix by direct mixing of surface modified TiO_2 nano particles with polyurethane resin. (78) Surface modification has been done using amino propyl trimethoxysilane. (78) TiO_2 polyurethane composites have also been prepared via the raft polymerization. (79) It was an *in situ* method and carried out using HEA terminated polyurethane emulsion, azobisisobutyronitrile (AIBN) and TiO_2 nano particles modified with 2-{[(Butylsulfanyl)carbonothioyl]sulfanyl}propanoic acid (BCSPA). (79) Nano zinc oxide particles have been introduced to waterborne polyurethane dispersion through ultrasonic probe sonication and were able to obtain polyurethane composite coatings with enhanced mechanical properties and increased corrosion resistance and UV resistance. (80) It has been reported that preparation of waterborne polyurethane/attapulgite nano composites via the direct emulsion bending was led to enhance the thermal stability and to increase the tensile strength of polyurethanes. (69) To achieve a good thermal stability, polyurethanes have been modified as a composite with surface modified SiO_2 nano particles. (81) Surface modification was done using poly(propylene glycol) phosphate ester. (81) To prepare magnetic polyurethane forms, flexible polyurethane (PU) foams as the matrix which is non-polarizable and carbonyl iron particles fillers which are polarizable have been used and confirmed that there is an increase in thermal stability compared to pure polyurethane forms. (82) Fe_2O_3/polyurethane nano fibers have been obtained via electrospinnig of a Fe_2O_3/polyurethane solution which was prepared by mixing Fe_2O_3 in a polyurethane solution by magnetic stirring. (83) Due to the enhanced properties such as magnetic heating capability of those nano fibers they can be developed to apply in hyperthermia therapy. (83)

Methodology

Materials and Analytical instruments

Materials

The three main monomers which were used during this research work polyether polyol; polytetrahydrofuran with average molar mass of 2000, 98% 4,4'-methylenebis(phenylisocyanate), and 98% 2,2-bis(hydroxymethyl)propionic acid were from Sigma Aldrich and used without further purification. As a catalyst 98% 1,4-diazabicyclo[2,2,2]octane, a photo initiator 98% 2-hydroxy-4'-(2-hydroxyethoxy)-2-methylpropiophenon, a chain terminator 98% trimethylolpropanediallyl ether and a quaternizing agent ≥99.5% diethylamine were also from Sigma Aldrich and used without further purification. N,N-dimethylacetamide(≥99.5%) , N,N-dimethylformamide (≥99.8) and acetone (≥99.5%) were used as solvents which were also obtained from Sigma Aldrich and were dried and stored over molecular sieves.

Analytical instruments

FT-IR data were obtained using ATR mode of Bruker VERTEX 80 FT-IR spectrophotometer (Germany). The related software was OPUS spectroscopy software version 6. UV-vis absorption spectra were recorded by SHIMADZU UV 3600 UV-VIS-NIR spectrophotometer (Japan). The applied software was UVProbe 2.33. Fluorescence analysis was carried out using HORIBA Fluorolog spectrofluorometer (Japan) with the help of FluorEssence V3.5 software. DSC and TGA data were obtained from TA Instruments (USA) Q200 DSC and Q600 TGA, respectively, while TA instrument explorer software was applied in both. Zetasizer nano series particle size analyzer from MALVERN Instruments (UK) was used to monitor the zeta potentials and particle sizes of the dispersions. In that case Zetasizer software was used. To obtain the XRD patterns, Bruker D8 FOCUS XRD (Germany) was used and Eva software was used for XRD analysis.

Polyurethane prepolymer synthesis and analysis

Polyurethane prepolymer synthesis

By changing the degree of polymerization, three different polyurethane prepolymer systems were synthesized. The formulations used to prepare those polyurethanes are listed in the Table 1. Several precautions were taken to avoid the isocyanate water side reaction. As the precautions, polytetrahydrofuran (PTHF) was dried in vacuum oven for 24 h at 105 ^{0}C prior to use, solvents were dried over the molecular sieves, and reactions were carried out under a nitrogen atmosphere. Required amount of 4,4'-methelenebis(phenyl isocyanate) (MDI) was dissolved in 30 ml of dimethylacetamide (DMAc). When MDI was completely dissolved, measured weight of PTHF was added. The catalyst 1,4-diazabicyclo[2,2,2]octane (DABCO) was added to the reaction mixture and DMAc was added to bring the total volume up to 100 ml. The reaction mixture was stirred at 300 rpm at 80 °C for 5 hrs. MDI and polytetrahydrofuran were reacted to form the polyurethanes as shown in Figure 5.

Table 1: Formulations used to synthesis polyurethane prepolymers

Polyurethane system	Amount of MDI	Amount of PTHF	Degree of polymerization
PUP-3	0.01 mol (2.5025 g)	0.02 mol (40.0000 g)	3
PUP-10	0.0083 mol (2.0853 g)	0.01 mol (20.0000 g)	10
PUP-∞	0.01 mol (2.5025 g)	0.01 mol (20.0000 g)	∞

Film preparation

The polyurethane solutions were cast onto dried glass slides which had been cleaned by tap water and then with distilled water. The solvent was then allowed to evaporate at 100 °C in a vacuum oven yielding smooth films.

DSC

DSC thermograms of dried films were obtained. The sample was first cooled to -30 ^{0}C and then heated at 5 ^{0}C /min up to a maximum temperature of 220 ^{0}C. The sample was cooled to -30 ^{0}C again and reheated to 220 ^{0}C at 5 ^{0}C min^{-1} cooling/heating rate.

XRD

XRD pattern of the film obtained from the prepolymer; PUP-3 were obtained by scanning at diffraction angle 2θ from 10° to 60°.

UV absorbance of polyurethane films

Absorption spectra of the polyurethane films were recorded in the range of 200 nm – 650 nm.

Fluorescence study

Fluorescence properties of the prepared films were studied by recording emission spectra. Excitation and emission slit widths were maintained at 3 nm for all the experiments. All the emission intensities presented in this study were normalized to excitation intensity. For each type of polyurethane film, fluorescence analysis was carried out as follows.

The fluorescence spectrum of the prepared polyurethane film was recorded using 293 nm as the excitation wavelength. The fluorescence spectrum of the film was recorded repeatedly (30 times). Each scan amounted to 30 s of UV irradiation at 293 nm wavelength. Then, the UV irradiated film was kept out of radiation for three days and spectrum was recorded again, after which the recording of the spectra was repeated for 30 times again. The above process was repeated for three complete cycles.

The curiosity was raised by two factors; the variations in the fluorescence spectra with extended UV exposure and the reversibility in those variations after UV ceasing. This was lead to an extended analysis to find the factors affecting this behavior, reasons for this nature and finally to propose a possible mechanism.

Effect of relaxation time on the fluorescence

The PUP-3 system was used to examine the effect of relaxation time on the reversibility. In this case number of continuous repeats per cycle was maintained at 30. Relaxation time was varied from 1 day to 1 month as 1 day, 3 days, 7days and 1month. Extent of reversibility was calculated using the collected data.

Effect of exposure time on the fluorescence

Using the PUP-3, the effect of exposure time on the reversibility was examined by varying the number of continuous repeats per cycle in such a way 20, 30, 40, 50, and 60 repeats per cycle while retaining a constant relaxation time of three days for each. Variations in fluorescence peak intensities were analyzed.

Effect of degree of polymerization

The results obtained related to the fluorescence behavior of three different polyurethane systems were compared to understand the effect of degree of polymerization.

Effect of solvent

In order to investigate the solvent effect, a new polyurethane system was prepared according to the formulations of PUP-3 given in Table 1 and procedure explained in the 0 changing the solvent from DMAc to DMF. The system was labeled as PUP-3$_{_DMF}$. The effect was discussed by comparing PUP-3 and PUP-3$_{_DMF}$.

FT-IR

To monitor the chemical changes during the UV exposure, IR spectra of polyurethane films before and after UV irradiation were obtained. For each sample 64 scans were carried out at 4 cm^{-1} resolution.

Optimization of the dispersion properties of hydrophilic polyurethane dispersions and thermal properties of their coatings by changing the hydrophilicity

Hydrophilic polyurethane synthesis and preparation of the aqueous dispersions

Via the introduction of the ionic groups to the polyurethane backbone, hydrophilicity of the polyurethane has been achieved. Five different kinds of polyurethane dispersions were obtained by varying the ionomer to polyol molar ratio while maintaining a constant ratio of total OH to total NCO at 1. The compositions used for the synthesis is given in Table 2. Reactions were carried under nitrogen atmosphere. The solvent N,N-dimethylformamide (DMF) was dried over molecular sieves. The ionomer, 2,2-bis(hydroxymethyl)propionic acid commonly known as Dimethylolpropionic acid (DMPA) and PTHF were pre-dried in vacuum oven at 105 ^{0}C for 24 hours prior to use. The required amount of DMPA was dissolved in minimum amount of DMF and was added to the measured PTHF. The mixture was stirred properly to obtain a homogenized mixture. MDI was dissolved in DMF. The DMF volume was measured in such a way the total DMF volume is 30 ml. After the complete dissolution of MDI, the DMPA PTHF mixture was added to it and stirred for 5 hours at 350 rpm speed. The temperature was maintained at 80 ^{0}C. The temperature was reduced to 30 ^{0}C and the chain terminator; trimethylolpropanediallyl ether (DiAE) was added and stirring was continued for 30 min. Ionomers were neutralized by adding diethylamine (DEA). After the addition of DEA, stirring was continued for another 30 min. To obtain the dispersion, 70 ml of distilled water was added drop wise while maintaining a vigorous stirring with speed of 1000 rpm. After the completion of water addition, the dispersion was stirred for another 30 min. It was able to obtain a polyurethane dispersion in a DMF-water mixture having 70% of water as shown in Figure 13.

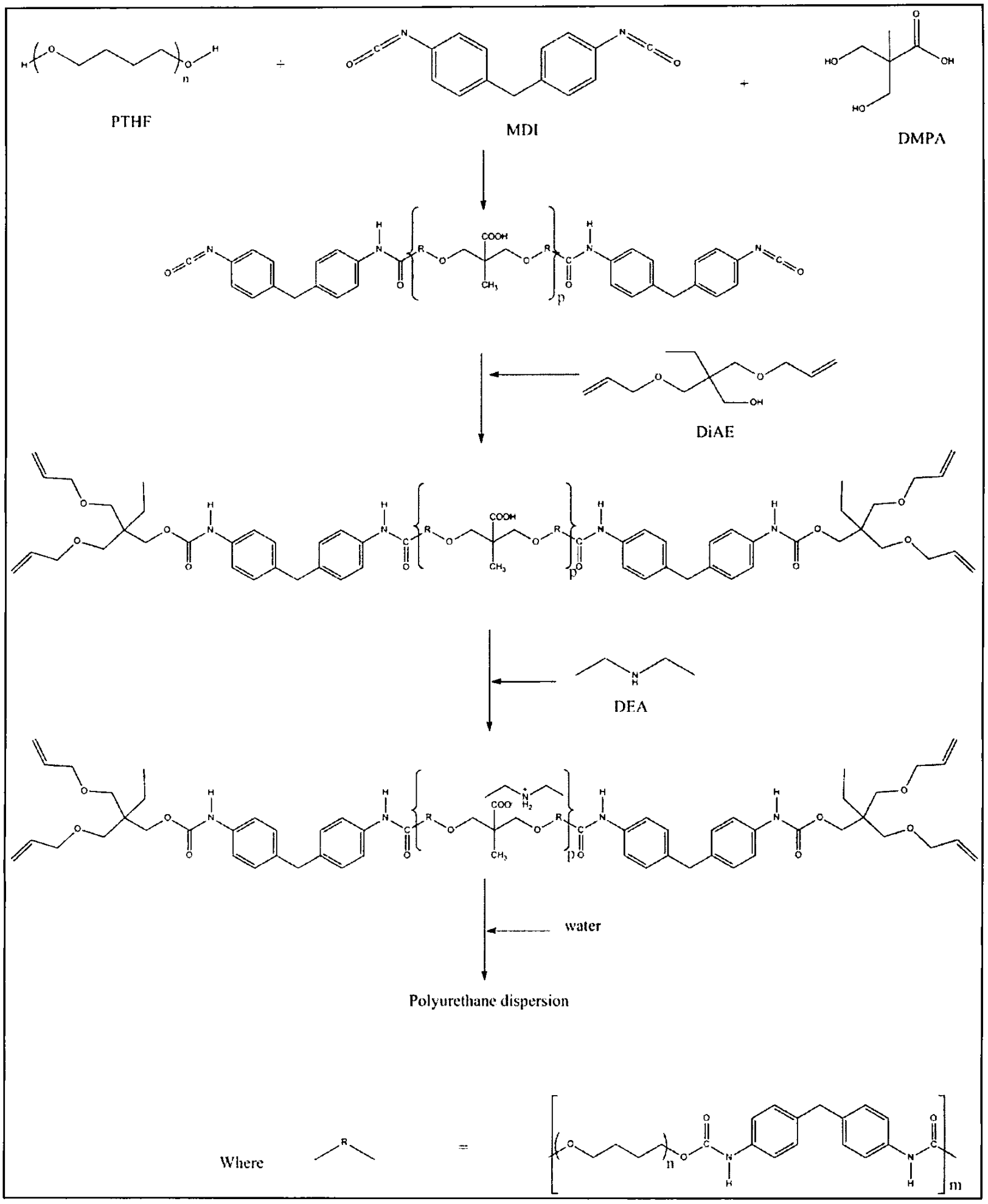


Figure 13: Synthesis of polyurethane dispersion

Table 2: Compositions used to prepare the polyurethane dispersions

Polyurethane dispersion	Amount of MDI (mol)	Amount of PTHF (mol)	Amount of DMPA (mol)	Amount of DiAE (mol)	Amount of DEA (mol)	Hard segment content (w%)
PUD-1	0.01	0.00175	0.00450	0.00750	0.00450	47.0
PUD-2	0.01	0.00225	0.00400	0.00750	0.00400	40.3
PUD-3	0.01	0.00275	0.00350	0.00750	0.00350	35.1
PUD-4	0.01	0.00325	0.00300	0.00750	0.00300	30.9

PUD-5	0.01	0.00375	0.00250	0.00750	0.00250	27.4

Dispersion stability

The two dispersion properties; the average particle size and the zeta potential were measured using the particle size analyzer. The average size of the particles was measured via the intensity based distribution and the particle size was measured over a two month of time period to discuss the stability of the dispersion. The zeta potential of the dispersion was also obtained to prove the dispersion stability and it was also continued over two months.

Preparation of polyurethane films

The polyurethane solutions were cast onto dried glass slides which had been cleaned by tap water and then with distilled water. The solvent was then allowed to evaporate at 100 °C in a vacuum oven.

XRD

XRD patterns of the prepared films were obtained by scanning at diffraction angle 2θ from 10° to 60°.

Thermal analysis

DSC thermogram of a dried polyurethane film was obtained. The sample was first cooled to -30 ^{0}C and then heated at 5 ^{0}C /min up to a maximum temperature of 300 ^{0}C. The sample was cooled to -30 ^{0}C again and reheated to 300 ^{0}C at 5 ^{0}C min^{-1} cooling/heating rate.

FT-IR spectroscopy

FTIR spectra of the prepared polyurethane films were recorded. Using the spectra, hydrogen bond index and NH peak shift were calculated. In order to monitor the micro-structural change in polyurethane films, the FTIR spectra of the films were recorded again just after the completion of the following DSC cycles. The sample was first cooled to -30 ^{0}C and then heated at 5 ^{0}C /min up to a maximum temperature of 220 ^{0}C. Then sample was cooled to -30 ^{0}C and reheated to 10 ^{0}C at 5 ^{0}C min^{-1} cooling/heating rate.

Fluorescence study

The fluorescence spectra of the prepared polyurethane films were recorded using 293 nm as the excitation wavelength. The fluorescence spectra of the film were recorded repeatedly (30 times). Each scan amounted to 30 s of UV irradiation at 293 nm wavelength. Then, the UV irradiated films were kept out of radiation for three days and spectra were recorded again, after which the recording of the spectra was repeated for 30 times again.

Iron –Polyurethane composites

Preparation

By following the method explained in section 3.2.1 three different polyurethane systems were obtained by varying the degree of polymerization. Polyurethane films were prepared as described in the section 3.2.2. Iron polyurethane composites were obtained using those polyurethane solutions and films. Through several changes in the way of composite preparation method, it was able to develop eight techniques to prepare the composites. Altogether twenty four different iron polyurethane composites were developed as shown in Table 3.

Technique 1: solution mixing method under dark conditions

To a portion of 25 ml of polyurethane solution, 0.5 ml of iron pentacarbonyl was added and stirred for 15 min at room temperature to obtain a homogenized mixture. The reaction environment was maintained under dark conditions by covering with aluminium foils. The composite solution was casted on to a glass slide and dried in vacuum oven to evaporate the solvents. Dark conditions were applied during the drying also.

Technique 2: solution mixing method followed by UV exposure

To a portion of 25 ml of polyurethane solution, 0.5 ml of iron pentacarbonyl was added and stirred for 15 min at room temperature to obtain a homogenized mixture. The reaction environment was maintained under dark conditions by covering with aluminium foils. After the preparation of homogenized mixture it was exposed to UV light for 15 min. The composite solution was casted on to a glass slide and dried in vacuum oven to evaporate the solvents.

Technique 3: surfactant added solution mixing method under dark conditions

To a portion of 25 ml of polyurethane solution, 0.5 ml of oleic acid was added and mixed properly prior to the addition of iron pentacarbonyl .To that mixture 0.5 ml of iron pentacarbonyl was added and stirred for 15 min at room temperature to obtain a homogenized mixture. The reaction environment was maintained under dark conditions by covering with aluminium foils. The composite solution was casted on to a glass slide and dried in vacuum oven to evaporate the solvents. Dark conditions were applied during the drying also.

Technique 4: surfactant added solution mixing method followed by UV exposure

To a portion of 25 ml of polyurethane solution, 0.5 ml of oleic acid was added and mixed properly prior to the addition of iron pentacarbonyl .To that mixture 0.5 ml of iron pentacarbonyl was added and stirred for 15 min at room temperature to obtain a homogenized mixture. The reaction environment was maintained under dark conditions by covering with aluminium foils. After the preparation of homogenized mixture it was exposed to UV light for 15 min. The composite solution was casted on to a glass slide and dried in vacuum oven to evaporate the solvents.

Technique 5: dipping method under dark condition

A prepared polyurethane film was dipped in iron pentacarbonyl solution for 30 min under dark conditions and dried in vacuum oven.

Technique 6: dipping method followed by UV exposure

A prepared polyurethane film was dipped in iron pentacarbonyl solution for 30 min under dark conditions and it was exposed to UV light for 15 min. The film was dried in vacuum oven.

Technique 7: vapour deposition method under dark conditions

The prepared polyurethane film was exposed to the vapour of iron pentacarbonyl for 30 min under dark conditions and dried in vacuum oven.

Technique 8: vapour deposition method followed by UV exposure

The prepared polyurethane film was exposed to the vapour of iron pentacarbonyl for 30 min under dark conditions and it was exposed to UV light for 15 min. The film was dried in vacuum oven.

Table 3: The list of iron polyurethane composites

Label number	Degree of polymerization	Method of Composite preparation
PUC-1	3	PU solution + $Fe(CO)_5$; under the dark conditions
PUC-2	3	PU solution + $Fe(CO)_5$; UV exposed

PUC-3	3	PU solution + oleic acid + $Fe(CO)_5$; under the dark conditions
PUC-4	3	PU solution + oleic acid + $Fe(CO)_5$; UV exposed
PUC-5	3	Pre prepared PU film dipped in $Fe(CO)_5$; under the dark conditions
PUC-6	3	Pre prepared PU film dipped in $Fe(CO)_5$; UV exposed
PUC-7	3	Pre prepared PU film exposed to $Fe(CO)_5$ vapour; under the dark conditions
PUC-8	3	Pre prepared PU film exposed to $Fe(CO)_5$ vapour; UV exposed
PUC-9	10	PU solution + $Fe(CO)_5$; under the dark conditions
PUC-10	10	PU solution + $Fe(CO)_5$; UV exposed
PUC-11	10	PU solution + oleic acid + $Fe(CO)_5$; under the dark conditions
PUC-12	10	PU solution + oleic acid + $Fe(CO)_5$; UV exposed
PUC-13	10	Pre prepared PU film dipped in $Fe(CO)_5$; under the dark conditions
PUC-14	10	Pre prepared PU film dipped in $Fe(CO)_5$;UV exposed
PUC-15	10	Pre prepared PU film exposed to $Fe(CO)_5$ vapour ; under the dark conditions
PUC-16	10	Pre prepared PU film exposed to $Fe(CO)_5$ vapour; UV exposed
PUC-17	∞	PU solution + $Fe(CO)_5$; under the dark conditions
PUC-18	∞	PU solution + $Fe(CO)_5$; UV exposed
PUC-19	∞	PU solution + oleic acid + $Fe(CO)_5$; under the dark conditions
PUC-20	∞	PU solution + oleic acid + $Fe(CO)_5$; UV exposed
PUC-21	∞	Pre prepared PU film dipped in $Fe(CO)_5$; under the dark conditions
PUC-22	∞	Pre prepared PU film dipped in $Fe(CO)_5$; UV exposed
PUC-23	∞	Pre prepared PU film exposed to $Fe(CO)_5$ vapour; under the dark conditions
PUC-24	∞	Pre prepared PU film exposed to $Fe(CO)_5$ vapour; UV exposed

Analysis

Fluorescence

A fluorescence study of above iron-polyurethane composites was carried out. The samples were excited at 293 nm excitation wavelength and emission spectra were recorded in the range of 320-500 nm. In parallel to earlier fluorescence study of the normal polyurethane film, the spectra were recorded continuously for 30 times and cease the exposure to 293 nm wavelength for three days and continuous recording were started again. Above cycle was repeated for four times.

RESULTS AND DISCUSSION

Polyurethane prepolymer synthesis and analysis

Polyurethane prepolymer synthesis

To elude the polyurea formation during the polyurethane synthesis it is necessary to avoid the contact of moisture with the reactants. So precautions such as doing the reaction in a nitrogen environment, drying the PTHF and DMPA above 100 ^{0}C prior to use, and use of solvents which were dried over molecular sieves were employed.

According to the Carothers' equation (10), the degree of polymerization was varied as 3,10 and ∞ by changing the polyol: diisocyanate molar ratio. The Carothers' equation which is used to calculate the degree of polymerization is given below in $\bar{X}_n = \frac{(1+r)}{(1+r-2rp)}$; Equation 2. The number average degree of polymerization $\bar{X}_n$ can be calculated using r and p where r and p represent the stoichiometric ratio and extent of reaction, respectively. Stoichiometric ratio (r) is always defined to have a value equal to or less than one. (10)

$\bar{X}_n = \frac{(1+r)}{(1+r-2rp)}$ **; Equation 2: Carothers' equation**

It was assumed that reaction approaches to the completion with in the period and extent of reaction was considered as 0.999.

When MDI:PTHF = 1:2

$r = {}^1/_2 = 0.5$

$\bar{X}_n = \frac{(1+0.5)}{(1+0.5-2(0.5)(0.999))} \approx 3$

When MDI:PTHF = 0.83:1

$r = {}^{83}/_{100} = 0.83$

$\bar{X}_n = \frac{(1+0.83)}{(1+0.83-2(0.83)(0.999))} \approx 10$

When MDI:PTHF = 1:1

$r = {}^1/_1 = 1$

$\bar{X}_n = \frac{(1+1)}{(1+1-2(1)(0.999))} \approx \infty$

MDI was dissolved in DMAc prior to react with PTHF as it will be helpful to confirm that unreacted residual MDI is not remained. The reaction mixture was further diluted to reduce the viscosity of the final polymer solution.

Film preparation

The films were obtained by evaporating the solvent. With the evaporation of the solvent smooth polyurethane films were deposited on the glass slides.

DSC

Thermal properties of the polyurethane films were analyzed using DSC thermograms. Both heating cycles (first heating cycle and second heating cycle) showed a single melting peak at comparatively low temperatures. In both case the melting peak is

located around 25 ^{0}C. The DSC thermograms of first and second heating cycles are shown in Figure 14 and Figure 15, respectively. During the cooling cycle which was proceeded in between these two heating cycles, a crystallization peak was shown at a temperature somewhat lower than melting temperature. As shown in Figure 16, it was around 10 ^{0}C. The appearance of this crystallization peak closure to the melting peak and at lower temperature compared to the melting temperature suggests that it is corresponding to the crystallization of the species that was melted during the first heating cycle. It was proven by the re-appearance of the melting peak in the second heating cycle around 25 ^{0}C which was similar to first heating cycle melting peak. It implies that the component which is melted in first heating cycle, get re-crystallized back during the cooling cycle and it is melted again during the second heating cycle.

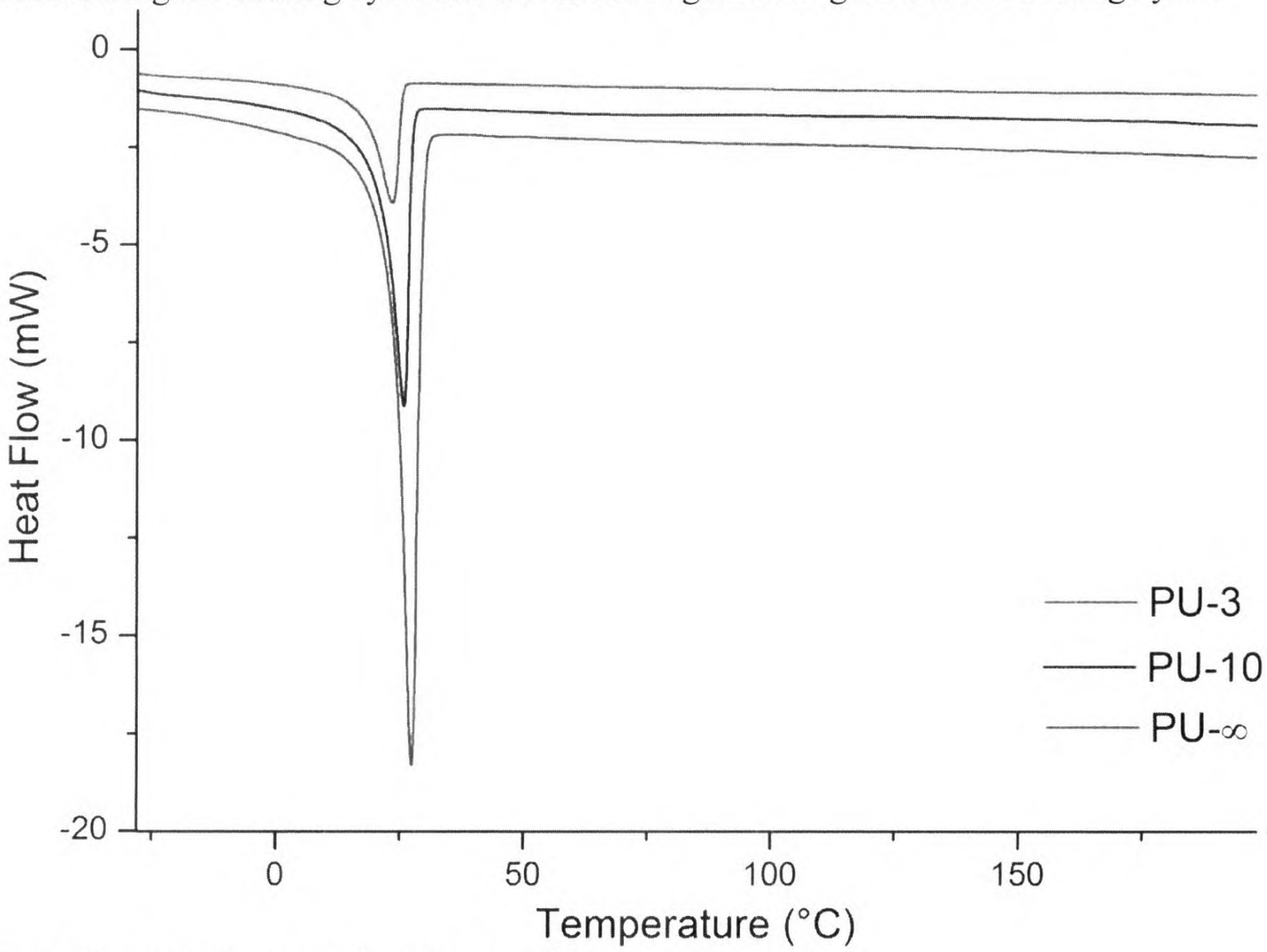


Figure 14: The first heating cycle of the polyurethane prepolymer films

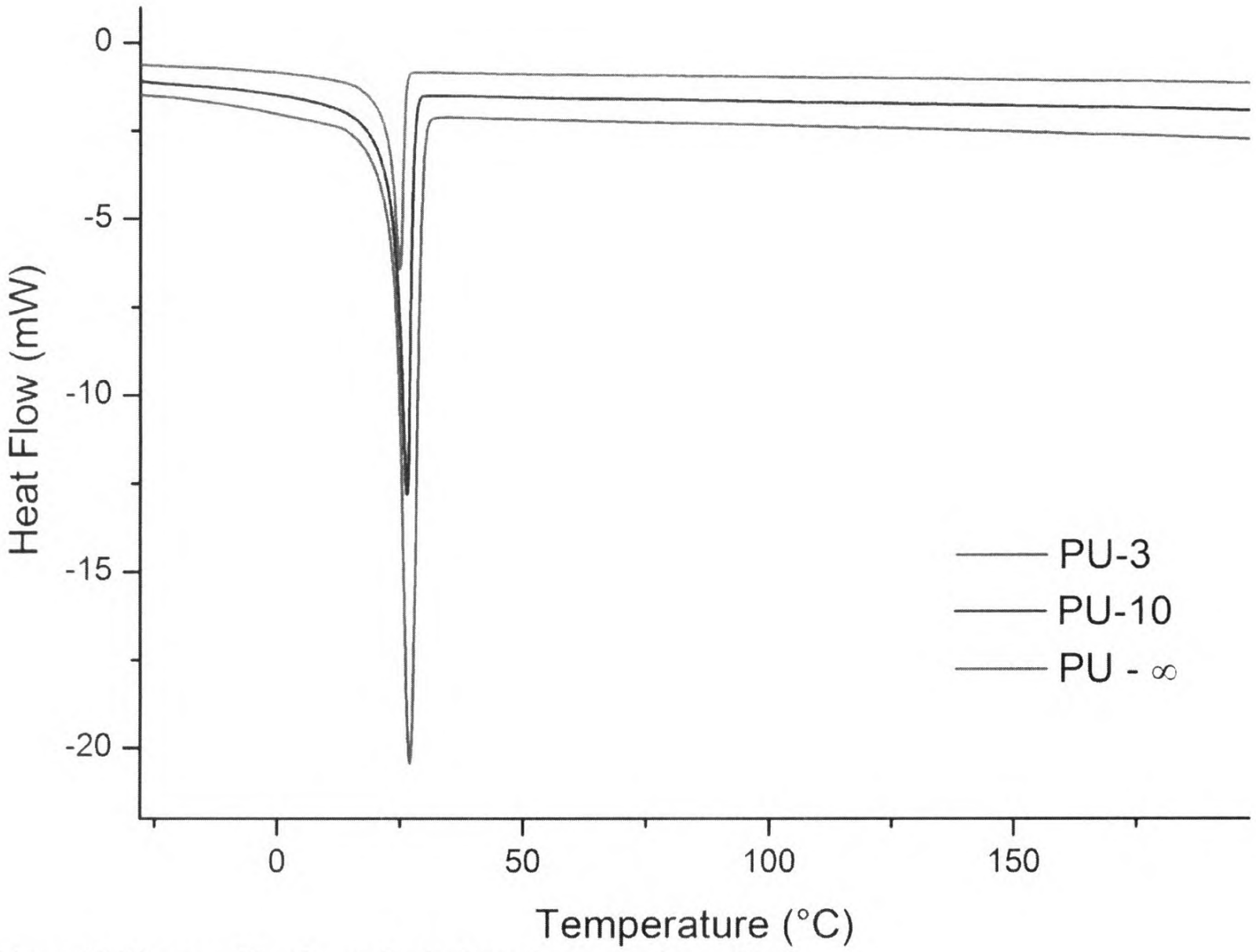


Figure 15: The second heating cycle of polyurethane prepolymer films

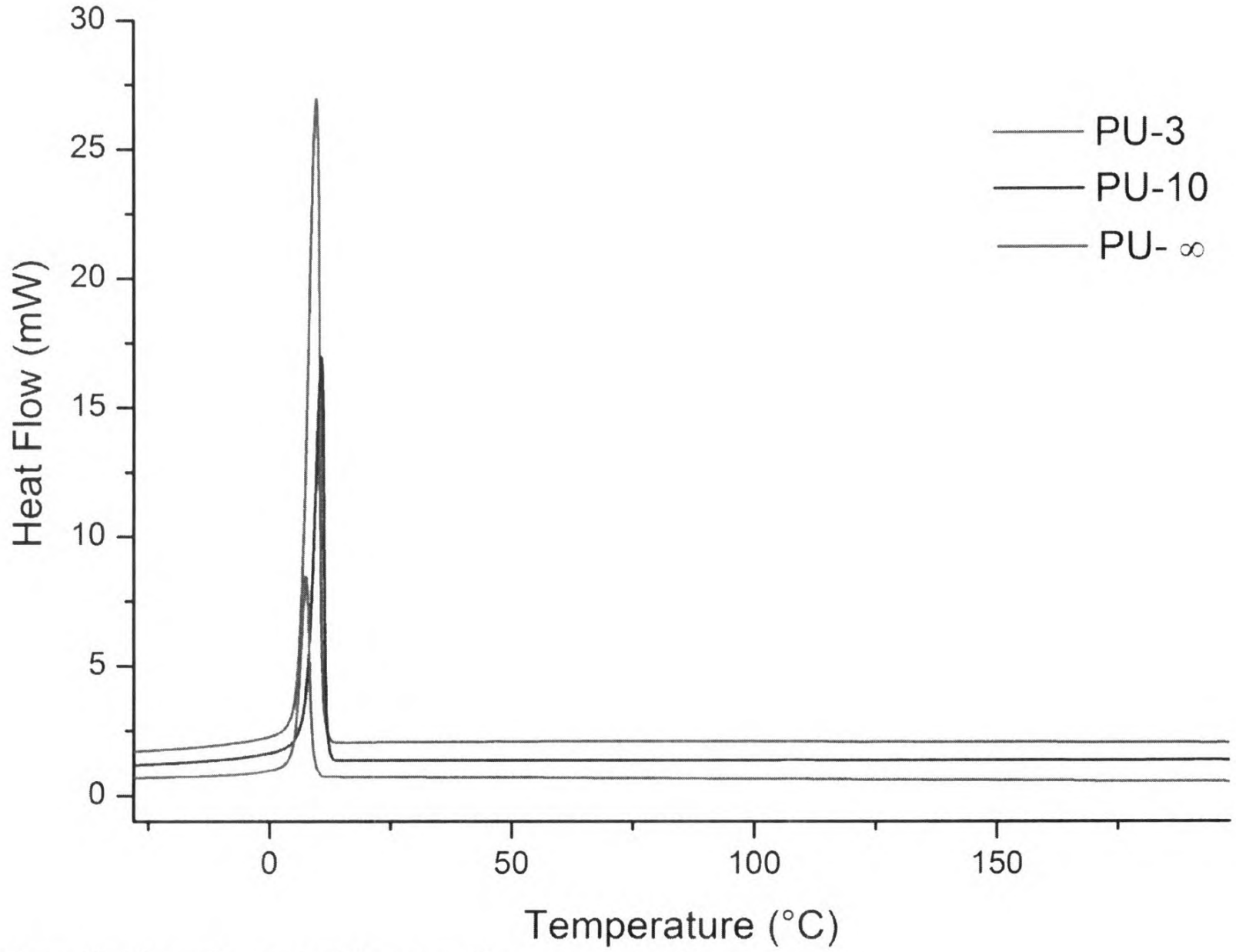


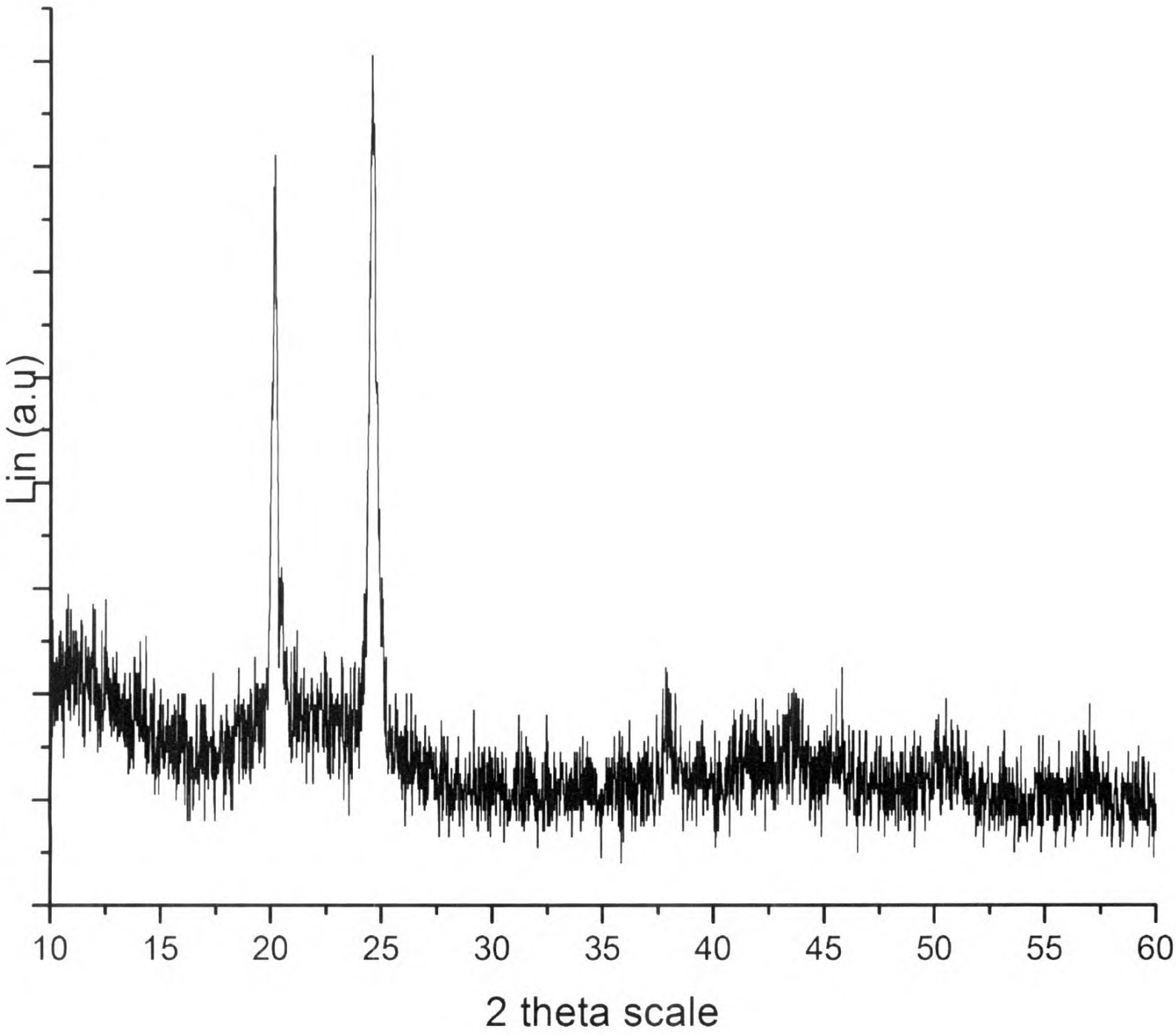
Figure 16: The cooling cycle of the polyurethane prepolymer films

The DSC analysis of the polyurethane film showed that the polyurethane films had a crystalline melting peak around 25 ^{0}C. The absence of an exothermic peak (T_c) before the melting endotherm (T_m) showed that the material had reached the highest possible crystallinity. As crystalline melting of PU hard segments generally occurs above 100 ^{0}C, this cannot be due to hard segment melting. According to literature melting of PTHF components in polyurethanes can be observed around 25 ^{0}C. (84,85) Hence, the melting endotherm of the DSC can be assigned to the crystalline melting of soft segment which is consisted of polytetrahydrofuran. The long chain polytetrahydrofuran occupies a large volume in the polymer and would produce highly crystalline areas. The absence of a glass transition in the thermogram confirms that the soft segment of the PU film formed by polytetrahydrofuran is not randomly oriented but highly crystalline. The highly crystalline nature of the long chain soft segments might have restricted the formation of crystalline hard segment bundles which are generally expected to be in the PU film. The unbound hard segments embedded in the crystalline soft segment areas should be highly entangled and hence hydrogen bond formation is sterically restricted which in turn could have prevented the formation of crystalline hard segment bundles and exist as unbound hard segments. These unbound hard segments are called "isolated hard segments". (86,87) The absence of crystalline hard segment bundles which are formed via hydrogen bonds at urethane linkages was able to confirm by the FT-IR spectra of the films. As there was no indication of hydrogen bonded NH groups in FT-IR spectra (Figure 36) it is fair enough to assume that crystalline hard segment bundles are not available in the polyurethane films. According to these observations, those polyurethanes have a microstructure consisting of randomly trapped isolated hard

segments with in the highly crystalline soft segment matrix. The soft segment crystallinity was able to confirm by the XRD results as well.

XRD

The XRD pattern of the PUP-3 prepolymer film is shown in Figure 17.


Lin (a.u)
10
15
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2 theta scale

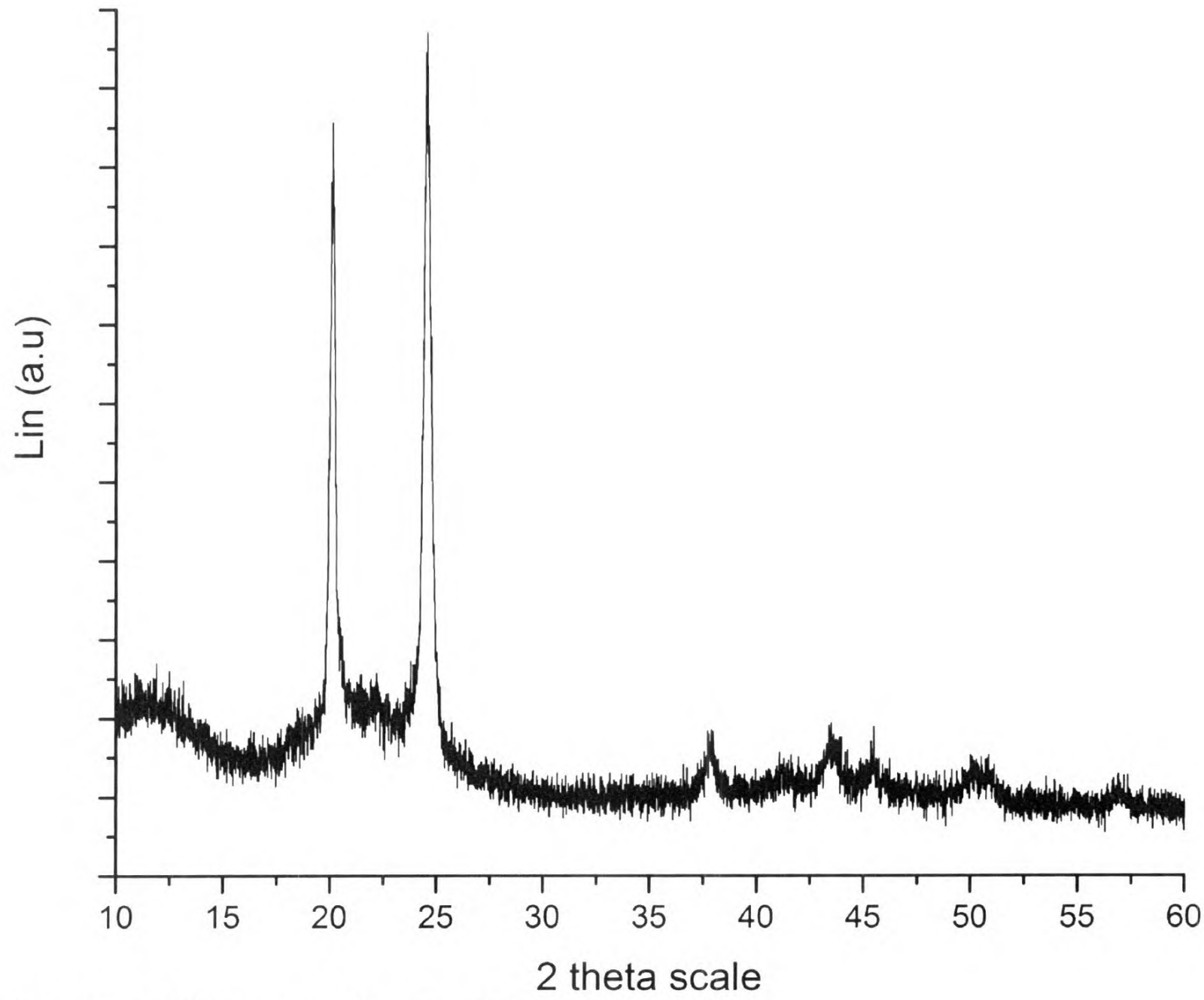


Figure 17 : The XRD pattern of the polyurethane prepolymer PUP-3

The diffraction pattern which is obtained from prepolymer is similar to the pattern corresponding to the crystalline PTHF. (88,89) This shows that the prepolymer PUP-3 has a microstructure consisting of crystallized soft segment matrix which is clearly matched with the DSC results.

UV absorbance of polyurethane films

In order to determine the wavelength corresponding to absorption maximum (λ_{max}), absorption spectra of the polyurethane films were obtained. The absorption spectra are shown in the Figure 18.

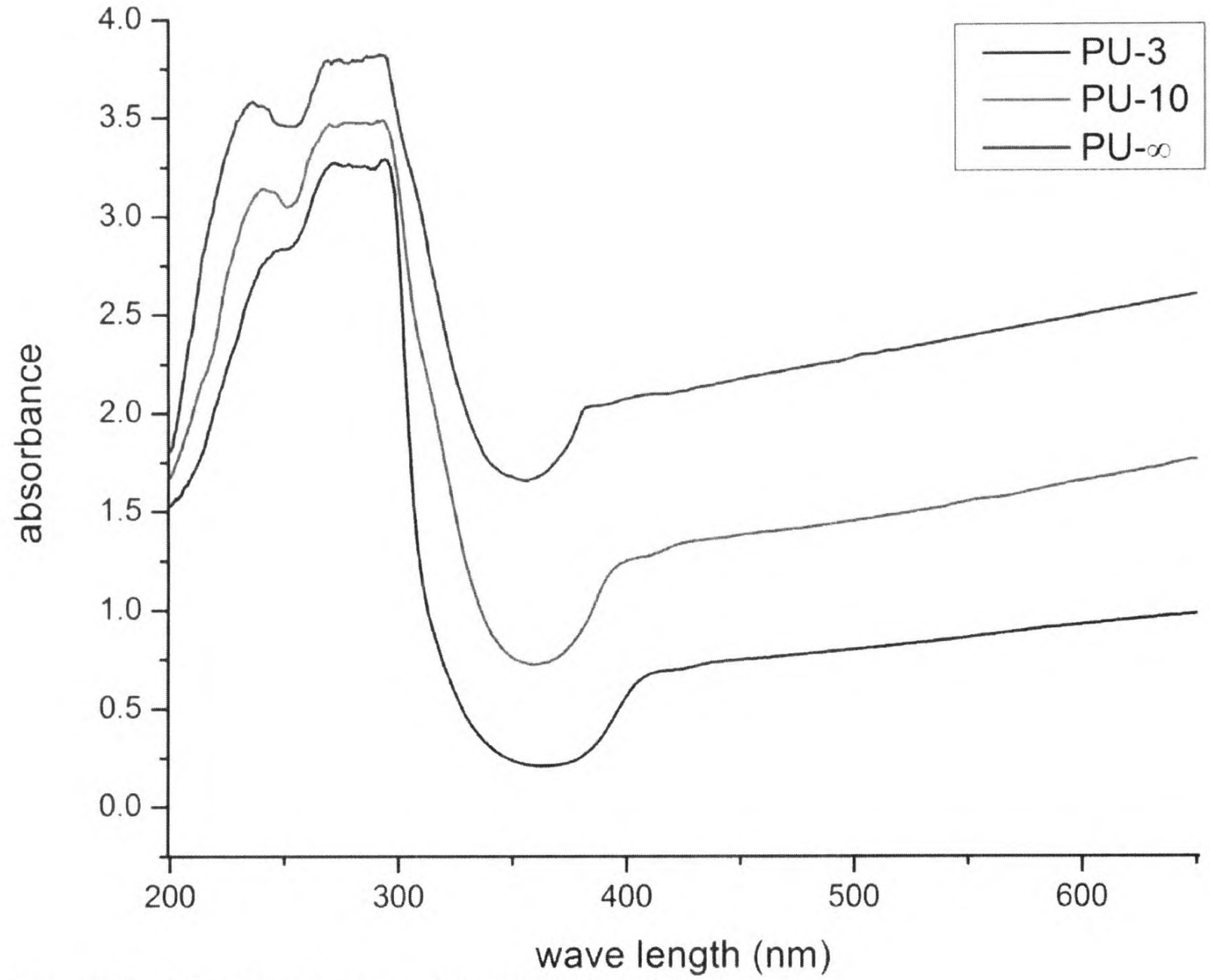


Figure 18: The UV absorption spectra of the polyurethane films

It was shown that PU films have an absorption maximum in the UV range and λ_{max} is located close to 293 nm.

Fluorescence study

Emission spectra of the polyurethanes were recorded while exciting the sample at 293 nm wavelength. The excitation wavelength was decided according to the UV-absorption spectrum of the polyurethane. The wavelength corresponding to absorption maximum was 293 nm, and hence it was selected as the excitation wavelength.

The initial study was started with the film obtained from the polyurethane having the degree of polymerization three. The emission spectrum of the polyurethane film was recorded and it was clear that the sample is fluorescing in such a way there was an emission peak. The emission spectrum of the polyurethane film is shown below.

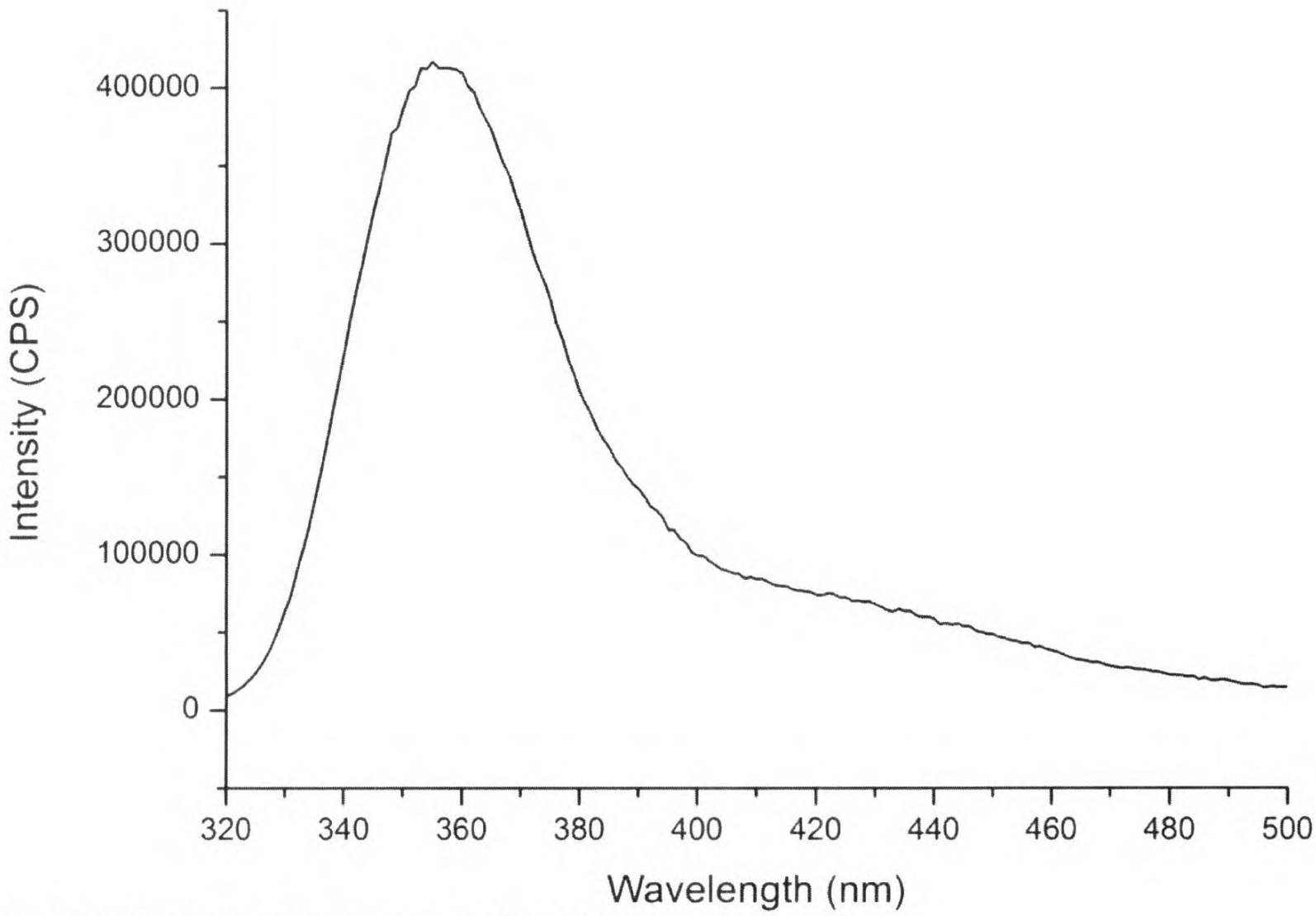


Figure 19: The initial emission spectrum of the PUP-3 film

Initially there was a single emission peak at 356 nm which was useful to prove that sample is fluorescing. Hence, a need to introduce an external fluorophore to the system to analyze the polyurethanes did not arise. Therefore, with the help of this internal fluorophore, fluorescence behavior of the polyurethane was further analyzed. It was observed that with the repeated recordings there were changes in spectrum. There was a reduction in intensity of the initially observed peak and the appearance of a new peak with continuous repeats. This interesting fluorescence behavior of PU films was focused for the further analysis. With the plan of studying this behavior, fluorescence spectrum of the polyurethane film was recorded repeatedly and variation of the peak intensities was considered. The variation in spectrums with number of repeats is shown below.

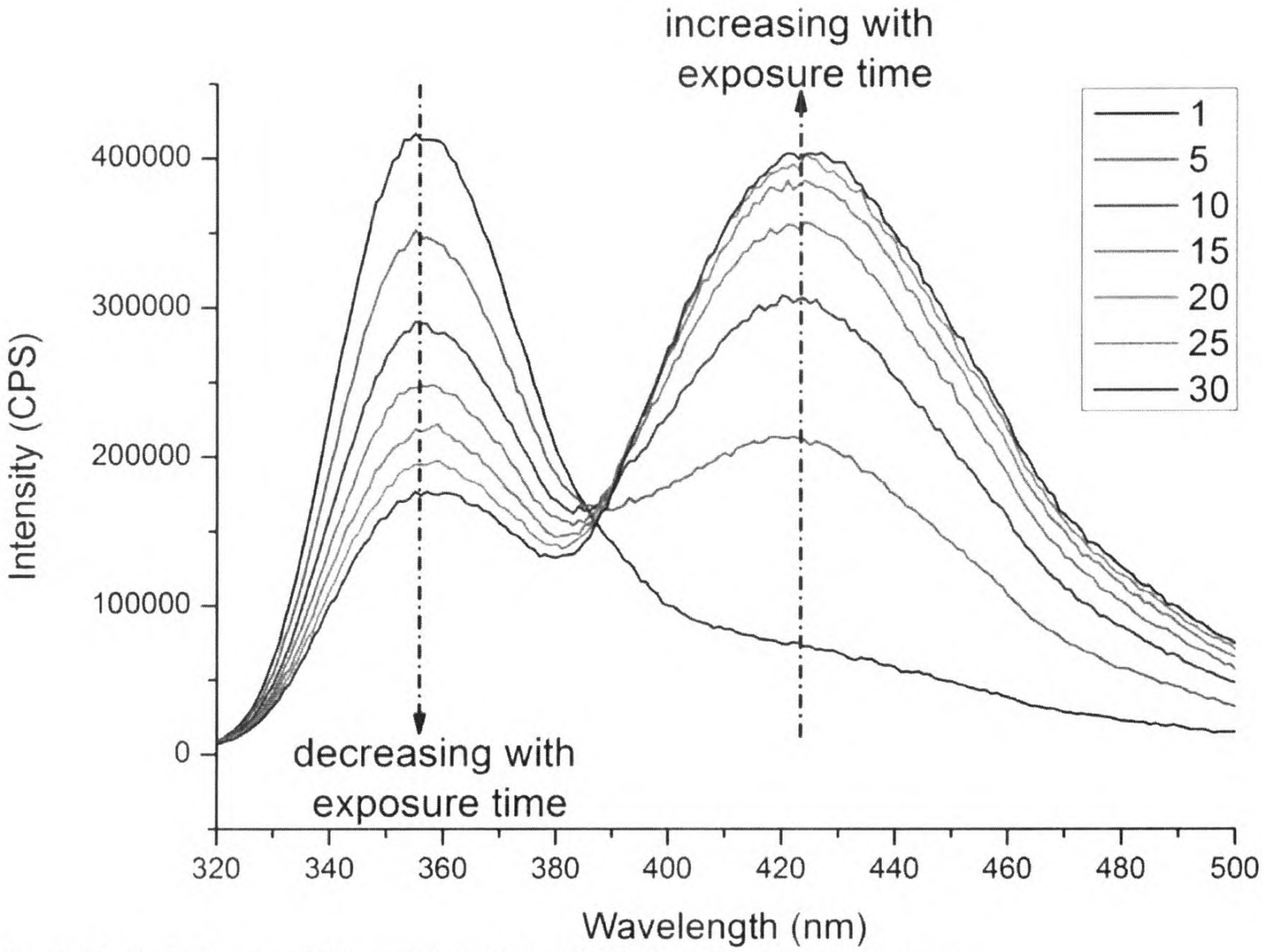


Figure 20: Variation of emission spectrum of the PUP-3 film with number of repeats

It was shown that the first peak which was at 356 nm was reduced with number of repeats and a second peak was appeared at 423 nm and intensity of that second peak was increased parallel to the decrease in first peak intensity. Variation of the intensities in two peaks is shown below.

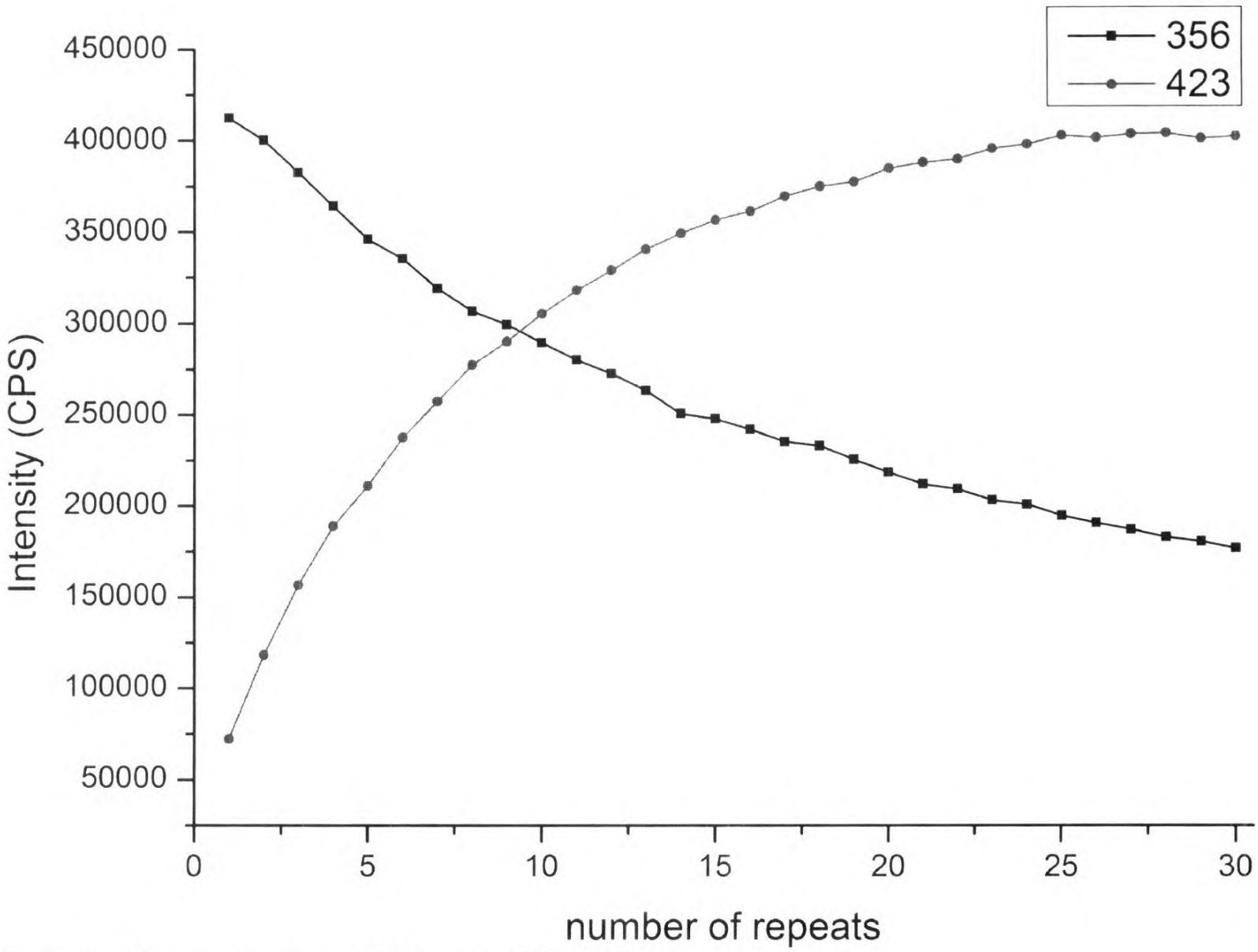


Figure 21: Variation of two peak intensities of PUP-3 film

As per the Figure 21, it indicates that, the intensity of the peak at 356 nm is reduced while that of the peak at 423 nm is increased. The extent of reduction and increase with respect to number of repeats was changed with time. When the number of repeats increases that extent was reduced. At initial repeats differences in intensities were high and at the later part of repeats the difference was very low. With number of repeats only a single factor of the system is varying. That is the exposure time to the 293 nm wavelength. It becomes higher and higher with number of repeats. Each scan can be accounted as a 30 s exposure to the 293 nm wave length. A smooth decrease of 356 nm emission with increasing exposure to 293 nm and a simultaneous increase of the intensity of the peak at the 423 nm indicate that 423 nm emitters were produced by a photo induced process at the expense of 356 nm emitters.

Before expand the study it was compulsory to identify the origin of the fluorophore. Fluorescence spectra of reactants were recorded. The emission spectra of reactants DMAc, DABCO, PTHF, and MDI are shown below.

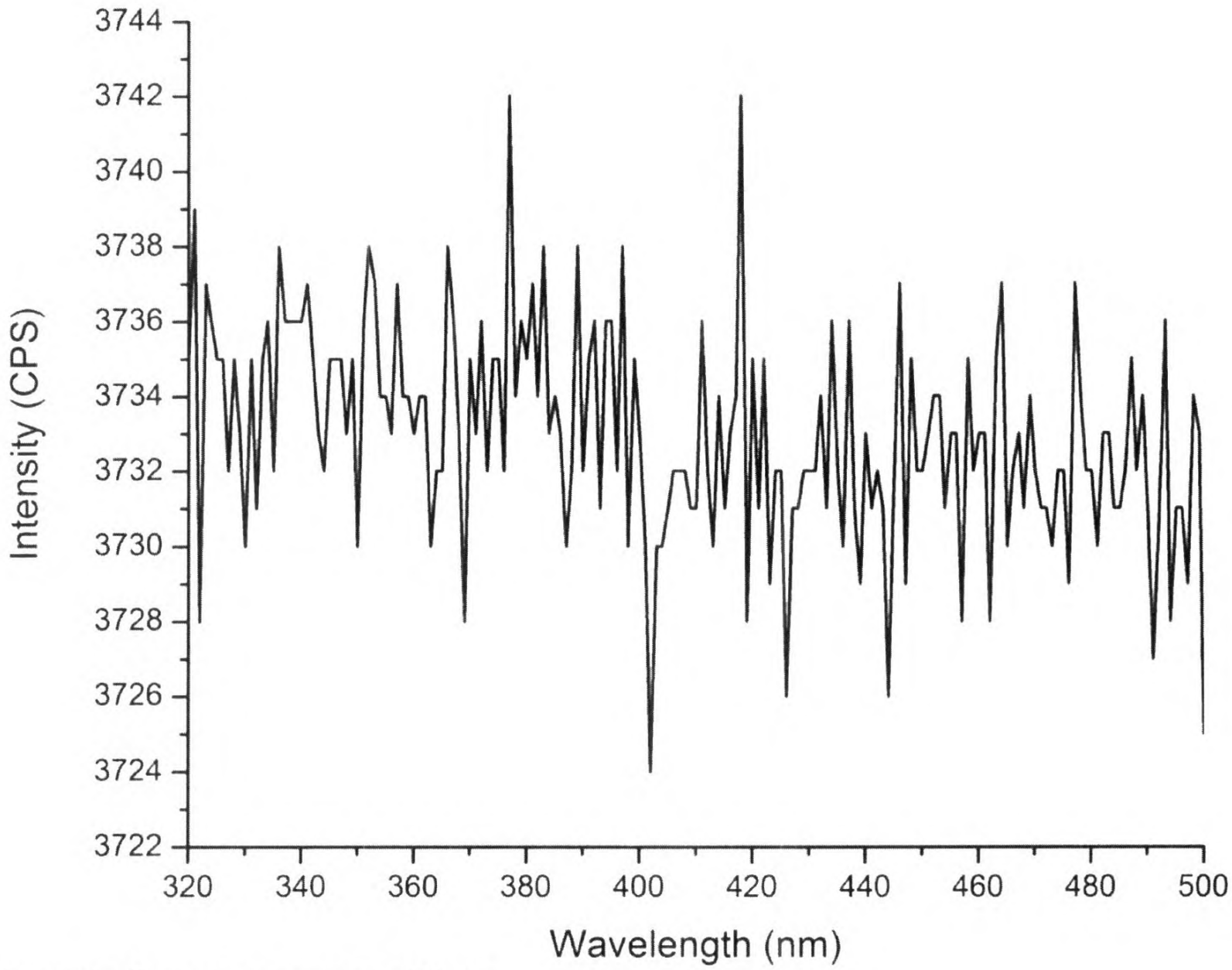


Figure 22: The emission spectrum of DMAc

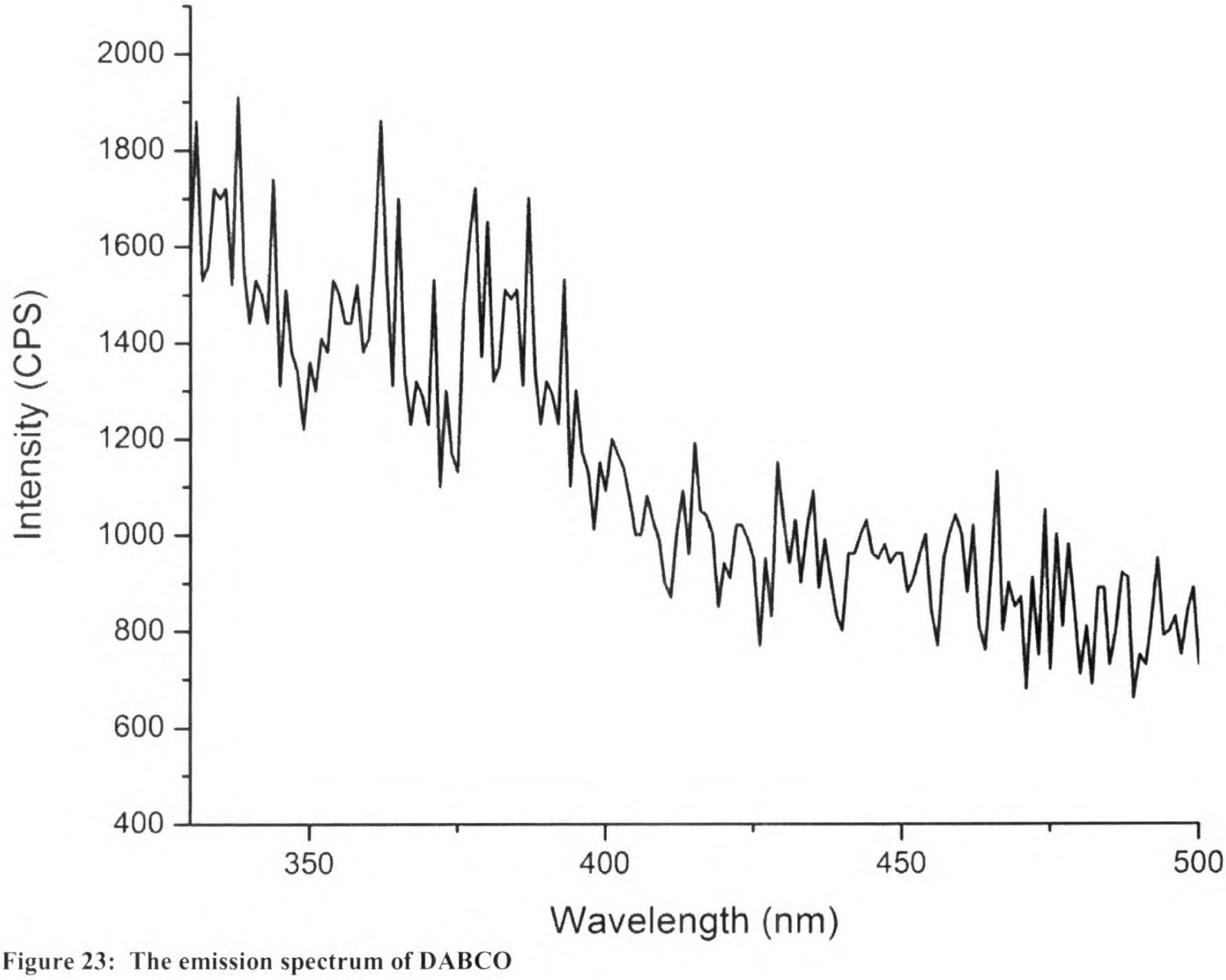


Figure 23: The emission spectrum of DABCO

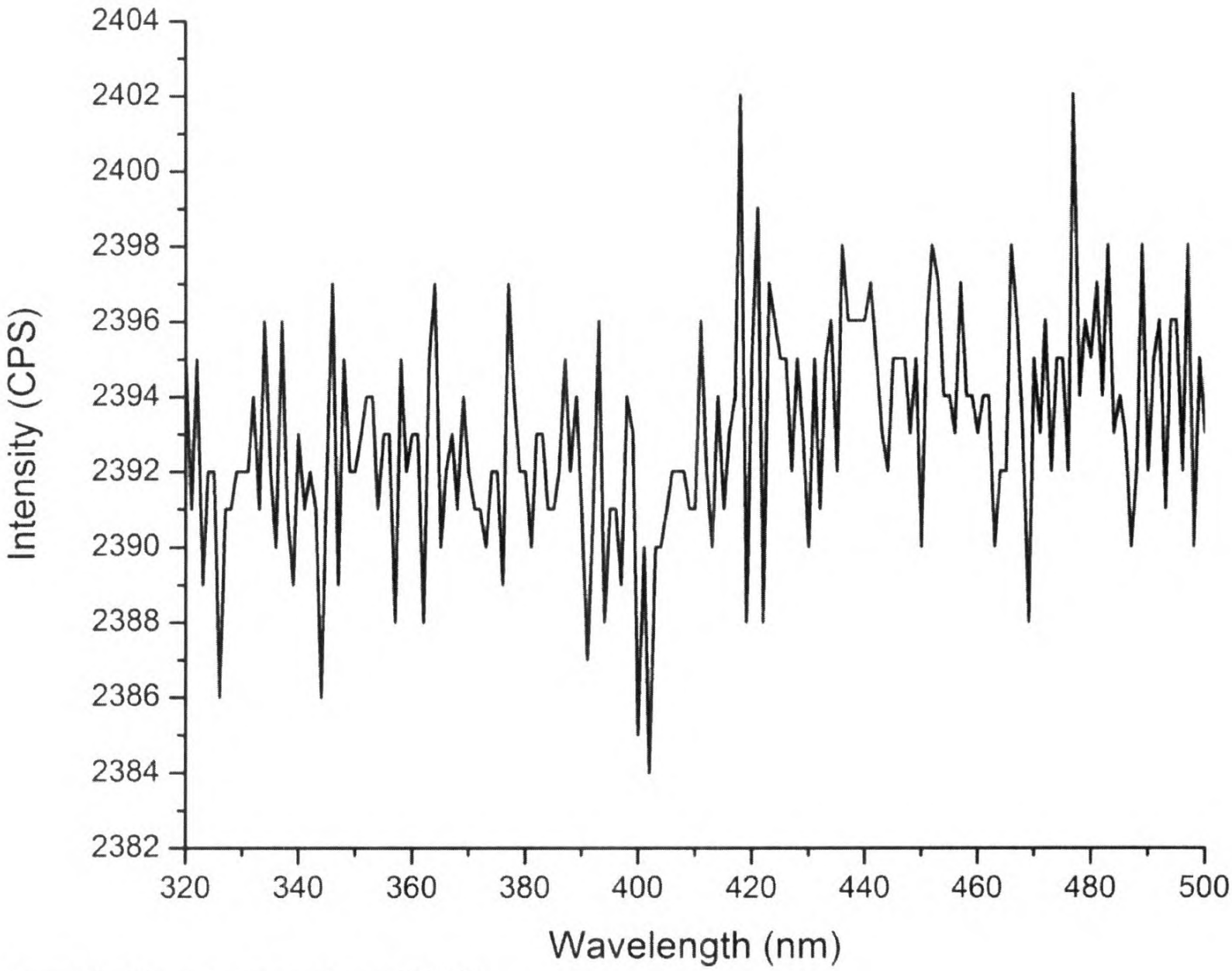


Figure 24: The emission spectrum of PTHF

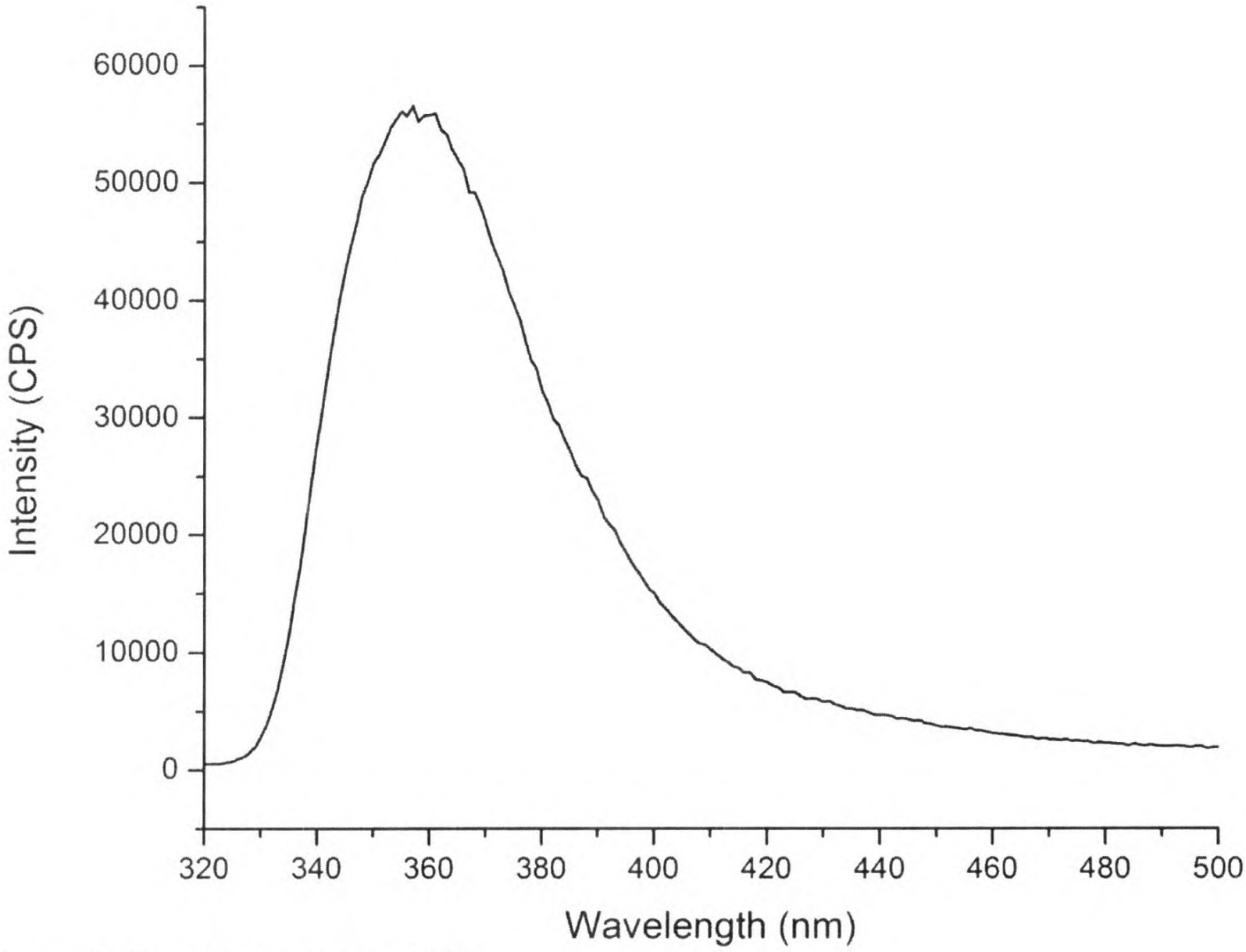


Figure 25: The emission spectrum of MDI

Therefore, it was clear that structure of MDI is responsible for the 356 nm emission and none of other reactants contribute to the emissions. However, there is a possibility that the observed fluorescence is due the unreacted MDI in the PU film. However, when highly reactive MDI was used in excess to have NCO:OH molar ratio of 1:2, possibility of finding an unreacted MDI in the solvent based system is very remote. The other evidence to prove this is that observed variation in emission intensities in polyurethane was not observed in MDI. That is MDI emission spectrum did not change with repeated exposure to UV irradiation. The comparison of emission spectra of MDI in the first and tenth repeat is shown below.

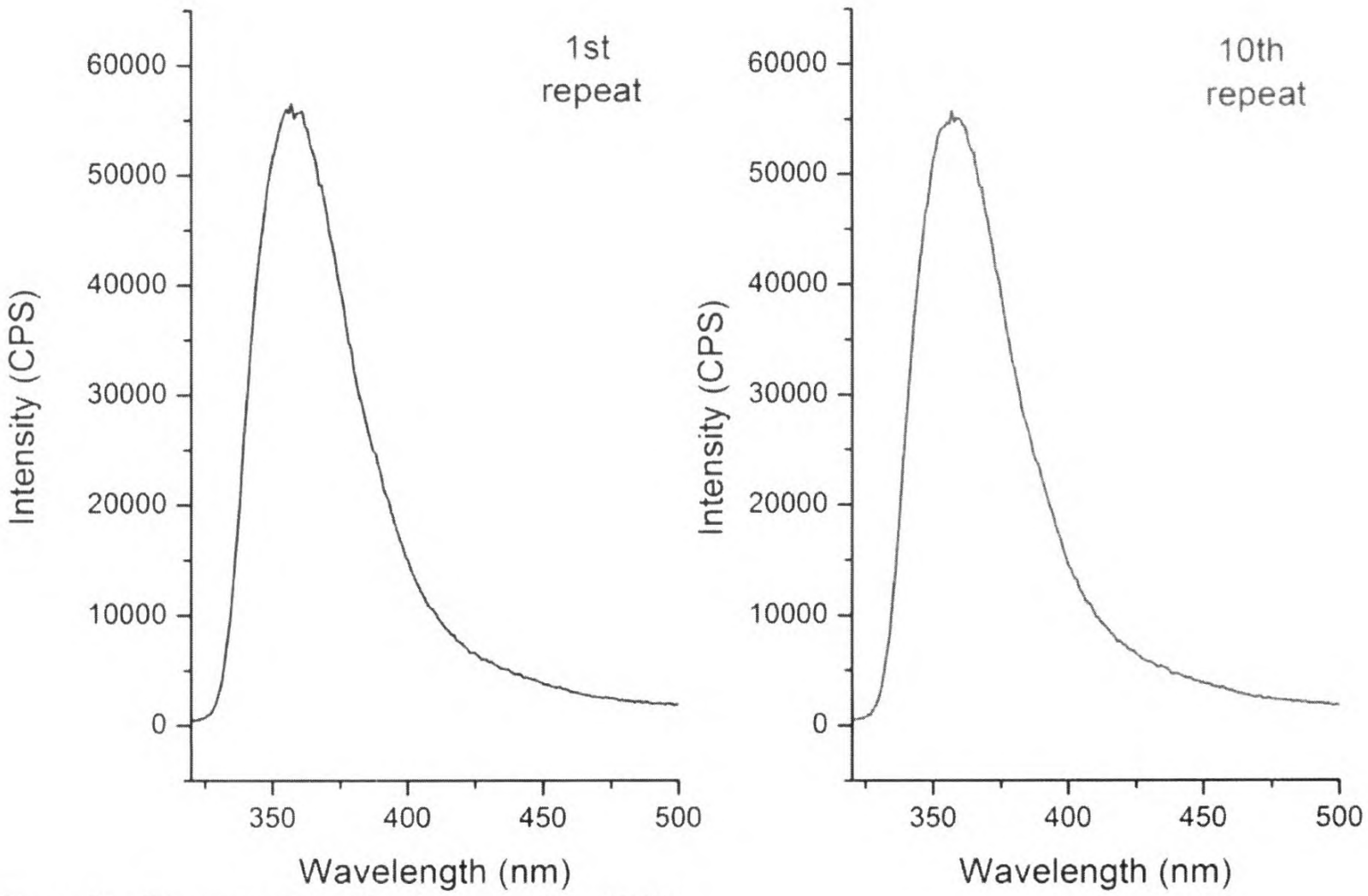


Figure 26: The comparison of emission spectra of MDI

The exposure of MDI to 293 nm light did not produce significant change in the emission at 356 nm compared to changes observed in spectra for PU films. By comparing the fluorescence behaviors shown by MDI and polyurethane, it can be assumed that the fluorescence behavior of the film had emanated from the hard segments of the polyurethane which contained the fluorophores originating from MDI but not from the free MDI.

Having identified the fluorophore, it is necessary to find the reasons for the behavior observed by polyurethane films. It is apparent that 423 nm emitters were generated by consuming the 356 nm emitters. There are several possibilities which can lead to the increase of 423 nm intensity with the reduction of 356 nm intensity. It may be due to formation of excimers, or formation of photo products via photo induced reactions such as degradation. One of the special features shown by the fluorescence behavior of polyurethane films was able to rule out that this is not due to a new photo product. It was the reversibility in fluorescence behavior. If this 423 nm emission is due to a photo product, just by discontinuing the UV exposure it is impossible to go back to initial state via bond breaks or formations. When the UV exposed polymer was kept out of light for three days, the peak at 356 nm increased and the peak at 423 nm decreased. Again with continuous recordings, the intensity of 356 nm peak was reduced and 423 nm peak was increased. These results suggest that the fluorescent behavior of the polymer is reversible. Therefore, it is clear that this behavior is not due to photo degradation product. The exposure to UV – cease of UV cyclic process was repeated for three complete cycles. The variations of two peak intensities are shown below.

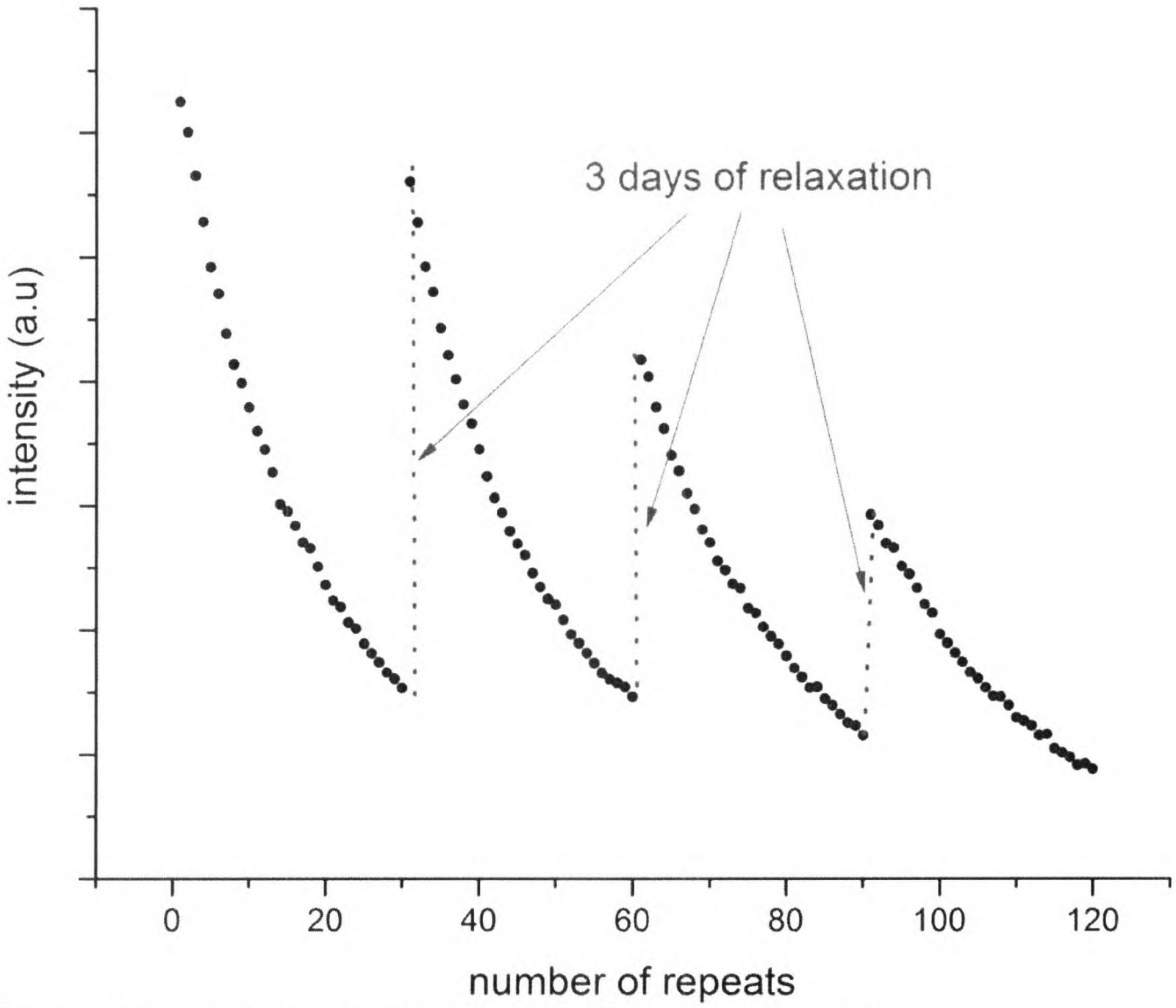


Figure 27: The variation in 356 nm peak intensity with UV exposure and relaxation

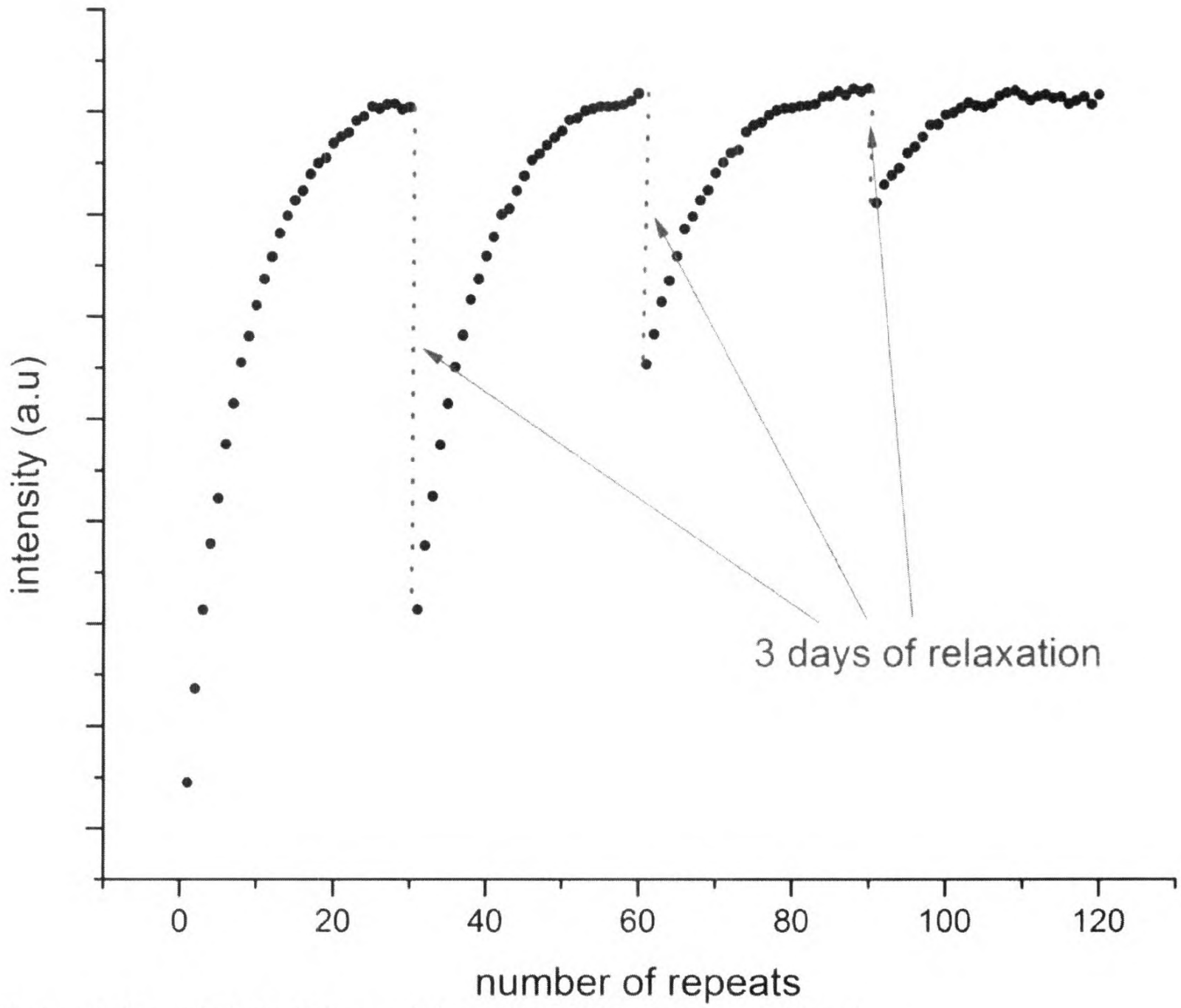


Figure 28: The variation in 423 nm peak intensity with UV exposure and relaxation

Exponential type decay was shown by the 356 nm emission intensity with respect to irradiation time while an exponential type growth was shown by the 423 nm emission intensity. When re-excited after 3 days of relaxation, the 356 nm emission intensity was increased while the 423 nm intensity was decreased.

As this reversibility is an important factor which helps to determine the actual process happens inside the polyurethanes with the UV exposure, study was expanded in such a way to analyze the effect of different variables on the reversibility shown in the polyurethane fluorescence behavior.

Effect of relaxation time on the fluorescence

In the above study, the relaxation time (UV cease time) after the continuous exposure was three days. In that case 100% reversibility was unable to achieve. With the purpose of check whether is there any possibility of achieving the complete reversibility by varying the relaxation time, the percentage reversibility with respect to different relaxation times was measured.

In each case of relaxation time, a similar fluorescence behavior was observed. In other words initially there was a single peak, and then with continuous exposure there was a reduction in first peak intensity while appearing a new peak and increase in second peak intensity, and also with the relaxation there was a partial re-increase in first peak intensity and parallel reduction in second peak intensity. The intensity variation of two peaks with respect to different relaxation times is shown in Figure 29.

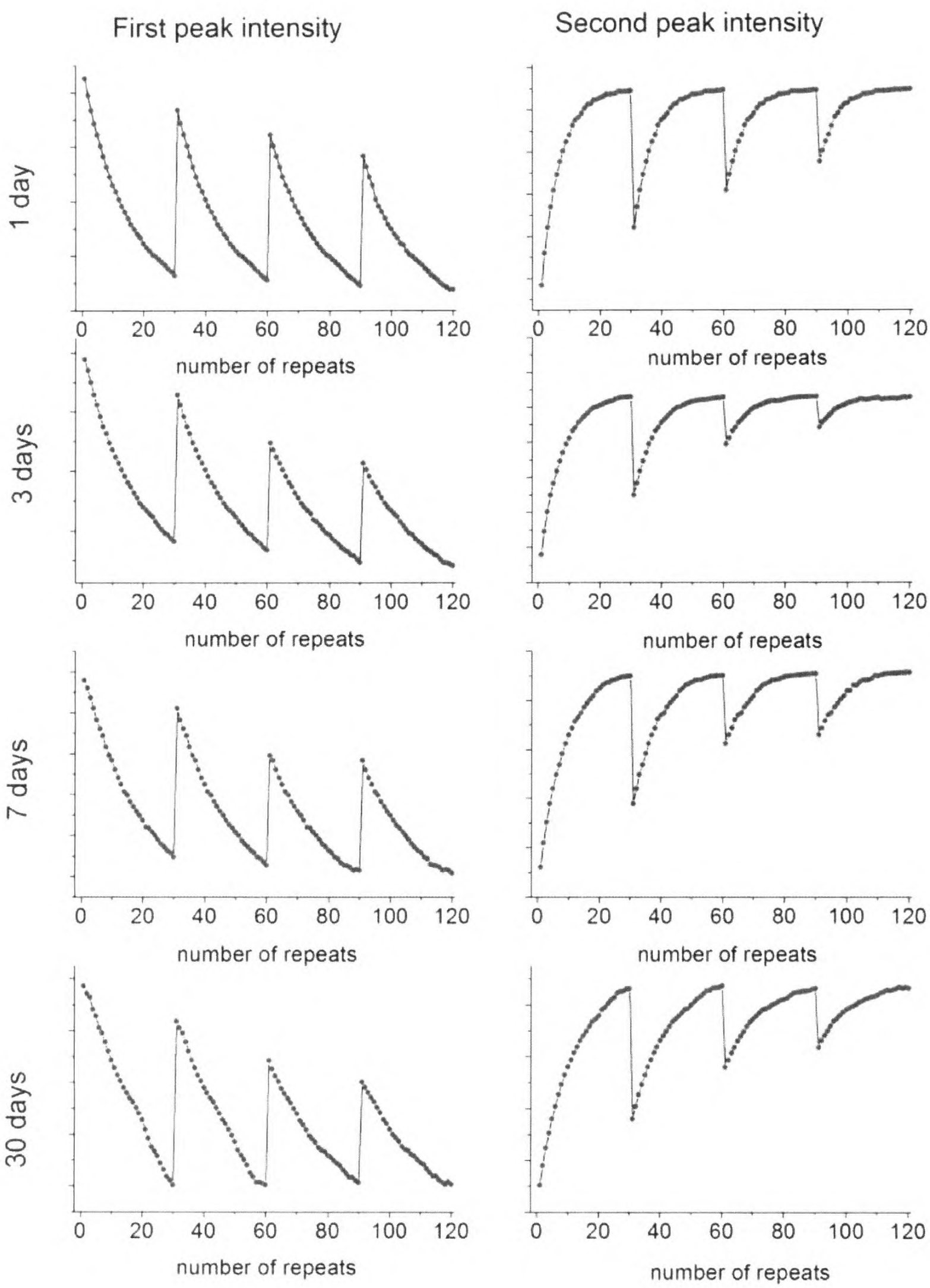


Figure 29: The intensity variation with relaxation time

The percentage reversibility was calculated according to the following equation.

$$\textbf{percentage recovery} = \frac{\textit{intensity of the 1st peak in the first repeat of second day}}{\textit{intensity of the 1st peak in the first repeat of first day}}$$

Equation 3: The equation which is used to calculate the percentage recovery

The effect of the relaxation times on percentage reversibility is tabled below (Table 4)

Table 4: Percentage reversibility with respect to different relaxation times

Relaxation time	Percentage recovery
1 day	90.6
3 days	89.8
7 days	92.1
30 days (1 month)	91.3

As shown in Table 4, percentage recovery after one day is greater than three days but smaller than seven days. So it was found that there was not any correlation between the percentage reversibility and relaxation times. Even after one month it was unable to achieve 100% reversibility. Hence, it can be assumed that only a partial reversibility is achievable even after infinite relaxation. In other words 100% reversibility cannot be obtained.

Effect of exposure time on the fluorescence

The exposure time is also one such factor which can be varied to check whether there is an effect from that to percentage reversibility. As each scan amounted to 30 s of UV irradiation at 293 nm wavelength, the exposure time was varied by changing the number of repeats per one continuous recording cycle. The intensity variation of two peaks with respect to different exposure times is shown below.

By calculating the percentage reversibility according to the Equation 3, the percentage reversibility with respect to exposure time is tabled below.

Table 5: The percentage reversibility w.r.t different exposure times

Number of repeats per cycle	Exposure time (min)	Percentage recovery (%)
20	10	92.2
30	15	86.8
40	20	89.8
50	25	89.7
60	30	89.8

According to the tabulated results, with the increase of exposure time there is a random variation in percentage recovery instead of smooth increase or decrease in percentage recovery. Therefore, it was able to conclude that the exposure time also does not have a correlation to the percentage reversibility.

Effect of degree of polymerization

By varying the degree of polymerization it was able to obtain three polyurethane systems having three different chain lengths. In other words, the average number of monomers per polymer chain was varied. Using these three systems the effect of chain

length on fluorescence behavior was analyzed. It was clear that once the precursors are same, even though the chain lengths were varied through the variation of degree of polymerization, a similar fluorescence behavior was shown by all three systems. In other words, all three systems showed a single peak at initially and with the exposure time there was a generation and growth of a second peak at higher wave length while reducing the first peak intensity. In addition to that the partial reversibility of the fluorescence intensity was also observed in all three systems.

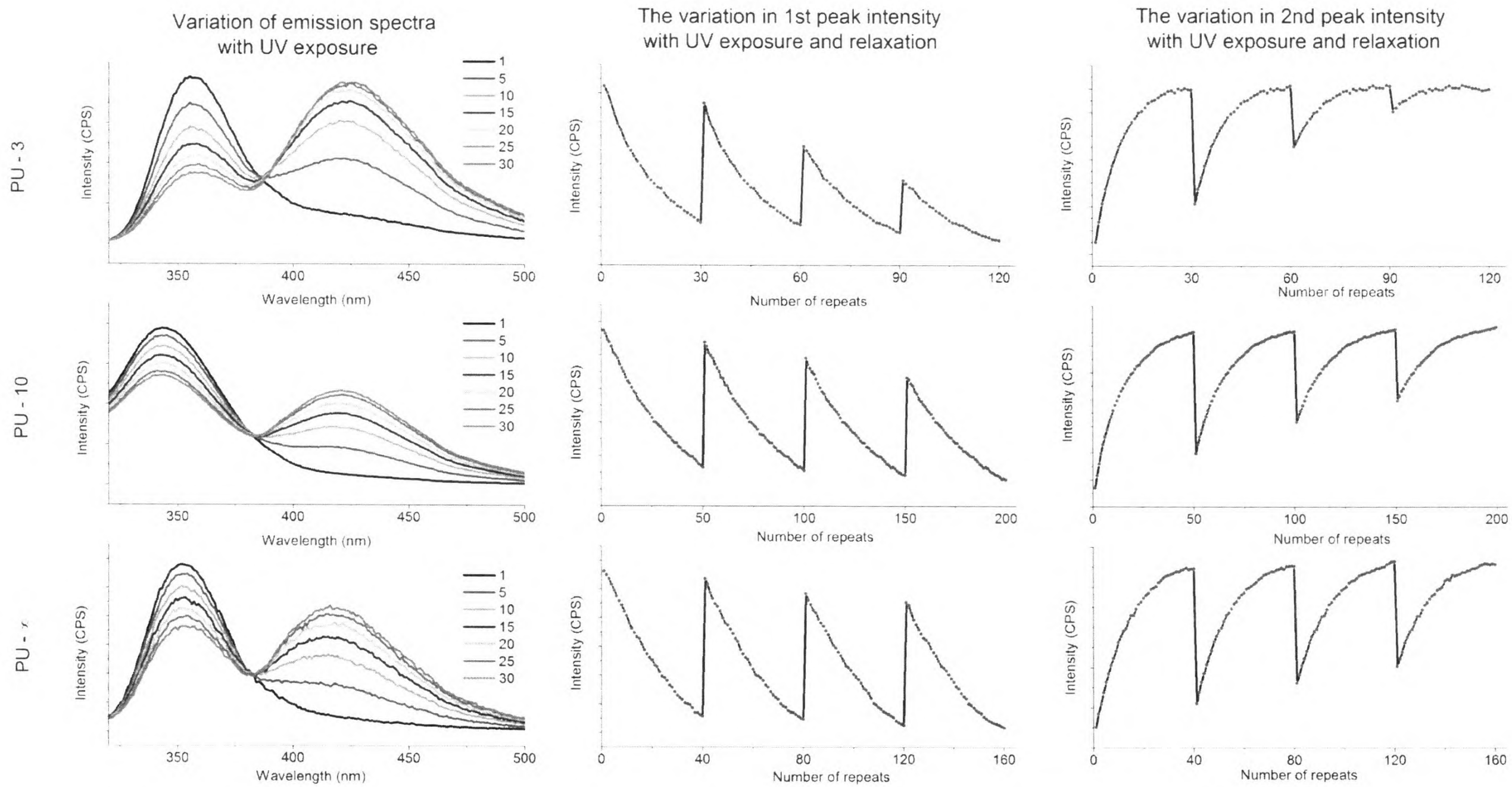


Figure 30: The fluorescence behavior of three polyurethane prepolymers

Hence, it was clear that this partially reversible florescence behavior was observed in polyurethanes prepared using MDI and PTHF irrespective to exposure time, relaxation time and the polymer chain length.

Effect of solvent

The solvent effect was investigated considering polyurethane having the degree of polymerization three. In order to investigate the effect of solvent, a new polyurethane system was prepared using a similar composition to the PUP-3 system but in a different medium. Instead of DMAc, DMF was used as the solvent here and was labeled as PUP-3_{DMF}. Similar to the PUP-3 system, initially there was a single peak and appearance and growth of a second peak while reducing the first peak was observed with continuous exposure. The Figure 31 shows the initial emission spectrum and how the fluorescence spectra varied with UV exposure.

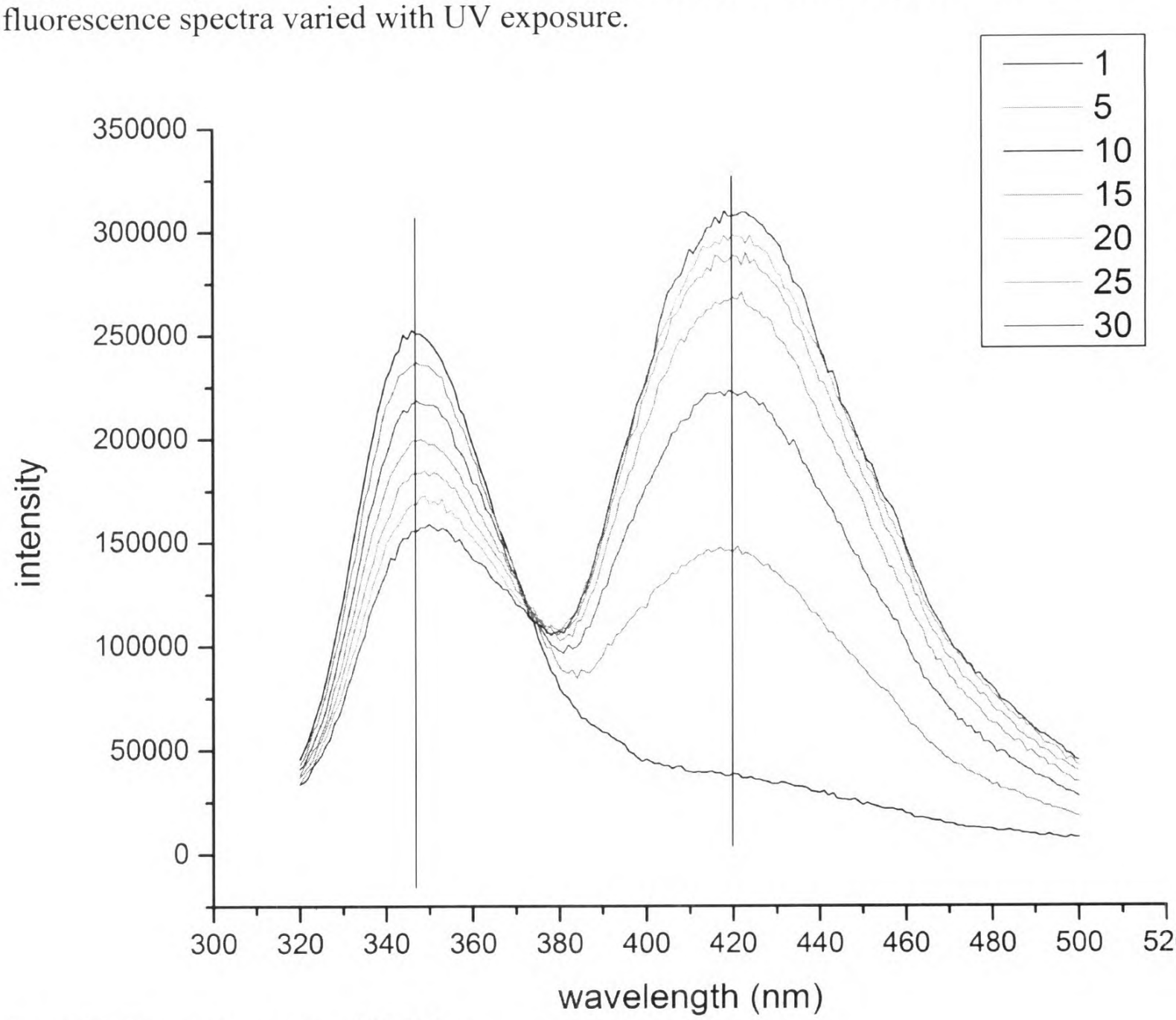


Figure 31: The spectra overlay of PUP-3_{DMF}

However, in contrast to PUP-3 system, PUP-3_{DMF} did not show reversibility in the fluorescence behavior. After 3 days of relaxation, the fluorescence signal was similar to the emission spectrum obtained in the last repeat of the first day.

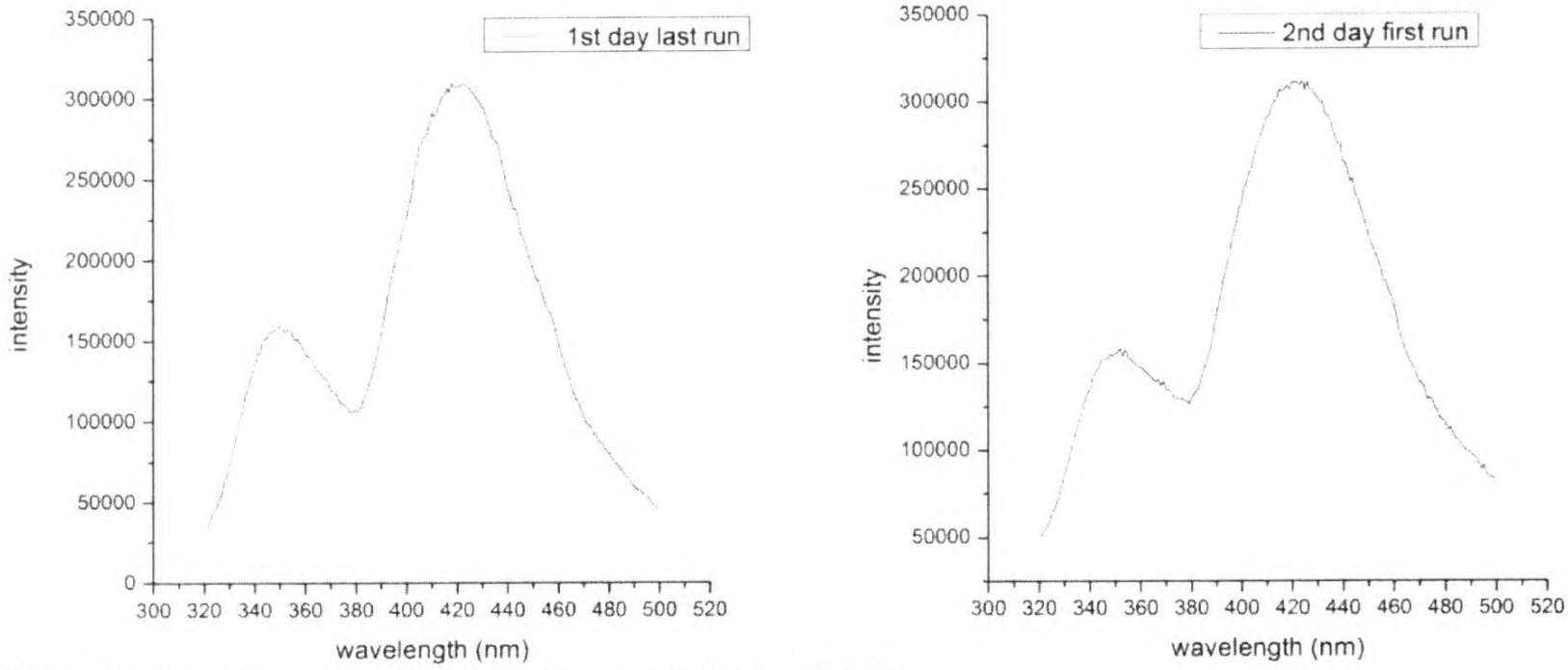


Figure 32: The non-reversibility of fluorescence behavior of PUP-3_DMF

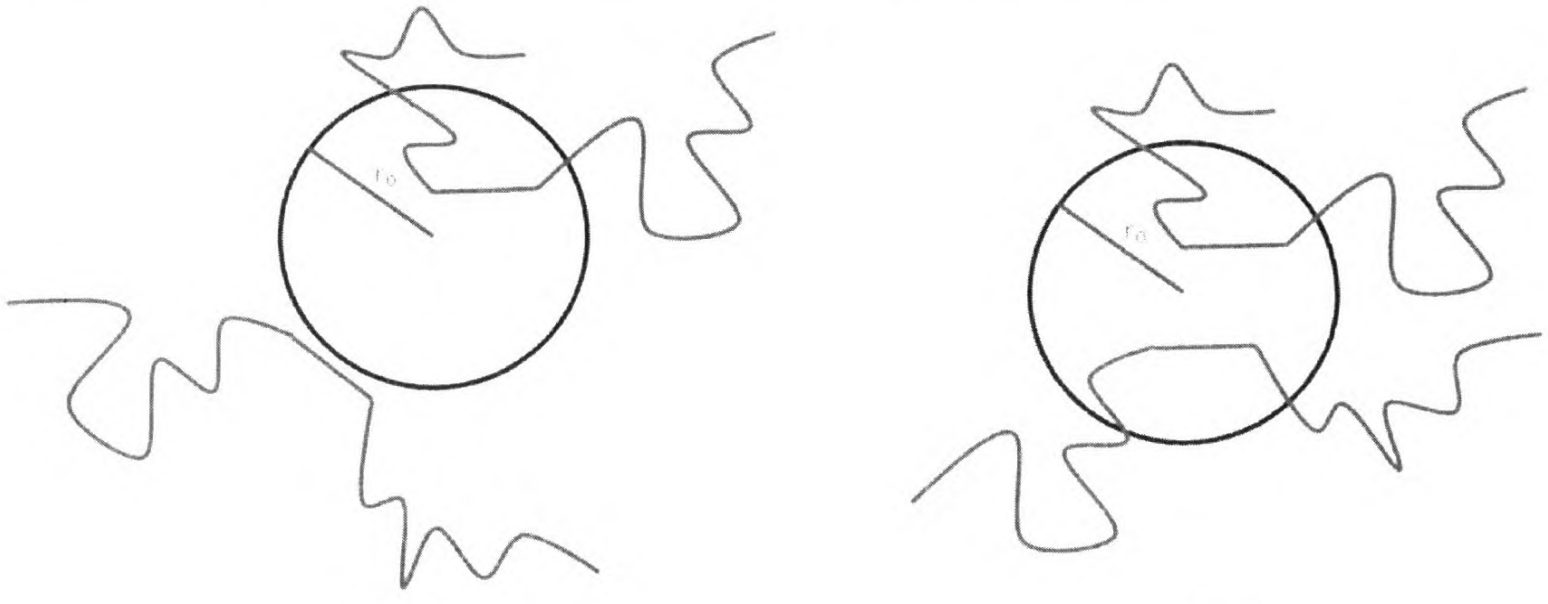
Hence, it is clear that there is an effect to the fluorescence behavior of the polyurethanes from the solvent. After explaining the overall picture of the fluorescence behavior in the following section, the way that solvent effects to the fluorescence behavior will be discussed.

The careful analysis of results shows that fluorescence behavior observed cannot be directly explained by the conventional excimer formation. (34) If it is a conventional excimer formation just after the UV cease the longer wavelength peak intensity should go back to its initial position. But the reversibility was partial. This suggests that this fluorescence behavior cannot be described directly via excimer formation.

Even though this reversible fluorescence behavior cannot be explained directly via a single process, it can be well explained using a series of interconnected processes.

The scenario behind this partially reversible fluorescence behavior

In order to explain this florescence behavior, it is important to explain when and how reactions get started. Generally reactions occur when molecules are close enough to interact with each other, thereby; the effective reaction rates depend on the local concentration of reactants rather than the global concentration. This can be mathematically modeled using an imaginary sphere drawn around a reactant molecule which is called the reaction sphere (Figure 33). Once a reactant meets the other member of the reaction within its reaction sphere, eventually the reaction occurs.



(a) (b)

Figure 33: The reaction spheres; the brown color lines indicate the hard segments of polyurethanes while blue color lines for soft segments (a) the situation where hard segments cannot react together (b) the situation where the hard segments can react together as they met each other within the reaction sphere

With that understanding, it was able to propose an explainable mechanism well matched with this fluorescence behavior. In order to explain this behavior the micro-structural arrangement of the polyurethane film is very important. According to the DSC thermograms of the polyurethane film (Figure 14, Figure 15, Figure 16) micro-structure of polyurethane is consisting of the unbound hard segments (isolated hard segments) embedded in the crystalline soft segment areas.

It was able to propose a mechanism based on the polyurethane micro-structure to explain what kind of photo chemical and physical processes are happened in the polyurethane film during the UV exposure. The proposed mechanism is shown below. In that mechanism; M stands for isolated hard segments while M_2 for ground state dimers. M^* and M_2^* stands for their excited species respectively. $M^{\#}$ represents an intermediate; the hard segments which are close enough to form H-bonds.

1) $M + h\nu_{293\ nm} \xrightarrow{k_1} M^*$ *(excitation of isolated hard segments)*

2) $M^* \xrightarrow{k_2} M + h\nu_{356\ nm}$ *(relaxation of excited isolated hard segments)*

3) $2M \xrightarrow{k_3} M_2$ *(dimer formation)*

   a. $2M \xrightarrow{k_{3a}} 2M^{\#}$ *(diffusion process)*

   b. $M^{\#} + M^{\#} \xrightarrow{k_{3b}} M_2$ *(hydrogen bond formation)*

4) $M_2 \xrightarrow{k_4} M_2^*$ *(excitation of the dimers)*

   i. $M^* + M_2 \xrightarrow{k_{4i}} M_2^* + M$ *(energy transfer process)*

   ii. $M_2 + h\nu_{293\ nm} \xrightarrow{k_{4ii}} M_2^*$ *(direct excitation process)*

5) $M_2^* \xrightarrow{k_5} M_2 + h\nu_{423\ nm}$ *(relaxation of excited dimers)*

6) $M2 \xrightarrow{k_6} 2M$ *(dimer dissociation due to tensile forces)*

Figure 34: The proposed mechanism to explain the fluorescence behavior

Before explain in detail, the mechanism consists of 6 basic steps. Simply isolated hard segments of the polyurethanes which contained the fluorophores originating from MDI (monomers) get excited by 293 nm wavelength and relaxed back to their ground state by emitting the 356 nm wavelength. Meanwhile the UV exposure leads to the formation of dimers via hydrogen bonding. The way it happens will be explained later. Then these dimers get excited and relaxed back to its ground state by emitting the 423 nm

wavelength. In addition to these photo chemical processes there is another process which is responsible to reversibility. It is the dissociation of the formed dimers.
By inspecting the mechanism in detail, it can be shown that the observed fluorescence behavior is well explainable through this mechanism. In the following section it will be explained that how properly this fluorescence behavior can be correlate with the mechanism.

Correlation of fluorescence behavior and the mechanism

Generation of the first peak

As per the proposed mechanism, the rate of reaction 2 corresponds to the emission intensity of 356 nm peak.

$$R_2 = k_2[M^*] \quad \text{; Equation 4}$$

In isothermal conditions the rate constant of reaction 2 (k_2) can assumed to be constant. Hence, the rate of the reaction 2 depends on the M* density. The M* density depends on the amount of available isolated hard segments. It is affected by excitation process (reaction 1), relaxation process (reaction 2) and energy transfer process (reaction 4_i).

$$\frac{\partial[M^*]}{\partial t} = k_1[M] - k_2[M^*] - k_{4i}[M^*][M_2] \quad \text{; Equation 5}$$

As excitation and relaxation processes are rapid compared to the time scale of the experiments, M* density cannot be affected by those two processes. Thereby, the contribution from $k_1[M]$ *and* $k_2[M^*]$ on the $\frac{\partial[M^*]}{\partial t}$ can be neglected. Therefore, the M* density depends on the available isolated hard segments and energy transfer process.
Initially the energy transfer process cannot happen as dimers (M_2) are not available in the system. Hence, the excitation process is only controlled by the availability of isolated hard segments.
Isolated hard segment density depends on initial isolated hard segment density and is affected by excitation process (reaction 1), relaxation process (reaction 2), dimer formation process (reaction 3) and dimer dissociation process (reaction 6).

$$\frac{\partial[M]}{\partial t} = -k_1[M] + k_2[M^*] - k_3[M]^2 + k_6[M_2] \quad \text{; Equation 6}$$

Excitation and relaxation processes can be considered rapid compared to the time scale of the experiments. Therefore, the time dependency of the availability of isolated hard segments is effectively controlled by the rates of dimer formation (reaction 3) and dimer dissociation (reaction 6).
At the initial excitation, contributions of reactions 3 and 6 are virtually absent due to the nonexistence of dimers at the beginning. The dimer formation is inhibited by the initial polyurethane microstructure. According to the DSC data (Figure 14, Figure 15, Figure 16) shows that the crystallinity of the polyurethane is governed by the soft segments. Hence, the isolated hard segments are trapped in the crystalline polytetrahydrofuran matrix. Those isolated hard segments are not close enough to form hydrogen bonds. The absence of hydrogen bonded hard segment bundles in the initial polyurethane film was proven by the FT-IR spectrum of the polyurethanes (Figure 36). The observed N-H peak at around 3367 cm^{-1} was corresponding to free NH and there was not any peak around the area corresponding to hydrogen bonded NH. Hence, initially dimers are not available in the system.
Initially, available isolated hard segments were not used for any other process but excited by 293 nm wavelength and relaxed back to their ground state while giving the

356 nm peak. As the maximum amount of isolated hard segments is available at this point, the intensity of 356 nm peak is highest here (initially).

Appearance and the growth of a second peak with reduction of first peak

According to DSC results, the initial polyurethane microstructure is consisting of isolated hard segments which are trapped in the crystalline polytetrahydrofuran matrix. The highly crystalline nature of the long chain soft segments has restricted the formation of hard segment bundles. In other words, dimers are not available. However, in subsequent excitations, the isolated hard segments can start to move to close to each other due to the localized melting in polyurethane films which is resulted owing to the UV exposure. Crystalline soft segments get melted and randomly oriented while allowing the hard segments to move. This facilitates the diffusion of isolated hard segments which were trapped in the crystalline polytetrahydrofuran matrix. This micro-structural change which occurred due to UV exposure is diagrammatically shown in Figure 35.

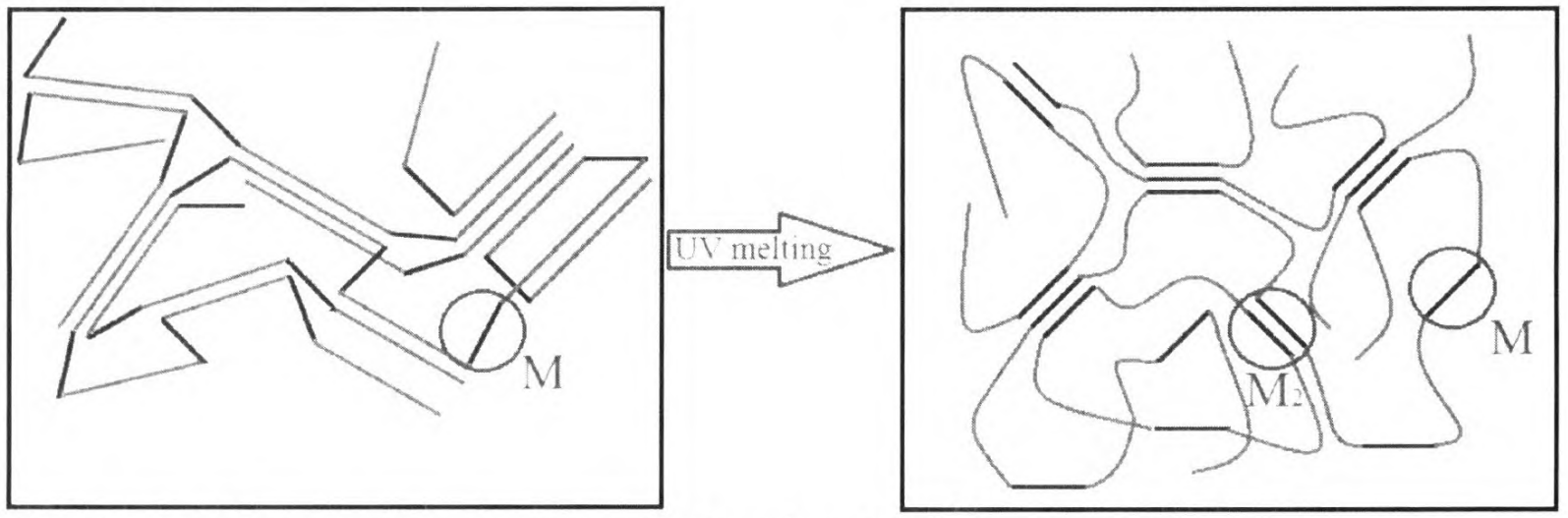


Figure 35: The alternative microstructures of polyurethane film; soft segments in blue and hard segments in brown color

When two of these moving hard segments get into a small enough volume fragment (reaction 3_a), represented by hypothetical sphere of radius r_0 (Figure 33), these hard segments form H-bonds (reaction 3_b). Subsequently, dimers are generated in the system. This H-bond formation after UV exposure was able to prove by comparing the FT-IR spectra recorded before and after UV exposure. According to Figure 36, IR spectral evidences confirm the formation of H-bonds. The intensity of peak at 3367.5 cm^{-1}(free N-H), which was initially present in the PU film, was reduced to a clearly distinct peak around 3196 cm^{-1}(H-bonded N-H) appearing after the UV irradiation. The appearance of hydrogen bonded NH peak with UV exposure confirms the formation of dimers via H-bonding after UV exposure.

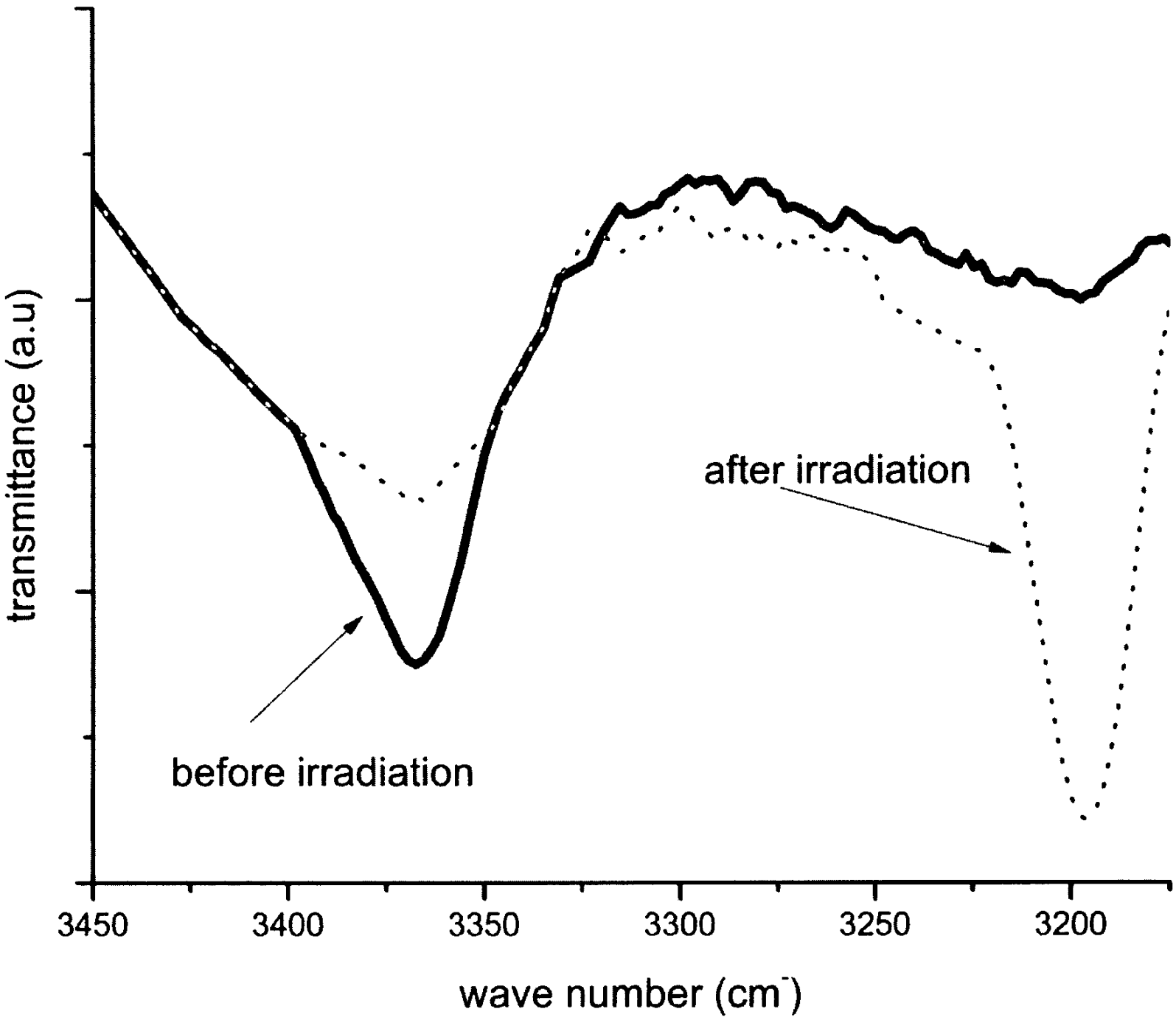


Figure 36: N-H absorption range of the FT-IR spectra before and after the UV exposure

This dimer formation process effectively depends on the diffusion rate of the hard segments (reaction 3_a) as this is the slowest step of the dimer formation process (reaction 3). The viscosity of the localized area decreases with the UV irradiation time. Hence, the rate of diffusion increases and thereby the rate of dimer formation increases. When these dimers get excited (reaction 4), they are relaxed back (reaction 5) to their ground state while generating the 423 nm peak.

The variation in intensities of 356 nm peak and 423 nm peak with UV exposure time can be well explained using this dimer formation scenario.

As explained in the above section, the 356 nm intensity at a given time is governed by the M* density at that time. M* density at a given time depends on the isolated hard segments (M) available at that time. As explained in $\frac{\partial[M]}{\partial t} = -k_1[M] + k_2[M^*] - k_3[M]^2 + k_6[M_2]$; Equation 6, isolated hard segment density depends on four processes excitation process (reaction 1), relaxation process (reaction 2), dimer formation process (reaction 3) and dimer dissociation process(reaction 6). Excitation and relaxation processes can be considered rapid compared to the time scale of the experiments. Therefore, the time dependency of the availability of isolated hard segments is effectively controlled by the rates of dimer formation (reaction 3) and dimer dissociation (reaction 6). With UV exposure time, the viscosity of the localized area decreases. Hence, the rate of diffusion increases and

thereby the rate of dimer formation increases. Hence, the availability of isolated hard segments for the excitation process reduces as dimer formation increases with the UV irradiation time. Subsequently, M* density reduces with the UV exposure time. Therefore, the 356 nm intensity reduces with UV exposure time. In addition to that, the increase in dimer formation increases the energy transfer process simultaneously which also reduces the M* density. It is also partially responsible to the 356 nm intensity reduction.

Rate of reaction 5 is the key to control the 423 nm emission intensity.

$$R_5 = k_5[M_2^*] \quad \text{; Equation 7}$$

In isothermal conditions the rate constant of reaction 5 (k_5) can assumed to be constant so the rate of reaction 5 or the intensity of 423 nm peak depends on the M_2* density. M_2* are generated from the excitation of ground state dimers (M_2). There are two possibilities for the excitation. Two possible reaction paths for the excitation of dimers are energy transfer from an excited isolated hard segments to a ground state dimer (reaction 4_i), and direct excitation of dimers with 293 nm light (reaction 4_ii). Importantly, we could not find any strong reasons to rule out the highly improbable direct excitation of dimmers with 293 nm radiation.

M_2* density depends on availability of M_2 and also affected by several reactions in the mechanism and demonstrated in $\frac{\partial[M_2^*]}{\partial t} = k_{4i}[M^*][M_2] + k_{4ii}[M_2] - k_5[M_2^*]$; Equation 8.

$$\frac{\partial[M_2^*]}{\partial t} = k_{4i}[M^*][M_2] + k_{4ii}[M_2] - k_5[M_2^*] \quad \text{; Equation 8}$$

As the relaxation and direct excitation processes are fast, the availability of M_2 is the factor which determines the intensity of 423 nm peak. M_2 availability can be explained using $\frac{\partial[M_2]}{\partial t} = k_3[M]^2 - k_{4i}[M^*][M_2] - k_{4ii}[M_2] + k_5[M_2^*] + k_6[M_2]$; Equation 9.

$$\frac{\partial[M_2]}{\partial t} = k_3[M]^2 - k_{4i}[M^*][M_2] - k_{4ii}[M_2] + k_5[M_2^*] + k_6[M_2] \quad \text{; Equation 9}$$

The excitation and relaxation processes are too fast and M_2 availability can be controlled by dimer formation dimer dissociation processes. With UV exposure, dimer formation increases due to the reduced viscosity of the polyurethane system which is caused by localized melting. Therefore, dimer availability increases with UV exposure. As a result of that M_2* density increases with UV exposure time, so the rate of reaction 5. Then the 423 nm peak intensity increases.

Reversibility observed during the UV cease time

The next interesting fact to consider here is hysteresis shown by both emission intensities. The peak at 356 nm re-increases and the peak at 423 nm re-decreases when UV irradiation is blocked for a considerable time period. However, both peaks do not come back to their original intensity even after UV cease time of one month. And also once the UV cease times were varied and percentage reversibility was calculated, it does not show that increase in that parameter affects on the percentage. This allows us to assume that 100% reversibility cannot be achieved even after infinite UV cease period.

The reversible nature of the fluorescence behavior can be explained using the micro structural changes in polymer system. When kept out of UV radiation, the melted polymer began to solidify reducing the entropy of molecules. This process re-

crystallizes soft segments back to highly crystalline areas which in turn create tensile forces on the hard segments. These tensile forces are capable of separating the dimers to re-produce isolated hard segments back (reaction 6). This reduction of dimer density can be attributed to reduction of 423 nm emission with simultaneous increase in 356 nm emission during the UV cease time. As the tensile forces cannot bring all the molecules back to the original spatial arrangement, some of the H-bonded hard segments will remain as dimers. This will result in a partial reversibility instead of complete reversibility.

It can be observed that the initial intensity of the peak at 423 nm increases while the initial intensity of the peak at 356 nm reduces with each cycle. It indicates that with each cycle of irradiation the density of dimers increases. Photo degradation could cleave some of the polymer molecules during the prolonged UV irradiation which in turn can reduce the tensile forces on H-bonded hard segments (dimers). Hence, the ground state dimer density increases with the number of excitation cycles.

As this proposed mechanism is well harmonized with the fluorescence behavior, it is fair enough to assume that this polyurethane film is behaved according to the given mechanism.

Blocking the reversibility by replacing the solvent from DMAc to DMF

It was pronounced that when the solvent is replaced from DMAc to DMF the reversibility of the fluorescence behavior has been vanished. There are several possibilities to explain this blocking of reversibility. The two possibilities which are postulated here are originated from the steric effect. When DMAc and DMF molecules are considered, in the DMAc molecule the formyl hydrogen of DMF has replaced by a methyl group which is arranged in a tetrahedral geometry while occupying a large volume of space. Hence, DMF is sterically less hindered compared to DMAc. Then the ability to embed inside the polymer matrix is high in DMF. In the films obtained by solvent casting method, the residual solvent molecules can be remained in the film. When attention goes to residual solvent molecules, the DMF molecules can more easily embed inside the polymer matrix compared to DMAc. Now the two possibilities which are caused to block the reversibility can be addressed. First one is; the embedded DMF molecules retard the tensile forces which were applied on hard segment bundles to make them separate. Therefore, the formed bundles are not separate apart to form isolated hard segments back and the intensities corresponding to isolated hard segments and hard segment bundles are remained as it is. That effect is somewhat similar to the role of plasticizers. In literature there are some articles explaining that residual solvent molecules act as plasticizers, the action of residual chloroform as a plasticizer to the polylactide (PLA) films has been reported. (90,91) The second possibility is, there is not any effect to the explained mechanism in such a way when UV cease the polymer molecules re-arranged as explained but, DMF molecules are embedded in to the polymer matrix during the localized melting step and when M2 separate to 2 M during the UV cease, DMF comes and joins with M to form MA type complex instead of M2 which also emits at 423 nm. There are several possibilities to form hydrogen bonds between urethane group and DMF molecules. (92) According to that article the DMF and urethane linkages are joined together via two pair of hydrogen bonds. This suggests that the MA type complex formation between DMF and isolated hard segments is feasible. This ability of complex formation enhances the reliability of second possibility. There is a third possibility with least probability. It is, when DMF is present instead of the explained mechanism it induces a photo degradation product which emits

at 423 nm. Even though it was able to postulate several possibilities, with the time constrains, it was unable to spend a considerable time on rule out the possibilities and find the exact reason for this reversibility blocking by DMF.

Hydrophilic polyurethane dispersions and their coatings

Hydrophilic polyurethane synthesis and preparation of the aqueous dispersions

A common obstruct in polyurethane synthesis is the formation of polyurea via the side reaction of the isocyanate group with water instead of hydroxyl group. Hence, it is necessary to avoid the water - isocyanate side reaction by removing the moisture from the reaction environment. Basically few precautions were taken to avoid the moisture contact. PTHF and DMPA were dried in vacuum oven at 105 ^{0}C prior to use and the DMF was dried over molecular sieves in order to remove the moisture. Inert reaction environment was maintained by carrying out the reaction in nitrogen atmosphere.

As polyurethane chain does not contain ionic centers, it is highly hydrophobic. Due to this hydrophobicity, organic solvents have to be used during the polyurethane synthesis processes. With the use of large amount of organic solvents, a huge problem regarding the environmental pollution was created due to the evaporation of volatile organic compounds (VOC) in the polyurethane industry. Now industry is focused to reduce the use of volatile organic solvents and shift to water based formulations. In this study it was focused to minimize the amount of dimethylformamide (DMF) consumed and to introduce water to the reaction medium in order to develop a DMF-WATER mixture as the solvent.

It was able to develop a DMF-WATER mixture as the solvent because DMF is properly miscible with water. DMF and water are miscible in such a way that they can be mixed in all proportions to give a homogenized mixture in other words they do not form two separate phases. (93)

In this research work MDI and PTHF are used as diisocyanate and the polyol, respectively. As both are non polar compounds the poyurethanes obtained from these monomers are highly hydrophobic. It is compulsary to have a hydrophilic nature in order to use a water based medium. It has been achieved by introducing a monomer containing a hydrophilic group. Dimethylolpropionic acid (DMPA) which is having a pendant carboxylic acid group was used as the ionomer.It is important to attain a uniform distribution of the ionic monomer inside the polyurethane chain in order to avoid the phase seperations of the polymer. It has been achieved by obtaining a homogenized mixture of PTHF and DMPA via a proper mixing of PTHF and DMPA which is dissolved in DMF through magentic stirring prior to the addition of MDI. Importancy of obtaining a homogenized mixture of polyol and ionomer prior to the addition of diisocyanate is emphasised by SM Cakic and his group in their publication. (94) The introduced ionic groups;the carboxylic acid groups were nutralized using diethyamine which is capable of fominng a carboxylate ion and quarternary ammonium group. Now these pendant carboxylate ions which are uniformely distributed in the polurethane backbone have the ability to convert the hydrophobic polyurethanes into hydrophilic polyurethanes.

The step growth polymerization was stopped using the chain terminator DiAE. It is consisting of a single hydroxyl group which can reacts with a isocyanate group and avoid further polymerization. It is important to talk about the other functional groups

present in DiAE. It contains two terminal 'ene' groups which are usefull in crosslinking via the UV curing.

Through dropwise addition of the water to the polyurethanes prepared in DMF, it was able to obtain a poyurethane dispersion in DMF-WATER mixture. In order to disperse properly it was needed to stir the reaction mixture vigouruosly. It was stirred with a very high speed of 1000 rpm.

Dispersion properties

When the attention was paid towards the polyurethane dispersions it is mandatory to discuss the stability of the dispersion. All the five dispersions which were prepared here are highly stable. There was not phase separation or sedimentation during the period of two months. The dispersion stability can be verified using the zeta potential. Dispersions having zeta potentials more positive than +30 mV or more negative than -30 mV are generally considered as stable. (95) And also higher the absolute value of the zeta potential higher the dispersion stability. (40) Particle size measurement taken over a long period of time is also an indirect evidence to the dispersion stability. In other words absence of significant changes in particle size indicates that dispersion is stable or no considerable agglomerations.

Particle size and zeta potential were measured using the Malvern Zetasizer nano series particle size analyzer at 30 ^{0}C. The material was selected as polyurethane and refractive index of the material was given as 1.50 according to the sample dispersion and refractive index guide of Malvern instruments. (96) Dispersant was given as 30% DMF-water. Dispersant properties were supplied using the literature values of refractive index, viscosity and dielectric constant of a 30% DMF-water mixture. As the measured values were not given, refractive index was back calculated as 1.368 using the given data and equations in the relevant article. (97) According to the literature viscosity was provided as 1.478 (98) while dielectric constant as 69.9 (99).

The average particle sizes and zeta potentials of the five dispersants over two months are given in the below.

Table 6: Particle sizes (diameter) and zeta potentials of polyurethane dispersions

Dispersion	PUD-1		PUD-2		PUD-3		PUD-4		PUD-5	
DMPA:POLYOL molar ratio	72:28		64:36		56:44		48:52		40:60	
Number of days	Average particle size (nm)	Zeta potential (mV)	Average particle size (nm)	Zeta potential (mV)	Average particle size (nm)	Zeta potential (mV)	Average particle size (nm)	Zeta potential (mV)	Average particle size (nm)	Zeta potential (mV)
1	63.4	-54.9	98.9	-51.2	156.6	-48.9	171.1	-45.9	205.2	-44.9
2	62.8	-57.6	99.3	-51.6	157.2	-47.8	171.5	-47.1	204.3	-45.2
3	63.5	-59.4	100.8	-54.4	159.0	-48.6	171.5	-48.5	206.9	-47.3
6	63.1	-58.4	97.4	-54.2	161.0	-47.6	172.2	-45.6	204.9	-45.0
7	63.4	-61.0	100.5	-56.1	163.7	-47.9	170.9	-48.1	205.0	-44.7
8	64.1	-59.8	101.7	-57.0	166.4	-48.6	168.5	-48.8	206.2	-45.0
9	63.0	-60.4	101.5	-59.5	166.9	-50.1	170.3	-49.8	205.8	-49.0
13	61.4	-58.2	102.5	-57.7	173.3	-46.2	170.5	-45.8	200.9	-44.8
14	64.2	-57.0	102.0	-53.6	173.6	-47.5	169.6	-47.5	204.5	-45.5
21	64.0	-50.6	102.6	-50.6	161.8	-46.9	170.8	-46.2	205.6	-43.2
28	63.1	-51.4	101.8	-51.0	173.1	-46.4	171.8	-45.1	208.7	-42.4
35	61.0	-52.9	101.9	-52.1	172.7	-46.7	176.5	-45.4	206.4	-45.1
42	62.0	-50.2	101.7	-49.6	171.5	-44.6	172.0	-44.7	205.4	-44.1
49	61.1	-52.8	101.2	-49.0	170.8	-46.9	173.5	-46.0	204.5	-44.7
56	60.6	-53.7	100.0	-51.8	173.6	-46.2	173.0	-44.0	206.0	-42.7
63	60.9	-54.1	100.1	-52.0	173.0	-48.7	173.7	-47.1	207.1	-46.8

It is clearly seen that higher the ionomer: Dimethylolpropionic acid lower the particle size. Inevitably increase in the DMPA percentage results in a subsequent increase in the hydrophilicity of the polyurethane due to the increase in the number of ionic groups per polyurethane chain. As a result of this higher hydrophilicity, the reduction in particle size can be predicted. The relationship between hydrophilicity and particle size has been discussed in literature. This inverse correlation has been attributed to the stabilization mechanism of dispersed particles which involves the diffusing electrical double layer formation. (100,101,102) And also with the increase in DMPA percentage, the PTHF percentage is decreased simultaneously. The molar mass of PTHF which is used is 2000 and hence it is a long chain polymer. It is obvious that decrease in the amount of these long chain monomers per polymer chain leads to a reduction in length of resulting polymer and subsequently to smaller polymer particles. Due to the increase in hydrophilicity and decrease in chain length, particle size is small in the polymers with higher percentage of DMPA. With the increase of DMPA percentage particle size shows a decrease.

Dispersion stability is a key feature to discuss in the field of polyurethane ionomers. Absolute zeta potentials of all the dispersions are greater than 30 mV which indicate that they are highly stable. With the increase in DMPA percentage there is an increase in absolute value of zeta potential which indicates increase of dispersion stability. The stability of aqueous dispersions is governed by the ionic groups. The polyurethane particles in aqueous dispersions are formed as tiny spheres having a core formed by hydrophobic segments and a boundary layer which is consist of ionic groups which are in general hydrophilic. (37) These tiny spheres of polyurethane particles form remarkably stable dispersions. (37) Hence, higher amount of ionic groups lead to higher dispersion stability. There was an indirect evidence to prove this dispersion stability. The average particle size of these dispersions were measured over a two months of period and it was clearly shown that variations in particle sizes with time are negligible compared to their particle sizes. It indicates that agglomerations of particles are poor indirectly showing that the dispersions are stable.

Preparation of polyurethane films

Smooth polyurethane films were obtained by evaporating the solvent from the polyurethane dispersions via overnight drying in a vacuum oven. It was a transparent film which was coated on glass slide.

Crystallinity

XRD

The XRD patterns of five PUD systems are shown in Figure 37.

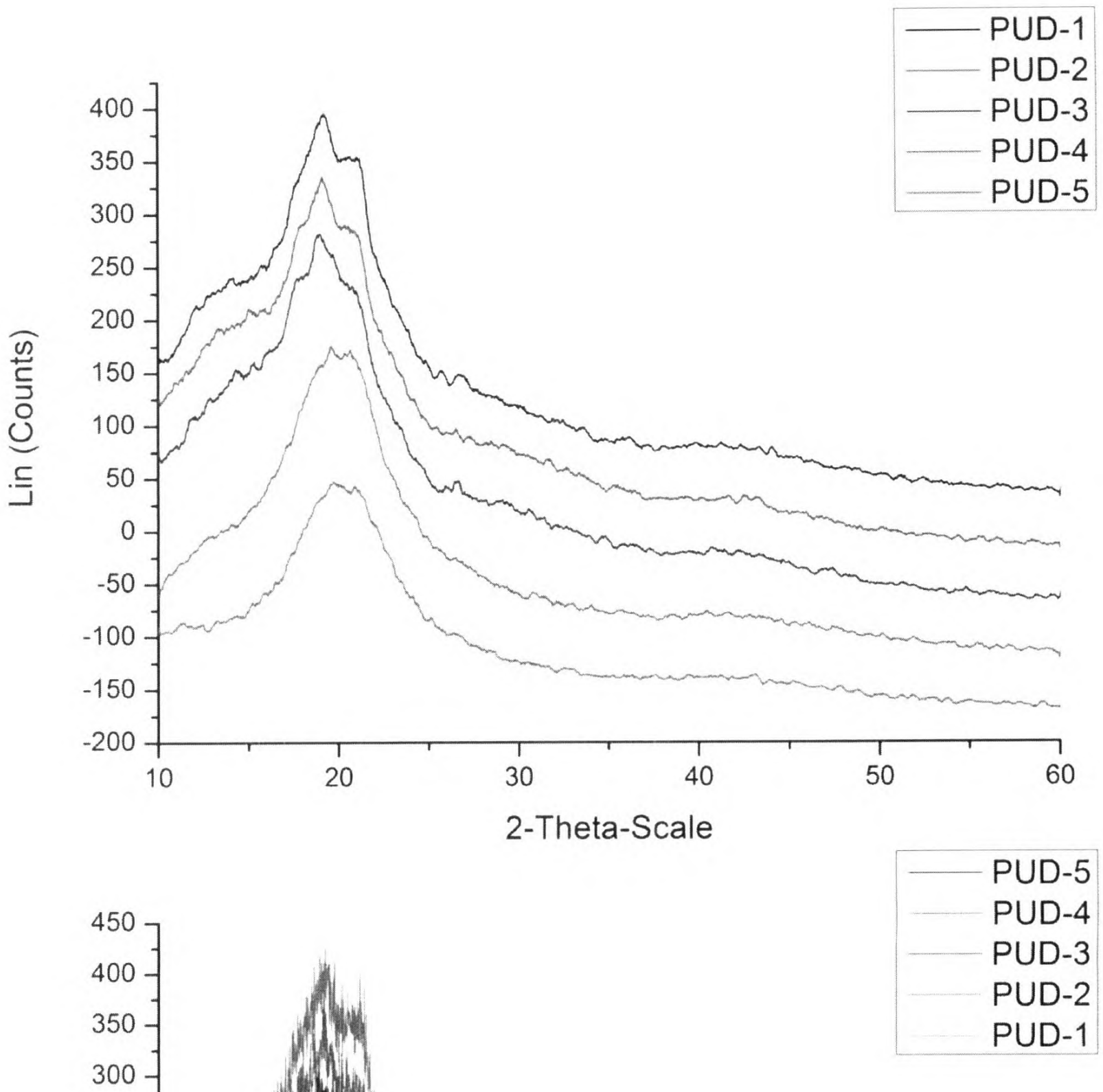


Figure 37: The XRD patterns of five PUD systems

All the five PUD systems have a XRD peak at 2θ around 20°. This peak is corresponding to the MDI based hard segment crystallinity. (103,104,84) When closely observe the five patterns there is an increase in the sharpness of the peak from PUD5 to PUD1 where in the order of increasing the hard segment content. It indicates that hard segment crystallinity becomes higher with the increase in hard segment content.

It is well established that crystalline hard segment bundles are existed due to the hydrogen bonds which are formed between the urethane linkages. With the increase of hard segment content, even though the degree of polymerization is same the chain length becomes shorter. So number of chains per unit volume becomes higher which increase the probability of finding two hard segments which are close enough to form hydrogen bonds. Therefore, with the increase of hard segment content the extent of hydrogen bonding is increased subsequently the amount of bundled hard segments. This will lead to an increase in the crystallinity of the system. In our systems the increase in hard segment content has been achieved by increasing the DMPA/PTHF molar ratio which leads to an increase in ionic centers. The coulombic interactions between the ionic centers make physical cross-links between polymer chains. As the number of ionic centers increases the inter-chain interactions become higher. Then polymer chains are attracted to each other strongly. Due to the increased interactions, crystallinity becomes stronger. In addition to that, inter chain coulombic interactions increase the attraction between the polymer chains and reduce the distance between chains. As a result of this, the strength of hydrogen bonds is increased eventually results in higher crystallinity.

FT-IR analysis

The increase in extent of hydrogen bonding and the increase in the strength of hydrogen bonding with respect to hard segment content can be explained using the FT-IR spectroscopy. According to the calculated values the hard segment content was gradually reduced from PUD-1 to PUD-5. By comparing the FT-IR spectra of five systems, the effect of hard segment content on hydrogen bonding can be discussed.

Generally, polyurethanes have a microstructure consisting of crystalline hard segment bundles and isolated hard segments trapped in the soft segment matrix. These crystalline hard segment bundles are produced due to the hydrogen bonds which are formed between the N-H group and C=O groups of the neighboring urethane linkages. Hence, polyurethanes having the microstructure of hard segment crystallinity show H bonded peaks due to crystalline bundles while peaks of free bonds due to isolated hard segments which are trapped in soft segment domain.

By the detailed analysis of the N-H region and the C=O regions (carbonyl region) of the FT-IR spectra, it is able to discuss about the hydrogen bonds. The characteristic absorption frequencies for free urethane carbonyl and urethane carbonyl which is H bonded to NH should appear in the ranges of 1730-1740 cm^{-1} and 1703-1710 cm^{-1} respectively. (105) Characteristic IR frequencies corresponding to free NH appear in the range of 3445-3450 cm^{-1} and that of NH which is hydrogen bonded to oxygen appears in the range 3260-3290 cm^{-1}. (105)

The Figure 38 & Figure 39 show the C=O region and N-H region of the five polyurethane films obtained from five dispersions respectively.

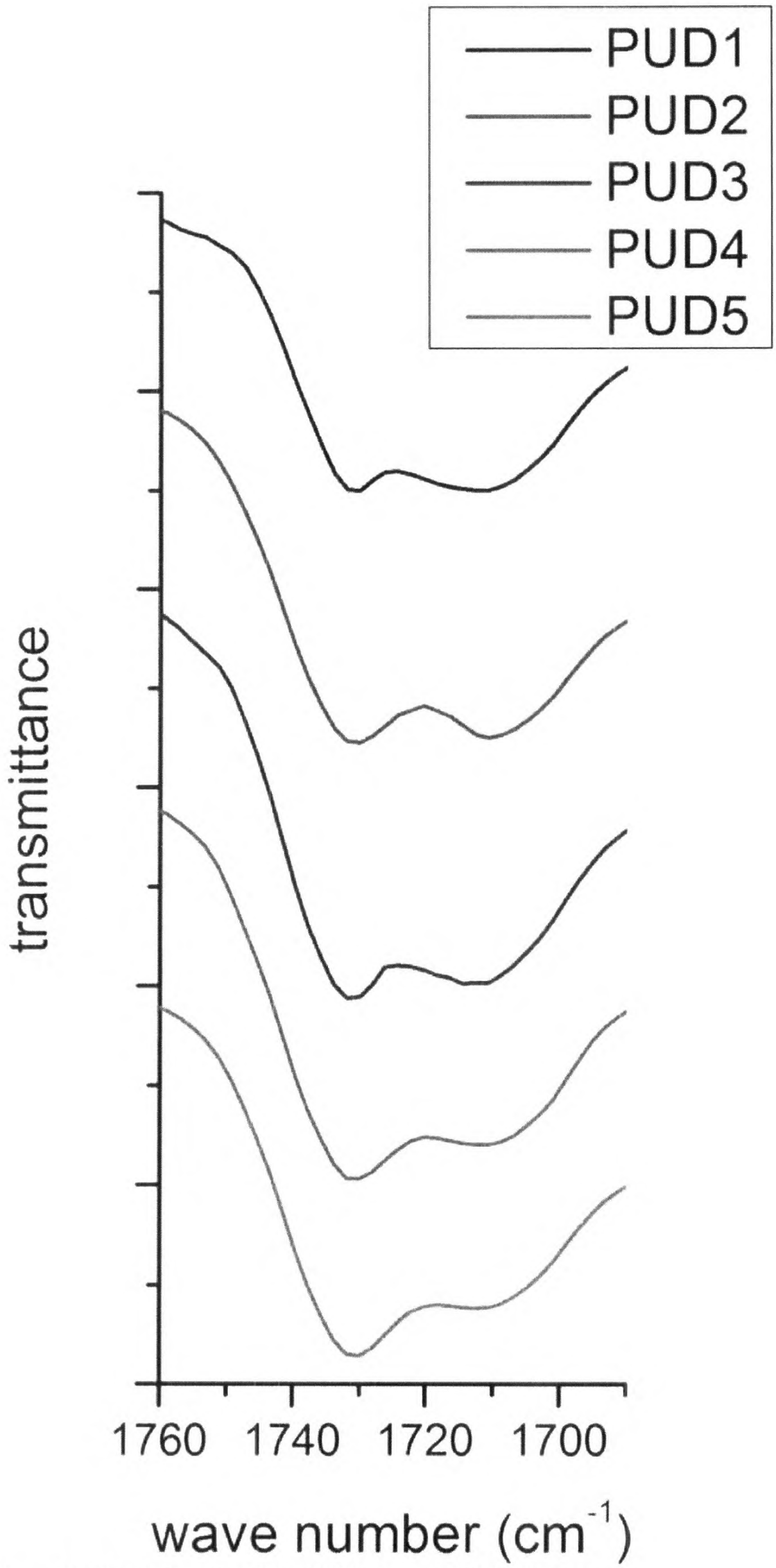


Figure 38: The C=O region of the FT-IR spectra of PUD films

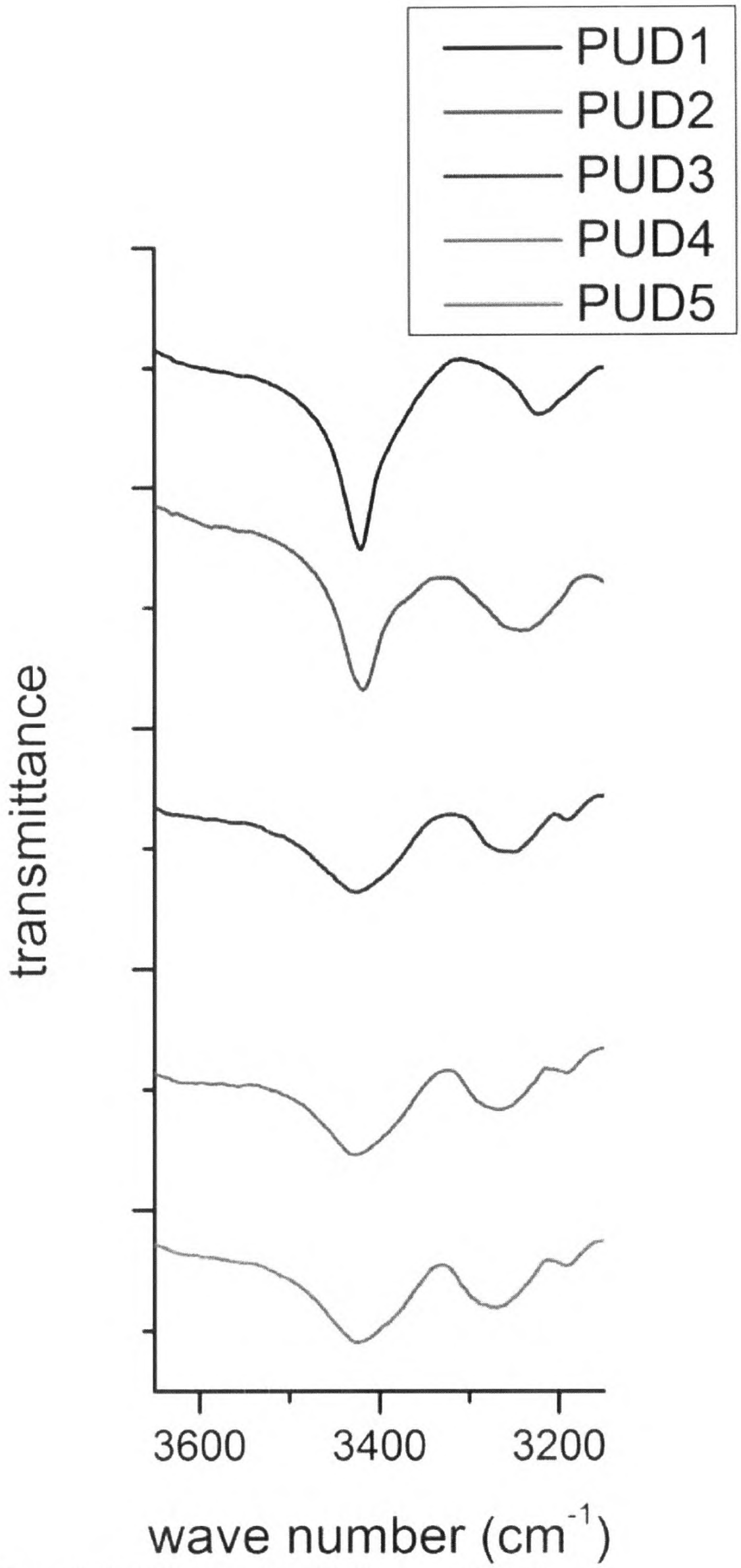
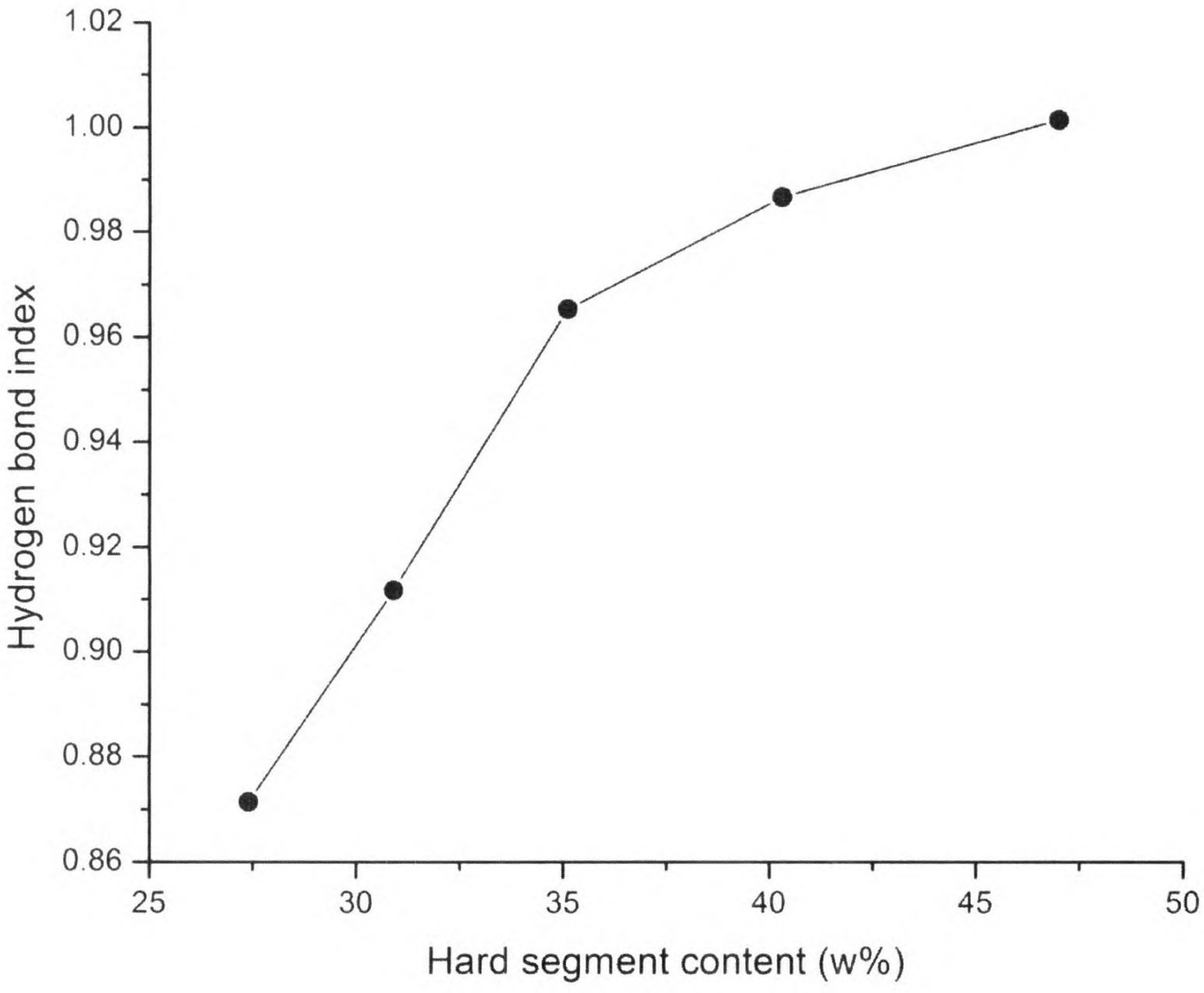


Figure 39: The N-H region of the FT-IR spectra of PUD films

In all five films, initially there are two peaks in the carbonyl region around 1730 cm^{-1} and 1710 cm^{-1} which can be assigned as free carbonyl peak and peak of carbonyl which is hydrogen bonded to NH, respectively. Similarly there are two peaks in the NH region, one is around 3425 cm^{-1} and the second peak varies in the range 3280-3220 cm^{-1}. Those two can be assigned to free NH and H bonded NH, respectively. The presence of hydrogen bonded NH and CO peaks in addition to free NH and CO peaks in all five films obtained from five dispersions proves the presence of crystalline hard segment bundles in all the films.

The extent of hydrogen bonding can be expressed using the hydrogen bond index (HBI) which is measured as the intensity ratio of hydrogen bonded carbonyl peak and free carbonyl peak which imply the relative absorbance of hydrogen bonded carbonyl peak to that of free carbonyl peak. (106)

Once the HBI is calculated, there is a trend of increase in HBI with respect to hard segment content. As shown in Figure 40, there is an exponential growth in hydrogen bond index with increasing hard segment content.


Hydrogen bond index
1.02
1.00
0.98
0.96
0.94
0.92
0.90
0.88
0.86
25
30
35
40
45
50
Hard segment content (w%)

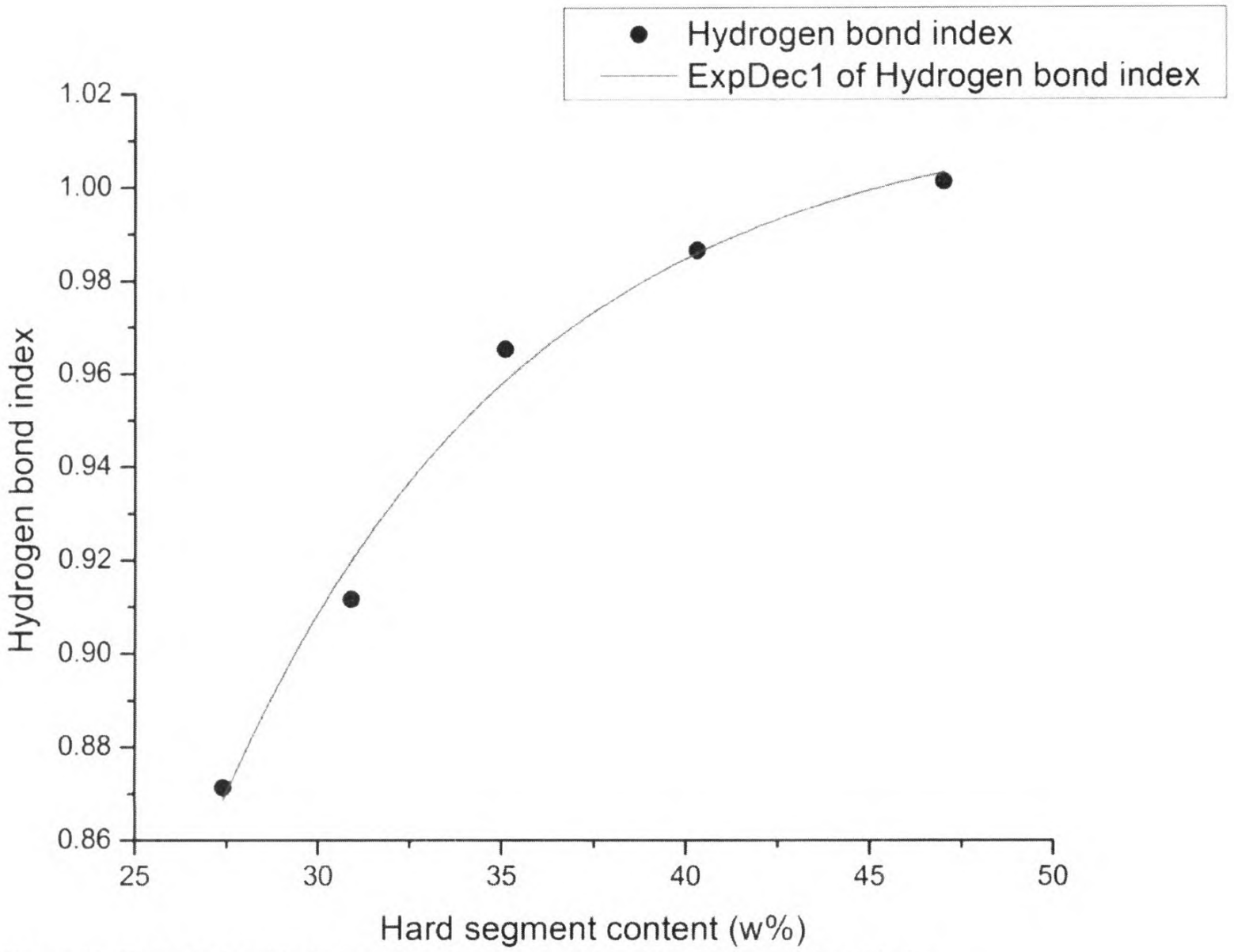
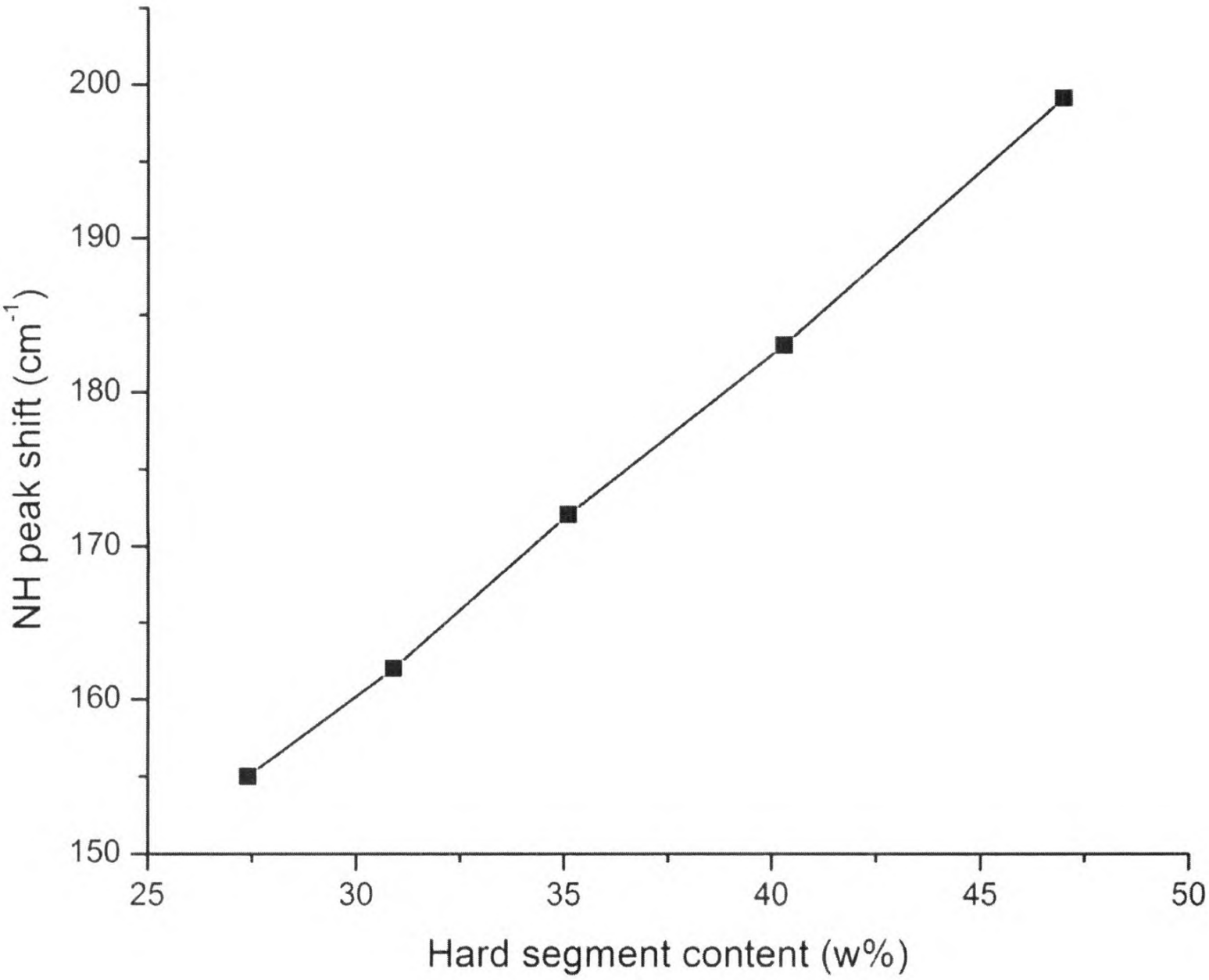


Figure 40: The relationship between hard segment content and hydrogen bond index

With the increase of hard segment content there is an increase in hydrogen bond index. This implies that extent of hydrogen bonding is increased with increased hard segment content (DMPA/polyol molar ratio). As explained earlier this increase in the extent of hydrogen bonding leads to an increase in crystallinity.

The shift in the NH peak position is a signal of the strength of hydrogen bonds. When NH bond involves with H bond formation, the NH bond strength becomes less and this will leads to a red shift in absorption frequency. (107) The magnitude of shifts in the NH peak position is a measure of Hydrogen bond strength. (105,108)

As shown in Figure 41, with the increase of hard segment content (DMPA/polyol molar ratio) the NH peak shift was increased.


NH peak shift (cm-1)
200
190
180
170
160
150
25
30
35
40
45
50
Hard segment content (w%)

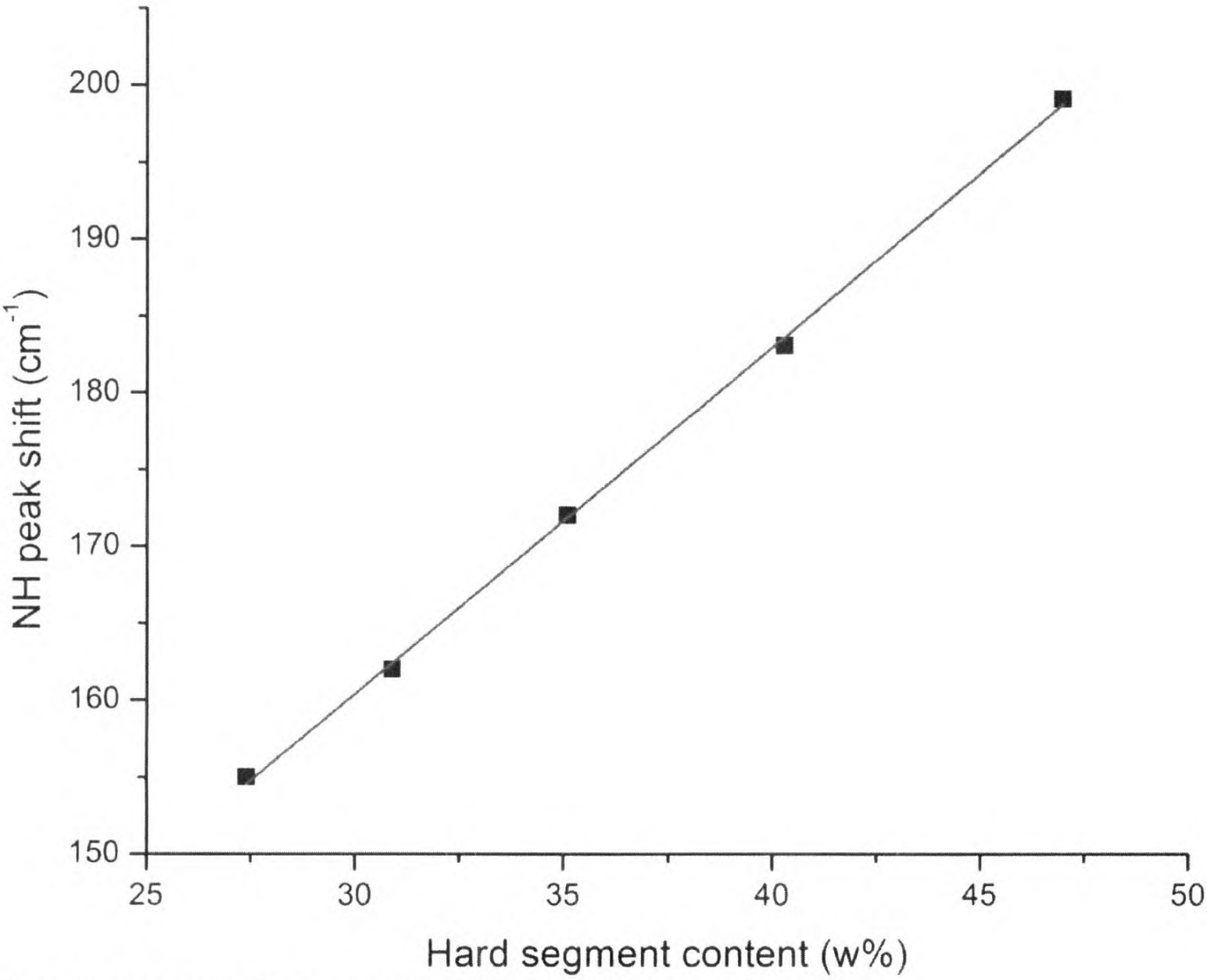


Figure 41: The relationship between NH peak shift and hard segment content

The increase in NH peak shift with increasing hard segment content implies that hydrogen bond strength become stronger when hard segment content is increased. As a result of this it is able to observe a growth in hard segment crystallinity.

Fluorescence behavior; new technique to address the crystallinity

As discussed in the section 0, isolated hard segments gave a peak at around 356 nm and dimers in the crystalline hard segment bundles gave a peak at comparatively higher wave length at around 423 nm. Even though in that section polyurethane prepolymer systems do not have crystalline hard segment bundles itself initially, as proven from afore discussed two sections in the films obtained from polyurethane dispersions have crystalline hard segment bundles itself initially. While providing an additional fact to prove the proposed mechanism is true, in the initial spectrum of these films has the second peak at higher wave length in addition to the first peak as shown in Figure 42. As suggested in the mechanism discussed above, the peak around 356 nm is due to the isolated hard segments remained in the system and peak at 423 nm is due to the initially available dimers located at crystalline hard segment bundles.

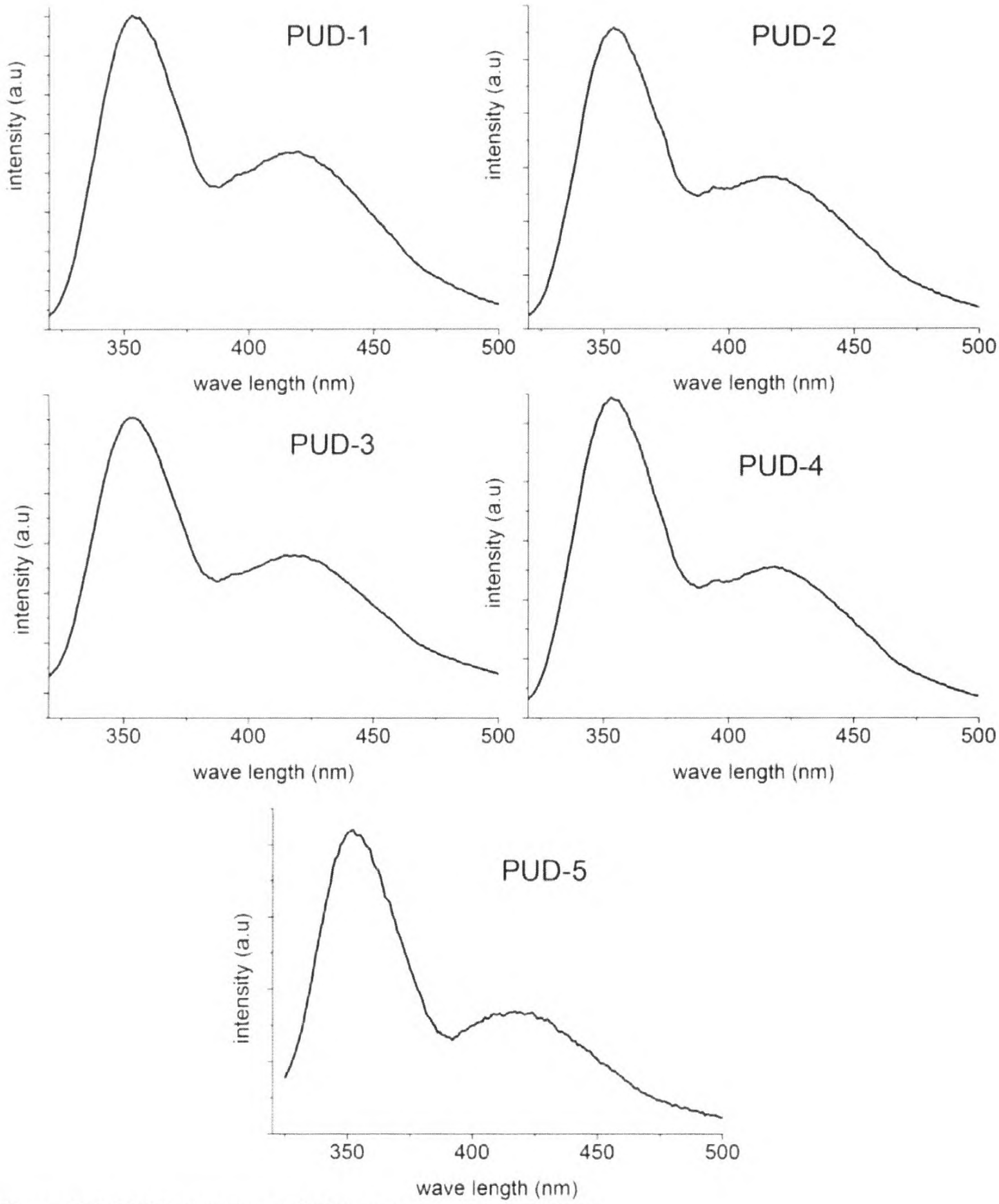


Figure 42: Initial fluorescence emission spectrum of five PUD films

According to the suggested mechanism, the 423 nm peak emission is due to the excited dimer relaxation. The increase in hard segment crystallinity with the increase of hard segment content can be explained through the comparison of relative intensity of the second peak compared to the first peak. As hard segment crystallinity increases, it leads to an increase in the available dimer amount in the system. Then the intensity of the peak corresponding to dimer relative to the peak intensity of isolated hard segments should increase with increased hard segment crystallinity. Hence, the relative intensity of second peak at higher wave length should be high in the systems

having higher crystallinity. As shown in Figure 43, the second peak intensity/first peak intensity ratio increases with increased hard segment content.

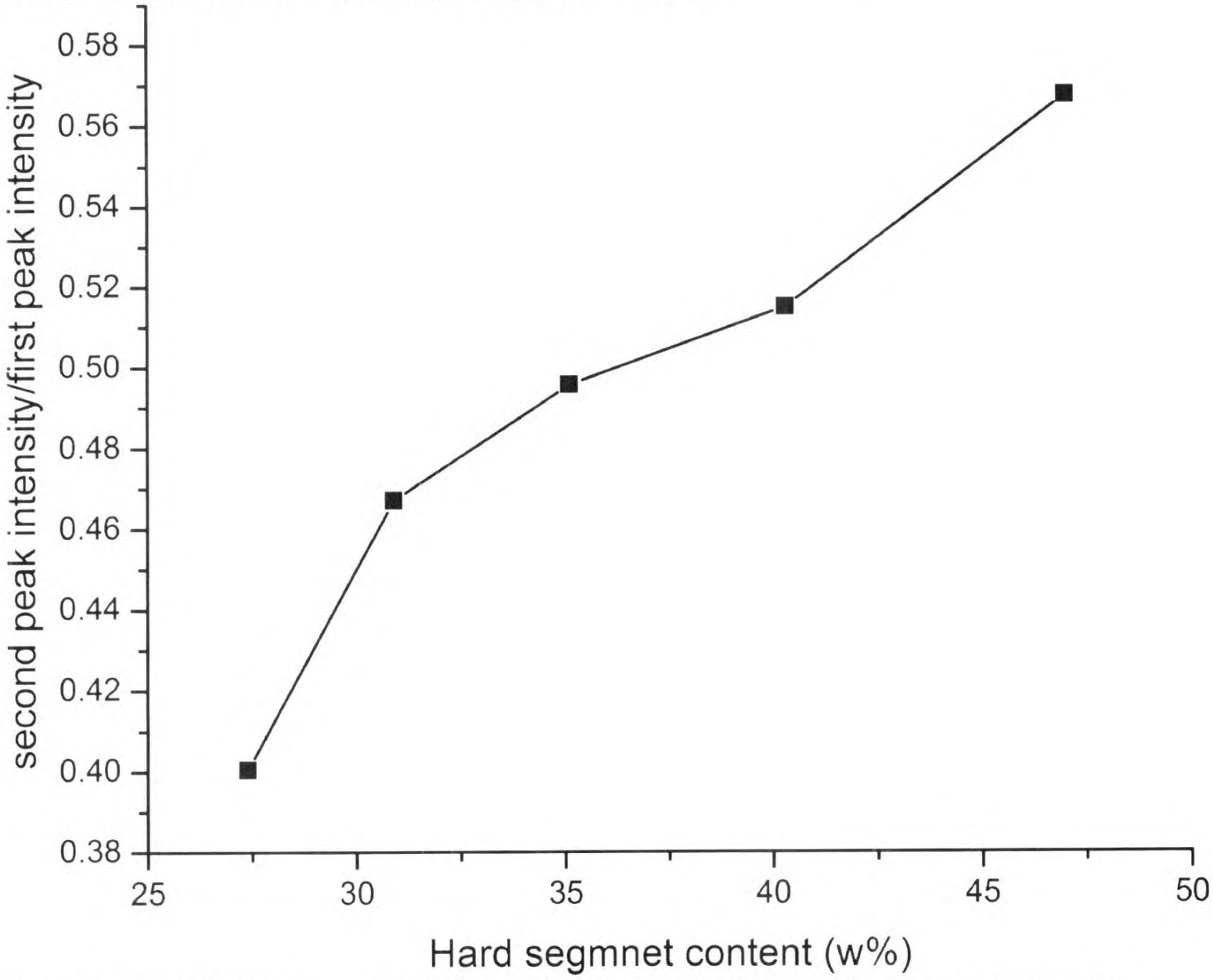


Figure 43: The variation in second peak/ first peak intensity ratio with respect to hard segment content

The five polyurethane films were synthesized and prepared in the same manner. The significant difference in five systems is the hard segment content. The increase in relative intensity of second peak with increasing hard segment content verifies that hard segment crystallinity becomes higher with hard segment content.

As the prepolymer systems increase their hard segment crystallinity with the UV exposure and in this section we are focusing on the hard segment crystallinity, it is necessary to consider whether the hard segment crystallinity of the films obtained from polyurethane dispersions also become higher with UV exposure (293 nm).

Similar to the prepolymer system, with UV exposure, the hard segment crystallinity was increased. It was indicated by continuous reduction of first peak intensity and simultaneous increase in second peak intensity with respect to exposure time (number of repeats). The variation in spectra of five PUD systems with number of repeats is shown in the Figure 44.

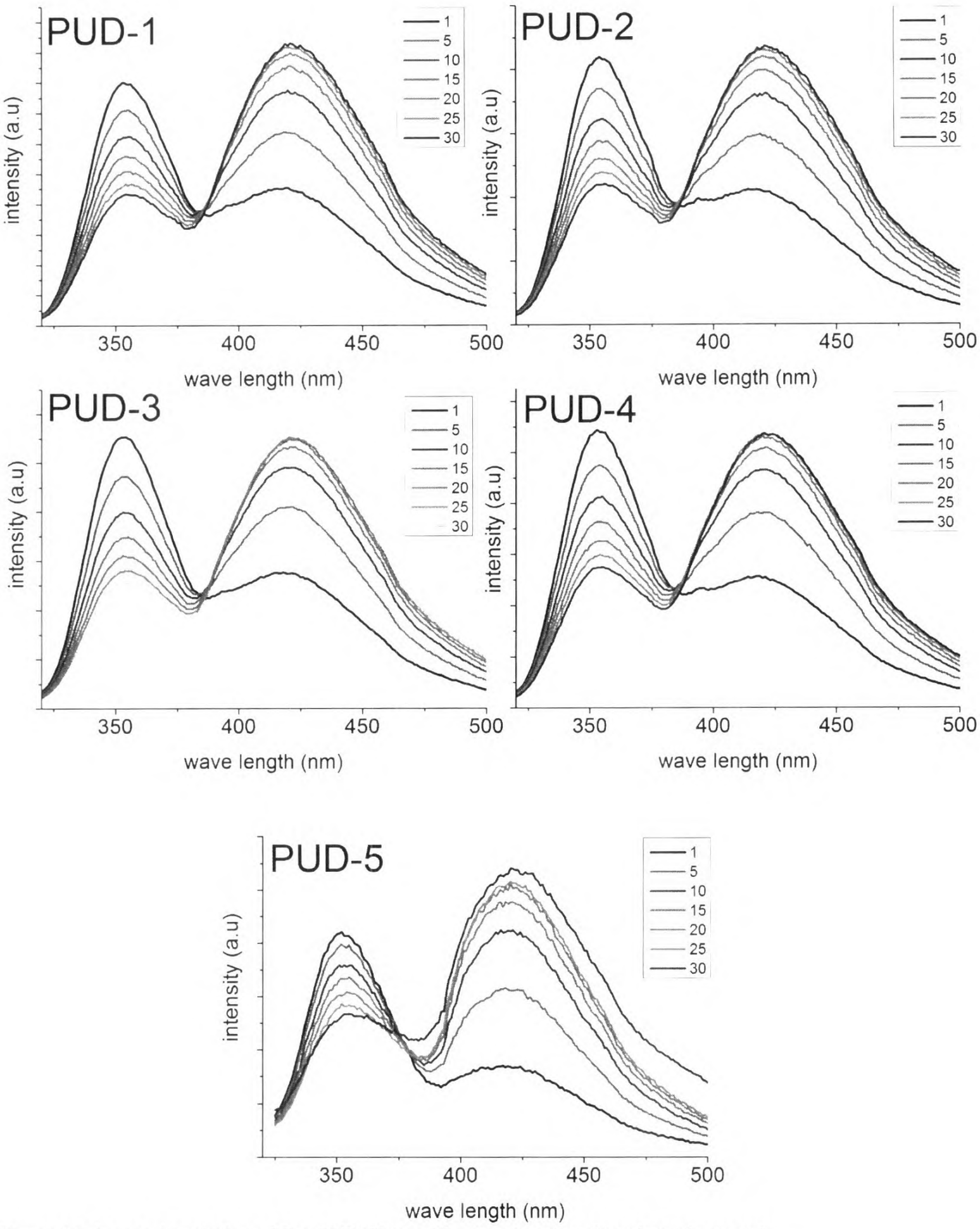


Figure 44: Spectral variation of five PUD films with exposure time (number of repeats)

Additional facts to confirm the given mechanism to explain the fluorescence behavior

The fluorescence behavior of the PUD systems helps to confirm the proposed mechanism of the fluorescence behavior of the MDI based polyurethanes.

As explained in the mechanism, 356 nm peak is generated from isolated hard segments and 423 nm emitters are generated from the hard segment bundles. The presence of hard segment bundles in the PUD films were confirmed by crystallinity study and the thermal study of those films. For

those films which are having the hard segment bundles, there is a second peak at 423 nm even in the initial fluorescence spectrum of those films. This is an additional support to confirm the 423 nm emitters are from hard segment bundles. The relative intensity of second peak increases with the increase of hard segment crystallinity (Figure 43). This is also a clue to prove that 423 nm emitters are from hard segment bundles.

Thermal properties

Thermal properties were analyzed using the DSC results. The thermal behavior of polyurethane films and the effect of ionic group percentage on thermal properties were analyzed. The first heating cycle, cooling cycle and second heating cycle of the DSC thermograms are shown in below figures (Figure 45, Figure 46, and Figure 47).

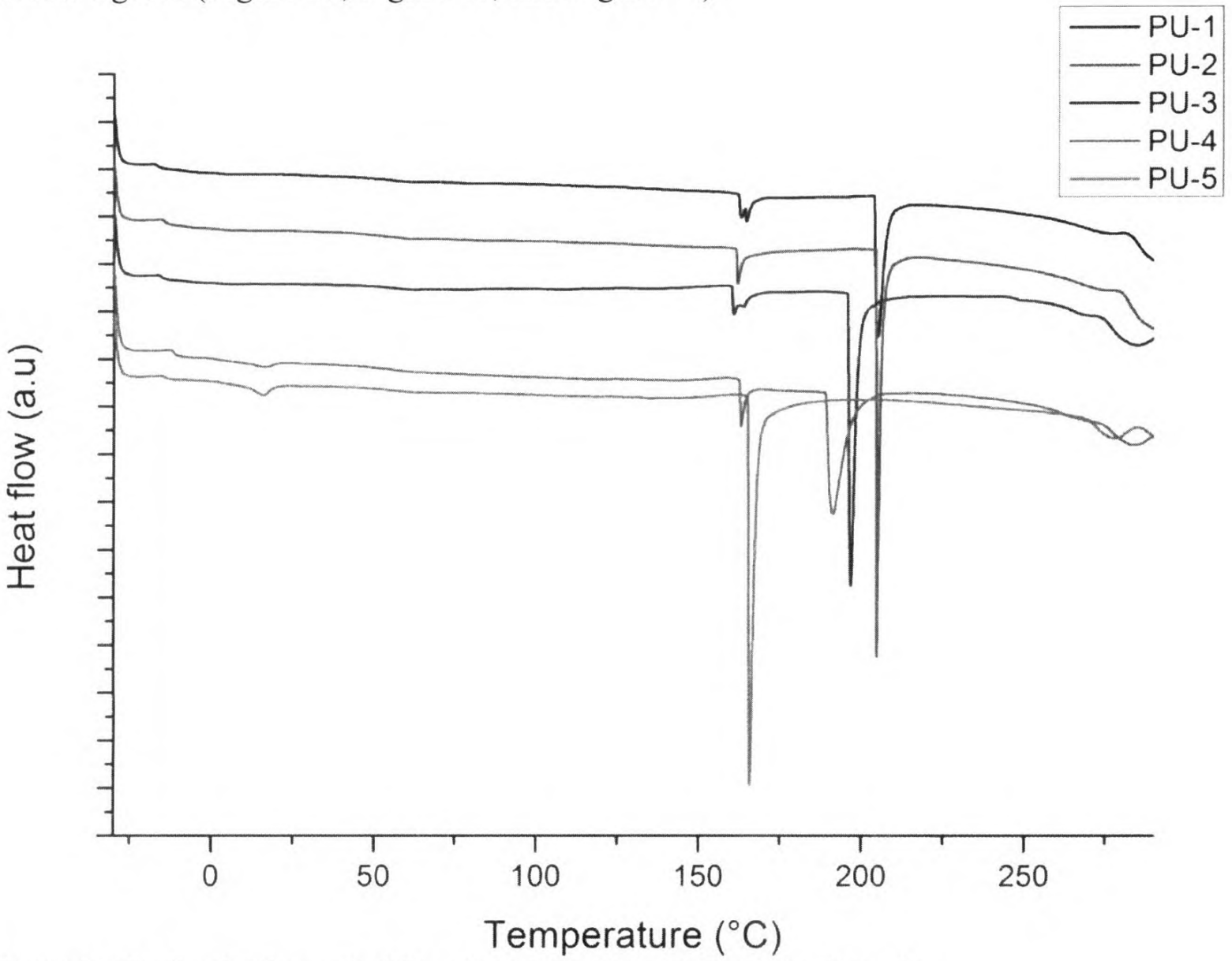
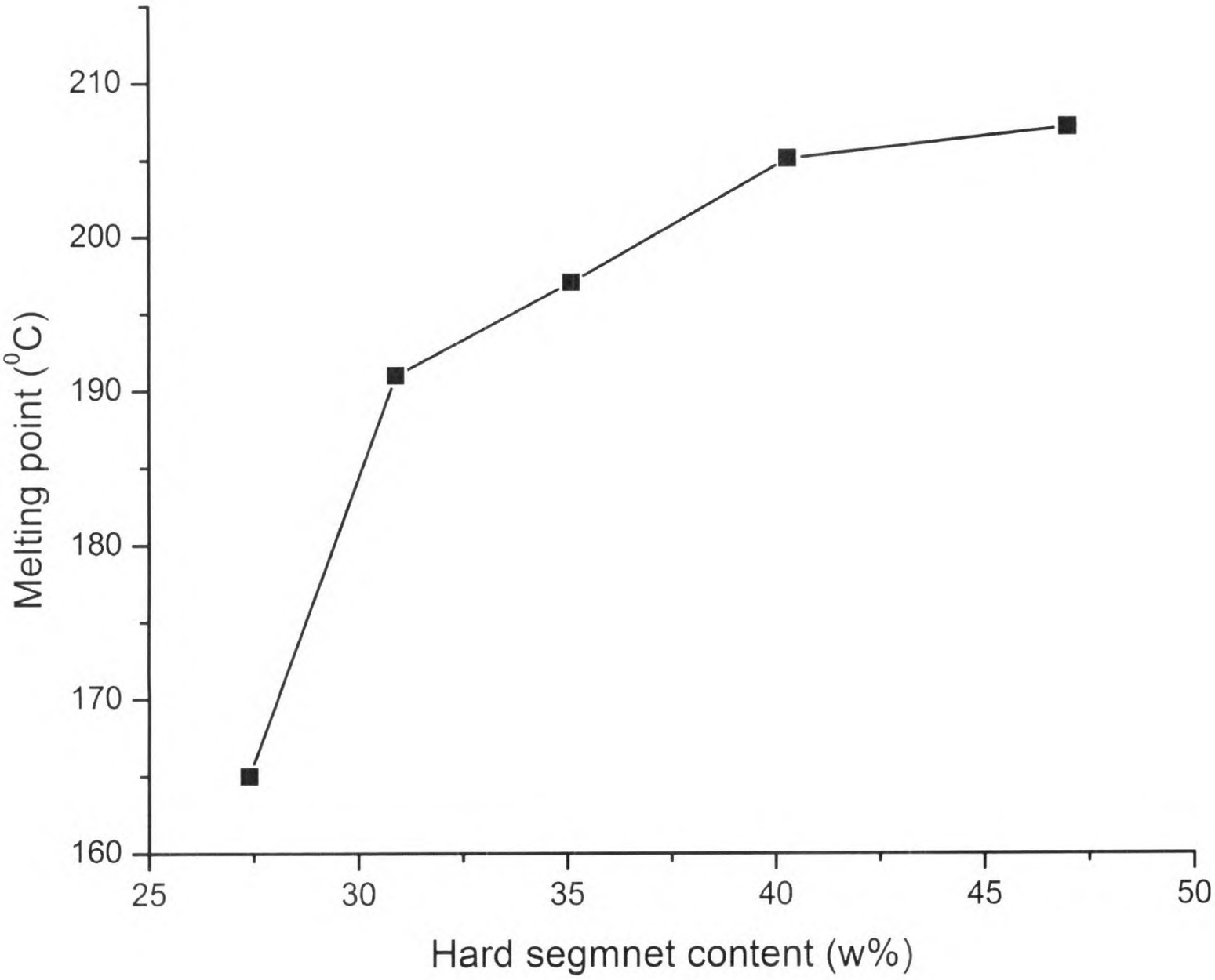


Figure 45: The first heating cycle of the polyurethane films obtained from dispersions

During the first heating cycle, all the five films had melting peaks at higher temperatures in the range of 150 ^{0}C to 225 ^{0}C. This can be attributed to hard segment melting. The melting peaks around 180 ^{0}C has been assigned to MDI based crystalline hard segment melting in the literature by Mishra and coworkers. (84) The appearance of this hard segment melting peak in the first heating cycle depicts that when polyurethane films were formed through solvent evaporation via oven drying, it leads to a micro structure of polyurethanes which is having crystalline hard segments. The other noticeable observation is the variation of melting temperature with the hard segment content. Hard segment content was varied by varying the polyol/ionomer molar ratio. As shown in Figure 46 the melting temperature was increased as the hard segment content is increased.


Melting point (^{0}C)
210
200
190
180
170
160
25
30
35
40
45
50
Hard segmnet content (w%)

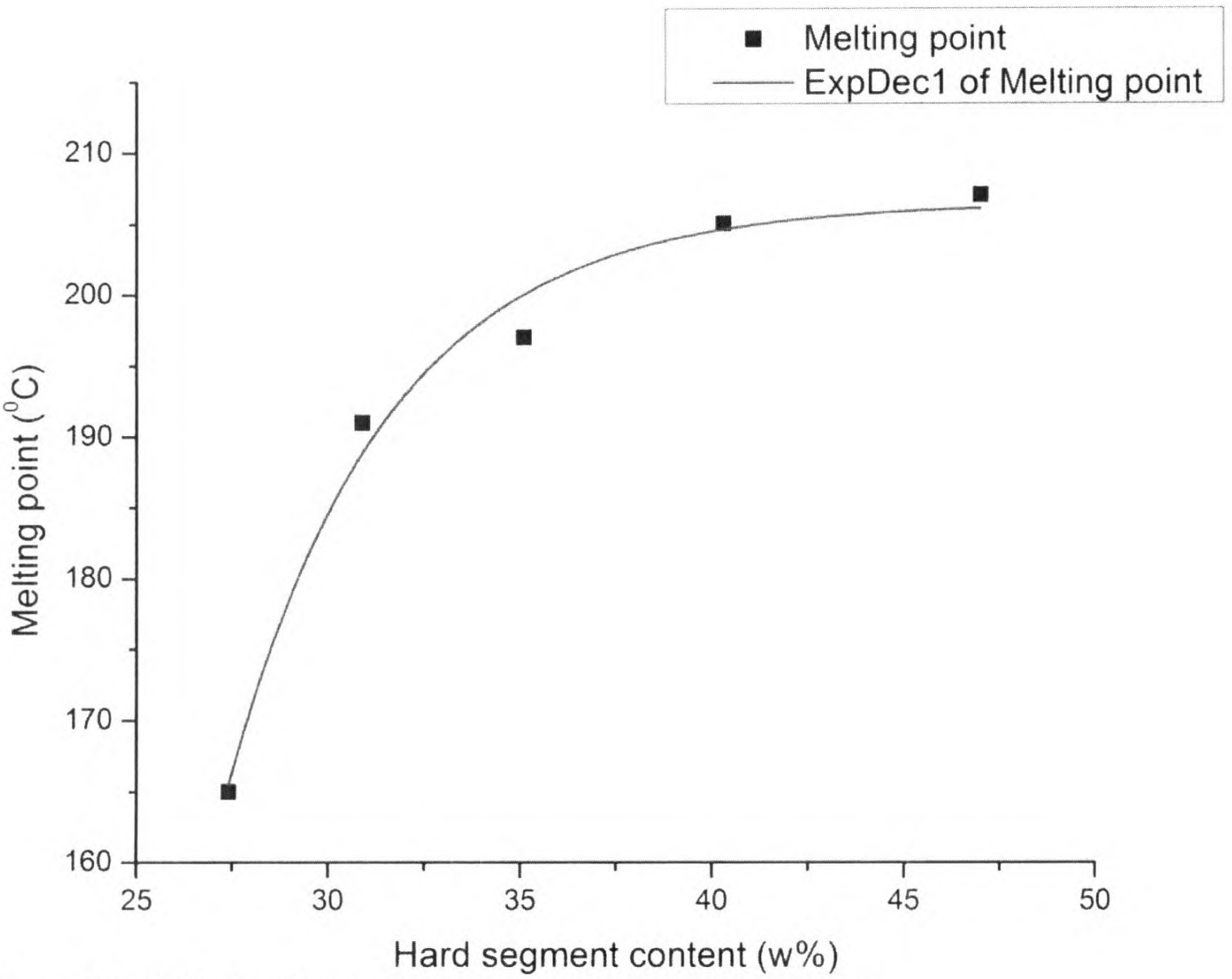


Figure 46: Variation in melting temperature compared to hard segment content

The increase in hard segment content has lead to an increase in crystallinity successively results in a higher melting temperature. The variation in crystallinity was explained in detail in afore section.

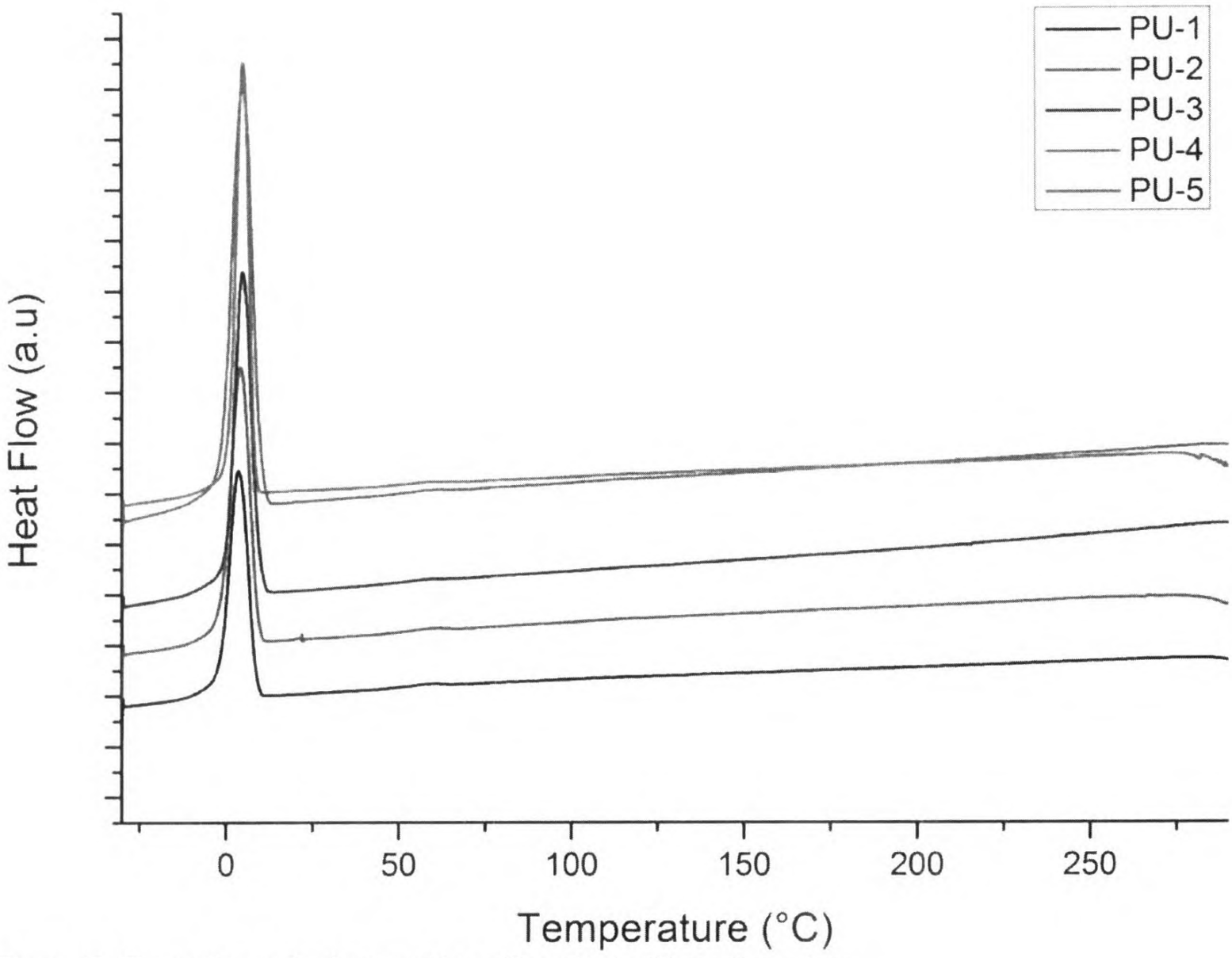


Figure 47: The cooling cycle of polyurethane films obtained from dispersions

During the slow cooling at a rate of 5 ^{0}C /min, PU samples produced a crystallization peak around 0 ^{0}C. Crystallization temperatures are almost same. If melted hard segments get crystalline back the crystallization peak should be at higher temperature. Hence, this crystallization is definitely not related to hard segment.

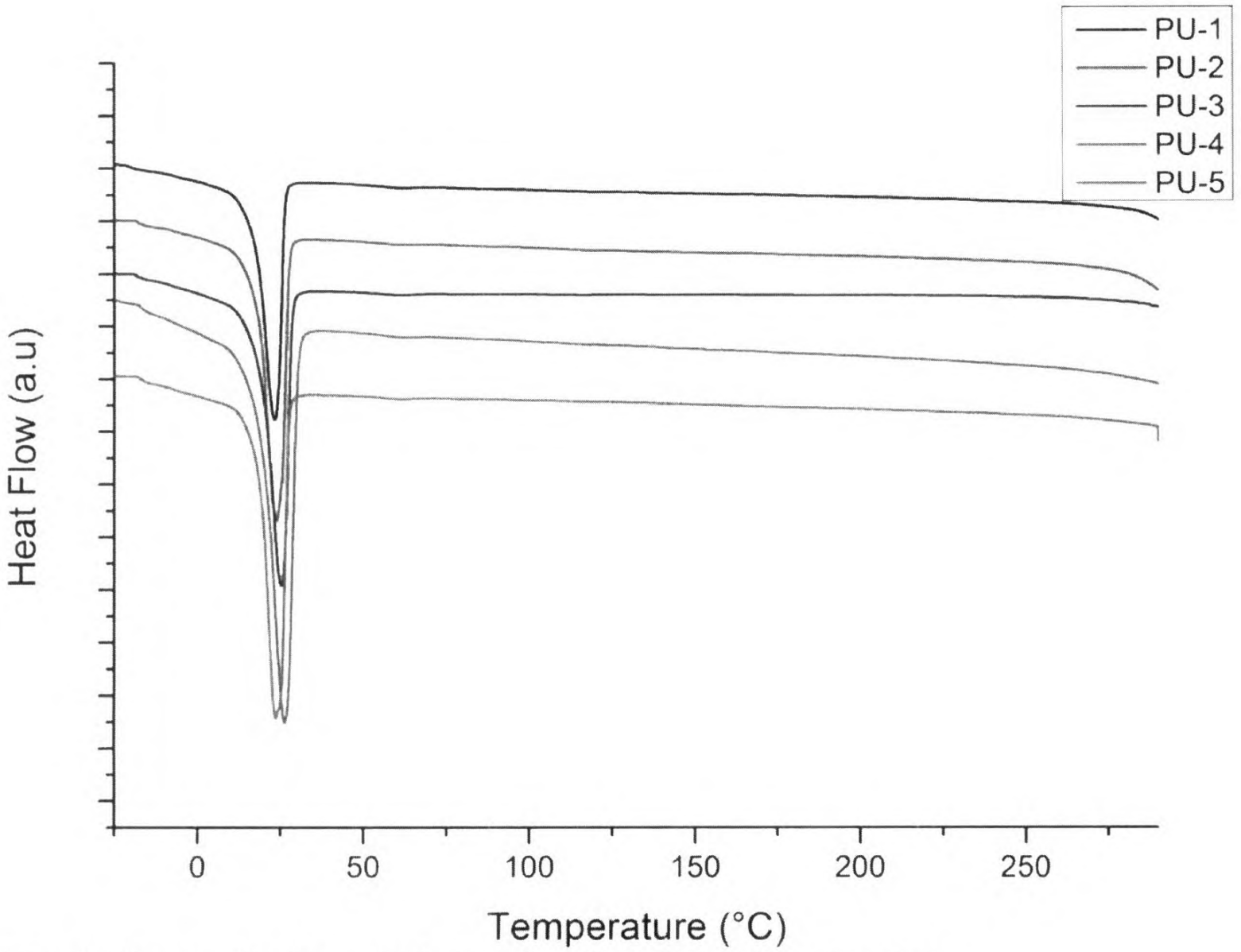


Figure 48: The second heating cycle of polyurethane films obtained from dispersions

In the second heating cycle the peak corresponding to hard segment melting is absent. Instead of that there is a distinct melting peak around 25 ^{0}C. This is due to the melting of the soft segment consisting of PTHF. In the second heating cycle of MDI and PTHF based polyurethane the disappearance of hard segment melting and appearance of soft segment melting has been observed by A Mishra and coworkers too and this melting at 25 ^{0}C has assigned to PTHF melting. (84) Hence, slow cooling of melted polyurethane at 5 ^{0}C /min leads to a micro structure of polyurethanes which is having crystalline soft segments instead of crystalline hard segments. It says that there is an exchange in micro-structural arrangement from hard segment crystallinity to soft segment crystallinity via the melting and re-crystallizing processes through a slow heat/cool route.

FT-IR technique can be used to collect the evidences to show these micro structural changes associated with heating/cooling processes during DSC thermogram.

The Figure 49 and Figure 50 show the CO region and NH region of the FT-IR spectra obtained from the films which were obtained from solvent evaporation after subjected to a gradual increase in temperature until it reaches to 220 ^{0}C via a DSC heating cycle which leads to hard segment melting followed by slow cooling process up to -30 ^{0}C via a DSC cooling cycle which leads to soft segment crystallization and re-heating up to 10 ^{0}C using another heating cycle. The temperature 10 ^{0}C was selected as the best suitable temperature, before crystallized soft segments start to melt, to open the DSC sample compartment.

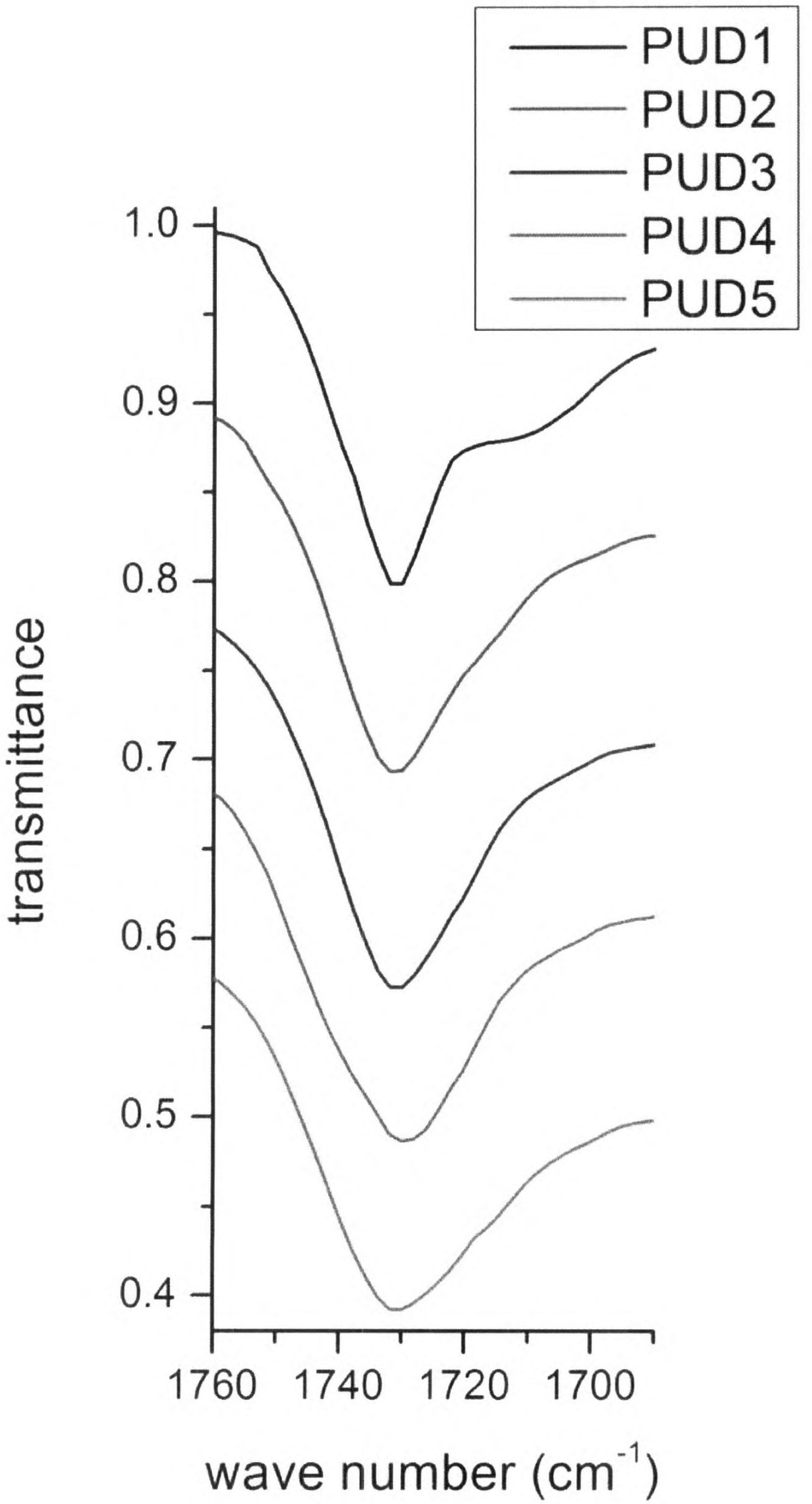

PUD1
PUD2
PUD3
PUD4
PUD5
1.0
0.9
0.8
0.7
0.6
0.5
0.4
transmittance
1760
1740
1720
1700
wave number (cm-1)

Figure 49: The C-O region of the FT-IR spectra of PUD films after the DSC profiling

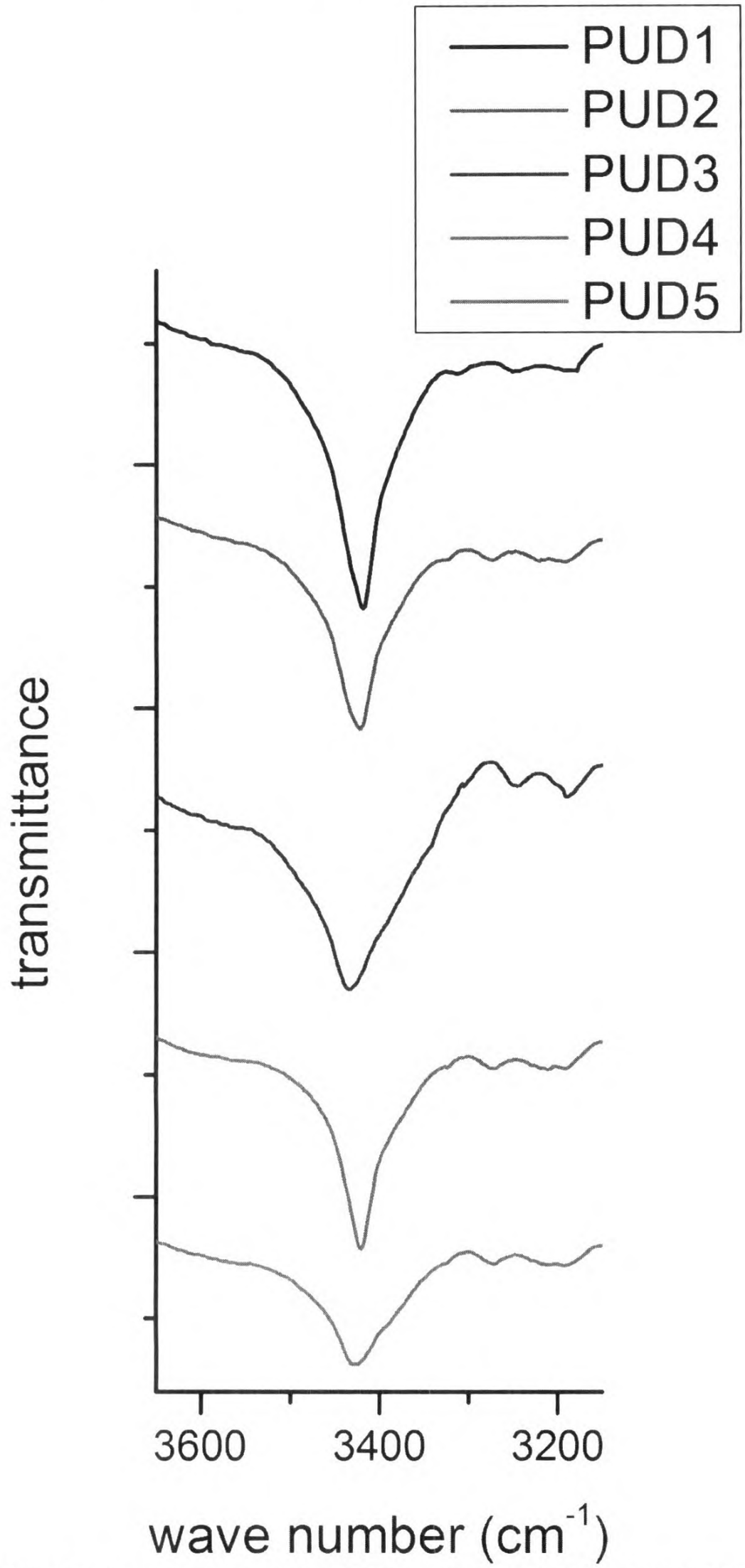


Figure 50: The N-H region of the FT-IR spectra of PUD films after the DSC profiling

By comparing those spectra (Figure 49 & Figure 50) with the spectra of the films obtained via solvent evaporation (Figure 38 & Figure 39) there is a disappearance of the hydrogen bonded NH and carbonyl peaks while increasing the intensity of free NH and carbonyl peaks. The replacement of hard segment crystallinity by soft segment crystallinity after the slow heating/cooling process occurred during the DSC recording can be well explained through this diminishment in the H bonded peaks and the growth in the free peaks of both carbonyl and NH bonds. When microstructure converts to soft segment crystallinity those hydrogen bonds are destroyed and then H bonded peaks are diminished.

Therefore, the required microstructure of polyurethane solid can be achieved through the way of their preparation. If the crystalline hard segment based polyurethane is needed just by evaporating the solvent it can be obtained. If the crystalline soft segment based polyurethane is required, it can be converted to crystalline soft segment based polyurethane by melting the former and slow back cooling.

Iron –Polyurethane composites

Preparation

Iron polyurethane composites were prepared using iron pentacarbonyl and three polyurethane prepolymer systems. The way that they prepared was discussed earlier under experimental section. The differences of those composites to each other were analyzed using the below analytical techniques.

Analysis

Fluorescence

The fluorescence behavior of these composites was analyzed similar to the fluorescence analysis of corresponding polyurethane prepolymer systems. It was able to compare the fluorescence behavior of each other as well as to compare the fluorescence behavior of composites and the corresponding polyurethane prepolymer. The observations for each film will be discussed under the corresponding label titles and analysis of those observations will be followed as a separate section.

PUC-1

The PUC-1 was obtained from PUP-3 system and prepared via solution mixing method under dark conditions.

Once the first spectrum was recorded a single peak was observed with very low intensity (Figure 51). Due to this low intensity the noises in the spectrum were significant.

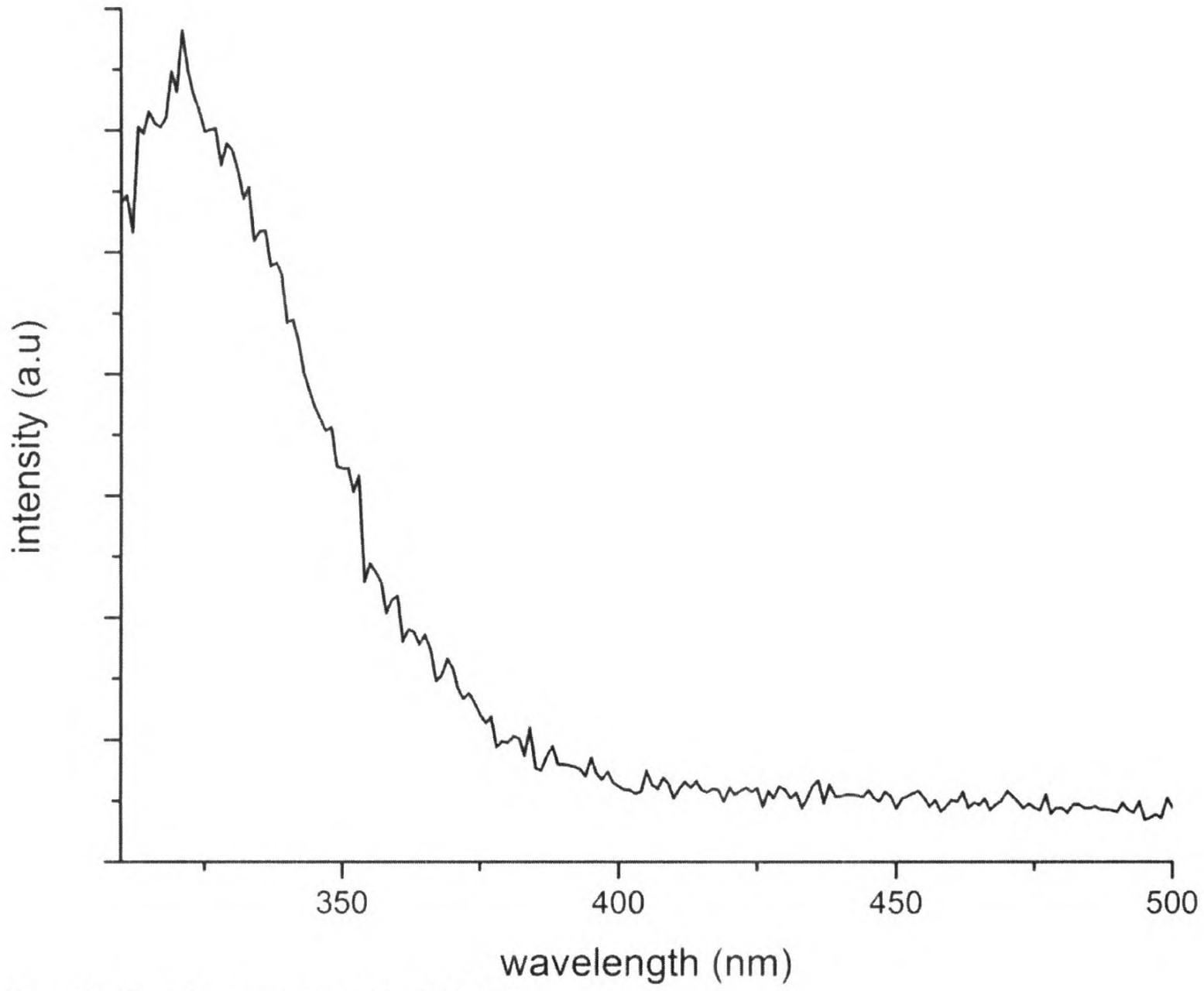


Figure 51: The initial spectrum of the PUC-1 film

With continuous exposure, a second peak was generated and its' intensity was increased by reducing the first peak intensity (Figure 52). However, the changes in intensities were comparatively slow.

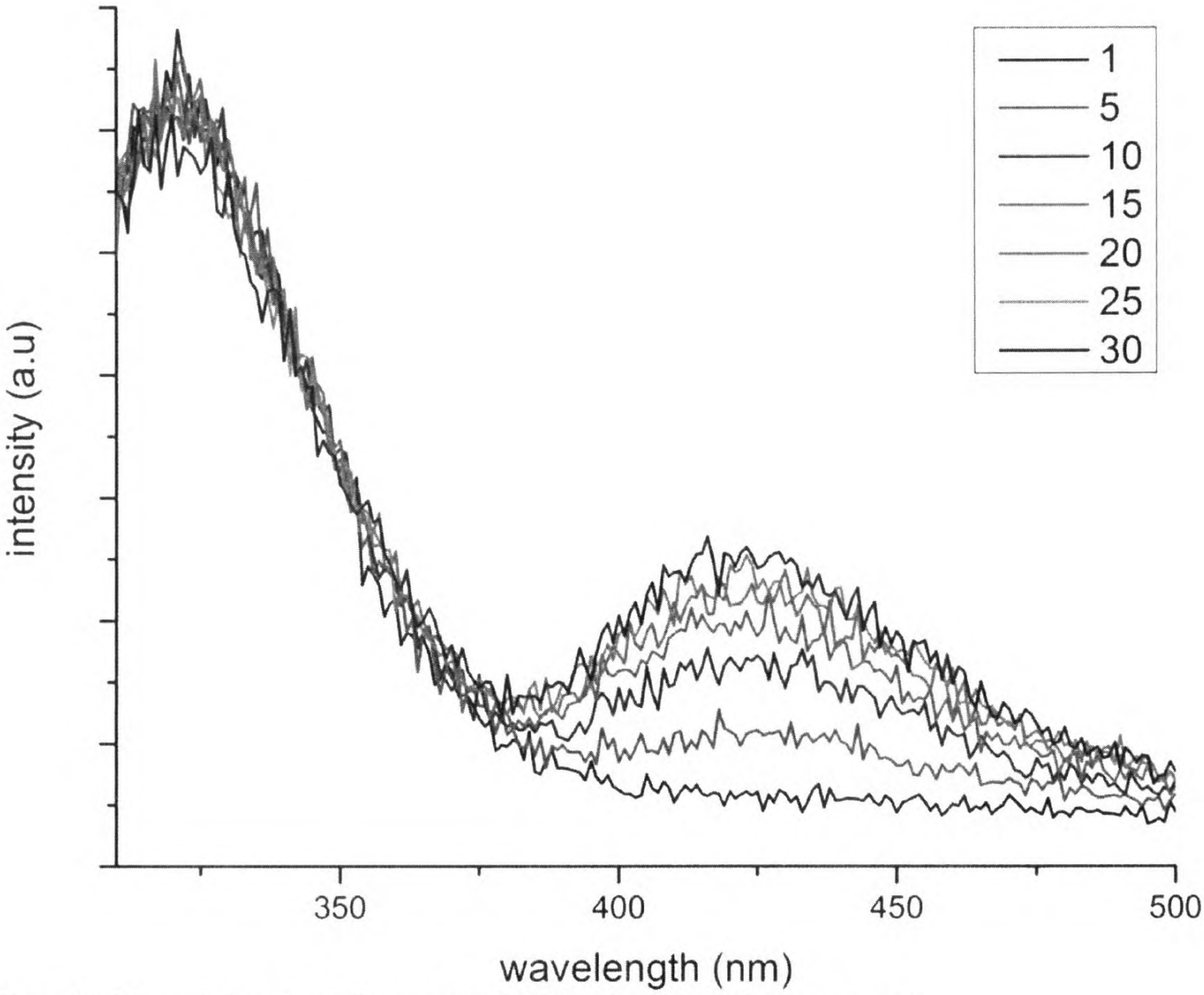


Figure 52: The variation of emission spectra of PUC-1 film with continuous exposure

Once the two peak intensity variation was considered, it was unable to observe a smooth increase and decrease in second peak and first peak intensities respectively. This is due to the significance of noises. Nevertheless, similar to the PUP-3 system, the tendency of increase in second peak and decrease in first peak during continuous exposure and hysteresis was observed (Figure 53 & Figure 54).

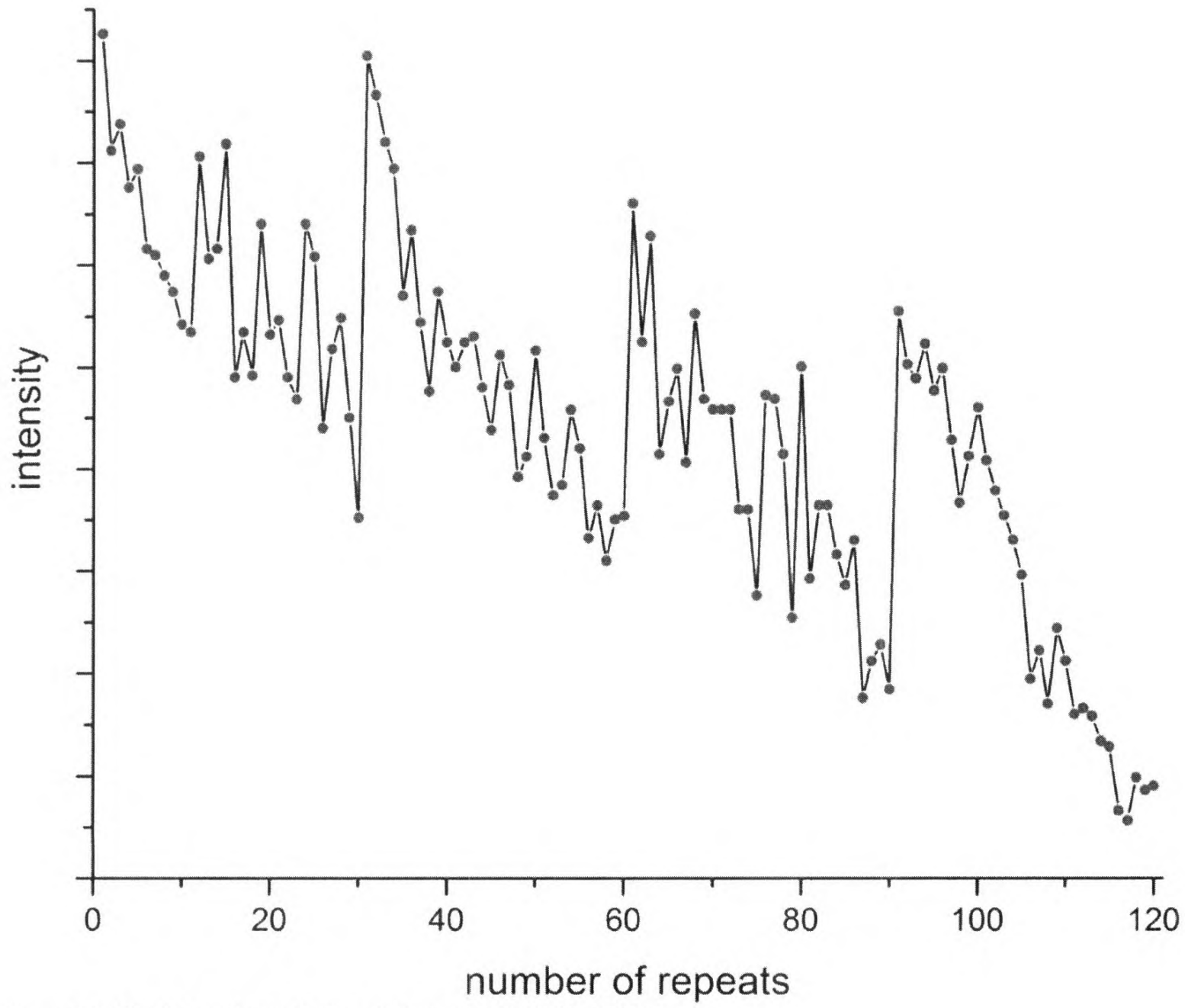


Figure 53: The intensity variation of first peak in PUC-1 film

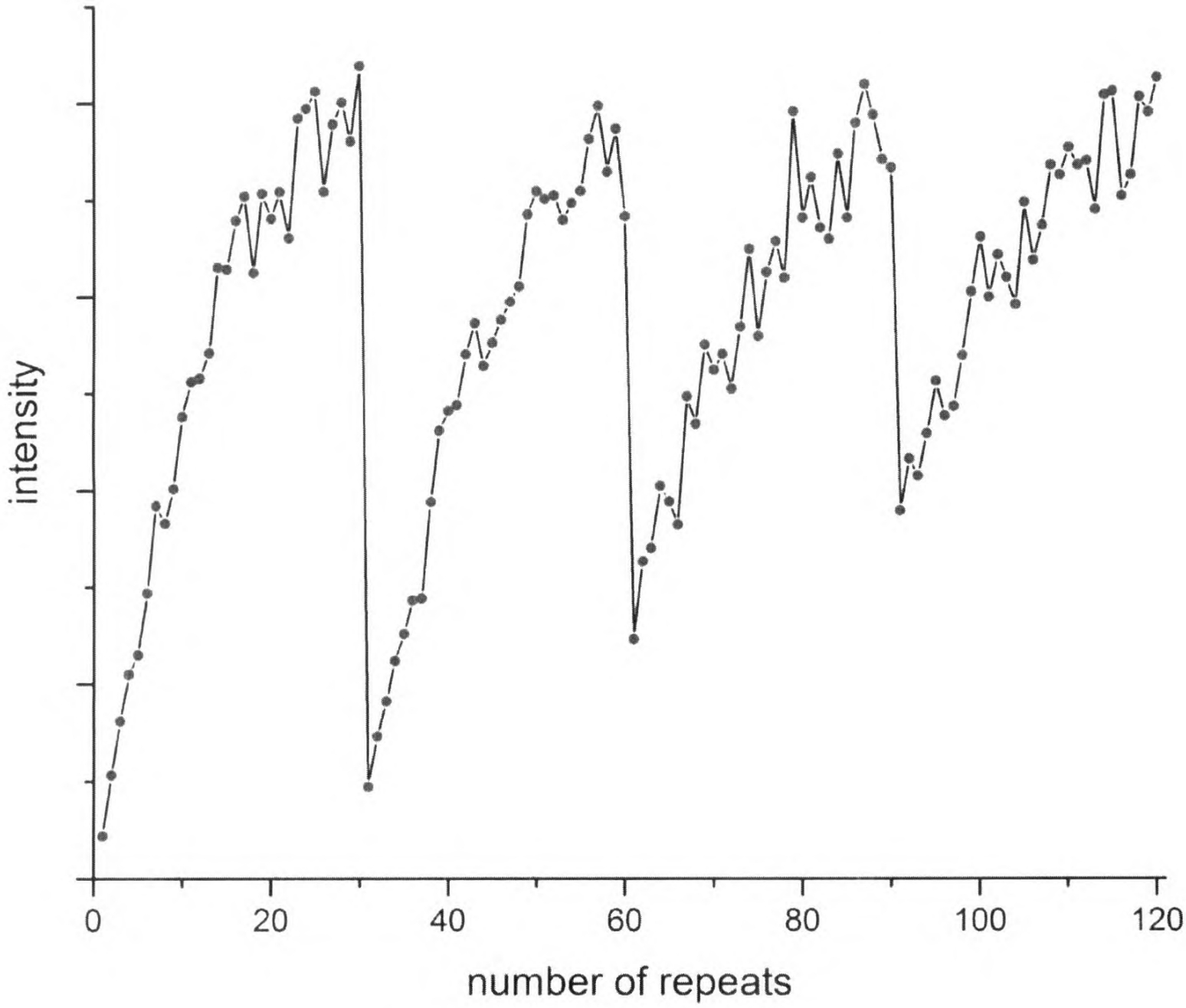


Figure 54: The intensity variation of second peak in PUC-1 film

PUC-2

The PUC-2 was obtained from PUP-3 system and prepared via solution mixing method followed by UV exposure.

Once the spectrum was recorded, it was observed that fluorescence emission has been quenched (Figure 55).

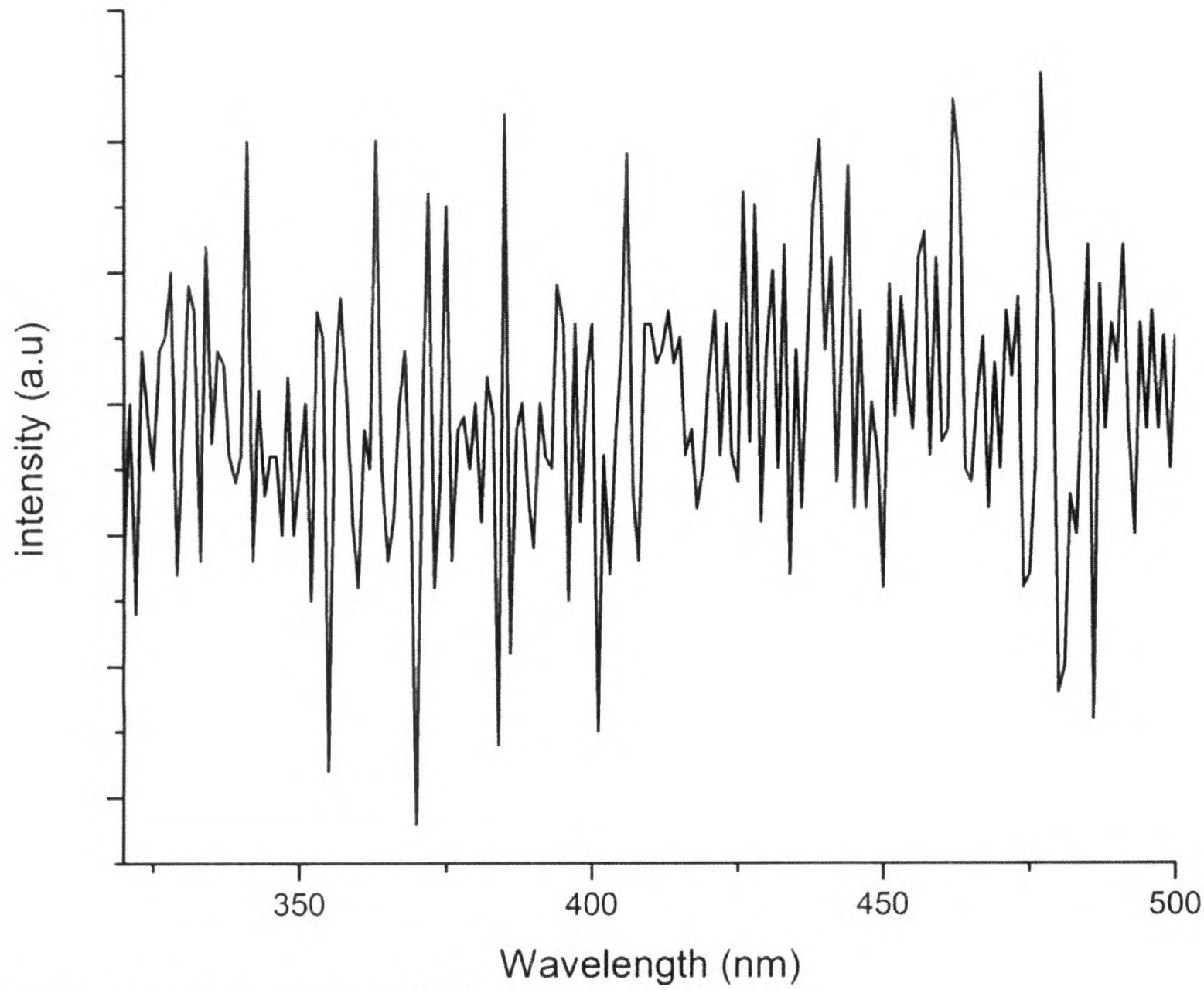


Figure 55: The emission spectrum of PUC-2 film

PUC-3

The PUC-3 was obtained from PUP-3 system and prepared via surfactant added solution mixing method under dark conditions. With the target of improving the compatibility between iron pentacarbonyl and polyurethanes, oleic acid was used as a surfactant.

Fluorescence emission has been quenched. Hence, there was no emission peak just a noise signal was appeared in the spectrum recorded (Figure 56).

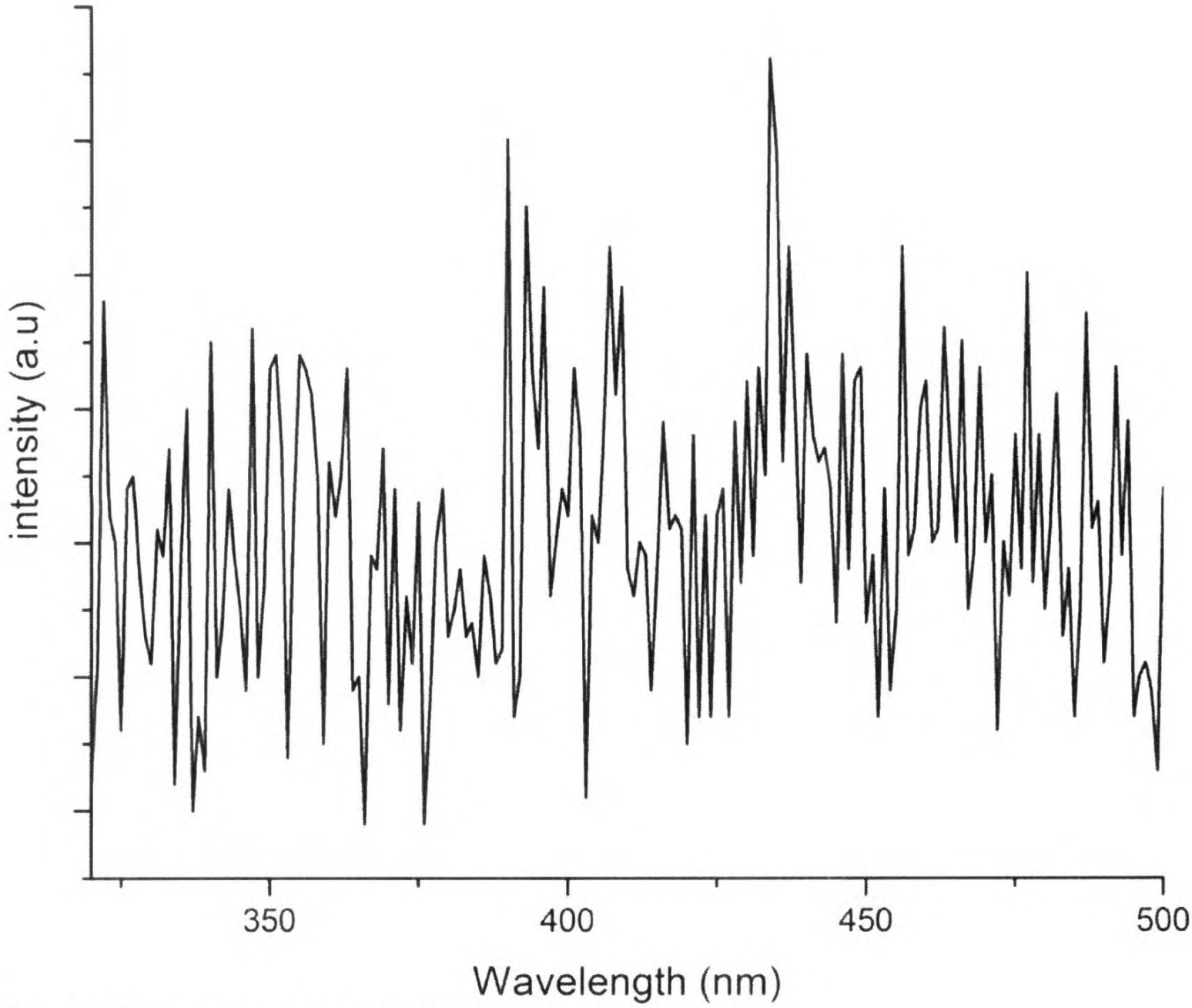


Figure 56: The emission spectrum of PUC-3 film

PUC-4

The PUC-4 was obtained from PUP-3 system and prepared via surfactant added solution mixing method followed by UV exposure. Oleic acid was used as the surfactant.

As shown in Figure 57, just a noise signal was appeared in the emission spectrum recorded due to the quenching of the fluorescence emission.

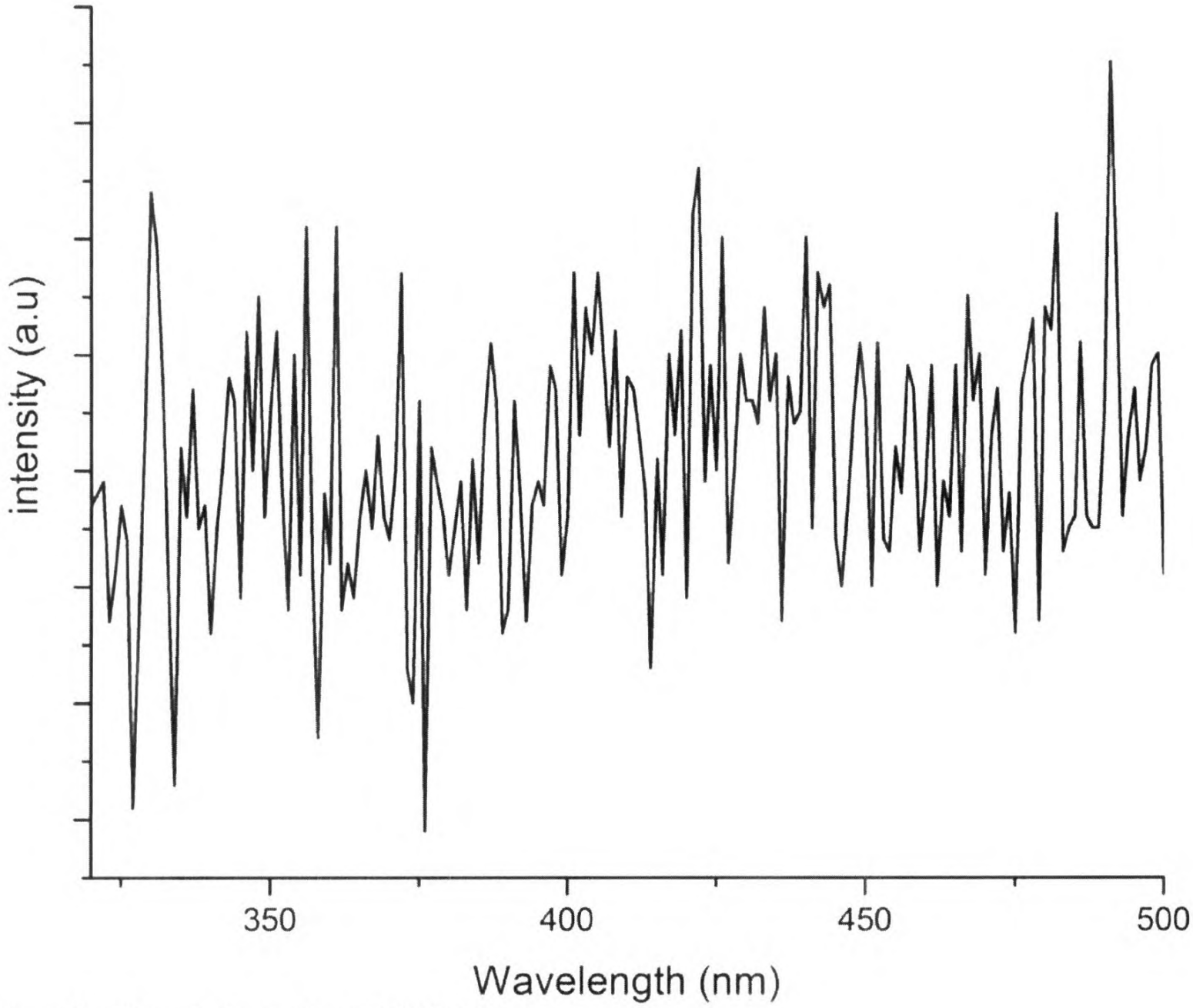


Figure 57: The emission spectrum of PUC-4 film

PUC-5

The PUC-5 was obtained from PUP-3 system and prepared via dipping method under dark conditions.

Initial emission spectrum was with a single peak (Figure 58). The intensity was less than PUP-3 film although higher than PUC-1 which was obtained from solution mixing method.

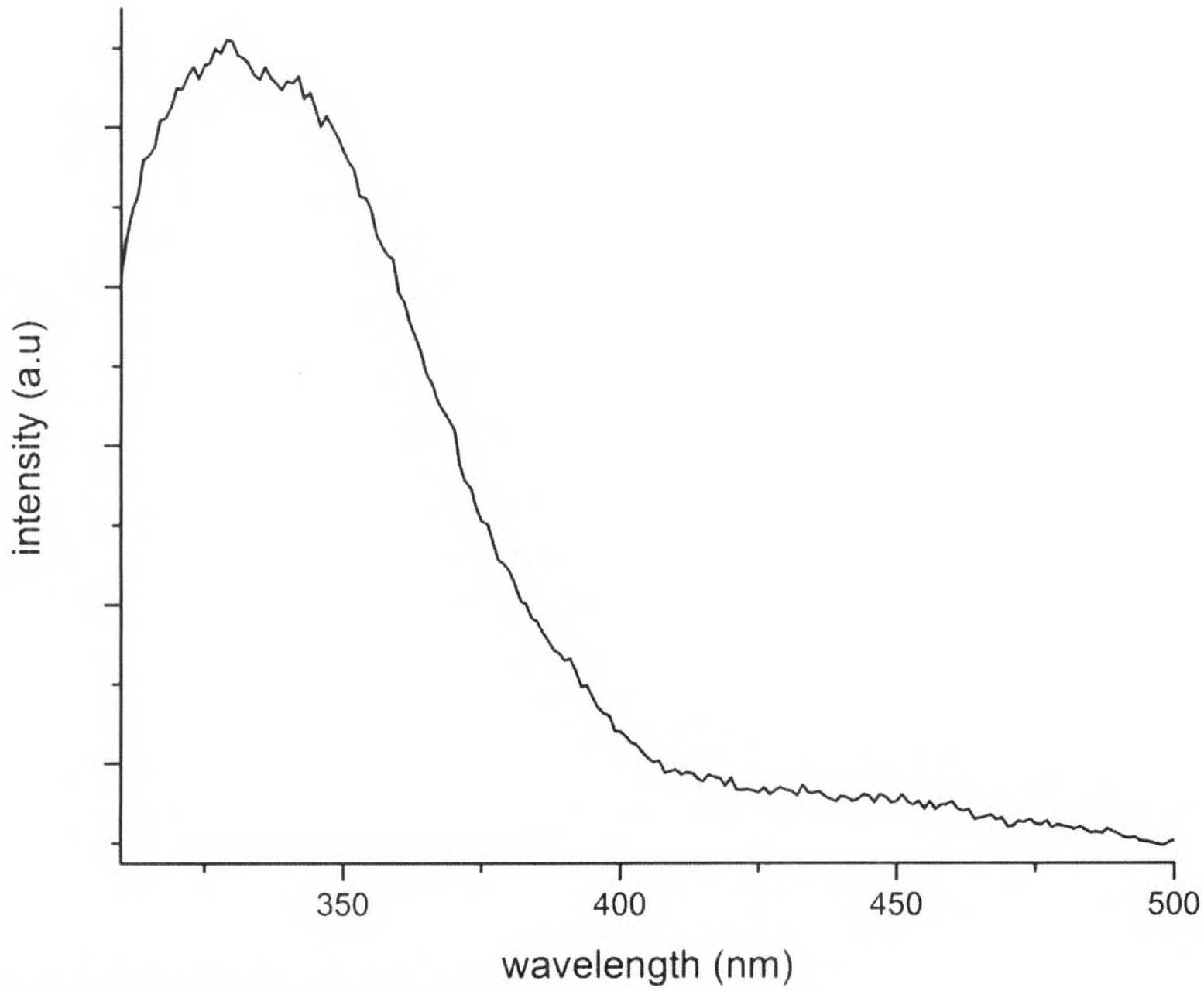


Figure 58: The initial spectrum of the PUC-5 film

The continuous exposure to 293 nm wave length was able to generate and grow a second peak while reducing the first peak intensity. It is shown in Figure 59 which shows the variation of emission spectra with number of repeats.

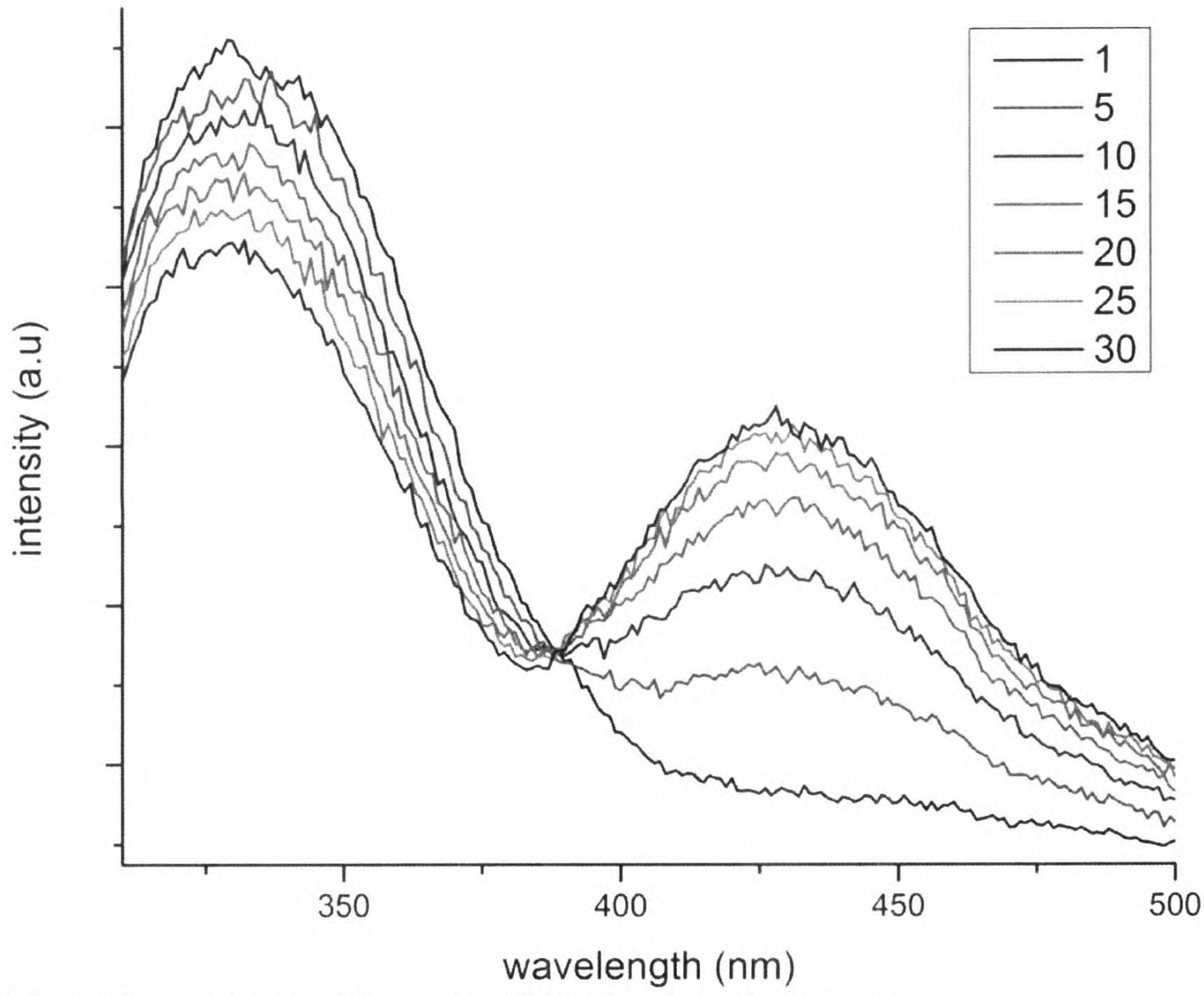


Figure 59: The variation of emission spectra of PUC-5 film with continuous exposure

The variation in intensities with number of repeats followed the trend of PUP-3 and also had the hysteresis as well (Figure 60 & Figure 61).

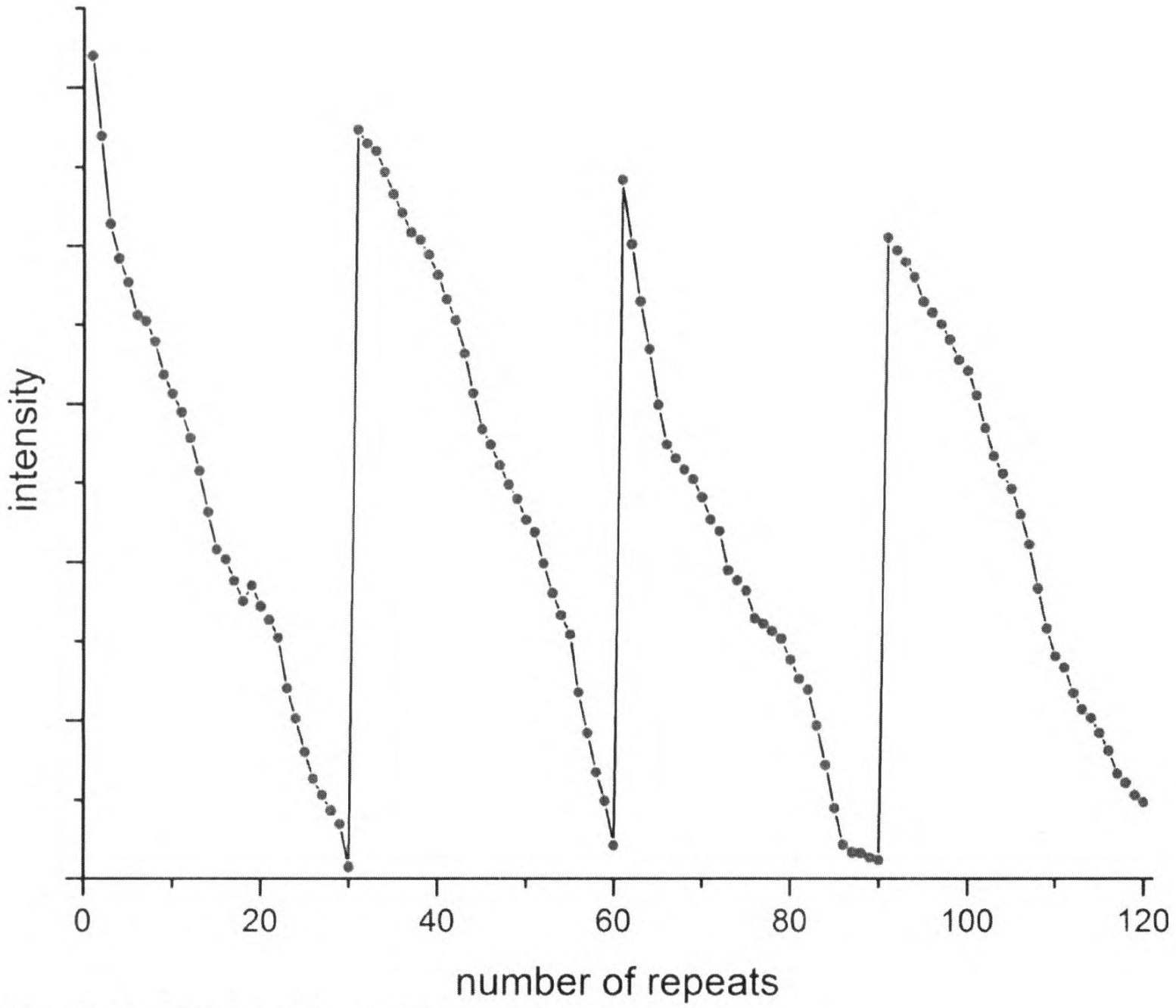


Figure 60: The intensity variation of first peak in PUC-5 film

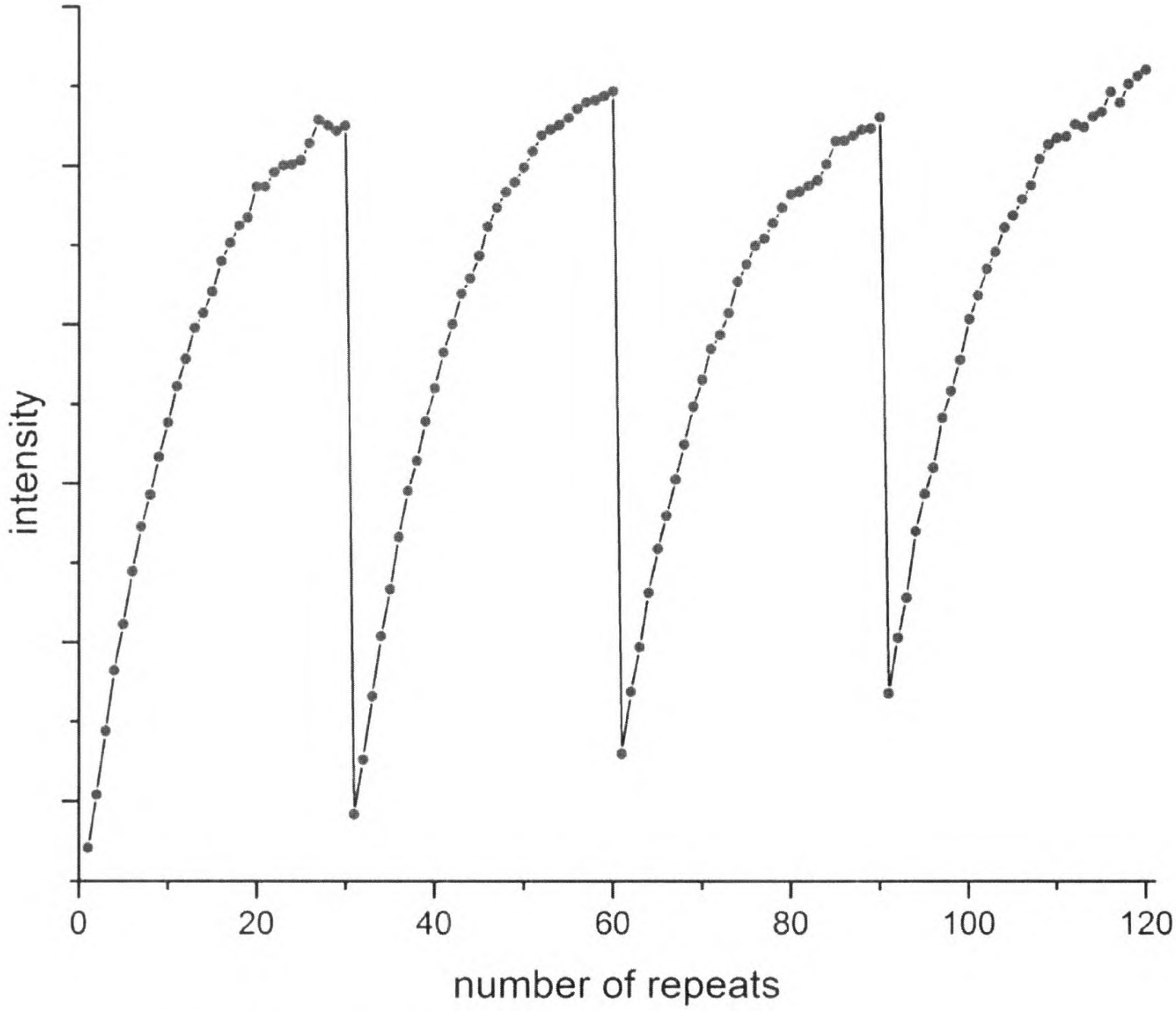


Figure 61: The intensity variation of second peak in PUC-5 film

PUC-6

The PUC-6 was obtained from PUP-3 system and prepared via dipping method followed by UV exposure.

There was no peak corresponding to an emission in the recorded emission spectrum (Figure 62). It has been quenched.

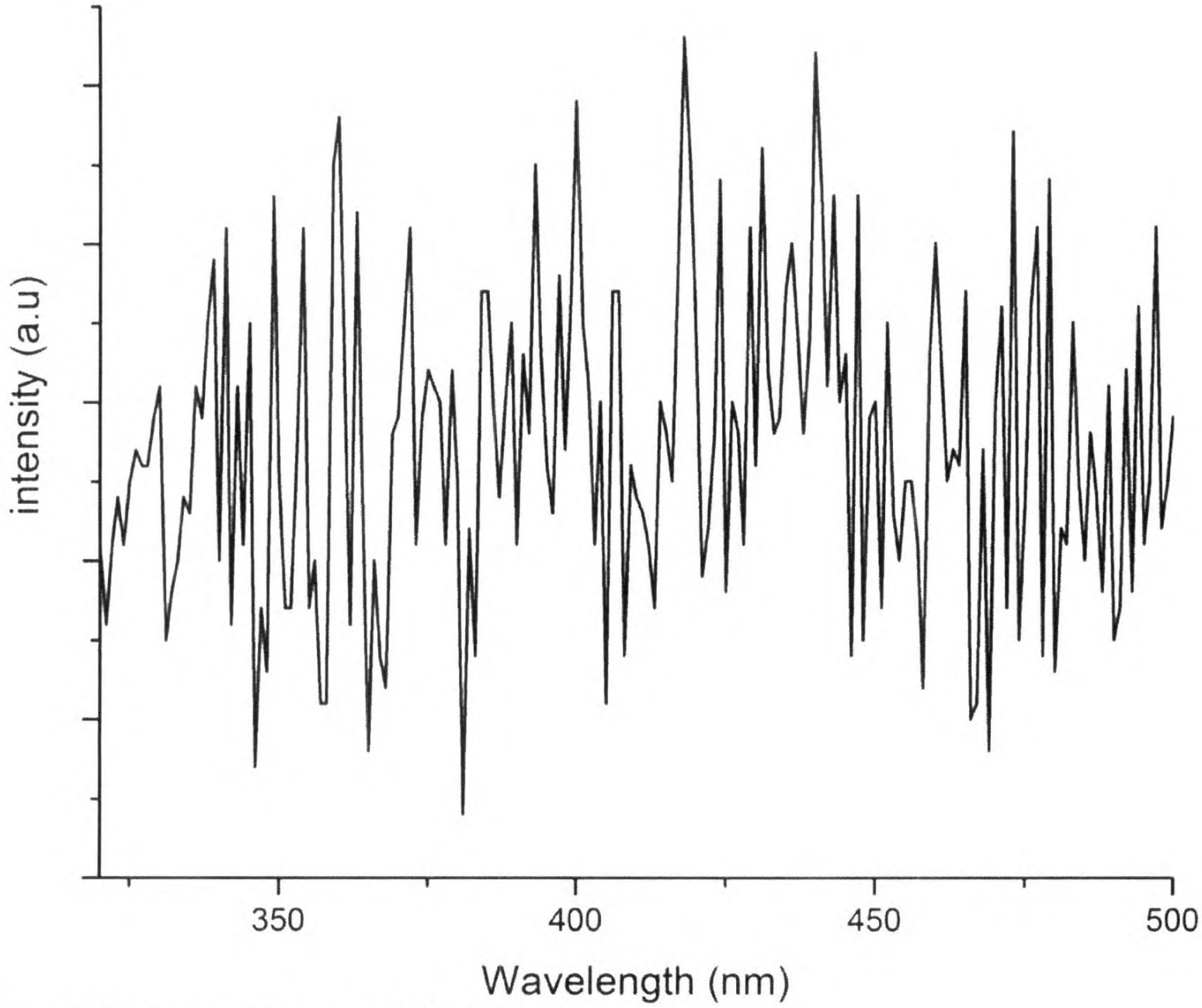


Figure 62: The emission spectrum of PUC-6 film

PUC-7

The PUC-7 was obtained from PUP-3 system and prepared via vapour deposition method under dark conditions.

A single peak was observed in the initial emission spectrum. The intensity of the signal was strong enough to achieve a noise free spectrum (Figure 63).

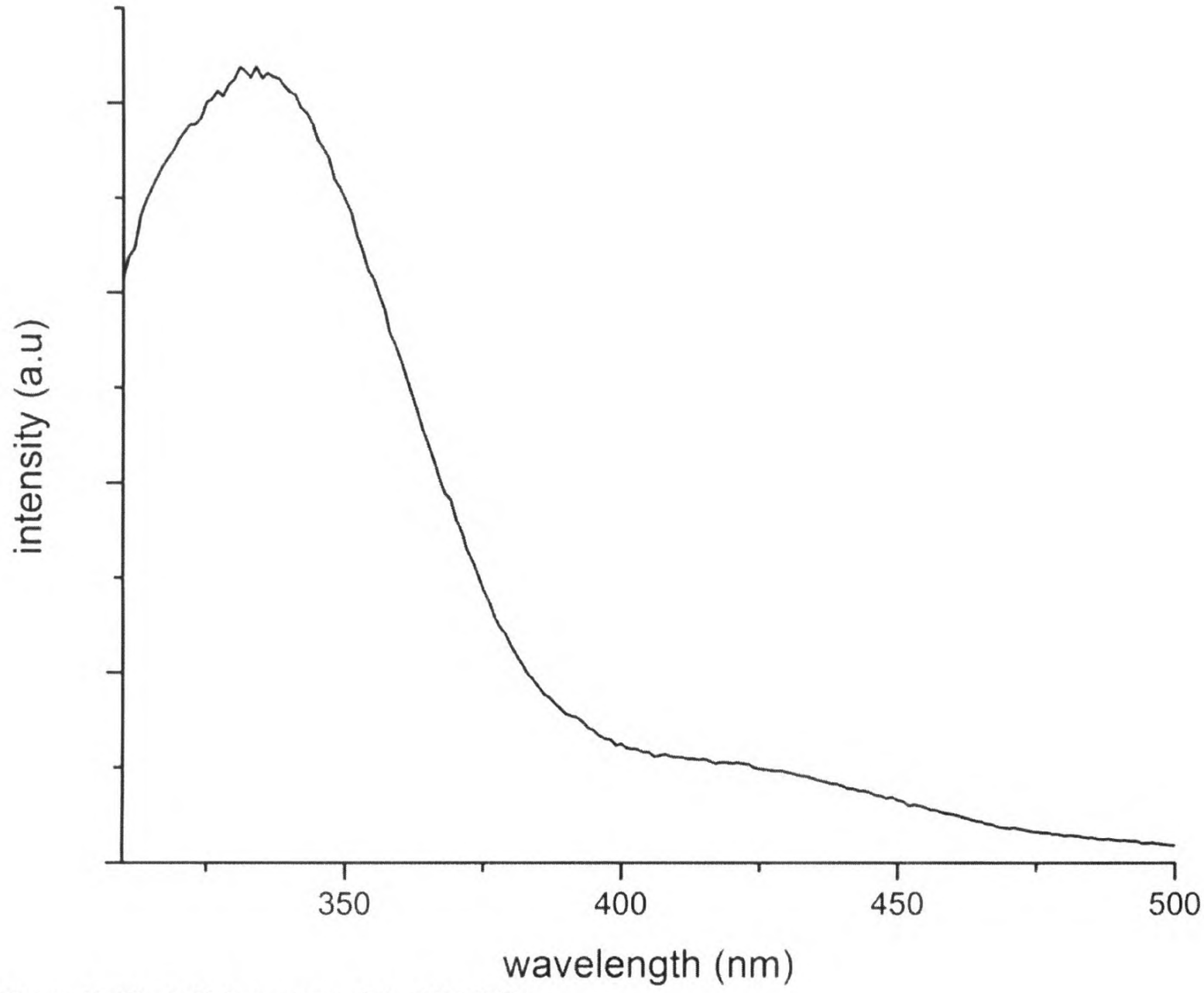


Figure 63: The initial spectrum of the PUC-7 film

With continuous exposure there is a generation in second peak at higher wave length which shows a further growth in its intensity while reducing the first peak intensity with exposure time (Figure 64).

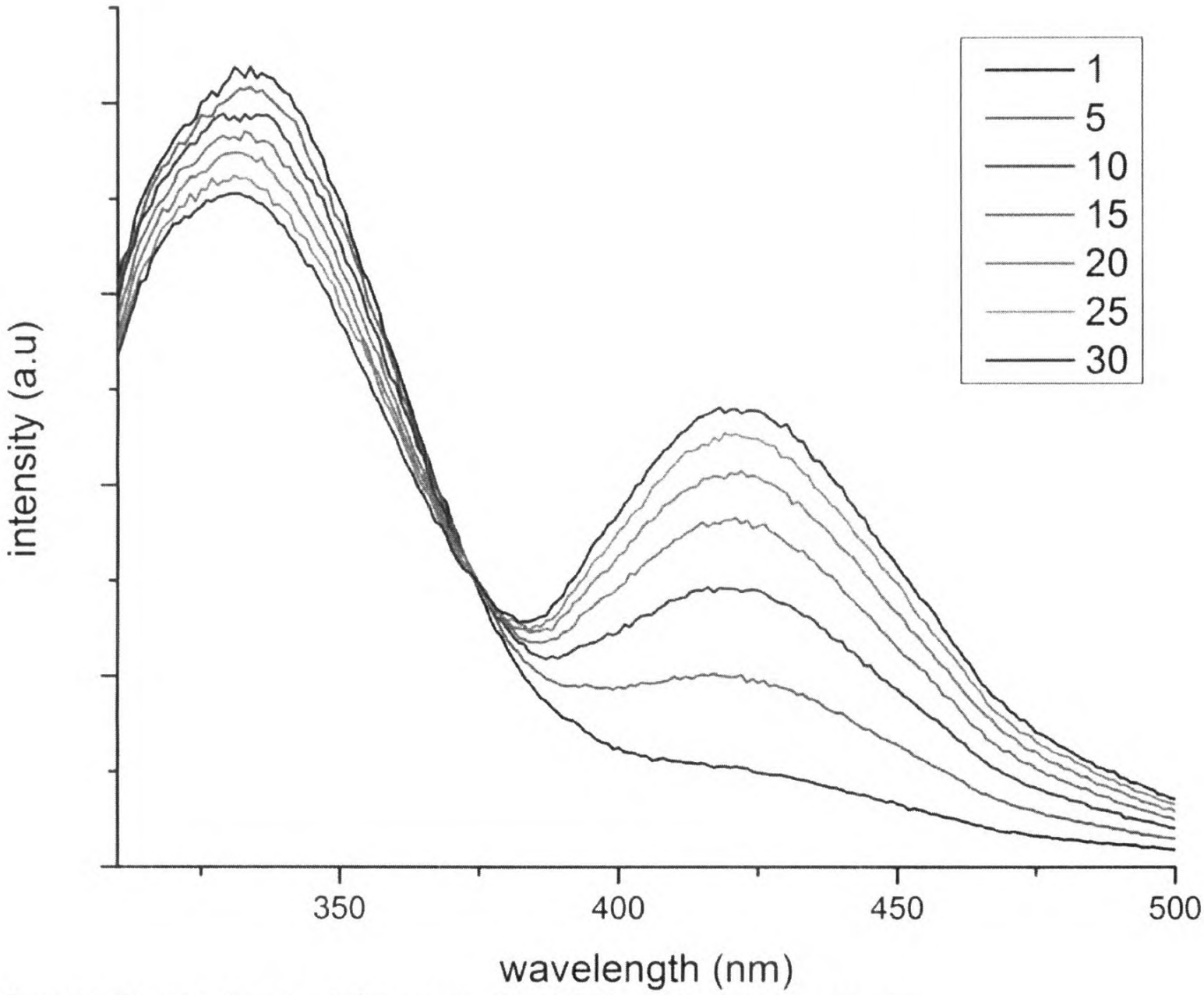


Figure 64: The variation of emission spectra of PUC-7 film with continuous exposure

Once the variations in two peak intensities were considered they showed a similar trend to the PUP-3 film. In such a way a gradual growth in second peak and reduction in first peak intensities were observed (Figure 65 & Figure 66).

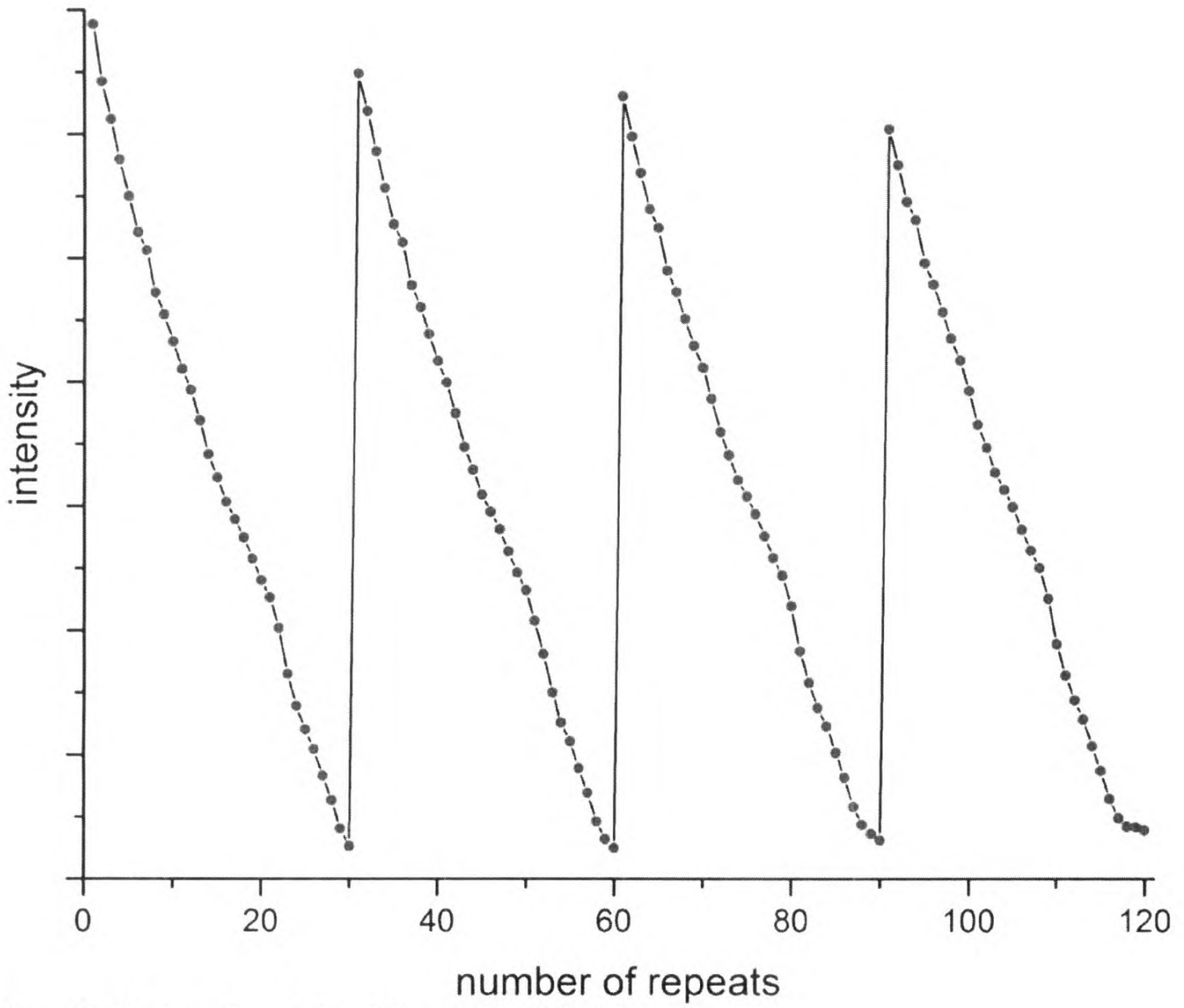


Figure 65: The intensity variation of first peak in PUC-7 film

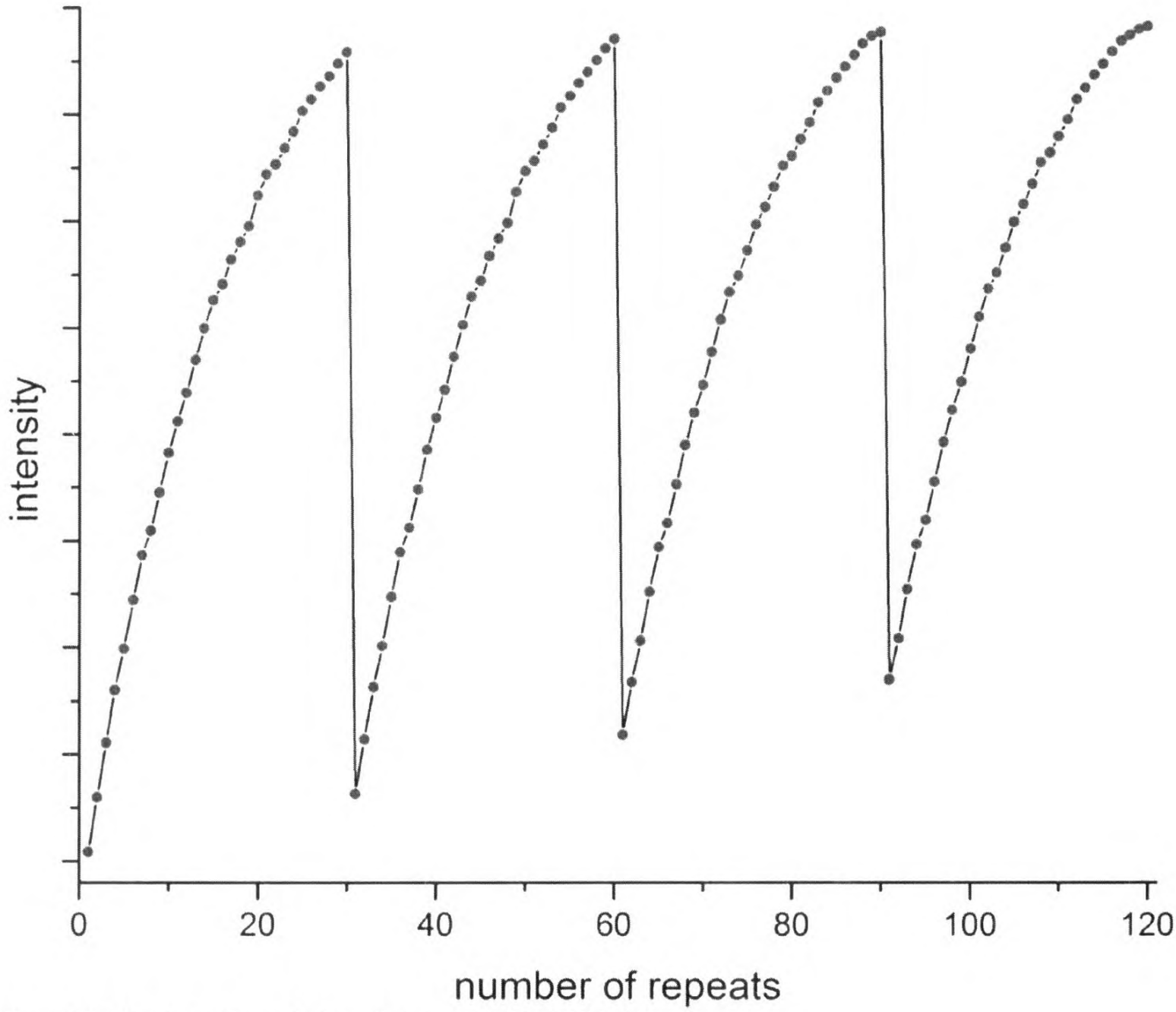


Figure 66: The intensity variation of second peak in PUC-7 film

PUC-8

The PUC-8 was obtained from PUP-3 system and prepared via vapour deposition method followed by UV exposure.

The fluorescence emission has been quenched and noisy signal without a peak was observed (Figure 67).

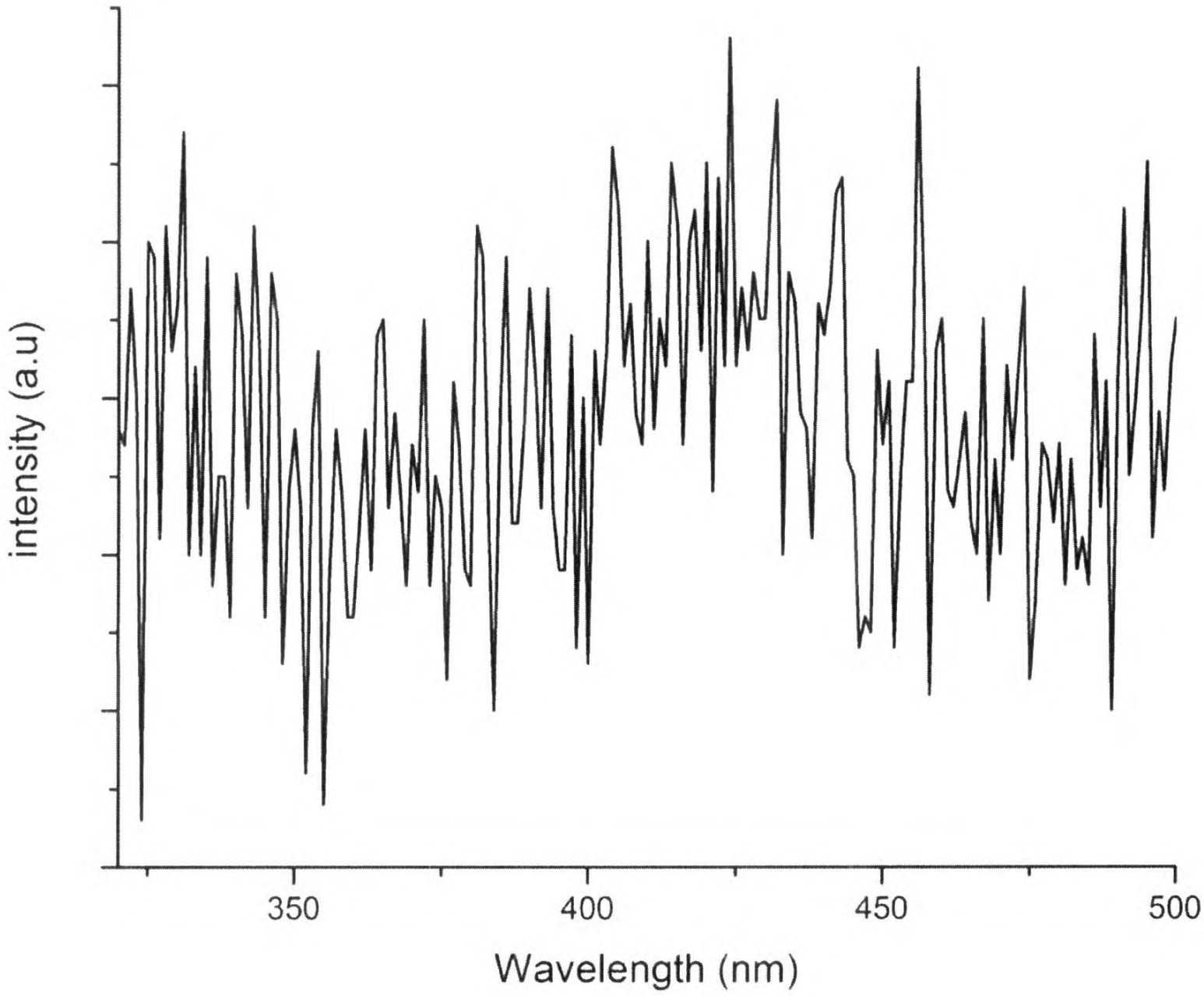


Figure 67

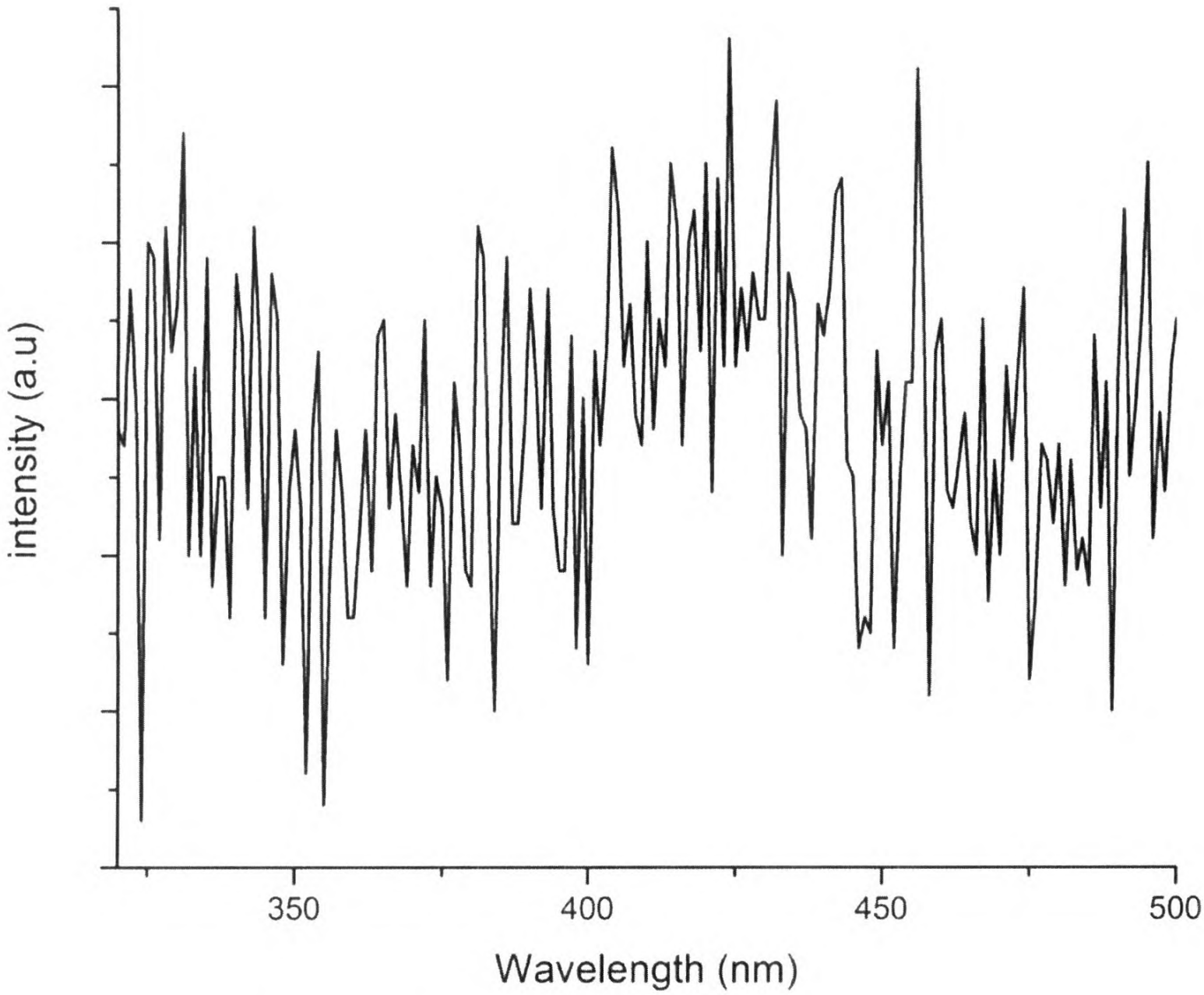


Figure 67: The emission spectrum of PUC-8 film

PUC-9

The PUC-9 was obtained from PUP-10 system and prepared via solution mixing method under dark conditions.

In the first spectrum of the sample, a single peak was observed with very low intensity (Figure 68). Due to this low intensity the noises in the spectrum were significant.

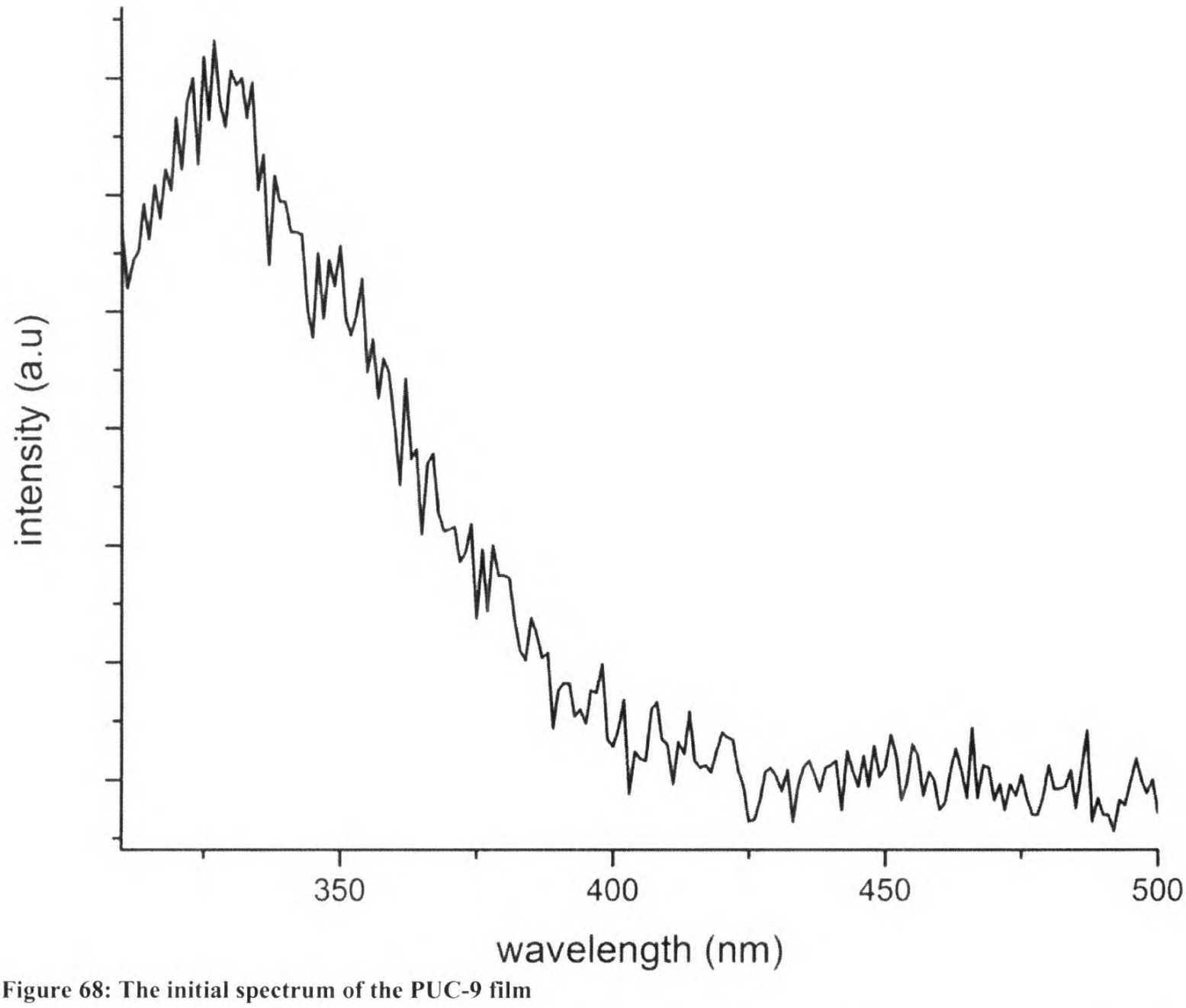


Figure 68: The initial spectrum of the PUC-9 film

With continuous exposure, a second peak was generated at higher wave length and its' intensity was increased while the first peak intensity was reduced (Figure 69). However, the changes in intensities were comparatively slow.

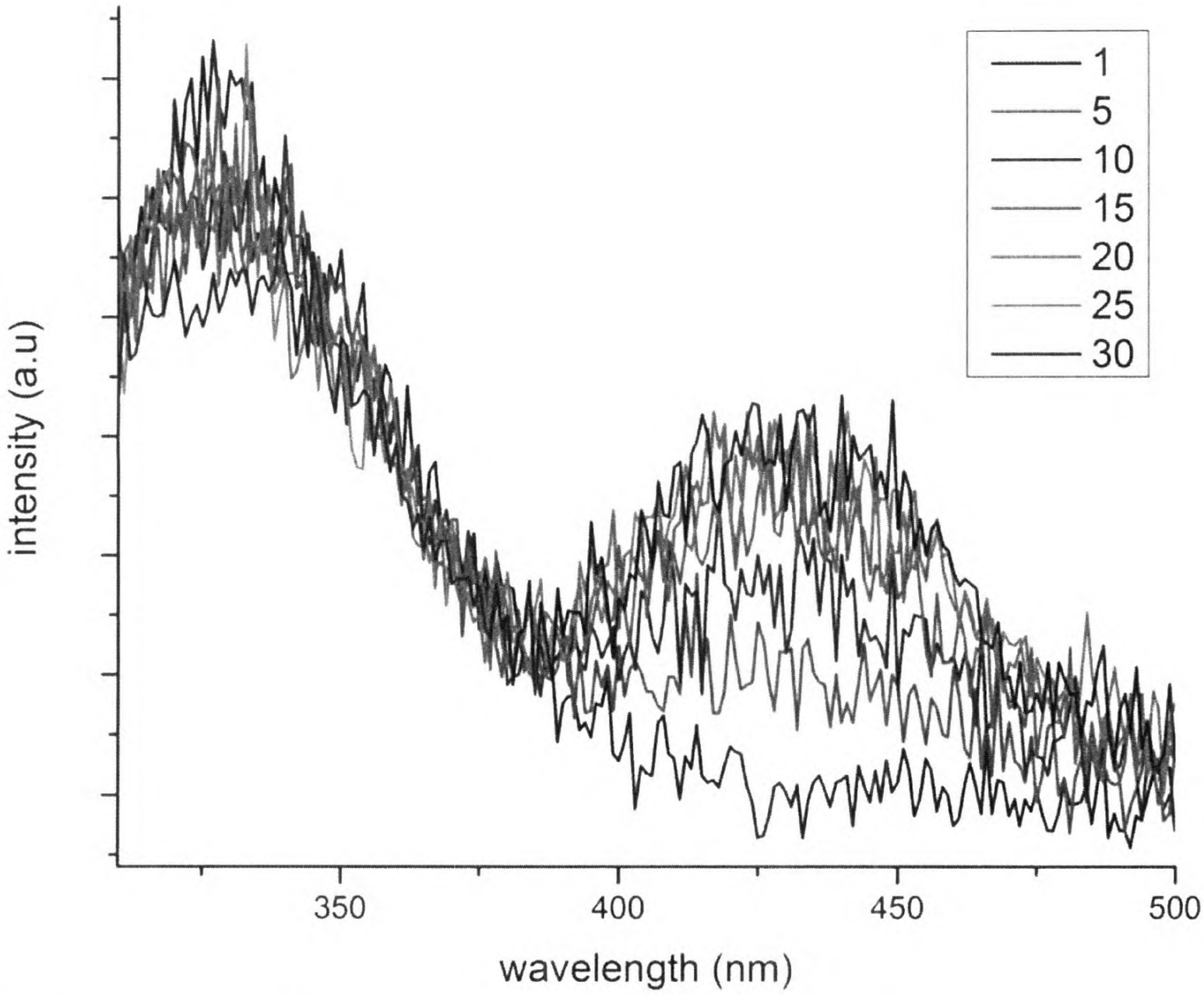


Figure 69: The variation of emission spectra of PUC-9 film with continuous exposure

Due to the significance of the noises in emission signals, the plots of intensity variation of two peaks are not smooth. Nevertheless, during the continuous exposure, it was able to observe the tendency of a diminishment and a growth of first and second peaks respectively and also the hysteresis (Figure 70 & Figure 71).

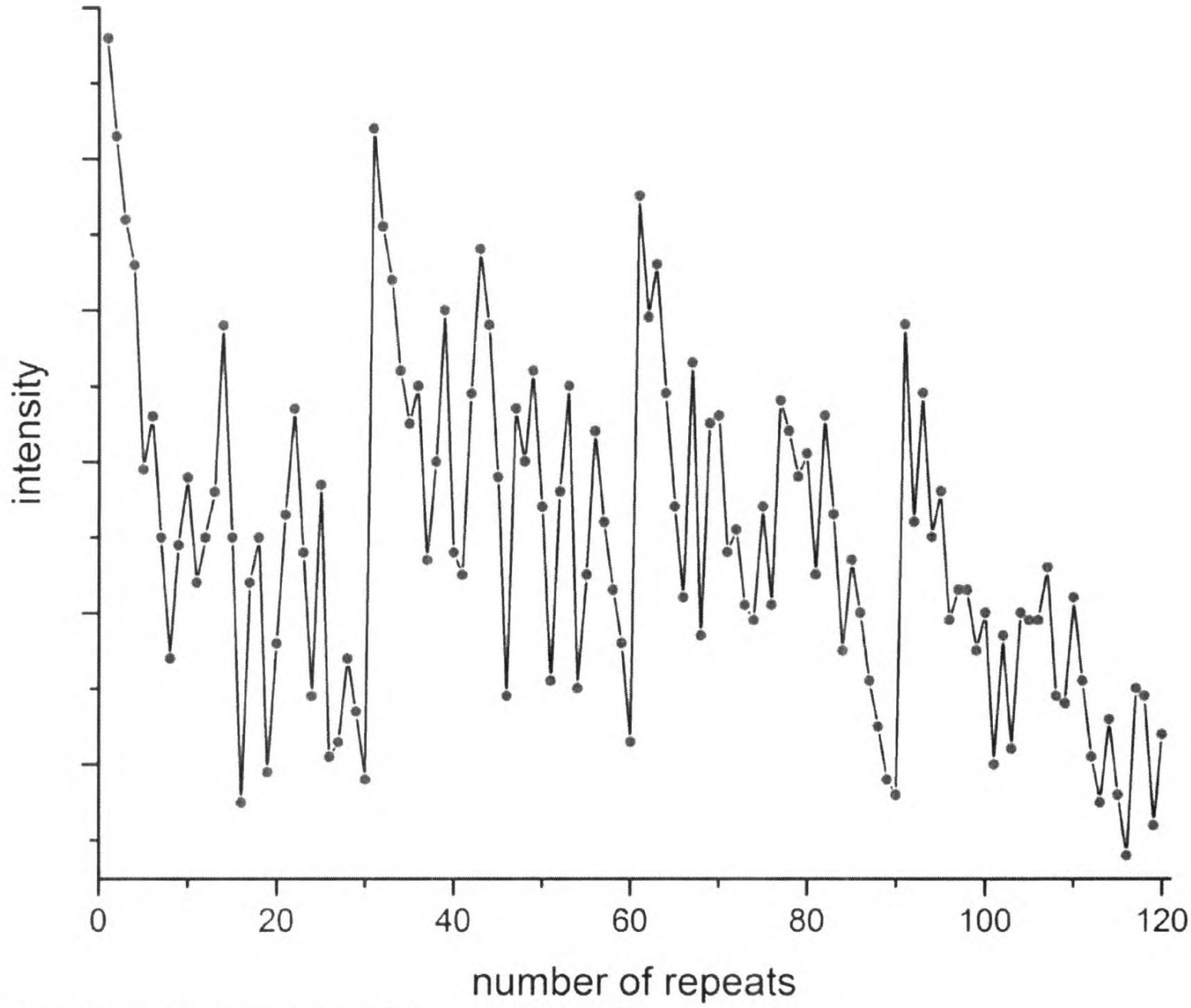


Figure 70: The intensity variation of first peak in PUC-9 film

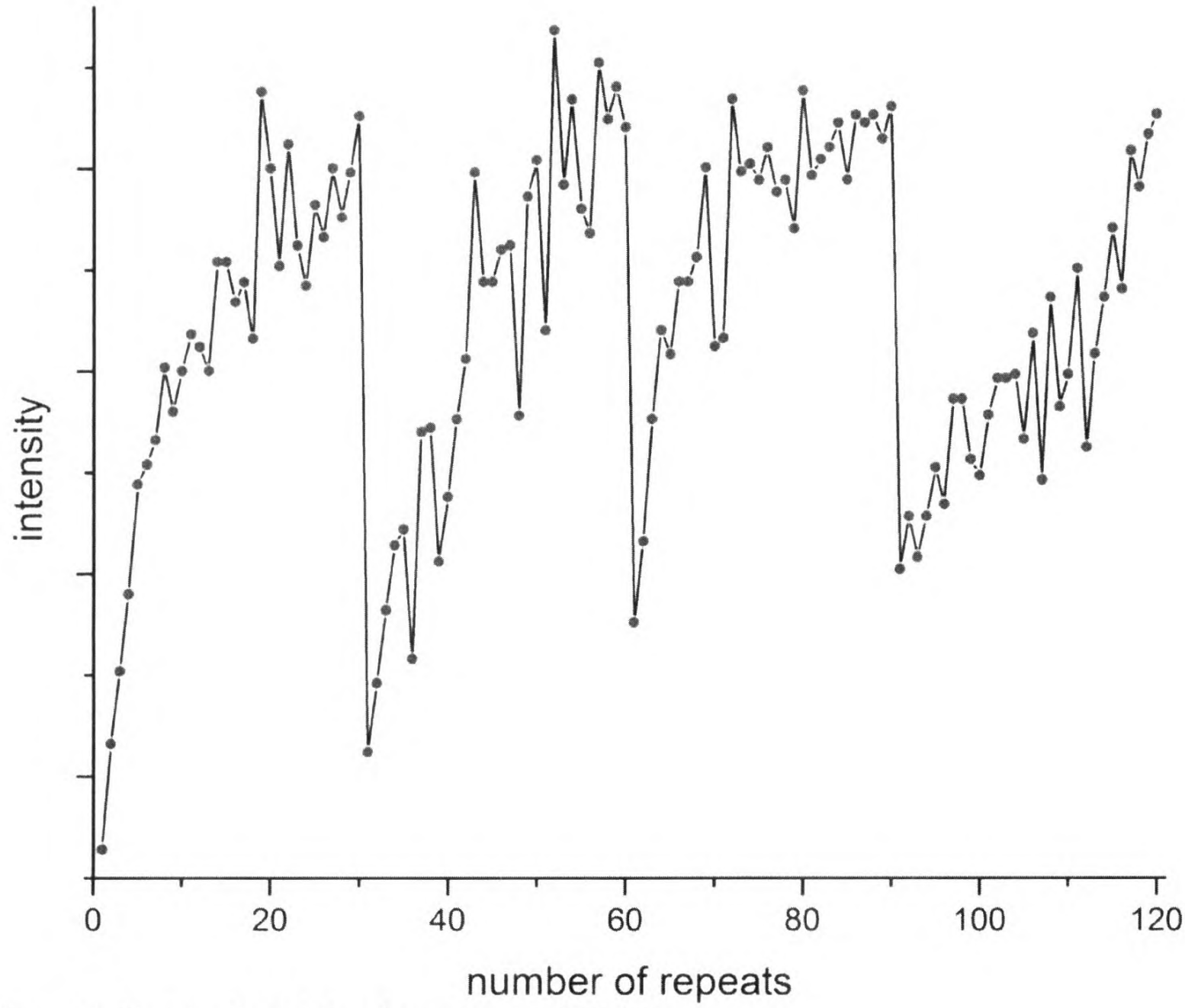


Figure 71: The intensity variation of second peak in PUC-9 film

PUC-10

The PUC-10 was obtained from PUP-10 system and prepared via solution mixing method followed by UV exposure.

The emission spectrum was a noisy signal without significant peak (Figure 72). Emission has been quenched.

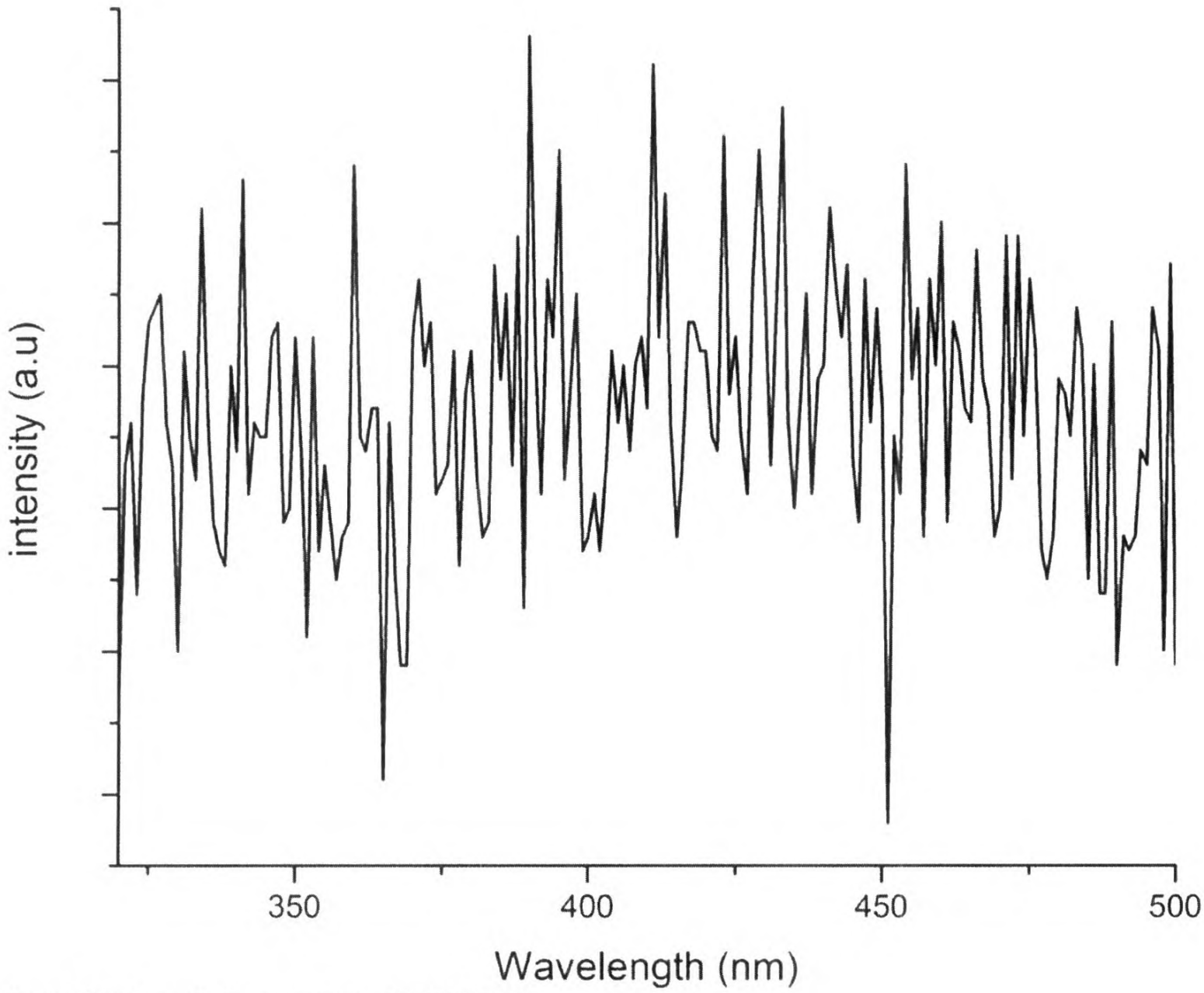


Figure 72: The emission spectrum of PUC-10 film

PUC-11

The PUC-11 was obtained from PUP-10 system and prepared via surfactant added solution mixing method under dark conditions. Here in addition to two main components, the surfactant oleic acid has been used to obtain the composite.

The emission peak has disappeared in the recorded emission spectrum due to quenching (Figure 73).

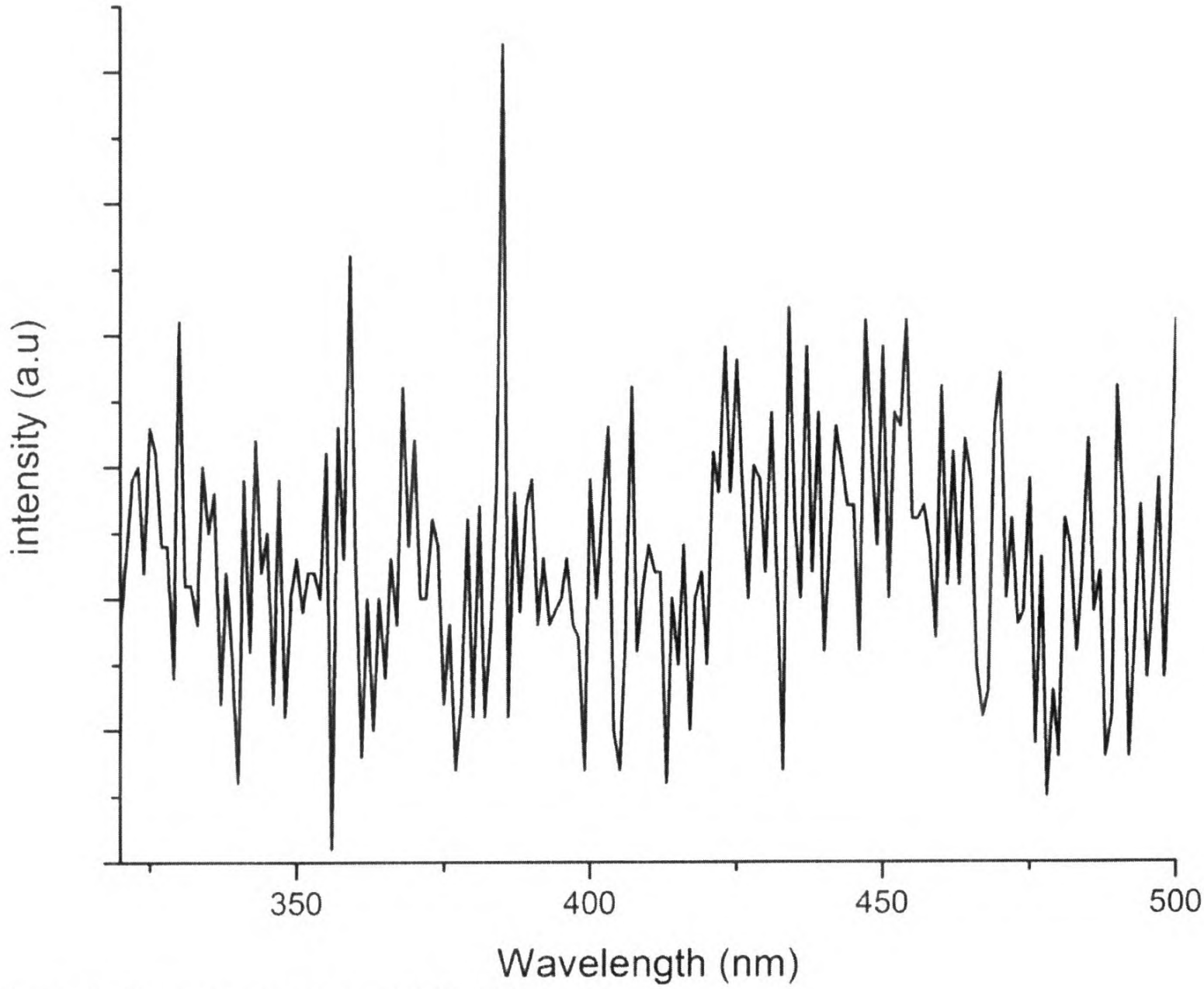


Figure 73: The emission spectrum of PUC-11 film

PUC-12

The PUC-12 was obtained from PUP-10 system and prepared via surfactant added solution mixing method followed by UV exposure. Oleic acid was the surfactant.

An emission spectrum without any peak was obtained because emission has been quenched (Figure 74).

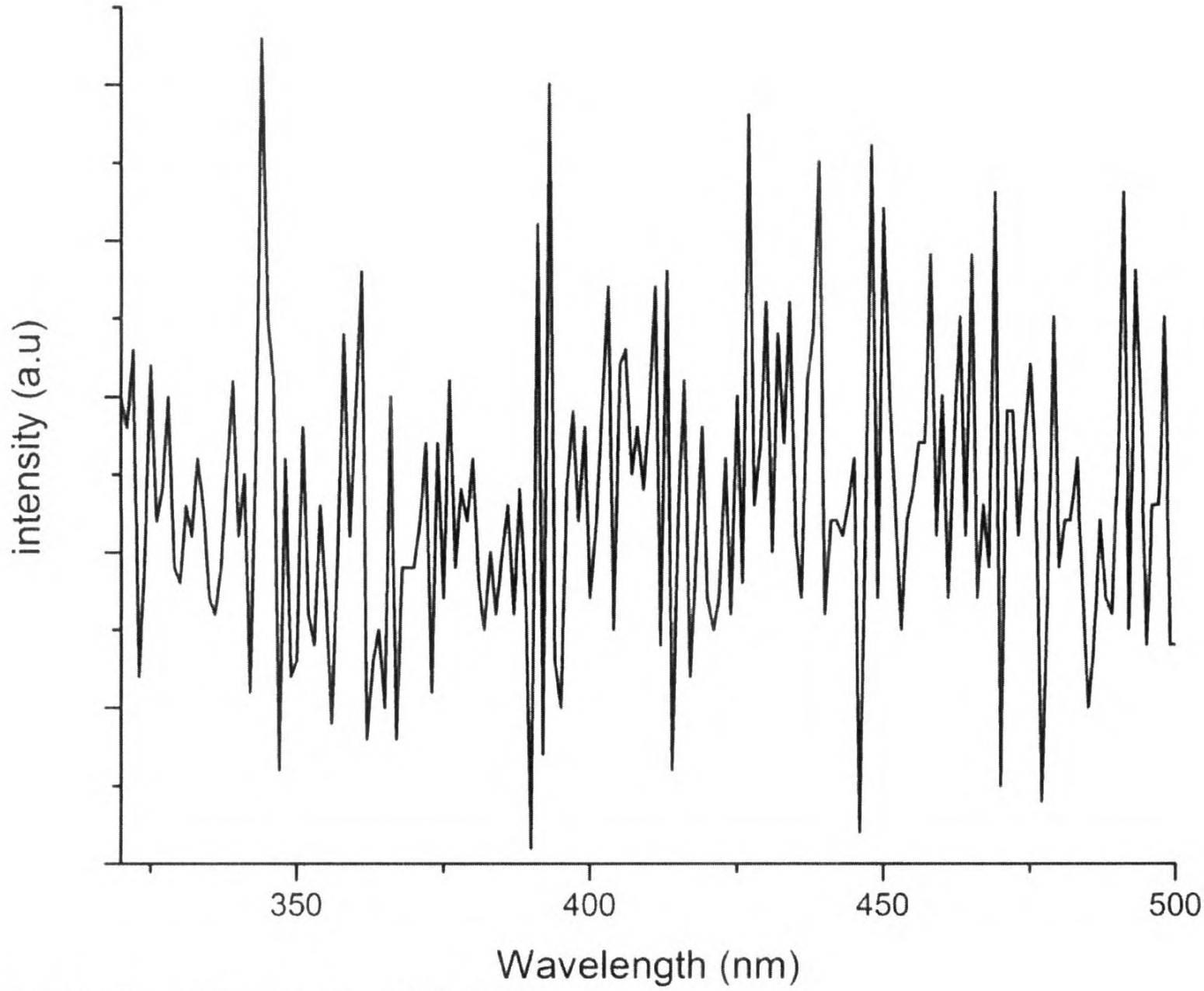


Figure 74: The emission spectrum of PUC-12 film

PUC-13

The PUC-13 was obtained from PUP-10 system and prepared via dipping method under dark conditions.

As a result of quenching, the emission peaks were not available in the recorded emission spectrum (Figure 75).

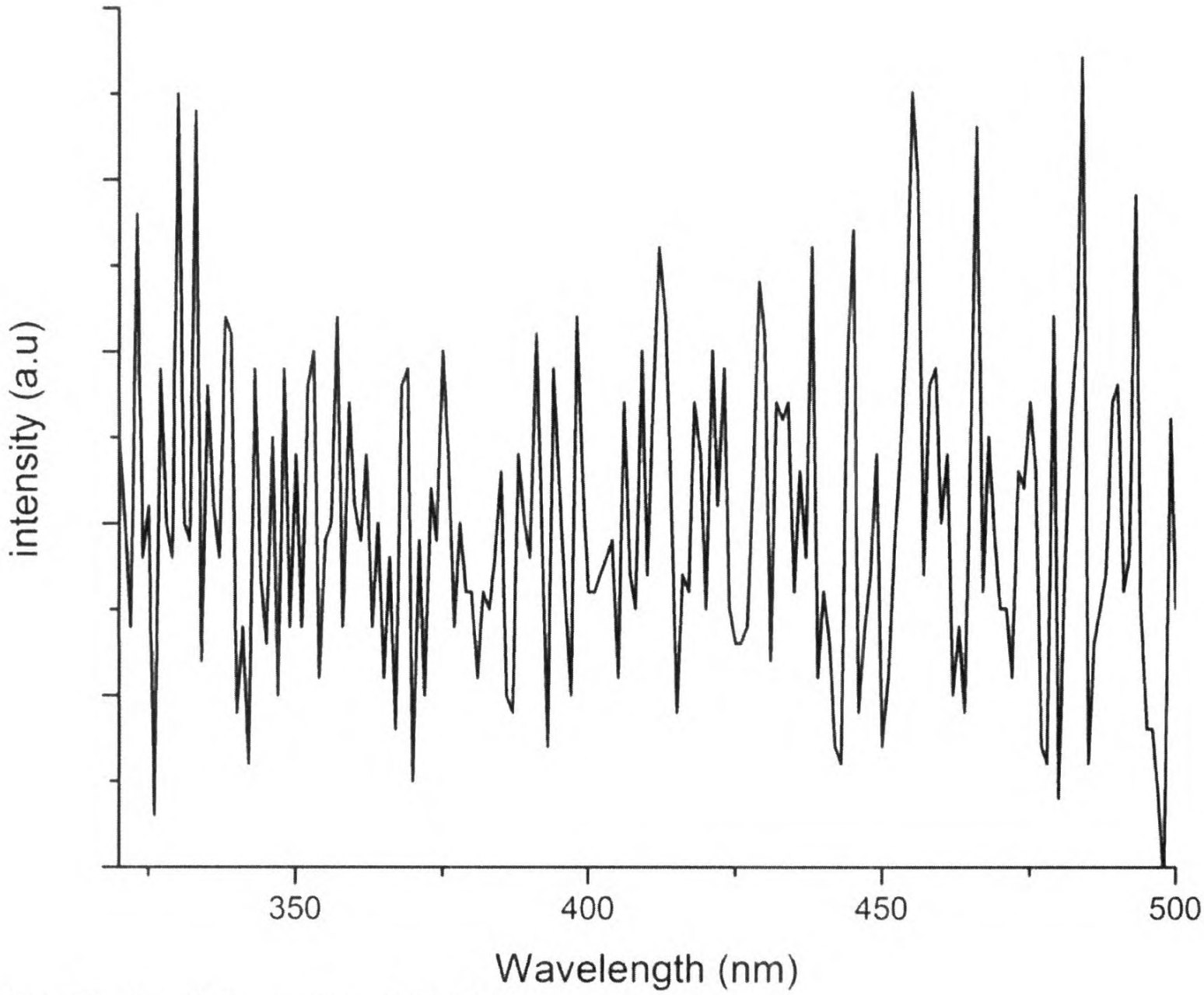


Figure 75: The emission spectrum of PUC-13 film

PUC-14

The PUC-14 was obtained from PUP-10 system and prepared via dipping method followed by UV exposure.

Fluorescence emission has been quenched and because of that no any peak in the spectrum (Figure 76).

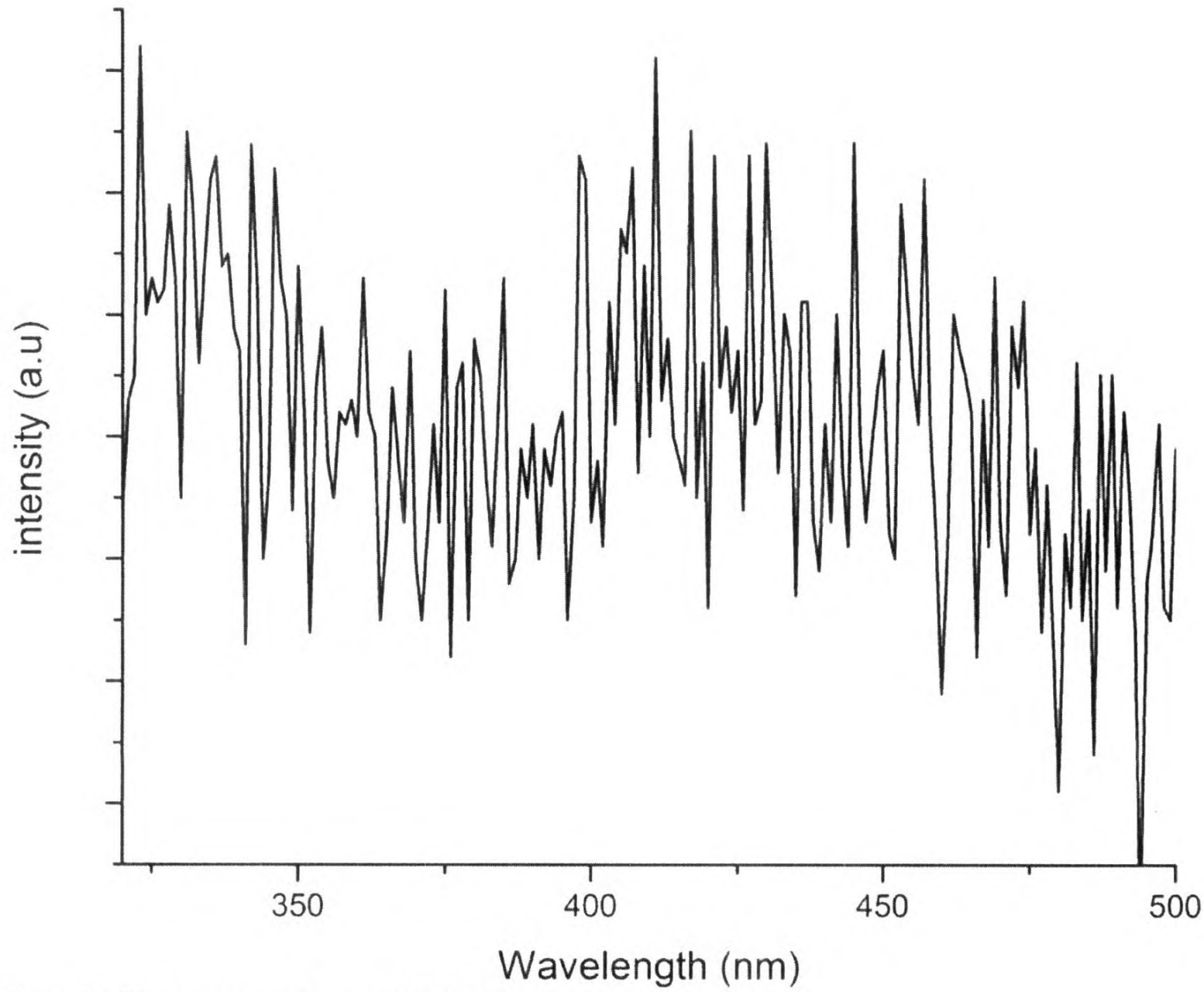


Figure 76: The emission spectrum of PUC-14 film

PUC-15

The PUC-15 was obtained from PUP-10 system and prepared via vapour deposition method under dark conditions.

The initial emission spectrum consists of a single peak. As the intensity of the signal was high, the signal was noise free (Figure 77).

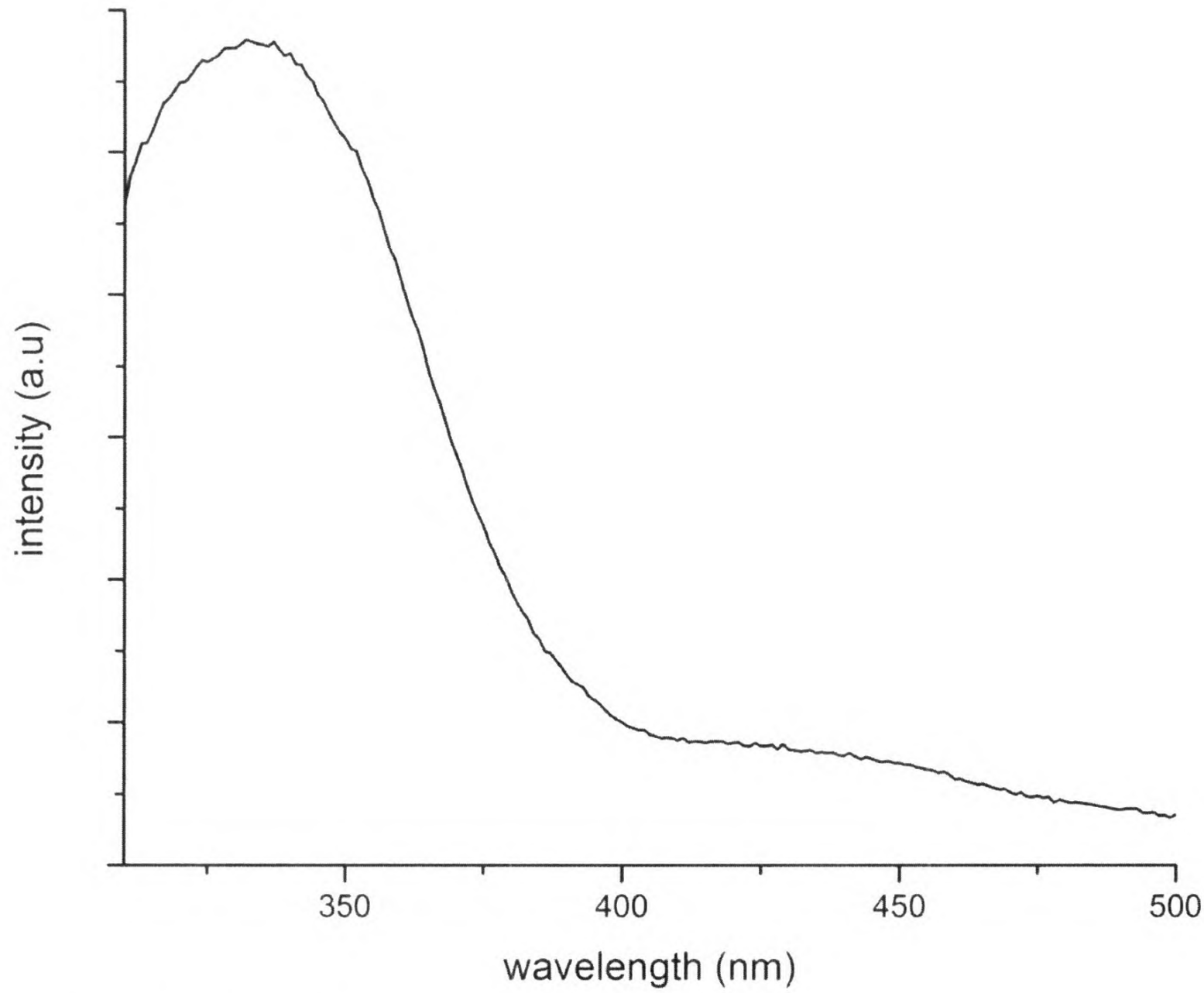


Figure 77: The initial spectrum of the PUC-15 film

The generation in second peak at higher wave length was observed with continuous exposure. That second peak shows a further growth in its intensity while reducing the first peak intensity with exposure time (Figure 78).

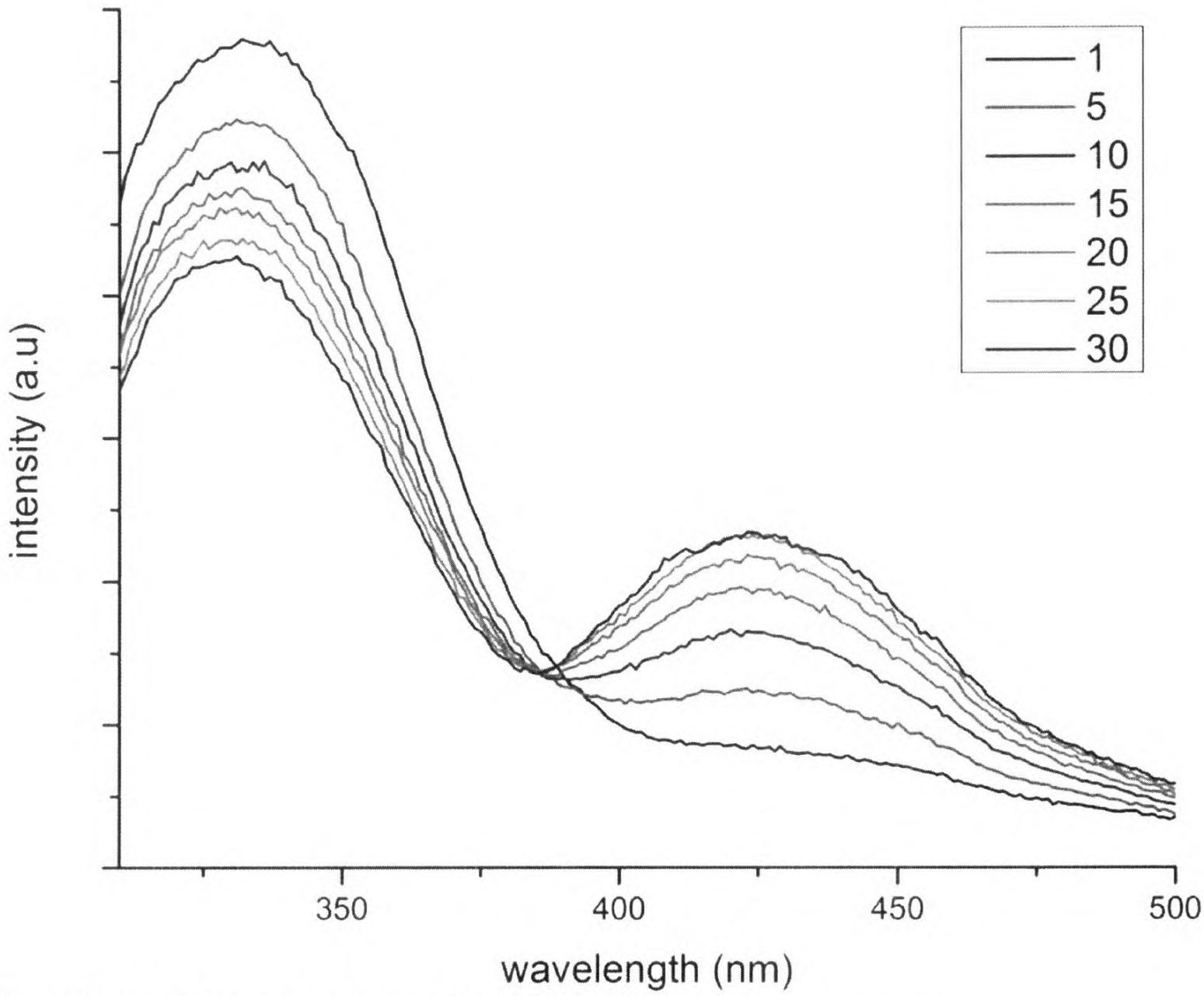


Figure 78: The variation of emission spectra of PUC-15 film with continuous exposure

The two peak intensity variations were able to show a similar trend to the PUP-10 film. It is a gradual growth in second peak and reduction in first peak intensities respectively (Figure 79 & Figure 80).

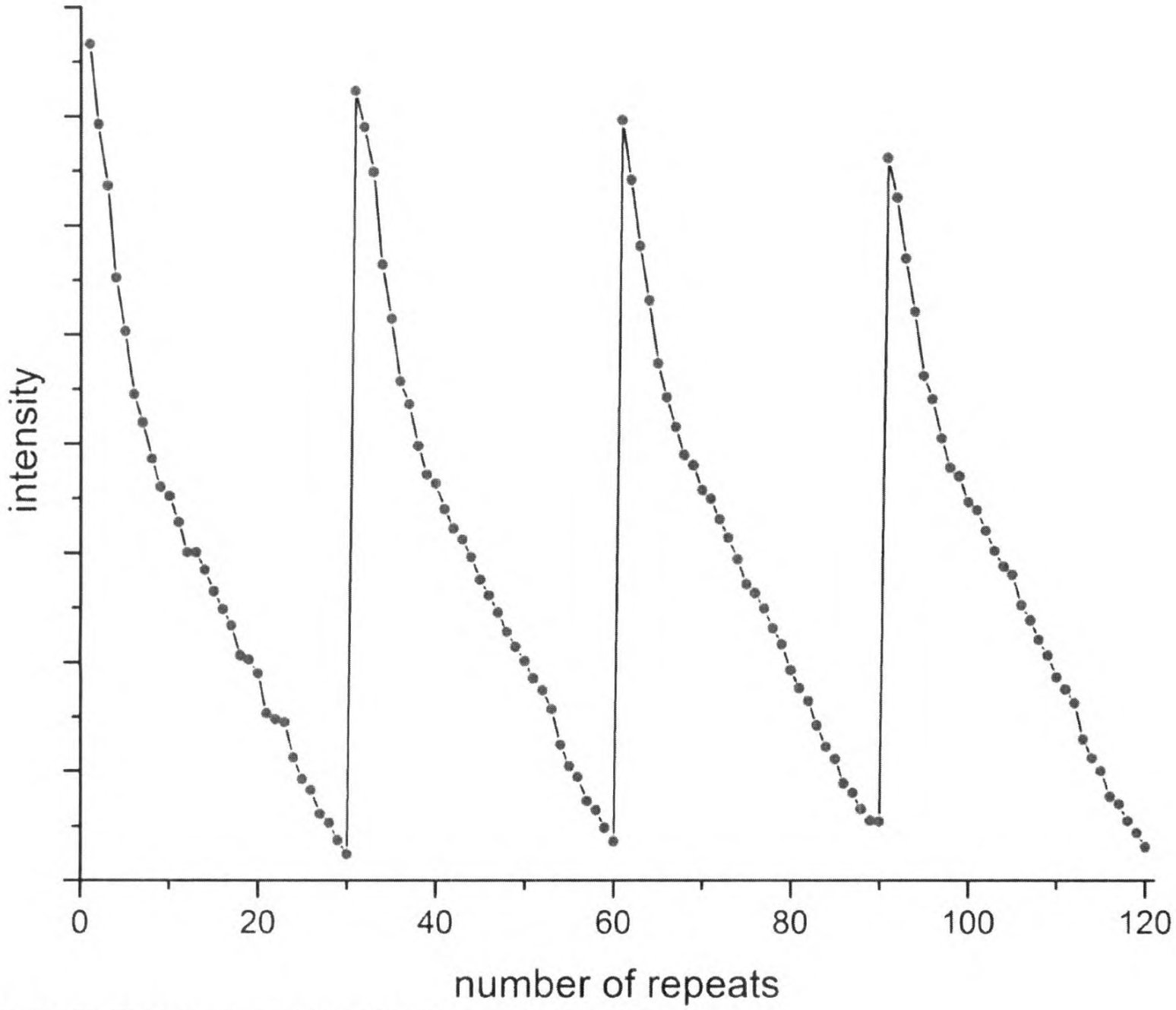


Figure 79: The intensity variation of first peak in PUC-15 film

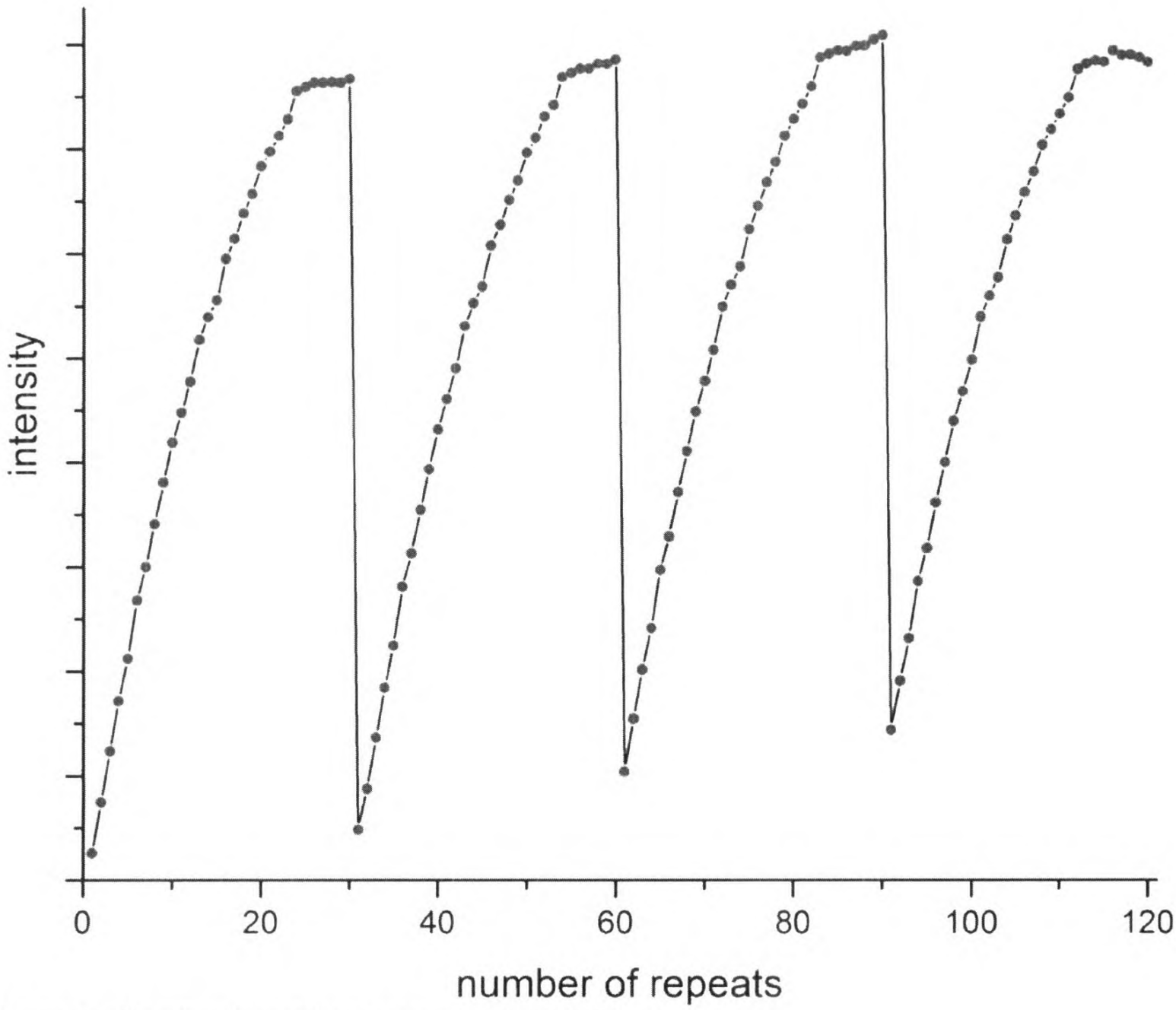


Figure 80: The intensity variation of second peak in PUC-15 film

PUC-16

The PUC-16 was obtained from PUP-10 system and prepared via vapour deposition method followed by UV exposure.

A noisy signal without emission peaks was resulted due to the fluorescence quenching (Figure 81).

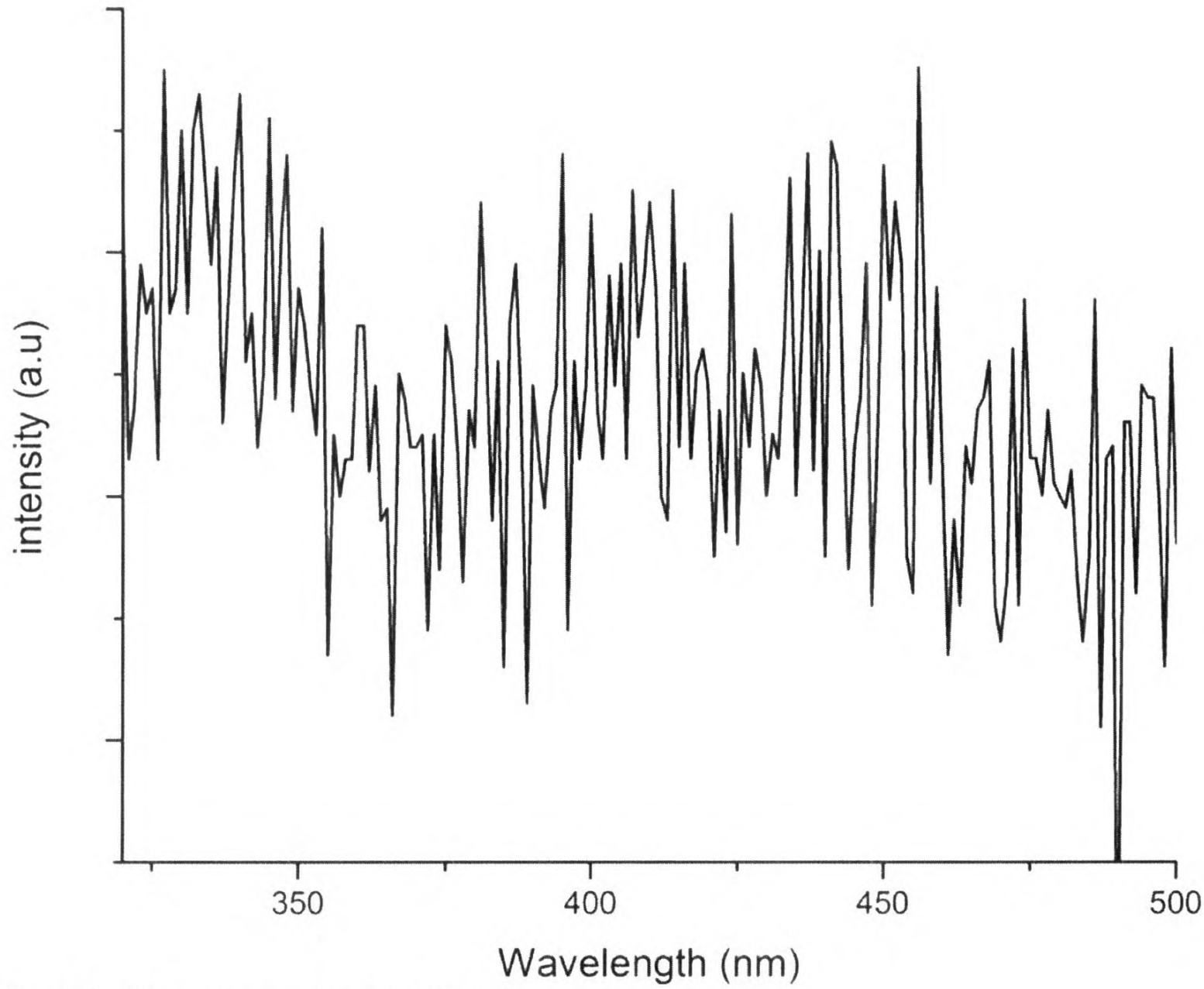


Figure 81: The emission spectrum of PUC-16 film

PUC-17

The PUC-17 was obtained from PUP-∞ system and prepared via solution mixing method under dark conditions.

An emission spectrum having a peak with very low intensity was obtained (Figure 82). With this low intensity of the signal, the noises were noticeable.

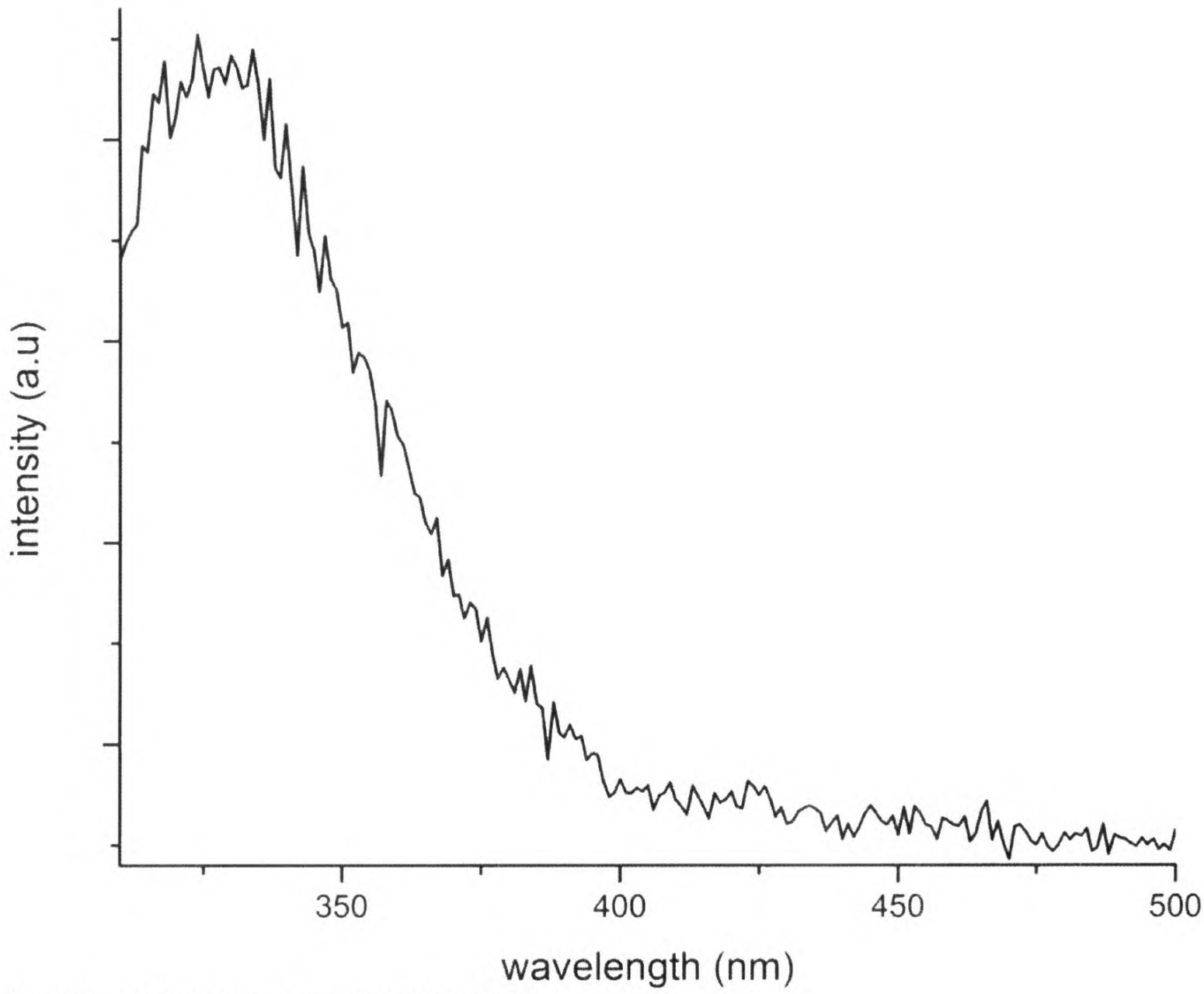


Figure 82: The initial spectrum of the PUC-17 film

As a result of the continuous exposure, the generation of an additional second peak at higher wavelength and increase in the intensity of that peak with decrease in first peak intensity was observed (Figure 83). But the intensity variation is comparatively less.

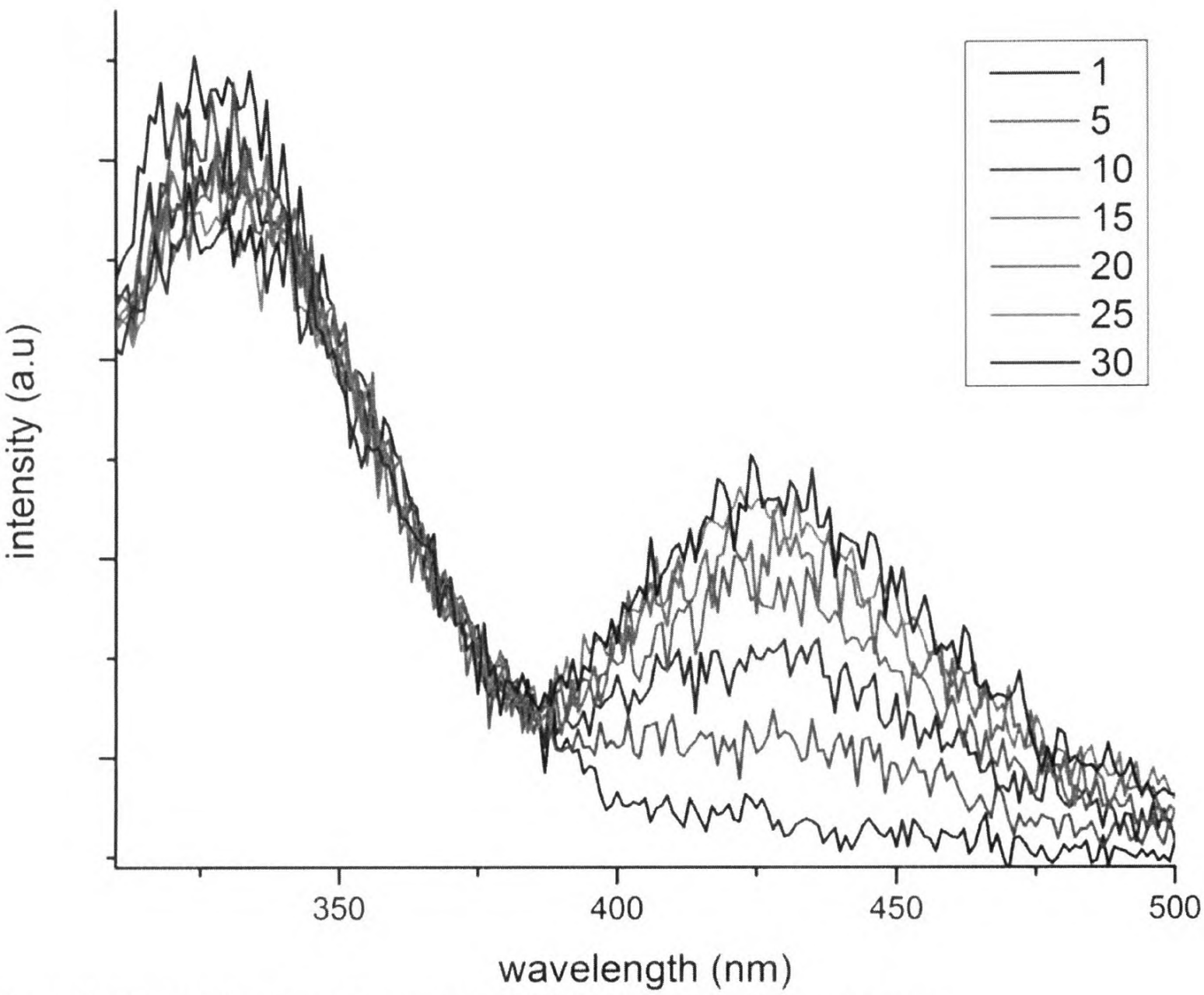


Figure 83: The variation of emission spectra of PUC-17 film with continuous exposure

Once the two peak intensity variation was considered, it was able to observe a tendency of increase in second peak and decrease in first peak during continuous exposure and hysteresis similar to PUP-10 (Figure 84 & Figure 85). However, the variation in intensity does not fit into smooth curves due to the significant noises associated with the emission signals.

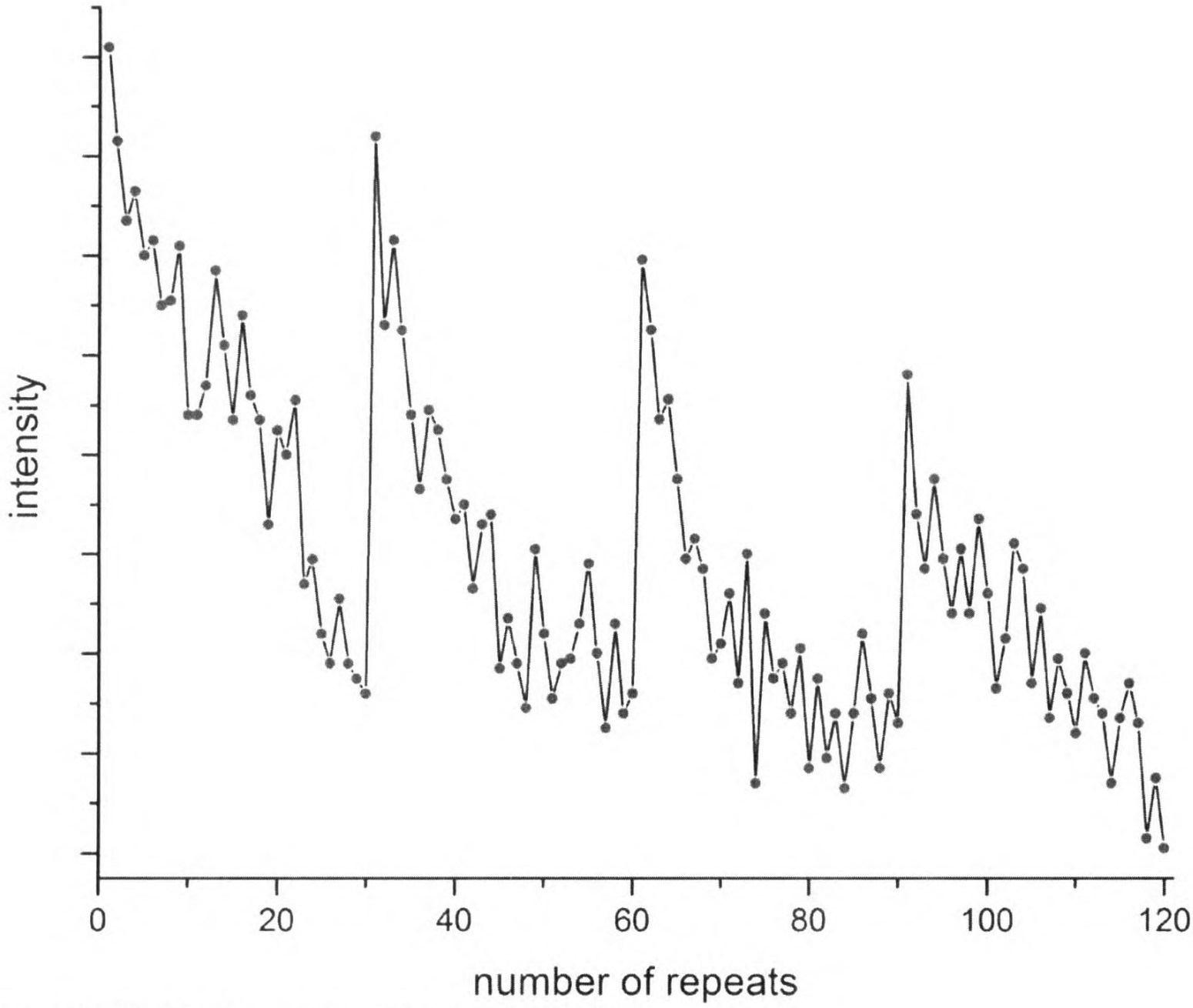


Figure 84: The intensity variation of first peak in PUC-17 film

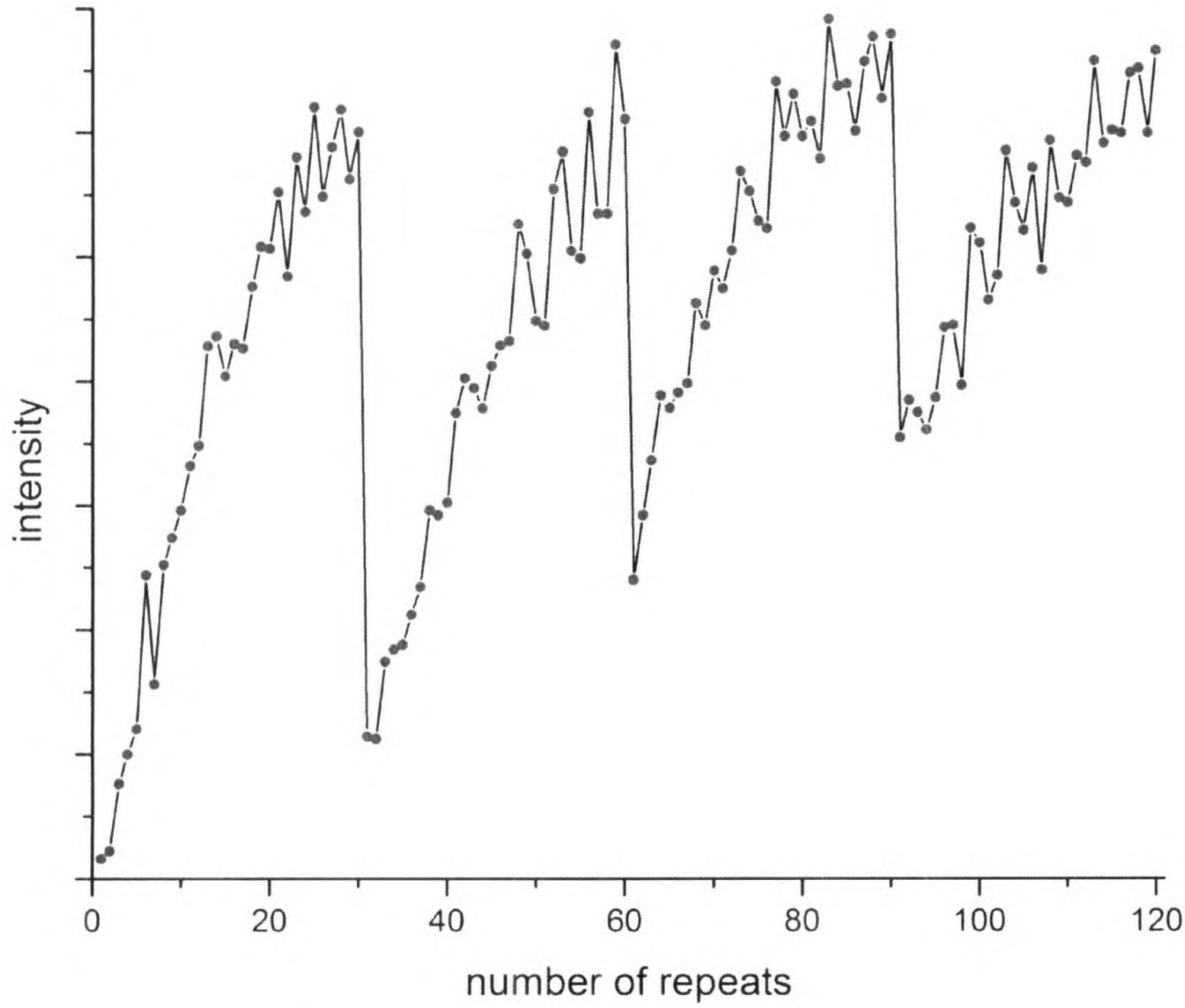


Figure 85: The intensity variation of second peak in PUC-17 film

PUC-18

The PUC-18 was obtained from PUP-∞ system and prepared via solution mixing method followed by UV exposure.

The emission spectrum did not contain any peak corresponding to an emission as emission has been quenched, instead of that a noisy signal is observed as shown in Figure 86.

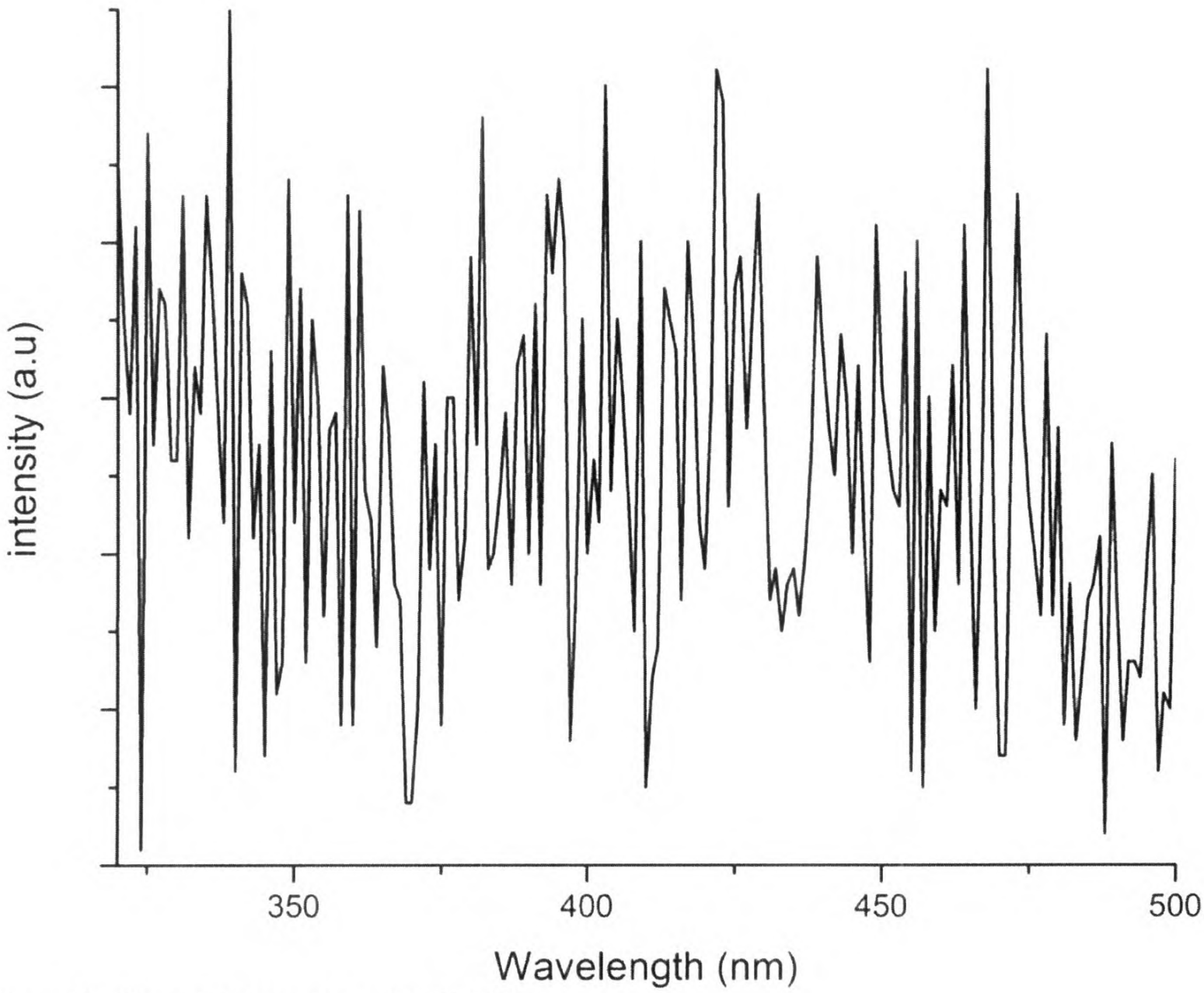


Figure 86: The emission spectrum of PUC-18 film

PUC-19

The PUC-19 was obtained from PUP-∞ system and prepared via surfactant added solution mixing method under dark conditions. The surfactant was oleic acid.

The emission spectrum has been quenched and subsequently there was not any peak (Figure 87).

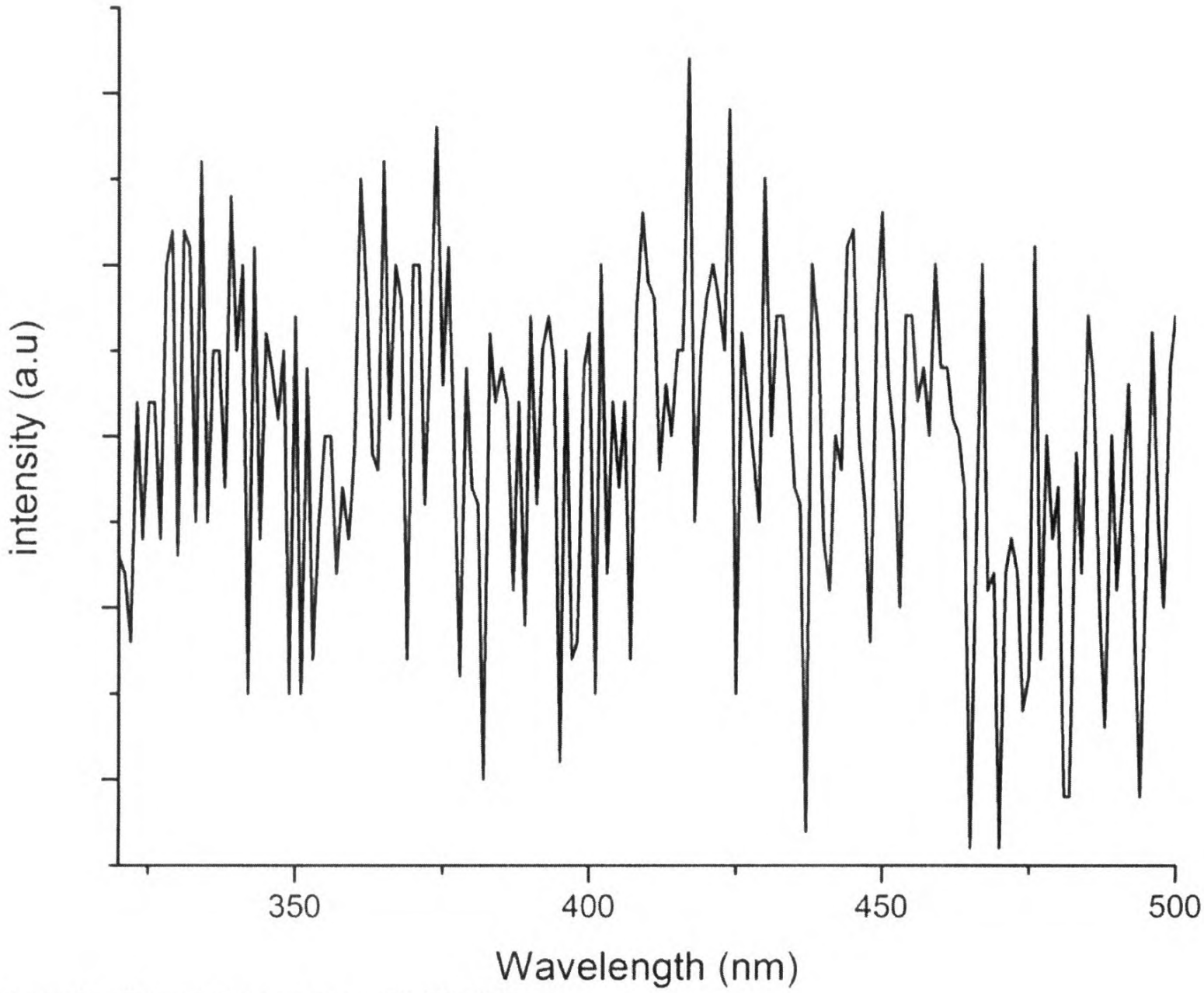


Figure 87: The emission spectrum of PUC-19 film

PUC-20

The PUC-20 was obtained from PUP-∞ system and prepared via surfactant added solution mixing method followed by UV exposure.

As shown in Figure 88, the emission spectrum was a noisy signal without any peak corresponding to an emission. Emission has been quenched.

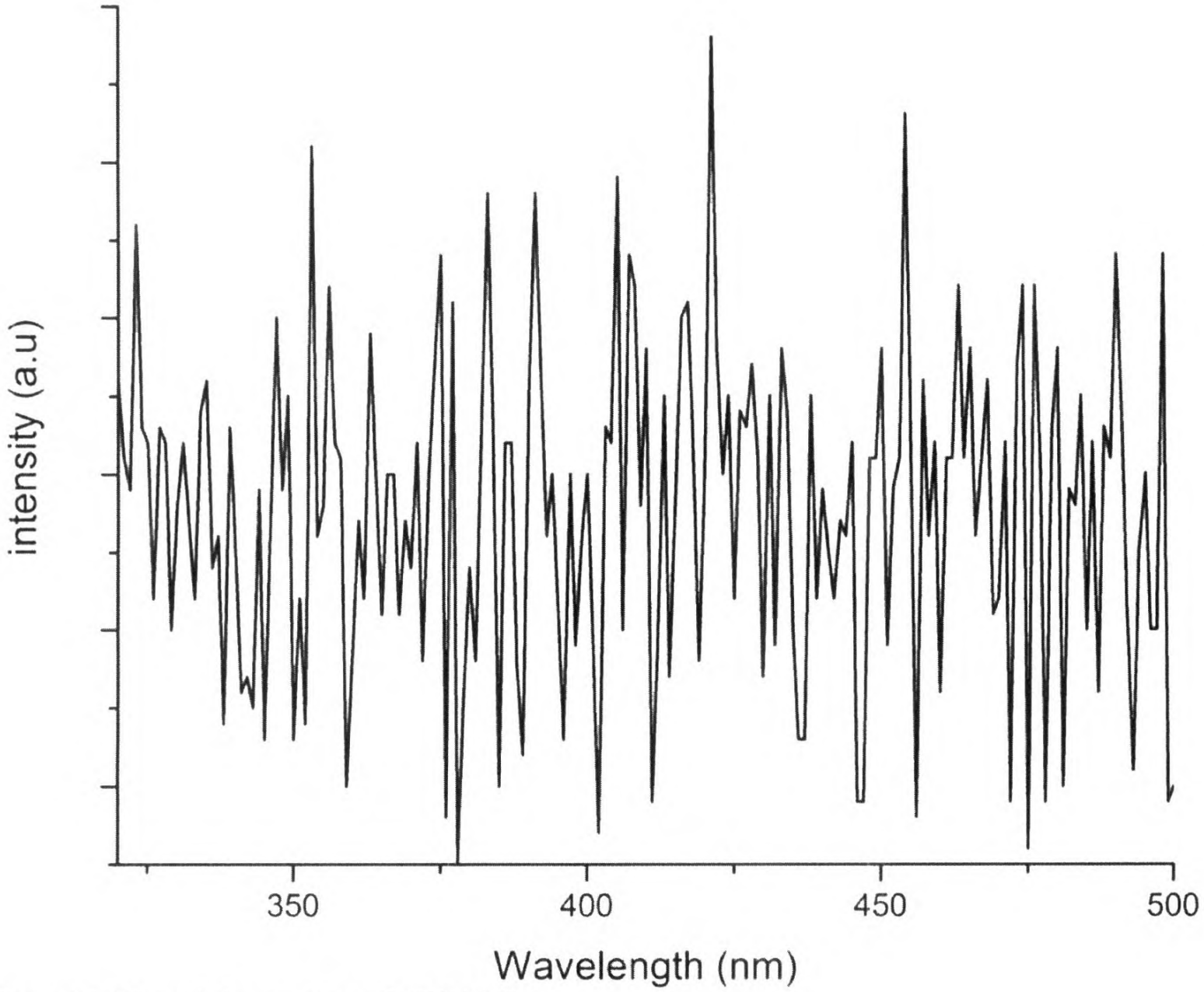


Figure 88: The emission spectrum of PUC-20 film

PUC-21

The PUC-21 was obtained from PUP-∞ system and prepared via dipping method under dark conditions.

Initial emission spectrum had a single peak (Figure 89). The intensity was less than PUP-∞ film but higher than PUC-17 which was from the film obtained from solution mixing method using PUP-∞.

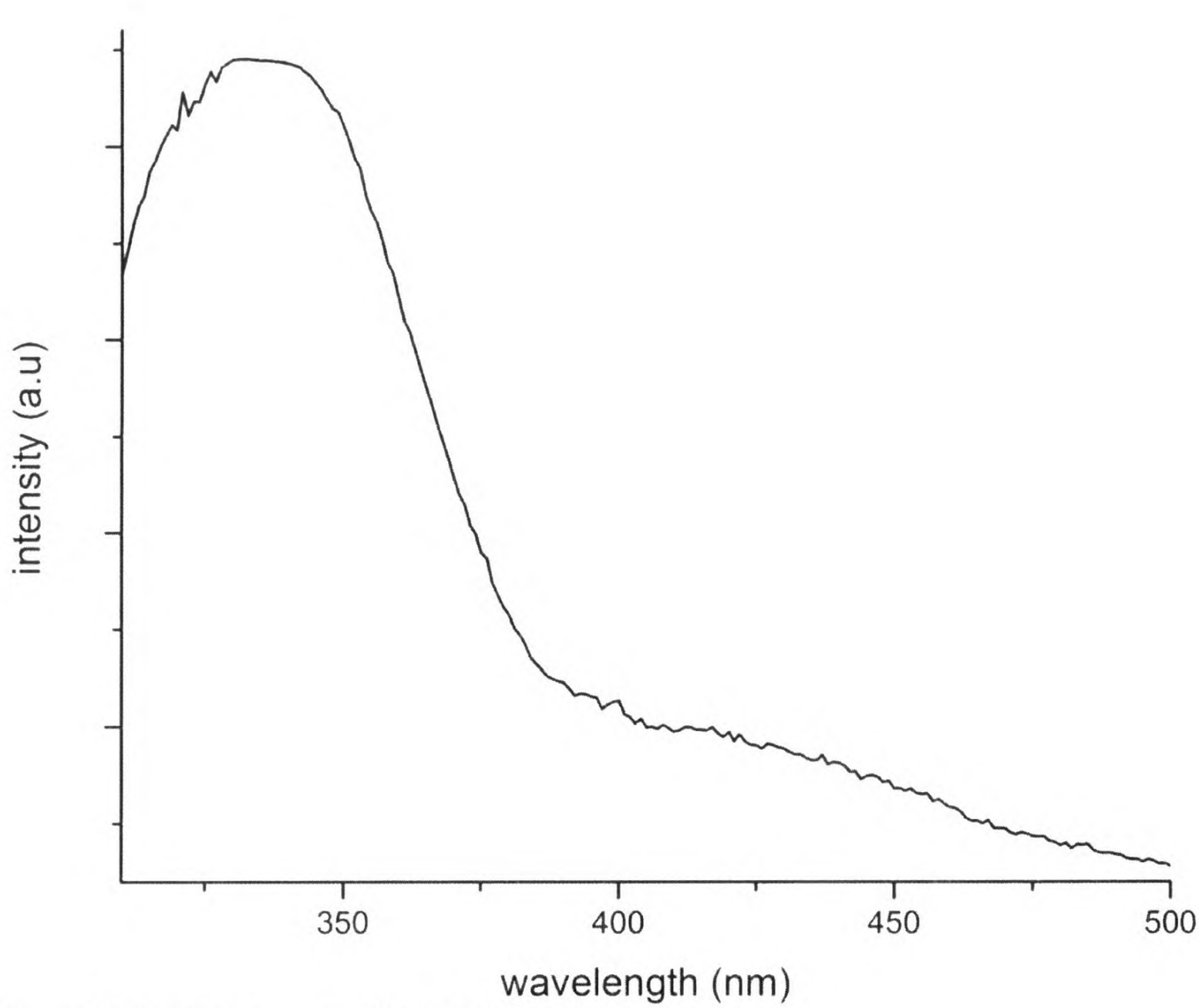


Figure 89: The initial spectrum of the PUC-21 film

Generation and growth of a second peak while reducing the first peak intensity were observed with continuous exposure (Figure 90).

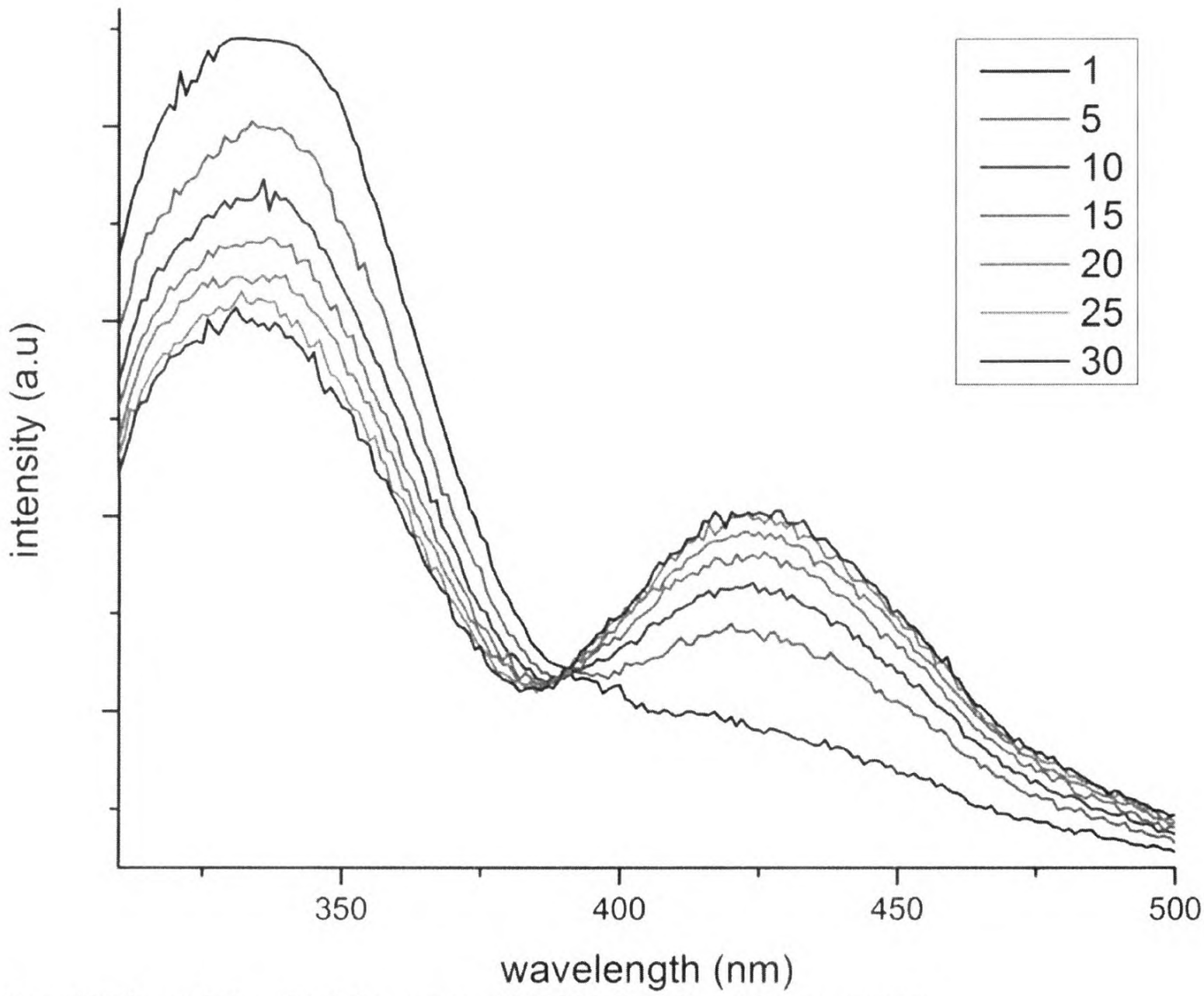


Figure 90: The variation of emission spectra of PUC-21 film with continuous exposure

The pattern of intensity variation with continuous exposure was closure to that of PUP-∞ and hysteresis was also observed (Figure 91 & Figure 92).

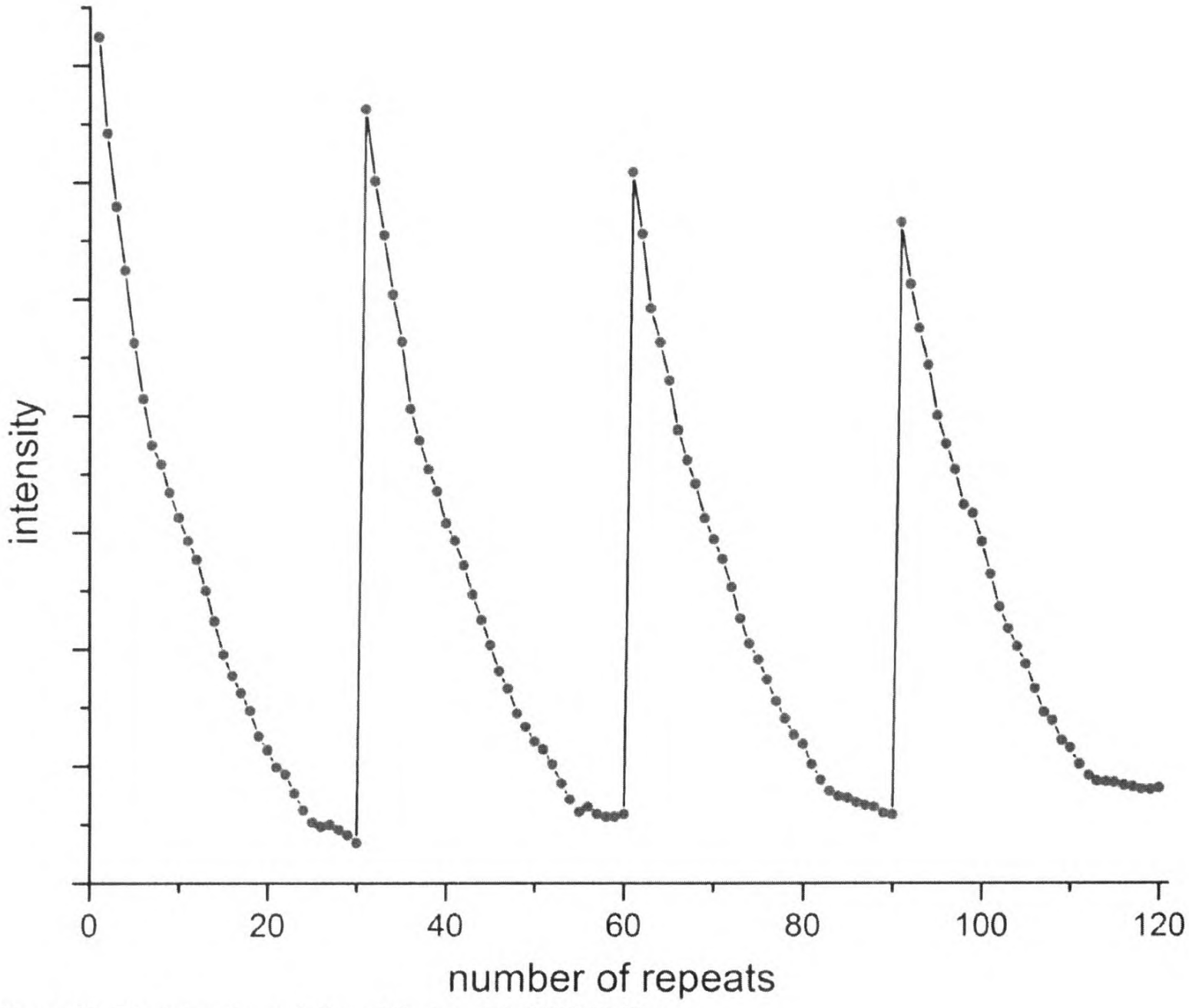


Figure 91: The intensity variation of first peak in PUC-21 film

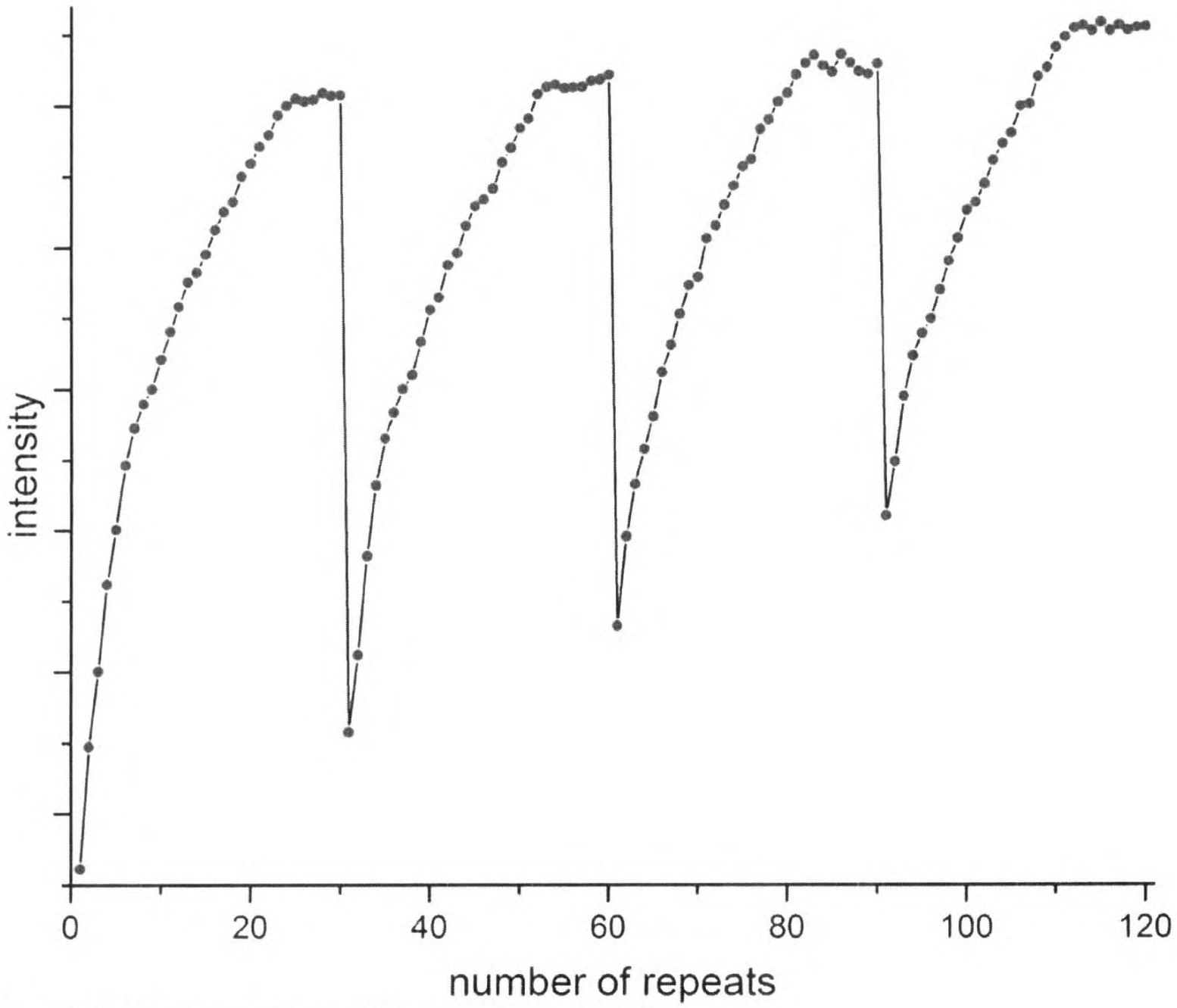


Figure 92: The intensity variation of second peak in PUC-21 film

PUC-22

The PUC-22 was obtained from PUP-∞ system and prepared via dipping method followed by UV exposure.

The emission has been quenched. Due to that, the peaks were not observed in the emission spectrum (Figure 93).

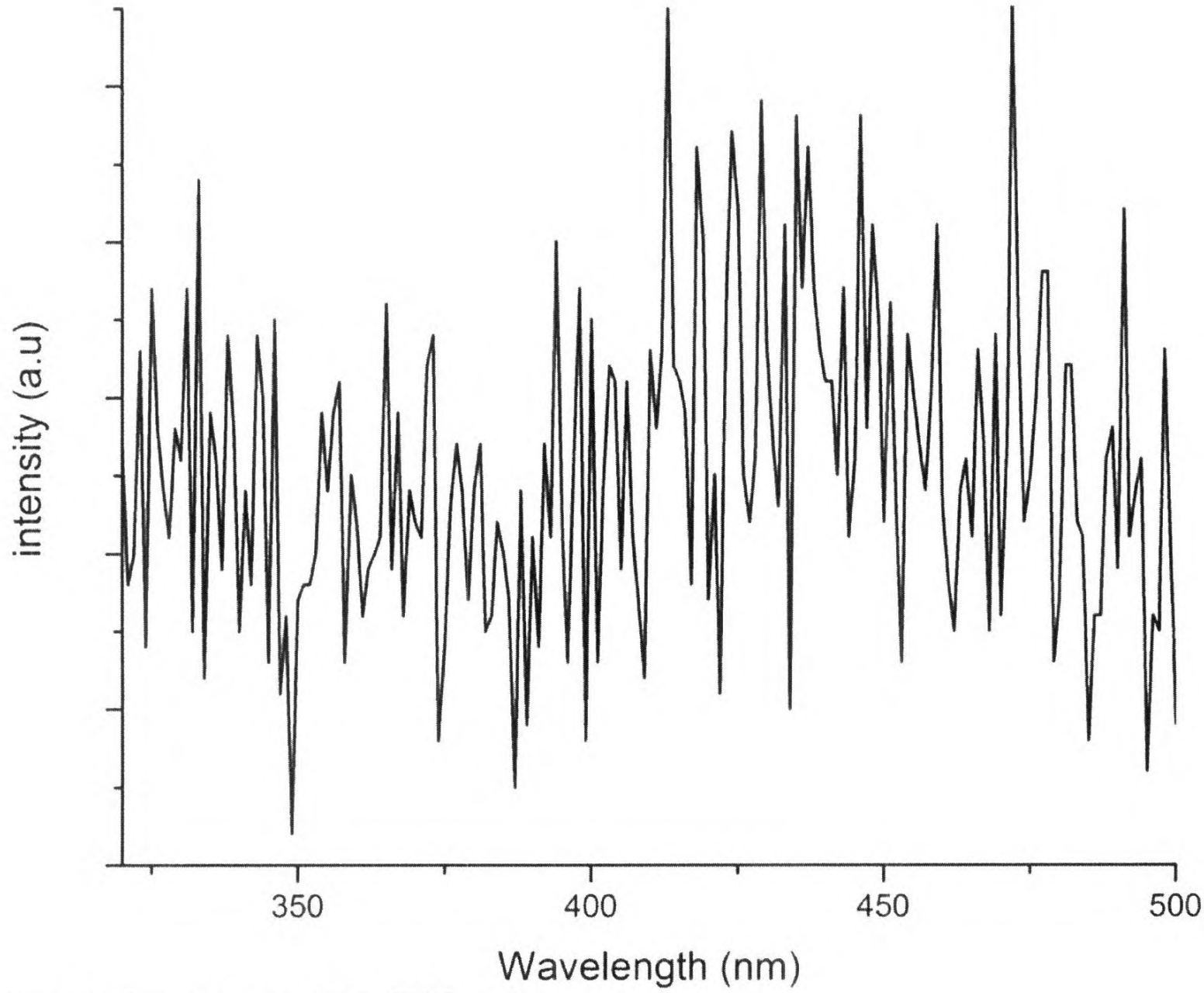


Figure 93: The emission spectrum of PUC-22 film

PUC-23

The PUC-23 was obtained from PUP-∞ system and prepared via vapour deposition method under dark conditions.

The initial emission spectrum consists of a noise free single emission peak (Figure 94).

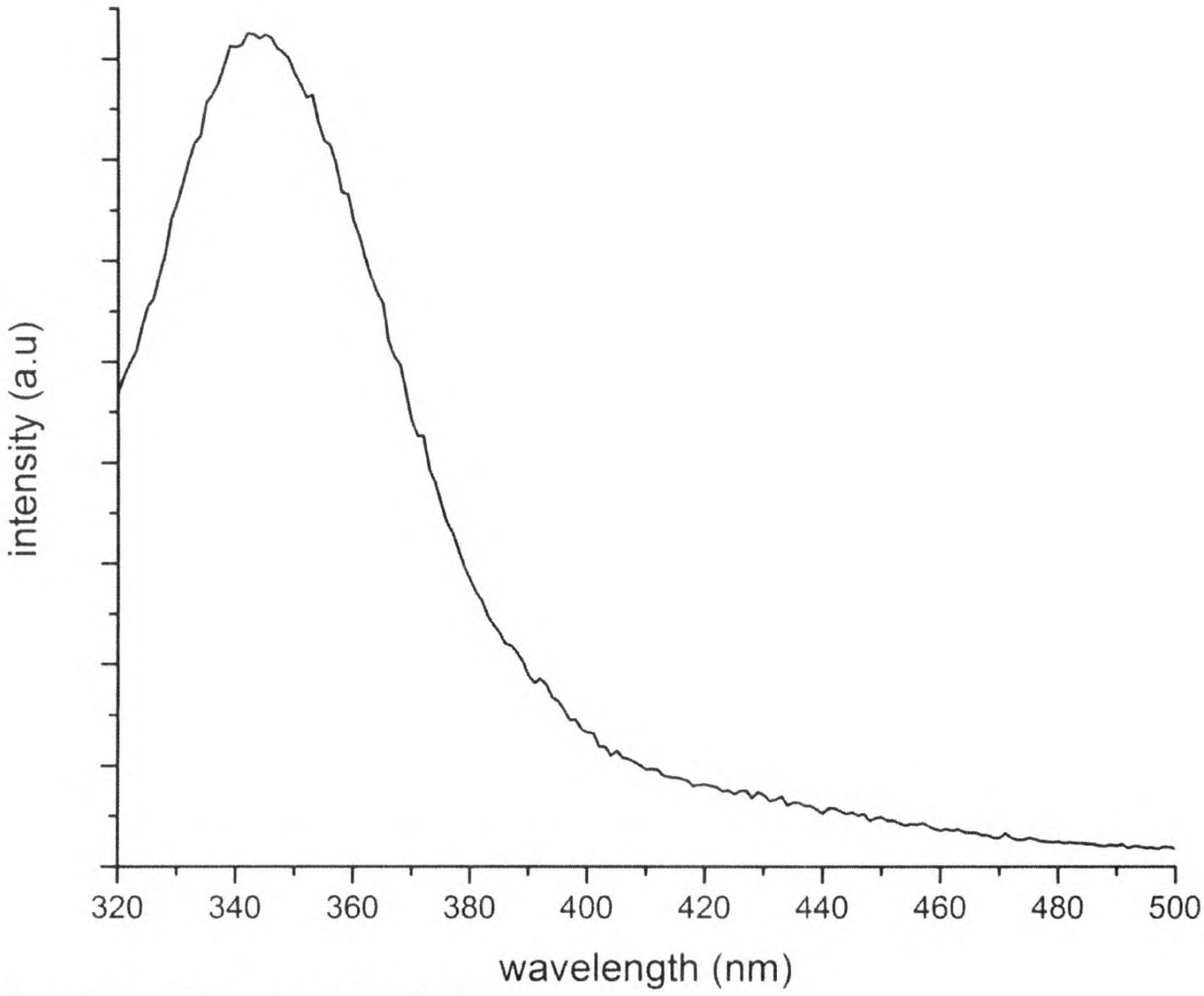


Figure 94: The initial spectrum of the PUC-23 film

The generation of a second peak and its growth while reducing the first peak intensity were observed with exposure time (Figure 95).

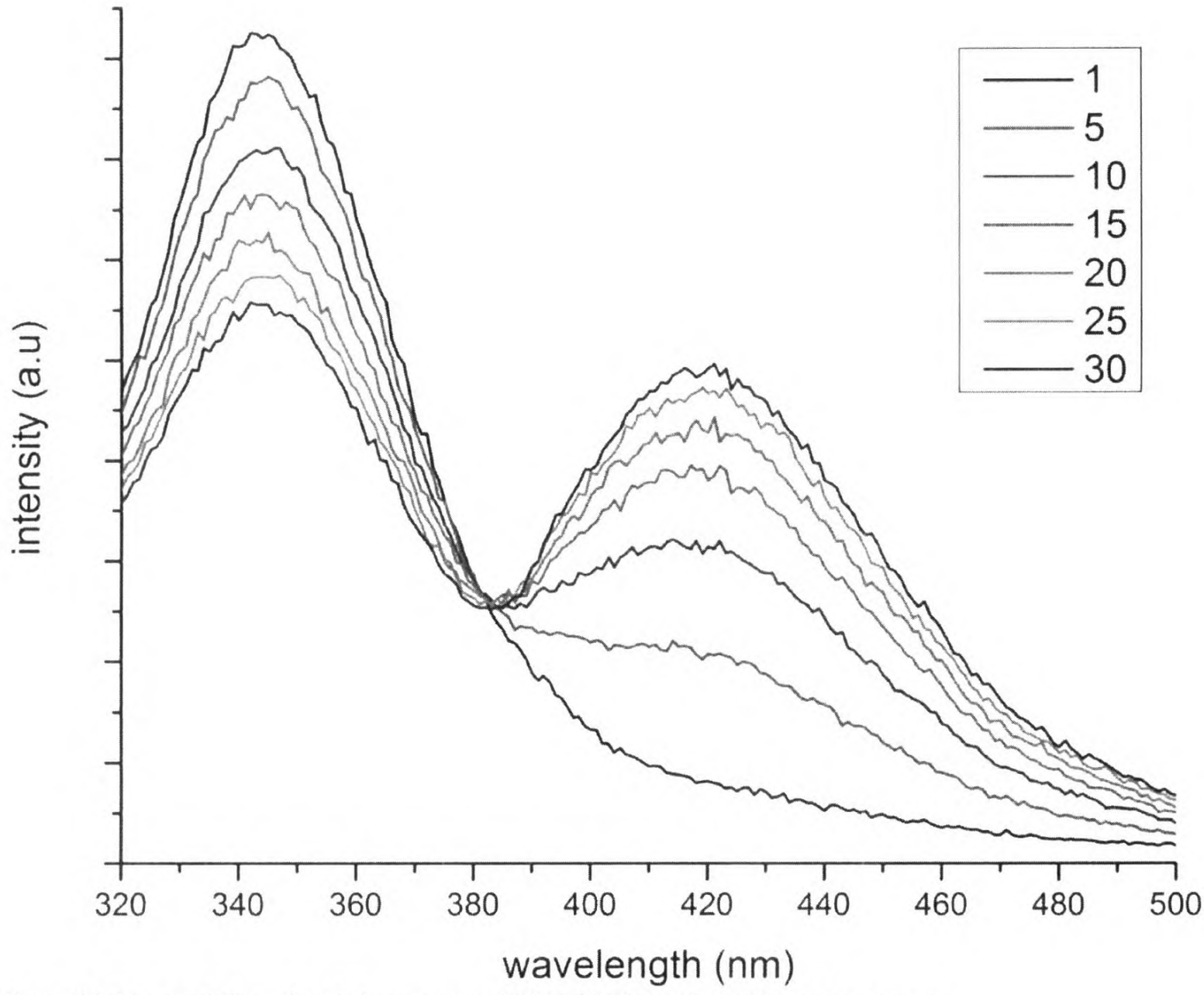


Figure 95: The variation of emission spectra of PUC-23 film with continuous exposure

A trend of a gradual growth in second peak and reduction in first peak intensities were observed similar to the corresponding PUP film PUP-∞ (Figure 96 & Figure 97).

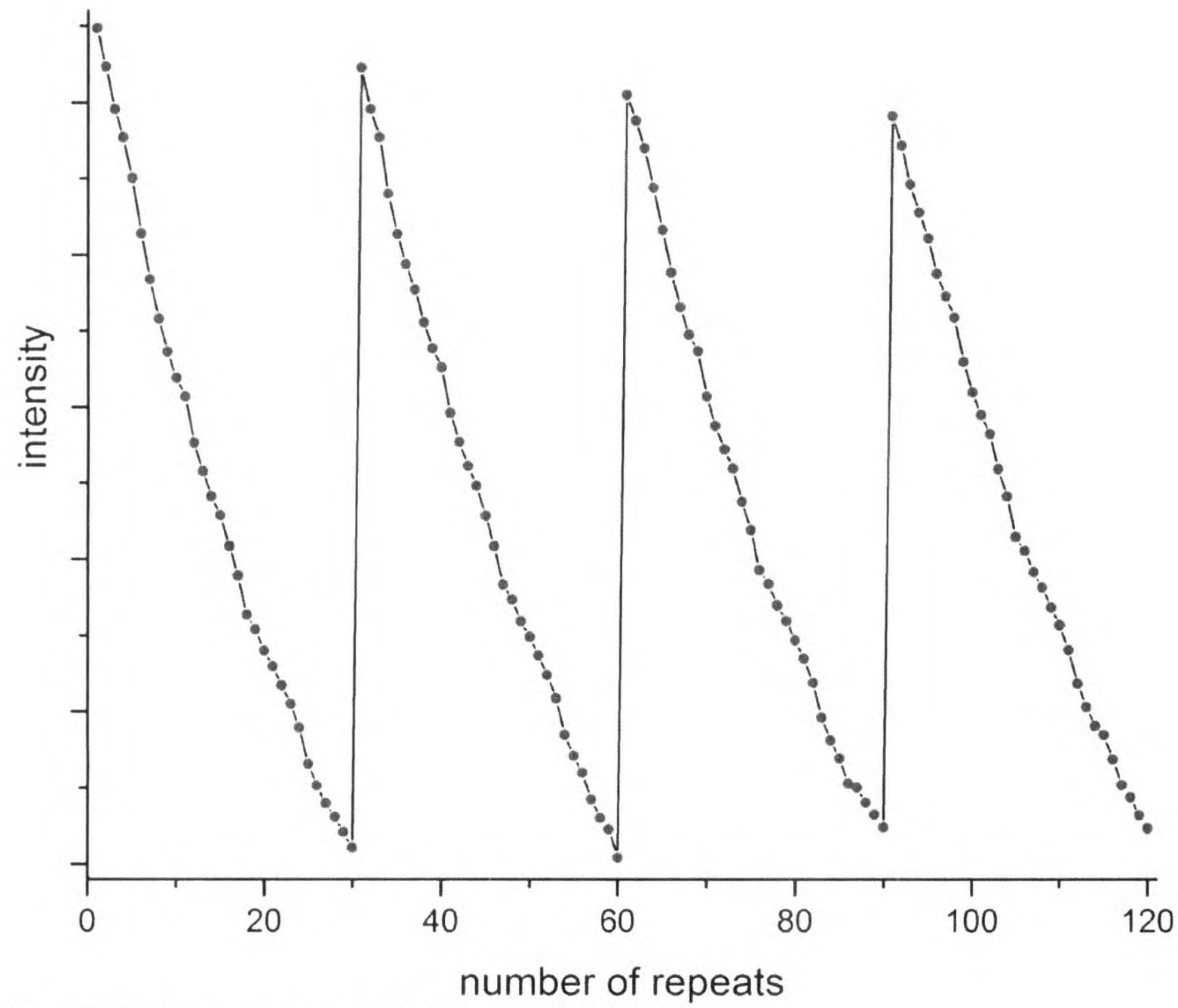


Figure 96: The intensity variation of first peak in PUC-23 film

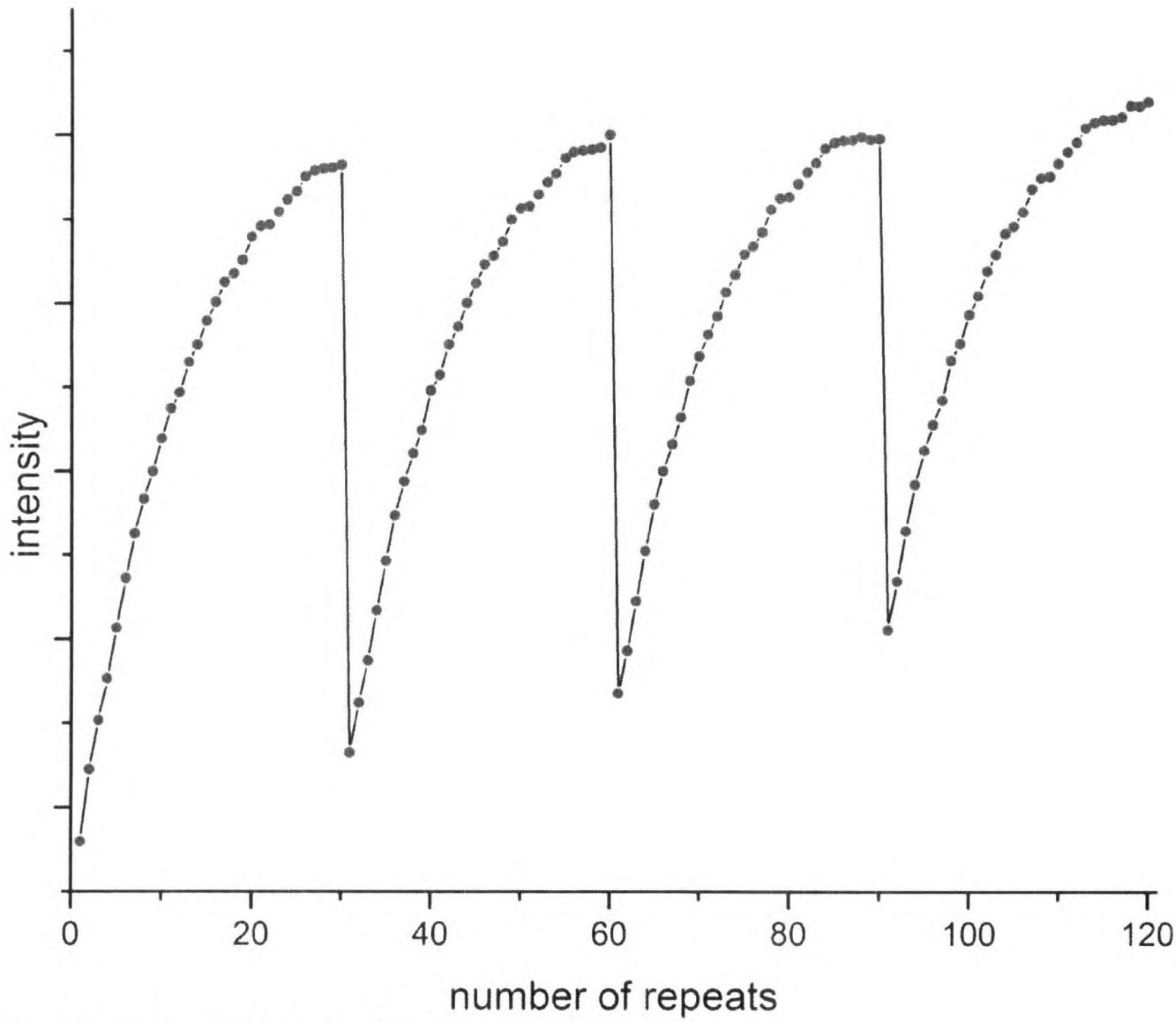


Figure 97: The intensity variation of second peak in PUC-23 film

PUC-24

The PUC-24 was obtained from PUP-∞ system and prepared via vapour deposition method followed by UV exposure.

The emission peaks were absent in the emission spectrum (Figure 98). It has been quenched.

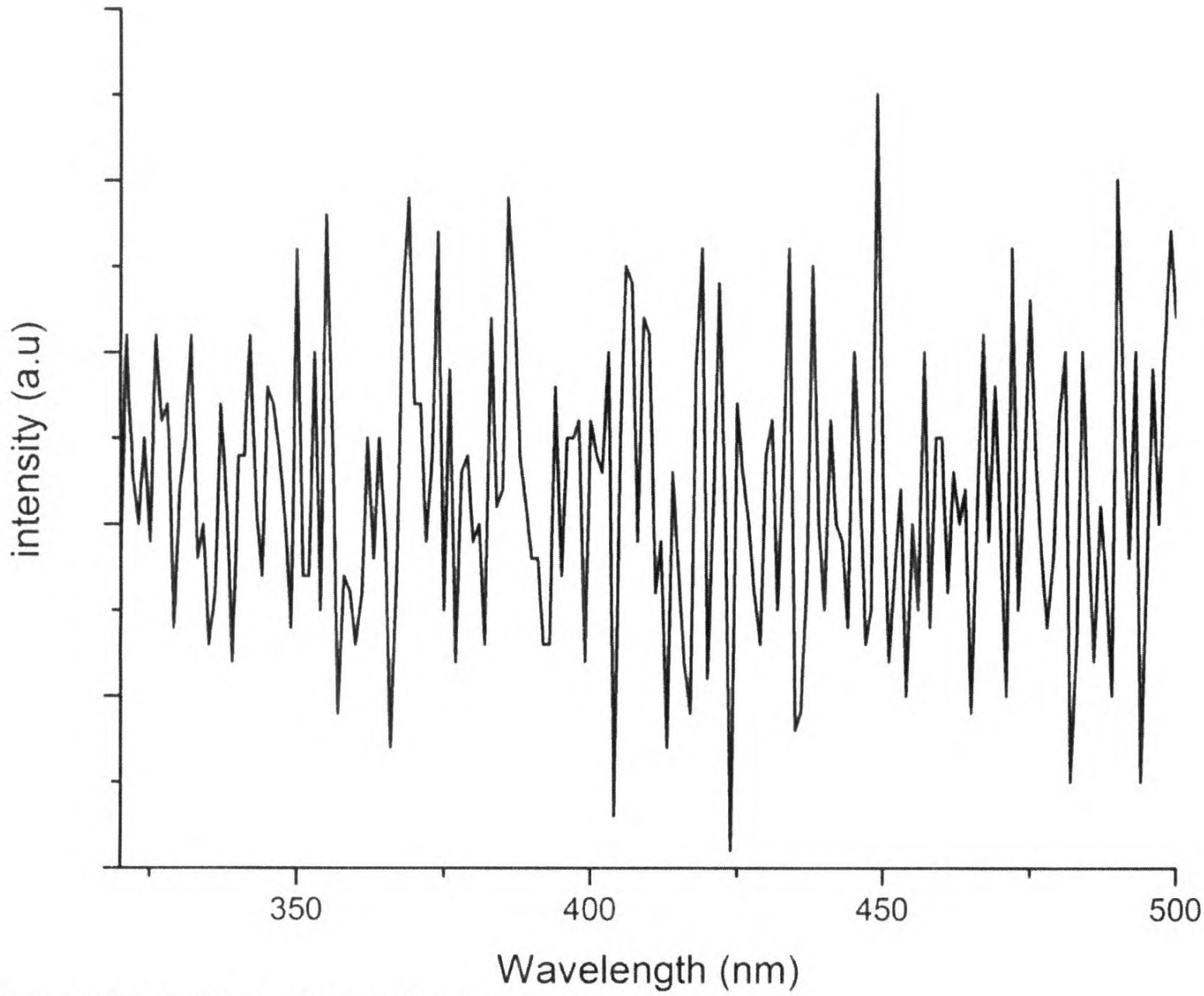


Figure 98: The emission spectrum of PUC-24 film

Overall discussion on fluorescence behavior of composites

The observations related to the fluorescence behavior of each composite were discussed above separately. However, the discussion of fluorescence behavior as groups will be more worth. First we will consider the systems where the fluorescence behavior has been quenched.

All the systems where samples get exposed to UV light did not give any emission (PUC-2, PUC-4, PUC-6, PUC-8, PUC-10, PUC-12, PUC-14, PUC-16, PUC-18, PUC-20, PUC-22, and PUC-24). In the field of polymer science, there is a phenomenon which is called as photo-stabilization. It involves a retardation or elimination of photo chemical processes. (109) UV absorbers are additives which prevent the photochemical reactions in other words UV absorbers are one type of photo-stabilizers. Those absorbers absorb the UV light and block the interaction of polymers with UV radiation and avoid the photo chemical processes. In order to happen this blocking of photo chemical processes of the polymers, it is necessary to those absorbers to absorb the UV range where the polymer shows the absorbance. (109) The quenching is a phenomenon addressed in photo chemistry. It is a process which reduces the emission intensity via the absorption of the energy of the excited species and relaxes them to their ground state in a non radiative way. (110) In order to quenching is taken place, it is necessary to overlap the absorption spectrum of the quencher and the emission spectrum of the excited species. It is generally accepted that when iron pentacarbonyl exposed to UV light they are converted to iron oxide. Iron oxides show a strong UV absorption and have a absorption band spreads in the range 275 nm-375 nm out of two broad absorption peaks observed. (111) The polyurethane prepolymers absorb

at 293 nm and emit at 356 nm. Both wavelengths are included in the absorption range of iron oxide. Hence, there are two possibilities to do not show any peak in the emission spectra. One is iron oxides can be behaved as a photo-stabilizer which absorbs the 293 nm radiations and do not allow 293 nm wavelengths to interact with polyurethanes. Subsequently isolated hard segments do not excited and therefore no emissions.

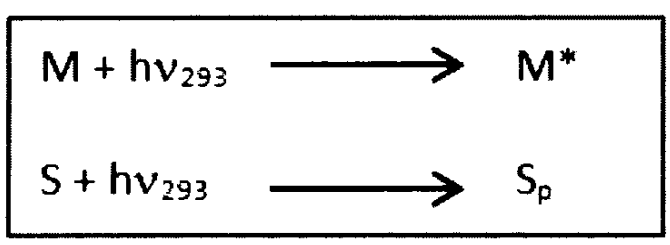


Figure 99: The competition between stabilizer and isolated hard segment towards the 293 nm wavelength; the isolated hard segment (M) is excited to M* and stabilizer (S) is converted to new product of S (S_p)

The other possibility is, iron oxide can be act as a quencher which absorbs the energy of the excited isolated hard segments and quench the 356 nm emission.

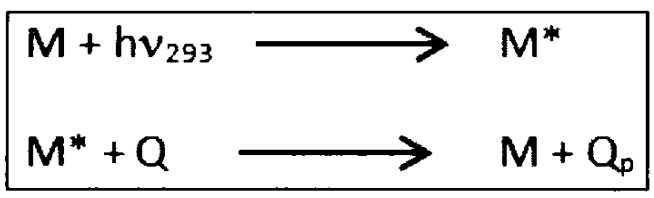


Figure 100: the quenching of excited isolated hard segments by quencher; the energy of excited isolated hard segment M* is absorbed by quencher Q and Q is converted new form Q_p.

Hence, in the presence of iron oxide it is impossible to observe an emission peak in the fluorescence spectrum of MDI based polyurethanes.

As the next set of composites it is possible to group the composites which were prepared in the presence of the surfactant: oleic acid. All the members in that group PUC-3, PUC-4, PUC-11, PUC-12, PUC-19, PUC-20 has quenched the emission signals which were shown in the corresponding polyurethane films. Oleic acid was used as a surfactant to enhance the compatibility between the iron pentacarbonyl and polyurethanes. Iron pentacarbonyl decomposition in the presence of oleic acid results in iron-oleate complex as an intermediate. (112) It has been reported that iron oleate complex and iron oxides have almost identical absorption spectra. (113) According to that, it is possible to quench the fluorescence signal in the presence of iron-oleate complex in the polyurethane matrix similar to the above explained reasons for quenching ability of iron oxide. However, due to time restrictions and lack of chemicals we were unable to identify the quencher exactly.

The three groups from the composites prepared under dark conditions; composites prepared by solution mixing method, dipping method and vapor deposition method show a similar trend in fluorescence behavior in such a way the presence of single peak initially and creation and development of a second peak with continuous exposure was observed and the hysteresis was also observed. The signal intensities are very low in composites from solution mixing method and intensities of the composites from vapor deposition method are very close to their corresponding prepolymer systems meanwhile composites from dipping method is in between these two. This can be explained by considering the iron pentacarbonyl absorption spectrum. According to the absorption of iron pentacarbonyl discussed by M Kotzian and co-workers, iron pentacarbonyl shows an absorption maximum around 200 nm and a shoulder peak around 240 nm and the important point to recognize is, absorption around 293 nm is very small and around 350 it is almost nil. (114) Hence it is clear that iron pentacarbonyl also absorbs the 293 nm wavelength however not in huge extent. Therefore the interaction of 293 nm wavelength with

polyurethane is affected in the presence of iron pentacarbonyl. This will result in a retardation of the extent of 293 nm absorption of polyurethanes and subsequently the amount of excited isolated hard segments. The amount of iron pentacarbonyl which is embedded in the polyurethane matrix is highest in the solution phase mixing method and least in the vapour deposition method. Therefore, the extent of retardation in 293 nm absorption of polyurethanes is highest in solution phase mixing method and least in vapour deposition methods. Hence, parallel to the amount of excited isolated hard segment density the signal intensities are highest in vapour deposition method and least in solution phase mixing method.

According to the observed results it is clear that composite formation effects to the prepolymer fluorescence. Depending on the technique applied the effect is different. It indirectly shows that the fluorescence behavior of polyurethane is sensitive to different species. These results indicate that polyurethane fluorescence can be used to develop an application in the field of sensors. Even though we were not continued this study up to that extent it will be continued in a separate study.

CONCLUSION

Large varieties of Polyurethanes are available in the world due to their feasibility of synthesis in different methods using different monomers in different molar ratios. In the polyurethane based researches, scientists have focused on different properties depending on their targeted applications. Fluorescence behavior is one such property which can be used to develop sensor type applications. In this work fluorescence behavior of MDI based polyurethane was analyzed and proposed a mechanism correlated with the microstructure of polyurethanes to explain that behavior. The polyurethane was synthesized using the 2000 molar mass PTHF and MDI. Films obtained from polyurethane prepolymers have a microstructure which is comprise of isolated hard segments embedded in a crystalline soft segment matrix. Those films showed a fluorescence emission around 356 nm initially, and it was proved that it is generated from isolated hard segments of the polyurethane chains which consist of MDI component and not from free MDI. With the UV exposure, there was a generation and growth of a second peak at higher wavelength while reducing intensity of the first peak. With the continuous UV exposure the localized melting could occur. The localized melting allows hard segments to move close to each other which results in formation of coupled hard segments via hydrogen bonds. Those coupled hard segments produce a new peak in fluorescence emission spectrum in higher wavelengths. When the UV irradiation is ceased, the intensity of the second peak reduces and intensity of the first peak re-increases partially. This partial reversibility is governed by tensile forces in the polyurethane matrix in such a way that the tensile forces pull apart some of the coupled hard segments to separate back to isolated hard segments. Meanwhile coupled hard segments which are formed by proper orientations are strongly bonded to each other and do not allow the tensile forces to separate them back. With this well explainable mechanism it was able to discuss the fluorescence behavior of MDI based polyurethane prepolymers.

To do a contribution towards the environmental protection, to reduce the volatile organic content, the polyurethane chains were converted to hydrophilic by uniformly distributing a pendant carboxylate group through the polyurethane chain via the use of DMPA as a monomer in addition to MDI and PTHF. By increasing the DMPA/PTHF molar ratio the dispersion stability was improved while reducing the size of the dispersed polyurethane particles. This is accredited to increased hydrophilicity associated with higher DMPA/PTHF molar ratios. When the films were prepared from those dispersions, the crystallinity was increased with DMPA/PTHF molar ratio. It was proven by XRD and DSC results and as the reason for the improvements in crystallinity it was explained that the inter chain interactions (coulombic attractions and hydrogen bonding) become stronger with the increase of DMPA/PTHF molar ratio. The hydrogen bond strength was correlated with DMPA/PTHF molar ratio with the FT-IR spectra of the films. It showed that there is an increase in hydrogen bonding with the increase in DMPA/PTHF molar ratio. Hence, it was able to propose a method to develop hydrophilic polyurethane dispersions and vary their properties by changing the DMPA/PTHF molar ratio.

Iron polyurethane composite was the other aspect of this project. Iron-polyurethane composites were prepared using polyurethane prepolymers and iron pentacarbonyl. Solution phase mixing techniques and depositions of iron pentacarbonyl s on polyurethane films were applied as the composite formation procedures and, it was able to obtain eight different kinds of composites for a single polyurethane system. Effect of composite formation on the fluorescence behavior was analyzed and it was able to show that some of the techniques results in fluorescence quenching. The other properties of the composites and use of those will be addressed in a separate study.

REFERENCES

1. Chattopadhyay DK, Raju KVSN. Structural engineering of polyurethane coatings for high performance applications. Progress in polymer Science. 2007; 32: p. 352-418.
2. Raghu AV, Jeong HM, Kim JH, Lee YR, Cho YB, Sirsalmat K. Synthesis and characterization of novel polyurethanes based on 4-((4-Hydroxyphenyl)iminomethyl)phenol. Macromolecular research. 2008; 16(3): p. 194-199.
3. Takami K, Matsuno R, Ishihara K. Synthesis of polyurethanes by polyaddition using diol compounds with methacrylate-derived functional groups. Polymer. 2011; 52: p. 5445-5451.
4. Nagle DJ, Celina M, Rintoul L, Fredericks PM. Infrared microspectroscopic study of the thermo-oxidativedegradation of hydroxy-terminated polybutadiene/isophorone diisocyanate polyurethane rubber. Polymer Degradation and Stability. 2007; 92: p. 1446-1454.
5. Clemitson IR. Castable polyurethane elastomers. New York: CRC press,Taylor and Francis Group; 2008.
6. Raftopoulos KN, Janowski B, Apekis L, Pielichowski K, Pissis P. Molecular mobility and crystallinity in polytetramethylene ether glycol in the bulk and as soft component in polyurethanes. European Polymer Journal. 2011; 47: p. 2120–2133.
7. Subramani S, Park YJ, Lee YS, Kim JH. New development of polyurethane dispersion derived from blocked aromatic diisocyanate. Progress in Organic Coatings. 2003; 48: p. 71-79.
8. Ashida K. Polyurethane and related foams: chemistry and technology.New York: CRC Press, Taylor & Francis Group; 2007.
9. Krol P. Synthesis methods, chemical structures and phase structures of linear polyurethanes. Properties and applications of linear polyurethanes in polyurethane elastomers, copolymers and ionomers. Progress in Materials Science. 2007; 52: p. 915–1015.
10. Odian G. Principles of Polymerization. 4th ed. New York: John Wiley & Sons, Inc; 2004.
11. Billiet L, Fournier D, Prez FD. Step-growth polymerization and 'click' chemistry: The oldest polymers rejuvenated. Polymer. 2009; 50: p. 3877–3886.
12. Szycher M. Szycher's Handbook of Polyurethanes. 2nd ed. New York: CRC press, Taylor and Francis group; 2013.
13. Houghton RP, Mulvaney W. Mechanism of tin (IV) - catalysed urethane formation. Journal of Organometallic Chemistry. 1996; 518: p. 21-27.
14. Silva AL, Bordado JC. Recent Developments in Polyurethane Catalysis:Catalytic Mechanisms Review. Catalysis Reviews: Science and Engineering. 2004; 46(1): p. 31–51.
15. Gabriel LP, Zavaglia CAC, Jardini AL, Dias CG, Filho RM. Isocyanates as precursors to biomedical polyurethanes. Chemical Engineering Transactions. 2014; 38: p. 253-258.
16. Stuart B. Infrared Spectroscopy: Fundamentals and Applications: John Wiley & Sons; 2004.
17. Madra H, Ersolmaz SBT, Guner FS. Monitoring of oil-based polyurethane synthesis by FTIR-ATR. Polymer Testing. 2009; 28: p. 773–779.
18. Rosu D, Rosu L, Cascaval CN. IR-change and yellowing of polyurethane as a result of UV irradiation. Polymer Degradation and Stability. 2009; 94: p. 591–596.
19. Yilgor E, Burgaz E, Yurtsever E, Yilgor I. Comparison of hydrogen bonding in polydimethylsiloxane and polyether based urethane and urea copolymers. Polymer. 2000;

41: p. 849–857.

20. Tanaka T, Yokoyama T, Yamaguchi Y. Quantitative study on hydrogen bonding between urethane compound and ethers by infrared spectroscopy. Journal of polymer science: part A-1. 1968; 6: p. 2137-2152.
21. Yilgor E, Yilgor I, Yurtsever E. Hydrogen bonding and polyurethane morphology. I. Quantum mechanical calculations of hydrogen bond energies and vibrational spectroscopy of model compounds. Polymer. 2002; 43: p. 6551–6559.
22. Hwang HD, Park CH, Moon JI, Kim HJ, Masubuchi T. UV-curing behavior and physical properties of waterborne UV-curable polycarbonate-based polyurethane dispersion. Progress in Organic Coatings. 2011; 72: p. 663–675.
23. Bai CY, Zhang XY, Dai JB, Li WH. A new UV curable waterborne polyurethane:Effect of C=C content on the film properties. Progress in Organic Coatings. 2006; 55: p. 291–295.
24. Lukas K, LeMaire PK. Differential Scanning Calorimetry: Fundamental Overview. Connecticut State University, Department of Physics; 2009.
25. Murakami H, Nishiide R, Ohira S, Ogata A. Synthesis of MDI and PCL-diol-based polyurethanes containing [2] and [3]rotaxanes and their properties. Polymer. 2014; 55: p. 6239-6244.
26. Mohamed HA, Badran BM, Rabie AM, Morsi SMM. Synthesis and characterization of aqueous (polyurethane/aromatic polyamide sulfone) copolymer dispersions from castor oil. Progress in Organic Coatings. 2014; 77: p. 965–974.
27. Pan J, Li G, Chen , Chen X, Zhu W, Xu. Alternative block polyurethanes based on poly(3-hydroxybutyrate-co-4-hydroxybutyrate) and poly(ethylene glycol). Biomaterials. 2009; 30: p. 2975–2984.
28. Kariduraganavar MY, Tambe SM, Tasaganva RG, Kittur AA, Kulkarni SS, Inamdar SR. Studies on nonlinear optical polyurethanes containing heterocyclic chromophores. Journal of Molecular Structure. 2011; 987: p. 158–165.
29. Tasaganva RG, Kariduraganavar MY, Inamdar SR. Synthesis and nonlinear optical properties of polyurethanes containing nitro-substituted 1,3,4-oxadiazole chromophores. Synthetic Metals. 2009; 159: p. 1812–1819.
30. Rodrigues JME, Pereira MR, Souza AGD, Carvalho ML, Neto AAD, Dantas TNC, et al. DSC monitoring of the cure kinetics of a castor oil-based polyurethane. Thermochimica Acta. 2005; 427: p. 31–36.
31. Owen T. Fundamentals of modern UV visible spectroscopy Germany : Agilent Technologies; 2000.
32. Simas ER, Akcelrud L. Fluorescent aggregates in naphthalene containing poly(urethane–urea)s. Journal of Luminescence. 2003; 105: p. 69–79.
33. Buruiana EC, Buruiana T, Strat G, Strat. Synthesis and fluorescence of polyurethane cationomers N-modified with a stilbene chromophore. Journal of Photochemistry and Photobiology A: Chemistry. 2004; 162: p. 23–31.
34. Lakowicz JR. Principles of Fluorescence Spectroscopy. 3rd ed. New York: Springer; 2006.
35. A basic guide to particle characterisation. Malvern instruments; 2012.
36. Mohaghegh SMS, Barikani M, Entezami AA. The effect of grafted poly(ethylene glycol monomethyl ether) on particle size and viscosity of aqueous polyurethane dispersions.

Colloids and Surfaces A: Physicochem. Eng. Aspects. 2006; 276: p. 95–99.

37. Liminana MAP, Ais A, Palau MT, Barcelo ACO, Martınez JMM. Characterization of waterborne polyurethane adhesives containing different amounts of ionic groups. International Journal of Adhesion & Adhesives. 2005; 25: p. 507–517.
38. Mequanint K, Sanderson R. Hydrolytic stability of nano-particle polyurethane dispersions: Implications to their long-term use. European Polymer Journal. 2006; 42: p. 1145–1153.
39. Pacios VG, Iwata Y, Colera M, Martinez JMM. Influence of the solids content on the properties of waterborne polyurethane dispersions obtained with polycarbonate of hexanediol. International Journal of Adhesion & Adhesives. 2011; 31: p. 787–794.
40. Ramos BGZ, Senna E, Cramail H, Cloutet E, Borsali R, Soldi V. The role of surfactant in the miniemulsion polymerization of biodegradable polyurethane nanoparticles. Materials Science and Engineering C. 2008; 28: p. 526–531.
41. Lee SK, Kim BK. High solid and high stability waterborne polyurethanes via ionic groups in soft segments and chain termini. Journal of Colloid and Interface Science. 2009; 336: p. 208–214.
42. Zhu X, Jiang X, Zhang Z, Kong XZ. Influence of ingredients in water-based polyurethane–acrylic hybrid latexes on latex properties. Progress in Organic Coatings. 2008; 62: p. 251–257.
43. Buruiana EC, Buruiana T, Strat G, Strat M. Synthesis and optical properties of new polyurethane cationomers with anchored stilbene chromophores. Journal of Polymer Science: Part A: Polymer Chemistry. 2002; 40: p. 1918–1928.
44. Peinado C, Allen NS, Salvador F, Corrales T, Catalina. Chemiluminescence and fluorescence for monitoring the photooxidation of an UV-cured aliphatic polyurethane-acrylate based adhesive. Polymer Degradation and Stability. 2002; 77: p. 523–529.
45. Chen XD, Wang Z, Liao ZF, Mai YL, Zhang MQ. Roles of anatase and rutile TiO2 nanoparticles in photooxidation of polyurethane. Polymer Testing. 2007; 26: p. 202–208.
46. Hoyle C, Kim KJ. Photolysis of Aromatic Diisocyanate-Based Polyurethanes in Solution. Journal of Polymer Science: Part A: Polymer Chemistry. 1986; 24: p. 1879-1894.
47. Hoyle CE, Kim KJ, No YG, Nelson GL. Photolysis of Segmented Polyurethanes.The Role of Hard-Segment Content and Hydrogen Bonding. Journal of Applied Polymer Science. 1987; 34: p. 763-774.
48. Hoyle CE, Kim KJ. Effect of Crystallinity and Flexibility on the Photodegradation of Polyurethanes. Journal of Polymer Science: Part A: Polymer Chemistry. 1987; 25: p. 2631-2642.
49. Bosch P, Almudena F, Salvador EF, Corrales T, Catalina F, Peinado C. Polyurethane-acrylate based films as humidity sensors. Polymer. 2005; 46: p. 12200–12209.
50. Buruiana C, Buruiana T, Olaru M, Zamfir M, Pohoata V. Fluorescent polymers for sensor applications. SCIENTIFIC STUDY & RESEARCH. 2006; VII (1): p. 141-150.
51. Palacios MA, Pohl R, Zyryanov , Anzenbacher. Anion Sensors in Polyurethane Matrices: Synergy Between Matrix and Sensor Materials Improves Selectivity of the Sensing Process. Polymeric Materials: Science and Engineering. 2007; 96: p. 595-596.
52. Buruiana EC, Olaru M, Simionescu BC. Photochemical aspects in anthracene-containing cationic polyurethanes. European Polymer Journal. 2007; 43: p. 1359–1371.

53. Hoyle E, Kim KJ. Excimer formation of a naphthalene diisocyanate based polyurethane in solution. Macromolecules. 1988; 21: p. 2100-2106.
54. Hu XH, Zhang Y, Dai JB, Liu J. Synthesis and fluorescent investigations of VBL-based waterborne polyurethane dye. Journal of Luminescence. 2011; 131: p. 2160–2165.
55. Hu X, Zhang X, Dai B. Synthesis and characterization of a novel waterborne stilbene-based polyurethane fluorescent brightener. Chinese Chemical Letters. 2011; 22: p. 997–1000.
56. Hu XH, Zhang XY, Dai JB. Synthesis and fluorescence enhancement behavior of a novel fluorescent aqueous polyurethane emulsion DDAQ-TDI-PU. Chinese Chemical Letters. 2012; 23: p. 855–858.
57. Buruiana EC, Buruiana T, Strat G, Strat M. Synthesis of Ionic Polyurethanes with Pyrene Rings:Spectral Properties and Fluorescence Quenching Study. Journal of Polymer Science: Part A: Polymer Chemistry. 2005; 43: p. 3945–3956.
58. Buruiana C, Buruiana , Pohoata V. Synthesis, properties and fluorescence quenching in a polycation based on polyetherurethane with pyrene fluorophore. Journal of Photochemistry and Photobiology A: Chemistry. 2006; 180: p. 150–156.
59. Nanda AK, Wicks DA. The influence of the ionic concentration, concentration of the polymer, degree of neutralization and chain extension on aqueous polyurethane dispersions prepared by the acetone process. Polymer. 2006; 47: p. 1805-1811.
60. Jhon Y, Cheong I, Kim JH. Chain extension study of aqueous polyurethane dispersions. Colloids and Surfaces A: Physicochemical and Engineering Aspects. 2001; 179 : p. 71–78.
61. Lee HT, Wu S, Jeng J. Effects of sulfonated polyol on the properties of the resultant aqueous polyurethane dispersions. Colloids and Surfaces A: Physicochem. Eng. Aspects. 2006; 276: p. 176–185.
62. Lei L, Zhong L, Lin X, Li , Xia. Synthesis and characterization of waterborne polyurethane dispersions with different chain extenders for potential application in waterborne ink. Chemical Engineering Journal. 2014; 253: p. 518–525.
63. Pacios VG, Costa V, Colera M, Martinez JMM. Waterborne polyurethane dispersions obtained with polycarbonate of hexanediol intended for use as coatings. Progress in Organic Coatings. 2011; 71: p. 136–146.
64. Liu X, Xu K, Liu H, Cai , Su J, Fu Z, et al. Preparation and properties of waterborne polyurethanes with natural dimer fatty acids based polyester polyol as soft segment. Progress in Organic Coatings. 2011; 72: p. 612– 620.
65. Sardon H, Irusta L, Berridi MJF, Luna J, Lansalot M, Lami EB. Waterborne Polyurethane Dispersions Obtained by the Acetone Process: A Study of Colloidal Features. Journal of AppliedPolymer Science. 2011; 120: p. 2054–2062.
66. Najafi F, Manouchehri , Shaabanzadeh. Synthesis and Characterization of Anionic Polyester-Polyurethane Dispersion as Environmentally-Friendly Water Based Resins. Journal of Chemical Health Risks. 2011; 1(2): p. 23-26.
67. Nanda AK, Wicks DA, Madbouly SA, Otaigbe JU. Effect of ionic content, solid content, degree of neutralization, and chain extension on aqueous polyurethane dispersions prepared by prepolymer method. Journal of applied polymer science. 2005; 98: p. 2514-2520.
68. Hwang HD, Kim HJ. UV-curable low surface energy fluorinated polycarbonate-based polyurethane dispersion. Journal of colloid and interface science. 2011; 362: p. 274-284.

69. Pan H, Chen. Preparation and characterization of waterborne polyurethane/attapulgite nano composites. European Polymer Journal. 2007; 43: p. 3766–3772.
70. Xin H, Shen Y, Li X. Novel cationic polyurethane-fluorinated acrylic hybrid latexes: synthesis, characterization and properties. Colloids and surfaces A: phisicochem. Eng. Aspects. 2011; 384: p. 205-211.
71. Daemi H, Rad RR, Barikani M, Adib M. Catalytic activity of aqueous cationic polyurethane dispersions:A novel feature of polyurethanes. Applied Catalysis A: General. 2013; 468: p. 10-17.
72. Pielichowska K, Król P, Król B, Pagacz. TOPEM DSC study of glass transition region of polyurethane cationomers. Thermochimica Acta. 2012; 545: p. 187–193.
73. Athawale VD, Kulkarni MA. Synthesis, characterization, and comparison of polyurethane dispersions based on highly versatile anionomer ATBS and conventional DMPA. J. Coat. Technol. Res. 2010; 7: p. 189-199.
74. Yang Z, Wicks DA, Hoyle CE, Pu H, Yuan J, Wan D, et al. Newly UV-curable polyurethane coatings prepared by multifunctional thiol- and ene-terminated polyurethane aqueous dispersions mixtures: Preparation and characterization. Polymer. 2009; 50: p. 1717–1722.
75. Yang Z, Wicks DA, Yuan J, Pu H, Liu Y. Newly UV-curable polyurethane coatings prepared by multifunctional thiol- and ene-terminated polyurethane aqueous dispersions: Photopolymerization properties. Polymer. 2010; 51: p. 1572–1577.
76. Guo Z, Park S, Wei S, Pereira T, Moldovan M, Karki AB, et al. Flexible high-loading particle reinforced polyurethane magnetic nanocomposite fabrication through particle-surface-initiated polymerization. Nanotechnology. 2007; 18: p. 1-8.
77. Guo Z, Park S, Hahn H. Magnetic and electromagnetic evaluation of the magnetic nanoparticle filled polyurethane nanocomposites. Jounal of applied physics. 2007; 101.
78. Sabzi M, Mirabedini SM, Mehr J, Atai M. Surface modification of TiO2 nano-particles with silane coupling agent and investigation of its effect on the properties of polyurethane composite coating. Progress in Organic Coatings. 2009; 65: p. 222–228.
79. Che XC, Jin YZ, Lee YS. Preparation of nano-TiO2 /polyurethane emulsions via in situ RAFT polymerization. Progress in Organic Coatings. 2010; 69: p. 534–538.
80. Dhoke SK, Rajgopalan , Khanna AS. Effect of Nano-Zinc Oxide Particles on the Performance Behavior of Waterborne Polyurethane Composite Coatings. International Journal of Material Science. 2012; 2(2): p. 47-55.
81. Gao X, Zhu Y, Zhao X, Wang , An D, Ma Y, et al. Synthesis and characterization of polyurethane/SiO2 nanocomposites. Applied Surface Science. 2011; 257: p. 4719–4724.
82. Zhang J, Li L, Chen G, Wee P. Influence of iron content on thermal stability of magnetic polyurethane foams. Polymer Degradation and Stability. 2009; 94: p. 246–252.
83. Park C, Kang SJ, Tijing LD, Pant H, Kim CS. Inductive heating of electrospun Fe2O3 /polyurethane composite mat under high-frequency magnetic field. Ceramics International. 2013; 39: p. 9785–9790.
84. Mishra A, Maiti P. Aromatic polyurethanes: the effect of hard segment and chain structure on their properties. Journal of Polymer Engineering. 2011; 31: p. 253–259.
85. Wang CH, Shieh YT, Guo G, Nutt S. Effects of Organophilic-Modified Attapulgite

Nanorods on Thermal and Mechanical Behavior of Segmented Polyurethane Elastomers. polymer composites. 2010; 31(11): p. 1890-1898.

86. Pielichowski K, Njuguna. Thermal Degradation of Polymeric Materials Crewe, UK: Smithers Rapra Technology; 2005.
87. Petrovic ZS, Ferguson J. Polyurethane elastomers. Progress in Polymer Science. 1991; 16: p. 695-836.
88. LIU LZ, CHU B. Crystalline Structure and Morphology of Microphases in Compatible Mixtures of Poly(tetrahydrofuran-methylmethacrylate) Diblock Copolymer and Polytetrahydrofuran. Journal of Polymer Science: Part B: Polymer Physics. 1999; 37: p. 779 –792.
89. Motokucho S, Furukawa M, Kawashima M, Kojio K, Yoshinaga K. Physical properties of poly(tetrahydrofuran)-block-poly(2-ethyl-2-oxazoline) triblock copolymer. Polymer Journal. 2013; 45: p. 1115–1119.
90. Rhim JW, Mohanty AK, Singh SP, Ng PKW. Effect of the Processing Methods on the Performance of Polylactide Films: Thermocompression Versus Solvent Casting. Journal of Applied Polymer Science. 2006; 101: p. 3736 –3742.
91. Pinto AM, Cabral J, Tanaka DP, Mendes AM, Magalhaes FD. Effect of incorporation of graphene oxide and graphene nanoplatelets on mechanical and gas permeability properties of poly(lactic acid) films. Polymer International. 2013; 62(1): p. 33-40.
92. Zhang C, Ren Z, Yin Z, Jiang L, Fang S. Experimental FTIR and simulation studies on H-bonds of model polyurethane in solutions. I: In dimethylformamide (DMF). Spectrochimica Acta Part A. 2011; 81: p. 598– 603.
93. Sadek PC. The HPLC solvent guide. 2nd ed. New York: A John Wiley and sons, Inc.; 2002.
94. Cakic SM, Stamenkovic JV, Djordjevic DM, Ristic IS. Synthesis and degradation profile of cast films of PPG-DMPA-IPDI aqueous polyurethane dispersions based on selective catalysts. Polymer Degradation and Stability. 2009; 94: p. 2015–2022.
95. Larsson M, Hill A, Duffy J. Suspension stability; Why particle size, zeta potential and rheology are important. Annual Transactions of the nordic rheology society. 2012; 20: p. 209-214.
96. Sample dispersion & refractive index guide England: Malvern Instruments Ltd.; 1997.
97. El-Dossoki FI. Refractive Index and Density Measurements for Selected Binary Protic-Protic, Aprotic-Aprotic, and Aprotic-Protic Systems at Temperatures from 298.15 K to 308.15 K. Journal of the Chinese Chemical Society. 2007; 54: p. 1129-1137.
98. Garcia JMB, Lopez AG, Torres AC, Baltazar EA, Silva GAI. Densities and Viscosities of (N,N-Dimethylformamide + Water) at Atmospheric Pressure from (283.15 to 353.15) K. J. Chem. Eng. Data. 2008; 53: p. 1024–1027.
99. Sengwa RJ, Khatri V, Sankhla S. Structure and hydrogen bonding in binary mixtures of N,N-dimethylformamide with some dipolar aprotic and protic solvents by dielectric characterization. Indian Journal of Chemistry. 2009; 48: p. 512-519.
100. KIM BK, LEE JC. Waterborne Polyurethanes and Their Properties. Journal of Polymer Science: Part A Polymer Chemistry. 1996; 34: p. 1095-1104.
101. Jang JY, Jhon YK, Cheong IW, Kim JH. Effect of process variables on molecular weight and mechanical properties of water-based polyurethane dispersion. Colloids and Surfaces

A: Physicochemical and Engineering Aspects. 2002; 196: p. 135– 143.

102. Son SH, Lee HJ, Kim JH. Effects of carboxyl groups dissociation and dielectric constant on particle size of polyurethane dispersions. Colloids and Surfaces A: Physicochemical and Engineering Aspects. 1998 ; 133: p. 295-301.
103. MARTIN DJ, MEIJS GF, GUNATILLAKE PA, YOZGHATLIAN SP, RENWICK GM. The Influence of Composition Ratio on the Morphology of Biomedical Polyurethanes. Journal of Applied Polymer Science. 1999; 71: p. 937–952.
104. Paul D, Paul S, Roohpour N, Wilks M, Vadgama P. Antimicrobial, Mechanical and Thermal Studies of Silver Particle-Loaded Polyurethane. Journal of Functional Biomaterials. 2013; 4: p. 358-375.
105. Yilgor E, Yilgor I, Yurtsever E. Hydrogen bonding and polyurethane morphology. I. Quantum mechanical calculations of hydrogen bond energies and vibrational spectroscopy of model compounds. Polymer. 2002; 43: p. 6551–6559.
106. Huang SL, Lai JY. Structure- tensile properties of polyurethanes. Eur. Polym. J. 1997; 33: p. 1563-1567.
107. Joseph J, Jemmis ED. Red-, Blue-, or No-Shift in Hydrogen Bonds: A Unified Explanation. Journal of american chemical society. 2007; 129: p. 4620-4632.
108. Brunette CM, Hsu SL, MacKnight WJ. Hydrogen-Bonding Properties of Hard-Segment Model Compounds in Polyurethane Block Copolymers. Macromolecules. 1982; 15: p. 71-77.
109. Halliwell SM. weathering of polymers Dolbey , editor.: RAPRA technology limited; 1992.
110. Montero T, Hernandez J, Estelrich J. Fluorescence Quenching of Albumin. A spectrofluorimetric experiment. Biochemical education. 1990; 18(2): p. 99-101.
111. Bhaumik A, Samanta S, Mal NK. Iron oxide nanoparticles stabilized inside highly ordered mesoporous silica. Pramana-J. Phys. 2005; 65(5): p. 855-862.
112. Mohapatra M, Anand S. Synthesis and applications of nano-structured iron oxides/hydroxides - a review. International Journal of Engineering, Science and Technology. 2010; 2(8): p. 127-146.
113. Kwon , Piao , Park , Angappane , Jo , Hwang NM, et al. Kinetics of Monodisperse Iron Oxide Nanocrystal Formation by "Heating-Up" Process. J. AM. CHEM. SOC. 2007; 129: p. 12571-12584.
114. Kotzian , Rosch , Schrode , Zerner C. Optical Spectra of Transition-Metal Carbonyls: Cr(CO)6, Fe(CO)5, and Ni(CO). J. Am. Chem. SOC. 1989; 11(20): p. 7687-7696.

i. Problems if any, encountered during the implementation of the project
As the polyurethane films made were quite different from the coatings made currently in the country by the industry, the attempts to check the quality of coatings according to industrial standards was not possible.

ii. Major findings and follow up activities.
The team is currently trying to write one more research proposal to continue the reaserch work. Specially, we are trying to explore the possibility of using PU films as a sensor. As we have already published in our first publication, it seems that the reversible fluorescent properties are sensitive to certain analytes such as Ca^{2+}.

Section 4

Impact of Research results:

i. Relevance of results achieved to scientific advancement:

In this project, we produced a water based polyurethane dispersion that can be used as a coating. The polyurethane molecules Films produced show special fluorescence properties. It has been found that fluorescence property can be made reversible. Hence, the possibility of using it as a sensor material would be studied in future. Nano-iron composites of the polyurethane were produced and fluorescence properties were investigated. The polyurethane produced were capped with ene-end groups to impart UV curing characteristics.

ii. Relevance of results achieved to national/socio-economic development

Water based polyurethanes are the current trend in the industry albeit information on production or the synthesis of water based polyurethane is not available in Sri Lanka. Hence, the acquiring of the basic chemistry of manufacture of this material is very valuable. Beside the economic value, if one can manufacture this material in Sri Lanka, it will be a very environmental friendly VOC free product.

In addition, as we have observed, there is an immense potential in this novel material to be developed as a sensor.

iii. Dissemination/application of research output

We have already published an abstract and are in the process of writing two or more research papers for indexed journals. Possibility of applying for a patent is also being evaluated.

Section 5

Miscellaneous

i. List of major equipment acquired during the project period and their functionality

None

ii. List of publications/communications arising from the project and/or presentations made at seminars, workshops etc. (Please attach copies)

Investigation of the potential to fabricate a conductive sensor based on fluorescence properties of polyurethane, M.V.L.Pathmakumari, S.Senevirathne, L.Karunanayake, V.Karunaratne and S.Amarasinghe, , Proceedings of IIUPST2015, 33 (2015)

Section 6

Summary Statement of Expenditure (indicate under Personnel, Equipment, Consumables, Travel and Subsistence and Miscellaneous)

Our Ref: FIN/04/10/2015/PP

RD/DOC/F/21

Schedule E

Format for Interim and Final Financial Report

The financial position of grant No **RG/2011/NANO/01** as at 28/10/2015.. awarded to Dr./Prof. Lakeen Karunaratne by National Science Foundation is as follows.

		Funds received By the Univ./ Institution	Total expenditure RS.	Balance available RS.
Personal-	Research Student	1,260,000/-	(1,580,000/-)	(320,000/-)
	Technical Assistant	.....	.....	.....
	Other	.....	.....	.....
Equipment- (Items Purchased Should be Stated)	Foreign	.....	.....	.....
	Local	698,000/-	(408,545/-)	289,455/-
Consumables-	Foreign	.....	.....	.....
	Local	.....	.....	.....
Travel & Subsistence		.....	.....	.....
Postgraduate Reg. Fees		213,500/--	(213,500/-)	-
Miscellaneous		....10,000/-	.....	...10,000/-
Lab services & Samples		60,000/-	(9,000)	51,000/-
TOTAL		2,241,500/-	2211,045	30,455/--

Unspent balance of the funds received

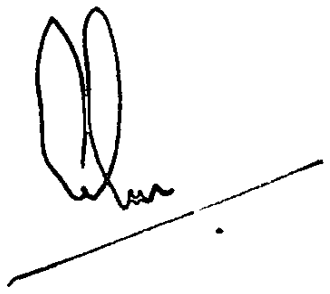
Funds received	- RS.	2,241,500/-
Actual expenditure	-	2,211,045/-
Balance		30,455/-.
Cash Imprest/Cash advance	-	.....
Balance as at 28/10/15	-	30,455/-

.....
Bursar / Accountant

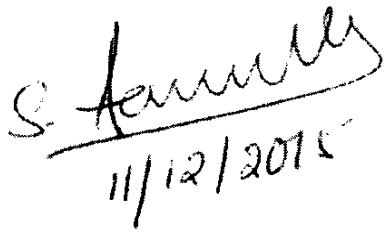
Date: 28/10/2015

Section 7

i. Grantees' signatures



Prof. L.Karunanayake



Dr.S.Amarasinghe

Prof.Veranja Karunaratne

Dr. Masilamani Koneswaran

ii. Comments of the Head of the Department/signature

iii. Head of the Institution's signature

Section 7

i. Grantees signatures

Prof. L. Karunanayake

Dr. S. Amarasinghe

Prof. Veranja Karunaratne

Dr. Masilamani Koneswaran

ii. Comments of the Head of the Department/signature

Project successfully completed

Head
Department of Chemistry
University of Sri Jayewardenepura
Nugegoda.

iii. Head of the Institution's signature

Professor Sampath Amaratunge
Vice-Chancellor
University of Sri Jayewardenepura
Nugegoda, Sri Lanka.

Investigation of the potential to fabricate a conductivity sensor based on fluorescence properties of polyurethane

M. V. L. Pathmakumari,[1] S. Senevirathne,[1,2] L. Karunanayake,[1] V. Karunaratne, [2] and S. Amarasinghe[3]

Conductivity is one of the major technical parameters employed in a wide variety of industries such as hydroponics, aquaculture and fresh water systems. Therefore, the potential to fabricate a conductivity sensor by utilizing fluorescence properties of 4,4'-Methylenebis(phenyl isocyanate)(4,4'-MDI) based polyurethane was investigated.

Anionic aqueous polyurethane dispersion (PUD) based on polytetramethylene ether glycol (PTMEG) and 4,4'-MDI was synthesized. Dimethylol propionic acid (DMPA) was used to obtain negatively charged polyurethane backbone. It was then neutralized into a salt with diethyl ammonium which aids in the aqueous phase dispersion in the prospective stages. Trimethylolpropane diallyl ether served as the chain terminator to prevent the isocyanate-water side reaction. Obtained stable aqueous PUD was characterized using FTIR spectroscopic technique.

PU films were casted on glass substrates by solvent and water evaporation from the dispersion, followed by drying of the resulted films to a sufficient extent. Fluorescence studies of the MDI based PU films showed a fluorescence emission around 340 nm when excited at 293 nm. Variations in PU fluorescence in response to a variety of electrolyte solutions such as $MgCl_2$, NaCl, $Ca(NO_3)_2$ and $CaCl_2$ were tested at ambient temperature. In this preliminary study, parameters such as pH, temperature and film thickness were kept constant.

Thereby, fluorescence of MDI based PU was found to be capable of sensing solution conductivities and there was a strong correlation between those two variables. Thus, PU is a potent candidate in fabricating conductivity sensors.

Keywords: Polyurethane / Sensor / Conductivity / Fluorescence / MDI

Acknowledgement: National Science Foundation, Sri Lanka(RG/2011/NANO/01)

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[2] SLINTEC, Pitipana, Homagama

[3] Department of Materials Science and Engineering, University of Moratuwa

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