

THE CHARGE-TRANSFER COMPLEXATION AND THE ALTERNATING COPOLYMERIZATION OF n-BUTYL VINYL ETHER AND MALEIC ANHYDRIDE IN CHLOROALKANES

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It has been proposed that the alternating copolymerization of acceptor-donor monomer pairs proceeds through the charge-transfer (CT) complexes formed between the comonomer pairs (Kokubo, Iwatsuki & Yamashita, 1968).

n-Butyl vinyl ether (BVE) and maleic anhydride (MA) form a CT complex showing the UV absorption maximum at 270 nm in 1,2-dichloroethane. The stoichiometry of the complexation is found to be 1:1. The equilibrium constant of the complexation is measured in carbon tetrachloride by NMR using Hanna-Ashbough equation (Hanna & Ashbough, 1964) to be $0.37 \text{ dm}^3/\text{mole}$, in chloroform by UV using Scott equation to be $0.27 \text{ dm}^3/\text{mole}$, and in 1,2-dichloroethane by UV using the equation of Ketelaar et al (Ketelaar, van de Storppe, Goudsmit & Dzcubas, 1952) to be $0.11 \text{ dm}^3/\text{mole}$ as the polarity of the solvent increases in this order. A 1:1 alternating copolymer is formed when BVE and MA are copolymerized in chloroform with 2,2'-azobisisobutyronitrile at 60°C. The rate of the copolymerization is rapid. The initial rate of copolymerization and the limiting conversion are maximum at 1:1 feed monomer ratio, and the limiting conversion is close to the theoretical maximum conversion for a pure alternating copolymerization.

The results are consistent with the mechanism that the weak 1:1 CT complex of BVE and MA homopolymerizes to form an alternating copolymer in chloroform.

References

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