Analysis of the role of complex in the alternating copolymerization of N-vinylpyrrolidone and maleic anhydride

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SUMMARY
Heterogeneous copolymerization of 1-vinyl-2-pyrrolidone (NVP) and maleic anhydride (MA) initiated with AIBN was studied in benzene at 60 °C, at two different total monomer concentrations. The existence of a charge transfer complex between the comonomers has been shown and its equilibrium constant determined. The chemical composition of the copolymer was examined as a function of the initial monomer ratio, and it was found nearly equimolecular in a wide range of relative monomer concentrations. Studying the dependence of the initial rate of copolymerization (\(W_0\)) on the monomer composition, significant increase in \(W_0\) was found at a mole ratio of NVP/MA = 1 when 3 mol dm\(^{-3}\) total monomer concentration was applied. The compositional equation for the NVP/MA copolymerization system was derived with the consideration of the effect of complex.

INTRODUCTION
Different models have been suggested for the mechanism of the radical alternating copolymerization of vinyl monomers. Most of them involve participation of a donor-acceptor complex formed between the two monomers, e.g. (1-7). For instance, alternating copolymerization of MA with different monomers was explained by "homopolymerization" of the comonomer charge-transfer complex (2-7). In a study of NVP, MA and methyl methacrylate (MMA) terpolymerization system, MMA was considered as a comonomer of NVP-MA charge-transfer complex (8). However, the idea of treating the complex as a monomer is rather objectionable by the reason of

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the theory of reaction kinetics. Inconsistency with the mechanism of homopolymerization of CTC was stated by several authors, e.g. (9-12). Therefore, in recent developments of theory of copolymerization, for the explanation of deviations from the terminal model of chain propagation, both the reaction of free monomers and the complex with the growing radical have been taken into account (9-12).

Most investigations for the mechanism of copolymerization involve an analysis of composition of the copolymer formed, but it is often difficult to distinguish between the various models for copolymerization on the basis of their fit to the composition data, which in turn are frequently determined with insufficient accuracy. It especially concerns the copolymers of MA.

The aim of the present work is to study the effect of C-T complex on the process of the copolymerization of NVP and MA, applying two independent methods for the determination of the chemical composition.

EXPERIMENTAL

Materials

1-vinyl-2-pyrrolidone (Fluka) was freshly distilled at a reduced pressure (60 Pa) before use (b.p. 46 °C, n_D^20 = 1.5115). Maleic anhydride (Reanal, Hungary) was purified by sublimation in vacuo (m.p. 52 - 53 °C). Azo-bis-isobutynitrile (Fluka, purum) was recrystallized twice from chloroform/ether (d.p. 103 - 109 °C). Thiophene free benzene was Na dried and distilled, in addition, refluxed with DPPH for several hours and redistilled.

Copolymerization

Copolymerization was carried out in 50 cm³ glass ampoules sealed in argon after deoxygenation of the reaction mixture.

Thermostat equipped with a shaking machine was used to maintain the constant temperature (60 ± 0.5 °C). The yield was determined gravimetrically. Suspension was cooled to 20 °C then poured into diethyl ether (3-fold excess by volume) to insure total precipitation of the copolymer.