

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. Inconsistence 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 , $n_{\text{D}}^{20} = 1.5115$). Maleic anhydride (Reanal, Hungary) was purified by sublimation in vacuo (m.p. $52 - 53^{\circ}\text{C}$). Azo-bis-isobutyronitrile (Fluka, purum) was recrystallized twice from chloroform/ether (d.p. $103 - 109^{\circ}\text{C}$). 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 cm^3 glass ampoules sealed in argon after deoxygenation of the reaction mixture.

Thermostat equipped with a shaking machine was used to maintain the constant temperature ($60 \pm 0.5^{\circ}\text{C}$). 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.

Determination of the chemical composition

Because of high sensitivity of poly(1-vinyl-2-pyrrolidone-co-maleic anhydride) / (NVP-co-MA) / to air moisture, poly(1-vinyl-2-pyrrolidone-co-maleic acid) / (NVP-co-MAC) / samples dried to constant weight were used for the determination of the chemical composition of the copolymer. Hydrolysis was carried out by boiling the 1 % aqueous solutions of samples for 3 h. Completeness of the hydrolysis was checked by IR spectroscopy after vacuum evaporation of the solvent.

Purification of P(NVP-co-MAC): 1 g of the copolymer was dissolved in 10 cm³ distilled water, diluted with 25 cm³ acetone, then the solution was pressed slowly through a G-4 glass filter into 150 cm³ THF stirred vigorously with a magnetic stirrer. The precipitated white powder was filtered, washed with THF and dried in vacuo at 50 °C until constant weight.

Elemental analysis: The chemical composition was evaluated from C,H,N data determined by usual microanalysis but the carbon/nitrogen content ratio was employed for calculations to avoid incidents due to absorbed water. Deviation of N content in parallel measurements were within ± 4 %.

Potentiometric titration: 0.01 M aqueous solution of P(NVP-co-MAC) samples were titrated with 0.1 M NaOH solution using RADELKISZ OP-208 type Precision Digital pH meter and RADELKISZ OP-08083 type combined glass electrode.

Determination of the complex equilibrium constant: It was carried out by UV-spectroscopy in CHCl₃, at 25 °C in the range of wave length 370 - 410 nm. Spectra were recorded by a SPECORD M 40 (Carl Zeiss, Jena) UV-VIS spectrophotometer after incubation of freshly prepared sample solutions for 10 min.

RESULTS AND DISCUSSION

The formation of CT complex was studied by UV-spectroscopy in CHCl₃. According to Caze et al. (13) this solvent does not form complex with MA. As the yellow complex of NVP-MA (14,15) has turned on standing pink then scarlet, sample solutions were always freshly prepared. The development of red colour ac-

celerated with increasing monomer concentration and temperature. Furthermore, the red solution obeyed Beer-Lambert's law. A supposition for the mechanism of the formation of these red compounds will be published elsewhere.

The complex equilibrium constant, K was determined by the linear graphic method assuming that the monomers M_1 and M_2 form an equimolar complex according to the equilibrium (1). The concentration of the complex (c) is given by Eqn. (2)



$$c = Km_1m_2 \quad (2)$$

Introducing the Lambert+Beer's law into (2), Eqn. (3) can be derived without any simplification

$$\frac{m_1}{E} = \frac{1}{\epsilon} + \frac{1}{\sqrt{\epsilon K}} \cdot \frac{1}{\sqrt{E}} \quad \text{if } m_1 = m_2 \quad (3)$$

Where E is the optical density, ϵ - the molar absorption coefficient, m_1 and m_2 - the concentration of M_1 and M_2 respectively. The complex equilibrium constant, $K = 0.15 \pm 0.03 \text{ dm}^3 \text{ mol}^{-1}$ was found to be constant in the range of the wave length 370 - 410 nm. This fact points to that the assumption of $m_1 = m_2$ in Eqn. (3) was correct. A slight temperature dependence of K , characteristic for molecular complexes (16) was found between 25 and 45 °C. The above value of K is in good agreement with $K = 0.18 \text{ dm}^3 \text{ mol}^{-1}$ determined by Tamura et al. in CHCl_3 at room temperature (8), and approximates $K = 0.29 \text{ dm}^3 \text{ mol}^{-1}$ obtained by Konsulov and Grozeva in dioxane (17).

The copolymerization initiated with AIBN ($0.02 \text{ mol} \cdot \text{dm}^{-3}$) was carried out in benzene at 60 °C. The dependence of the initial rate of copolymerization (W_0) on the monomer composition was studied at two different monomer concentrations. W_0 values were determined at early stage of copolymerization, 8 - 10 % conversion, where straight lines were obtained for conversion vs. time function. Fig. 1 shows the difference in shape of curves obtained at $2 \text{ mol} \cdot \text{dm}^{-3}$ and $3 \text{ mol} \cdot \text{dm}^{-3}$ total monomer concentrations. As comonomers form an equimolar CT complex, the sharp increase in W_0 (cf. curve 2 in Fig. 1) at the monomer mole fraction of 0.5 can be attributed to the effect of complex be-

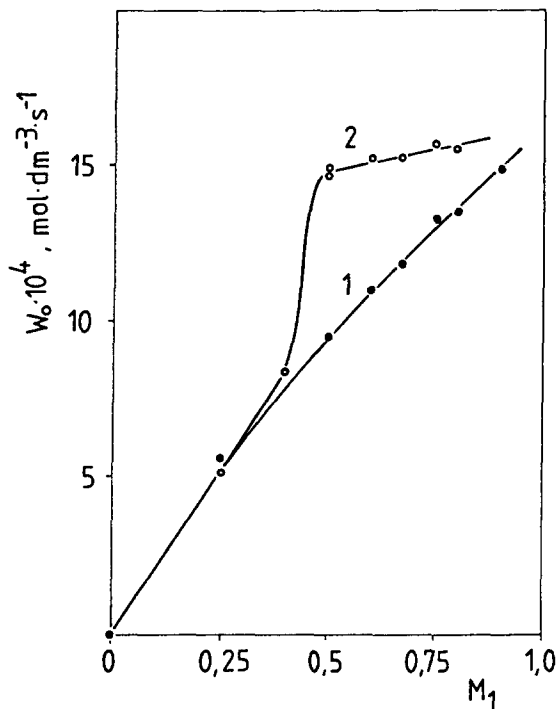


Figure 1.

The initial rate of copolymerization (W_0) of 1-vinyl-2-pyrrolidone with maleic anhydride plotted against the mole fraction of NVP (M_1). Total monomer concentrations: $2 \text{ mol} \cdot \text{dm}^{-3}$ (curve 1) and $3 \text{ mol} \cdot \text{dm}^{-3}$ (curve 2), (AIBN): $0.02 \text{ mol} \cdot \text{dm}^{-3}$, temperature: 60°C .

ing in an appreciable concentration. Unfortunately, the employment of higher monomer concentrations encountered experimental difficulties.

Determination of the copolymer composition

The dependence of the copolymer composition on the initial monomer mole ratio was studied by two independent methods, i.e. elemental analysis and potentiometric titration. The results obtained were concordant within $\pm 6\%$. Proper conditions for the titration and a precise approach for the evaluation of the results applied in this work were reported earlier (18).

The chemical composition of the copolymer formed was found to be 1:1 in a broad range of monomer composition. The data in Table 1 however indicate a slight but systematic increase in dm_1/dm_2 values (i.e. relative content of NVP in the copolymer) by increasing m_1/m_2 and the total monomer concentration.

Table 1. Potentiometric titrational measurements of the copolymer composition as a function of the initial monomer feed. Total monomer concentrations ($m_1 + m_2$): $2 \text{ mol}\cdot\text{dm}^{-3}$ and $3 \text{ mol}\cdot\text{dm}^{-3}$; [AIBN]: $0.02 \text{ mol}\cdot\text{dm}^{-3}$; temperature: 60°C

Monomer mole ratio of NVP/MA	Copolymer composition (dm_1/dm_2)	
	($m_1 + m_2 = 2 \text{ mol}\cdot\text{dm}^{-3}$)	($m_1 + m_2 = 3 \text{ mol}\cdot\text{dm}^{-3}$)
0.6	-	1.00
1.0	0.98	1.01
1.5	1.03	1.03
2.0	1.05	1.07
3.0	1.06	1.11
4.0	1.08	1.12
6.0	1.09	1.13
9.0	1.10	1.15

For the description of the above finding, the method for the determination of copolymerization constants elaborated by Tüdös et al. (19) has been applied. By plotting the calculated η - ξ data pairs, a slight curvature in Fig. 2 referring to the deviation from the terminal model can be observed.

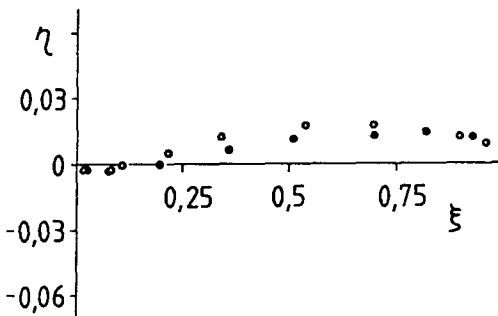


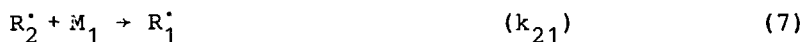
Figure 2.

The η - ξ representation of *N*-vinylpyrrolidone/maleic anhydride copolymerization system. Monomer concentrations: $2 \text{ mol}\cdot\text{dm}^{-3}$ (•) and $3 \text{ mol}\cdot\text{dm}^{-3}$ (○).

Composition equation has been derived starting from the Eq1. (1) and Eqn. (2) with the consideration that homopolymerization of MA under the given conditions does not occur (7). The latter statement was checked by us in several experiments. Then, the chain propagation consists of the following six reaction steps



and respectively



The principle of short sequences (19), in this case, can be given as follows

$$k_{12}r_1m_2 + k_{14}r_1c = k_{21}r_2m_1 + k_{23}r_2c \quad (9)$$

Considering Eqn. (9) in terms of the suggested mechanism, the rate expression for the copolymerization of individual monomers are:

$$\frac{dm_1}{dt} = k_{11}r_1m_1 + k_{13}r_1c + k_{12}r_1m_2 + k_{14}r_1c \quad (10)$$

and

$$\frac{dm_2}{dt} = k_{12}r_1m_2 + k_{14}r_1c \quad (11)$$

By the use of Eqn. (2), Eqn. (10) and (11) can be brought into the following form

$$\frac{dm_1}{dt} = k_{12}r_1m_2 \left\{ \frac{k_{11}}{k_{12}} \cdot \frac{m_1}{m_2} + \frac{k_{13}}{k_{12}} \cdot K \cdot m_1 + 1 + \frac{k_{14}}{k_{12}} \cdot K \cdot m_1 \right\} \quad (12)$$

and

$$\frac{dm_2}{dt} = k_{12}r_1m_2 \left\{ 1 + \frac{k_{14}}{k_{12}} \cdot K \cdot m_1 \right\} \quad (13)$$

Introducing the following notations

$$\rho_1 = k_{11}/k_{12} \quad (14)$$

$$\rho_1' = K \cdot k_{13}/k_{12} \quad (15)$$

$$\rho_1'' = K \cdot k_{14}/k_{12} \quad (16)$$

and

$$x = m_1/m_2 \quad (17)$$

from Eqn. (12) and (13) the equation of the copolymer composition is

$$dm_1/dm_2 = \frac{\rho_1 x + (\rho_1' + \rho_1'')m_1 + 1}{\rho_1''m_1 + 1} \quad (18)$$

Using experimental data in Tab. 1, copolymerization constants determined are $\rho_1 = 0.005$; $\rho_1' = 0.05$, and $\rho_1'' = 0.2$. Substituting these values into Eqn. (18), it has been found that the derived equation (18) fits the experimentally determined copolymer composition with the accuracy of $\pm 4\%$.

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