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Relative Reactivity of Free Monomers and Donor-Acceptor Complex in Alternating Copolymerization of Isobutyl Vinyl Ether with Maleic Anhydride from the Rate of Polymerization

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ABSTRACT

Radical copolymerization of isobutyl vinyl ether (IBVE) with maleic anhydride (MA) gave 1:1 alternating copolymer in a wide range of monomer composition. IBVE and MA formed a 1:1 donor-acceptor complex which showed an absorption maximum at 273 nm in $CHCl_3$. The equilibrium constant of the complexation was measured to be 0.052 M^{-1} in CCl_4 at 37°C by NMR, 0.036 M^{-1} in $CDCl_3$ at 37°C by NMR, and 0.033 M^{-1} in $CHCl_3$ at 23°C by UV. The dilatometrically measured rate of copolymerization in $CHCl_3$ at 50°C was a maximum at a feed MA mole fraction of 0.350, 0.405, and 0.435 when the total monomer concentration was 0.5, 1, and 1.5 M, respectively. The Georgiev-Zubov method, based on the reactions of free monomers and the complex, was applied to obtain α = 0.210, β_1 = 65.6, and β_2 = 4.42.

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INTRODUCTION

The initial rate of an alternating copolymerization is maximum at a feed composition when both comonomers do not homopolymerize. The 1:1 alternating copolymerization can be regarded as the result of exclusive cross-propagation reactions of free monomers on one hand [1, 2] or, on the other hand, as the result of the homopolymerization of the donor-acceptor complex formed between the comonomers [3, 4]. In the latter case the initial overall rate of polymerization should be maximum at 1:1 monomer composition in the feed, and in the former case the rate maxima should always occur at the same monomer composition. There are numerous examples in which the rate maxima do not coincide with the 1:1 monomer composition [5]. It is now generally accepted that free monomers and the complex compete for a propagating chain end [6].

This article describes the copolymerization of isobutyl vinyl ether (IBVE) with maleic anhydride (MA) in chloroform, both monomers being unable to homopolymerize in ordinary conditions. The dilatometrically measured rate is analyzed according to the method developed by Georgiev and Zubov [7, 8].

EXPERIMENTAL

Reagent grade MA (BDH) and 2,2'-azobisisobutyronitrile (AIBN) (BDH) were recrystallized from dry benzene and methanol, respectively. Reagent grade IBVE (Fluka) was fractionally distilled before use. Solvents were purified according to the usual methods [9].

The UV absorption of the donor-acceptor complex of MA and IBVE was measured with a Unicam SP8-100 spectrophotometer with a 1-cm path length. The absorptivity due to the uncomplexed components was subtracted either numerically or by placing the solution of the same concentration in the reference cell. A Varian EM-360 60 MHz NMR spectrometer was used to measure the chemical shift of the protons of MA. Linear regression was applied when evaluating the equilibrium constants of the complexation. The correlation coefficients were better than 0.997 in all cases.

Polymerization was carried out in glass ampules in which the required quantities of the reagents were placed. The ampules were sealed after freeze-thaw degassing under high vacuum and placed in an oil bath at 60 ± 0.1°C. After the reaction, the mixture was poured into a large amount of dry diethyl ether and the precipitated copolymer was separated by filtration. The copolymer was purified by reprecipitation from acetone solution in diethyl ether. The composition of the copolymer was determined by conductometrically backtitrating the MA unit in acetone/water solution with standard 0.05 M NaOH and 0.05 M HCl. Approximately 150 mg of the sample was used in each titration.

Dilatometric determination of the initial overall rate of copolymerization was carried out at 50 ± 0.1°C in an oil bath. The degassed reaction mixture was placed in a glass dilatometer whose capacity at 50°C was 17.4320 cm^3. The copolymer was not soluble in $CHCl_3$, but a homogeneously dispersed colloidal solution without coagulation was formed when conversion was less than a few percent, which enabled accurate measurement of the initial rate. Since the copolymer composition was found to be 1:1 in a wide range of monomer composition, it was assumed that only alternating copolymer was formed at the initial stage of the polymerization at different feed compositions. The following densities (ρ, in g/cm^3) of the compounds were measured pyconometrically at 50°C: $\rho(CHCl_3) = 1.4123$, $\rho(IBVE) = 0.7617$, $\rho(MA) = 1.2816$ measured in $CHCl_3$ solution, and ρ(1:1 copolymer) = 2.1072 measured after complete swelling in $CHCl_3$. The volume decrease was very close to linear versus the reaction time until a few percent of conversion was reached. The rate was determined by the initial slope of the plot. The dilatometrically measured conversion and the gravimetrically determined conversion agreed well when the reaction mixture in a dilatometer was dropped in dry diethyl ether after a period of polymerization.

RESULTS AND DISCUSSION

The donor-acceptor complex of IBVE and MA shows an absorption maximum at 273 nm in $CHCl_3$. Figure 1 shows the continuous variation of the absorptivity with respect to the composition of the component in $CHCl_3$. The position of the maxima of the plots indicates a 1:1 stoichiometry for the complex [10]. The equilibrium constant of the complexation (K in M^{-1}) was determined by UV and NMR methods. Figure 2 shows the Bensi-Hildegrand plot [11] based on the following relation:

$$\frac{[A]}{abs} = \frac{1}{K\epsilon[D]} + \frac{1}{\epsilon} \qquad (1)$$

where [A] and [D] are the overall concentrations of the acceptor (MA) and the donor (IBVE), respectively, and abs and ϵ are the absorptivity and the molar extinction coefficient of the complex, respectively. K = 0.033 is obtained with ϵ = 2 300 in $CHCl_3$ at 23°C. Hanna-Ashbough plots based on the NMR measurements are shown in Fig. 3, where the difference of the chemical shift of MA protons in the pure state and in

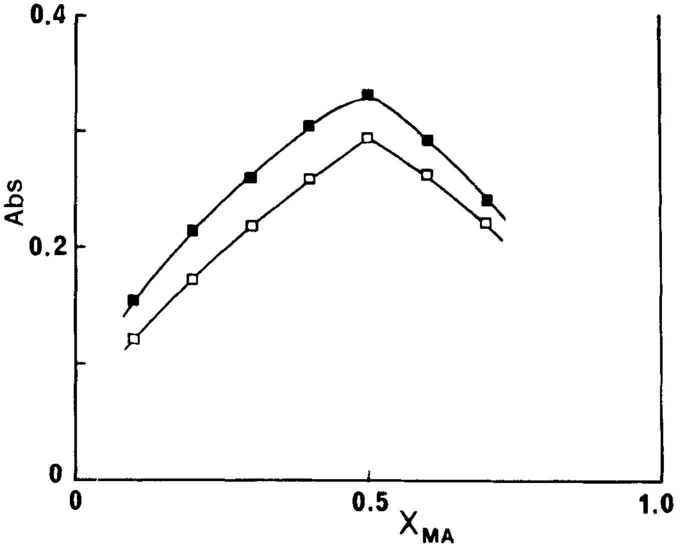

FIG. 1. Continuous variation of the absorptivity (Abs) of donor-acceptor complex of IBVE and MA against mole fraction of MA in the mixture (X_{MA}). [IBVE + MA] = 0.1624 M in $CHCl_3$, path length = 1 cm; (■) at 280 nm, (□) at 300 nm.

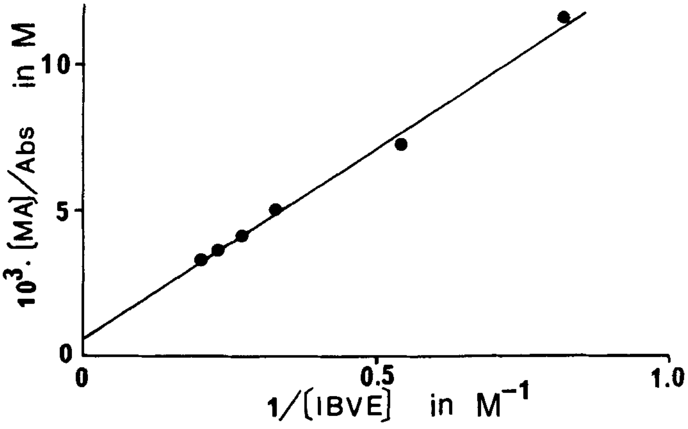

FIG. 2. Bensi-Hildebrand plot for determination of the equilibrium constant of complexation by UV. In $CHCl_3$, 23°C, path length = 1 cm.

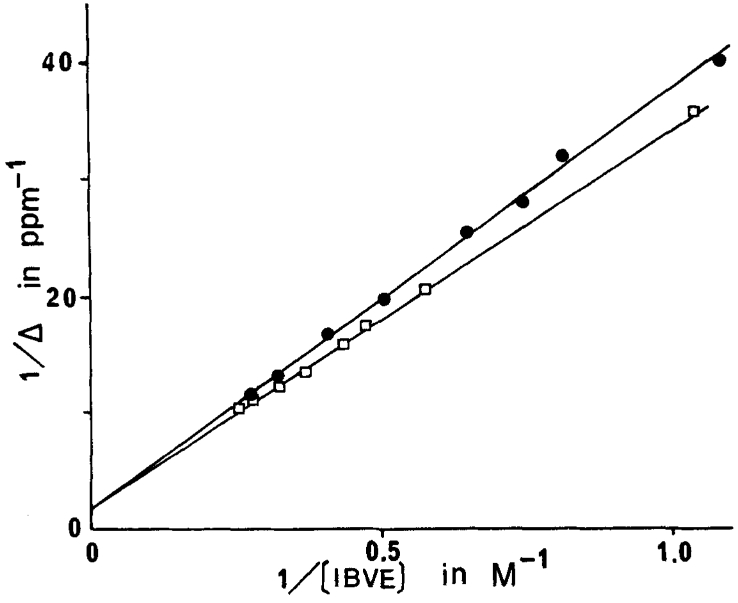

FIG. 3. Hanna-Ashbough plot for determination of the equilibrium constant of complexation by NMR at 37°C: (●) in $CDCl_3$, (□) in CCl_4, [MA] = 5.00×10^{-3} M.

the mixture (Δ) is related to the difference in chemical shift of MA protons in the pure state and in the pure complex (Δ_c) by the following relation [12]:

$$\frac{1}{\Delta} = \frac{1}{K\Delta_c[D]} + \frac{1}{\Delta_c} \tag{2}$$

The equilibrium constants of the complexation were found to be 0.052 in CCl_4 and 0.036 in $CDCl_3$ at 37°C. The complexation is more favorable in less polar CCl_4 (dielectric constant, DC = 2.238/20°C [9]) than in chloroform (DC = 4.806/20°C [9]). The equilibrium constants measured in chloroform by UV and NMR methods agree well, and the magnitude of the constants indicate that IBVE and MA form a relatively weak complex [4].

The composition of the copolymer was found to be 1:1 in a wide range of feed composition as shown in Fig. 4. The copolymer was

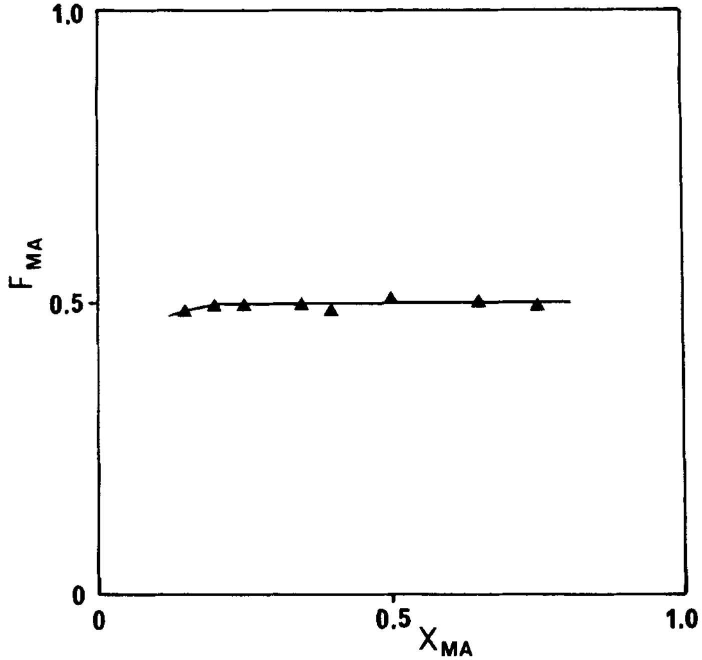

FIG. 4. Copolymer composition of IBVE-MA copolymer. Mole fraction of MA unit in copolymer (F_{MA}) against mole fraction of MA in feed (X_{MA}). [IBVE + MA] = 1.200 M. [AIBN] = 6.1×10^{-3} M, polymerized in $CHCl_3$ at 60°C.

prepared in $CHCl_3$ at 60°C and the conversion was close to 5%. Since neither IBVE or MA homopolymerizes with radicals in ordinary conditions, it is considered that a 1:1 alternating copolymer is formed.

The alternating copolymer is thought to be formed by the combination of free monomer cross-propagations, Eqs. (3) and (4), and the reaction of the donor-acceptor complex C, Eqs. (5) and (6):

$$-A\cdot + D \xrightarrow{k_{AD}} -D\cdot \tag{3}$$

$$-D\cdot + A \xrightarrow{k_{DA}} -A \tag{4}$$

$$-A\cdot + \bar{C} \xrightarrow{k_{AC}} -A \tag{5}$$

$$-D\cdot + C \xrightarrow{k_{DC}} -D\cdot \tag{6}$$

Since gravimetric determination of the rate generally involves large uncertainty, the initial rate was measured dilatometrically. Excellent linear correlation was observed in all cases between the volume decrease of the reaction mixture and the reaction time, enabling the determination of initial rate with four significant figures. The initial rate in $CHCl_3$ at 50°C with a constant initiator concentration is shown in Fig. 5. It is seen that the rate maxima do not coincide with the 1:1

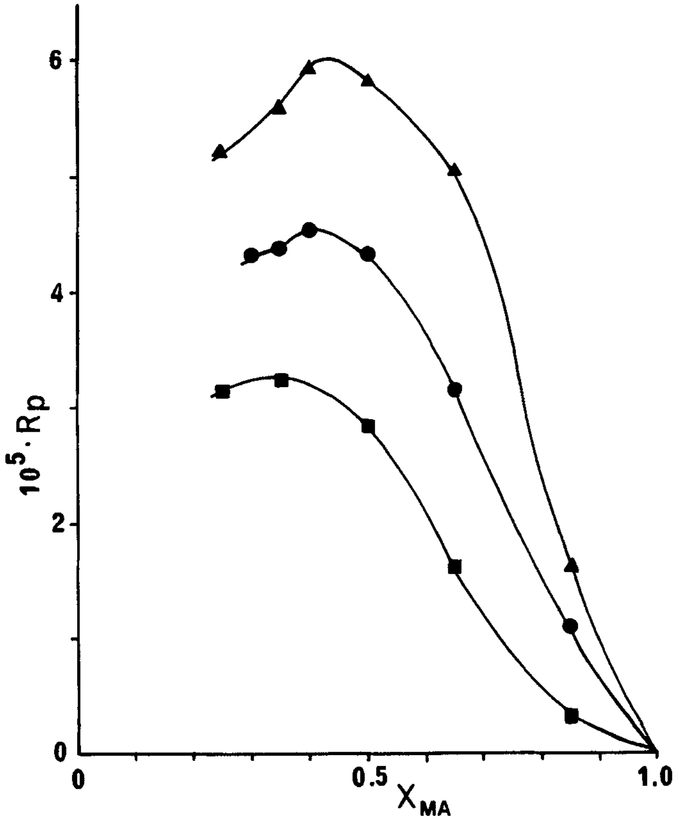

FIG. 5. Initial rate of copolymerization (R_p in mol/L·s) of IBVE with MA in $CHCl_3$ at 50°C against mole fraction of MA in feed (X_{MA}). [AIBN] = 1.220×10^{-2} M. (■) [IBVE + MA] = 0.5010 M, (●) [IBVE + MA] = 1.002 M, (▲) [IBVE + MA] = 1.503 M.

feed composition but they are dependent on feed composition, indicating that the alternating copolymerization is not purely by the cross-propagations of the free monomers nor the homopolymerization of the complex alone. The position of the maxima shifts toward the 1:1 feed composition as the total monomer concentration increases. This is consistent with the fact that the concentration of the complex, [C], increases as the total monomer concentration becomes larger: $[C] \simeq K[A][D]$.

In order to evaluate the relative reactivity of the free monomers and the complex, Georgiev and Zubov developed a method based on the shift of the rate maximum with total monomer concentration, the rate being expressed as

$$\begin{aligned}\overline{RP} &= k_{AD}[A\cdot][D] + 2k_{AC}[A\cdot][C] + k_{DA}[D\cdot][A] + 2k_{DC}[D\cdot][C] \\ &= k_{AD}(\overline{RI}/k_{to})^{1/2}\{[A]([D] + 2\beta_1[C]) + [D]([A] \\ &\quad + 2\beta_2[C])\}/\alpha([D] + [A])\end{aligned} \qquad (7)$$

where $\overline{RP}$ is the overall rate, $\overline{RI}$ is the rate of initiation, k_{to} is the total rate constant of termination, $\alpha = k_{AD}/k_{DA}$, $\beta_1 = k_{AC}/k_{AD}$, and $\beta_2 = k_{DC}/k_{DA}$ (see "Method I" described in Ref. 8). The rate is a maximum at the monomer concentrations of $[\overline{A}]$ and $[\overline{D}]$. By applying the conditions for a maximum, the following form of Eq. (7) obtained:

$$a\alpha\beta_1 + b\alpha\beta_2 + c\alpha + d\beta_1 + e\beta_2 = f \qquad (8)$$

where $a = 2K[\overline{A}][\overline{D}]$, $b = K([\overline{D}]^2 - [\overline{A}][\overline{D}])$, $c = [\overline{D}]$, $d = (1/[\overline{D}])k[\overline{A}]^2([\overline{D}] - [\overline{A}])$, $e = 2K[\overline{A}]^2$, and $f = [\overline{A}]^2/[\overline{D}]$. Equation (8) can be solved for α, β_1, and β_2 by determining the ratio $[\overline{A}]/[\overline{D}]$ for three different total monomer concentrations.

One application of the Georgiev-Zubov method has been for the radical copolymerization of vinyl acetate (D) with MA (A) based on gravimetrically measured data by Caze and Loucheux [13], the following relative reactivity ratios being reported [8]: $\alpha = 3.25 \times 10^{-3}$, $\beta_1 = 26.1$, $\beta_2 = 0.3$.

It is seen in Fig. 5 that the rate of copolymerization of IBVE with MA is maximum at the mole fraction of MA in the feed, $X_{MA} = 0.350$, $X_{MA} = 0.405$, and $X_{MA} = 0.435$ when the total monomer concentration is 0.5, 1, and 1.5 M, respectively, in $CHCl_3$. Equation (8) is solved with $K = 0.035\ M^{-1}$ which is the average of the equilibrium constants measured by UV and NMR methods in $CHCl_3$. The following relative reactivity ratios were obtained: $\alpha = k_{AD}/k_{DA} = 0.120$, $\beta_1 = k_{AC}/k_{AD} = 65.6$, and $\beta_2 = k_{DC}/k_{DA} = 4.42$. Small values of α and very large β_1 indicate the importance of resonance stabilization of the MA radical, which is relatively easily formed but much less reactive than the unconjugated IBVE radical because of the magnitude of activation energies involved [14]. β_1 and β_2 indicate enhanced reactivity of the complex compared with free monomers. However, β_1 is much larger than β_2 because Reactions (4) and (5) lead to formation of stabilized MA radicals. From $\alpha\beta_1/\beta_2 = k_{AC}/k_{DC} = 1.78$, it is estimated that the complex is about twice as reactive toward the MA radical reproducing the stabilized MA radical than toward the IBVE radical.

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