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Initial rate of alternating copolymerization of anethole with maleic anhydride in methyl ethyl ketone

Analysis by a complex model

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Summary

Dilatometrically determined initial rate of alternating copolymerization of anethole (M_1) and maleic anhydride (M_2) in methyl ethyl ketone (MEK) is reported for the total monomer concentrations of 1M, 2M and 3M polymerized at 50°C with AIBN. The rate is larger than the first order with respect to the monomer concentration. The simplified complex model adopted by Shirota et al is found to be consistent with the data. The equilibrium constant of donor-acceptor complexation (C) of the comonomers is measured to be $K=0.057$ M^{-1} in MEK at 26°C. The ratios of the propagation rate constants are calculated to be $k_{1c}/k_{12}=\beta_D=2$ and $k_{2c}/k_{21}=\beta_A=6$.

Introduction

We have previously reported dilatometric determination of initial rates of the alternating copolymerization of maleic anhydride (MA) with butyl vinyl ether (1), isobutyl vinyl ether (2), styrene (3) and vinyl acetate (4). It has been found that the rate maxima always appear only in one side of the feed monomer compositions which are richer in the monomer that forms less resonance-stabilized growing radical. This, of course, is contrary to the concept of homopolymerization of the donor-acceptor complexes (C), which predicts the rate maxima at the 1:1 feed composition. On the other hand, we have found the position of the rate maxima shifts toward the 1:1 feed composition as the total monomer concentration increases. This is consistent with the participation of 1:1 donor-acceptor complex in the alternating copolymerization.

We wish to report the initial rate of the alternating copolymerization of MA with anethole(1-methoxy-4-propenylbenzene) (ANE) in methyl ethyl ketone (MEK) solution initiated with 2,2'-azobisisobutylnitrile (AIBN) at 50°C.

Experimental

MA(Fluka) and AIBN(Fluka) were recrystallized from dry benzene and methanol, respectively. ANE(British Drug House) and MEK were distilled before use. The initial rate of copolymerization was determined dilatometrically about 8 cm^3 capacity in a thermostated oil bath at 50±0.1°C. Required amounts of MA, ANE and AIBN were accurately weighed out and dissolved in MEK in a standard volumetric flask. The solution was degassed by the freeze-thaw method under vacuum before being placed in the dilatometer. The following densities in g/cm^3 at 50°C were determined pycnometrically; ANE 0.9547, MA 1.2816, MEK 0.77400 and 1:1 ANE-MA copolymer 1.4946 (measured in MEK).

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The copolymerization proceeded homogeneously in MEK. The volume decrease of the system was assumed to be proportional to the conversion. UV absorption spectra were obtained by using UNICAM SP8-100 spectrophotometer with 1 cm path length.

Results and discussion

When ANE and MA are mixed in MEK, an intense yellow color develops indicating the formation of a donor-acceptor complex. The equilibrium constant (K) of the complexation between ANE and MA was determined by measuring the UV absorption due to the complex in MEK at 26°C, in which the absorption due to the donor (ANE) was subtracted numerically. Small concentration of MA (2.305×10^{-3} M) was used. The results at 360 and 370 nm are shown in Fig. 1.

As there is virtually no detectable absorption by MA at this concentration at 360 and 370 nm, the Ketelaar equation (5) reduces to Hildebrand (6) or Scott (7) equation. The version of the equation by Bensi and Hildebrand is used for the determination of the equilibrium constant.

$$[MA]1/d_c = 1/(\varepsilon_c K[ANE]) + 1/\varepsilon_c \quad (1)$$

where [MA] and [ANE] are concentrations in M, 1, d_c and ε_c are path length in cm, the absorptivity by the complex alone and the molar extinction coefficient of the complex, respectively. The linear plots in Fig.1 confirm the 1:1 stoichiometry of the complexation. In this rather polar solvent (dielectric constant of MEK at 20°C is 18.51(8)), the equilibrium constant is determined to be 0.054 M^{-1} at 370 nm and 0.059 M^{-1} at 360 nm. The average value of K = 0.057 M^{-1} is used for the rate analysis.

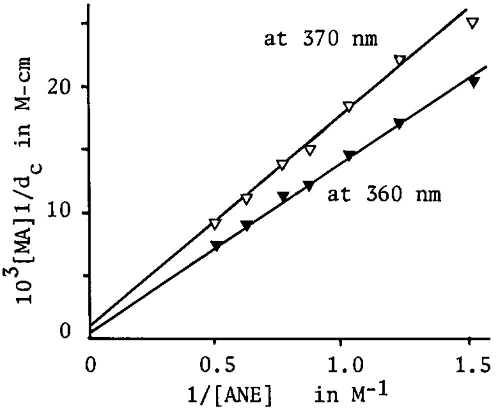

Fig.1. Hildebrand plot for the determination of equilibrium constant of complexation at 26°C in MEK. [MA] = 2.305×10^{-3} M.

It is reported that ANE and MA form alternating copolymer when the mole fraction of MA in feed is larger than 0.4(9). The initial rate of the copolymerization is shown in Fig.2 against the mole fraction of MA in feed (x_{MA}) for $x_{MA} \geq 0.4$. The data shows that the overall rate increases faster than the first order of total monomer concentration, which suggests a complex participation. The formation of a 1:1 alternating copolymer can be conceived as the result of crosspropagations by the free donor (D) and acceptor (A) monomers, and the addition of the donor-acceptor complex (c) formed between the comonomers.

$$—D\cdot + A \xrightarrow{k_{12}} A\cdot \quad (2)$$

$$—A\cdot + D \xrightarrow{k_{21}} D\cdot \quad (3)$$

$$—D\cdot + C \xrightarrow{k_{1c}} D\cdot \quad (4)$$

$$—A\cdot + C \xrightarrow{k_{2c}} A\cdot \quad (5)$$

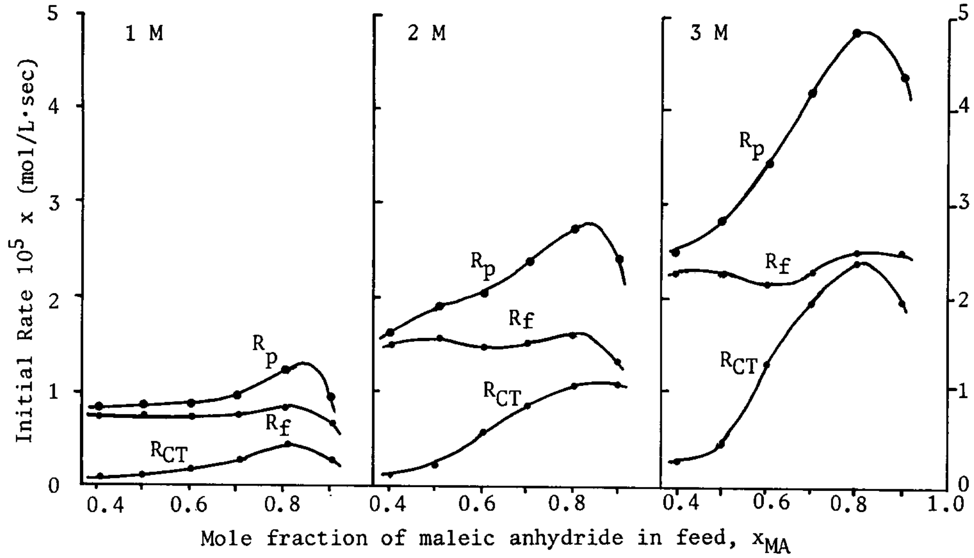

Fig. 2. Initial rate of copolymerization of NAE with MA (R_p) in MEK at 50°C. [AIBN]=1.220×10^{-2} M. R_f and R_{CT} are calculated contributions to R_p.

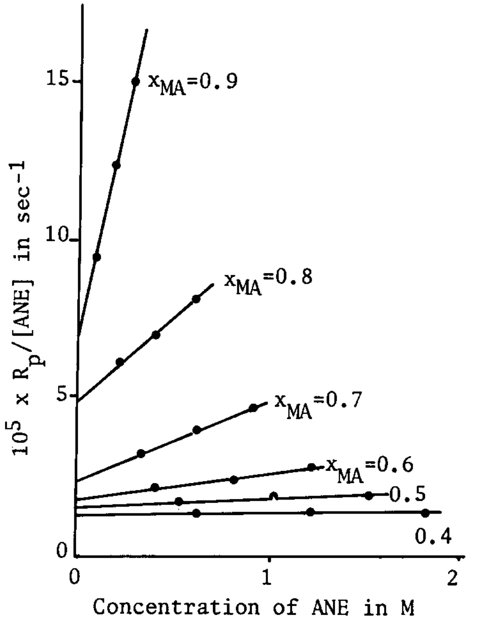

Fig. 3. Shirota plot of R_p/[ANE] vs. [ANE] at each x_{MA}

Since free monomer additions are first-order reactions but the complex additions are second-order reactions with respect to the monomer concentration, Shirota et al (10) have shown that the overall rate of copolymerization, R_p, can be a sum of a first-order reaction and a second-order reaction.

$$R_p/[M_1] = A(x)K\{(k_{1c}/k_{12})+x(k_{2c}/k_{12})\} \cdot [M_1] + A(x) \qquad (6)$$

where $A(x) = (2k_{21}k_{12}R_i^{\frac{1}{2}}x)/(k_{t11}k_{21}^{2} + 2k_{t12}k_{21}k_{12}x + k_{t22}k_{12}^{2}x^2)^{\frac{1}{2}}$ in which R_i is the initiation rate, k_t's are the termination rate constants, and $x=[M_2]/[M_1]=[MA]/[ANE]$. According to the above scheme, if the complex is involved the overall rate should be larger than the first order with respect to the monomer concentration. It follows from equation (6) that, at a fixed x, the plot of $R_p/[M_1]$ agsint $[M_1]$ should give a straight line. These Shirota plots are shown in Fig. 3. The positive slopes in the Shirota plots are consistent with a complex participation. The contribution of the free propagation, R_f, by the Reactions (2) and (3) to the overall rate is $R_f = A(x)[M]$, and that by the complex addition by Reactions (4) and (5) is $R_c = A(x)K\{(k_{1c}/k_{12}) + x(k_{2c}/k_{21})\}\cdot[M_1]^2$, and $R_p = R_f + R_c$. The calculated results are shown in Fig. 2. It is seen that R_c is small when the total monomer concentration is low, partly reflecting the fact that the K is small in this polar solvent, but R_c becomes substantial at higher concentrations. The ratios of the propagation rate constants, k_{1c}/k_{12} and k_{2c}/k_{22} (which are identical to Georgiev and Zubov's β_D and β_A, respectively, (11)) are estimated from the plot of $\{(k_{1c}/k_{12}) + x(k_{2c}/k_{21})\}$ against x to be $k_{1c}/k_{12} = 2$ and $k_{2c}/k_{21} = 6$. The values indicate that the complex is slightly more reactive than the free monomers. As the ANE radical, which is more extensively conjugated, is more stable and therefore longer living, the growing chains ending with ANE radical may be present in the copolymerization system predominantly. Thus, in polar MEK where the concentration of the complex is relatively small, the overall rate depends more critically on the MA concentration, making the rate maximum to appear in MA-rich side of the feed composition.

It is not possible to determine the positions of the rate maxima unequivocally. But it appears in Fig. 2 that the rate maxima shift toward 1:1 feed composition as the total monomer concentration increases. Thus the rate data is consistent with the simplified complex model adopted by Shirota and co-workers.

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