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FREE-RADICAL-INITIATED COPOLYMERIZATION OF α-METHYLSTYRENE WITH MALEIMIDE

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ABSTRACT

Alternating copolymers of α-methylstyrene (α-MeSt) and maleimide (MI) were prepared by free-radical initiated polymerization at different monomer-to-monomer concentrations in the feed in $CHCl_3$ as solvent. The equilibrium constant of α-MeSt and MI was determined by the transformed Benesi–Hildebrand NMR method in $CDCl_3$ and has a value of 0.03 L/mol. From the equation $R_p = R_p(\text{f}) + R_p(\text{CT})$ proposed by Shirota and coworkers, $R_p(\text{f})$ and $R_p(\text{CT})$ were calculated, and it was found that the copolymerization of α-MeSt with MI proceeds predominantly through participation of the CT complex. Alternating copolymers have a glass transition temperature of 567 K (DSC method). Alternating copolymer decomposes via a one-step reaction at 350°C.

INTRODUCTION

In a recent paper we described the high conversion copolymerization of α-methylstyrene (α-MeSt) with maleimide (MI) at different monomer-to-monomer ratios in the feed [1], and it was shown that in the presence of an excess of MI the alternating copolymer was formed quantitatively before the formation of homopolymer. In the present paper we wish to describe the mechanism of copolymerization of α-MeSt with MI in $CHCl_3$ in the presence of 2,2′-azobis(isobutyronitrile) (AIBN) as initiator. The polymerizations in all cases were carried out to a conversion not exceeding 10-15% by applying the "point-by-point" method.

Several approaches have been used in the literature to treat the kinetic data of systems with the anticipated participation of CT complexes in the copolymerization systems. As shown in previous papers from our Laboratories [2-4], the treatment of Shirota and coworkers [5, 6] makes it possible to separate the copolymerization reaction into two parts signifying the influence of propagation via cross propagation of free monomers and by the addition of a CT complex. The same treatment is also applied in the present study with the aim of determining the monomer complex contribution to the mechanism of chain growth in the copolymerization of α-MeSt with MI.

EXPERIMENTAL

Physicochemical Measurements

NMR spectra were obtained on a Varian EM 390 spectrometer. The copolymer composition was determined by NMR spectrometry in deuterated dimethylsulfoxide as solvent and by elemental analysis. The equilibrium constant of charge-transfer complexation was determined by the NMR continuous variation method in deuterated chloroform at 35°C, with TMS used as the internal reference [7, 8]. Differential scanning calorimetry (DSC) was carried out on a Perkin-Elmer model DSC-2 with a scanning rate of 20°C/min in nitrogen with a sample size of 15 mg. The only distinctive feature of the DSC thermograms was the glass transition temperature, T_g, which was taken as the temperature at which the midpoint of the heat capacity change at transition was achieved. The thermogravimetric analysis was carried out on a Perkin-Elmer TGS-2, Thermogravimetric System, in a nitrogen stream with a heating rate of 10°C/min.

Materials

α-MeSt was a commercial product of 99% purity (Aldrich Europe). A freshly distilled fraction, boiling at 50°C at 1.3 kPa (10 mmHg), was used in the copolymerization procedure. MI of 99% purity (Aldrich Europe) was recrystallized from $CHCl_3$ and hexane and dried in high vacuum, mp 93-94°C.

Copolymerization Procedure

Copolymerization was performed in vacuum-sealed 10 mL glass vials which were thoroughly degassed, filled with purified nitrogen before sealing, and placed into an oil bath thermostated to 60°C. Copolymerization was performed in $CHCl_3$ at different monomer-to-monomer ratios in the feed at a total monomer concentration of 1 mol/L (60 min), 2 mol/L (60 min), and 3 mol/L (45 min), respectively, with 0.3 wt% (based on monomer) AIBN as initiator. The viscous solution of copolymers was diluted with $CHCl_3$ and precipitated by dropwise addition to methanol. The precipitated polymer was filtered off and dried in vacuum at 70°C overnight. The T_g of poly(α-MeSt-*alt*-MI) is 567 K (294°C); thermal decomposition proceeds via a one-step reaction. Less than a 1% weight loss is observed below ca. 350°C in nitrogen, and at 410°C there is an abrupt decomposition with a residue of 7% at 500°C.

RESULTS AND DISCUSSION

In previous papers from our Laboratories it was shown that in the copolymerization of α-MeSt with *N*-phenylmaleimide (NPhMI) [4] or with *N*-methylmaleimide (NMeMI) [9] at different ratios of comonomers in the feed there is a strong tendency toward alternation. The same was also found in this paper for the copolymerization of α-MeSt with MI in $CHCl_3$ with AIBN as initiator (Fig. 1).

On admixture of α-MeSt with MI in $CHCl_3$, there was no change of color (often associated with the formation of a CT complex). The formation of a CT complex in the present work is proved by the change of chemical shifts of MI protons in the presence of varied concentrations of α-MeSt.

The equilibrium constant for monomer complexation was determined by a transformed Benesi-Hildebrand method [7] in deuterated chloro-

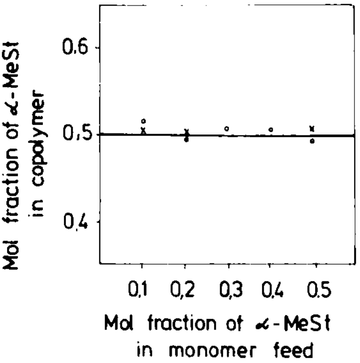

FIG. 1. Monomer-copolymer composition curve for the copolymerization of α-MeSt with MI in $CHCl_3$ at 60°C with AIBN: (○) by NMR spectrometry; (×) by elemental analysis.

form at 35°C. The concentration of MI was constant and very small, 0.1 mol/L, so that self-association could be neglected, while the concentration of α-MeSt varied from 1.35 to 1.98 mol/L. Figure 2 shows the plot of the reciprocal of the molar concentration of α-MeSt against the reciprocal of chemical shifts of the difference of complexed and

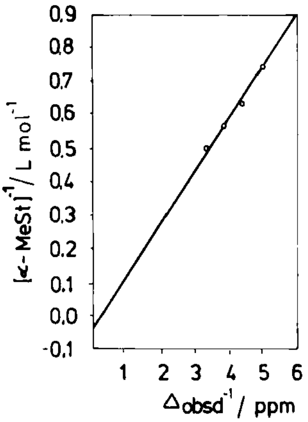

FIG. 2. Plot of Δ_{obsd}^{-1} vs $[\alpha\text{-MeSt}]^{-1}$ for chemical shifts of MI protons in the presence of α-MeSt as electron donor in $CDCl_3$ at 35°C.

uncomplexed MI molecules. The constant of complexation (K) was calculated from the intercept of the straight line in Fig. 2 by applying Eq. (1) [10]:

$$1/[D_0] = (1/\Delta_{\text{obsd}})\, K\Delta_{\text{compl}} - K \qquad (1)$$

where$[D_0]$ is the molar concentration of α-MeSt, $\Delta_{\text{obsd}} = \delta_{\text{fr}} - \delta_{\text{obsd}}$, $\Delta_{\text{compl}} = \delta_{\text{fr}} - \delta_{\text{compl}}$, δ_{fr} is the chemical shift of the free MI, δ_{obsd} are chemical shifts of MI in the presence of different molar concentrations of α-MeSt, and Δ_{compl} is the chemical shift of the complexed MI. The numerical value of K obtained by the least-squares method is 0.03 ± 0.01 L/mol.

Although the complexation constant of the charge-transfer complex in the mixture of α-MeSt and MI is very low, it was found that the copolymerization follows the mechanism proposed by Shirota et al. [5] and Tsuchida and coworkers [10]. This mechanism is based on the assumption that alternating copolymers are formed by the simultaneous cross-propagation of free monomers and the addition of the CT complex.

The dependence of the initial copolymerization rate, R_p, on the monomer composition in the feed but at constant total monomer concentrations of 1, 2, and 3 mol/L, respectively, are plotted in Fig. 3. Initial

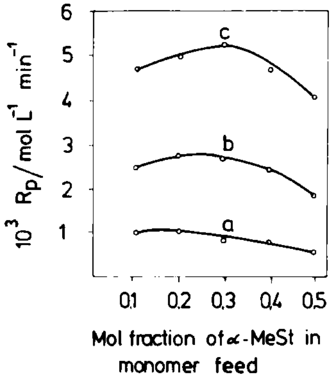

FIG. 3. Initial copolymerization rates vs monomer feed molar ratios in the copolymerization of α-MeSt with MI; 0.3% AIBN at 60°C in $CHCl_3$; total monomer concentration (in mol/L): (a) 1.0; (b) 2.0; (c) 3.0.

rates of copolymerization, $R_p/\mathrm{mol}\cdot\mathrm{L}^{-1}\cdot\mathrm{min}^{-1}$, are determined by the "point-by-point" method. By assuming that the overall rate of copolymerization is given by the sum of rates of copolymerization of the CT complex $R_p(\mathrm{CT})$ and of free monomers $R_p(\mathrm{f})$, Shirota and coworkers [5] showed that a plot of $R_p/[\mathrm{M}_1]$ against $[\mathrm{M}_1]$ according to

$$R_p/[\mathrm{M}_1] = A(X)\cdot K(k_{1c}/k_{12} + k_{2c}/k_{21}X)[\mathrm{M}_1] + A(X) \qquad (2)$$

gives a straight line for each given ratio of comonomer concentration $X = [\mathrm{M}_2]/[\mathrm{M}_1]$ as shown in Fig. 4. $[\mathrm{M}_1]$ and $[\mathrm{M}_2]$ are molar concentrations of MI and α-MeSt, respectively; K is the equilibrium constant of the CT complex ($K = 0.03$ L/mol); $A(X)$ is given by

$$A(X) = \frac{2k_{21}k_{12}R_i^{1/2}X}{(k_{t11}k_{21}^2 + 2k_{t12}k_{21}k_{12} + k_{t22}k_{12}^2X)^{1/2}} \qquad (3)$$

where R_i is the rate of initiation and k_{12}, k_{21}, k_{1c}, k_{2c}, k_{t11}, k_{t12}, and k_{t22} are rate constants of monomers, complex and termination rate constants [5], respectively.

$A(X)$ can be calculated from the intercepts of straight lines in Fig. 4, while slopes give the values of k_{1c}/k_{12} and k_{2c}/k_{21} through

$$F(X) = K(k_{1c}/k_{12} + k_{2c}/k_{21}X) \qquad (4)$$

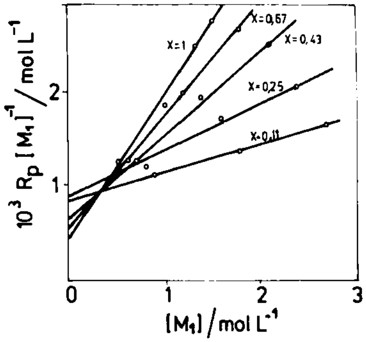

FIG. 4. Plot of $R_p[\mathrm{M}]^{-1}$ vs $[\mathrm{M}_1]$ at different $X = [\mathrm{M}_2]/[\mathrm{M}_1]$ ratios in the copolymerization of α-MeSt (M_2) and MI (M_1).

The numerical values of reactivity ratios are calculated from the plot of $F(X)$ vs X (Fig. 5): $Kk_{1c}/k_{12} = 0.26$ (intercept) and $Kk_{2c}/k_{21} = 3.2$ (slope). The ratio $(k_{1c}k_{21})/(k_{2c}k_{12}) = 0.08$ indicates that the rate of formation of α-MeSt free radicals is much faster than the rate of formation of MI free radicals, thus indicating that α-MeSt free radicals are formed preferably through complex addition in alternating copolymerization. This explains the mechanism of high conversion copolymerization of electron-donor-acceptor monomers in the presence of an excess of homopolymerizable electron acceptor as described in previous papers from our Laboratories [1, 4, 11].

Based on the assumption that $R_p = R_p(\text{f}) + R_p$ (CT) and that $R_p(\text{f}) = A(X)[\text{M}_1]$, R_p(CT) was calculated as the difference of R_p and R_p(f) [5] (Fig. 6).

It is evident from Fig. 6 that the copolymerization of α-MeSt with MI proceeds predominantly via the addition of a CT complex, and that an increase of monomer concentration in the feed promotes participation of the CT complex. The average contributions of R_p(CT) as calculated from Fig. 5 are 51% (1 *M*), 65% (2 *M*), and 73% (3 *M*), respectively (Fig. 7). It is of interest to note that similar results were obtained in the copolymerization of α-MeSt with maleic anhydride [2], while in the copolymerization of α-MeSt with NPhMI [4] or NMeMI [9], cross-propagation of free monomers predominates.

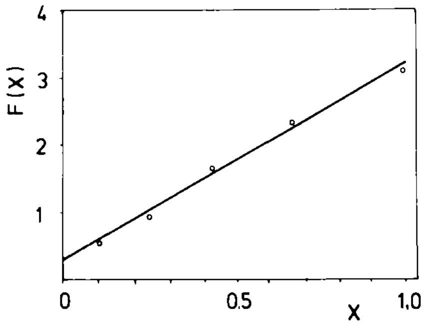

FIG. 5. Plot of $K(k_{1c}/k_{12} + k_{2c}/k_{21}X) = F(X)$ vs $X = [\text{M}_2]/[\text{M}_1]$ in the copolymerization of α-MeSt (M_2) with MI (M_1).

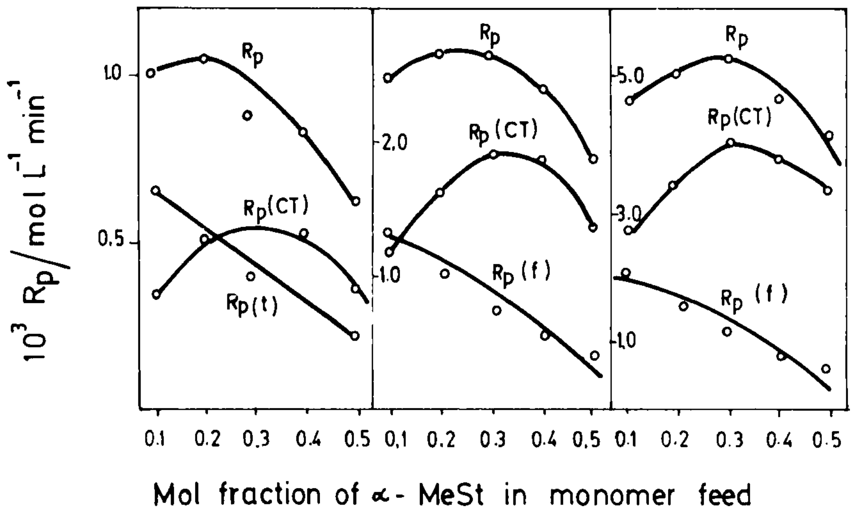

FIG. 6. Relative participation of free monomers and CT complex in the copolymerization of α-MeSt with MI at different monomer feed concentrations in $CHCl_3$; 2 and 3 mol/L.

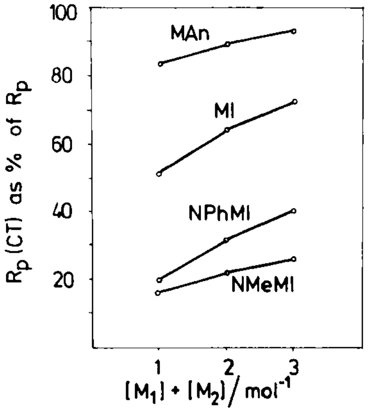

FIG. 7. Plot of R_p(CT) against molar concentration of monomers in the copolymerization of α-MeSt with the following electron acceptors: MI (in $CHCl_3$), NMeMI (in $CHCl_3$), NPhMI (in toluene), and MAn (in benzene).

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REFERENCES

[1] F. Ranogajec, D. D. Fleš, R. Vuković, and D. Fleš, *Polym. Bull.*, *24*, 597 (1990).

[2] I. Javni, D. Fleš, and R. Vuković, *J. Polym. Sci., Polym. Chem. Ed.*, *20*, 977 (1982).

[3] R. Vuković, V. Kurěsević, and D. Flešs, *Croat. Chem. Acta*, *60*, 139 (1987).

[4] D. D. Flěs, R. Vuković, and F. Ranogajec, *J. Polym. Sci., Polym. Chem. Ed.*, *27*, 3227 (1989).

[5] Y. Shirota, M. Yoshimura, A. Matsumoto, and H. Mikawa, *Macromolecules*, *7*, 4 (1974).

[6] M. Yoshimura, H. Mikawa, and Y. Shirota, *Ibid.*, *11*, 1085 (1978).

[7] H. A. Benesi and J. H. Hildebrand, *J. Am. Chem. Soc.*, *71*, 2703 (1949).

[8] M. W. Hanna and A. L. Ashlaugh, *J. Phys. Chem.*, *68*, 811 (1964).

[9] D. D. Fleš, R. Vuković, F. Ranogajec, M. Zuanić, and D. Fleš, Polimeri, 10(6), 143 (1989).

[10] E. Tsuchida, T. Tomono, and H. Sano, *Makromol. Chem.*, *151*, 245 (1972).

[11] D. Fleš, R. Vuković, F. Ranogajec, and D. D. Fleš, *J. Macromol. Sci.–Chem.*, *A27*, 1621 (1990).

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