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Polymerization of Styrene Initiated by Photoexcited Charge-Transfer Complex

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ABSTRACT

Photopolymerization of styrene in the presence of pyromellitic dianhydride, an electron acceptor which forms a charge-transfer complex with the monomer, was studied. Polymerization was initiated by illumination with a light of wavelength longer than 350 nm, where only the charge-transfer absorption band exists. It was found that the reaction involves cationic and radical polymerizations and that the reaction course strongly depends on polarity of the system. It was also suggested by the dependence of the rate of polymerization on light intensity and temperature that the cationic polymerization consists of free ion and ion-pair polymerizations. These results were compared with those of the photoinduced cationic polymerization of α-methylstyrene, which has previously been studied.

INTRODUCTION

Photoinduced ionic polymerizations initiated by charge-transfer interaction have been reported for several monomers such as N-vinylcarbazole [1, 2]. In our previous studies it has been established that the cationic polymerization of α-methylstyrene [3-7] or cyclohexene oxide [7-9], and anionic polymerization of acrylonitrile [7] or nitroethylene [7, 10] are initiated by radical cation from the excited charge-transfer complex.

In the present investigation, photopolymerization of styrene was carried out in the presence of pyromellitic dianhydride, which is an electron acceptor forming a charge-transfer complex with the monomer, to elucidate the initiation, propagation, and termination mechanisms of the polymerization. The effects of temperature, monomer concentration, and polarity of solvent on the polymerization were analyzed in detail. The dependence of the rate of polymerization on the light intensity was also studied.

EXPERIMENTAL

Styrene was washed several times with an aqueous solution of sodium hydroxide and with water and distilled onto calcium hydride. The middle fraction was distilled twice onto molecular sieves (4Å 1/16) which had been baked for 24 hr at 400° C at a pressure of less than 1×10^{-5} Torr and then distilled over barium oxide which had been baked for 48 hr at 400° C at a pressure of less than 3×10^{-5} Torr. Methylene chloride, 1,2-dichloroethane, chloroform, and tetrachloromethane were purified in the same way as styrene. Pyromellitic dianhydride was purified by sublimation in vacuo before use.

All reaction mixtures were prepared in vacuo at less than 1×10^{-5} Torr pressure. Illumination was carried out with a super high-pressure mercury lamp, and the wavelength was selected with Toshiba filter UV-35. The molecular weight distribution of the polymer was measured by gel-permeation chromatography (GPC), Toyo Soda Model HLC801. The polymers were measured as 0.3 wt % solution in tetrahydrofuran. The composition of the copolymers was calculated from the elemental analysis. The intensity of light was controlled with neutral filters.

RESULTS

Absorption Spectra

Curves A and B in Fig. 1 show the absorption spectra of styrene (1.7 M) in methylene chloride and pyromellitic dianhydride (1 × 10^{-3} M) in ethanol, respectively. The spectrum of a solution of styrene(1.7 M) and pyromellitic dianhydride(1 × 10^{-3} M) in methylene chloride, shown in Fig. 1C, has an additional absorption band around 380 nm. This is interpreted as due to the charge-transfer complex.

Polymerization was initiated by illumination with light of wavelength longer than 350 nm (with UV 35 filter), where only the charge-transfer absorption band exists. Light through the filter(UV-35) irradiates only the charge-transfer band.

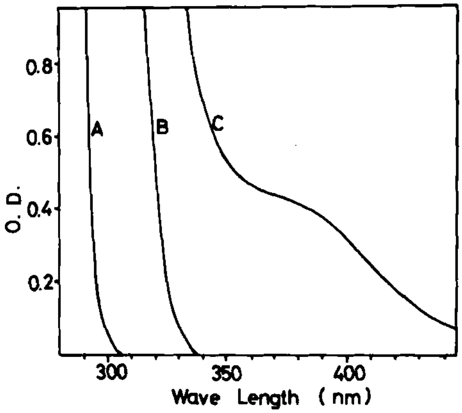

FIG. 1. Absorption spectra of styrene, pyromellitic dianhydride and their complex at 18° C: (A) methylene chloride solution containing styrene(1.7 M); (B) methanol solution containing pyromellitic dianhydride(1 × 10^{-3} M); (C) methylene chloride solution containing styrene(1.7 M) and pyromellitic dianhydride(1 × 10^{-3} M).

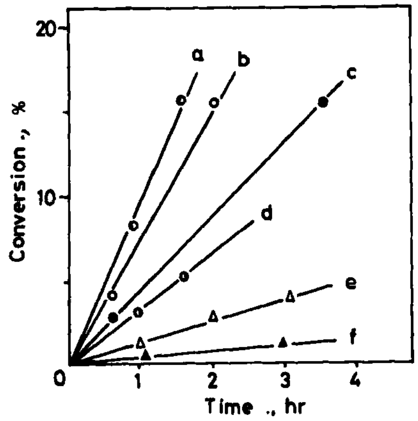

FIG. 2. Time-conversion curves of the photopolymerization of styrene in the presence of pyromellitic dianhydride (1×10^{-3} M): (a), (b), (c), (d) at -74° C, -50° C, 4° C, and 18° C, respectively, in bulk; (e), (f) at 18° C and 4° C, respectively, with 0.6 M monomer concentration in methylene chloride solution.

Photopolymerization of Styrene

Coexistence of Radical and Cationic Polymerizations

Photopolymerization of styrene was observed in the presence of pyromellitic dianhydride(1×10^{-3} M) in bulk and in methylene chloride solutions at various temperatures from -74° C to 18° C as shown in Fig. 2, while no polymer was obtained in the dark. The polymerization started without an induction period, and the yield increased proportionally with the time of illumination.

The rate of polymerization was dependent on the monomer concentration, and the results at 18° C are shown in Fig. 3. When the monomer concentration was above about 4 M, the rate of polymerization decreased with decreasing monomer concentration. On the other hand, below about 4 M it increased with decreasing monomer concentration.

The molecular weight distributions of the polymers obtained at 18° C were measured by GPC (gel permeation chromatography) and are shown in Fig. 4. The polymer obtained in bulk has a unimodal distribution. The height of this peak decreased with decreasing monomer concentration. In the case of polymerization in methylene

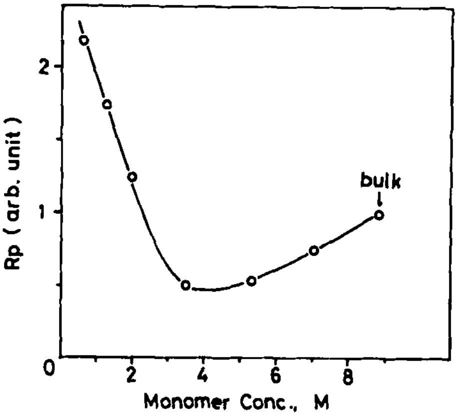

FIG. 3. Dependence of the rate of polymerization on the monomer concentration of styrene in methylene chloride at 18° C. Concentration of pyromellitic dianhydride, 1×10^{-3} M.

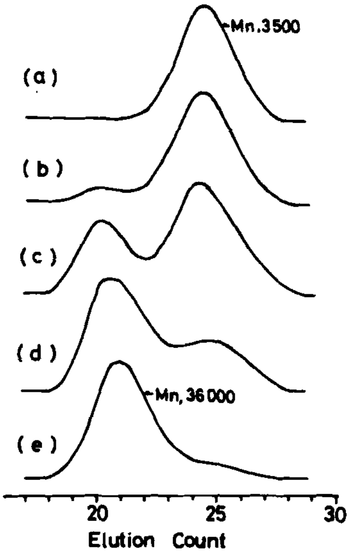

FIG. 4. Molecular weight distribution of polystyrene measured by GPC method. Polymerization was done in the presence of pyromellitic dianhydride(1×10^{-3} M) at 18° C at various monomer concentrations in methylene chloride: (a) 8.8 M (bulk); (b) 7.0 M; (c) 5.3 M; (d) 3.5 M; (e) 1.9 M.

chloride solutions, another peak appeared in the higher molecular weight region and its height increased with decreasing monomer concentration. These results indicate that there are two mechanisms of polymerization, whose relative contributions depend on the monomer concentration.

In order to reveal these mechanisms, the effect of the addition of ether, which is a typical inhibitor of cationic polymerization, was examined at 3.5 M of monomer concentration at 18° C. On the addition of 0.01 M ether, the rate of the polymerization decreased to 7.1% of that in the absence of ether and the molecular weight distribution changed as shown in Fig. 5. The higher molecular weight peak completely disappeared.

The copolymerization with methyl methacrylate initiated by illumination in the presence of pyromellitic dianhydride was carried out at 18° C, and the results are shown in Fig. 6. The content of styrene in the copolymers obtained in bulk were close to that reported for the radical copolymerization [11]. When the concentration of the mixture of two monomers in methylene chloride was 1.7 M, the content of styrene in the copolymers were close to that reported for the cationic polymerization initiated by $SnCl_4$ [11]. These results indicate that the lower molecular weight peak of the bimodal distribution may be attributed to radical polymerization and the higher molecular weight peak, to cationic polymerization.

The photopolymerization of styrene was also carried out in other chlorinated hydrocarbon solutions at 18° C. Figure 7 shows the molecular weight distribution curves of the polymers obtained in

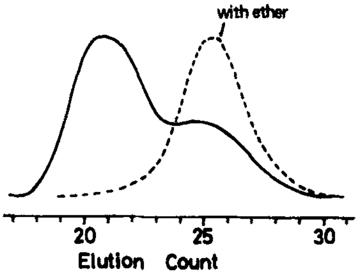

FIG. 5. Effect of the addition of diethyl ether (0.01 M) on the molecular weight distribution of polystyrene. Polymerization was done in the presence of pyromellitic dianhydride (1×10^{-3} M) at 18° C; monomer concentration in methylene chloride, 3.5 M.

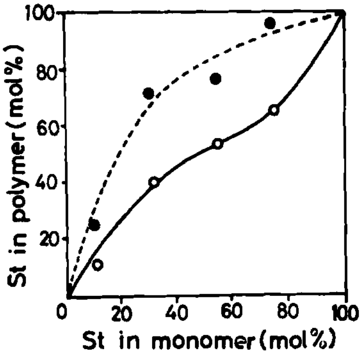

FIG. 6. Photoinduced copolymerization of styrene(St) with methyl methacrylate(MMA) in the presence of pyromellitic dianhydride (1 10^{-3} M) at 18°C: (○) in bulk (●) 1.7 M(St + MMA) in methylene chloride.

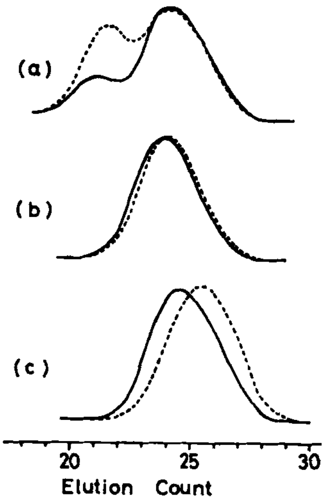

FIG. 7. Molecular weight distribution of polystyrene obtained by polymerization at 18° C in the presence of pyromellitic dianhydride (1×10^{-3} M) in several solvents: (a) 1,2-dichloroethane; (b) chloroform; and (c) tetrachloromethane; concentrations of styrene were (· ·) 3.5 M and (—) 5.3 M.

1,2-dichloroethane, chloroform, and tetrachloromethane. The polymers obtained in 1,2-dichloroethane, which is polar as well as methylene chloride, had bimodal distributions. The higher molecular weight peak was larger at a monomer concentration of 3.5 M than that at 5.3 M. This tendency was the same as that in methylene chloride solution. On the other hand, the polymers obtained in chloroform and tetrachloromethane, which are less polar solvents, had only the lower molecular weight peak. These results indicate that the relative contributions of the radical and cationic polymerizations depend on the polarity of the solvent, that is, the larger the polarity the larger is the contribution of the cationic polymerization. Thus, the effect of the monomer concentration on the molecular weight distribution (Fig. 4) can be explained by the fact that the polarity of the system increases with decreasing monomer concentration resulting in the larger contribution of the cationic polymerization.

Coexistence of Free Ion and Ion-Pair Polymerizations

The Arrhenius plot of polymerization rate is shown in Fig. 8. The rate of polymerization in bulk decreased with decreasing temperature (Fig. 8A). The activation energy of this system was 8.5 kcal/mole. This value is close to that of the radical polymerization of styrene reported in the radiation-induced polymerization in a wet system, 6.7 kcal/mole [12]. On the other hand, when the monomer concentration was low the cationic polymerization alone occurred, the rate of polymerization increased with decreasing temperature (Fig. 8B). The activation energy was about -1 kcal/mole at monomer concentrations of 1.3 and 0.6 M. In the case of the photoinduced cationic polymerization of α-methylstyrene, it was also observed that the rate of the polymerization increased with decreasing temperature. These results should be attributable to the fact that an increase in the polarity of the solution facilitates the ionic dissociation of the excited charge-transfer complex and the dissociation of ion pair to free ions, and that the free-ion propagation has a larger rate than the ion pair one.

The Arrhenius plot of molecular weight is shown in Fig. 9. The molecular weight of the polymers obtained in bulk, where radical polymerization occurs, decreased with decreasing temperature (Fig. 9A). On the other hand, when the monomer concentration was low, the molecular weight increased with decreasing temperature (Fig. 9B). The plot was broken at about -30° C, and the slope decreased below -30° C. The activation energy of molecular weight for styrene above -30° C was -3.4 kcal/mole, close to the reported value [13] of cationic polymerization of styrene by catalyst. On the other hand, the activation energy below -30° C was near zero. These results suggest that two

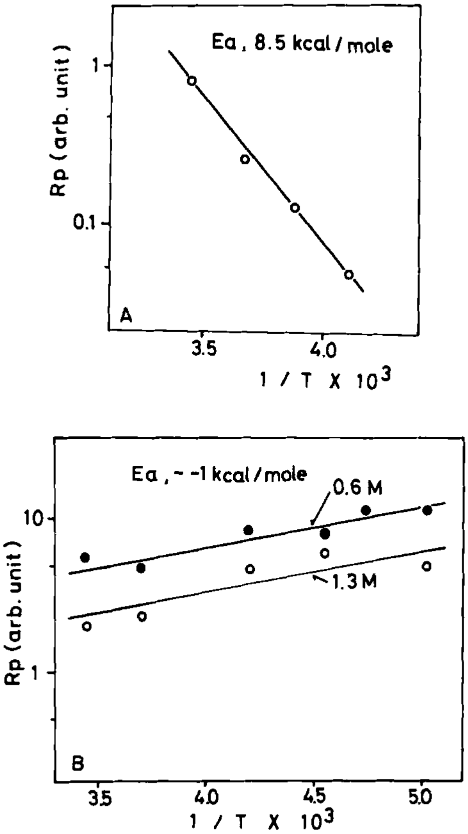

FIG. 8. Arrhenius plot of the rate of polymerization of styrene in the presence of pyromellitic dianhydride(1×10^{-3} <u>M</u>): (A) in bulk and (B) in methylene chloride.

propagation mechanisms of the cationic polymerization coexist, and that the propagating species at high temperature is the ion-pair.

Figure 10 shows the dependence of the rate of polymerization, R_p on the light intensity. When the chain ends are radical, the dependence should be $R_p \propto I^{0.5}$. In the polymerization in bulk at 18° C the dependence was $R_p \propto I^{0.56}$ (Fig. 10A), supporting the assumption that the chain ends are radicals. In ionic polymerization, the

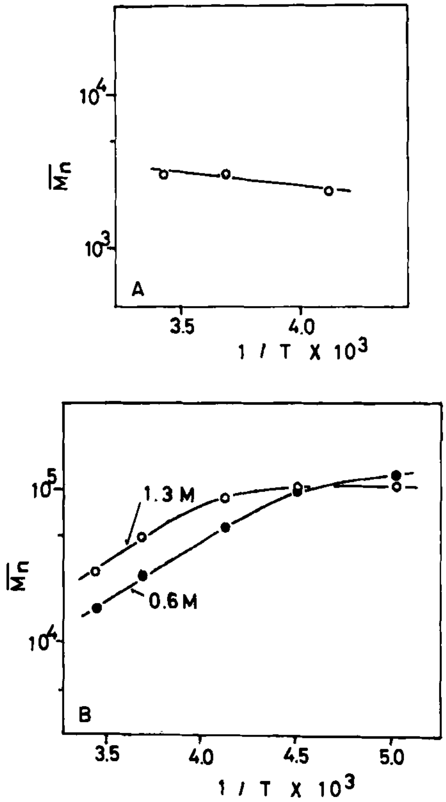

FIG. 9. Arrhenius plot of the molecular weight of polystyrene obtained (A) in bulk and (B) in methylene chloride. Concentration of pyromellitic dianhydride was 1×10^{-3} M.

dependence of R_p on the light intensity can give information on the propagating chain ends, whether they are free ions or ion pairs. When the chain ends are free, the dependence should be $R_p \propto I^{0.5}$. For ion pairs the dependence should be $R_p \propto I$. Figures 10B and 10C show the results at monomer concentrations of 1.7 M and 0.6 M, respectively, at -74° C. In these conditions cationic polymerization occurs exclusively, as described above. It is indicated that the

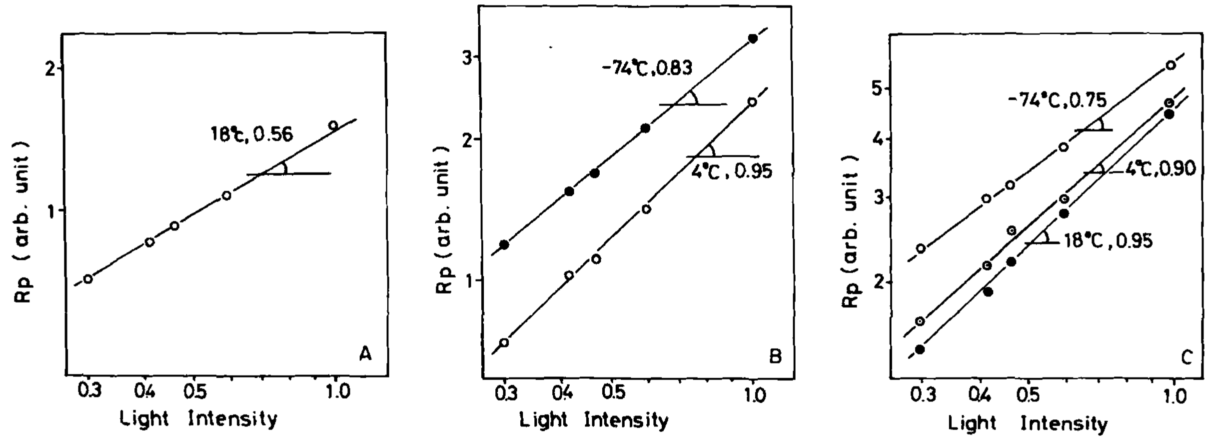

FIG. 10 Dependence of the rate of polymerization of styrene on light intensities on polymerization in the presence of pyromellitic dianhydride (1×10^{-3} $\underline{M}$); (A) in bulk, (B) in methylene chloride 1.7 $\underline{M}$ solution, and (C) in methylene chloride, 0.6 $\underline{M}$ solution at several temperatures.

ion-pair polymerization predominantly occurs at 4° C, and that when temperature is low the chain ends are mixtures of ion pairs and free ions. It is also suggested that the contribution of the free ion to the polymerization increases by lowering the monomer concentration. The increase in the contribution of the free ion polymerization with decreasing temperature and monomer concentration can be attributed to the increase in the polarity of the solution.

These results suggesting the coexistence of the free ion and ion-pair polymerizations are analogous to those obtained in the photoinduced cationic polymerization of α-methylstyrene, which has previously been studied [7].

In the case of polymerization of α-methylstyrene, the contributions of the two propagating species are successfully revealed by the molecular weight distributions. Thus, to obtain further information on the propagating ends of the photoinduced cationic polymerization of styrene, the molecular weight distributions of the polymers obtained at low monomer concentrations were measured. While the charts of GPC were almost unimodal below 1.7 $\underline{M}$ at various temperatures, the peaks sometimes had small shoulders, suggesting that two chain ends with different reactivities propagate independently. In Fig. 11, the molecular weight distributions are depicted as plots of the number of polymer chain, which was obtained by dividing the height of the GPC curve by the molecular weight, against the elution count in order to mark the existence and behavior of the two peaks.

The temperature dependence of the molecular weight distribution of the polymers obtained at 0.6 $\underline{M}$ is shown in Fig. 11A. The molecular weight distributions were bimodal below -30° C of the polymerization temperature. The higher molecular weight peak shifted to larger elution volume (small molecular weight) with increasing temperature, while the position of the lower one was not affected by temperature, and then the distribution was unimodal at 18° C.

Figure 11B shows the dependence of the molecular weight distribution on the monomer concentration at a polymerization temperature of -74° C. The relative height of the lower molecular peak increased with decreasing monomer concentration, while the positions of the two peaks were little affected by the monomer concentration. Considering the facts that the lower the monomer concentration, the larger is the polarity of the solution, and that an ion-pair tends to dissociate more to free ions at larger polarity, it appears that the lower polymers are formed by the free ion polymerization. This is also supported by the result of the dependence of the rate of polymerization on light intensity at the different monomer concentrations at -74° C (Figs. 10B and 10C).

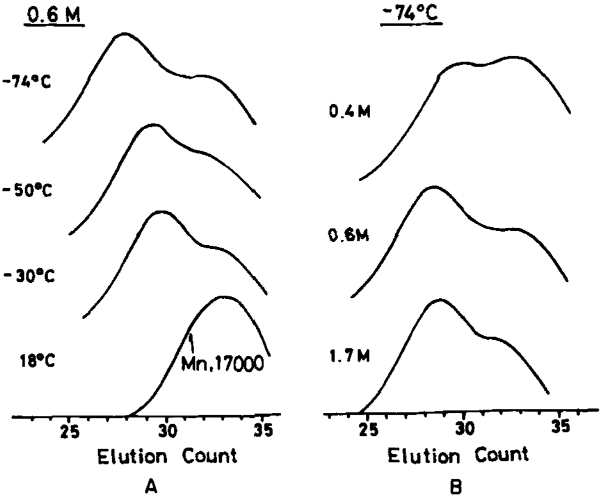

FIG. 11. Molecular weight distribution (number of polymer chains by elution count) of polystyrene obtained by polymerization in the presence of pyromellitic dianhydride (1×10^{-3} M) in methylene chloride: (A) monomer concentration 0.6 M; (B) temperature, -74° C.

DISCUSSION

Styrene forms a charge-transfer complex with pyromellitic dianhydride as well as α-methylstyrene whose photoinduced cationic polymerization has previously been studied [3-7]. Both radical and cationic polymerizations were initiated by the illumination of the complex, whereas only cationic polymerization occurred in the case of α-methylstyrene, which is hardly polymerized by the radical mechanism. The dependence of the rate of polymerization on the monomer concentration (Fig. 3), and the molecular weight distributions of the obtained polymers (Fig. 4) suggest that the radical and cationic polymerizations are competitive. The results shown in Fig. 7 indicate that the cationic polymerization occurs only in polar solvents such as methylene chloride and 1,2-dichloroethane but not in less polar solvents, chloroform and tetrachloromethane. On the basis of the fact that the ionic dissociation of the photoexcited charge-transfer complex is favored in polar solvents, the competition of the radical and cationic polymerizations is determined by the extent of ionic dissociation of the excited charge-transfer complex. Thus, the radical polymerization should be initiated by the excited charge-transfer complex before ionic dissociation.

Furthermore, it was indicated that the photoinduced cationic polymerization of styrene involves the two propagating species, free ions and ion-pairs, as well as that of α-methylstyrene [3-7]. The dependence of the rate of polymerization on light intensity shows that the contribution of the free ion polymerization increases with increasing polarity of the solution. Thus, the process of photopolymerization of styrene can be expressed as in Eqs. (1)-(6).

$$D + A \rightleftharpoons (D{\cdot}A) \tag{1}$$

$$(D \cdot A) \xrightarrow{h\nu} (D \cdot A)^* \tag{2}$$

$$(D \cdot A)^* \longrightarrow (D_s^{\cdot +} \cdots A_s^{\cdot -}) \rightleftharpoons D_s^{\cdot +} + A_s^{\cdot -} \tag{3}$$

$$(D \cdot A)^* \longrightarrow \text{Polymer (radical polymerization)} \tag{4}$$

$$(D_s^{\cdot -}) \cdots A_s^{\cdot -}) \longrightarrow \text{Polymer (ion-pair polymerization)} \tag{5}$$

$$D_s^{\cdot +} \longrightarrow \text{Polymer (free-ion polymerization)} \tag{6}$$

Here D and A denote the electron donor (styrene) and the electron acceptor (pyromellitic dianhydride), respectively. The increase in the polarity of the solution results in an increase in the contribution of the cationic polymerization, especially the free-ion polymerization.

In contrast to the photoinduced cationic polymerization of α-methylstyrene [3-7], the molecular weights of the polymers produced by the free-ion and ion-pair polymerizations did not differ so mcuh from one another, and the GPC charts were almost unimodal for the polymers obtained at low monomer concentrations. On plotting the number of polymer chains against elution volume, bimodal distributions were obtained (Fig. 11). The lower molecular weight peak was assigned to the free-ion polymerization on the basis of increase in its height with decreasing monomer concentration. It has recently been reported that in the cationic polymerization of styrene by acetyl perchlorate [14, 15] and perchloric acid [16] the polymers possess bimodal molecular weight distributions and that two propagating species, ion-pairs and free ions (or a loose ion-pair) contribute to the polymerization. In these studies the higher molecular weight peaks have been assigned to the free-ion polymerization. In the photoinduced cationic polymerization the lower molecular weight peak may be assigned to the free-ion polymerization as described above, while the molecular weights of the polymers produced by the two propagting species did not differ so much. The molecular weight of the lower polymer was of the same order as that of the higher polymer from the cationic polymerization with acetyl perchlorate [14, 15]. On this basis it seems reasonable to assume that the different assignments of the two peaks in the photoinduced and catalytic polymerizations may be attributed to a difference in the anion, that is, ion-pairs from the propagating cation with pyromellitic dianhydride radical anion give much higher polymer than that from perchlorate anion.

REFERENCES

[1] M. Yamamoto, S. Nishimoto, M. Ohoka, and Y. Nishijima, Macromolecules, 3, 706 (1970).
[2] K. Tada, Y. Shirota, and H. Mikawa, J. Polym. Sci. Polym. Chem. Ed., 11, 2961 (1973).
[3] M. Irie, S. Tomimoto, and K. Hayashi, J. Polym. Sci. B, 8, 585 (1970).
[4] M. Irie, S. Tomimoto, and K. Hayashi, J. Polym. Sci. A-1, 10, 3235 (1972).
[5] M. Irie, S. Tomimoto, and K. Hayashi, J. Phys. Chem., 76, 1419 (1972).
[6] M. Irie, S. Tomimoto, and K. Hayashi, J. Phys. Chem., 78, 341 (1974).
[7] M. Irie, Y. Yamamoto, and K. Hayashi, J. Macromol. Sci.-Chem., A9, 817 (1975).
[8] M. Irie, S. Tomimoto, and K. Hayashi, J. Polym. Sci. A-1, 10, 3243 (1972).
[9] M. Irie, S. Tomimoto, and K. Hayashi, J. Polym. Sci., Polym. Chem. Ed., 11, 1859 (1973).
[10] M. Irie, S. Tomimoto, and K. Hayashi, J. Polym. Sci. Polym. Letters Ed., 10, 699 (1972).
[11] G. E. Ham, Copolymerization, Wiley, New York, 1964.
[12] D. S. Ballantine, et al., Chem. Eng. Progr. Symp. Ser., 56, 267 (1954).

[13] P. H. Plesch, The Chemistry of Cationic Polymerization, Pergamon Press, Oxford, 1963.
[14] T. Masuda and T. Higashimura, J. Polym. Sci. B, 9, 783 (1971).
[15] T. Higashimura and O. Kishiro, J. Polym. Sci. B, 12, 967 (1974).
[16] D. C. Pepper, Makromol. Chem., 175, 1077 (1974).

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