# Effects of an Electron Acceptor on the Radiation-Induced Cationic Polymerization of α-Methylstyrene

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ABSTRACT: The radiation-induced cationic polymerization of α-methylstyrene has been carried out in methylene chloride solution in the presence and absence of an electron acceptor, pyromellitic dianhydride (PMDA), which forms a stable electron donor–acceptor (EDA) complex with the monomer, in order to investigate the contribution of the EDA complex to the polymerization. The polymer yield appreciably increases by the addition of a small amount of PMDA (~$10^{-3}$ mol/L). The molecular weight distribution of the resulting polymer indicated that two kinds of propagating species possessing different reactivities coexist in the presence of PMDA. The results have been explained by the occurrence of the polymerizations both via the dissociation of the excited EDA complex into an ion pair (ion-pair polymerization) and via direct ionization (free-ion polymerization).

There has been much interest recently in photochemistry of electron donor–acceptor (EDA) complexes. One of the most interesting behaviors of photoexcited EDA complexes is their ionic dissociation to the radical ions of the donor and acceptor molecules.[1] In polymer chemistry attention has been paid to photoinduced ionic polymerization, where monomer is the electron donor or acceptor and ionized by photoillumination.[2] In our previous papers it has been reported that the cationic polymerization of α-methylstyrene is initiated by the photoillumination of the chlorinated hydrocarbon solutions of the monomer in the presence of an electron acceptor, pyromellitic dianhydride (PMDA) or tetracyanobenzene, which forms a stable EDA complex with the monomer.[3,4]

On the other hand, we have previously studied the effect of the irradiation of ionizing radiation on the EDA complexes between aromatic hydrocarbons and PMDA and revealed that the ion-pair formation via the excited EDA complexes is important in the irradiated system.[5] The present investigation of the radiation-induced cationic polymerization of α-methylstyrene in the presence of an electron acceptor, PMDA, was carried out in order to obtain information about the contribution of the EDA complex to the polymerization.

It is known that the propagating ion of radiation-induced polymerization is a free ion, which is kinetically distinguishable from an ion pair.[6] In the present study the results were obtained which suggest that the ion-pair polymerization occurs via the ionic dissociation of the excited EDA complex produced by γ-ray irradiation as well as the free-ion polymerization. This seems to be the first example of an ion-pair polymerization initiated by ionizing radiation.

## Experimental Section

**Materials.** α-Methylstyrene obtained from Wako Pure Chemical Industrial Co. was washed three times with aqueous solution of sodium hydroxide and water and distilled over calcium hydride. The middle fraction was distilled onto barium oxide, which had been baked for 72 h at 400 °C, with a high vacuum operation (~$10^{-6}$ mm). Methylene chloride, 1,2-dichloroethane, chloroform, and carbon tetrachloride were purified and dried by the same method as α-methylstyrene. Pyromellitic dianhydride was purified by sublimination before use.

**Procedures.** The reaction mixtures were prepared in vacuo as follows. Weighed pyromellitic dianhydride was sublimed into an irradiation tube, a Pyrex tube of 10 mm diameter, and then the monomer and the solvents, whose volumes had been measured in tubes of accurately determined diameter, were introduced into the irradiation tube by trap-to-trap distillations. In these operations breakable seals were used instead of cocks in order to avoid contamination by impurities separated from grease. The samples were irradiated with γ rays from $^{60}$Co source. The dose rate was determined by Fricke's dosimetry. Poly(α-methylstyrene) was precipitated from irradiated solution in an excess of methanol. The polymer was filtered, dried in a vacuum oven, and then weighed. The molecular weight distribution was measured by gel permeation chromatography using a polystyrene gel column, and the molecular weight of the polymer was calculated from the gel permeation chromatograph.

## Results and Discussion

It is known that the radiation-induced polymerizations of styrene and α-methylstyrene are very sensitive to impurities, particularly to water.[6] Evidence that the polymerizations under extensively dried conditions are due to cationic propagation mechanisms comes from scavenger studies and from the determination of reactivity ratios in copolymerization experiments.[6] It has also been revealed that the initiation species of the polymerizations in methylene chloride solutions are not derived from the acid formed by radiolysis of the solvent.[7] On the basis of these previous studies it appears that the radiation-induced polymerization of α-methylstyrene in methylene chloride solution is propagated by free cations.

The results of the radiation-induced polymerization in methylene chloride solution in the presence and absence of PMDA are shown in Table I. The polymer yields are apparently increased by the addition of small amounts of PMDA except in the case of an experiment in bulk at 0 °C.

No polymer was obtained in the presence and absence of PMDA when α-methylstyrene and methylene chloride were not dried with baked barium oxide indicating that a trace amount of water inhibits the polymerization, as reported for the photoinduced cationic polymerization.[3]

**Polymerizations at −78 °C.** When small amounts of PMDA (~$10^{-3}$ mol/L) were added at −78 °C at 2.0 mol/L of the monomer concentration, the polymer yield increased by a factor of 7 to 8 as is shown in Table I. The molecular weight of the polymer also increased by the addition of PMDA as well as the $\bar{M}_w/\bar{M}_n$ ratio reflecting the degree of dispersion. The molecular weight distributions of the polymers obtained in the presence and absence of $2 \times 10^{-3}$ mol/L of PMDA are shown in Figure 1. The molecular weight distribution appears to be bimodal in the presence of PMDA, indicating the coexistence of two types of propagating species possessing different reactivities. The lower molecular weight peak of the bimodal distribution coincides in position with the peak of the polymer obtained in the absence of PMDA and can be assigned to the free-ion polymerization. Thus, the results show that the increase in the polymer yield caused by the addition of PMDA is due to the occurrence of polymerization by another propagation mechanism which produces the higher molecular weight polymer than the free cationic propagation. The molecular weight of the higher peak can be estimated to be approximately $2.0 \times 10^4$.

The polymerization was completely inhibited by a trace amount of water as described above. This indicates that a

**Table I**
**The Radiation-Induced Cationic Polymerization of α-Methylstyrene in the Presence and Absence of Pyromellitic Dianhydride (PMDA) in Methylene Chloride Solution [a]**

| Temp, °C | Concn, mol/L | | Irradiation time, h | Polymer yield | | | |
|---|---|---|---|---|---|---|---|
| | Monomer | PMDA | | Conversion, % | $G(-m)$ [b] | $\overline{M}_n$ | $\overline{M}_w/\overline{M}_n$ |
| −78 | 2.0 | None | 4.5 | 3.2 | 24 | $3.5 \times 10^3$ | 2.0 |
| −78 | 2.0 | $2 \times 10^{-3}$ | 4.5 | 21 | 170 | $9.5 \times 10^3$ | 4.9 |
| −78 | 2.0 | $4 \times 10^{-3}$ | 4.5 | 22 | 180 | $7.9 \times 10^3$ | 4.7 |
| −78 | 2.0 | $5 \times 10^{-3}$ | 4.5 | 24 | 200 | $8.2 \times 10^3$ | 4.9 |
| 0 | 2.0 | None | 4.5 | c | c | c | c |
| 0 | 2.0 | $2 \times 10^{-3}$ | 2.0 | 16 | 270 | $4.5 \times 10^3$ | 2.6 |
| 0 | 2.7 | None | 3.3 | 1.2 | 17 | $4.8 \times 10^3$ | 2.2 |
| 0 | 2.7 | $2 \times 10^{-3}$ | 0.91 | 7.5 | 410 | $5.8 \times 10^3$ | 2.1 |
| 0 | 4.6 | None | 0.91 | 2.2 | 170 | $1.2 \times 10^4$ | 2.1 |
| 0 | 4.6 | $1 \times 10^{-3}$ | 0.91 | 5.5 | 430 | $1.3 \times 10^4$ | 2.1 |
| 0 | 5.4 | None | 0.91 | 5.7 | 540 | $1.7 \times 10^4$ | 2.1 |
| 0 | 5.4 | $1 \times 10^{-3}$ | 0.42 | 2.9 | 610 | $1.2 \times 10^4$ | 2.5 |
| 0 | 6.6 | None | 0.91 | 2.7 | 590 | $1.8 \times 10^4$ | 2.2 |
| 0 | 6.6 | $1 \times 10^{-3}$ | 0.42 | 1.8 | 870 | $1.6 \times 10^4$ | 2.4 |
| 0 | bulk | None | 0.33 | 2.1 | 780 | $2.0 \times 10^4$ | 2.2 |
| 0 | bulk | $1 \times 10^{-3}$ | 0.33 | 1.3 | 560 | $2.0 \times 10^4$ | 2.3 |

[a] The dose rate was $5.8 \times 10^5$ rad/h. [b] The number of the consumed monomer molecules per 100 eV energy absorbed by the solution. [c] The yield of polymer was negligible and the molecular weight could not be determined.

radical polymerization does not occur in the present system. Moreover, it is known that methylene chloride is a good electron acceptor,[8] and an anionic polymerization cannot be initiated by ionizing radiation in methylene chloride. Thus, it appears that the propagating species producing the higher molecular weight polymer in the presence of PMDA is also cationic. In our previous study it has been established by the use of the optical absorption technique that ion pairs are formed by γ-ray irradiation from EDA complexes of aromatic hydrocarbons with PMDA in glassy matrices at 77 K.[5] The result has been explained in terms of the ionic dissociation of the EDA complexes excited by ionizing radiation. On these bases it is reasonable to conclude that the polymerization is initiated by the ion pair formed from the EDA complex, that is, the propagating species producing the higher molecular weight polymer appears to be the ion pair of the propagating cation and the PMDA radical anion which is similar to that in the photoinduced cationic polymerization.[3]

Since the concentration of the EDA complex is very low, the probability of its direct excitation by radiation is neglected and the excited EDA complex is produced mainly via the energy transfer from the solvent. Thus, the process of the polymerization in the presence of PMDA can be expressed as follows.

$$D + A \rightleftarrows (D\,A)$$

$$S \rightsquigarrow S^{+}\cdot, S^{*}$$

$$S^{+}\cdot + D \rightarrow S + D^{+}\cdot$$

$$S^{*} + (D\,A) \rightarrow S + (D\,A)^{*}$$

$$D^{+}\cdot \text{ — polymer (free-ion polymerization)}$$

$$(D\,A)^{*} \rightarrow (D^{+}\cdot\cdots A^{-}\cdot) \rightleftharpoons \text{polymer (ion-pair polymerization)}$$

where D, A, and (D A) denote the electron donor, α-methylstyrene, and acceptor, PMDA, and their EDA complex, respectively, and S and $(D^{+}\cdot\cdots A^{-}\cdot)$ the solvent and the radical ion pair, respectively.

As is shown in Table I, the yield of polymer is little affected by the concentration of PMDA in the range $2 \times 10^{-3}$ to $5 \times 10^{-3}$ mol/L, although the concentration of the EDA complex is proportional to that of PMDA. Thus, it can be considered that the excitation transfer from the solvent to the EDA complex is almost complete at $2 \times 10^{-3}$ mol/L of the PMDA concentration.

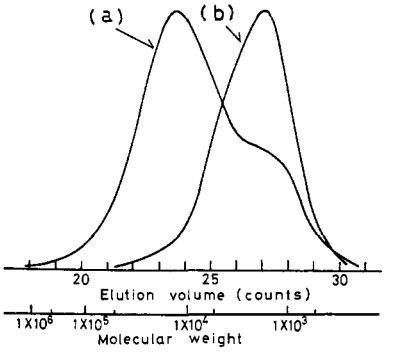


**Figure 1.** The molecular weight distributions of the polymers produced at −78 °C at 2.0 mol/L of the monomer concentration in the presence (a) and absence (b) of $2 \times 10^{-3}$ mol/L of PMDA.

**Polymerizations at 0 °C. Dependence on the Monomer Concentration.** The dependence of the polymerization on the monomer concentration was examined in the presence and absence of PMDA at 0 °C (Table I). It is shown that the polymer yield and the molecular weight of the polymer decrease with decreasing monomer concentration in both the presence and absence of PMDA. The increase in the polymer yield caused by the addition of PMDA is significant at low monomer concentrations, while the $G$ values of the monomer consumption, $G(-m)$, do not vary too much with the addition of PMDA at high monomer concentrations. In order to clarify this phenomenon, experiments with other solvents having different polarities, 1,2-dichloroethane, chloroform, and carbon tetrachloride, were carried out at 0 °C at 2.7 mol/L of the monomer concentration, and the results are shown in Table II. In the case of 1,2-dichloroethane, which is a polar solvent as well as methylene chloride, the polymer yield appreciably increases by the addition of PMDA. On the other hand, the polymer yield is little affected by the addition of PMDA in the lesser polar solvents, chloroform and carbon tetrachloride. These results mean that the addition of PMDA

**Table II**
**The Radiation-Induced Cationic Polymerization of α-Methylstyrene in the Presence and Absence of Pyromellitic Dianhydride (PMDA) in the Solvents of Various Polarities [a]**

| Solvent | $\epsilon_{25°C}$ [b] | Concn of PMDA, mol/L | Irradiation time, h | Polymer yield | | $\overline{M}_n$ | $\overline{M}_w/\overline{M}_n$ |
|---|---|---|---|---|---|---|---|
| | | | | Conversion, % | $G(-m)$ [c] | | |
| 1,2-Dichloroethane | 10.3 | None | 1.6 | 15.9 | 440 | $7.5 \times 10^3$ | 2.1 |
| | | $2 \times 10^{-3}$ | 0.50 | 9.2 | 810 | $7.3 \times 10^3$ | 2.3 |
| Chloroform | 4.8 | None | 1.6 | 2.9 | 80 | $6.2 \times 10^3$ | 2.3 |
| | | $2 \times 10^{-3}$ | 1.6 | 3.4 | 90 | $5.6 \times 10^3$ | 2.5 |
| Carbon tetrachloride | 2.2 | None | 0.55 | 4.4 | 360 | $7.8 \times 10^3$ | 2.8 |
| | | $2 \times 10^{-3}$ | 0.55 | 5.1 | 380 | $7.4 \times 10^3$ | 3.1 |

[a] The monomer concentration and temperature were 2.7 mol/L and 0 °C, respectively. The dose rate was $5.8 \times 10^5$ rad/h. [b] The dielectric constant of the solvent at 25 °C. That of methylene chloride is 9.5. [c] The number of the consumed monomer molecules per 100 eV energy absorbed by the solution.

enhances the polymer yield only in the polar solvents, and can be explained by the fact that the excited EDA complex tends to dissociate more to the ion pair in more polar medium. The small effect of the addition of PMDA on the polymer yield in a high concentration region is attributable to the low polarity of the medium. The ion-pair polymerization cannot be initiated in bulk because the ionic dissociation of the excited EDA complex does not occur, and the molecular weight is not affected by the addition of PMDA (Table I).

The molecular weight of the polymer obtained at 0 °C in the presence of PMDA did not so much differ from that in the absence of PMDA, as is shown in Table I, and its molecular weight distribution was apparently unimodal throughout the monomer concentrations studied. However, it is possible to conclude that the molecular weight increases at the low monomer concentrations, 2.7 and 4.6 mol/L, and decreases at the high monomer concentrations, 5.4 and 6.6 mol/L, when PMDA is added. This result indicates that the molecular weight of the polymer produced by the ion-pair polymerization is larger at the low monomer concentrations and smaller at the high monomer concentrations than that of the polymer produced by the free-ion polymerization, that is, the former is affected by the monomer concentration to a smaller extent than the latter.

**Comparison with the Photoinduced Cationic Polymerization.** In a recent study of the photoinduced cationic polymerization of α-methylstyrene, which is initiated by the photoexcitation of the EDA complex in methylene chloride, it has been found that the molecular weight distributions of the polymers are bimodal at low monomer concentrations and at low temperatures.[9] This result has been attributed to the coexistence of the ion-pair and free-ion polymerizations on the basis of the fact that the ion pair formed from the excited EDA complex dissociates to the free ions when the polarity of the medium is increased by lowering the monomer concentration and temperature.[10] Furthermore, the dependence of the rate of photoinduced cationic polymerization, $R_p$, on light intensity, $I$, was examined in order to elucidate whether the form of propagating chain ends is a free ion or an ion pair.[11] In the expression $R \propto I^n$, the values of $n$ are 0.5 and 1.0 for the free-ion and ion-pair polymerizations, respectively. When the monomer concentration and temperature were lowered, the value of $n$ decreased within the range of $0.5 < n < 1.0$ indicating that the contribution of the free-ion polymerization increased. At 1.9 mol/L of the monomer concentration, the values of $n$ were 1.0, 0.94, and 0.84 at −15, −35 and −74 °C, respectively.[11] On this basis, it can be considered that in the radiation-induced polymerization in the presence of PMDA the free-ion polymerization via the dissociation of the ion pair hardly occurs at 0 °C in the range of the monomer concentration studied (above 2.0 mol/L). On the other hand, at −78 °C the free-ion polymerization may occur via the dissociation of the ion pair as well as via the direct ionization process at low monomer concentrations. In the previous study it has also been revealed that the molecular weight of the polymer produced by the ion-pair polymerization is little affected by the monomer concentration, while that produced by the free-ion polymerization increases with increasing monomer concentration. This is in agreement with the present results of the polymerization at 0 °C as described above.

Furthermore, it has been shown that in the photoinduced ion-pair polymerization the molecular weight decreases with increasing temperature.[9] In the present study the polymer produced at 0 °C at 2.0 mol/L in the presence of PMDA is considered to be due to the ion-pair polymerization since the polymer yield is negligible in the absence of PMDA under the same condition (Table I), and its molecular weight, $4.5 \times 10^3$, is smaller than that at −78 °C at the same monomer concentration, approximately $2.0 \times 10^4$ (the higher molecular weight peak in Figure 1). Such a temperature dependence of the molecular weight agrees with that in the photoinduced ion-pair polymerization.

## References and Notes


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