Recent Progress of Photo- and Radiation-Induced Ionic Polymerizations

M. Irie[a]; Y. Yamamoto[a]; K. Hayashi[a]

[a] The Institute of Scientific and Industrial Research Yamadakami, Suita, Osaka, Japan

PLEASE SCROLL DOWN FOR ARTICLE

Recent Progress of Photo- and Radiation-Induced Ionic Polymerizations

M. IRIE, Y. YAMAMOTO, and K. HAYASHI*

The Institute of Scientific and Industrial Research
Yamadakami, Suita, Osaka, 565 Japan

ABSTRACT

Photoinduced ionic polymerizations of the monomers
α-methylstyrene, cyclohexeneoxide, nitroethylene, and
acrylonitrile were carried out in the presence of electron
acceptor or donor molecules. These polymerizations are
proved to be initiated by ions formed through the dissoci-
ation of the photoexcited electron donor-acceptor complex
and to proceed by ionic mechanism.
The molecular weight distribution of the polymer and the
light intensity dependency on the rate of polymerization
indicate that free ionic and ion-pair propagations coexist
in the cationic polymerization of α-methylstyrene.
Anionic polymerizations were observed for the nitroethylene-
tetrahydrofuran and acrylonitrile-dimethylformamide
systems.
Radiation-induced cationic polymerizations of styrene and
α-methylstyrene were found to proceed by free cationic
propagation. The effect of added electron acceptors in
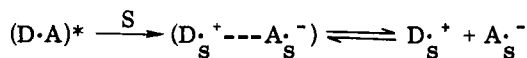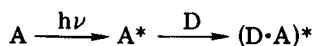these polymerizations was investigated.

---

*The paper was presented by K. Hayashi.

PHOTOINDUCED IONIC POLYMERIZATION

α-Methylstyrene

Although several photoinduced ionic polymerizations by charge transfer interaction have been reported [1], the monomers used have been limited to those containing hetero atoms, such as N-vinylcarbazole, which have a very low ionization potential and a high reactivity in cationic polymerization. We have found the photoinduced cationic polymerization of α-methylstyrene [2], which is a weak electron donor monomer and contains no hetero atom, in the presence of tetracyanobenzene (TCNB). Extremely well-dried α-methylstyrene polymerized in methylene chloride by the photoillumination of the charge transfer band of the α-methylstyrene—TCNB complex, though no polymer was obtained in the dark. There was no polymerization after the light was turned off. Water or triethylamine, which are typical inhibitors of cationic polymerization, stopped the polymerization. This result indicates that the photoinduced polymerization proceeds by a cationic mechanism. This conclusion was further confirmed by a copolymerization with styrene at 0°C. The monomer reactivity ratios are r_1 (α-methylstyrene) = 2.0 and r_2 (styrene) = 0.11. These reactivity ratios are close to those reported for cationic polymerization initiated by $SnCl_4$ [3] ($r_1 = 2.90$, $r_2 = 0.55$), but different from those of radical [4] ($r_1 = 0.36$, $r_2 = 1.18 \pm 0.04$) and anionic [5] ($r_1 = 0.08$, $r_2 = 10.5 \pm 0.5$) copolymerizations. Both the effect of additives and the reactivity ratios in copolymerization prove that the propagating ends in the photopolymerization have a cationic nature.

This polymerization is thought to be initiated through ions formed by the dissociation of the excited electron donor-acceptor complex as follows:

$$D + A \rightleftharpoons (D \cdot A) \qquad\qquad (D \cdot^+ \text{---} A \cdot_s^-) \rightleftharpoons \text{Polymer}$$

$$(D \cdot A) \xrightarrow{h\nu} (D \cdot A)^* \qquad\qquad D \cdot_s^+ + A \cdot_s^- \rightleftharpoons \text{Polymer}$$

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

$$(D \cdot A)^* \xrightarrow{S} (D \cdot_s^+ \text{---} A \cdot_s^-) \rightleftharpoons D \cdot_s^+ + A \cdot_s^-$$

where D, A, and S indicate α-methylstyrene, TCNB, and solvent, respectively.

We previously reported the fundamental processes involved in the formation of initiating species from the photoexcited complex by the use of various physicochemical methods, such as optical absorption and emission spectroscopies, laser flash photolysis, ESR, and photoconductivity [6, 7].

Figure 1 represents the cationic polymerization of α-methylstyrene in the presence of TCNB at -30°C. Curve A in Fig. 1 shows the yield of polymer obtained by illumination with wavelengths longer than 350 nm (with UV 31 filter), which involves both the charge-transfer band (363 nm) and the absorption band of TCNB (316 nm). Polymerization was also initiated by illumination with light of wavelength longer than 350 nm (with UV 35 filter), where only the charge-transfer absorption band exists, but the rate of polymerization was decreased by one-third (Curve B in Fig. 1). Illumination with light passed through a VY 42 filter, where the tail of the charge-transfer absorption band exists, scarcely initiates the polymerization, as shown in Curve C in Fig. 1 [8].

In ionic polymerization the dependence of the rate of polymerization, R_p, on the light intensity can give information on the form of propagating chain ends, whether they are free ions or ion pairs. When the chain ends are free, the dependence should be $R_p \propto I^{1/2}$. For ion pairs the dependence is expressed by $R_p \propto I$.

Figure 2 shows the dependence of the rate of polymerization on the
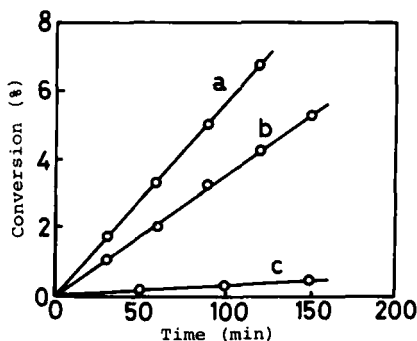
FIG. 1. Photopolymerization of α-methylstyrene (1.9 $\underline{M}$) in the presence of tetracyanobenzene (10^{-3} $\underline{M}$) in methylene chloride at -30°C. (a), (b), and (c): yields of polymer obtained by illumination with light passed through UV 31, UV 35, and VY 42 filters, respectively.
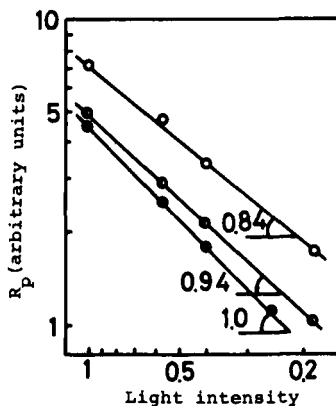
FIG. 2. Light intensity dependence of the rate of polymerization at various temperatures: (O) -74°C, (◐) -35°C, and (●) -15°C. [α-MeSt] = 1.9 $\underline{M}$, [PMDA] = 4 × 10^{-4} $\underline{M}$. Solvent: CH$_2$Cl$_2$.

light intensity at three temperatures [9]. Hereafter we use pyromellitic dianhydride (PMDA) as electron acceptor instead of TCNB. The dependence decreased from first order at -15°C to 0.84 at -74°C. The result suggests that free growing chain ends also contribute to the propagation process at the lower temperature.

The molecular weight distributions of the polymers obtained at four temperatures measured by GPC (gel permeation chromatography) are shown in Fig. 3. The polymer obtained at -74°C has a bimodal distribution, which clearly indicates that two chain ends with different structures propagate independently. The height of the polymer peak at the lower molecular weight decreased to a great extent with an increase of the temperature, though the peak positions are the same. On the other hand, the other peak increased both in its intensity and elution volume counts with increasing temperature. The deviation from first-order dependency at the lower temperature shown in Fig. 2 indicates the lower molecular weight peak arises from free propagating ends. The other peak is presumably caused by the ion-pair ends. The relative contributions of these two mechanisms, free ion and ion pair, are considered to depend on the polarity of the systems. Upon lowering the temperature the polarity of the system is expected to increase, and the facilitates ionic dissociation of ion pairs into free ions [10].

The relationship between the propagation mechanism and the polarity was also revealed by the effect of the monomer concentration.
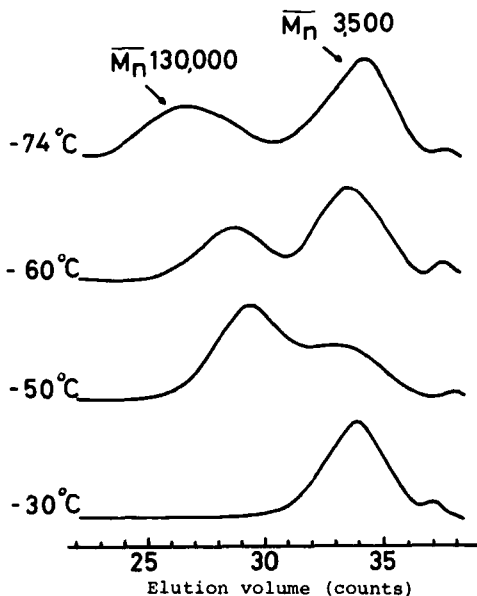
FIG. 3. Molecular weight distribution of poly-α-methylstyrene formed by GPC method. Polymerization was accomplished with a monomer concentration of 0.57 $\underline{M}$ at various temperatures.

When the concentration of α-methylstyrene in the system is decreased, so that the system is made more polar, the light intensity dependence also approached 0.5, as shown in Fig. 4. The molecular weight distribution curves shown in Fig. 5 indicate that the relative intensity of the peak at lower molecular weight, due to free ionic polymerization, increases with decreasing monomer concentration.

The rate of polymerization increased when the monomer concentration and temperature were lowered. This result is attributable to the facts that an increase in the polarity of the solution facilitates the dissociation of the ion pair to free ions, and the free ionic propagation has a higher rate than the ion pair one.

The light intensity dependencies of the photocurrents during photoillumination, which corresponds to the concentration of free ions, was always 0.5 as shown in Fig. 6. The photocurrent increased with decreasing temperature as expected. It also increased with a decrease in the concentration of α-methylstyrene
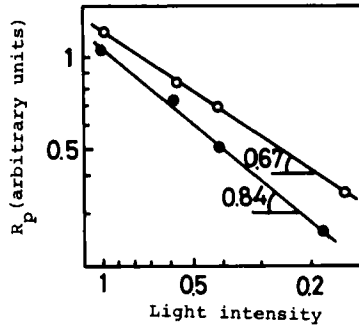
FIG. 4. Light intensity dependence of the rate of polymerization at various monomer concentrations. (○) [α-MeSt] = 0.53 M, (●) [α-MeSt] = 1.9 M, [PMDA] = 4 × 10⁴ M, Solvent: CH₂Cl₂. Temperature: −74°C.
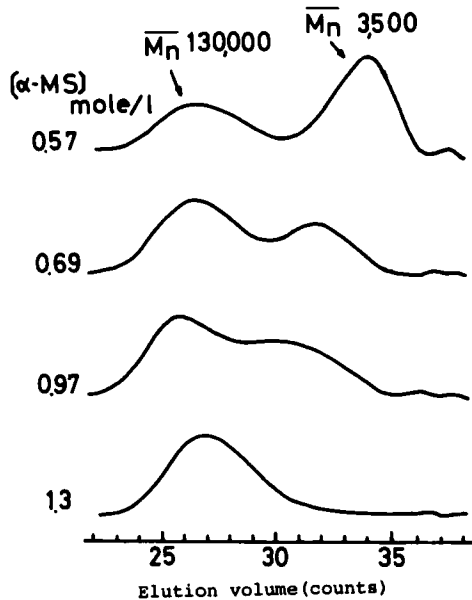

FIG. 5. Molecular weight distribution of poly-α-methylstyrene formed by GPC method. Polymerization was done at −74°C for various monomer concentrations.
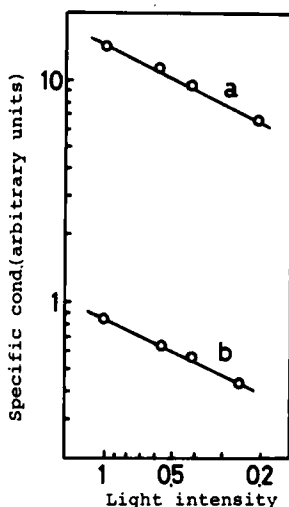
FIG. 6. Light intensity dependence of photocurrent. $[\alpha\text{-MeSt}]$ = 1.9 $\underline{M}$, $[\text{PMDA}]$ = 4×10^{-4} $\underline{M}$. (a) -74°C, (b) -15°C.

in the system, and this results in an increase of the polarity of the system. The steady-state yield of the free ions at monomer concentrations of 0.53 $\underline{M}$ is four times higher than that at 1.9 $\underline{M}$.

On the assumption that the mobility of ion is 5×10^{-4} $\text{cm}^2/(\text{V})(\text{sec})$ [11], the rate constant of free ionic propagation is obtained tentatively to be $(3.5 \pm 1.8) \times 10^3$ $\underline{M}^{-1}\text{sec}^{-1}$ at -74°C by the use of the above photocurrent value and the rate of the polymerization measured by dilatometry. This value is one order less than that of free ions obtained in radiation-induced ionic polymerization [12], even when it is extraporated to room temperatures by the use of an activation energy of 4 kcal/mole. A part of the decrease is possibly due to the solvation of the propagating chain ends by the polar solvent during the photopolymerization.

Cyclohexene Oxide [13]

Not only π-electron-donor monomers, such as styrene or α-methylstyrene, but also n-electron-donor monomers, such as cyclohexene oxide, are expected to be photoionized when complexed with suitable acceptors.

Photopolymerization of cyclohexene oxide was observed in the presence of TCNB or PMDA, while no polymer was obtained in the dark. The molecular weight of the polymer formed in the presence of PMDA at -78°C was 477,000, which is as large as that obtained by γ-irradiation. Small amounts of triethylamine inhibited the polymerization, which indicates that this polymerization proceeds by a cationic mechanism. The yield of polymer obtained in the presence of PMDA is three times that obtained in the presence of TCNB.

The dependence of the rate of polymerization of cyclohexene oxide on the wavelength of illuminating light in the presence of PMDA are shown in Fig. 7. The photopolymerization of cyclohexene oxide induced by the light exciting the acceptor band is much faster than that of α-methylstyrene. Hardly any poly-(cyclohexene oxide) is obtained by illumination with light of wavelengths larger than 390 nm.

Nitroethylene [14]

Anionic as well as cationic polymerization is expected to occur in photoexcited charge transfer systems, since laser photolysis studies have proved that cations and anions are formed simultaneously from the excited complex [7]. The photoinduced anionic

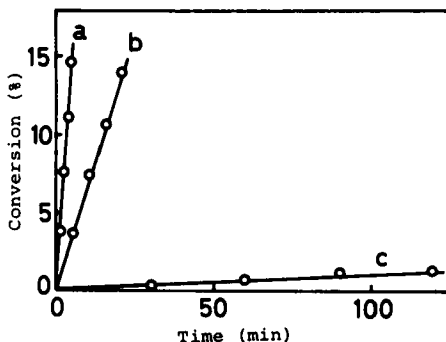FIG. 7. Polymerization of cyclohexene oxide in the presence of pyromellitic dianhydride at -78°C. (a), (b), and (c): yields of polymer obtained by illumination with light passed through Toshiba UV 31, UV 35, and UV 39 filters, respectively. Concentrations of cyclohexene oxide and pyromellitic dianhydride were 2.5 and 1×10^{-3} $\underline{M}$ respectively.

polymerization of nitroethylene and acrylonitrile was carried out with the purpose of extending the scope of photoinduced ionic polymerization to anionic systems. It is well known that nitroethylene has a high electron affinity, that it is readily polymerized by anionic catalysts, and that tetrahydrofuran is a suitable solvent for anionic polymerization as well as an n-electron donor.

The spectrum of the mixture of nitroethylene and tetrahydrofuran has a weak charge transfer band around 450 nm, which indicates the existence of a charge-transfer interaction between these compounds. Photoexcitation of the charge-transfer band by the light passed through a VY-45 filter ($\lambda > 450$ nm) gives rise to polymerization of nitroethylene as shown in Fig. 8(b). No polymer was obtained in the dark. In this system there was neither an induction period nor postpolymerization after turning off the light. Elemental analysis and the IR spectrum proved that the polymer obtained is poly(nitroethylene). The molecular weight was determined by viscometry to be 17,000.

The light which covers both the charge-transfer band and the acceptor band gives a high polymer yield, although hardly any polymer was obtained with light of wavelength longer than 520 nm, as shown in Figs. 8(a) and 8(c). In addition, no polymer was obtained in the absence of tetrahydrofuran. These results imply that the polymerization is initiated by the photoexcited charge-transfer interaction between nitroethylene and tetrahydrofuran.

A trace of hydrogen chloride (5×10^{-3} $\underline{M}$) inhibited the polymerization completely, which suggests that this reaction proceeds by an anionic mechanism. This was confirmed by a
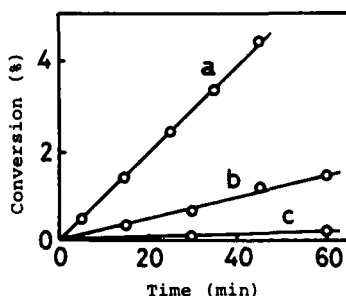

FIG. 8. Photopolymerization of nitroethylene in tetrahydrofuran at 4°C. Time-conversion curves were attained by the light passed through UV-39 filter (a), VY-45 (b), and VO-52 (c). Concentration of nitroethylene in tetrahydrofuran was 3.0 $\underline{M}$.

copolymerization with acrylonitrile, for which the light was passed
through a VY-45 filter to avoid a direct radical polymerization of
the acrylonitrile. The content of nitroethylene in the copolymer is
shown as a function of monomer composition in Fig. 9. The monomer
reactivity ratios were estimated to be r_1 (nitroethylene) = 25 ± 10
and r_2 (acrylonitrile) = 0.24 ± 0.20, which are similar to those for the
radiation-induced anionic copolymerization in tetrahydrofuran at
-78°C (r_1 = 63 ± 15, r_2 = 0.01 ● 0.01) [15].

Acrylonitrile [16]

The intermolecular interaction between acrylonitrile and DMF
in the ground state is very weak, because the absorption spectrum
of DMF was scarcely shifted to longer wavelength by the addition
of acrylonitrile. The excitation of the DMF band by the light passed
through Toshiba UV-29 filter ($\lambda > 290$ nm) induced the polymerization
of acrylonitrile. The light hardly excites the acrylonitrile band.
    The polymerization was completely inhibited by the addition of
small amount of hydrogen chloride or a trace of moisture. In
addition, preilluminated DMF cannot initiate the polymerization.
These results indicate that the polymerization is initiated by the
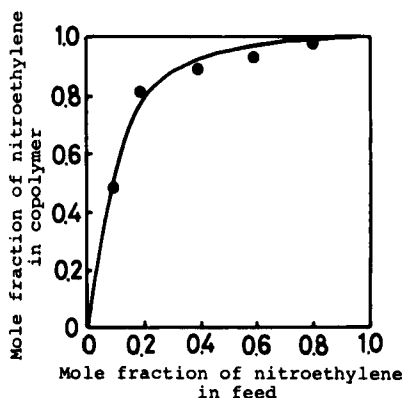excited complex between acrylonitrile and DMF and proceeds by
anionic mechanism.

FIG. 9. Photoinduced copolymerization of nitroethylene and
acrylonitrile in tetrahydrofuran at 4°C. The concentration of the
mixture of nitroethylene and acrylonitrile in tetrahydrofuran was
3.0 M. r_1 (nitroethylene) = 25 ± 10; r_2 (acrylonitrile) = 0.24 ± 0.20.

The mechanism was further confirmed by copolymerization with methacrylonitrile at -30°C, and the monomer reactivity ratio agreed with the value reported for anionic polymerization initiated by NaNH₂ [17].

The dependence of the rate of polymerization on the light intensity was measured at -30°C to clarify the structure of the propagating chain ends, as shown in Fig. 10. The slope is found to be 0.63. The dependence of close to 0.5 indicates that almost all propagating chain ends are free at -30°C in this system. The free ion mechanism in this very polar solvent agrees well with that proposed for the case of the cationic polymerization of α-methylstyrene.

Simultaneous Cationic and Anionic Polymerizations [18]

Simultaneous polymerization is expected when two monomers can form an excited complex by photoirradiation, and the donor monomer can be polymerized cationically and the acceptor monomer anionically. In this study, cyclohexene oxide and nitroethylene were used as the electron-donor and -acceptor monomers, respectively.

Nitroethylene has an absorption tail around 470 nm. The addition of cyclohexene oxide to nitroethylene causes a small red shift in the absorption, which indicates a weak contact-type charge-transfer interaction between these monomers.

The excitation of the charge-transfer band by light passing through the Toshiba UV-39 filter induces the polymerization of both monomers at 4°C. Polymerization was not observed in the
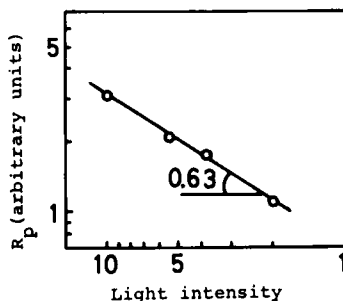

FIG. 10. Light intensity dependence of the rate of photopolymerization of acrylonitrile in DMF at -30°C. The concentration of acrylonitrile was 3.0 M.

absence of either nitroethylene or cyclohexene oxide or in the dark.
There was neither an induction period nor postpolymerization after
turning off the light.

Figure 11 shows the dependence of the rate of polymerization
on the feed composition. The maximum rate was attained at almost
equimolar monomer composition, and the rate decreased markedly
on deviating from this composition. The fact that the highest rate
of polymerization occurs at equimolar composition seems to be
due to the formation of the highest concentration of initiating active
species by photoirradiation of the 1:1 EDA complex. Fractionation
of the polymer obtained indicates that it is a mixture of the homo-
polymers of cyclohexene oxide and nitroethylene and a copolymer,
probably a block copolymer.

RADIATION-INDUCED IONIC POLYMERIZATION

It has been found that the radiation-induced polymerizations of
styrene and α-methylstyrene are considerably enhanced by the use
of the extreme drying technique [19, 20]. Evidence that those
polymerizations are due mainly to a cationic propagation mechanism
comes both from scavenger studies and from the determination of
reactivity ratios in copolymerization experiments. k_p values in
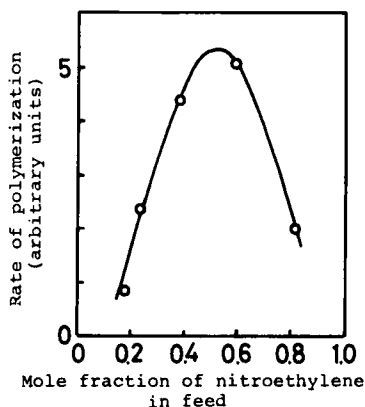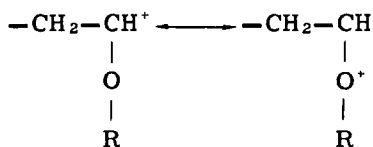bulk were determined to be 10^6 $\underline{M}^{-1}sec^{-1}$ for both monomers by

FIG. 11. Dependence of the rate of photopolymerization of
mixture of cyclohexene oxide and nitroethylene on the composition
of the two monomers in the feed at 4°C.

the electrical conductivity method [21]. The large k_p values are explained as a characteristic ion-dipole reaction for the free ionic propagation [22, 23]. The propagation reaction of styrene in free cationic process in bulk is characterized by a lower activation energy as compared with that in other mechanisms [24]. A decrease of k_p value owing to the solvation by polar solvent such as CH_2Cl_2 to growing cation was observed preliminary [25]. The radiation-induced cationic polymerization of superdried isobutyl vinyl ether (IBVE) in bulk gave a half-power dose rate dependence of the rate of polymerization [26]. A propagation reaction of this monomer was found to be characterized by a high activation energy of 9.6 kcal/mole. In order to elucidate the reason for the considerable difference in the activation energies for the propagation of styrene and IBVE, radiation-induced copolymerization of these monomers was carried out in bulk at various temperatures [27]. It is found that in the reactivity of cation, styrene is greater than IBVE; however, the relation is reversed in relative reactivity of monomer. The extraordinary high activation energy (E_p) of IBVE is presumably explained in terms of the solvation of IBVE to cation and resonance stabilization of the growing IBVE cation as follows.

$$-CH_2-CH^+ \longleftrightarrow -CH_2-CH$$
$$\quad\quad\; | \quad\quad\quad\quad\quad\quad | $$
$$\quad\quad O \quad\quad\quad\quad\quad O^+$$
$$\quad\quad\; | \quad\quad\quad\quad\quad\quad | $$
$$\quad\quad R \quad\quad\quad\quad\quad R$$

On the other hand, radiation-induced anionic polymerization was achieved by using well-purified nitroethylene [28] and acrylonitrile [29].

Recently the formation of an ion-pair by ionizing radiation was found for electron-donor acceptor (EDA) systems by the use of the optical absorption technique in glassy matrices at low temperature [30]. By the addition of ethylbenzene the yield of radical anion of pyromellitic anhydride (PMDA) increased and the absorption band of this intermediate shifted from 664 to 668 nm. These results are explained in terms of the formation of ion pairs through the ionization of the EDA complex of PMDA and ethylbenzene. The rate of polymerization in the radiation-induced ionic polymerization of α-methylstyrene in methylene chloride was increased by the addition of an electron acceptor such as PMDA [31]. Figure 12 represents the increase of molecular weight of polymer formed
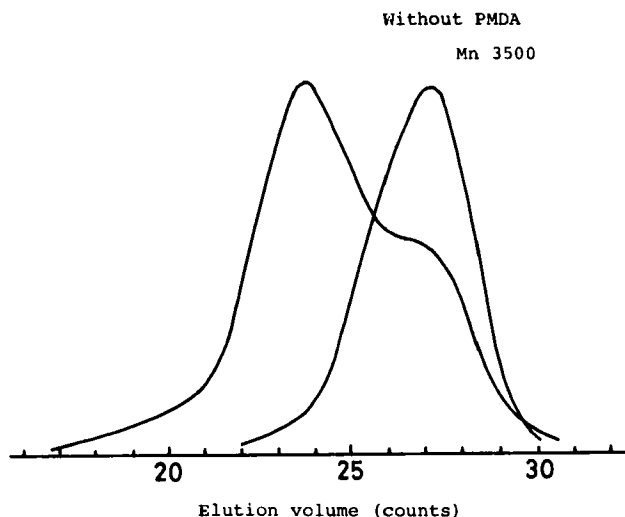
Without PMDA

Mn 3500

Elution volume (counts)

FIG. 12. Molecular weight distribution of poly-α-methylstyrene obtained by ionizing radiation; effect of added PMDA (3×10^{-3} $\underline{M}$) at -78°C in CH_2Cl_2.

caused by the addition of PMDA in this polymerization. These results indicate that the polymerization mechanism changes from free cationic propagation to ion-pair as discussed previous for the photopolymerization of this monomer.

REFERENCES

[1] For example: (a) S. Tazuke, Adv. Polym. Sci., 6, 321 (1969); (b) M. Yamamoto, S. Nishimoto, M. Ohoka, and Y. Nishijima, Macromolecule, 3, 706 (1970); (c) K. Tada, Y. Shirota, and H. Mikawa, J. Polym. Sci., Polym. Chem. Ed., 11, 2961 (1973).

[2] M. Irie, S. Tomimoto, and K. Hayashi, J. Polym. Sci., Part B, 8, 585 (1970).

[3] E. B. Lindvig, A. P. Gantmakker, and S. S. Medvedev, Dokl. Akad. Nauk SSSR, 119, 90 (1950).

[4] A. V. Golubera, N. F. Usmanova, and A. A. Vansheidt, J. Polym. Sci., 52, 63 (1961).

[5] A. V. Tobolsky and R. J. Boudreau, Ibid., 51, S53 (1961).

[6] M. Irie, S. Tomimoto, and K. Hayashi, J. Phys. Chem., 76, 1419 (1972).

[7] M. Irie, M. Masuhara, K. Hayashi, and N. Mataga, Ibid., 78, 341 (1974).

[8] M. Irie, S. Tomimoto, and K. Hayashi, J. Polym. Sci., Polym. Chem. Ed., 10, 3235 (1972).

[9] M. Irie, S. Irie, and K. Hayashi, To Be Published.

[10] M. Szwarc, Carbanions, Living Polymers and Electron Transfer Processes, Wiley-Interscience, New York, 1968, p. 416.

[11] M. Katayama, H. Yamazaki, and Y. Ozawa, Bull. Chem. Soc. Japan, 42, 2410 (1969).

[12] F. Williams, K. Hayashi, K. Ueno, K. Hayashi, and S. Okamura, Trans. Faraday Soc., 63, 1501 (1969).

[13] M. Irie, S. Tomimoto, and K. Hayashi, J. Polym. Sci., Polym. Chem. Ed., 10, 3243 (1972).

[14] M. Irie, S. Tomimoto, and K. Hayashi, J. Polym. Sci., Polym. Lett. Ed., 10, 699 (1972).

[15] H. Yamaoka, P. Uchida, K. Hayashi, and S. Okamura, Kobunshi Kagaku, 24, 79 (1967).

[16] M. Irie, S. Sasaoka, and K. Hayashi, To Be Published.

[17] F. Dawans and G. Smets, Makromol. Chem., 59, 163 (1963).

[18] M. Irie, S. Tomimoto, and K. Hayashi, J. Polym. Sci., Polym. Chem. Ed., 11, 1859 (1973).

[19] K. Ueno, Ff. Williams, K. Hayashi, and S. Okamura, Trans. Faraday Soc., 63, 1478 (1967).

[20] R. C. Potter, R. H. Bretton, and D. J. Metz, J. Polymer Sci., Part A-1, 4, 2295 (1966).

[21] Ka. Hayashi, Y. Yamazawa, T. Takagaki, F. Williams, K. Hayashi, and S. Okamura, Trans. Faraday Soc., 63, 1489 (1967).

[22] F. Williams, Ka. Hayashi, K. Ueno, K. Hayashi, and S. Okamura, Ibid., 63, 1501 (1969).

[23] K. Hayashi, Actions Chim. Biol. Radiat., 15, 145 (1971).

[24] K. Hayashi, K. Hayashi, and S. Okamura, Polym. J., 4, 426 (1973).

[25] T. Hibi, K. Hayashi, M. Irie, and K. Hayashi, To Be Published.

[26] K. Hayashi, K. Hayashi, and S. Okamura, J. Polym. Sci., Part A-1, 9, 2305 (1971).

[27] K. Hayashi, K. Hayashi, and S. Okamura, Polym. J., 4, 495 (1973).

[28] H. Yamaoka, F. Williams, and K. Hayashi, Trans. Faraday Soc., 63, 376 (1967).

[29] S. Iiyama, S. Abe, and K. Namba, Kobunshi Kagaku, 30, 134
      (1973).
[30] M. Irie, S. Irie, Y. Yamamoto, and K. Hayashi, J. Phys.
      Chem., 79, 699 (1975).
[31] Y. Yamamoto, M. Irie, and K. Hayashi, 15th Annual Meeting
      of the Polymer Society, Japan, Tokyo, June 1974.