PHOTO AND RADIATION INDUCED IONIC POLYMERIZATION

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ABSTRACT

Photo-induced cationic polymerizations of styrene and α-methylstyrene, which are weak electron donors and contain no hetero atom, were carried out in the presence of electron acceptors such as tetracyanobenzene and pyromellitic dianhydride to elucidate the polymerization mechanism initiated through an excited charge transfer interaction. Cyclohexene oxide was also polymerized by photo-illumination in the presence of these electron acceptors. The mechanism of this ring-opening polymerization was thought to be a cationic one. Photo-polymerization of nitroethylene in tetrahydrofuran was carried out with the purpose of extending this process to anionic systems. The results obtained have been compared with the cases of ionic polymerizations by ionizing radiation and conventional catalysts.

It has been found that the radiation induced polymerization of styrene is considerably enhanced by the use of an extremely rigorous drying technique[1, 2]. Evidence that this polymerization is due mainly to a cationic propagation, comes both from scavenger studies and from the determination of reactivity ratios in copolymerization experiments with α-methylstyrene and isobutyl vinyl ether. The large k_p value ($>3 \times 10^6$ M^{-1} sec^{-1}) is explained as a characteristic ion–dipole reaction for the free ionic propagation process[3, 4].

On the other hand, photo-induced ionic polymerization of styrene and α-methylstyrene which are weak donors and contain no hetero atom, were carried out in the presence of tetracyanobenzene and pyromellitic dianhydride to elucidate the polymerization mechanism initiated through an excited charge transfer interaction[5].

Photo-illumination was carried out with a high pressure mercury lamp through filters which cut off wavelengths shorter than 300 nm. The photo-induced polymerizations of these monomers were observed in 1,2-dichloroethane and methylene chloride in the presence of electron acceptors as shown in *Table 1*. The degree of polymerization of the poly(α-methylstyrene) formed at $-30°C$ was estimated to be 660 by viscometry. No polymer was obtained in the dark, in the absence of acceptors or without rigorous drying of monomer and solvent. This polymerization was completely inhibited by the addition of a trace amount of proton scavenger such as triethylamine as reported for the radiation-induced ionic polymerization. This polymerization was also retarded by durene or oxygen. A copolymerization with styrene at 0°C confirms a cationic mechanism, that is, the monomer reactivity

Table 1. Photo-induced cationic polymerization

Monomer	Acceptor	Additives	Time h	Temperature °C	Yield %
αMeSt	TCNB	None	4	−30	7.18
αMeSt	TCNB	None	4	+30	1.23
αMeSt	None	None	4	−30	0
αMeSt	TCNB	H_2O 2×10^{-3} M	4	−30	0
αMeSt	TCNB	$N(C_2H_5)_3$ 5×10^{-3} M	4	−30	0
αMeSt	TCNB	Durene 2×10^{-2} M	4	−30	1.79
αMeSt	PAH	None	1	−78	9.8[a]
CHO	PAH	None	3	0	57.3

αMeSt: α-methylstyrene, [Monomer]: 1.9 M in 1,2-dichloroethane or methylene chloride[a]
CHO: Cyclohexene oxide · [Monomer] = 2.5 M in methylene chloride
TCNB: Tetracyanobenzene, [Acceptor]: 1×10^{-3} M
PAH: Pyromellitic dianhydride · [Acceptor] = 1×10^{-3} M

ratios are r_1(α-methylstyrene) = 2.0 and r_2(styrene) = 0.11 and these values are close to those reported for cationic polymerization initiated by $SnCl_4$. A new band with absorption maximum at 363 nm is due to a charge transfer interaction between α-methylstyrene and tetracyanobenzene in methylene chloride. The extinction coefficient of the band and the equilibrium constant to form an electron donor–acceptor complex were determined to be 1500 and 0.23 M^{-1} respectively by applying the Benesi–Hildebrand method at 0°C.

The curve A in *Figure 1* shows the yield of polymer with light of longer wavelength than 310 nm which involves both charge transfer band and acceptor band. The polymerization is also initiated by illumination at wavelengths longer than 350 nm. In this range, only the charge transfer absorption band exists, though the apparent rate of polymerization was

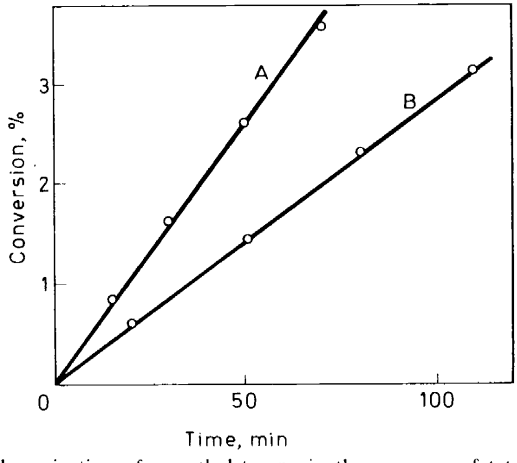

Figure 1. Photopolymerization of α-methylstyrene in the presence of tetracyanobenzene in methylene chloride at −74°C. The concentrations of α-methylstyrene and tetracyanobenzene are 1.9 M and 1×10^{-3} M, respectively. A and B show the yields of polymer obtained by illumination at wavelengths longer than 310 nm and 350 nm, respectively.

decreased to one half as shown by curve B in *Figure 1*. No polymerization was observed after turning off the light. A large rate of polymerization was obtained at low monomer concentration. The dependence of the rate of polymerization on the light intensity derived from *Figure 2*, was found to be first order. The stereoregularity of poly(α-methylstyrene) formed by photo-illumination was found to be the same as the polymer by ionizing radiation. In addition the temperature dependence of the molecular weight distribution made by the use of GPC suggests the coexistence of two kinds of propagation mechanisms.

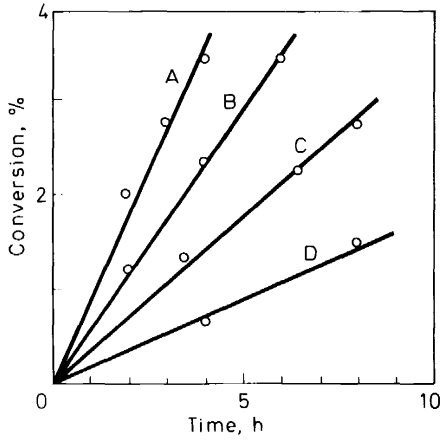

Figure 2. Photopolymerization of α-methylstyrene in the presence of tetracyanobenzene in methylene chloride as a function of light intensity at −30°C. The concentrations of α-methylstyrene and tetracyanobenzene are the same as for *Figure 1*. The relative light intensities are A = 1.0, B = 0.64, C = 0.43 and D = 0.18.

To elucidate the initiation mechanism some spectroscopic measurements were carried out. The fluorescence of tetracyanobenzene at 324 nm was quenched by the addition of a small amount of α-methylstyrene and a new emission spectrum appeared at 520 nm which is thought to be the fluorescence of the excited electron donor–acceptor complex. This fluorescence decreased with increasing polarity of the solvent, because of the dissociation of the excited complex to solvated ions. This polymerization is thought to be initiated through ions formed by the dissociation of the excited electron donor–acceptor complex as follows.

$$\begin{aligned} &A \xrightarrow{h\nu} A^{\star} \xrightarrow{D} {}^{1}(D\cdot A)^{\star} \longrightarrow {}^{3}(D\cdot A)^{\star} \\ &D + A \rightleftharpoons D\cdot A \xrightarrow{h\nu'} \end{aligned} \tag{1}$$

$$\left.\begin{aligned} {}^{1}(D\cdot A)^{\star} &\searrow \\ {}^{3}(D\cdot A)^{\star} &\nearrow \end{aligned}\right\} (D_s^{+\cdot} \ldots A_s^{-\cdot}) \rightleftharpoons D_s^{+\cdot} + A_s^{-\cdot} \tag{2}$$

$$D_s^{+\cdot} + D \rightarrow \cdot D - D_s^{+} \xrightarrow{D} \text{polymer} \tag{3}$$

$$(D_s^{+\cdot} \ldots A_s^{-\cdot}) + D \rightarrow (\cdot D - D_s^{+} \ldots A_s^{-\cdot}) \xrightarrow{D} \text{polymer} \tag{4}$$

D: Monomer
A: Acceptor

The existence and behaviour of ion radicals formed by photo-illumination were detected by the use of e.s.r. and laser photolysis[7]. The similarity with radiation induced ionic polymerization on the complete inhibition by trace amounts of proton scavengers and stereoregularity of polymer obtained suggests that this polymerization proceeds by free ions. However, an important role of loosely coupled solvated ion pairs should be emphasized from the observations of the first order dependence of the rate of polymerization on the intensity of incident light.

Recently, cyclohexene oxide was also polymerized by photo-illumination in the presence of pyromellitic dianhydride or tetracyanobenzene, as shown in *Table 1* and *Figure 3*. A weak charge transfer band of this system was found around 340 nm. The mechanism of this polymerization was thought to be a cationic one as with radiation-induced polymerization of this monomer[8].

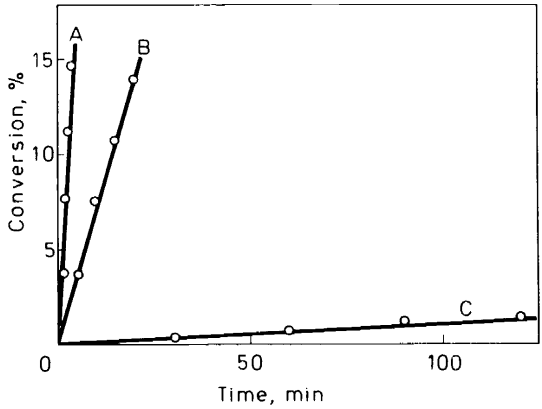

Figure 3. Photopolymerization of cyclohexene oxide in the presence of pyromellitic dianhydride in methylene chloride at $-74°C$. The concentrations of cyclohexene oxide and pyromellitic dianhydride are 2.5 M and 1×10^{-3} M respectively. A, B and C are the yields of polymer obtained by illumination of light at wavelengths longer than 310 nm, 350 nm and 390 nm respectively.

The studies on photo-induced ionic polymerization are so far limited to a cationic one and any report of an anionic one has not yet been made. Photopolymerization of nitroethylene in tetrahydrofuran was carried out with the purpose of extending the photo-induced ionic polymerization to the anionic system.

It has already been reported that the radiation induced polymerization of nitroethylene proceeds by a free anionic mechanism[9]. The spectrum of the mixture of nitroethylene and tetrahydrofuran has a weak charge transfer band around 450 nm. The light which covers both charge transfer band and acceptor band results in the formation of polymer, though little polymer was obtained by light of wavelength longer than 520 nm as shown in *Figure 4*. No polymer was obtained in the absence of tetrahydrofuran. Elemental analysis and the infra-red spectrum proved that the polymer obtained is poly-(nitroethylene). Molecular weight was determined to be 17000 by

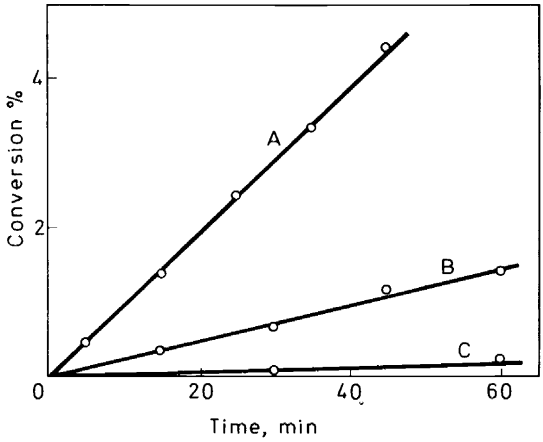

Figure 4. Photopolymerization of nitroethylene in tetrahydrofuran at 4°C. Time/conversion curves A, B and C were obtained by illumination of light at wavelengths longer than 390 nm, 450 nm and 520 nm respectively.

viscometry in DMF[10]. By the addition of a trace amount of hydrogen chloride the polymerization was inhibited completely. The monomer reactivity ratios in the copolymerization with acrylonitrile were estimated to be r_1(nitroethylene) = 25 ± 10 and r_2(acrylonitrile) = 0.24 ± 0.20, which are similar to those of radiation-induced anionic copolymerization at −78°C[11]. These results prove that the photopolymerization of nitroethylene in tetrahydrofuran proceeds by an anionic mechanism.

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