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Radiation and Photo-Induced Ionic Polymerization

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Radiation-Induced Ionic Polymerization

It has been found that the radiation-induced polymerization of styrene is considerably enhanced by the use of extremely rigorous drying techniques.¹⁾²⁾ Evidence that this polymerization is due mainly to a cationic propagation mechanism comes both from scavenger studies and from the determination of reactivity ratios in copolymerization experiments with α -methylstyrene and isobutyl vinyl ether. On the other hand, k_p values are determined to be $>3 \times 10^6 \text{ M}^{-1} \text{ sec}^{-1}$ by electrical conductivity method.³⁾ The large k_p value is explained as a characteristic ion-dipole reaction for the free ionic propagation process.⁴⁾ Free ionic polymerization of this monomer was carried out at 0, 25 and 40°C. The propagation reaction of styrene in free cationic process in bulk is characterized with lower activation energy as compared with that in other mechanisms while the frequency factor does not change so much in its magnitude from these in radical and free anionic mechanisms.⁴⁾⁵⁾

The radiation-induced cationic polymerization of superdried isobutyl vinyl ether in bulk gave a half power dose rate dependence of the rate of polymerization at the temperature range $0 \sim 50^\circ\text{C}$.⁶⁾⁷⁾⁸⁾ The propagation rate constant of the polymerization of this monomer was estimated as shown in Figure 1, for example $1.2 \times 10^5 \text{ M}^{-1} \text{ sec}^{-1}$ at 25°C , by parallel measurement of the rate and electrical conductivity. These k_p values obtained are much larger than the values reported for the conventional cationic polymerization in ion-pair mechanism, $0.083 \text{ M}^{-1} \text{ sec}^{-1}$ (in CCl_4)⁹⁾ and $6.5 \text{ M}^{-1} \text{ sec}^{-1}$ (in $\text{C}_2\text{H}_4\text{Cl}_2$)¹⁰⁾. A propagation reaction of this monomer was found to be characterized by a high frequency factor and also high activation energy, $9.6 \text{ Kcal mol}^{-1}$. This is explained by the mutual interaction between propagating carbonium cation and oxygen atom of this monomer molecule.⁸⁾ The number average degree of polymerization of polymer formed at 25°C was evaluated to be 930 and therefore the monomer chain transfer rate constant, k_m , was $130 \text{ M}^{-1} \text{ sec}^{-1}$ at the same temperature. The activation energy for monomer transfer reaction are obtained to be $8.1 \text{ Kcal mol}^{-1}$. The molecular weight of the polymer obtained in free cationic process seems to be relatively high comparing with polymers by catalysts.

A cationic mechanism was proposed for the radiation-induced polymerization of dry α -methylstyrene with the evidence of strong retardation by low concentration of amine¹¹⁾ and copolymerization experiments with styrene which demonstrated a cationic monomer reactivity ratios.¹²⁾

The stereoregularity of poly α -methylstyrene obtained by γ -irradiation has been analyzed by NMR method¹⁶⁾ and compared with polymer formed by cationic catalyst,¹⁴⁾ as shown in Table 1. At 0°C, it was observed that polymer formed by radiation has higher content of syndiotactic structure than polymer by catalyst. This might be interpreted on the basis of the difference of the structure at the growing cation, that is, on the effect of counter ion.

Photo-Induced Ionic Polymerization

Photo-induced ionic polymerization of styrene and α -methylstyrene which are weak donors and contain no hetero atom, was carried out in the presence of tetracyanobenzene and pyromellitic anhydride to elucidate the polymerization mechanism initiated by excited charge transfer complex.¹³⁾

Photo-illumination was carried out with a high pressure mercury lamp through filters of water and n-hexane solution containing 1 % of monomer which cuts off of wavelength shorter than 300 nm. The photo-induced polymerization of α -methylstyrene was observed in the presence of either tetracyanobenzene or pyromellitic anhydride in 1,2-dichloroethane solution. The molecular weight of the polymer formed at -30°C was estimated to be 77600. No polymer was obtained in dark or without rigorous drying of monomer and solvent. (Table 2) This polymerization was completely inhibited by the addition of a trace amount of triethylamine, as reported for the radiation-induced ionic polymerizations. A copolymerization with styrene at 0°C confirms a cation mechanism. The monomer reactivity ratios are

γ_1 (α -methylstyrene) = 2.0 and γ_2 (styrene) = 0.11 and close to those reported for cationic polymerization initiated by SnCl_4 ¹⁵⁾. The stereoregularity of poly α -methylstyrene formed by photo-illumination was found to be the same as the polymer by radiation. (Table 1)¹⁶⁾ Recently, cyclohexene oxide was also polymerized by photo-illumination and the mechanism was thought to be cationic one.¹⁶⁾

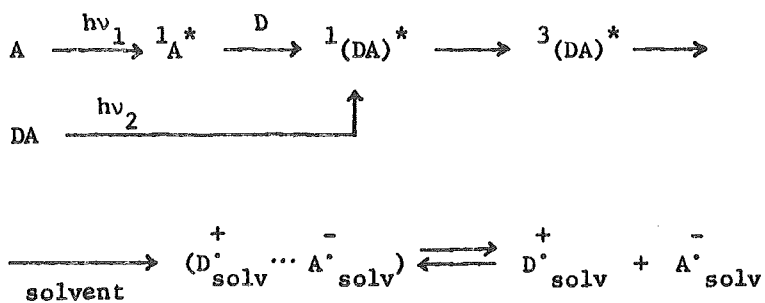
To elucidate the initiation mechanism, some spectroscopic measurements were carried out. Tetracyanobenzene has an absorption maximum at 316 nm and a fluorescence maximum at 324 nm in the mixed solvent 1,2-dichloroethane and cyclohexane (volume ratio of 1:2). The fluorescence of tetracyanobenzene was quenched by the addition of a small amount of α -methylstyrene ($\sim 10^{-2}\text{M}$) and a new emission spectrum appeared at 520 nm. The new emission is thought to be the fluorescence of the excited charge transfer complex of tetracyanobenzene with α -methylstyrene. The fluorescence decreased with increasing polarity of the solvent, because of the dissociation of the excited complex to ion pairs in the polar solvent.

The absorption spectrum of the mixture of tetracyanobenzene ($5 \times 10^{-4}\text{M}$) and α -methylstyrene has a charge transfer band at 363 nm, which indicates the existence of a weak charge transfer interaction between these compounds. However, our results indicate that the charge transfer interaction in the ground state does not initiate the polymerization, but that the excited state plays an important role. This is also supported by the fact that the addition of durene, which quenches the fluorescence of the excited complex

of tetracyanobenzene with α -methylstyrene, retards the polymerization, as shown in Table 2.

The first order dependence of the formation of ionic species measured by photo conductivity method and of the rate of polymerization on incident light intensity were observed as shown in Figures 2 and 3.

The initiation mechanism of this ionic polymerization is deduced as follows.



A: Acceptor, D: Monomer

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Figures

- Fig. 1 Radiation-induced polymerization of isobutyl vinyl ether.
Arrhenius plots of the rate constants for propagation k_p
and monomer transfer, k_{tm} .⁸⁾
- Fig. 2 Dependence of slope of initial photo-current of α MeSt-TCNB
on incident light intensity.¹⁶⁾
 $[\alpha\text{MeSt}] = 7.6 \times 10^{-1} \text{M}$, $[\text{TCNB}] = 5 \times 10^{-3} \text{M}$
Solvent; n-amyl alcohol 163V/cm
- Fig. 3 Dependence of rate of polymerization of α -methylstyrene
on incident light intensity at -30°C .¹⁶⁾
 $[\alpha\text{MeSt}] = 1.9 \text{M}$, $[\text{TCNB}] = 1 \times 10^{-3} \text{M}$, in $\text{C}_2\text{H}_4\text{Cl}_2$.

Table 1

Tacticity of Poly- α -methylstyrene

Polymerization temperature 0°C

Tacticity	Photo 16)		Bulk	Radiation 16)		Catalyst 14)
	CH_2Cl_2	$(\text{CH}_2\text{Cl}_2)_2$		CH_2Cl_2	$(\text{CH}_2\text{Cl})_2$	CH_2Cl_2
S %	67.8	70.9	64.6	65.7	70.1	37.3
H %	23.9	21.5	21.2	19.5	25.3	46.0
I %	8.3	7.6	14.2	14.8	4.6	16.7

Table 2
Photo-induced Cationic Polymerization¹³⁾¹⁶⁾

Monomer	Acceptor	Additives	Time hr	Temperature °C	Yield %
α MeSt	TCNB	None	4	-30	7.18
α MeSt	TCNB	None	4	+30	1.23
α MeSt	None	None	4	-30	0
α MeSt	TCNB	H ₂ O	4	-30	0
α MeSt	TCNB	$2 \times 10^{-3} M$ N(C ₂ H ₅) ₃ $5 \times 10^{-3} M$	4	-30	0
α MeSt	TCNB	Durene $2 \times 10^{-2} M$	4	-30	1.79
α MeSt	PAH	None	4	-78	4.9
CHO	PAH	None	3	0	57.3

α MeSt: α methylstyrene, [Monomer]: 1.9 M in 1.2 dichloroethane

CHO : Cyclohexene oxide

TCNB : Tetracyanobenzene [Acceptor]: $1 \times 10^{-3} M$

PAH : Pyromellitic anhydride

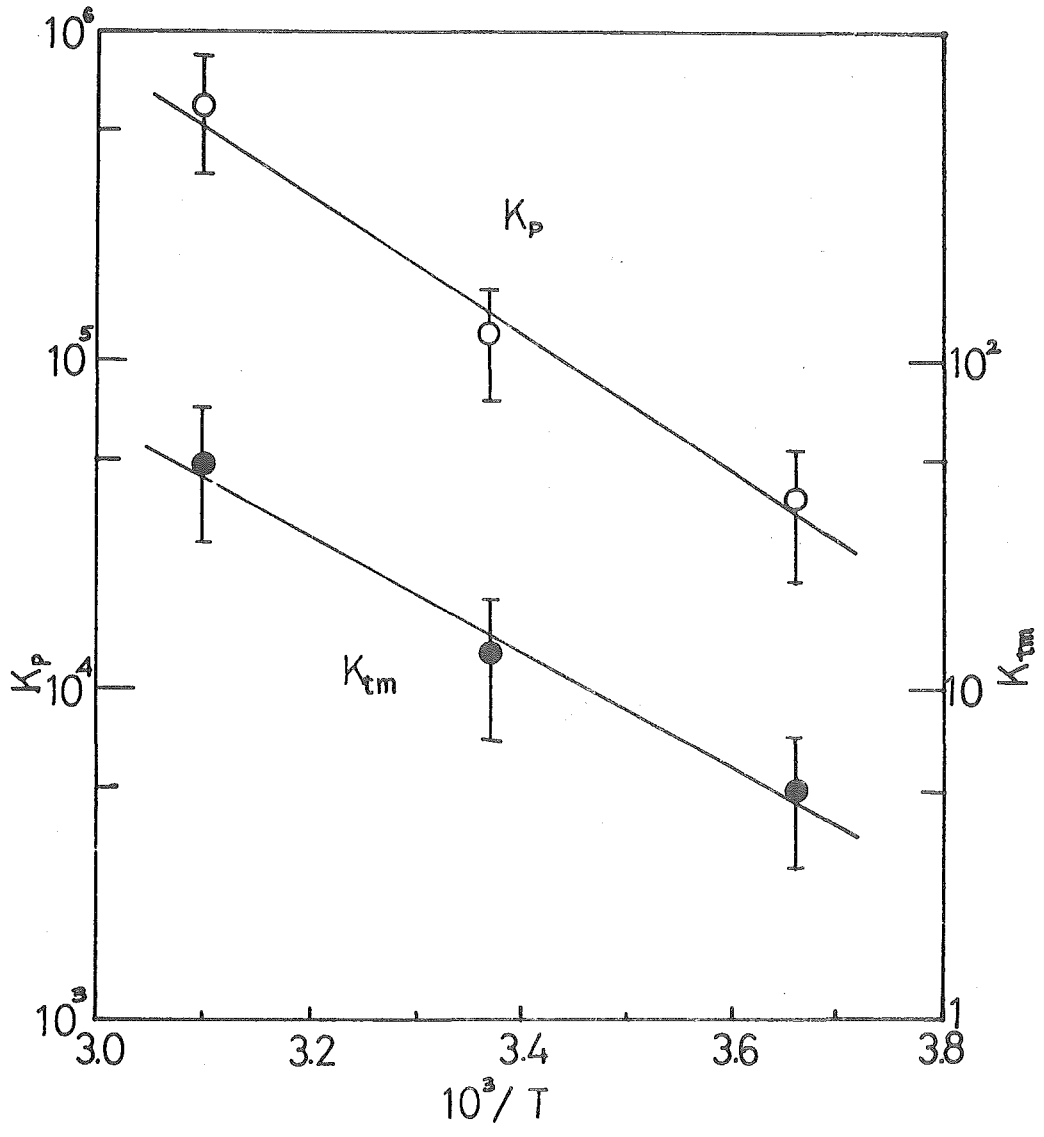


FIGURE 1.

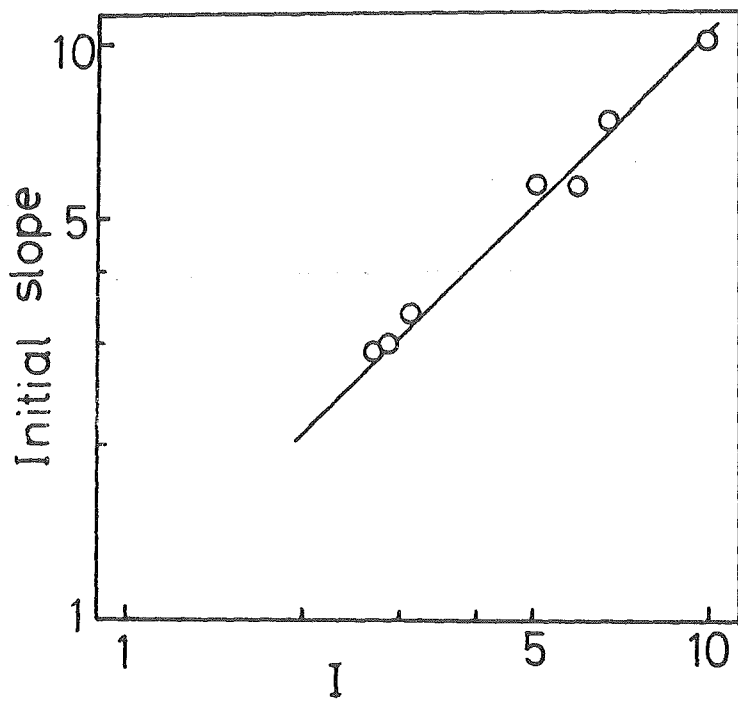


FIGURE 2.

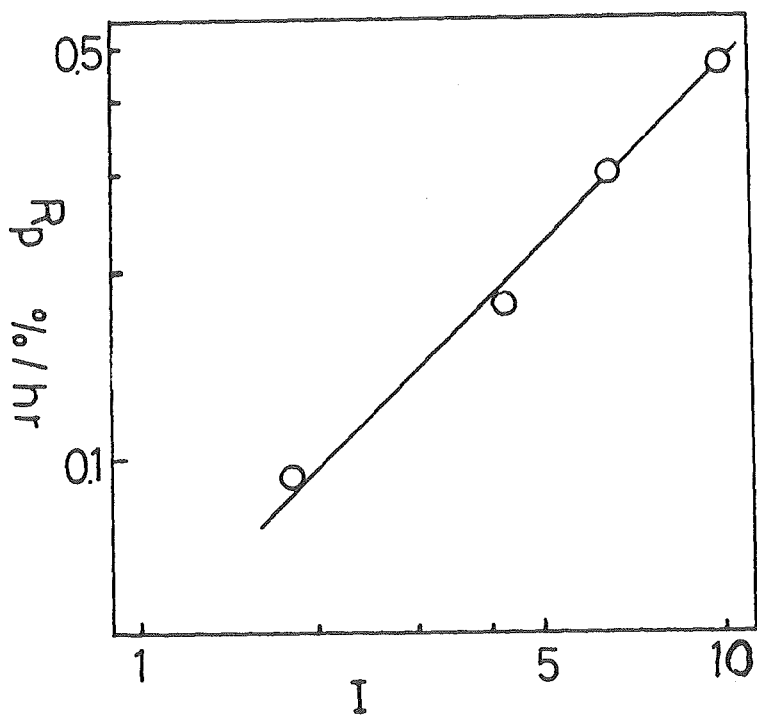


FIGURE 3.