

## RECENT ADVANCES IN PHOTOINDUCED IONIC POLYMERIZATIONS

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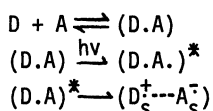
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**Abstract** - Photoinduced ionic polymerizations of styrene, cyclohexene oxide and acrylonitrile were studied. The molecular weight distributions of the polymer and the light intensity dependences proved that three kinds of mechanisms coexist in the photopolymerization of styrene, namely the radical, the ion-pair and the free-ion polymerization of which the contributions depend on the polarity of the system. Cyclohexene oxide in the presence of an electron acceptor polymerizes in solid state by photoillumination. The quantum yield of monomer consumption is equal to  $8 \times 10^3$  at  $-65^\circ\text{C}$ . Anionic polymerization was observed for the acrylonitrile-dimethylformamide system and its propagating rate constant was estimated to be  $2 \times 10^4 \text{ M}^{-1} \text{ sec}^{-1}$ .

### INTRODUCTION

Photoinduced ionic polymerizations based on charge transfer interactions in the excited state have been extensively studied, starting with the first observation of Ellinger (1) in 1964. Until recently however, the studies were limited to N-vinylcarbazole, on accounts of its high reactivity in cationic polymerization. We have extended the photoinduced ionic polymerisation in the other monomers in order to establish their ionic, cationic or anionic, mechanisms during photopolymerization.

For ionic polymerization to proceed, ionic entity has to be formed in some way. The energy of a photon is, however, usually small when compared to the ionization energy of monomers or solvent molecules. One possible way of forming ion is the irradiation of an electron donor-acceptor complex. The energy of ultraviolet light is high enough to transfer an electron from a donor molecule, D, of low ionization potential to an acceptor molecule, A, of high electron affinity. The photoexcited polar complex is expected to dissociate in polar solvents into separated ion-pairs.



The primary process of photodissociation of the excited complex has been recently studied in detail with laser flash photolysis (2), and it is now well established that ionic dissociation is one of the prevalent non-radiative deactivation processes of the singlet or triplet excited state of the complex in polar solvents. This implies that monomers can be ionized in the presence of suitable electron acceptor or -donor molecules by photoexcitation of the charge transfer band or local band of each component, which lies in the visible or ultraviolet wavelength region. Monomeric radical cations or anions thus formed are expected to initiate cationic or anionic polymerizations.

The monomers we have studied until now are summarized in Table I.

TABLE 1. Monomers studied in the photoinduced ionic polymerizations

Mechanism	Monomers <sup>3-16</sup>
Cationic	$\alpha$ -methylstyrene styrene isobutylvinylether
Anionic	cyclohexene oxide nitroethylene acrylonitrile

$\alpha$ -Methylstyrene (3-9), styrene (10), isobutylvinylether (11) and cyclohexene oxide (12,13) have been polymerized through a cationic mechanism in the presence of suitable electron acceptors, such as tetracyanobenzene or pyromellitic dianhydride. On the other hand, anionic propagation was observed in the photopolymerizations of nitroethylene in tetrahydrofuran (14,15) and of acrylonitrile in *N,N*-dimethylformamide (8,16). In the discussion presented here we are concerned mainly with the photopolymerization of styrene, cyclohexene oxide and acrylonitrile. Three kinds of mechanisms, radical, ion-pair and free ionic polymerizations, were observed in the photopolymerizations of styrene, their respective contributions being dependent on the polarity of the system. Cyclohexene oxide polymerizes in the solid state under irradiation. Anionic polymerization of acrylonitrile was proved by copolymerization and inhibitor experiments and its rate constant was estimated.

## RESULTS AND DISCUSSION

### styrene

In previous papers (3-9) we have shown that  $\alpha$ -methylstyrene polymerizes through a cationic mechanism on irradiation in the presence of tetracyanobenzene or pyromellitic dianhydride. The choice of  $\alpha$ -methylstyrene in the previous study is based on its reluctance to polymerize by a radical mechanism. The absence of a radical mechanism simplifies indeed considerably the interpretation of the experimental results. After having established the cationic mechanism in the photopolymerization of  $\alpha$ -methylstyrene, we extended the study to styrene, which is capable of polymerizing by both radical and ionic mechanisms. Figure 1 shows the concentration dependence of the rate of photopolymerization of styrene in the presence of pyromellitic dianhydride in dichloromethane.

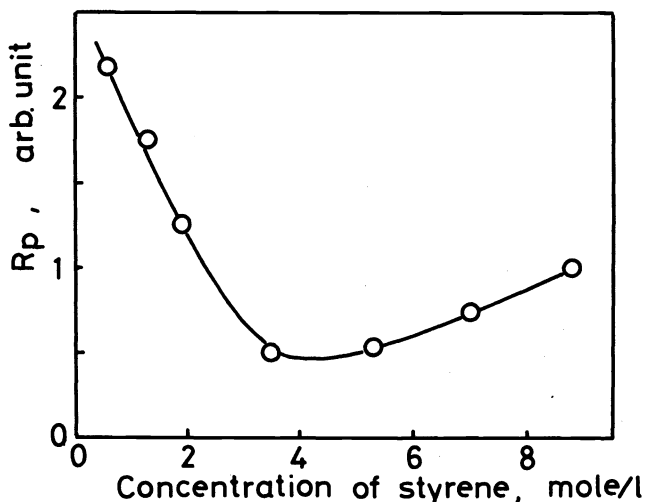


Fig. 1 Dependence of the rate of polymerization on the concentration of styrene in dichloromethane at 18°C. Concentration of pyromellitic dianhydride is  $1 \times 10^{-3}$  M.

The irradiation wavelength was chosen within the charge transfer band of the complex styrene-pyromellitic dianhydride by using a cut-off filter, Toshiba UV-35 ( $\lambda > 350$  nm). The rate decreases with a decrease of monomer concentration in the high concentration region. At lower concentrations, however, the rate increases with dilution. This characteristic concentration dependence indicates that the polymerization mechanism changes with the concentration of styrene in dichloromethane. In order to elucidate the mechanism we adopted two methods. One based on the molecular weight distribution of the polymer, the other on the copolymerization with methylmethacrylate.

Figure 2 shows the concentration dependence of the molecular weight distribution of the product polymer.

In bulk the polymer has unimodal molecular weight distribution and its molecular weight is 3,500. Upon decreasing the concentration of styrene a new peak appears at about 20 of elution count and clear bimodal distribution was observed at 5.3 M of styrene. At concentration lower than 1.9 M the distribution again becomes unimodal and the molecular weight is 36,000, i.e. ten times higher.

These two distribution peaks are affected in different ways by addition of ether, which is a typical inhibitor of cationic polymerization.

A small amount of ether eliminated the higher molecular weight peak, while the lower peak remains unchanged.

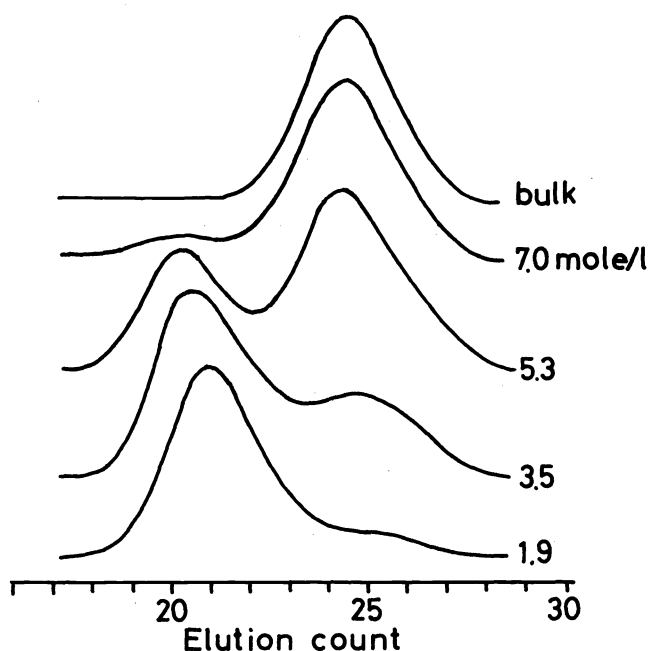


Fig. 2 Molecular weight distribution of polystyrene measured by GPC method. Polymerization was carried out in the presence of pyromellitic dianhydride ( $1 \times 10^{-3}$  M) in dichloromethane at  $18^\circ\text{C}$ .

This result clearly indicates that the higher molecular weight polymer is due to cationic polymerization and the lower molecular weight polymer due to radical mechanism. This assignment suggests that the radical mechanism is predominant in bulk; while the contribution of the cationic mechanism increases with the decrease of the concentration of styrene. Figure 3 shows the copolymerization data at two different concentrations of styrene.

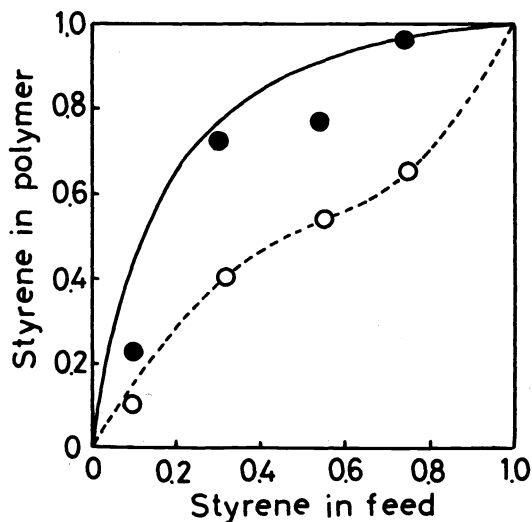


Fig. 3 Photoinduced copolymerization of styrene (st) with methylmethacrylate (MMA) in the presence of pyromellitic dianhydride ( $1 \times 10^{-3}$  M) in bulk (o) and in solution of 1.7 M in dichloromethane (●) at  $18^\circ\text{C}$ .

The diagram of the polymerization in bulk is similar to the radical copolymerization diagram as initiated by benzoyl peroxide (17), while the curve of low concentration of styrene resembles the curve of cationic copolymerization initiated by tin tetrachloride (17). These copolymerizations thus confirm the coexistence of radical and cationic mechanism during the photopolymerization and the contribution of the latter mechanism increases at a lower concentration of styrene.

The concentration dependences indicate that when the solution was made polar the ionic dissociation becomes the dominant deactivation process of the photoexcited complex, leading to the higher yield of ions. These ions initiate the ionic polymerizations. In a less polar solvent, e.g. at higher concentration of styrene, the ionic dissociation of the excited complex is greatly suppressed and only few ions can initiate the ionic polymerization. Consequently, in the bulk system radical mechanism becomes largely predominant.

The polarity effect was also examined by the use of different solvents. In polar 1,2-dichloroethane, the molecular weight is bimodal. A higher molecular weight peak due to cationic mechanism is clearly observed and its contribution increases with the decrease in the concentration of styrene. However, in a less polar medium as chloroform and tetrachloromethane, the distribution is unimodal and it does not show any concentration dependence, indicating a radical mechanism.

The light intensity dependence of the rate of polymerization also gives valuable information concerning the mechanism. When the chain ends are free, for example in radical or free ionic polymerizations, a half power dependence should be observed. It should become first order when the propagating chain end is terminated with its partner, for example counter ion in ion-pair polymerizations. First order dependence is also expected as the termination due to the presence of impurity becomes important. Figure 4 shows the light intensity dependence of the rate of polymerization in the different concentration of styrene and at different temperatures.

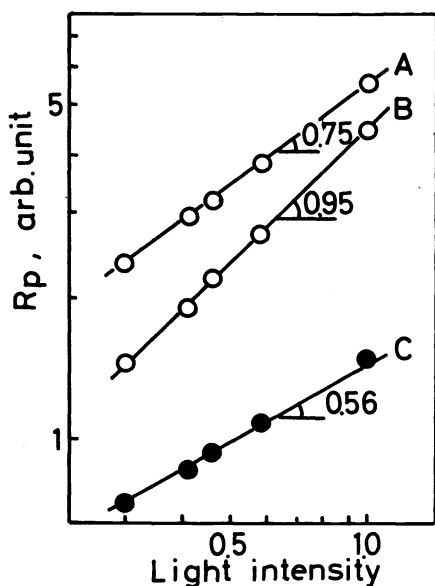
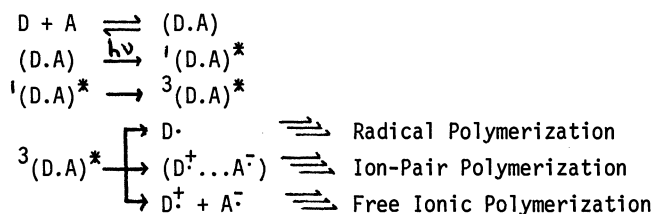


Fig. 4 Dependence of the rate of photopolymerization of styrene on light intensities in bulk (●) and in solution of 0.6 M (○) in dichloromethane at 18°C (B,C) and -74°C (A)

The slope in bulk is close to a half power dependence. This coincides with the radical mechanism. When the concentration of styrene is decreased at the same temperature as observed in bulk, the slope increases close to first order. The slope of 0.95 indicates that the termination of the propagating chain end is caused by charge neutralization within ion-pairs. When lowering the temperature, the slope again becomes closer to a half and at the same time the rate of polymerization increases. These two effects suggest a contribution of an additional mechanism, which is considered to be the free ionic one. Its contribution increases by lowering the polymerization temperature, as observed in the photopolymerization of  $\alpha$ -methylstyrene (9).

In order to substantiate the free ionic mechanism, molecular weight distribution of the product polymer was also measured at low temperature and at low concentration of styrene. At 18°C the distribution is unimodal, while new low molecular weight peak appears at low temperature and the distribution becomes bimodal at -74°C. The contribution of the lower molecular weight peak increases at low temperature. The lower molecular weight peak is safely ascribed

to the free ionic polymerization, since the identical molecular weight polymer was obtained by  $\gamma$ -irradiation in similar condition. The higher molecular weight polymer is due to the ion-pair polymerization and its peak increases with the rise in temperature. A similar temperature dependence has been observed in the photopolymerization of  $\alpha$ -methylstyrene (9). The lower molecular weight peak, which we ascribed to free ionic polymerization, increases with the decrease of styrene concentration at  $-74^\circ\text{C}$ , so that the solution is made polar. This behavior coincides with the fact that the slope of the light intensity dependence becomes closer to a half power at a lower temperature in the low concentration. These two results, light intensity dependences and molecular weight distributions, indicate that both ion-pair and free ionic mechanisms play important roles in the photopolymerization. In conclusion the mechanism of photopolymerization of styrene, D, in the presence of electron acceptor molecule, A, can be summarized as follows,



The contribution of the three mechanisms depends on the polarity of the medium. In a less polar solution the radical mechanism predominates, while in polar solution contribution of ion-pair mechanism increases; finally in very polar medium free ionic mechanism plays a major part.

#### Cyclohexene oxide in solid state

We have shown in a previous paper (12) that cyclohexene oxide in dichloromethane solution polymerizes by cationic mechanism on irradiation in the presence of an electron acceptor. Cationic polymerization is expected not only in dichloromethane solutions but also in bulk system, since cyclohexene oxide has a similar dielectric constant as methylene chloride. One of the interesting natures of cyclohexene is that it forms a plastic crystal phase at low temperature between  $-36^\circ\text{C}$  and  $-81^\circ\text{C}$  (18). We focused our attention on the photopolymerization in the solid state, since no work dealing with the photoinduced ionic polymerization in solid phase has yet been reported.

In a plastic crystal phase the sample is almost transparent. This enables us to illuminate it homogeneously. The yield of polymer increases linearly with the illumination time. The polymerization was observed in so far as the irradiation light covers the absorption band of pyromellitic dianhydride used as electron acceptor. A trace amount of water or triethylamine, which are typical inhibitors of cationic polymerizations, inhibited the polymerization. The temperature dependence of the rate of polymerization is shown in Fig. 5. A discontinuous phenomenon of the rate was not observed between liquid and plastic crystal phases, the rate in the crystal phase being higher than the rate in the liquid state. The polymerization is, however, remarkably suppressed below  $-81^\circ\text{C}$  even taking into account the reflection due to the polycrystalline state.

In the plastic crystal phase even when the temperature is changed, no change is observed in the rate. This suggests that the initial ion yield and the polymerization mechanism does not change with temperature in this phase. The non-variance of the mechanism was further confirmed from the temperature dependence of molecular weight of the product polymer, as shown in Fig. 5. The molecular weight does not show any noticeable change in the solid phase. The rate of polymerization of cyclohexene oxide in the solid phase is much higher, about three orders of magnitude higher, than the rate observed in the photopolymerization of styrene or  $\alpha$ -methylstyrene. The high rate predicts a high quantum yield of forming initiating ions, a high propagating rate and a long kinetic chain length. The quantum yield of the monomer consumption was measured and found to be as high as  $8 \times 10^3$  at  $-65^\circ\text{C}$ . The value means that the kinetic chain length is more than  $8 \times 10^3$  and the chain transfer occurs at least ten times in a single kinetic chain, considering the molecular weight of the polymer of  $8 \times 10^4$ . The quantum yield of monomer consumption of  $8 \times 10^3$  is, so far as the authors know, the highest value observed in the photoinduced ionic polymerization. Such high value must be related to the tension of the oxizane ring.

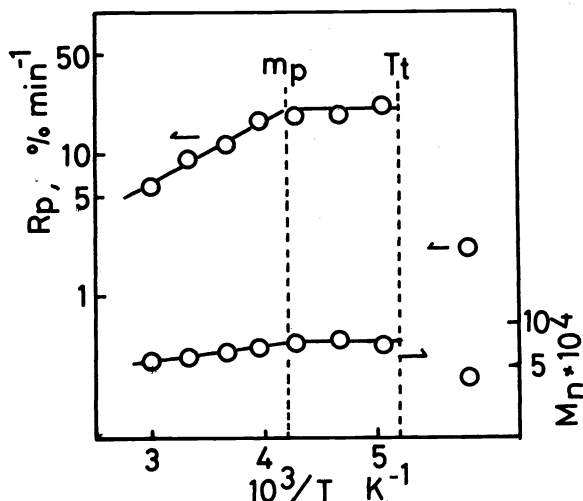


Fig. 5 Temperature dependences of the rate of photopolymerization of cyclohexene oxide in bulk in the presence of pyromellitic dianhydride and its molecular weight

### Acrylonitrile

Photopolymerization of acrylonitrile was carried out in carefully dry conditions in dimethylformamide. Acrylonitrile polymerizes on irradiation with light which excites the absorption of dimethylformamide or the charge transfer bands. The polymerization was completely inhibited by the addition of a trace amount of moisture or hydrogen chloride. In addition preilluminated dimethylformamide could not initiate the polymerization. The monomer reactivity ratio obtained from the copolymerization with methacrylonitrile at  $-30^{\circ}\text{C}$  agreed with the value reported for anionic polymerization initiated with sodium amide (19). All these results support the anionic mechanism, which is initiated by the ions formed from the excited complex between acrylonitrile and dimethylformamide.

The rate of polymerization increases with the decrease of monomer concentration, presumably due to the increase of the polarity of the medium. On the other hand, the highest molecular weight is obtained at almost equimolar mixture of acrylonitrile and dimethylformamide.

The light intensity dependence of the rate of polymerization was measured to be 0.66 at  $0^{\circ}\text{C}$  and 0.63 at  $-30^{\circ}\text{C}$ . Such values relatively close to a half power dependence indicate free ionic polymerization. On assuming a free ionic mechanism and the absence of chain transfer during the propagation, a propagation rate constant can be evaluated from the measurement of the rate of polymerization,  $R_p$ , and of the molecular weight of the polymer,  $\overline{DP}$ , by eq. (1).

$$k_p = (\overline{DP} \cdot R_p \cdot kt)^{1/2} / [M] \quad (1)$$

were  $[M]$  and  $kt$  are monomer concentration and termination rate, respectively.

A propagation rate constant of  $2 \times 10^4 \text{ M}^{-1} \text{ sec}^{-1}$  was obtained at  $0^{\circ}\text{C}$  by assuming  $kt$  of  $10^{10} \text{ M}^{-1} \text{ sec}^{-1}$ . This rate constant is two orders of magnitude higher than that for a radical mechanism (20) and is comparable with the value of free anionic polymerization of nitroethylene in bulk by  $\gamma$ -irradiation (21).

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