

Stabilizing Ion Pairs in Poly(methyl methacrylate)

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Received: December 2, 2002; In Final Form: March 17, 2003

Decay of ions trapped in γ -irradiated poly(methyl methacrylate) (PMMA)-containing ion scavengers was examined. Cations in PMMA migrate through diffusion and by a hopping transfer of the charge. They encounter anions, combine, and thereby decay. The diffusion of cations was confirmed by a comparison of decay of ions in PMMA-containing pyrene and that in a copolymer of methyl methacrylate and 1-pyrenylmethyl methacrylate. Cations in the former sample decay faster than those in the latter sample. The ions in the copolymer are chemically bonded to the polymer chains, preventing the diffusion of the ions. However, the dependence of the decay of the ions on the concentration of pyrenyl groups indicated that the ions decay through a hopping transfer of the charge on pyrenyl groups. The hopping transfer was suppressed by triphenylamine. The suppression is ascribed to structural difference in neutral triphenylamine and its cation. Anions in PMMA are ketyl-type anions at the side chains of the polymer. Their migration is suppressed, since they are connected to the polymer chains and the structures of the neutral state and its anion are different.

Introduction

Positive ions and electrons are generated by the irradiation of materials with ionizing radiation. An ejected electron thermalizes a few nanometers from the parent molecule.^{1,2} If an electron scavenger exists near the electron, a negative ion is generated a few nanometers from the positive ion. The positive ion is also converted to a more stable ion, if a cation scavenger exists near it.

Decay of the ion pairs in irradiated materials has practical importance as well as fundamental interests. An ion pair of positive and negative ions has a dipole. By trapping the ion pairs in a nonpolar material, dipoles of 10^{-28} – 10^{-27} Cm (10–100 D) can be introduced into the material, and in this way, functional materials can be produced. For example, ion pairs in electric fields induce polarization in the material. If the polarization of the ion pairs is fixed, piezo- and pyroelectric material can be made. This method enables us to prepare piezo- and pyroelectric materials from various polymers other than ferroelectric polymers such as polyvinylidene fluoride and polar polymers such as copolymers of vinylidene cyanide.³

In this paper, we examine the mechanism of decay of the ions trapped in poly(methyl methacrylate) in an effort to find a method of fixing the dipoles due to the ion pairs and in this way to fabricate new functional materials.

Experimental Section

Poly(methyl methacrylate) (PMMA) was supplied by Wako Pure Chemical Industries. Its number-averaged molecular weight is 2.3×10^5 . 1-Pyrenylmethyl methacrylate was synthesized from methacryl chloride supplied by Tokyo Kasei Kogyo and 1-pyrenemethanol supplied by Aldrich (stated purity of 98%). The copolymer of 1-pyrenylmethyl methacrylate and methyl methacrylate was polymerized with α, α' -azobis(isobutyronitrile) (AIBN, 98%) supplied by Junsei Chemical. PMMA and the copolymer were purified by dissolving them in tetrahydrofuran

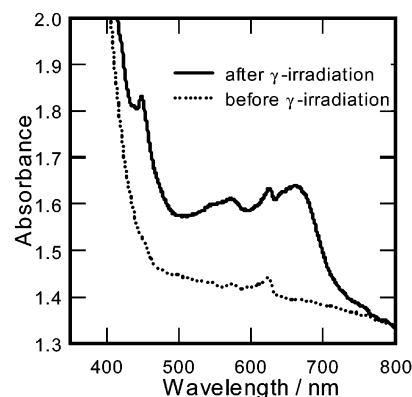


Figure 1. Photoabsorption spectra generated from a PMMA film containing 0.1 mol of triphenylamine/kg and 0.1 mol of chloranil/kg before and after γ -irradiation to a dose of 5 kGy at 77 K. The thickness of the film was 0.6 mm.

and reprecipitating with methanol or water. Pyrene (98%) and chloranil (98%) were supplied by Wako Pure Chemical Industries, and benzene (99.5%) was supplied by Jusei Chemical and triphenylamine by Tokyo Kasei Kogyo (99%). They were used without further purification.

Sample films were prepared by two methods. In the first method, solutions of PMMA and scavengers in benzene were cast on a glass plate and air-dried overnight (method 1). In the second method (method 2), a mixture of powdered PMMA and the scavengers or the copolymer were pressed at 160 °C under vacuum with a Vacuum Press (Shibayama Scientific, VP-50) and molded to a film.

The films were γ -irradiated at 77 K. Photoabsorption of the films, which were in a cryostat (Oxford, DN1704), was monitored with a spectrophotometer (Shimadzu, UV-3101PC).

Results and Discussion

Decay of Ions in PMMA through Diffusion. Figure 1 shows photoabsorption spectra of a film containing 0.1 mol of triphenylamine/kg and 0.1 mol of chloranil/kg before and after

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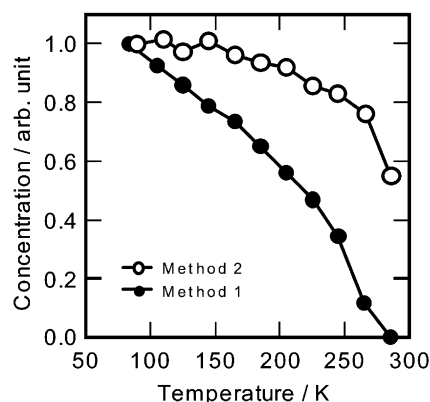


Figure 2. Temperature dependence of the concentration of the triphenylamine cation in two irradiated PMMA films containing 0.1 mol of triphenylamine/kg and 0.1 mol of chloranil/kg irradiated with γ -rays to a dose of 5 kGy at 77 K. One film was prepared by casting a solution of PMMA and the scavengers in benzene on a glass plate and overnight air-drying [method 1 (●)]. The other film was prepared by pressing the mixture of powdered PMMA and the scavengers at 160 °C under vacuum [method 2 (○)].

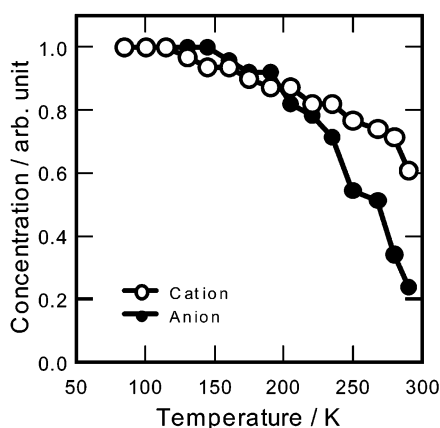


Figure 3. Dependence of the concentration of the triphenylamine cation (●) and the chloranil anion (○) on the temperature in an irradiated PMMA film containing triphenylamine and chloranil. The film was prepared by pressing the mixture of powdered PMMA and the scavengers at 160 °C under vacuum. The sample was γ -irradiated to a dose of 5 kGy at 77 K.

γ -irradiation to a dose of 5 kGy at 77 K. The film was made by casting a solution of PMMA and the scavengers (method 1). The peak at 450 nm is due to chloranil anion,⁴ while the peak at 660 nm is due to triphenylamine cation.⁴ A film generated by pressing the fused mixture of PMMA and the scavengers without solvent (method 2) showed essentially the same spectra. The anion and the cation in both films were stable at 77 K.

However, when the temperature was increased, the stability of the ions in the two films was different. Figure 2 shows the dependence of the concentrations of the cations in the two films on temperature. The film prepared with solvent (method 1) has a lower concentration at a given temperature than the film made without solvent (method 2). The residual solvent facilitates diffusion of the ions. Photoabsorption peaks due to benzene were observed for a neat PMMA film prepared by casting a solution of PMMA in benzene and dried overnight. The estimated concentration is 0.2–0.3 mol/dm³.

PMMA has a positive electron affinity, and negative charge can be trapped in the polymer.⁵ Figure 3 compares the variation of the concentration of the cations and the anions in the film prepared with method 2. The films were γ -irradiated at 77 K,

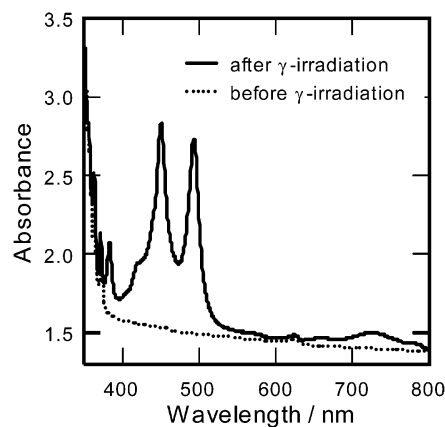


Figure 4. Photoabsorption spectra generated from a PMMA film containing 0.1 mol of pyrene/kg before and after γ -irradiation to a dose of 5 kGy at 77 K. The thickness of the film was 0.6 mm.

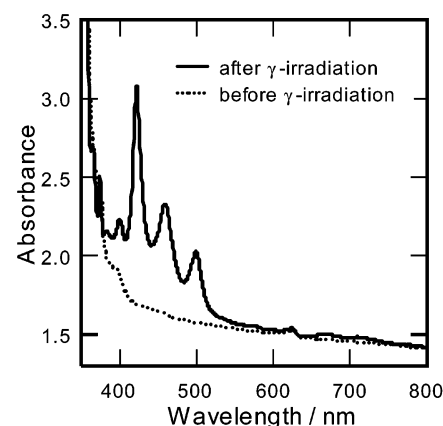
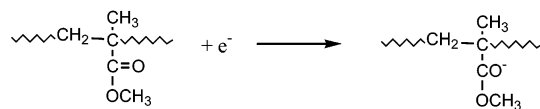


Figure 5. Photoabsorption spectra generated from a film of a copolymer of 1-pyrenylmethyl methacrylate and methyl methacrylate before and after γ -irradiation to a dose of 5 kGy at 77 K. The concentration of the pyrenylmethyl group is 0.01 mol/kg. The thickness of the film was 0.6 mm.

and the variation of the concentration with increasing temperature was evaluated from the absorbance of the peaks. The chloranil anion decays faster than the triphenylamine cation. The film should be electrically neutral. Negative charge corresponding to the difference between the cation and anion concentration will be trapped in PMMA. The anionic species in PMMA will be ketyl-type anions at side chains of the polymer:^{5–8}



The diffusion of the ions in PMMA is confirmed by comparison of the stability of ions in PMMA-containing pyrene with that in the copolymer of 1-pyrenylmethyl methacrylate and methyl methacrylate.

Figure 4 shows the photoabsorption spectrum of a PMMA film containing 0.1 mol of pyrene/kg before and after γ -irradiation to a dose of 5 kGy at 77 K. The peak at 449 nm is due to the pyrene cation, while the peak at 492 nm is due to the pyrene anion.⁴ Figure 5 shows the photoabsorption spectra of a film of the copolymer of 1-pyrenylmethyl methacrylate and methyl methacrylate before and after γ -irradiation to a dose of 5 kGy at 77 K. The copolymer contains 0.1% 1-pyrenylmethyl methacrylate in a monomer unit. The peak at 455 nm is due to

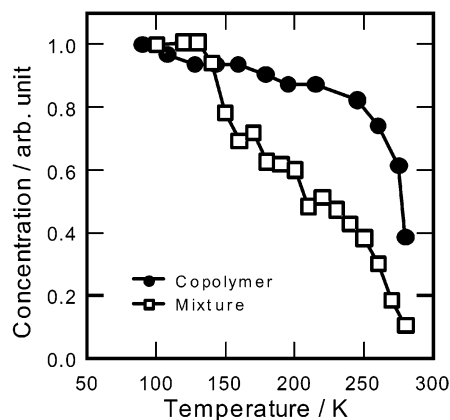


Figure 6. Temperature dependence of the cation concentration in an irradiated PMMA film containing 0.01 mol of pyrene/kg (\square) prepared without a solution and an irradiated film of the copolymer of 1-pyrenylmethyl methacrylate and methyl methacrylate (\bullet). The concentration of the pyrenylmethyl group in the copolymer is 0.01 mol/kg. The sample was γ -irradiated to a dose of 5 kGy at 77 K.

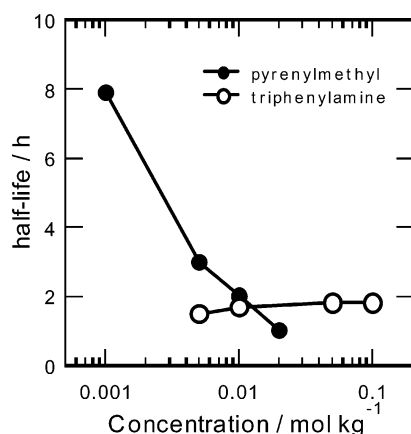


Figure 7. Half-lives of cations in a PMMA film containing triphenylamine and chloranil (\circ) and in a film of the copolymer of 1-pyrenylmethyl methacrylate and methyl methacrylate (\bullet) at room temperature.

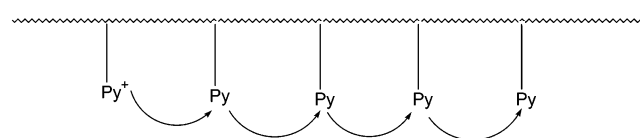
the cation, while the peak at 498 nm is due to the anion. The peak at 420 nm is due to a neutral radical. These assignments were based on the following measurements. A photoabsorption spectrum of a solution of 1-pyrenylmethyl methacrylate in *sec*-butyl chloride γ -irradiated at 77 K exhibited a peak at 460 nm, while a photoabsorption spectrum of a solution of 1-pyrenylmethyl methacrylate in methyltetrahydrofuran γ -irradiated at 77 K exhibited a peak at 498 nm. Cations of the solute are selectively generated in *sec*-butyl chloride, while anions of the solute are selectively generated in methyltetrahydrofuran.⁴ The peak at 460 nm can be assigned as the cation of 1-pyrenylmethyl methacrylate, while the peak at 498 nm can be assigned as its anion. The peaks at 455 and 498 nm in the spectrum of the copolymer will hence be assigned as the cation and anion, respectively. The wavelengths of the peaks are nearly the same as those of the cation and anion of pyrene, suggesting that the charges are trapped at the pyrenyl groups. The photoabsorption spectrum of a film of the copolymer after 254 nm photolysis exhibits a peak at 421 nm, which can be assigned as the neutral radical. Benzyl-type radicals are generated with photolysis of alkyl benzenes, tetralin, and 9,10-dihydrophenanthrene.^{9,10} Similar types of radicals will be generated by photolysis. The peak at 420 nm in the spectrum of the copolymer will hence be assigned as a neutral radical.

Figure 6 compares the temperature dependence of cation concentration in the films of PMMA-containing pyrene and the

copolymer. The cation concentration in the film of PMMA-containing pyrene decreased faster than that in the copolymer with increasing temperatures; at 280 K, it was 10% of the initial concentration, whereas the concentration in the film of the copolymer remains at \sim 40% of the initial concentration. The copolymer suppresses the decay of the cations.

The concentration of anions is lower than those of the cation in both films. The difference in the concentrations is due to the anions trapped at the side chains of PMMA as described above. The anions in both films disappeared at temperatures higher than 150 K. They are converted to the ketyl-type anion at a side chain of PMMA or combine with the cations.

Decay of Ions in PMMA by a Hopping Transfer. The decay of ions in PMMA films is reduced by suppressing the diffusion of the ions. However, the ions in the copolymer still decay with increasing temperatures and with time at room temperature. It is due to migration of positive charge by hopping on the pyrenyl groups:



The half-life for the cations in the copolymer at room temperature is shown in Figure 7. It depends on the concentration of the pyrenyl groups, which indicates the hopping mechanism. This charge migration is an electron transfer from the π orbital of neutral pyrenyl groups to the π orbital of cationic ones, and occurs through electron tunneling. The rate of electron tunneling between π orbitals depends on the orientation of the orbitals.¹¹ The hopping rate increases with increasing rotational and vibrational motions.

The hopping transfer was suppressed in PMMA-containing triphenylamine where the ions decay only through their diffusion. The decay rate is nearly constant for the triphenylamine cation with increasing concentrations of triphenylamine as shown in Figure 7. It is due to the structural change in neutral and cationic triphenylamine. The hopping transfer of cations is a transfer of an electron from a neutral molecule to a cation. If the structure of the neutral molecule and cation is different, this electron transfer must be accompanied by a change in molecular geometry. Nuclear motion occurs on a slower time scale than electron motion. The hopping rate hence decreases according to the Franck–Condon principle.¹²

Structure differences between the neutral molecule and its cation can be evaluated by the difference in the vertical and adiabatic ionization potentials. The vertical ionization potential for triphenylamine is 7.00 eV,¹³ whereas the adiabatic ionization potential is 6.75–6.80 eV.^{14,15} The vertical and adiabatic ionization potentials for pyrene are the same within experimental error.¹⁶ The structures of neutral and cationic triphenylamine are different, whereas the structures of neutral and cationic pyrene are nearly the same, which causes the difference in the hopping rate.

Anions in PMMA are the ketyl-type anions. The structures of the neutral side chain of PMMA and its anion are different. The hopping transfer of the anions is hence slower than that of the cations at the pyrenyl groups, which was confirmed by the following. The half-life for the cations in the copolymer [$\tau_{1/2}(\text{Py})$] is expressed as follows:

$$\tau_{1/2}(\text{Py})^{-1} = (k_{\text{PMMA}}[\text{MMA}]) / (\ln 2) + (k_{\text{Py}}[\text{Py}]) / (\ln 2) \quad (1)$$

where k_{PMMA} is the hopping rate of the anions in neat PMMA, $[\text{MMA}]$ is the monomer basis concentration of PMMA, k_{Py} is the hopping rate of the cations on the pyrenyl groups, and $[\text{Py}]$ is the concentration of the pyrenyl groups. The constants k_{PMMA} and k_{Py} are evaluated by fitting the equation to the experimental values. The estimated values are $0.012 \text{ mol}^{-1} \text{ kg h}^{-1}$ for k_{PMMA} and $65 \text{ mol}^{-1} \text{ kg h}^{-1}$ for k_{Py} . The hopping rate of the anions is less than 1/500 of that of the cations.

Conclusions

Ions trapped by scavengers in PMMA films decay through their diffusion and by hopping transfer of the charge. The diffusion is suppressed by chemically connecting the scavengers to the polymer chain. The hopping transfer is suppressed by using scavengers whose structures of neutral and ionic states are different. If we can make a film in which such a scavenger is bonded to the polymer chain, the stability of the ions in the film will be increased. Preparation of such films is in progress. A study on the stability of ions in these films will be reported shortly.

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