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Pulse Radiolysis Study on Electron-Transfer Reactions in Polymer Solutions at Low Temperatures

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Introduction

Intermolecular reactions of polymers with reactive chemical species, particularly polymer–polymer reactions, are of interest from the viewpoint of polymer science as well as chemical kinetics. A number of studies on diffusion-controlled intermolecular polymer–polymer reactions have been reported previously. These reactions of polymers are mainly concerned with free radicals and excited molecules.[1] The reactions of polymer anions have not been studied until recently. The formation of polymer anions has been investigated by the pulse radiolysis of the systems 2-methyltetrahydrofuran (MTHF)–poly(4-vinylbiphenyl) (PVB),[2,3] hexamethylphosphoramide–poly(methyl methacrylate),[4] and tetrahydrofuran–organopolysilane[5] systems.

Intermolecular polymer–polymer electron-transfer reactions, however, have not been reported as yet. It is generally difficult to separate clearly the electron-transfer reaction of anions from their neutralization reaction with cations. In the present work, we attempt to observe the electron-transfer reaction of polymer anions by pulse radiolysis at low temperature where the neutralization reaction of the anions are retarded remarkably.

Experimental Section

Poly(4-vinylbiphenyl) (PVB) was supplied by Aldrich Chemical Co., and poly(1-vinylpyrene) (PVPy) was synthesized by radical polymerization of 1-vinylpyrene, which was synthesized by Wittig's reaction from 1-pyrenecarboxyaldehyde.[6,7] The average molecular weights of PVB and PVPy were 1.35×10^5 obtained by viscosity measurement and 5×10^4 determined by gel permeation chromatography, respectively. The purification of the polymers was described in a previous paper.[2] Zone-refined biphenyl (Ph_2) and pyrene (Py) (Tokyo Kasei Chemical Co.) were used without further purification. A mixture of 2-methyltetrahydrofuran (MTHF)–tetrahydrofuran (THF) (1:1 in volume) was used as the solvent, since both PVB and PVPy are soluble in the mixture, which is transparent even at low temperature. The purification of the solvents was also described previously.[2] Pulse irradiations were made by generating electron beams with a Febetron 707 accelerator operated at an energy of 2 MeV, and the duration time of a pulse was 20 ns. The radiation dose delivered by one pulse is about 6×10^4 rad. The temperature of the sample can be controlled to a given temperature within ±0.1 K by use of a metal Dewar.[8]

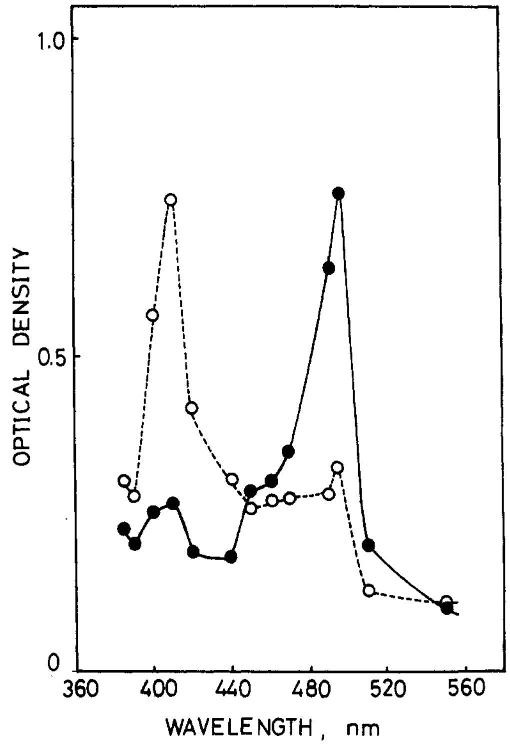

Figure 1. Optical absorption spectra for MTHF–THF–PVB (0.6 M)–PVPy (0.2 M) system at 140 K immediately after pulse irradiation (○) and 60 μs after pulse irradiation (●), respectively.

Results and Discussion

Figure 1 shows optical absorption spectra for the pulse-irradiated MTHF–THF mixtures containing two polymers, PVB and PVPy, as solutes at 140 K. The concentrations of PVB and PVPy are represented by biphenyl and pyrene monomer units (M; mol L^{-1}), respectively. A sharp absorption peak at 410 nm, denoted by open circles, is observed immediately after the pulse irradiation and decays almost to zero within 60 μs. Since the absorption peak at 410 nm is very similar to the absorption spectrum of biphenyl anions, which has a sharp absorption maximum at 408 nm,[9] the absorption peak at 410 nm is attributed to PVB anions (PVB^-),[2] formed by an electron-capture reaction of biphenyl molecules hanging to the polymer chain. A strong absorption band around 496 nm, denoted by filled circles, appears about 60 μs after the pulse irradiation. Since the absorption band around 496 nm coincides with the well-known absorption spectrum of Py anions at 492 nm,[10] the absorption band around 496 nm is ascribed to PVPy anions. Figure 2 shows that the absorption of PVPy anions at 496 nm increases complementarily with a decrease in that of PVB anions at 410 nm. The results demonstrate unambiguously that the electron-transfer reaction occurs from PVB anions to PVPy molecules. A similar electron-transfer reaction from biphenyl anions to PVPy molecules was also observed for the MTHF–THF–Ph_2–PVPy system. The mechanism of formation and decay of the anions in the radiolysis of MTHF–THF mixtures containing both PVB and PVPy is described by the following reaction scheme.

$$\mathrm{M} \rightsquigarrow \mathrm{M}^+ + \mathrm{e}^- \tag{1}$$

$$\mathrm{PVB} + \mathrm{e}^- \rightarrow \mathrm{PVB}^- \tag{2}$$

$$\mathrm{PVPy} + \mathrm{e}^- \rightarrow \mathrm{PVPy}^- \tag{3}$$

$$\mathrm{PVB}^- + \mathrm{PVPy} \rightarrow \mathrm{PVB} + \mathrm{PVPy}^- \tag{4}$$

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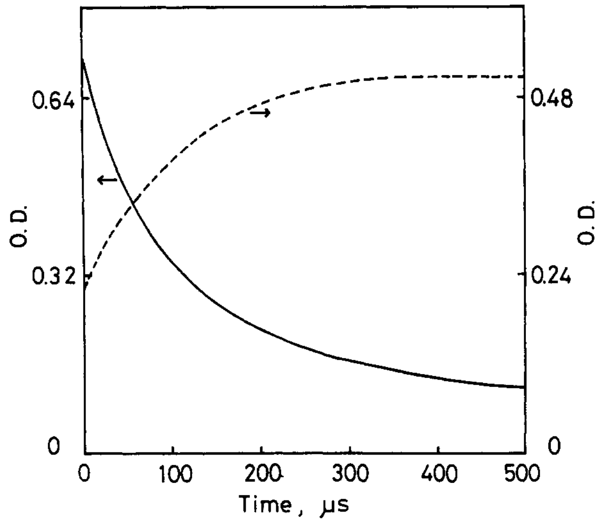

Figure 2. Decay of PVB anions (solid line) and the growth of PVPy anions (dashed line) in the MTHF-THF mixture containing 0.6 M PVB and 0.2 M PVPy after pulse irradiation at 130 K.

Table I
Rate Constants for Electron-Transfer Reactions in the MTHF-THF (1:1 Mixture) Solvents[a]

reaction	k, L mol^{-1} s^{-1} 130 K	k, L mol^{-1} s^{-1} 140 K
$Ph_2^- + Py \rightarrow Ph_2 + Py^-$	3.1×10^7	8.1×10^7
$PVB^- + Py \rightarrow PVB + Py^-$	7.2×10^6	1.5×10^7
$Ph_2^- + PVPy \rightarrow Ph_2 + PVPy^-$	1.0×10^6	2.5×10^6
$PVB^- + PVPy \rightarrow PVB + PVPy^-$	2.8×10^4	8.9×10^4

[a] Ph_2, Py, PVB, and PVPy represent biphenyl, pyrene, poly(4-vinylbiphenyl), and poly(1-vinylpyrene), respectively.

M represents MTHF or THF. Though reactions 2 and 3 are competitive processes for electron capture, PVB captures electrons more efficiently than PVPy immediately after pulse irradiation under our experimental conditions. This is shown in Figures 1 and 2. Then, $PVPy^-$ is formed by an electron-transfer reaction from PVB^- to PVPy. The decay rate of PVB anions by the electron-transfer reaction is represented by the following equation

$$-d[PVB^-]/dt = k[PVPy][PVB^-] \qquad (5)$$

where k is a decay rate constant. Since the concentration of PVPy, [PVPy], is sufficiently high compared to the concentration of PVB anions, $[PVB^-]$, and consequently [PVPy] is approximately constant, the decay of PVB anions can be regarded as a pseudo-first-order process. In fact, the decay of the PVB anions shown in Figure 2 can be represented by a first-order kinetic plot. Thus, the rate constant, k, for the electron-transfer reaction from PVB anions to PVPy molecules was obtained as 2.8×10^4 L mol^{-1} s^{-1} at 130 K. Similar kinetic treatments were operative for other electron-transfer reactions in the MTHF-THF-Ph_2-PVPy, MTHF-THF-PVB-Py, and MTHF-THF-Ph_2Py systems.

The rate constants obtained for all the systems studied in the present work are summarized in Table I. The electron-transfer rates from biphenyl anions to pyrene molecules are about as thousand times as large as those from PVB anions to PVPy molecules at 130 and 140 K. The rate for the electron-transfer reaction decreases with decreasing temperature and is probably controlled by a diffusion process. The much larger electron-transfer rate for the $Ph_2^- + Py$ reaction than that for the $PVB^- + PVPy$ reaction corresponds to the large diffusion coefficient for biphenyl anions and pyrene molecules as compared with that for PVB anions and PVPy polymers.

Since, the radius of gyration of PVB polymer coils is 107 Å in MTHF,[3] the critical concentration of the polymer coil overlap is estimated as 0.3 M. In the MTHF-THF-PVB-PVPy system, the concentration of PVB used is 0.6 M, which is higher than the critical concentration. Thus it appears that the electron-transfer reaction from PVB anions to PVPy polymers is caused by the diffusion of polymer chains. The rate constant, k, for a bimolecular diffusion-controlled reaction of spherical particles is represented by the following Stokes-Einstein equation

$$k = 4\pi RD \qquad (6)$$

where R is the radius of the reaction sphere and D is the sum of the diffusion coefficients of two reacting particles. In the electron-transfer reaction of the polymer system, the reaction takes place between biphenyl anions and pyrene molecules hanging to polymer chains. Thus, R is regarded as the sum of the radii of biphenyl and pyrene molecules and is taken to be 7 Å. D equals $D_{PVB} + D_{PVPy}$, where D_{PVB} and D_{PVPy} are the diffusion coefficients of PVB and PVPy polymer chain, respectively. Thus the values of D can be obtained from the experimental value of k for the electron-transfer reaction, and they were estimated as 5.3×10^{-11} cm^2 s^{-1} at 130 K and 1.7×10^{-10} cm^2 s^{-1} at 140 K. It appears that the rate of the electron transfer in the semidilute region of polymer solution is closely related to the diffusional motion of polymer chains. Since the optical absorption of the anions in this system is very strong, the electron-transfer reaction can be used in the future as a probe of diffusional motion of polymer in the glassy state.

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Registry No. PVB, 25232-08-0; PVPy, 25120-43-8; MTHF, 96-47-9; THF, 109-99-9.

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Anionic Synthesis of Isotactic Polystyrene

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Introduction

The synthesis of isotactic polystyrene (iPS) is usually accomplished using some form of coordination chemistry such as Ziegler-Natta catalysis. Early experiments by

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