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Photoinduced Electron Transfer in Acceptor Polymer Poly(vinyl methyl terephthalate) and Its Anion Radical Behavior Studied by Laser Photolysis

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ABSTRACT: Photoinduced electron transfer in a heteroexcimer system of excited *N*-ethylcarbazole (electron donor)–poly(vinyl methyl terephthalate) (electron acceptor) was studied by nanosecond ruby-laser photolysis in benzonitrile at room temperature. The behavior of the ion radicals thus formed in the polymer system was investigated in comparison with those in model compounds: dimethyl terephthalate and three dimer model compounds. The transient absorption spectrum of the acceptor polymer system was the same as those of the monomer and dimer model compounds. However, anion radical transfer experiments show that the anion radical formed in the polymer chain does not transfer to an acceptor *p*-dicyanobenzene, while the anion radical in the monomer and dimer systems easily transfers the electron to the acceptor *p*-dicyanobenzene. The results suggest that the anion radical in the polymer system is stabilized by the interaction with neighboring chromophores and its electron transfer is suppressed.

Introduction

Polymer systems show several photophysical and photochemical behaviors characteristic of a high local concentration of chromophores in contrast to dilute homogeneous systems. For example, efficient energy migration along the polymer chain[1] and considerable annihilation of excited states under high-intensity excitation have been reported.[2,3] As for the photoionization process of polymer systems, peculiar solvent effects,[4–6] e.g., emission spectra of transient excited species are not much affected by solvent polarity and have been observed for copolymers that have pendant electron donor and acceptor groups. Also, the cation radical formed in poly(*N*-vinylcarbazole) (PVCZ) was reported to be stabilized by the neighboring chromophores.[7] As for the stabilization of ion radicals, dimer cation radicals have been well investigated by ESR[8] and optical spectroscopy after γ-ray irradiation in rigid media[9–12] and by the pulse radiolysis method.[13] However, very little knowledge about dimer anion radicals has been obtained thus far,[14] since only under special conditions are the dimer anion radicals of aromatic compounds formed.[15]

It is known that excited singlet carbazole residue interacts with dimethyl terephthalate (DMTP) and forms a heteroexcimer in nonpolar solvents and that in polar solvents photoionization occurs and carbazole cation radical and DMTP anion radical are produced.[16,17] In this study, the photoinduced electron-transfer process and the behavior of ion radicals thus formed were investigated for the system of *N*-ethylcarbazole (ECZ)–poly(vinyl methyl terephthalate) (PMTP). With regard to photoinduced electron transfer, the electron-transfer rate constant, the quantum yield of ion radical formation, and the ion radical recombination rate constant for the polymer were compared with those of the monomer and dimer model compounds. The stabilization of anion radicals in the polymer was investigated by the ion radical transfer method.[18] The results show several polymer effects, e.g., higher yield of ion radical formation and stabilization of ion radicals in the polymer chains.

Results

Photoionization of Methyl Terephthalate (MTP) Derivatives. The compounds studied in this investigation are denoted in Figure 1 with their abbreviations. DMTP is a monomer model of PMTP, whereas, 1,2-MTP, 1,3-MTP, and 2,4-MTP (racemate) are the dimer models of PMTP. In this paper, MTP represents the methyl terephthalate residue $CH_3OCOPhCOO$–.

The fluorescence quenching rate constant of $^1ECZ^*$ by MTP residue was obtained from the Stern–Volmer plot and is listed in Table I. Quenching rate constants (k_q) for DMTP and dimer models are all approximately the diffusion-controlled values, ca. 10^{10} M^{-1} s^{-1}. The k_q value for the $^1ECZ^*$–PMTP system is not listed since the effective chromophore concentration of the polymer system cannot be estimated.

Laser photolysis experiments were carried out for the systems of ECZ–electron acceptors in benzonitrile solvent at room temperature. ECZ was excited by a second harmonic pulse of a *Q*-switched ruby laser (347 nm, 14-ns pulse width). The electron-transfer process from excited singlet ECZ ($^1ECZ^*$) to MTP residue produces the cation

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Table I
Photoionization and Anion Radical Properties of PMTP Compared with Other Methyl Terephthalate Derivatives[a]

	PMTP	1,2-MTP	1,3-MTP	2,4-MTP	DMTP
$E_{1/2}$ vs. Ag/Ag$^+$		-1.99	-1.98	-1.99	-2.11
k_q/M^{-1} s^{-1} [b]		1.6×10^{10}	1.1×10^{10}	9.8×10^9	8.8×10^9
OD_{530}/OD_{780} [c]	1.5	1.4	1.4	1.5	1.4
Φ_{ion} [d]	3.5	1.1	1.0	1.2	1.0
k_r/M^{-1} s^{-1} [e]	1.5×10^9	3.2×10^9	4.5×10^9	5.0×10^9	6.6×10^9
$k_{tr,D}$/M^{-1} s^{-1}	no transfer	2×10^8	6×10^8	1×10^9	1×10^9
$k_{tr,T}$/M^{-1} s^{-1}	1.5×10^9				

[a] Abbreviations are given in Figure 1 and in the scheme. All measurements were made in benzonitrile solution at room temperature. [b] Quenching rate constants of $^1ECZ^*$ by MTP. [c] Optical density ratios at 530 nm (absorption maximum of MTP$^-\cdot$) and at 780 nm (absorption maximum of ECZ$^+\cdot$). The ratios were obtained at 300 ns after photoexcitation. [d] Relative quantum yields of free ion radical formation at the condition of 60% quenching of $^1ECZ^*$. [e] Recombination rate constants of MTP$^-\cdot$ with ECZ$^+\cdot$.

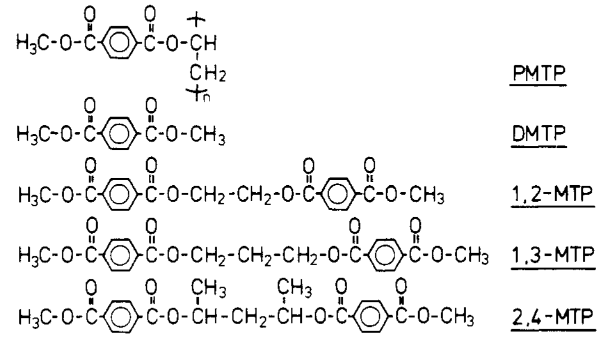


Figure 1. Methyl terephthalate derivatives with their abbreviations.

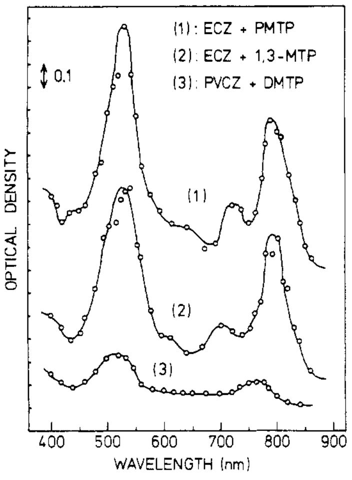
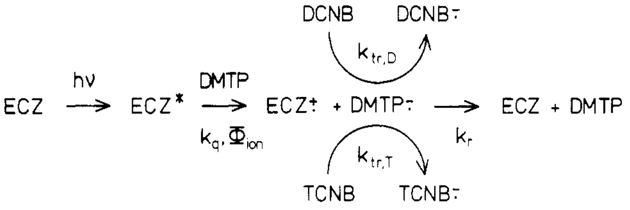


Figure 2. Transient absorption spectra obtained at 300 ns after photoexcitation in benzonitrile at room temperature: (1) [ECZ] = 2.8×10^{-4} mol/L and [PMTP] = 1.0×10^{-1} unit mol/L; (2) [ECZ] = 2.8×10^{-4} mol/L and [1,3-MTP] = 2.0×10^{-2} mol/L; (3) [PVCZ] = 4.6×10^{-4} unit mol/L and [DMTP] = 2.0×10^{-2} mol/L.

radical of ECZ (ECZ$^+\cdot$) and the anion radical of MTP (MTP$^-\cdot$). Curves no. 1 and no. 2 in Figure 2 are the transient absorption spectra obtained for PMTP and 1,3-MTP as acceptors, respectively. Curve no. 3 is the reference spectrum of PVCZ as a donor and DMTP as an acceptor. The absorption band around 780 nm and around 530 nm for spectra no. 1 and no. 2 are ascribed to ECZ$^+\cdot$ and MTP$^-\cdot$, respectively.[2,3,16b] These two spectra show practically no difference, and other anion radicals of 1,2-MTP, and 2,4-MTP studied in this investigation showed the same spectra. The ratios of optical density at 530 nm to that at 780 nm (OD_{530}/OD_{780}) are listed in Table I. Almost the same values of these ratios indicate the identical nature of these spectra. As for spectrum no. 3, the absorption bands are small and the absorption band of PVCZ$^+\cdot$ appears at ca. 750 nm. High-intensity excitation of PVCZ by a laser pulse causes S_1–S_1 annihilation in PVCZ polymer chain,[2,3] and therefore the amount of produced ion radicals is reduced compared with the systems for spectra no. 1 and no. 2. The shift of a band peak from 780 (ECZ$^+\cdot$) to 750 nm (PVCZ$^+\cdot$) is due to some interaction of CZ$^+\cdot$ with the neighboring CZ chromophores.

Scheme I



The comparison of the relative quantum yield of photoionization for PMTP with those for monomer and dimer models is made in Table I. To do this, it is necessary to normalize the excitation intensity and the quenching value of ECZ fluorescence. The former condition is attained by exciting the same concentration of ECZ at a constant laser intensity, and the latter is normalized at the condition of 60% quenching of ECZ fluorescence with MTP residue. Under these conditions, the relative yields of transient absorption of ECZ$^+\cdot$ give the relative quantum yields of photoionization (Φ_{ion}) and these values are listed in Table I. The system of ECZ–PMTP gives a markedly high value of 3.5.

The recombination rate constant of ion radical of ECZ$^+\cdot$ with MTP$^-\cdot$ is obtained by the analysis of transient absorption decay of ion radicals. The values of the recombination rate constant (k_r) are also listed in Table I. It is noted that the k_r for ECZ$^+\cdot$–PMTP$^-\cdot$ is the smallest and it is only a quarter of the value for the ECZ$^+\cdot$–DMTP$^-\cdot$ pair.

Anion Radical Transfer Systems. Ion radicals produced by photoexcitation deactivate by recombination; e.g., DMTP$^-\cdot$ recombines with ECZ$^+\cdot$. However, the addition of 1,4-dicyanobenzene (DCNB) (reduction potential: $E_{1/2}$ = −1.97 V vs. Ag/Ag$^+$),[19] which is a stronger acceptor than DMTP ($E_{1/2}$ = −2.11 V vs. Ag/Ag$^+$),[19] to the system as a third solute accelerates the decay of DMTP$^-\cdot$ accompanying the formation of DCNB$^-$. By the analysis of DMTP$^-\cdot$ decay with DCNB$^-\cdot$ growth, it is possible to determine the anion radical transfer rate constant $k_{tr,D}$, where the suffix D denotes the electron transfer to DCNB. The processes of anion radical transfer are shown in Scheme I, and the analysis of ion radical transfer processes are described elsewhere.[18] 1,2,4,5-Tetracyanobenzene (TCNB) ($E_{1/2}$ = −1.02 V vs. Ag/Ag$^+$),[19] which is a stronger acceptor than DCNB, was also used as a third solute: the electron-transfer rate constant is represented by $k_{tr,T}$, where the suffix T denotes the electron transfer to TCNB. Of course, DCNB or TCNB quenches $^1ECZ^*$ and produces their ion

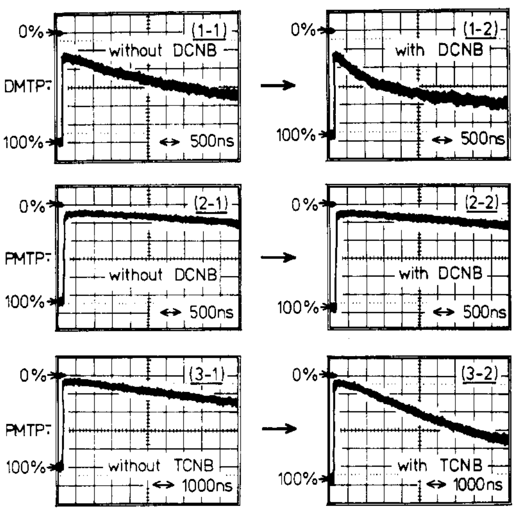


Figure 3. Oscillograms of transient absorption of MTP$^-\cdot$ at 530 nm in benzonitrile at room temperature: (1-1) [ECZ] = 2.8×10^{-4} mol/L and [DMTP] = 2.0×10^{-2} mol/L; (1-2) [DCNB] = 4.0×10^{-4} mol/L was added to (1-1); (2-1) [ECZ] = 2.8×10^{-4} mol/L and [PMTP] = 1.0×10^{-1} unit mol/L; (2-2) [DCNB] = 4.0×10^{-4} mol/L was added to (2-1); (3-1) the same decay as (2-1) with a different time scale; (3-2) [TCNB] = 1.0×10^{-4} was added to (3-1).

radicals, however, by proper adjustment of each concentration, this process can be made negligible. Figure 3 shows the oscillograms obtained at 530 nm, which is the absorption maximum of MTP$^-\cdot$. Oscillogram 1-1 is the decay of DMTP$^-\cdot$ in the absence of DCNB. The decay was well analyzed by the bimolecular recombination of DMTP$^-\cdot$ with ECZ$^+\cdot$. This decay behavior observed at 530 nm agreed with that of ECZ$^+\cdot$ (780 nm). By the addition of 4.0×10^{-4} mol/L DCNB to the system, the absorption decay of DMTP$^-\cdot$ was accelerated as shown in oscillogram 1-2. At the wavelength 430 nm, which corresponds to the absorption maximum of DCNB$^-\cdot$, the concordant growing up with DMTP$^-\cdot$ decay was observed.

In the polymer system of PMTP, however, addition of DCNB to the system does not accelerate the decay of PMTP$^-\cdot$, as shown in oscillograms 2-1 and 2-2 in Figure 3. The anion radical formed in PMTP did not transfer to DCNB. However, the addition of TCNB to this polymer system caused the anion radical transfer from PMTP$^-\cdot$ to TCNB as shown in the oscillograms 3-1 and 3-2. The formation of TCNB$^-\cdot$ was confirmed by the growth of absorption at 457.5 nm, which is the absorption maximum of TCNB$^-\cdot$. The rate constants of anion radical transfer are listed in Table I, where $k_{\mathrm{tr,D}}$ and $k_{\mathrm{tr,T}}$ are the ones from MTP$^-\cdot$ to DCNB and from MTP$^-\cdot$ to TCNB, respectively (see Scheme I).

The values of $k_{\mathrm{tr,D}}$ are obtained from the decay of MTP$^-\cdot$ and the rise of DCNB$^-\cdot$. At the short time range (<3 μs in oscillogram 1-2 of Figure 3), the decay of MTP$^-\cdot$ agreed well with the expected curve from the scheme, and the calculation of $k_{\mathrm{tr,D}}$ was made in this time range. However, for longer time after the excitation (>3 μs), the decay of MTP$^-\cdot$ at 530 nm deviates from the expected curve, since some unknown absorption overlaps. Since UV absorption of the samples after the laser photolysis shows no evidence of irreversible chemical reactions, a longer component at the 530-nm band may be some transient intermediates. In the system of TCNB as a second acceptor, no absorption of such transient intermediates was found.

Discussion

As shown in Table I, the quenching rate constants (k_q) for DMTP and dimer model compounds are almost the same and they are approximately diffusion-controlled. The reduction potentials of three dimer models are almost the same and that of DMTP is slightly more negative but very close to the other three. The reduction potential of PMTP is also considered to be nearly the same as the values of DMTP and dimer models, because the reduction potential is for MTP residues in the ground state and there is no specific interaction between MTP residues.

The transient absorption spectra of no. 1 and no. 2 in Figure 2 and the values of $\mathrm{OD}_{530}/\mathrm{OD}_{780}$ in Table I show that the shape of the absorption bands, peak wavelength, and molar extinction coefficient are the same for all MTP anion radicals. Electronic transition of the anion radical for the dimer models seems not to be affected by the interaction of MTP$^-\cdot$ with the neighboring chromophores. In the system PVCZ–DMTP (no. 3 in Figure 2), the absorption bands observed were weak. This is because the S_1–S_1 annihilation process in PVCZ diminishes the photoionization and because the molar extinction coefficient of PVCZ$^+\cdot$ is reduced by the interaction of CZ$^+\cdot$ with neighboring chromophores.[2,3] Intramolecular interaction of chromophores in the excited singlet state and in the ionic states has been studied on the dimer models of PVCZ. The photoexcitation of two diastereoisomers of 2,4-di(*N*-carbazolyl)pentane gives different excimers: the sandwich type and the second excimer.[20] The electron-transfer quenching of these excimers by an electron acceptor gives two types of cation radicals.[21] As far as the absorption spectrum is concerned, the racemic isomer of 2,4-MTP did not show any evidence of specific interaction of MTP$^-\cdot$ with another MTP moiety. This suggests a rather weak interaction of the anion radical MTP$^-\cdot$ with another chromophore MTP.

As for photoionization quantum yield, PMTP produced 3.5 times as many ion radicals as DMTP. One explanation for this result is that the fast stabilization of PMTP$^-\cdot$ by the neighboring MTP residue suppresses the geminate recombination of PMTP$^-\cdot$ with ECZ$^+\cdot$. The relaxation time of small conformational change of pendant chromophores may be fast enough to suppress the geminate recombination. In fact, in good solvents such as benzonitrile, the relaxation time of molecular motion of pendant chromophores, which is less than a few nanoseconds, allows efficient intramolecular exciplex formation.[4] Another explanation is that this result is due to the heterogeneous microenvironment in polymer solutions. The methylene chain of PMTP forms a nonpolar field around the polymer backbone in polar benzonitrile solvent. After electron transfer from ^{1}ECZ* to PMTP at a certain distance, ECZ$^+\cdot$ thus produced is solvated immediately by benzonitrile solvent and is taken apart from the nonpolar polymer chain, and the geminate recombination of PMTP$^-\cdot$ with ECZ$^+\cdot$ may be suppressed.

As for the recombination rate constant (k_r) of MTP$^-\cdot$ with ECZ$^+\cdot$, PMTP$^-\cdot$ shows the smallest k_r. The value of k_r for PMTP$^-\cdot$ is only a quarter of that for DMTP$^-\cdot$. According to the diffusion-controlled reaction model, k_r is expected to be half of the value of the recombination of DMTP$^-\cdot$ with ECZ$^+\cdot$. However, if the anion radical sites in PMTP$^-\cdot$ migrate along the polymer chain, the increase of active sphere radius is expected to overcome the decrease of diffusion constant and then k_r should become large.

This is not the case for the recombination of PMTP$^-\cdot$ with ECZ$^+\cdot$: the value is reduced to one-quarter. Therefore, the anion radical site in PMTP$^-\cdot$ does not seem to migrate. Decrease of the recombination rate constant may be due to the anion radical stabilization by neighboring chromophores and/or the steric hindrance of the polymer backbone. For all the samples, the decrease of k_r parallels the decrease of $k_{tr,D}$, which may reflect the increase of the anion radical stabilization as described below.

As mentioned above, the electronic transition for all MTP anion radicals in this study was not affected by the neighboring chromophores. However, the anion radical transfer experiments revealed the stabilization of $MTP^{-\cdot}$ for PMTP, 1,2-MTP, and 1,3-MTP. In this study, the electron-transfer rates of the produced anion radical $MTP^{-\cdot}$ to stronger acceptors, DCNB and TCNB, were examined. The value of $k_{tr,D}$ or $k_{tr,T}$ is a measure of the anion radical stabilization. The anion radical of PMTP did not transfer to DCNB. 2,4-$MTP^{-\cdot}$ ($E_{1/2}$ = −1.99 V vs. Ag/Ag^+) gave the same transfer rate constant as $DMTP^{-\cdot}$. The value of $k_{tr,D}$ (6×10^8 M^{-1} s^{-1}) for 1,3-$MTP^{-\cdot}$ ($E_{1/2}$ = −1.98 V vs. Ag/Ag^+) is smaller than that for $DMTP^{-\cdot}$, and the value of $k_{tr,D}$ for 1,2-$MTP^{-\cdot}$ ($E_{1/2}$ = −1.99 V vs. Ag/Ag^+) is one-fifth of the value for $DMTP^{-\cdot}$. It is noted that 1,2-$MTP^{-\cdot}$ has a smaller $k_{tr,D}$ than 1,3-$MTP^{-\cdot}$. The structure of a dimer anion radical is expected to be of a sandwich type where π electrons of the two chromophores have the strongest interaction.[14,15] This sandwich type structure is most stable for the excimer when two moieties are linked by three methylene chains,[22] which corresponds to 1,3-MTP in this study. However, 1,2-MTP has a stronger interaction than 1,3-MTP. This is explained by the fact that the oxygen atom in the ester linkage modifies the C3 rule and the moieties linked by two methylene chains have a stronger interaction than those linked by three methylene chains. The fact that 2,4-$MTP^{-\cdot}$ and $DMTP^{-\cdot}$ have the same $k_{tr,D}$ value indicates that the conformation of two chromophores for 2,4-$MTP^{-\cdot}$ does not allow appreciable interaction. The situation is not similar to the case of the racemic isomer of 2,4-di(*N*-carbazolyl)pentane: large carbazole chromophores of racemic isomer partially overlap to form a second excimer type of dimer cation radical.[21]

The anion radical of PMTP does not transfer to DCNB ($E_{1/2}$ = −1.97 V vs. Ag/Ag^+), but it transfers to TCNB ($E_{1/2}$ = −1.02 V vs. Ag/Ag^+). This is because the anion radical formed in the polymer chain is stabilized by the interaction with the neighboring chromophores or steric hindrance of polymer backbone. When the electron-transfer process is diffusion-controlled, the rate between the polymer and a small molecule is expected to be roughly half of that for the system of small molecules. In this study, no electron transfer was observed. The steric factor for a small molecule to approach pendant chromophores in polymer chain is also small: anion radical transfer could be observed for the copolymer of vinyl acetate with a low fraction (12%) of vinyl methyl terephthalate. Therefore, thermodynamic stabilization of $MTP^{-\cdot}$ seems to be a main cause. The free energy change of anion radical transfer from $DMTP^{-\cdot}$ to DCNB and to TCNB is estimated to be 3 and 25 kcal/mol, respectively, from the electrochemical data.[19] Therefore, it is estimated that the anion radical formed in PMTP is stabilized more than 3 kcal/mol but less than 25 kcal/mol by the neighboring chromophores when thermodynamic stabilization is assumed. As for the case of $CZ^{+\cdot}$ in PVCZ, this stabilization energy is estimated to be 9–17 kcal/mol.[7]

In the present system, stabilization of the anion radical $MTP^{-\cdot}$ was observed, but the transient absorption spectra for both PMTP and dimer models were the same as that for the monomer anion radical. This is different from the case of cation radicals whose dimers show a rather large spectral shift. For the anion radical, however, the interaction may not be so large as to induce the spectral shift. The dimer ion radicals are known to have charge-resonance bands in the IR region.[14,15] The study of this band may give further information on the ion radicals formed in polymer systems.

In conclusion, the anion radical formed in PMTP is stabilized by the interaction of $MTP^{-\cdot}$ with the neighboring pendant chromophores, resulting in a more stable anion radical that cannot be transferred to DCNB. However, the interaction is not so large as to change the shape of the absorption band of $MTP^{-\cdot}$. The quantum efficiency of photoionization for PMTP was found to be 3.5 times as large as DMTP. This is also ascribed to the stabilization of anion radical.

Analysis of anion radical behavior suggests that the produced anion radical in PMTP is localized and it does not migrate along the polymer chain.

Experimental Section

Materials. Polymers. PVCZ (Tokyo Kasei Kogyo Co.) was purified by reprecipitation and the estimated weight-average molecular weight was about 8×10^5. The synthesis of vinyl methyl terephthalate was made by the ester-exchange reaction of vinyl acetate with terephthalic acid monomethyl ester (Tokyo Kasei Kogyo Co.).[23] Vinyl methyl terephthalate was purified by silica-gel column chromatography, and radical polymerization initiated by AIBN in benzene solution gave PMTP. GPC analysis gave the number-average and the weight-average molecular weight of PMTP as 1.3×10^4 and 2.5×10^4, respectively.

Dimer Model Compounds. 1,2-Bis[*p*-(methoxycarbonyl)-benzoyloxy]ethane (1,2-MTP), 1,3-bis[*p*-(methoxycarbonyl)-benzoyloxy]propane (1,3-MTP), and 2,4-bis[*p*-(methoxycarbonyl)benzoyloxy]pentane (2,4-MTP) were prepared from their corresponding diols. These dimer models were purified by recrystallization. Identification was made by IR, NMR spectra, and elemental analysis. The existence of two diastereoisomers of 2,4-MTP was confirmed by NMR analysis for the crude product of 2,4-pentanediol (Aldrich Chemical Co.) with terephthalic acid monomethyl ester chloride. However, the recrystallization gave only the crystalline racemic isomer, and this isomer was used as 2,4-MTP in this study: δ_H (90 MHz; $CDCl_3$; Me_4Si) 1.30–1.44 (CH_3 for racemi), 1.04–1.16 (CH_3 for meso).

Other Chemicals. ECZ (Aldrich Chemical Co.), dimethyl terephthalate (DMTP, Wako Pure Chemical Industry Ltd.), and DCNB (Wako Pure Chemical Industry Ltd.) were purified by recrystallization. TCNB was synthesized from pyromellitic dianhydride[24] and was purified by recrystallization. Benzonitrile (Wako Pure Chemical Industry Ltd.) was purified by distillation under reduced pressure several times.

Spectroscopic Measurements. The transient absorptions were obtained by the nanosecond laser photolysis method. Photoexcitation was made by a *Q*-switched giant pulse ruby laser (NEC SLG2009) fitted with a KDP frequency doubler. The 347-nm light pulse has 10-mJ pulse energy and 14-ns pulse duration. All samples for laser photolysis were degassed by the freeze–pump–thaw method in a Pyrex ampule fitted with a 1-cm quartz cell. Measurements were carried out in benzonitrile solvent at room temperature. The absorption spectra of ion radicals ($ECZ^{+\cdot}$, $DMTP^{-\cdot}$, $DCNB^{-\cdot}$, and $TCNB^{-\cdot}$) were identified by γ-ray irradiation in rigid matrices at 77 K.[25] Molar extinction coefficients of these anion radicals for kinetics were determined by the comparison of these spectra with that of $ECZ^{+\cdot}$ by laser photolysis at room temperature.[18] The values of molar extinction coefficient of ion radicals used in these experiments are as follows: 9.4×10^3 M^{-1} cm^{-1} for $ECZ^{+\cdot}$ (780 nm), 12.3×10^3 M^{-1} cm^{-1} for $DMTP^{-\cdot}$ (530 nm), 6.5×10^3 M^{-1} cm^{-1} for $DCNB^{-\cdot}$ (430 nm), and 10.0×10^3 M^{-1} cm^{-1} for $TCNB^{-\cdot}$ (457.5 nm).

Absorption spectra were measured by a Shimadzu UV-200S spectrophotometer, and fluorescence spectra were measured by a Shimadzu RF-501 spectrofluorophotometer.

Electrochemical Measurements. Oxidation and reduction potentials were measured by cyclic voltammetry in acetonitrile vs. Ag/0.01 N Ag^+ as a reference electrode.

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Registry No. DCNB, 623-26-7; TCNB, 712-74-3; PVCZ, 25067-59-8; PMTP, 101199-72-8; 1,2-MTP, 2225-04-9; 1,3-MTP, 101199-70-6; 2,4-MTP, 101199-71-7; DMTP, 120-61-6; ECZ, 86-28-2.

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Propagation Rate Coefficients from Electron Spin Resonance Studies of the Emulsion Polymerization of Methyl Methacrylate

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ABSTRACT: The first results are reported for the quantitative application of ESR spectroscopy to emulsion polymerization kinetics. When this technique, in conjunction with dilatometric rate measurements, was applied to the seeded emulsion polymerization of methyl methacrylate at 50 °C, the dependence of the propagation rate coefficient (k_p) on the weight fraction of polymer (w_p) was found to be $k_p = k_p{}^0$ ($0.33 \le w_p \le 0.84$) and $k_p = k_p{}^0 \exp\{-29.8[w_p - 0.84]\}$ ($0.84 \le w_p \le 0.99$), where $k_p{}^0 = 790 \pm 300$ dm^3 mol^{-1} s^{-1}. These results reflect the passage of the latex particles through their glass transition point (at $w_p = 0.84$), leading to the propagation step being controlled by the diffusion of monomer to the propagation site. The observed decrease in k_p for $w_p > 0.84$ appears to be less dramatic than that predicted by current free volume theories.

Introduction

We have reported previously[1] how it is possible to utilize modern ESR spectrometers (possessing both long-term field stability and high sensitivity) for the detection of free radicals in the emulsion polymerization of certain monomers (e.g., methyl methacrylate). The accumulation of ESR spectra using frozen samples opens up the possibility of measuring directly the time evolution of the free-radical concentration during emulsion polymerizations. Furthermore, such direct quantitative measurements of the free-radical concentration when coupled with concomitant measurements of the instantaneous polymerization rate allow the propagation rate coefficient (k_p) to be determined directly over a relatively wide range of polymer concentrations. We report here the first application of this method, the system chosen for study being the emulsion polymerization of methyl methacrylate. The values determined for k_p by this direct ESR method are virtually independent of any model-based assumptions. The major uncertainty in the method arises from the necessity of calibrating the ESR spectrometer.

The method provides in principle a means of measuring absolute values for k_p. In practice, it provided in this study accurate results for the relative values of k_p as the system passed through the glass transition point and then proceeded beyond it, due to the consumption of monomer. Melville and co-workers[2] have previously reported that the propagation rate coefficient for methyl methacrylate de-

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