

Stabilization of an Anion Radical Formed in Poly(vinyl methyl terephthalate) Studied by Anion Radical Transfer Method

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ABSTRACT: Photoexcitation of *N*-ethylcarbazole (donor) in the presence of a polymer having terephthalate chromophores (acceptor) in solution produces a terephthalate anion radical in the polymer. The stability of the terephthalate anion radical (TP⁻) in the polymer chain was investigated by the anion radical transfer method using nanosecond laser photolysis. The samples were poly(vinyl methyl terephthalate) (PVMTTP), copolymers of vinyl methyl terephthalate (VMTP) with vinyl acetate (VAc), and the monomer model compound, dimethyl terephthalate (DMTP). The anion radical TP⁻ formed in the homopolymer, PVMTTP does not transfer an electron to 1,4-dicyanobenzene (DCNB), but the monomer model compound, DMTP does, although the two systems have the same transient absorption spectrum. As for the anion radical TP⁻ in the copolymer, the anion radical transfer to DCNB has two components, a fast and a slow component: the fast component has a rate constant of $7.7 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ and the slow component is extremely slow. The fraction of the slow component increases with the VMTP fraction. The results show that the neighboring interactions of TP residues in the polymer chain stabilize the anion radical of the TP residue. The anion radical TP⁻ formed in the polymer is stabilized partly due to neighboring interactions and partly due to the steric hindrance of the polymer chain to an approaching DCNB.

KEY WORDS Stabilization / Neighboring Chromophore Interaction / Anion Radical / Anion Radical Transfer / Laser Photolysis / Poly(vinyl methyl terephthalate) / Poly(vinyl methyl terephthalate-co-vinyl acetate) / Dicyanobenzene /

In photophysical and photochemical processes in polymers having chromophores as pendant groups, interactions between neighboring chromophores play important roles. Recently extensive investigations have been made on interactions between an excited chromophore and a ground state one (excimer and exciplex) or between an ion radical chromophore and a neutral one (dimer ion radical).¹⁻⁶

As for excited chromophores in polymers, the excitation energy migrates efficiently along the polymer chain,⁷⁻⁹ and an intramolecular excimer is formed through energy migration.^{10,11} Annihilation of excited states also occurs frequently through energy migration under a high photon-density excitation such as laser excitation.^{12,13}

A dimer ion radical is formed by interactions between an ion radical chromophore and

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an adjacent ground state chromophore. The properties of cation radicals formed in polymers and in the dimer model compounds have been investigated using ESR,^{14,15} CIDNP,¹⁶ gamma-ray experiment,¹⁷⁻²⁰ pulse radiolysis,^{21,22} and laser photolysis.^{23,24} Recently, we reported the stabilization of the cation radical formed photochemically in poly(*N*-vinylcarbazole) (PVCz) and its dimer model compounds (1,3-di(*N*-carbazolyl)propane and 2,4-di(*N*-carbazolyl)pentanes). We used the cation radical transfer method with nanosecond laser photolysis, and estimated quantitatively the stabilization energy of the dimer cation radical for the dimer model compounds.²⁵ On the other hand, there are only a few reports about the formation of aromatic dimer anion radicals.^{26,27} Recently, we reported the stabilization of the anion radical formed in poly(vinyl methyl terephthalate) (PVMTP) and its dimer model compounds by the anion radical transfer method.²⁸ For both PVMTP and the dimer model compounds, where the terephthalate groups are linked by a methylene chain, the anion radical transfer to 1,4-dicyanobenzene (DCNB) or to 1,2,4,5-tetracyanobenzene (TCNB) was found to be suppressed in comparison with a monomer model compound, dimethyl terephthalate (DMTP). Furthermore the suppression for PVMTP was much stronger than that for the dimer model compounds and no anion radical transfer to DCNB could be observed for PVMTP. This is considered due to the stabilization of the anion radical by interactions with the neighboring chromophores.

In this study, we investigated the anion radical transfer to DCNB using nanosecond laser photolysis for the copolymer of vinyl methyl terephthalate (VMTP) with vinyl acetate (VAc). The relation between the sequence of TP chromophores and the stabilization was studied in detail to elucidate the behavior of the anion radical formed in PVMTP.

EXPERIMENTAL

Copolymers

Vinyl methyl terephthalate (VMTP) was synthesized by the ester exchange reaction of vinyl acetate with terephthalic acid monomethyl ester (Tokyo Kasei Kogyo Co.)²⁹ and was purified by a silica-gel column chromatography with the eluent of dichloromethane and by recrystallization from hexane. Vinyl acetate (VAc, Wako Pure Chem. Ind., Ltd.) was purified by distillation. Four samples of the copolymer of VMTP with VAc were prepared by a radical copolymerization initiated by AIBN in a benzene solvent at 60°C and their conversions of the copolymerization were suppressed to below 30 mol%. They were purified by precipitation three times from a benzene solution into hexane. The molecular weight (\bar{M}_w) of these copolymers was measured by GPC (Toyo Soda HLC 802 UR) with a G4000H and a GMH6 column. The fraction of terephthalate units (f_{TP}) in these copolymers was determined by UV absorption spectra on the basis of the molar extinction coefficient of dimethyl terephthalate (DMTP, $\epsilon = 1.87 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ at 286 nm) in dichloromethane. These data are shown in Table I with the feed ratios. These copolymers were designated as P1, P2, P3, and P4 in the order of increasing f_{TP} . The monomer reactivity ratios, r_1 and r_2 , were determined by the Fineman-Ross

Table I. Characterization of copolymers of VMTP with VAc

Copolymer	F^a	f_{TP}^b	$\bar{M}_w/10^4^c$
P1	0.20	0.18	1.9
P2	0.52	0.31	2.9
P3	1.2	0.49	3.4
P4	3.5	0.62	3.4

^a Monomer feed ratio of the copolymerization ($F = [\text{VMTP}]_0/[\text{VAc}]_0$).

^b Mole fraction of TP unit in the copolymer determined by UV absorption.

^c Molecular weights determined by GPC (polystyrene equivalent).

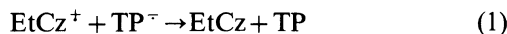
method³⁰ to be 0.26 and 0.64, respectively.

Other Chemicals

N-Ethylcarbazole (EtCz) was synthesized by *N*-alkylation of carbazole and was purified by recrystallization. Dimethyl terephthalate (DMTP, Wako Pure Chem. Ind., Ltd.) and 1,4-dicyanobenzene (DCNB, Wako Pure Chem. Ind., Ltd.) were purified several times by recrystallization. Dimer model compounds, 1,3-bis[*p*-(methoxycarbonyl)propane] (1,3-MTP) and 2,4-bis[*p*-(methoxycarbonyl)pentane] (2,4-MTP) were synthesized and purified as reported previously.²⁸ A racemic isomer of two diastereoisomers was used as 2,4-MTP. Dichloromethane (Dotite Spectrosol) was used without further purification. Benzonitrile (Wako Pure Chem. Ind., Ltd.) was fractionally distilled.

Measurements

When an electron donor, EtCz, is excited in the presence of an electron acceptor, a TP chromophore in benzonitrile, a cation radical of EtCz (EtCz⁺) and an anion radical of TP (TP⁻) are produced by the electron transfer. These ion radicals decay by recombination (eq 1). Then, the addition of an anion radical acceptor, DCNB, which has a lower reduction potential than the TP chromophore, causes the anion radical transfer (an electron transfer) from TP⁻ to DCNB and an anion radical of DCNB (DCNB⁻) is produced (eq 2). The formed DCNB⁻ also decays by recombination with EtCz⁺ (eq 3).



The absorption spectra and decays of EtCz⁺, TP⁻, and DCNB⁻ were measured by nanosecond laser photolysis. Selective photoexcitation of EtCz was made by a second harmonic pulse (347 nm, 10 mJ, 14 ns) of a Q-switched giant pulse ruby laser (NEC SLG2009) for

copolymer systems and by an excimer laser pulse of XeF (Lambda Physik EMG101MSC, 351 nm, 60 mJ, 18 ns) for model compound systems. All samples for the laser photolysis were degassed by the freeze-pump-thaw method. In the measurement of the laser photolysis, the absorbance of EtCz was adjusted to about unity at an excitation wavelength and the TP chromophore concentration was adjusted to 1.0×10^{-1} M for copolymers and to 5.0×10^{-2} M for model compounds. For the anion radical transfer experiments, 1.0×10^{-2} M DCNB for copolymer systems and 2.0×10^{-3} M DCNB for model compound systems were added to the above systems.

The UV absorption spectra of these copolymers in dichloromethane were measured by a Shimadzu UV-200s spectrometer.

The reduction potentials of DMTP and DCNB were measured by cyclic voltammetry with the reference electrode (Ag/0.01 N Ag⁺ in acetonitrile) and were determined to be -2.11 V and -1.97 V, respectively.

RESULTS AND DISCUSSION

Transient Absorption Spectra

Figure 1 shows the transient absorption spectrum of the EtCz-P1 system in benzonitrile.

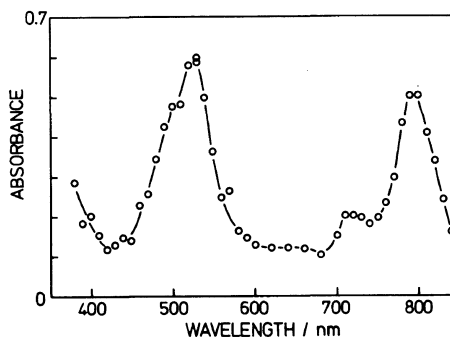


Figure 1. Transient absorption spectrum of EtCz-P1 system in benzonitrile measured by nanosecond laser photolysis at 298 K at $1 \mu\text{s}$ after excitation. The absorbance of EtCz at 347 nm is about unity. The concentration of TP chromophore in the copolymer is 1.0×10^{-1} M.

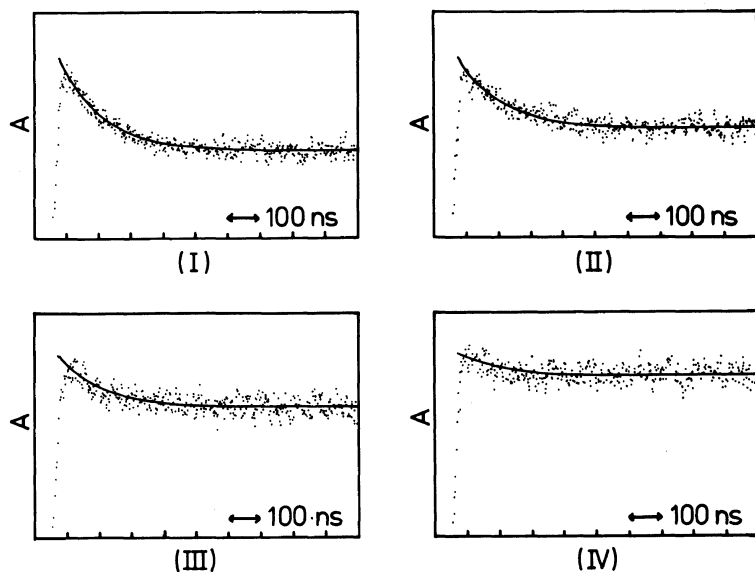


Figure 2. Transient absorbance decay measured at 530 nm in benzonitrile. (I), EtCz-P1-DCNB system; (II), EtCz-P2-DCNB system; (III), EtCz-P3-DCNB system; (IV), EtCz-P4-DCNB system. The absorbance of EtCz is about unity. The concentrations of TP chromophore in the copolymers and DCNB in each system are 1.0×10^{-1} M and 1.0×10^{-2} M, respectively.

trile. This spectrum is almost the same as that of the monomer model compound, EtCz-DMTP system. The absorption bands around 780 nm and 530 nm are assigned to EtCz^+ and TP^- in the copolymer, respectively. Other copolymer systems give similar transient absorption spectra as that shown in Figure 1. The molar extinction coefficient of TP^- for each copolymer at 530 nm was determined to be *ca.* $1.3 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ on the basis of that of EtCz^+ at 780 nm ($\epsilon = 9.4 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$). The molar extinction coefficient of TP^- in the copolymer was independent of f_{TP} . This value is almost the same as that of DMTP^- ($\epsilon = 1.2 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$). The fact that no change was observed in the transient absorption spectra means weak interactions between the neighboring chromophores.

Anion Radical Transfer from TP^- to DCNB

Figure 2 shows the decay at 530 nm which was mainly assigned to TP^- in the copolymer. In the absence of DCNB, TP^- decays by the recombination with EtCz^+ , but its decay is

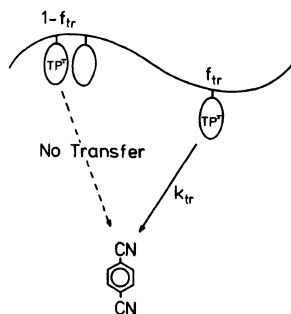


Figure 3. Scheme of anion radical transfer from TP^- in copolymers to DCNB.

hardly observed in this time region ($< 1 \mu\text{s}$). On the contrary, addition of DCNB to this system accelerates the decrease of TP^- as shown in Figure 2. This is due to the anion radical transfer from TP^- in the copolymer to DCNB. The decay consists of a fast decay component in the short time region ($< \text{ca. } 200 \text{ ns}$) and a slow decay component after the fast decay. As f_{TP} increases from 0.18 to 0.62, the fast decay component decreases.

We simulated these decay curves using the

scheme shown in Figure 3. One part of TP^- in the copolymer transfers an electron to DCNB in the rate constant k_{tr} with a fraction of f_{tr} and the others that are stabilized by the neighboring interaction do not. The concentration of TP^- ($[\text{TP}^-]$) at time t is expressed by eq 4, as the decrease of TP^- by the recombination with EtCz^+ is negligible in this time region ($< 1 \mu\text{s}$).

$$[\text{TP}^-] = [\text{TP}^-]_0 (f_{\text{tr}} \exp(-k_{\text{tr}}[\text{DCNB}]t) + (1 - f_{\text{tr}})) \quad (4)$$

where $[\text{TP}^-]_0$ and $[\text{DCNB}]$ are the concentration of TP^- and DCNB at $t=0$, respectively. The first term in the parentheses corresponds to the fast decay component in the observed decay curve and represents the decrease through the anion radical transfer. The second term corresponds to the slow decay component which does not decrease in this time region.

The observed decay curves at 530 nm were simulated using eq 4. As the absorbances of EtCz^+ and DCNB^- overlap slightly on that of TP^- , the contribution of these ion radicals was subtracted on simulation. The initial concentration $[\text{TP}^-]_0$ was also determined from the absorbance at $t=0$ at 530 nm in consideration of the overlap contribution of EtCz^+ and DCNB^- . The formation of DCNB^- through direct quenching of an excited EtCz was also taken into account. The results are summarized in Table II and the simulation lines are given by the solid line in Figure 2. The rate constant k_{tr} was found to be $7.7 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ for each system. The fraction of electron-transferable TP, f_{tr} , decreases in the order, P1

Table II. Simulation parameters of decay curves at 530 nm

Copolymer	f_{tr}	$k_{\text{tr}}/10^8 \text{ M}^{-1} \text{ s}^{-1}$
P1	0.83	7.7
P2	0.64	7.7
P3	0.48	7.7
P4	0.21	7.7

($f_{\text{tr}}=0.83$), P2 ($f_{\text{tr}}=0.64$), P3 ($f_{\text{tr}}=0.48$), and P4 ($f_{\text{tr}}=0.21$) with the increase of f_{TP} .

Interactions of Neighboring Chromophores in the Copolymer

In this system, the degree of interactions between the neighboring chromophores depends on the sequence distribution of VMTP in the copolymer. The fraction (f_i) that the TP group is isolated in the copolymer, that is, the fraction of the sequence, VAc-VMTP-VAc was calculated from r_1 and the feed ratio ($F = [\text{VMTP}]/[\text{VAc}]$) using eq 5.³¹

$$f_i = (1 + r_1 F)^{-2} \quad (5)$$

The calculated values f_i of P1, P2, P3, and P4 are 0.90, 0.78, 0.58, and 0.27, respectively. Figure 4 shows the relation between the transferable fraction f_{tr} and the calculated value f_i . The value f_{tr} is somewhat smaller than f_i for each copolymer. One reason for the difference is considered due to the underestimation of the initial absorbance of TP^- : the anion radical transfer occurs within the excitation pulse width of 14 ns. It is concluded that the transferable fraction f_{tr} is roughly proportional to f_i . This means that the electron-transferable anion radical TP^- is the one formed in the sequence, VAc-VMTP-VAc, and that the other TP^- 's formed in the more than two VMTP sequences cannot transfer any electrons to DCNB.

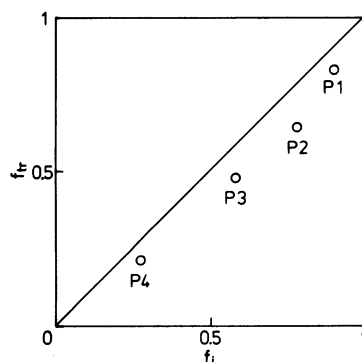


Figure 4. Transferable fraction f_{tr} versus isolated fraction f_i .

As for TP^- formed in the homopolymer VMTP, the anion radical transfer to DCNB does not occur at all. It is stabilized by interactions among more than two TP chromophores.

Comparison with Dimer Model Compounds

To compare the diad sequence of VMTP in the copolymer with the dimer model compounds, we investigated again the anion radical transfer from the TP^- of dimer model compounds and DMTP to the acceptor DCNB and determined k_{tr} more exactly by the initial transient absorption decay of TP^- at 530 nm in the time region ($< 1 \mu\text{s}$) where the recombination process can be neglected. The measured rate constants are as follows, $1.2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ for DMTP, $1.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ for 2,4-MTP, and $7.2 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ for 1,3-MTP. The anion radicals of dimer model compounds transfer their electron to DCNB more slowly than that of DMTP by the stabilization through interactions between the neighboring chromophores. Furthermore, the stability of 1,3-MTP is stronger than that of 2,4-MTP, which can be explained by the difference in the conformation of the dimer model compounds, *i.e.*, 1,3-MTP is easier to take sandwich-like conformation than 2,4-MTP.

On the other hand, the anion radical TP^- formed in the sequence, VAc-VMTP-VMTP-VAc on the copolymer does not transfer its electron to DCNB as described above. This suggests that TP^- in the dimer sequence, VAc-VMTP-VMTP-VAc on the copolymer is more stable than the dimer model compound. This large stabilization seems to be caused partly by the stronger neighboring interaction and partly by steric hindrance of the polymer chain to an approaching DCNB. In the latter case, it is plausible that the electron transfer in polymer systems occurs at a longer distance than in low-molecular compounds system since DCNB cannot approach the TP^- by the steric hindrance. This reduces electron transfer rate constants. Figure 5 shows a summary of the

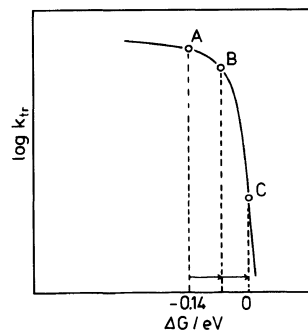


Figure 5. Relation between k_{tr} and free energy change in the anion radical transfer from TP^- to DCNB.

above situation. The relation between k_{tr} and free energy change (ΔG) for the electron transfer is shown by the solid curve: k_{tr} decreases slowly with increase of ΔG in the exothermic region and drops rapidly at *ca.* $\Delta G=0$.³² For monomer model compounds system, the free energy change (ΔG) of the anion radical transfer to DCNB is estimated to be *ca.* -0.14 eV from the difference of the reduction potentials of DMTP ($E_{1/2} = -2.11 \text{ V}$) and DCNB ($E_{1/2} = -1.97 \text{ V}$). This case is represented by point A. For the dimer model compound, k_{tr} becomes smaller than that of the monomer model compound by stabilization through interactions between the neighboring chromophores. The system is denoted by point B. As for the anion radical in consecutive TP's in the copolymer, they are further stabilized by neighboring interactions or steric hindrance. This makes ΔG larger and the system may correspond to point C. In this case, even a slight increase of ΔG causes a large decrease of k_{tr} around $\Delta G=0$. As for the homopolymer, anion radical transfer was not observed in our experimental resolution; therefore, TP^- in the homopolymer is estimated to be at least 0.1 eV more stable than DMTP⁻.

CONCLUSION

The anion radical TP^- formed in the copolymer of VMTP with VAc is stabilized depending on the location of the VMTP. That

is, $TP^{\cdot-}$ isolated by a comonomer VAc in the copolymer transfers an electron to DCNB with a rate constant of $7.7 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$, whereas $TP^{\cdot-}$ formed in the VMTP sequences does not transfer an electron to DCNB; neither does the anion radical $TP^{\cdot-}$ in the homopolymer PVMTP transfer an electron to DCNB. This is partly due to neighboring interactions and partly due to the steric hindrance of the polymer chain to an approaching DCNB. The steric hindrance is considered to be one reason why $TP^{\cdot-}$ formed in the dimer sequence in the copolymer is more stable than the one in a dimer model compound.

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