Radical Ions of Vinyl Polymers Having Aromatic Side Groups. Polystyrene and Poly(2-vinylnaphthalene)

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ABSTRACT: Absorption spectra of radical ions of polystyrene, poly(2-vinylnaphthalene), and their bichromophoric model compounds have been measured in rigid matrices as well as in solution in an attempt to get information concerning the conformation of these polymer chains. New bands ascribable to the intramolecular interaction between two aryl groups were observed in the spectra of radical cations of the polymers and the bichromophoric compounds, though spectra of their radical anions were identical with the spectrum of the monomeric unit. The peak position of the new band observed in the infrared region, a charge-resonance band, was found to serve as a sensitive tool for evaluating weak intramolecular interaction of the side groups of the polymers and their mobility in rigid matrices. Pulse radiolysis study at room temperature revealed that the geometrical structure of the intramolecular dimer radical cation of the polymers is different from the structure of the intermolecular dimer radical cations of the monomeric units.

Introduction

Photophysical studies of vinyl polymers having aromatic side groups have given invaluable information on the conformation of polymer chains.[1] Intramolecular excimer fluorescence, for example, has been successfully applied to the study of conformational changes with relaxation times in the nanosecond region.[2] An equilibrium conformation of polymer chains in rigid matrices has also been examined by use of the fluorescence spectrum.[3]

Although several attempts have been carried out to use absorption spectra of side groups of a polymer as an indicator of conformation,[4,5] the method is of limited usefulness because spectral changes require strong intramolecular interactions. The purpose of this study is to characterize the absorption spectra of radical ions of polystyrene and poly(2-vinylnaphthalene) in rigid matrices as well as in solution and to use them as a measure of the side-chain conformation of these polymers. Radical cations have high promise as probes for conformational studies because their spectra are known to be highly sensitive to intermolecular interactions.[6,7] Absorption spectra of radical ions of bichromophoric compounds bounded by two or three methylene chains were also carefully examined as model systems of a unit in the polymer chains.

Experimental Section

Poly(2-vinylnaphthalene) (P2VN) and polystyrene (PS) were polymerized in benzene, using *n*-BuLi as an initiator. The polymers were purified by repeated reprecipitation in methanol from methylene chloride solution.

2-Methyltetrahydrofuran (MTHF), *n*-butyl chloride (BuCl), tetrahydrofuran (THF), methylene chloride, and ethylbenzene (EB) were purified by repeated distillation. 2-Ethylnaphthalene (2EN) and dinaphthylpropane (DNP) were purified by vacuum distillation. Dinaphthylethane (DNE) and 1,3-di-β-naphthylpropane (DNP) were synthesized according to the method of Chandross and Dempster.[8]

All samples were prepared under reduced pressure of less than 10^{-5} mmHg. The solution in a Suprasil cell was degassed, and the frozen solution was γ-irradiated with a dose rate of 6×10^{18} eV/(g·h) at 77 K. The optical change induced by irradiation and by subsequent warming was measured with a Hitachi 323 spectrophotometer. Emission spectra were measured with a Hitachi MPF-2A spectrofluorimeter. The pulse radiolysis apparatus has been described in detail elsewhere.[9] The energy of the electron pulse was 10 MeV, and the duration was 0.5 μs.

Results

Emission Spectra. Figure 1 shows fluorescence spectra of 2EN, DNE, DNP, and P2VN (MW 8×10^4) in BuCl in a rigid glassy state at 77 K. The spectra of the polymer and the bichromophoric compounds are identical with the spectrum of 2EN. No excimer emission can be observed at wavelengths above 400 nm. These fluorescence spectra imply no intramolecular interaction between side groups of the polymer or between the two chromophores of the dinaphthylalkanes at 77 K.

Figure 2 depicts phosphorescence spectra of 2EN, DNE, DNP, and P2VN (MW 8×10^4) under the same conditions as used for fluorescence measurement of Figure 1. The phosphorescence near 470 nm is assigned to the 0–0 band of the monomeric unit. Although the spectra of DNE and DNP are identical with the spectrum of 2EN, the spectrum of P2VN is noticeably different from other three spectra. The spectrum of P2VN clearly shows a red shift. The red shift indicates intramolecular interaction between side groups of the polymer exists in the triplet state. In a previous paper,[10] it has been shown that the intramolecular interaction in the triplet state for the copolymer of phenyl vinyl ketone and 2-vinylnaphthalene exists in the high-content region of 2-vinylnaphthalene. The different behavior between fluorescence and phosphorescence spectra suggests that the phosphorescence spectrum can give information concerning weak interaction between the side groups which cannot be detected in the fluorescence spectrum.

Figure 3 shows fluorescence and phosphorescence spectra of EB, DPE, DPP, and PS (MW 1×10^5). Although the fluorescence spectrum of PS is very similar to the spectra of diphenylalkanes and EB, its phosphorescence spectrum shows a clear difference in band position and intensity from the other three spectra. The band shift of PS, a blue shift, is in the direction opposite to the shift observed in P2VN. The decrease of intensity in the polymer system is considered to be due to the triplet–triplet annihilation caused by migration of triplet states along the polymer chain.[11]

Absorption Spectra of Radical Ions at 77 K. It is well established that a solute radical anion is produced in

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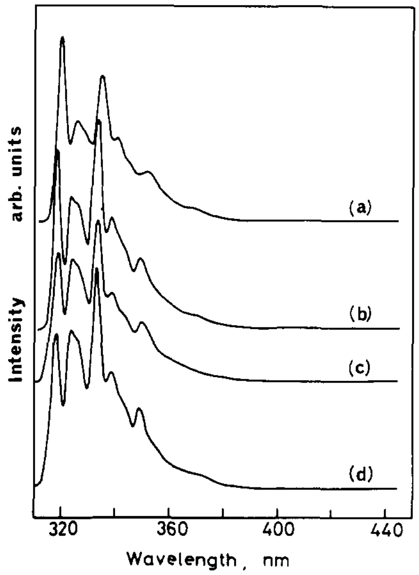

Figure 1. Fluorescence spectra of (a) P2VN, (b) DNP, (c) DNE, and (d) 2EN in BuCl at 77 K.

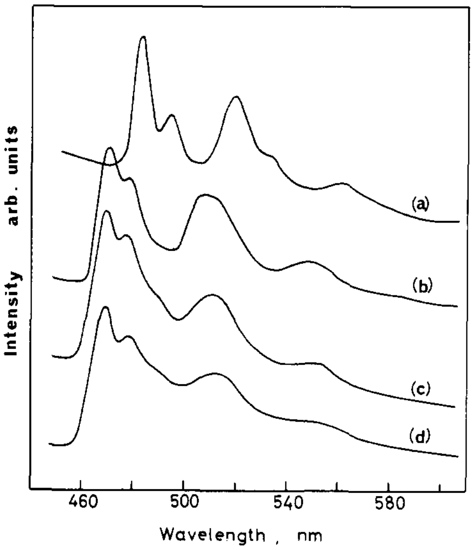

Figure 2. Phosphorescence spectra of (a) P2VN, (b) DNP, (c) DNE, and (d) 2EN in BuCl at 77 K.

irradiated MTHF by the reaction of a electron with a solute molecule.[12] Figure 4 shows the absorption spectra of MTHF solutions containing 1×10^{-1} M P2VN and 2×10^{-2} M 2EN, DNE, and DNP at 77 K irradiated with a dose of 3×10^{19} eV/g. According to Hamill's criterion,[12] these spectra in MTHF are ascribable to radical anions of P2VN, 2EN, DNE, and DNP. These four radical anions have absorption peaks at identical positions of 327 and around 800 nm and have similar band shapes. Both of these bands disappeared simultaneously when photoirradiated with light longer than 390 nm. The similarity of the spectra of the polymer and the bichromophoric compounds with that of 2EN indicated that there is no appreciable intramolecular interaction between the radical anion and the adjacent neutral side groups. This suggests that the electron is localized in one naphthyl chromophore in the bichromophoric systems as well as in the polymer systems at 77 K.

Radical cations of solute molecules are produced by the γ-irradiation of alkyl halide glass matrices at 77 K.[12] Figure 5 shows the absorption spectra of BuCl solutions containing 1×10^{-1} M P2VN and 2×10^{-2} M 2EN, DNE, and DNP irradiated with a dose of 3×10^{19} eV/g at 77 K.

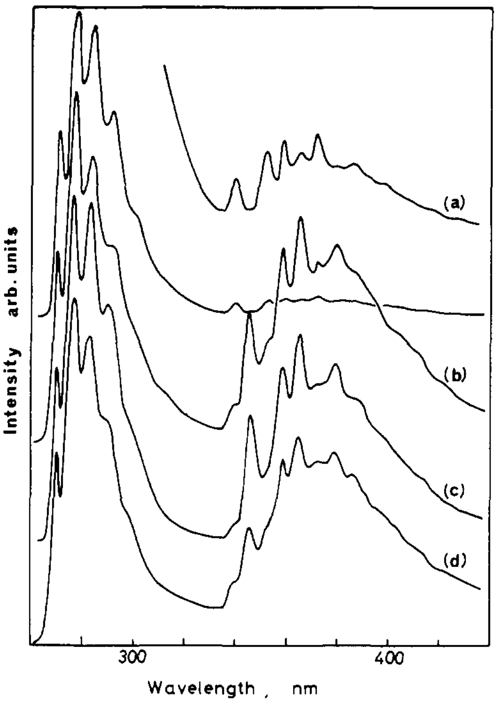

Figure 3. Fluorescence and phosphorescence spectra of (a) PS, (b) DPP, (c) DPE, and (d) EB in BuCl at 77 K.

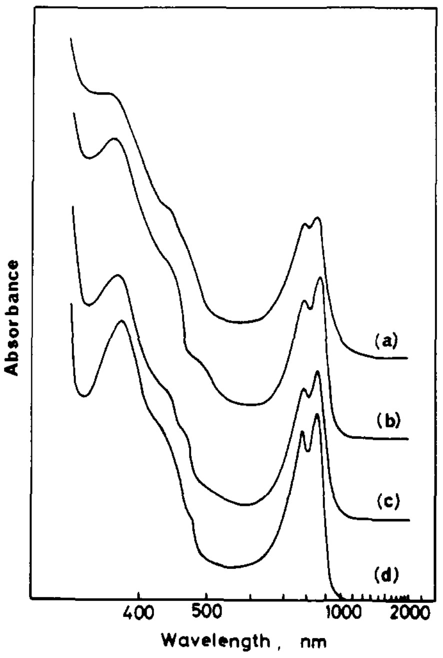

Figure 4. Absorption spectra of MTHF solutions containing (a) 1×10^{-1} M P2VN, (b) 2×10^{-2} M DNP, (c) 2×10^{-2} M DNE, and (d) 2×10^{-2} M 2EN irradiated with a dose of 3×10^{19} eV/g at 77 K.

The absorption bands at 397 and around 690 nm of 2EN are ascribable to the monomeric radical cation of 2EN. In the spectra of P2VN and the two bichromophoric compounds two new bands appear in the infrared region and around 460 nm besides the monomeric bands around 400 and 690 nm. The new bands in the infrared region are due to a charge-resonance interaction between two naphthyl chromophores.[13] The appearance of these new bands is clear evidence of the interaction of two naphthyl side groups in the radical cation state. The peak position of the charge-resonance band is different for each of these three compounds. The band peak of P2VN is around 2100

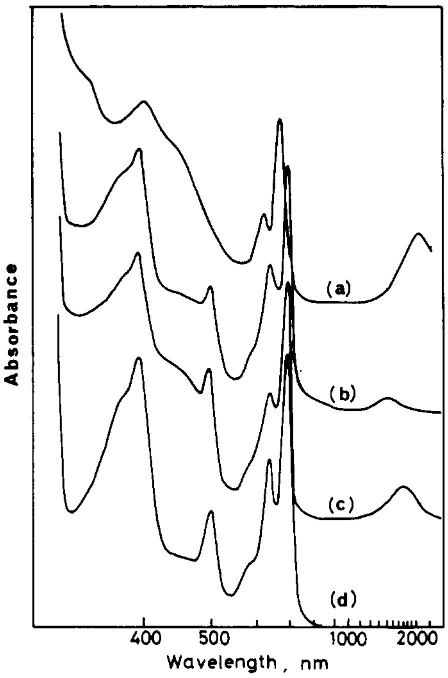

Figure 5. Absorption spectra of BuCl solutions containing (a) 1×10^{-1} M P2VN, (b) 2×10^{-2} M DNP, (c) 2×10^{-2} M DNE, and (d) 2×10^{-2} M 2EN irradiated with a dose of 3×10^{19} eV/g at 77 K.

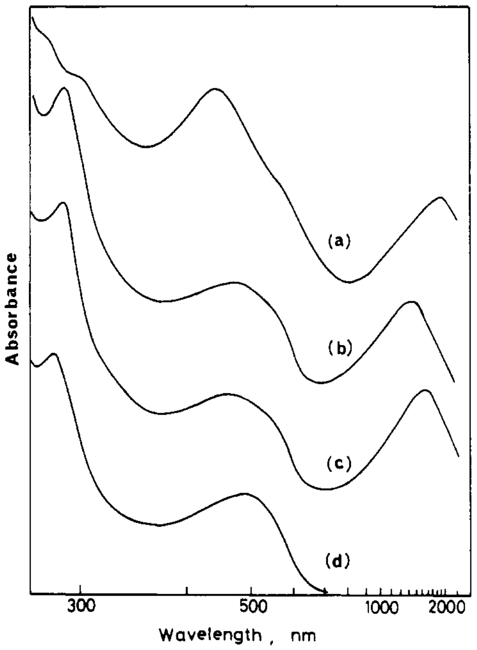

Figure 6. Absorption spectra of BuCl solutions containing (a) 1×10^{-1} M PS, (b) 2×10^{-2} M DPP, (c) 2×10^{-2} M DPE, and (d) 2×10^{-2} M EB irradiated with a dose of 3×10^{19} eV/g at 77 K.

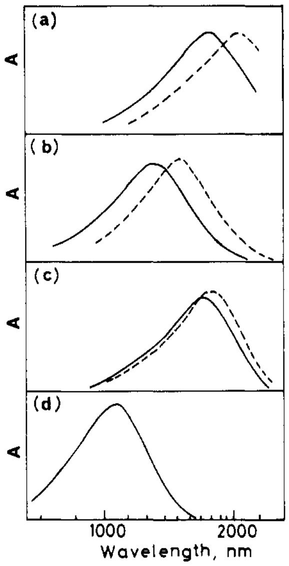

Figure 7. Absorption spectra of BuCl solutions containing (a) 1×10^{-1} M P2VN, (b) 2×10^{-2} M DNP, (c) 2×10^{-2} M DNE, and (d) 2×10^{-2} M 2EN irradiated with a dose of 3×10^{19} eV/g: (---) immediately after irradiation; (—) after annealing.

nm and of DNP is around 1450 nm. The peak position of DNE, 1700 nm, is between the peak of positions of the polymer and DNP.

Also in the polymer spectrum, another new band around 460 nm has the highest intensity, being weakest in DNP, in agreement with the intensity of the charge-resonance band in the infrared region. This band is considered to reflect the intramolecular interaction of naphthyl side groups.[13]

In addition to the new bands, the polymer spectrum clearly shows a blue shift of 13 nm for the band around 690 nm, though the peak positions of the bichromophoric compound are identical with those of 2EN. The similarity of the behavior of the peak shift observed in the phosphorescence spectrum suggests that the geometrical orientation of the naphthyl side groups in the polymer system is slightly different from that of the bichromophoric systems.

As in the naphthalene systems, BuCl solutions of PS, DPP, and DPE after irradiation also exhibited new bands in the infrared region and around 450 nm in addition to the known bands of the monomer radical cation of EB, as shown in Figure 6. The band around 500 nm has been assigned to the monomer cation.[13] The new band in the infrared region and the band at 450 nm are analogous to the dimer radical cation of benzene derivatives.[7,13] These results show that interaction of two phenyl side groups also exists in the radical cation states of PS as well as DPP and DPE.

Thermal and Photoannealing of Radical Ions. It is well-known that the radical ion changes its conformation to a relaxed state by thermal annealing or by photoillumination in visible and/or infrared light.[14] The photoillumination is considered to cause local heating in the surroundings of radical ions by the absorption of photon energy, resulting in thermal annealing. We carefully examined the spectral changes induced by photoillumination in order to examine side-chain conformational changes and mobility of the polymer chains at low temperature. The most dramatic change was observed in near-infrared bands of radical cations in BuCl. Absorption spectra immediately after irradiation of P2VN and PS systems in BuCl matrices at 77 K are shown by broken curves in Figures 7 and 8. Annealing of the irradiated sample in the BuCl matrices caused the spectral changes shown by the solid curves in Figures 7 and 8. The bottom spectra of 2EN and EB were obtained by thermal annealing of the irradiated solution of these two compounds. In these monomer systems, photoillumination did not give rise to spectral changes. The band at 1040 nm of 2EN is similar to that of the relaxed naphthalene dimer radical cation.[15] After annealing, all charge-resonance bands showed remarkable blue shifts. In P2VN, the charge-resonance band shifted from 2100 to 1700 nm.

A similar shift was observed in P2VN and DNP but the shift was small in DNE. These shifts are considered to

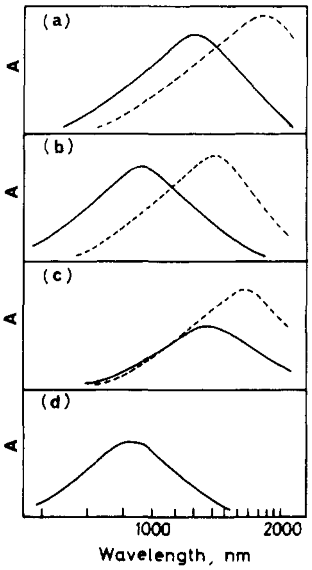

Figure 8. Absorption spectra of BuCl solutions containing (a) 1×10^{-1} M PS, (b) 2×10^{-2} M DPP, (c) 2×10^{-2} M DPE, and (d) 2×10^{-2} M EB irradiated with a dose of 3×10^{19} eV/g: (---) immediately after irradiation; (—) after annealing.

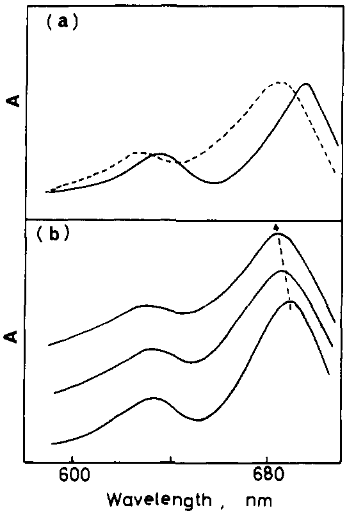

Figure 9. (a) Absorption spectrum of the monomeric radical cation of 2EN (—) and the spectrum of the relaxed radical cation of P2VN (---). (b) Spectral changes of the irradiated BuCl solutions containing 1×10^{-1} M P2VN (MW 1900) after illumination with visible light.

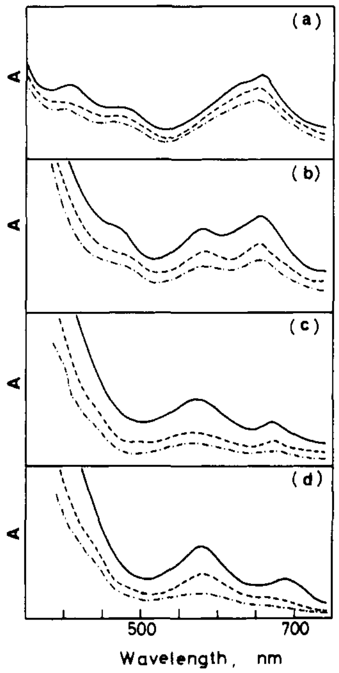

Figure 10. Transient absorption spectra of methylene chloride solutions containing (a) 1×10^{-1} M P2VN, (b) 1×10^{-2} M DNP, (c) 1×10^{-2} M DNE, and (d) 5×10^{-3} M 2EN at room temperature immediately (—), 1.25 μs (---), and 2.5 μs (-·-) after the pulse.

be due to the conformational change from the unrelaxed to relaxed dimer radical cation state about the connecting methylene chains.[7,15] The final peak position of the relaxed state is, however, still quite far from the position of the dimer radical cation of 2EN. Although the definite configuration of the dimer radical cation is still under discussion even for naphthalene,[7] it is generally assumed that the configuration is a distorted-sandwich pair. The difference in the peak position among these spectra is possibly due to the fact that the geometrical reorientation of the two naphthyl groups is restricted by the connecting methylene chains in the polymers as well as in the bichromophoric compounds. The similarity of the peak positions of the annealed radical ions of P2VN and DNE suggests that the interchromophore distance of adjacent naphthyl units in the side group of the polymer is similar to the distance of the naphthyl units of DNE in BuCl matrices.

A similar discussion can be applied to the conformation of PS in BuCl as shown in Figure 8. The larger shifts of the charge-resonance band of PS suggest a difference in the mobility of P2VN and PS. The peak position of PS is similar to that of DPE, while the peak position of DPP is found to be very close to that of EB. These peak positions also indicate the similarity of the interchromophore distance of phenyl groups in PS and DPE.

In addition to the spectral shift in the charge-resonance band, the band at 690 nm showed interesting relaxation behavior in P2VN. The solid curve in Figure 9a is the absorption spectrum of the monomeric radical cation of 2EN, and the broken curve is the spectrum of the relaxed radical cation of P2VN. Figure 9b demonstrates the changes in the spectrum of P2VN of lower molecular weight (MW 1900) by visible-light illumination at 77 K. The absorption band at 690 nm observed immediately after irradiation shifted gradually toward the shorter wavelength of 684 nm. The shift indicates that the conformation of the polymer changed to the relaxed conformation by photoannealing.

Absorption Spectra of Radical Ions at Room Temperature. On the basis of fundamental knowledge of the spectra of the transient radical ions of polymers at low temperature, we carried out a pulse radiolysis study at room temperature in methylene chloride solution. Figure 10 shows the transient absorption spectra of P2VN, 2EN, DNE, and DNP in the methylene chloride solution at the end of the pulse and 1.25 and 2.5 μs after the pulse. The spectrum of 2EN in the visible region is composed of two bands at 580 and 700 nm. The peak around 700 nm is due to the monomeric radical cation and the band at 580 nm is considered to be due to the so-called dimer band,[13] which appeared along with the charge-resonance band in the near-infrared region by annealing the irradiated sample of 2EN at low temperature. The identical band is observed at 580 nm in both bichromophoric compounds. Therefore, this band at 580 nm can be ascribed to an intermolecular dimer band. In bichromophoric compounds, the monomer band shows a quite large blue shift of 20–40 nm. The blue shift is due to the intramolecular interaction between a naphthyl radical cation and a neutral naphthyl chromo-

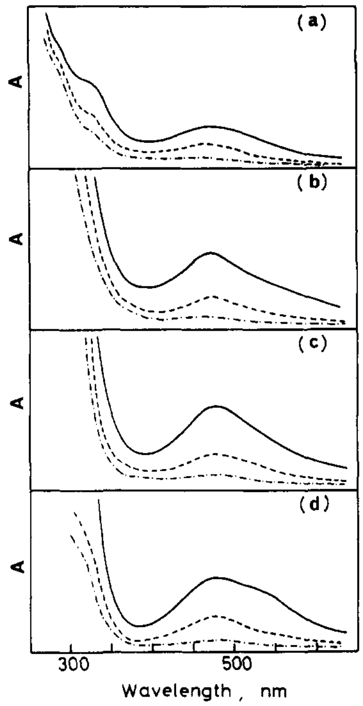

Figure 11. Transient absorption spectra of methylene chloride solutions containing (a) 5×10^{-2} M PS, (b) 2×10^{-2} M DPP, (c) 2×10^{-2} M DPE, and (d) 5×10^{-3} M EB at room temperature immediately (—), 1.25 μs (- - -), and 2.5 μs (-·-) after the pulse.

phore as discussed earlier. The band at 650 nm is, therefore, ascribable to an intramolecular dimer band. The spectral difference between the two intermolecular and intramolecular dimer bands is possibly due to the difference in the geometry of the two naphthyl groups. In the case of P2VN an intermolecular dimer is not observed; only an intramolecular dimer remained after an electron pulse of 0.5 μs. In addition to the band around 650 nm a new band appears around 470 nm for P2VN and DNP. This band is also assigned to the intramolecular dimer band because a similar band is observed in the rigid matrices of Figure 5. The nonappearance of this band for DNE indicates that the intramolecular interaction is weak in this compound in fluid solution.

Figure 11 shows the transient absorption spectra of PS, DPP, DPE, and EB observed in methylene chloride solution at the end of pulse and 1.25 and 2.5 μs after the pulse. The shoulder around 520 nm observed for EB is assigned to the monomeric radical cation of EB on the basis of the spectra at low temperature. The band around 460 nm observed for EB, for the two diphenylalkanes, and for PS is considered to be due to dimeric radical ions. In these systems the difference of the spectrum between intra- and intermolecular dimer radical cations was indistinguishable because of the broadness of the spectra.

Discussion

The absorption spectrum of a radical cation is a powerful tool for the study of conformational change of polymers having aromatic side groups, especially at low temperature. The spectrum can give information concerning intramolecular interaction of the side groups, even if the interaction is very weak. Even under conditions where the fluorescence spectrum does not give any indication of intramolecular interaction of side groups of P2VN at 77 K in BuCl (Figures 1 and 3), the absorption spectrum of the radical cation showed a clear charge-resonance band (Figures 5 and 6), which is unambiguous evidence of the intramolecular interaction of side groups. We could follow the relaxation process of the methylene chains after photoannealing at low temperature by observing the spectral shifts of the charge-resonance band in the infrared region (Figures 7 and 8) and the monomer band around 690 nm (Figure 9). The spectral change is not due to the relaxation of solvent around the radical cations because the photoannealing process was not observed for monomer systems of EN and EB. The possibility of translational diffusion by photoannealing can also be ruled out because the annealing did not cause any spectral changes for the monomer systems. The spectral shifts of P2VN, DNP, and DNE by annealing are summarized in Table I.

Table I
Absorption Bands of Radical Cations of DNE, DNP, and P2VN

	λ_{max} at 77 K, nm			
	monomer and charge-resonance bands			charge-resonance bands after annealing
DNE	397	696	1700	1620
DNP	397	696	1450	1270
P2VN (MW 8×10^4)	402	683	2100	1700
EN	397	696		1040

The phosphorescence spectra of P2VN and PS at 77 K are also quite different from the spectra of bichromophoric and monomeric compounds (Figures 2 and 3). The difference suggests that a phosphorescence spectrum can be used as a tool for the study of weakly interacting systems. Weak intramolecular interaction in copolymer systems has previously been studied by the use of phosphorescence spectra.[10] This method is, however, not as straightforward as the absorption spectra of radical cations, since the triplet state can migrate along the polymer chains and be trapped in rather strongly interacting sites. The absence of the spectral shift in the bichromophoric systems can be explained by the lack of migration in these systems.

The charge-resonance bands of the radical cations of P2VN and PS do not coincide in position with the bands of the corresponding diarylpropane and diarylethane at 77 K (Figures 5 and 6). It is supposed from this observation that the intramolecular interactions between two side groups of the polymers at 77 K are not representd by either of these model compounds. On annealing, the peak positions shifted to shorter wavelength, indicating an increase in intramolecular interaction. The peak positions of the polymers after annealing are, however, still far from the peak positions of the intermolecular dimers of monomeric compounds, the conformations of which are assumed to be a distorted-sandwich structure.[6] This result indicates that the mobility of side groups in the polymers is too restricted to form the same sandwich structure at low temperature.

The peak positions of the charge-resonance band of P2VN and the bichromophoric compounds around 2000 nm are close to the band of the unrelaxed dimer of naphthalene, which is reported to be observed only in alkane matrices and not in BuCl.[15] The appearance of these bands in BuCl even in diluted samples is due to the presence of two naphthyl groups close to each other in the polymers as well as in the bichromophoric systems.

It is worthwhile to consider the possible site conformation of the polymer chain which is responsible for the dimer formation. Since the polymers examined in this study were atactic, we will analyze both syndiotactic and isotactic cases. The excimer fluorescence intensity in the solid state is associated with the population of racemic g^-t

and tg$^-$ dyads in syndiotactic sequences and meso tt dyads in isotactic sequences.[3] The absence of an excimer fluorescence in BuCl at 77 K (Figures 1 and 3) implies that among various conformations the fraction of these chain conformational sites available for excimer formation is very low at the freezing temperature of BuCl in comparison with the number of migration steps an exciton can make during its lifetime at 77 K. Possible conformations for the dimer formation besides the excimer conformations are tt and g$^-$g$^-$ of the syndiotactic chain and g$^-$t and tg$^-$ of the isotactic chain. Although a sandwich geometry is not attained and the interchromophore distance is fairly large in these conformations, the dimer radical cation formation is highly expected when the conformation is slightly distorted, since small rotational adjustments in these conformations significantly reduce the interchromophore distance to close to the value found in diarylethanes.[16] In addition, the appearance of the charge-resonance band in diarylethane radical cations suggests that a sandwich geometry is not necessary for making the dimer radical cation. Among these possible site conformations the distorted tt conformation is most probable, since the conformation is one of the lowest energy conformational states for the syndiotactic chain segment, the others having higher energy than the excimer-forming site conformations.[3] The similarity in the peak positions of the annealed radical cations of the polymers with those of the corresponding diarylethanes is well interpreted by the conformation in which the interchromophore distance is close to the value found in diarylethanes. The relaxation process of the charge-resonance band on annnealing is ascribable to the rotational adjustment of the paired aryl groups in the conformation.

Two different kinds of dimer radical cation bands, intra- and intermolecular dimer bands, were observed in bichromophoric systems at room temperature (Figures 10 and 11). In DNE the absorption spectrum in methylene chloride is mainly composed of an intermolecular dimer radical ion band at 580 nm, while in DNP the intramolecular dimer radical cation bands at 650 and 470 nm are dominant. This result suggests that the naphthyl groups connected by three methylene chains can easily form an intramolecular dimer in contrast with two naphthyl groups connected by two methylene chains, as expected from excimer experiments.[1] The difference in the peak positions of inter- and intramolecular dimer radical ions indicates that the geometrical structures of these two dimers are quite different from each other. This observation is consistent with the results for excimer fluorescence of bichromophoric systems,[17] though the absorption spectrum of the radical cation is more sensitive to the geometrical structure of the two aryl groups than is the excimer fluorescence.

The absorption spectrum at room temperature of the radical cation of P2VN after an electron pulse of 0.5 μs is exclusively composed of the intramolecular dimer radical cation (Figure 10). The monomer radical cation is considered to be stabilized immediately by the formation of an intramolecular dimer radical cation between side groups in the polymer systems. The geometrical structure of the two naphthyl side groups in the radical cation state is similar to the conformation of DNP at room temperature but is quite different from the intermolecular dimer radical cation of 2EN.

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