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An Electron Spin Resonance Study of the Phosphorescent Triplet State of Poly(vinylnaphthalene)s

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The electron spin resonance (ESR) of poly(1-vinylnaphthalene) and poly(2-vinylnaphthalene) in their phosphorescent triplet states is studied in glassy solutions and in plastic hosts. The zero-field splitting parameters thus obtained are discussed in comparison with those of 1- and 2-methylnaphthalene. Through the ESR measurement, the possibility of detecting the triplet energy transfer through the naphthyl groups is examined.

The lowest triplet state of vinyl polymers with aromatic groups attached has been investigated mainly in connection with their intramolecular energy transfer through aromatic chromophores, by measuring the delayed fluorescence and phosphorescence spectra at low temperatures.[1] Nevertheless, comparatively little attention has been paid to studies of their electron spin resonance (ESR), especially for synthetic polymers. If the naphthyl groups are attached to polymeric chains, their fairly strong phosphorescent ESR signals may be expected to be observed in rigid glasses, judging from those of the naphthalene molecule. In the present work, therefore, ESR studies of poly(1-vinylnaphthalene) (P1-VN) and poly(2-vinylnaphthalene) (P2-VN) in their lowest triplet states are taken up as typical examples of such works.

Experimental

The P1-VN and P2-VN were purchased from Polysciences, Inc., and were purified repeatedly by dissolving in tetrahydrofuran and by precipitation with methanol (after a purification, the molecular weights of P1-VN and P2-VN were $M_w=3.4\times10^3$ and $M_n=2.0\times10^3$, and $M_w=1.93\times10^4$ and $M_n=9.2\times10^3$, respectively). The 1-methylnaphthalene (1-MN) and 2-methylnaphthalene (2-MN) were obtained from Tokyo Kasei Co. and were used without further purification, because the ESR signals of the other molecules could not be detected. The ESR spectra were observed in 2-methyltetrahydrofuran (MTHF) glasses. As the plastic host of these polymers, stretched atactic polystyrene (PS) film was used, because it is very hard for isotactic PS to form transparent films from either a toluene or a 1,3,5-trimethylbenzene solution. By evaporating the toluene from a solution containing a 50 : 1 (*w*/*w*) mixture of PS and a sample in a glass vessel on a hot plate, a transparent film was obtained on the glass. Then the film was stretched at 80 °C. The films thus obtained had about 200% of stretch in the stretched direction.

The details of the ESR experiment are exactly the same as in our previous works,[2,3] except for the use of an additional apparatus of JES-UCT-2AX variable-temperature adapter and a JES-VT-3 variable-temperature controller when the measurements were carried out at temperatures above 77 K.

Results and Discussion

In comparison with the ESR spectrum of the naphthalene molecule, the line shapes for P1-VN and P2-VN resemble each other closely, but their intensities are relatively weak in MTHF glasses at 77 K. The zero-field splitting (ZFS) parameters obtained under the same conditions are listed in Table 1. For the naphthalene molecule, the coordinate axes were taken as follows: the x axis is parallel to the longest direction of the molecule, and the y axis is perpendicular to it in the molecular plane, while the z axis is perpendicular to the molecular plane. The directions of the magnetic principal axes of the PVN and MN molecules were assumed not to deviate largely from those of the naphthalene molecule, although they could not be determined in the present work. The results for the ZFS parameters may be summarized as follows: for naphthalene and 1- and 2-MN, the present values are slightly different from those obtained in EPA glasses by Yamanashi and Bowers.[5] (1) The D and $|E|$ values of 1-MN are both smaller than the respective values of 2-MN, although such a relation is completely reversed in the latter work. (2) Similarly, the D and $|E|$ values of P1-VN are both smaller than the corresponding values of P2-VN. (3) Each D value of these polymers is smaller than that of the corresponding MN, while such differences are hardly found at all for the E values.

These relations can reasonably be explained in terms of the spin distributions of these molecules, except for the E values described in (3). That is, since, in the naphthalene molecule, the spin density at the 2 position of the carbon atom is smaller than that at the 1 position, the spin delocalization from the naphthyl group in 2-naphthyl substituents is smaller than that in 1-

Table 1. Zero-field splitting parameters in the phosphorescent triplet states (cm^{-1})$^{a)}$

Molecule	$\|X\|$	$\|Y\|$	$\|Z\|$	$\|D\|$	$\|E\|$	$D^{*b)}$	$D^{*c)}$
Naphthalene	0.0489	0.0181	0.0669	0.1004	0.0154	0.1039	0.1040
1-Methylnaphthalene	0.0472	0.0180	0.0652	0.0978	0.0146	0.1012	0.1008
2-Methylnaphthalene	0.0478	0.0179	0.0657	0.0986	0.0150	0.1020	0.1022
Poly(1-vinylnaphthalene)	0.0469	0.0177	0.0643	0.0967	0.0146	0.1000	0.0992
Poly(2-vinylnaphthalene)	0.0476	0.0177	0.0653	0.0980	0.0150	0.1014	0.1031

a) Observed in MTHF glasses at 77 K. b) $D^*=(D^2+3E^2)^{1/2}$. c) Obtained from the observed resonance field of the $\Delta m=\pm2$ transition with Kottis-Lefebvre's correction.[4]

naphthyl ones. Also, such spin delocalization may generally be larger for P1- and P2-VN than for the corresponding MN molecule. The above elucidation is actually based on the hyperconjugation-type consideration. On the other hand, the results of (3) may possibly be interpreted as being caused by the influence of the triplet-energy transfer which occurs slightly through the naphthyl groups at 77 K. The intramolecular triplet-energy transfer through naphthyl groups has been demonstrated by Cozzens and Fox for P1-VN in a THF: diethyl ether (1 : 1) glass at 77 K through the measurements of the delayed fluorescence due to triplet-triplet annihilation.6) In P1- and P2-VN, therefore, the triplet exciton may mainly move along the polymer chain if the normal axes of naphthyl groups are locally aligned on this direction. In that case, only the D value of PVN slightly decreases from that of the corresponding MN, while the E value is hardly changed.

Until now, the intramolecular triplet-energy transfer through naphthyl groups has been optically studied in P1-VN6-8) and P2-VN.8-11) In the present work, the possibility of detecting such a triplet exciton was examined from the change in the ESR line shapes at different temperatures where the rates of triplet-energy transfer may be appreciably changed. Generally, the use of glassy solutions does not permit the detection of the phosphorescent ESR signals at temperatures where the host glass is not rigid. For observing the line shapes over a fairly wide range of temperature, therefore, a stretched PS film was used as a host.

The ZFS parameters obtained in the PS films at 77 K are slightly smaller than those in MTHF glasses, although the line shapes become rather broad. With a rise in the temperature, the intensity of each peak with the $\Delta m = \pm 1$ transition decreases and the line shapes become broad. The peak intensities for P2-VN are quite weak as compared with those of P1-VN. Therefore, further experiments were carried out for only P1-VN and its reference compound of 1-MN. The signals of the $\Delta m = \pm 1$ transition observed at 77 K barely showed a little anisotropy due to the directions of the stretched film against the applied magnetic field. Because of the lowering of the peak intensities, it may be impossible to deduce some meaningful information from its detection at higher temperatures. Actually, its Z peaks could not be detected near 160 K.

On the other hand, it is possible to detect the triplet ESR signal of P1-VN with the $\Delta m = \pm 2$ transition with an appreciable deformation of line shape at a temperature not higher than 160 K. Figure 1 shows the ESR spectra of the $\Delta m = \pm 2$ transition for P1-VN and 1-MN in stretched PS films at 77 K and 160 K. It may be noted here that these samples all contain roughly the same amount of naphthyl groups. For P1-VN, the line shape observed at 160 K becomes fairly broad as compared with that at 77 K, while that of 1-MN is hardly changed over the temperature range studied. This may suggest that some intramolecular triplet-energy transfer through naphthyl groups in the same polymer chain occurs for P1-VN, for the distances between adjacent naphthyl groups along a polymer chain are fairly small as compared with those of separated molecules. Such a consideration may generally support the interpretation of observation (3) described above. At 160 K, the D^* values of P1-VN and 1-MN were also obtained according to Kottis-Lefebvre's correction.4) They are each 0.002 cm^{-1} smaller than that of the corresponding molecule observed at 77 K. In addition to the effect of triplet-energy transfer in P1-VN, the lowering of D^* values may be partly attributed to the motion of naphthyl groups in the host polymer.12)

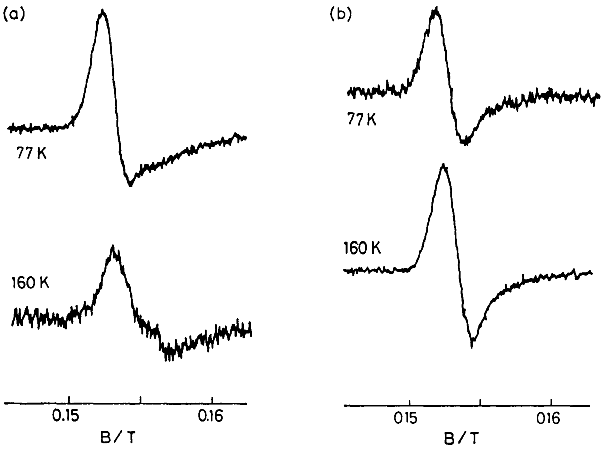

Fig. 1. ESR spectra of the $\Delta m = \pm 2$ transitions for the phosphorescent triplet states of poly(1-vinylnaphthalene) (a) and 1-methylnaphthalene (b) in stretched polystyrene films.

Several years ago, Avakian *et al.*9) studied the magnetic-field modulation of delayed fluorescence for P2-VN in a THF: diethyl ether (1 : 1) glass at 77 K. In comparison with the fluorescence intensity calculated by assuming that the D value is nearly equal to that of naphthalene and $E=0$, they deduced tendencies for the normal axes of naphthyl groups to be locally aligned approximately parallel to one another and for the naphthyl planes to have orientations tending to an average of the in-plane components. The last part of their assumption is evidently different from our value of $E \neq 0$. Compared with the present results, their interpretation may overestimate the triplet-energy transfer for P2-VN at 77 K, although the steric hindrance between the naphthyl group and the polymer chain is rather small as compared with the case of P1-VN.

In the present work, the host polymer consists of stretched atactic PS films without perfect ordering. Although the isotactic polymers were used, PS and P1-VN have different molecular symmetries, with threefold and fourfold screw axes respectively.13,14) Therefore, the present selection of guest and host polymers may not always be suitable if we are to expect even the partial ordering of guest molecules. Under these circumstances, a more detailed analysis of the observed spectra could not actually be carried out. Also, the characterization of the molecular weight or polymerization degree of the polymers may possibly be meaningless unless the aforementioned points are improved.

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