Mobility of spin probes having an amide group in nylon films

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The mobility of spin probes having an amide group in dried nylon films was investigated by means of an electron spin resonance (e.s.r.) technique. The results for 4-acetylamino-2,2,6,6-tetramethyl-1-piperidinyloxy (SPVII) and 4-benzoylamino-2,2,6,6-tetramethyl-1-piperidinyloxy (SPVIII) were compared with that for 4-((*p*-phenylazobenzoyl)amino)-2,2,6,6-tetramethyl-1-piperidinyloxy (SPI) examined previously. The mobility of all the spin probes increased with increasing methylene chain length of the nylon, and a small effect of drawing was observed. The mobility of SPVII was a little lower than that of SPI, whereas SPVIII gave the same mobility as SPI. From this, it was concluded that the mobility of spin probes having an amide group was affected by interactions between the amide group of the probe molecules and the nylons rather than by the molecular volumes of the spin probes.

(Keywords: spin probes; electron spin resonance; nylon; molecular motion; nitroxide; interaction of spin probes with nylon)

INTRODUCTION

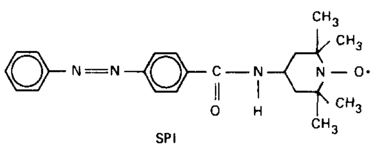
In our previous paper[1], we studied the mobility of three non-ionic spin probes with different molecular volumes in dried nylon films by means of an electron spin resonance (e.s.r.) technique. Their mobility was affected not only by probe volumes but also by interactions between the probe molecules and the nylon chains. In particular, effects of drawing of the nylon films were observed solely for spin probes having an amino or amide group. Furthermore, we investigated the mobility of spin probes having an anionic group[2] or a hydrophilic group[3] with a similar molecular volume in nylon films by means of e.s.r. measurements. The results clearly indicated that the chemical structures of the spin probes play an important role. From this point of view, it is interesting to examine the mobility of spin probes having a functional group, e.g. hydrogen-bond-forming group, with different molecular volumes, to make clear the effects of probe volumes.

The effects of probe molecular size on the rotational motions of spin probes have been interpreted[4–6] by using Bueche's free-volume theory[7]. However, in the interpretation, one should consider the interactions between polymers and probe molecules[5] and the free rotation around single bonds in spin probes[6]. Therefore, a relationship based simply on the free-volume theory just mentioned has been applied to systems where the spin probe–polymer interaction is rather weak[8,9].

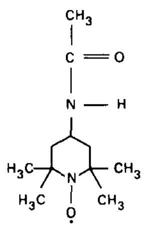
In the present study, we investigate the mobility of spin probes having an amide group with different molecular volumes in order to elucidate the effects of the amide group and the molecular volume. Here our attention is focused on the interaction between the amide group of the spin probes and the nylons.

EXPERIMENTAL

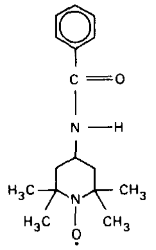
To compare with 4-((*p*-phenylazobenzoyl)amino)-2,2,6,6-tetramethyl-1-piperidinyloxy (SPI), which was investigated in our previous paper[1], 4-acetylamino-2,2,6,6-tetramethyl-1-piperidinyloxy (SPVII) and 4-benzoylamino-2,2,6,6-tetramethyl-1-piperidinyloxy (SPVIII) were used:



SPI



SPVII



SPVIII

SPVII was prepared as follows. First, 1.25 g (7.3×10^{-3} mol) 4-amino-2,2,6,6-tetramethyl-1-piperidinyloxy was dissolved in 20 ml benzene together with 2 ml (2.5×10^{-2} mol) pyridine. Then 0.5 ml (7.3×10^{-3} mol) acetyl chloride dissolved in 5 ml benzene was dropped into the above benzene solution. After reaction at room temperature for 14 h, the pyridinium salt was removed by filtration and the solvent was evaporated under reduced pressure. The residue was purified by

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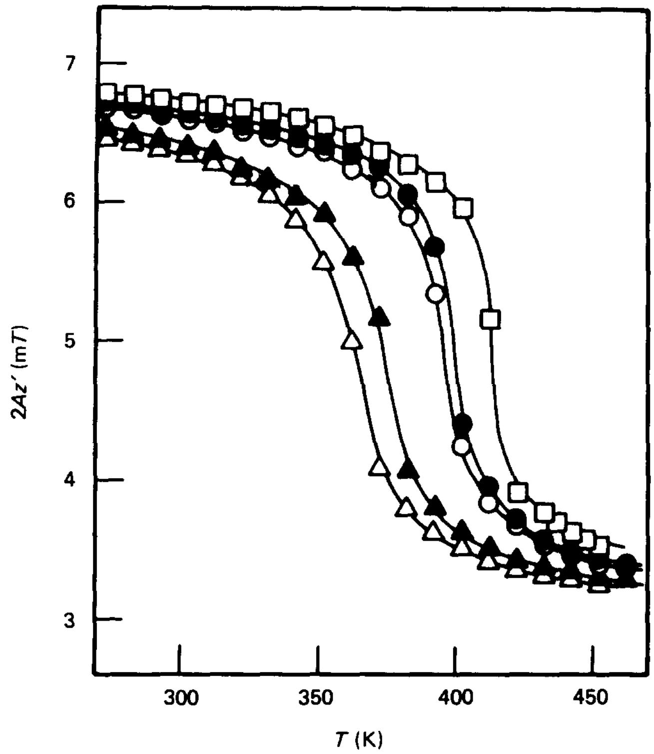

Figure 1 Plot of 2*Az*′ vs. temperature for SPVII: (□) NY-4; (●) NY-6(2D); (○) NY-6(ND); (▲) NY-11; (△) NY-12

repeated recrystallization from benzene. Red crystals (m.p. 409 K) were obtained (calculated for $C_{11}H_{21}N_2O_2$: C 61.94, H 9.92, N 13.14; observed: C 61.73, H 9.94, N 12.83). SPVIII was prepared in a similar manner to SPVII using benzoyl chloride instead of acetyl chloride. After recrystallization from 25% aqueous ethanol solution, red crystals (m.p. 398 K) were obtained (calculated for $C_{16}H_{23}N_2O_2$: C 69.78, H 8.42, N 10.18; observed: C 70.25, H 8.45, N 10.36).

Five nylon films were used. Undrawn nylon-4 film (NY-4) was prepared as described in our previous papers[1,2]. Biaxially drawn nylon-6 film (NY-6(2D)) and undrawn nylon-6 film (NY-6(ND)) were kindly supplied by Unitika Co. Nylon-11 film (NY-11) and nylon-12 film (NY-12), both drawn by inflation, were kindly supplied by Daicell Co. The nylon films were pretreated in boiling water as reported in our previous paper[1].

The spin probes were sorbed by the nylon films from aqueous probe solutions at 343 K for 2 days. The amounts of the spin probes sorbed were determined as about 5×10^{-6} mol g^{-1} nylon by spectrophotometric measurements of the initial and final bath concentrations. After sorption, the film was put into an e.s.r. tube, dried *in vacuo* at 393 K for 1 day, and sealed in the presence of air. E.s.r. spectra were obtained under the same conditions as described in our previous paper[1].

RESULTS AND DISCUSSION

Extrema separation

The extrema separation of the e.s.r. spectra 2*Az*′ is an appropriate measure of the mobility of spin probes, and decreases with increase in mobility. The temperature dependence of 2*Az*′ has often given important information about the mobility: the dependences vary from system to system as reported in our previous paper[1].

Figure 1 shows plots of 2*Az*′ against temperature for SPVII. The change of 2*Az*′ with temperature became more gentle with increasing methylene chain length of the nylon. The same pattern was observed for SPI and SPVIII. These gentle curves of 2*Az*′ suggest that the mobility of the spin probes changes gently with temperature and is not sensitive to changes of the nylon chain motion. In the case of NY-12, the temperature dependences of 2*Az*′ for the three spin probes were compared (*Figure 2*). The curves for SPI and SPVIII were superimposed on each other, while that for SPVII was not overlapped, suggesting that the mobility is affected by the amide group rather than by the molecular volume.

The temperature, T_{50G}, at which 2*Az*′ becomes 5 mT (50 gauss), was determined from the curves of 2*Az*′ against temperature, and is given in *Table 1*. For all the spin probes T_{50G} decreased with increasing methylene chain length, while the effects of drawing on T_{50G} were very small. This behaviour of T_{50G} was different from that of the glass transition temperature T_g, which was determined by dynamic mechanical measurement at 10 Hz. These discrepancies between T_{50G} and T_g are attributed to differences in the methods used[1,2].

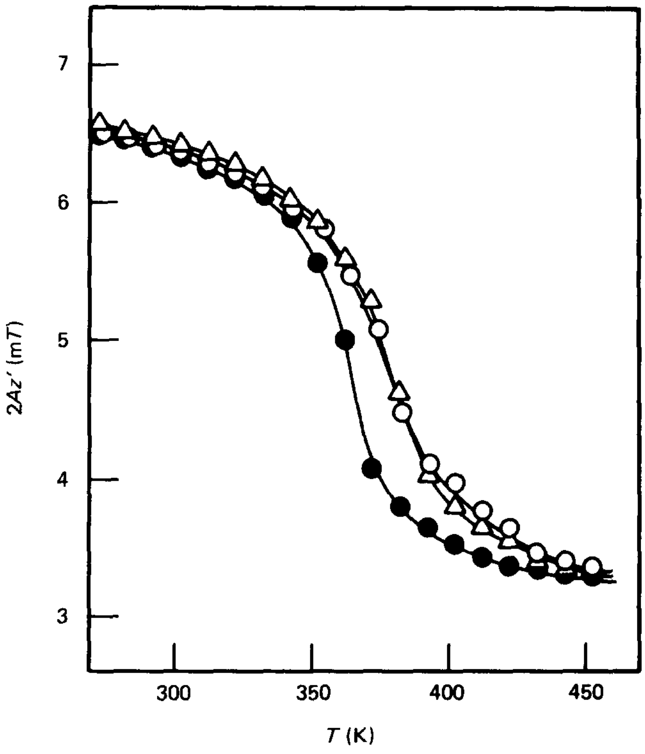

Figure 2 Plot of 2*Az*′ vs. temperature for NY-12: (○) SPI (cf. ref. 1); (●) SPVII; (△) SPVIII

Table 1 Values of T_{50G} (K) and T_g (K)

		NY-4	NY-6(2D)	NY-6(ND)	NY-11	NY-12
T_{50G}	SPVII	415	398	395	375	363
	SPVIII	419	407	405	385	377
	SPI[a]	424	408	404	388	376
T_g[b]		373	358	318	340	331

[a] Cf. ref. 1
[b] Determined by dynamic mechanical measurement at 10 Hz

Table 2 The f and v_m values for NY-6(ND) determined from equation (1)

	$T_{50G}-T_g$ (K)	f $(=v_p/v_m)$	$v_p{}^a$ (nm^3)	v_m (nm^3)
SPVII	77	0.51	0.217	0.43
SPVIII	87	0.63	0.276	0.44
SPI	86	0.62	0.371	0.60

[a] Evaluated by Kitaigorodskii's method[10]

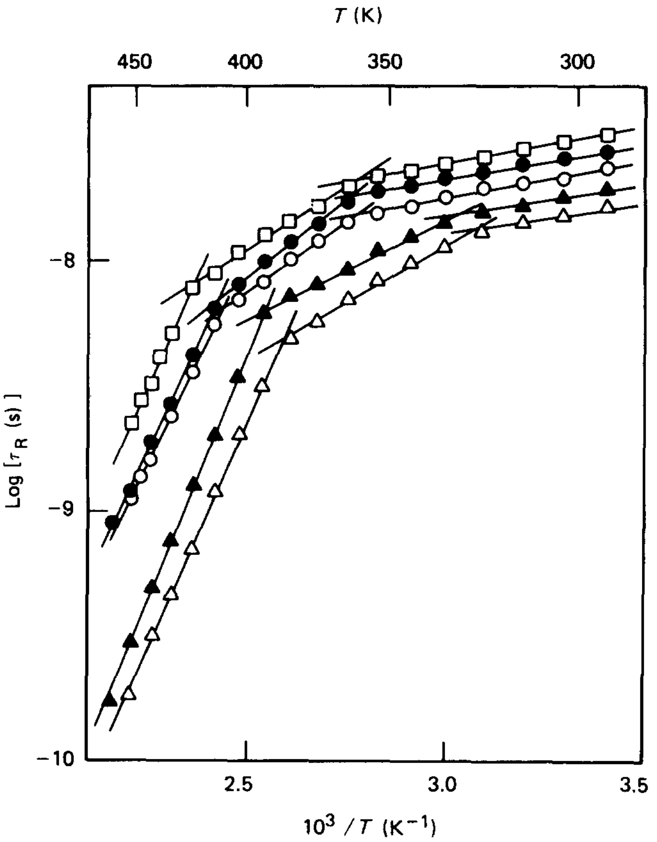

Figure 3 Arrhenius plots of τ_R for SPVII: (□) NY-4; (●) NY-6(2D); (○) NY-6(ND); (▲) NY-11; (△) NY-12

Here it is interesting to note the effects of spin probe structures on the mobility. The T_{50G} values for SPI and SPVIII were almost the same, whereas SPVII had a somewhat smaller T_{50G} value than SPI and SPVIII. Now if we interpret the above results by a simple relation between T_{50G} and T_g which was derived by Kusumoto *et al.*[4], the following conclusions may be drawn. Using Bueche's free-volume theory[7], they derived:

$$T_{50G}-T_g=52\{2.9f[\ln(1/f)+1]-1\} \qquad (1)$$

where f is the ratio of the molecular volume of the spin probe to that of the polymer segments participating in the local motion at T_g. Assuming that the probe molecules are located in an amorphous region of the nylon, we calculated the f value and the molecular volume of the polymer segments, v_m, for undrawn nylon film NY-6(ND), in which T_g reflects the properties of the amorphous region. In this calculation, the molecular volumes of the spin probes, v_p, were estimated by means of Kitaigorodskii's method[10]. As a result, v_m evaluated from the results for SPVII and SPVIII coincided quite well, whereas v_m calculated from the data for SPI was larger (*Table 2*). At least two reasons for this discrepancy can be presumed. One is that equation (1) takes no account of polymer–probe interactions. In the systems examined here, the interaction between the amide groups of both the spin probes and nylons through hydrogen bonding should be taken into consideration. The other is that rotation of a piperidine ring around a single bond takes place. All the spin probes used in the present study have a single bond link with the other part of the probe molecules, so that rotation around the single bond may be observed. The above reasons have been pointed out by other authors: Bullock *et al.*[5] mentioned that it is quite conceivable that the polymer–probe interactions and the flexibility of spin probes mask the effects of probe volume, and Hlouskova *et al.*[6] used the effective molecular volumes of spin probes, taking into account the non-rigid behaviour of the probe molecules. It is thus concluded that the interaction between the amide group of the spin probes and the nylons, and the single-bond rotation strongly affect the T_{50_G} values.

Rotational correlation times

Rotational correlation times τ_R were determined from the e.s.r. spectra. As in our previous paper[1], the equations derived by Kivelson[11] and Kuznetsov *et al.*[12] were used for the calculation of τ_R. As τ_R used here was determined assuming an isotropic rotation, the value should be termed 'apparent rotational correlation time', and was used for the purpose of comparison.

Arrhenius plots of τ_R are shown in *Figures 3* and *4*. For all the spin probes, the Arrhenius plots gradually shifted to lower temperatures along the abscissa as the methylene

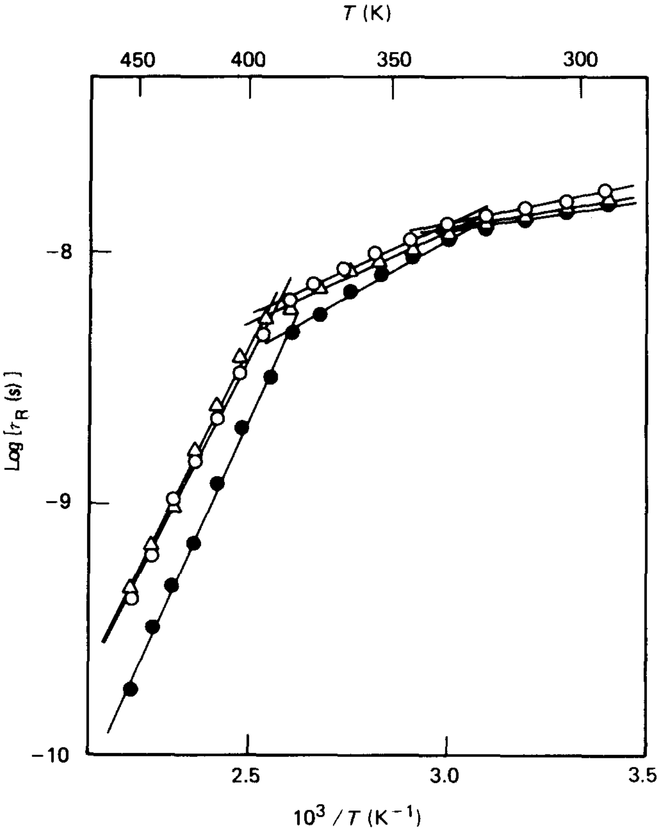

Figure 4 Arrhenius plots of τ_R for NY-12: (○) SPI (cf. ref. 1); (●) SPVII; (△) SPVIII

Table 3 Values of T_n' and T_n (K)

		NY-4	NY-6(2D)	NY-6(ND)	NY-11	NY-12
T_n'	SPVII	361	360	358	328	325
	SPVIII	379	364	365	349	329
	SPI[a]	381	371	362	354	336
T_n	SPVII	422	412	408	393	384
	SPVIII	433	424	423	399	395
	SPI[a]	441	423	425	403	389

[a] Cf. ref. 1

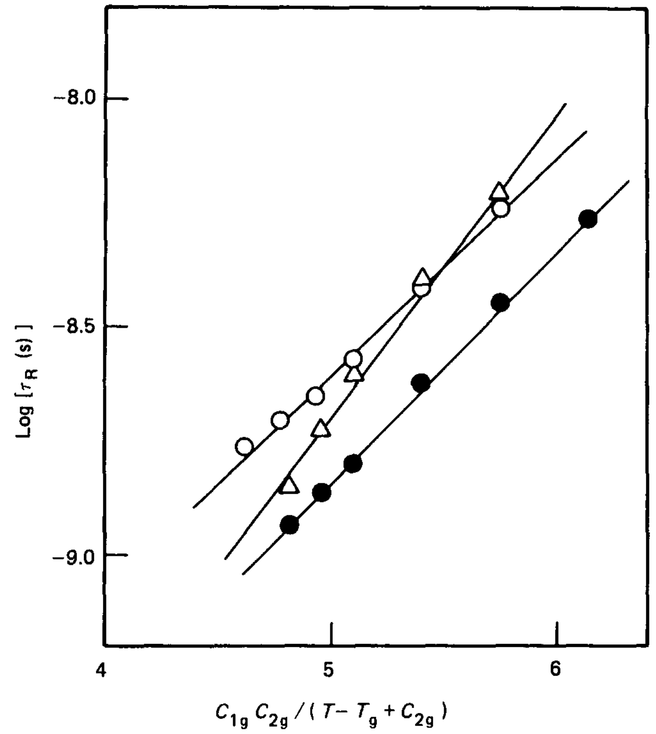

Figure 5 Plot of log τ_R vs. $C_{1g}C_{2g}/(T-T_g+C_{2g})$ for NY-6(ND): (○) SPI; (●) SPVII; (△) SPVIII

chain length of the nylon increased (*Figure 3*). Small effects of drawing on τ_R were observed in the low-temperature region, but no significant effects were found in the high-temperature region, suggesting vigorous motion of the nylon chains in the high-temperature region regardless of their orientation. The Arrhenius plots for SPI and SPVIII were virtually superimposed on each other, while that for SPVII was not overlapped (*Figure 4*). This result was the same as that for $2Az'$, suggesting that the mobility of the spin probes cannot be explained solely by their molecular volumes.

As shown in *Figures 3* and *4*, two distinct crossover points were defined for all the systems. The crossover points in the low- and high-temperature regions were designated as T_n' and T_n, respectively. As described in our previous paper[1], at T_n' rotation around the single bond between the probe moiety and the NH group is assumed to occur: rotation around other single bonds hardly takes place owing to the resonance of the π-orbitals. T_n is believed to correspond to the temperature at which the rotational motion of the whole probe molecule takes place: above T_n the spin probe rotates without any restriction by specific bonding with the macromolecules. Values of T_n' and T_n are given in *Table 3*. Both the T_n' and T_n values behave in a similar manner to the T_{50G} values. This also indicates that the mobility is influenced by the ineraction between the probe molecules and the nylon chains rather than by the probe volumes.

Using the values of τ_R, we evaluated the f values for NY-6(ND) again by means of the following relation derived by Bullock *et al.*[5]:

$$\log \tau_R = \log \tau_R^{\infty} + f C_{1g} C_{2g}/(T - T_g + C_{2g}) \qquad (2)$$

where C_{1g} and C_{2g} are the WLF parameters (universal values $C_{1g} = 17.44$ and $C_{2g} = 51.60$ were used for the calculation) and τ_R^{∞} is the rotational correlation time at the limit $T \rightarrow \infty$. For the three spin probes in NY-6(ND), log τ_R was plotted against $C_{1g}C_{2g}/(T-T_g+C_{2g})$ in the temperature region above T_n where the rotation of the whole probe molecule is assumed to occur (*Figure 5*). The plots for all the three spin probes gave good linearity. The f and τ_R^{∞} values were determined from the slope and intercept of the straight lines (*Table 4*). The f values determined from equation (2) were comparable with those determined from equation (1), in which τ_R^{∞} is assumed to be constant (10^{-14} s): in equation (2) τ_R^{∞} is different for each individual spin probe (*Table 4*). Thus neither of the equations gave a simple correlation between the probe volumes and f values, indicating that other factors should be considered.

For further discussion, the activation energies for rotation E_a^R were determined from Arrhenius plots of τ_R (*Table 5*). The behaviour of E_a^R for all the spin probes was almost the same. E_a^R in the 'low'-temperature region below T_n' was similar for all the systems. The spin probes are supposed only to vibrate rotationally in this region owing to the difficulty of nylon chain motion. The values of E_a^R in the 'medium'-temperature region between T_n' and T_n showed a complicated tendency. The E_a^R value in this region was larger for NY-6(2D) than for NY-6(ND), i.e. a noticeable effect of drawing was observed. This may be explained by considering the hydrogen bonding between the amido group of the spin probes and the nylons, as discussed in the study on 4-amino-2,2,6,6-tetramethyl-1-piperidinyloxy (SPIII)[1,3]. Orientation of the nylon chains is assumed to facilitate hydrogen bonding sterically, as illustrated schematically in *Figure 6a*, leading to greater difficulty of rotation. On the other hand, in the undrawn film the hydrogen bonds may be formed in the manner shown in *Figure 6b*, in contrast to the crosslinking modes. It is thus estimated that the ratio of the two modes of hydrogen bonding determines the magnitude of E_a^R.

The E_a^R values in the 'high'-temperature region above T_n did not show any regular tendency. Since hydrogen bonding between the amide group of the spin probes and the nylons is thought to be broken in this region, E_a^R may include the energy of this break. The complicated behaviour of E_a^R in this region is attributed to the difference of the breaking energy in each system.

Table 4 The f, v_m and τ_R^{∞} values for NY-6(ND) determined from equation (2)

	f $(=v_p/v_m)$	v_m (nm^3)	$10^{12}\tau_R^{\infty}$ (s)
SPVII	0.519±0.010	0.418±0.008	10.3
SPVIII	0.66±0.07	0.42±0.04	3.66
SPI	0.48±0.02	0.77±0.03	1.03

Table 5 Values of E_a^R (kJ mol^{-1})

		NY-4	NY-6(2D)	NY-6(ND)	NY-11	NY-12
'Low'	SPVII	5.71 ± 0.07	4.56 ± 0.12	5.24 ± 0.10	3.99 ± 0.13	4.46 ± 0.13
	SPVIII	6.41 ± 0.10	4.86 ± 0.10	5.31 ± 0.07	5.6 ± 0.2	4.37 ± 0.10
	SPI[a]	5.7 ± 0.2	5.3 ± 0.3	4.9 ± 0.3	6.1 ± 0.4	6.3 ± 0.2
'Medium'	SPVII	19.7 ± 0.7	24.2 ± 1.1	20 ± 2	15.3 ± 0.6	17.2 ± 1.3
	SPVIII	23.8 ± 1.0	25.0 ± 1.5	21.1 ± 0.7	14.8 ± 1.9	13.8 ± 1.0
	SPI[a]	21.8 ± 1.0	27 ± 2	22.5 ± 1.6	19.6 ± 1.2	14.1 ± 1.1
'High'	SPVII	65.2 ± 1.6	63.7 ± 1.6	61.1 ± 0.9	73.5 ± 0.7	67.3 ± 1.9
	SPVIII	52 ± 7	57.7 ± 1.7	59.0 ± 1.4	72 ± 4	61.9 ± 1.4
	SPI[a]	66 ± 3	59 ± 4	59.5 ± 1.7	63.2 ± 1.9	60.9 ± 1.9

[a] Cf. ref. 1

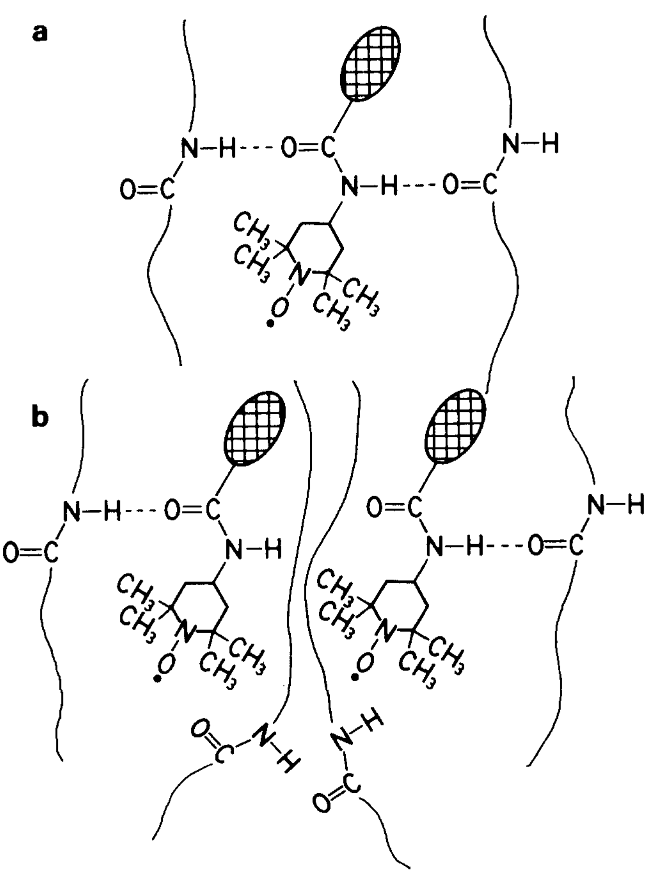

Figure 6 Model of the interaction between nylon chains and spin probes having an amide group

Anisotropy of rotation

The anisotropy parameter ε was calculated from the e.s.r. spectra, as described in our previous paper[1]. The ε value proposed by Kuznetsov *et al.*[13] is a useful measure to estimate the degree of anisotropic rotation in the region $\tau_R < 1 \times 10^{-9}$ s. The behaviour of ε did not vary in all the nylons used, so that the results for NY-12 are discussed because it had the smallest measured τ_R in all the nylons. As shown in *Figure 7*, ε for all the spin probes was less than zero in the region $\tau_R < 1 \times 10^{-9}$ s, indicating that they rotate anisotropically around the x axis[14], which corresponds to the N–O bond direction. The long axis of the three spin probes corresponds to the x axis and they rotate most easily around this axis. In addition, ε for SPI was more negative than those for SPVII and SPVIII, indicating that the longer probe molecule rotates more anisotropically.

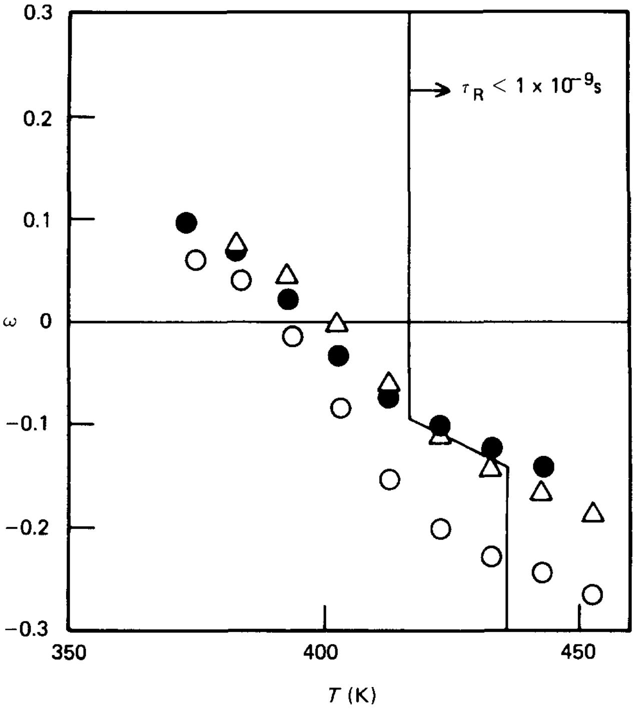

Figure 7 Plot of ε vs. temperature for NY-12: (○) SPI (cf. ref. 1); (●) SPVII; (△) SPVIII

CONCLUSIONS

From the above results, we can conclude that spin probes having an amide group interact with the amide groups of the nylons through hydrogen bonding. Consequently the mobility of the spin probes in nylon films is influenced much more strongly by this interaction than by the probe volumes. This fact makes it difficult to apply a simple relation between the probe motion and the segmental motion of the polymer chain. In addition, the behaviour of the crossover points in the Arrhenius plots and the activation energies hardly varied in different probe molecules. It is thus concluded that the amide group of the spin probes plays a dominant role in modifying the probe motions in nylon films.

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