

THE ROTATION BARRIER OF ELECTRON SPIN PROBE IN THE STUDY OF POLYMER SYSTEM*

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ABSTRACT

In the study of molecular motion of polymer by means of ESR in combination with spin probe, owing to that the ESR spectrum depicts only the behavior of spin probe, the information obtained is of indirect nature. Hence the relationship between them must first be investigated before any conclusion could be drawn. In this paper, two parameters T_R and C_R are introduced to characterize the changing of tumbling rate of spin probe, and the concept of rotation barrier of spin probe is proposed. It is considered that the magnitude of the rotation barrier is determined by the internal cavity size and distribution in polymer. When the temperature is raised, the size and distribution of the cavities change accordingly, thus the tumbling of spin probe changes gradually from a slower to a higher rate.

The application of spin probe in the ESR study of molecular motion of polymer is developed recently. Many papers have been published using stable nitroxide free radical as the probe material^[1,2]. However, the ESR spectra obtained in this way respond only to the motion of spin probe, the relationship between the spectra and the molecular motion of polymer must first be sought before any useful information can be obtained.

In this paper, the spectra of various polymers doped with five stable nitroxides are studied (T spectra). Similar spectra are obtained by varying the solvent content in the polymers (C spectra). Further spectra are worked out by confining the spin probe in the pores of macroreticular resin (D spectra). By analyzing these spectra, the concept of rotation barrier of nitroxide radical is proposed, and the latter is determined by the pore sizes and their distribution in the host polymer at different temperature.

EXPERIMENTAL

Instrument

Hilger Watts ESR-5 (X-band)

Spin probes used

2,2,6,6-tetramethyl-4-hydroxypiperidine-1-oxyl (HONO); 2,2,6,6-tetramethyl-4-piperidone-1-oxyl (ONO); 2,2,6,6-tetramethyl-4-hydroxypiperidine-1-oxyl benzoate (BzONO);

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2,2,5,5-tetramethyl-3-carbamidopyrroline-1-oxyl (NH_2CONO); 2,2,6,6-tetramethyl-4-amino-piperidine-1-oxyl (NH_2NO).

Polymers studied

Polystyrene (PS), $\bar{M}=1.0\times 10^5$; poly(methyl methacrylate) (PMMA), $\bar{M}=3.6\times 10^4$; *cis*-polybutadiene (*cis*-PB), $\bar{M}=5\times 10^3$; poly(dimethyl siloxane) (PDMS), $\bar{M}=5.3\times 10^5$; atactic polypropylene (a-PP), $\bar{M}=1.2\times 10^5$; polyethylene (PE), $\bar{M}=1.0\times 10^4$; polycarbonate (PC), $\bar{M}=2.4\times 10^4$; poly(ethylene glycol) (PEG), $\bar{M}=2.0\times 10^4$; chlorinated poly(vinyl chloride) (ch-PVC).

ESR samples preparation

By dissolving the polymer in appropriate solvent in which a small amount of probe was added, usually 0.05% of polymer by weight. The solvent was driven off in the air and the polymer was dried in vacuum. The PE sample was specially made by mixing the probe and the polymer in molten state.

Macroreticular styrene-divinyl benzene copolymers (MR resin) preparation: They were made by suspension polymerization in the presence of 30% stearic acid, 30% toluene and 20% *n*-hexane as diluent, the crosslinking densities were 30% for MR-1, 35% for MR-2 and MR-3^[3].

RESULTS AND DISCUSSION

From the respective spectra at programmed increasing temperature (the increment of temperature is 10°C) for each sample, the parameter $2A_{11}$ were evaluated (Fig. 1). In plotting the $2A_{11}$ value against the respective temperature (Fig. 2), three regions can usually be distinguished: the region of broad spectrum, the region of narrow spectrum and the region of mixed spectra. Taking the spectra of HONO in chlorinated PVC as an example, the temperature

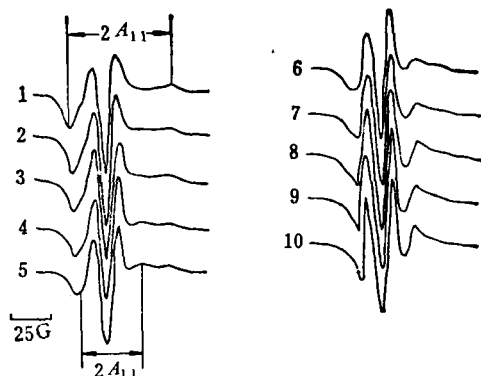


Fig. 1 T spectra-ESR spectra of nitroxide HONO in chlorinated PVC at various temperature

Upper $2A_{11}$ =the peak-to-peak separation of broad spectrum;

Lower $2A_{11}$ =the peak-to-peak separation of narrow spectrum;

Temperature ($^\circ\text{C}$): 1, 18.5; 2, 29.0; 3, 40.0; 4, 50.0; 5, 60.0,
6, 70.0; 7, 80.0; 8, 90.0; 9, 99.5; 10, 110.

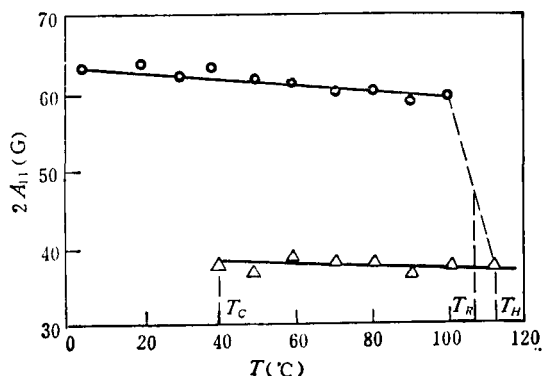


Fig. 2 $2A_{11}$ values as function of temperature in chlorinated PVC doped with nitroxide HONO

—○— $2A_{11}$ value for broad spectrum;

—△— $2A_{11}$ value for narrow spectrum.

T_L the temperature at which the mixed spectra appears;

T_H the temperature at which the mixed spectra ends.

range of the three regions are: below 40°C, above 110°C, between 40°C and 110°C respectively. It can be seen that the mixed spectra are the duplication of broad and narrow spectra, so actually there are only two kinds of nitroxide radical. According to Freed's formula^[4] in calculating the rotation time (τ_R) of nitroxide radical, the broad spectrum corresponds to the slower tumbling rate of the probe ($10^{-9} \text{ s} < \tau_R < 10^{-7} \text{ s}$), while that of narrow one corresponds to faster rate ($5 \times 10^{-11} \text{ s} < \tau_R < 10^{-9} \text{ s}$). The mixed spectra region represents the transition of spin probe from slower tumbling rate to faster rate, therefore the mixed region could be considered as transition region. The temperature range of transition region varies with the nature of polymer, it ranges from 20°C for PDMS to 120°C for PC in our case (Table 1). In literature^[2], the temperature at which $2A_{11}$ equals to 50 Gauss, called as T_{50G} , is taken as the transition temperature for nitroxide radical and is correlated with the T_g of polymer. From our experiment, the T_{50G} is influenced by many factors, including the structure of polymer, the size of probe, the affinity between them, so this parameter bears no physical meaning, at least from the theoretical point of view.

In order to characterize the transition of tumbling rate of nitroxide radical, we designate the interface temperature between region of mixed spectra and that of narrow spectrum as T_R , which is the temperature at which all the probes in the polymer just turn from slower tumbling rate to faster rate. In Fig. 2, when the temperature is raised up to T_H (110°C), the broad spectrum disappears. Since the temperature increment in the experiment amounts to 10 degrees, so 105°C would be the best value for T_R .

For the purpose to analyze the relation between the spectra and the molecular motion of polymers, we have performed the following two kinds of experiments. (1) The polymers were treated with solvent vapor up to different concentrations, then the ESR spectra were taken (Fig. 3) and the $2A_{11}$ value at certain specific temperature was plotted against the percentage of solvent (w/w) (Fig. 4). Figs. 3 and 4 show that the C spectrum also consists of three regions: the region of broad spectrum, the region of narrow spectrum and the region of mixed spectra, similar to that of T spectrum. Here, we designate the interface concentration

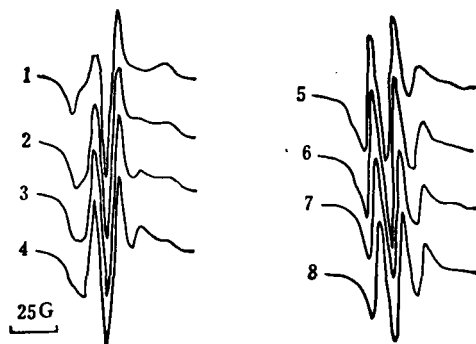


Fig. 3 The ESR spectra of nitroxide BzONO in PMMA-CHCl₃ system at different chloroform concentration

Temperature: 29°C.

Weight % CHCl₃: 1, 0; 2, 11.4; 3, 17.3; 4, 24.3;
5, 31.6; 6, 38.9; 7, 44.3; 8, 52.2.

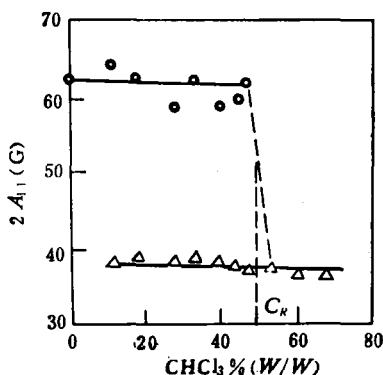


Fig. 4 A plot of $2A_{11}$ against chloroform concentration in PMMA-CHCl₃ system, with BzONO as spin probe

Temperature: 29°C.

—○— $2A_{11}$ value of broad spectra; —△— $2A_{11}$ value of narrow spectra.

of solvent between the region of mixed spectra and the region of narrow spectrum as C_R (referring to certain specific temperature). (2) MR resins of different pore size were used to observe the relationship between the pore size and the tumbling rate of probes. A certain amount of nitroxide (0.05% of resin by weight) was diffused into MR resins by means of solvent, the latter was removed afterwards. Because the three MR resins are highly crosslinked, their gel phase is tightly packed in which the probe can not diffuse into, so the pores are the only place for the probe to disperse. Figs. 5 and 6 clearly show that similar changes of tumbling rate of probes NH₂CONO and BzONO appear, as in the case of T and C spectra. In the present case, the variance is the pore size inside the MR resins.

From these experiments, it is evident that the change of tumbling rate of probe mainly depends on the size of internal cavity in polymer. Since the transition is not limited to a single temperature, but covers a wide range, so there must be a distribution of the size of cavities in polymer. When the temperature is raised or the polymer is doped with solvent, the mobility of polymer segments increases. As a result, the rotation barrier of nitroxide radical decreases, which gives rise to the change of tumbling rate of the probe. Thus, the ratio of the

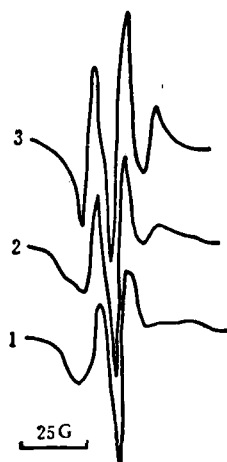


Fig. 5 D spectra-ESR spectra of nitroxide NH_2CONO in MR resins at room temperature
1, MR-3; 2, MR-2; 3, MR-1.

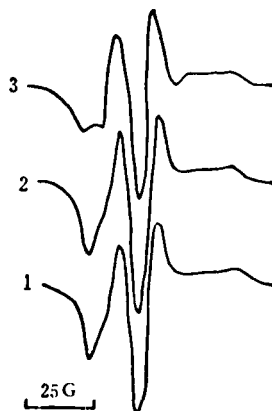


Fig. 6 D spectra-ESR spectra of nitroxide BzONO in MR resins at room temperature
1, MR-3; 2, MR-2; 3, MR-1.

population of slower tumbling species of the probe to that of faster ones depends on the distribution of cavity size in the transition region.

It is natural then to correlate the change of size cavity in polymer with the change in specific volume of the polymer. It turns out that the relative increase of specific volume in the transition region (using HONO as probe in the present case) for most polymers is around 2.1%, that is to say, although the expansion coefficients of different polymers vary greatly, their relative thermal expansions in the transition regions are approximately equal.

In Table 2 are listed the value of T_R and C_R of five probes in three systems. It can be seen that the T_R values for different probes doped in the same polymer are different, and the C_R values for different probes doped in the same polymer-solvent system are different; yet in the same polymer, the T_R values for the five probes are in the same order as that of the C_R values, the only exception is PMMA, in which some ester change might occur. This phenomenon may be due to the following causes. In the case of T spectrum, if the probe with a larger T_R value changes from slower tumbling rate to faster rate, the host polymer must be heated to a higher temperature, i.e., greater thermal expansion of the polymer, it means larger space is required for the probe to tumble. For the same reason, in the case of C spectrum, more solvent must be taken by the host polymer and the internal cavities are swollen to larger volume, which leads to the decrease of rotation barriers of the probes and makes the C_R value of this polymer higher. These facts described above further confirm the concept that the cavity size and distribution inside the polymer and their variation with temperature determine the rotation barrier of the probe.

Finally, in comparing the T_R values with T_g (Table 1), we find that for polymers with rigid chains, such as PS, PMMA, chlorinated PVC and PC, T_R is smaller than T_g ; while for polymers with soft chains, such as *cis*-PB, PDMS, *a*-PP, PE and PEG, T_R is greater than T_g . Therefore, the spin probe test may serve as a measure of flexibility of different polymer chains.

Table 1

Polymer	T_L (°C)	T_H (°C)	$T_H - T_L$ (°C)	$\beta \times 10^4$	$\frac{V_{T_H} - V_{T_L}}{V_{T_L}}$ (%)	T_R (°C)	T_g (°C)
PE	-5	85	90	2.59	2.3	80	100
PMMA	10	90	80	2.62	2.1	85	114
ch-PVC	40	110	70	—	—	105	179
cis-PB	-60	-30	30	6.53	2.0	-35	-108
PDMS	-90	-70	20	9.26	2.0	-75	-123
a-PP	-45	26	71	—	—	20	-18
PE	-23	26	49	—	—	20	-68
PC	-20	100	120	1.88	2.3	95	150
PEG	-15	5	20	—	—	0	-66

- Note: 1. V_{T_L} and V_{T_H} are the specific volume of polymer at temperature T_L and T_H .
 2. $(V_{T_H} - V_{T_L})/V_{T_L}$ is the relative change of specific volume in the transition region.
 3. All these values are referred to HONO as the probe.

Table 2

Nitroxide	Polymer						
	PMMA		PS		a-PP		
	T_R (°C)	C_R (29°C) chloroform (%)	T_R (°C)	C_R (24°C) benzene (%)	T_R (°C)	C_R (-50°C) n-hexane (%)	C_R (-30°C) n-hexane (%)
HONO	85	37.0	80	12.7	20	27	22
ONO	95	32.0	85	18.0	8	17	7
NH ₂ CONO	143	63.5	85	17.8	—	—	—
NH ₂ NO	—	48.5	115	29.1	28	52	32
BzONO	120	52.0	125	29.7	55	57	39

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