E.p.r. studies of spin-probed and spin-labelled poly(vinyl benzoate), poly(vinyl cinnamate) and poly(vinyl diisophthalate)

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E.p.r. relaxation measurements have been made on polymers derived from poly(vinyl alcohol). Poly(vinyl alcohol) was esterified with three carboxylic acids, one of which was bifunctional, leading to formation of a polymer network. Polymeric samples were studied with two nitroxide sonds and a nitroxide label copolymerized in the main chain. The label had longer correlation times than the sonds. However, the activation energy calculated for the rotational diffusion of the label was lower than that for the radical sonds. In the linear polymers, the size of the side group affected only slightly the rotational motion of the sonds, whereas the rate of motion of the label was very sensitive to variations in the side group.

(Keywords: poly(vinyl benzoate); poly(vinyl cinnamate); poly(vinyl diisophthalate); spin-labelled; e.p.r.)

INTRODUCTION

Electron paramagnetic resonance (e.p.r.) spectroscopy has been utilized during the past 25 years to study local dynamics in various macromolecular systems. With this method it is possible to study the nature of motion of polymer chain segments in bulk and in solution. The molecular relaxations detectable by e.p.r. have profound effects upon the mechanical behaviour, solid state reactivity, diffusion, melt rheology and solution properties[1]. The monitoring of the sudden change in the width of the spectrum as a measure of the glass transition temperature, and the temperature dependence of the rotational correlation times as a means to compare activation energies with those determined by other dynamic measurements are some of the data derivable from the analysis of e.p.r. spectra of stable nitroxide radicals embedded in polymeric materials[2].

Nitroxide probes may be used as sonds dispersed in polymeric matrices or as labels covalently bound at different parts of the polymer molecule. For example, the label could be bonded to the polymer as a side group, as in poly(methyl methacrylate)[3–5], in the main chain segment as in poly(vinyl acetate)[6] and poly(vinyl alcohol)[7], or as an end group, as in segmented polyurethanes[8].

The present work is a study of the molecular motions in spin-labelled and spin-probed poly(vinyl benzoate), poly(vinyl cinnamate), and poly(vinyl diisophthalate) in thin films. The effects of the olefinic bond in the side group as well as the effect of crosslinking on the local segmental motion of these polymers is examined.

EXPERIMENTAL

Raw material

Poly(vinyl alcohol) (Aldrich) with average molar mass 115 000 was purified by precipitation from water into methanol and dried in a vacuum oven.

Spin-labelled polymers

The procedures of Bullock *et al.*[6] and Tenhu and Sundholm[7] were adopted with little modification. Vinyl acetate was copolymerized with 2,2,5,5-tetramethylpyrroline-3-carboxamide prepared as described by Rozantsev[9] in dry benzene using AIBN as initiator. The pyrrolidine moieties of the copolymer were oxidized with *m*-chloroperbenzoic acid to nitroxides. Hydrolysis of the poly(vinyl acetate) nitroxide radical was performed by dissolving it in methanol and refluxing with 40% aqueous sodium hydroxide solution. Soxhlet extraction with methanol removed free nitroxide, excess NaOH and sodium acetate from the hydrolysed polymer. The polymer, having a number-average molar mass of 40 000, was esterified using excess acid chloride (benzoyl chloride or *trans*-cinnamoyl chloride). Purification was carried out by Soxhlet extraction using water as solvent to remove unreacted labelled poly(vinyl alcohol). The polymers are referred to as PVBNO and PVCMNO, corresponding to benzoyl and cinnamoyl chloride respectively.

Spin-probed polymers

Poly(vinyl alcohol) (PVAL) was esterified with excess amounts of (1) benzoyl chloride, (2) *trans*-cinnamoyl chloride, and (3) isophthaloyl dichloride to obtain poly(vinyl benzoate) (PVB), poly(vinyl cinnamate) (PVCM), and poly(vinyl diisophthalate) (PVDI)[10].

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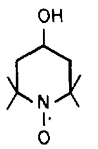
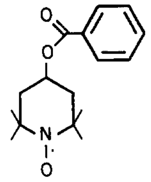
Purification was performed to remove unreacted PVAL and other impurities. PVCM was partially soluble in chloroform. Thus it was extracted with chloroform for 3 days. PVCM1 refers to the chloroform-soluble component, and PVCM2 to the chloroform-insoluble part.

Thin films of polymers PVB and PVCM1 were cast from chloroform solution containing about 0.01% 4-hydroxy-2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPOL) or 4-benzoxy-2,2,6,6-tetramethylpiperidine-1-oxyl (BZONO). PVCM2 and PVDI containing 0.01% nitroxide were swollen in chloroform. The solvent was removed in a vacuum oven for several days.


TEMPOL


BZONO

Electron paramagnetic resonance

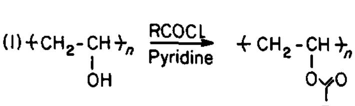
E.p.r. spectra were recorded with Varian E4 and E109 spectrometers. The samples were cooled to −150°C to register the immobilized spectra, and then gradually heated to 150–160°C. The labelled polymers were observed to degrade at temperatures above 150°C, whereas the sonds were still stable.

Differential scanning calorimetry

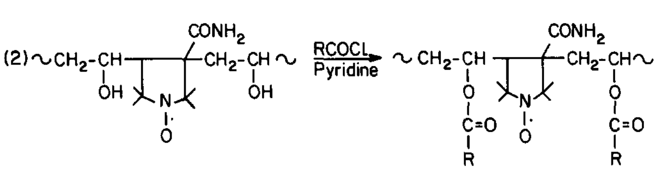
D.s.c. measurements were performed with a Perkin–Elmer DSC 2 with a heating rate of 20°C min^{-1}.

RESULTS AND DISCUSSION

Poly(vinyl alcohol) molecules were esterified with acid chloride. The reaction equations for unlabelled (A) and labelled (B) polymers are shown below.



$$(1)\ \underset{OH}{+CH_2-CH+_n} \xrightarrow[Pyridine]{RCOCl} \underset{\underset{R}{O\diagup O}}{+CH_2-CH+_n}$$



PVDI is a crosslinked polymer owing to the nature of the acid chloride. As mentioned above, part of the poly(vinyl cinnamate) was insoluble in chloroform. The insolubility may be due to chemical heterogeneity of the polymer, i.e. to incomplete esterification of the hydroxyl groups of poly(vinyl alcohol). Furthermore, poly(vinyl cinnamate) is known to be a photocrosslinkable polymer, so the insoluble fraction may be slightly crosslinked material.

The e.p.r. signal for the labelled polymers was very weak, and the number of labelled units in the polymer is estimated to be about one nitroxide group per 20000 repeating units. Samples doped with nitroxide sonds showed strong e.p.r. signals. The spectra registered at low temperatures, i.e. well below the glass transition temperature, are typical broadened, asymmetric spectra indicative of a slow tumbling rate of the radicals. With increasing temperature the width of the spectra decreases; the temperature region where the spectra change from slow-motional ones to symmetric three-line spectra typical of rapidly rotating nitroxides generally correlates with the glass transition temperature measured by other methods. *Figures 1* and *2* show plots of the outermost extrema separation against temperature. As is convenient and customary, the temperatures where the extrema separation is 50G is denoted as T_{50G} and the aim is to use it as a measure of the glass transition of the polymers. *Table 1* summarizes the T_{50G} values obtained and the T_g

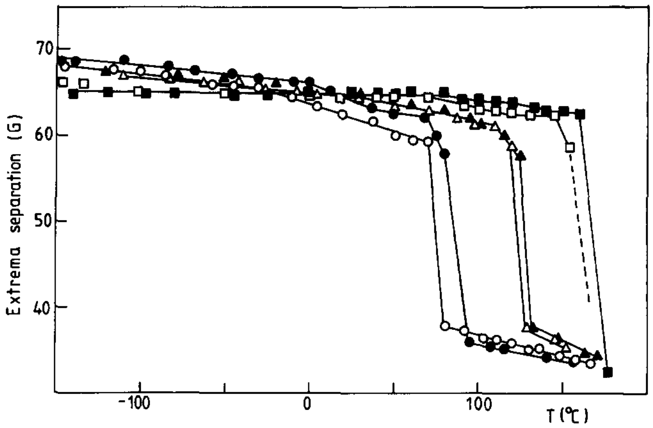


Figure 1 Width of the e.p.r. spectra of TEMPOL (○, ●), BZONO (△, ▲) and the labelled polymers (□, ■) as a function of temperature. Open symbols refer to poly(vinyl benzoate), filled symbols to the chloroform-soluble fraction of poly(vinyl cinnamate), PVCM1

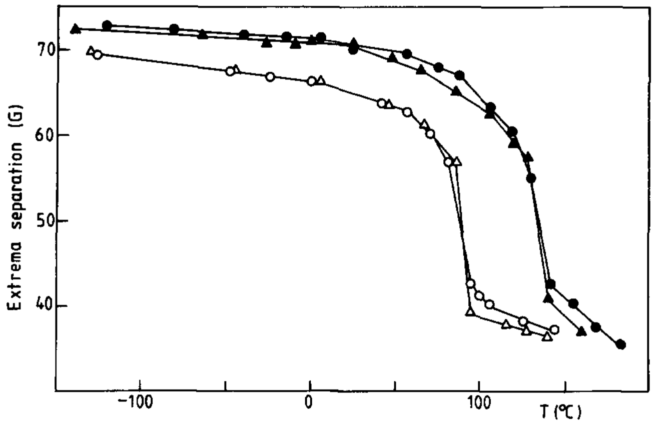


Figure 2 Width of the e.p.r. spectra of TEMPOL (○, ●) and BZONO (△, ▲) in the insoluble fraction of poly(vinyl cinnamate), PVCM2 (open symbols) and in the crosslinked polymer PVDI (filled symbols)

Table 1 T_g and T_{50G} values

Sample	T_g (°C)	T_{50G} (°C) TEMPOL	BZONO	LABEL
PVB	91	75	124	–
PVCM1	95	86	128	–
PVCM2	95	87	87	–
PVDI	–	133	133	–
PVBNO	72	–	–	158
PVCMNO	92	–	–	166

values from d.s.c. measurements. As expected, T_{50G} is found to increase with increasing probe size. It is noteworthy that T_{50G} values measured with TEMPOL are lower than the calorimetrically measured values of T_g. On the other hand, the labelled polymers have a high T_{50G}. Unfortunately the nitroxide-containing polymers begin to degrade above T_{50G}; at high temperatures the e.p.r. signal rapidly loses intensity, and thus the estimation of the correlation times is impossible at $T > T_{50G}$.

Polymers PVCM2 and PVDI show the peculiar feature that with both nitroxide sonds the same T_{50G} value is obtained; T_{50G} is 87°C for PVCM2 and 133°C for PVDI. T_g measured by d.s.c. is 95°C for PVCM2, similar to that of PVCM1. It is somewhat surprising that both nitroxides, TEMPOL and BZONO, give a T_{50G} value below the glass transition temperature of PVCM2. PVDI is a tightly crosslinked polymer showing no glass transition by d.s.c. In PVCM2 and PVDI, the probes are rotating in holes in the polymer matrix, and thus T_{50G} does not reflect glass transition but a structural relaxation of the polymer network.

In principle, the e.p.r. spectrum obtainable for a nitroxide radical mixed with a polymer gives information only on the motion of the 'guest' molecule, modulated by the motion of the 'host' polymer. In some instances radical dopants may perturb the polymer system, e.g. by binding to the polymer. However, if there is no specific interaction between the probe and the polymer, an increase in the rate of probe motion detected at temperatures above T_g is correlated with an increase of free volume in the polymer. The free volume in turn may be correlated with the volume of the chain segment relaxing at T_g. The size of the motional chain segment was estimated by the Kusumoto equation[11], modified by Bullock *et al.*[12]:

$$T_{50G} - T_g = c_2((2.303c_1 f)/9.1 - 1) \qquad (1)$$

where c_1 and c_2 are constants in the WLF equation, and f is volume of the probe divided by the volume of the relaxing segment. Since c_1 and c_2 are not known for poly(vinyl benzoate) and poly(vinyl cinnamate), the 'universal' constants $c_1 = 17.4$ and $c_2 = 51.6$ were used. Tsay and Gupta[3] estimated the volumes of TEMPOL and BZONO probes. Using these values, and estimated volumes of the repeating units in PVBZ and PVCM[13], the size of the motional segment in both polymers was calculated. The results are collected in *Table 2*.

As can be seen in *Table 2*, TEMPOL gives higher values of the segment volume than does BZONO. This is due to the ability of TEMPOL to form a hydrogen bond to the carbonyl group in the polymers. Because of specific binding of TEMPOL to the polymer side group, it does not report purely the glass transition; this conclusion may also be drawn from the fact that the T_{50G} values are lower than T_g of the host polymer. In PVB and PVCM1, the probe BZONO reflects the changes in free volume more accurately than does TEMPOL, and thus the number of repeating units in the relaxing segment is approximately four in PVB and three in PVCM1. Several authors have estimated the smallest segments involved in the glass–rubber relaxation. For example, the number of repeating units in the segment was estimated to be three in polyisoprene, five in polybutadiene, seven to ten in styrene–butadiene rubber[14], and four to seven in poly(vinyl acetate)[15].

Table 2 Values of f, volume of the relaxing segment (V), and number of repeating units in the segment (N)

	TEMPOL			BZONO			Label
Sample	f	V (Å^3)	N	f	V (Å^3)	N	f
PVB	0.156	1130	6	0.372	764	4	0.606
PVCM1	0.188	943	4	0.372	764	3	0.553

PVB and PVCM differ from each other because PVCM contains an olefinic bond between the carbonyl group of the ester and the benzene ring. A double bond in the main chain has been shown to increase the size of the relaxing chain segment by hindering the segmental motion in its vicinity[16]. The present results show that an olefinic bond in the side chain does not change the volume of the relaxing segment.

For a given polymer, T_{50G} increases with increasing probe size. In a labelled polymer the nitroxide moiety has a certain degree of motional independence over the other parts of the polymer, and thus the difference between a probe and a label is not necessarily as great as might be expected[17]. Because the number of nitroxide radicals in the labelled polymers PVBNO and PVCMNO is very low, it is to be expected that the volume of the relaxing segment is equal to that of polymers PVB and PVCM. Knowing the value of f for the labelled polymers, one should obtain the effective volume of the nitroxide moiety in the polymer chain. It is clear that the effective volume of the label must be much lower than the volume of the whole polymer. According to the data in *Table 2* the label behaves as a sond built up of the nitroxide ring itself and one or two repeating units of the polymer.

The advantage of a labelled polymer lies not in its size but in the ability to study very closely the local dynamics of the chain. Especially in the present case, the nitroxide is copolymerized rigidly in the main chain and has no motional independence over the segment to which it is bound. The rotational correlation times (τ_c) of the labels and sonds have been estimated assuming the motion of the nitroxides to be isotropic. This often leads to some error in the absolute values of τ_c, especially when the radical is covalently bound to the polymer and thus rotates anisotropically. However, the main interest here is to compare polymers that are chemically very close to each other. For example, Tsay and Gupta[3] and Shiotani and Sohme[4] have shown that there is no significant difference in the activation energies of the nitroxide rotation in spin-labelled and spin-probed PMMA, whether the rotation is assumed isotropic or anisotropic. The absolute values of τ_c are model-dependent and vary with the method and parameters used for the calculation. As will be shown, using approximate methods outlined by Freed and co-workers[18,19] and the Kivelson theory[20], the differences between the polymer samples in the present work are clearly detected.

The rotational correlation times from the slow motional spectra have been calculated using the equation

$$\tau_c = a(1 - S)^b \qquad (2)$$

where $S = A'_{zz}/A_{zz}$. A'_{zz} is one-half the separation of the outer hyperfine extrema in slow motional spectrum, and A_{zz} is the corresponding rigid limit value. Adopting[19] the moderate jump diffusion model and intrinsic linewidth equal to 3*G*, $a = 1.0 \times 10^{-9}$ s and $b = -1.01$. In the rapid tumbling regime the correlation times have been calculated using the intensities of the three lines and the width of the central line[20].

Spin labels have longer correlation times than the spin probes because the labels report the motion of the polymer backbone. Furthermore, labelled PVCM has a higher τ_c than does labelled PVB. This is due to the bulkier side group in PVCM, which slows the segmental motion of the polymer. Crosslinking reduces the mobility of the chains; spin-probed PVDI has longer correlation times than uncrosslinked PVB and PVCM.

Figures 3–6 show the Arrhenius plots of log τ_c against inverse absolute temperature for the spin labels and sonds. Apparent activation energies calculated from these plots are summarized in *Table 3*.

Ishida *et al.*[21] obtained an activation energy of 46 kJ mol^{-1} for β-relaxation of poly(vinyl benzoate) using dielectric measurements. The values of E_a obtained for the nitroxide sonds in PVB and PVCM1 in this work at high temperature (region 1) is attributable to the relaxation of the ester side groups. Activation energies in region 2 (and region 3) are due to the main chain carbon–carbon bond rotation at medium and low temperature respectively. Ishida *et al.*[21] found that the activation energy of poly(vinyl benzoate) was larger than that of poly(vinyl acetate) in the α- and β-relaxation because of the bulky side groups. The activation energies for the PVCM samples are lower than those of the PVB. This raises the role of the olefinic bond in the ester side group on the relaxation process. Although it can hinder the motion of the segments in its vicinity, an increased methine content in the side chain tends to enhance the flexibility or reduce the apparent bulkiness of the side group. Thus these roles contradict each other and may alter both the correlation times and activation energy.

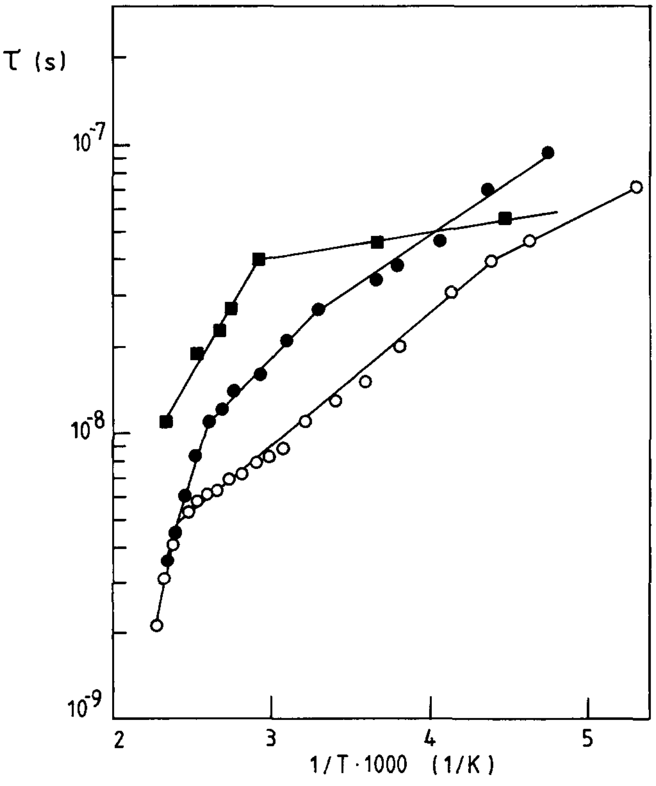


Figure 3 Correlation times for the sonds and the label in poly(vinyl benzoate). (○), TEMPOL; (●), BZONO; (■), the label

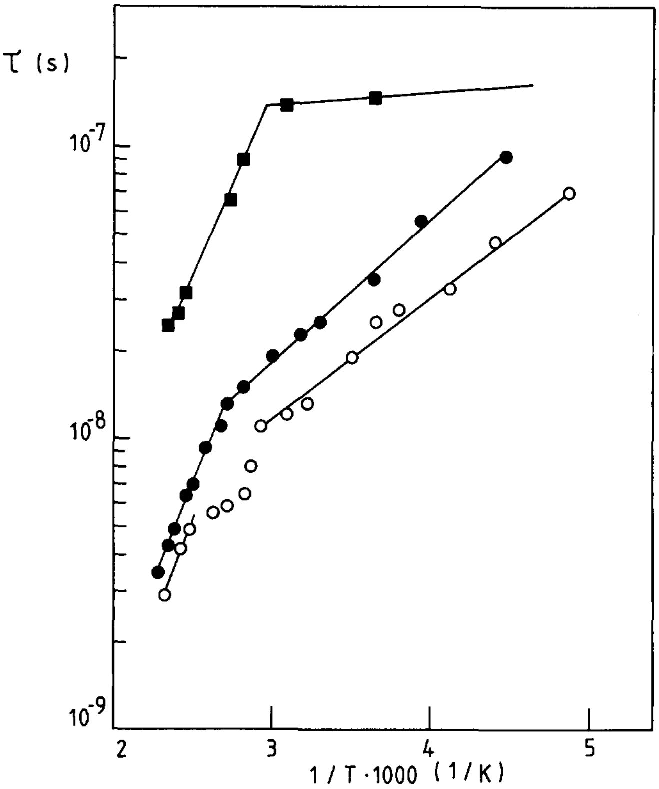


Figure 4 Correlation times for TEMPOL (○), BZONO (●) and the label (■) in chloroform-soluble poly(vinyl cinnamate)

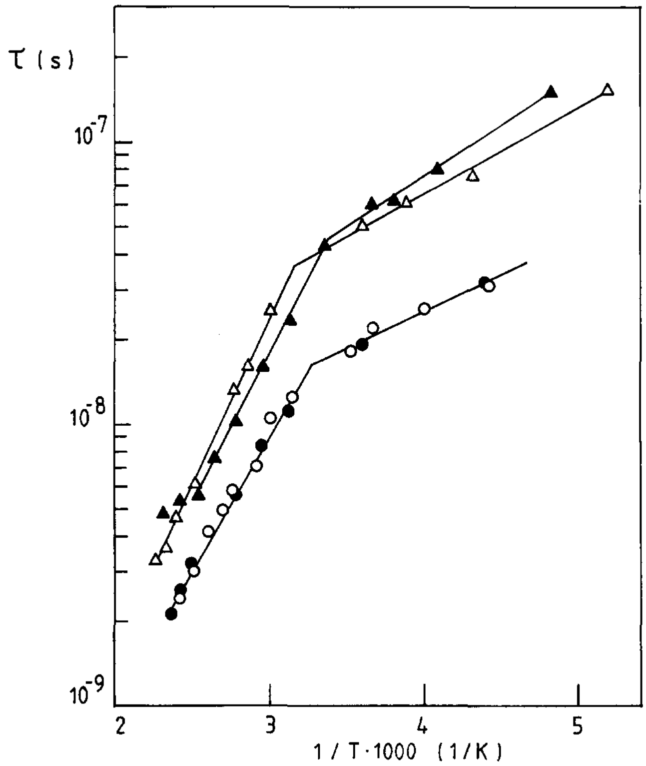


Figure 5 Correlation times for TEMPOL (open symbols), BZONO (filled symbols) in PVCM2 (○, ●) and PVDI (△, ▲)

The E_a values obtained refer to different molecular relaxation processes in each sample. For example, E_a for the sonds in PVB is 35.2–38.7 kJ mol^{-1} in the high-temperature region, whereas the corresponding value for the labelled PVB is 17.8 kJ mol^{-1}. The former value

Table 3 Apparent activation energies for the nitroxide sonds and labels determined by e.p.r.

		Activation energy (kJ mol^{-1})		
Sample	Probe	Region 1	Region 2	Region 3
PVB	BZONO	35.2	11.0	10.0
	TEMPOL	38.7	8.6	7.1
PVCM1	BZONO	24.8	10.2	–
	TEMPOL	29.5	8.0	–
PVCM2	BZONO	19.1	5.5	–
	TEMPOL	18.2	5.0	–
PVDI	BZONO	19.8	7.0	–
	TEMPOL	23.0	5.8	–
PVBNO	label	17.8	1.7	–
PVCMNO	label	22.7	1.0	–

was stated to be due to the relaxation of the benzoate group; the latter value describes local motion of the main chain. In the network polymer PVDI, the isophthalate side groups act as crosslinks whose motion is strongly limited. In the high-temperature region, E_a for the sonds (19.8–23.0 kJ mol^{-1}) is considerably lower than that of the linear polymers PVB and PVCM1. The low value, it is concluded, is a result of a combination of the main chain local motion and the limited motion of the side groups. It should be noted that the radicals in the polymers PVDI and PVCM2 show activation energies very close to each other over the whole temperature range, these values being much lower than those for the linear polymers.

Activation energies obtained from e.p.r. studies may depend on radical probe size, as found by Wasserman *et al.*[22] and Cameron *et al.*[23]. However, Tsay and Gupta[3] observed that the apparent activation energy was independent of the size, shape and mass of the probes and the label, in their e.p.r. studies of poly(methyl methacrylate).

CONCLUSIONS

A slight increase in the size of the side group has been shown to have a profound effect on the dynamics of the polymer main chain. The correlation time of a nitroxide label bound into the polymer backbone increases when a benzoate side group is replaced by a cinnamate group. Increasing the size of the side group does not affect very much the rate of motion of the sonds. The apparent activation energy for the sond rotation is observed to be higher in PVB than in PVCM. This indicates that although cinnamate groups slow down the segmental motion, these side groups have considerable motional freedom over the polymer main chain.

Crosslinking has been shown to decrease the rate of sond rotation, owing to hindered motion of the polymer chains. The apparent activation energy for a nitroxide sond is lower in a polymer network than in linear polymers. Crosslinking alters the local relaxation processes in polymers, and thus the radicals rotate more independently of the host polymer in a network structure than in a linear polymer.

The effective volume of the label has been estimated to correspond to that of a sond consisting of the nitroxide ring and one or two repeating units of the polymer. This emphasizes the local nature of information obtainable with spin probes.

T_{50G} has been used as a measure of the glass transition temperature, and to estimate the volumes of the chain segments relaxing at T_g. Two cases have been observed (crosslinked PVDI and chemically heterogeneous, possibly slightly crosslinked PVCM2) where correlation between T_{50G} and T_g was lost.

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