Electron paramagnetic resonance application to polymers: 4. The segmental volume of poly(phenylacetylene) using different nitroxide spin probes

J. S. Hwang*, M. M. Saleem and C. P. Tsonis
Department of Chemistry, King Fahd University of Petroleum and Minerals,
Dhahran 31261, Saudi Arabia

(Received 13 November 1989; revised 16 February 1990; accepted 22 February 1990)

Electron paramagnetic resonance (e.p.r.) studies of $T_{50\,G}$ of poly(phenylacetylene) have been carried out at X-band as a function of spin probe size over a wide range of temperatures. It was found that $T_{50\,G}$ increased with increasing probe size. The polymer glass transition temperature T_g, determined from the break on the plot of ln T_R *versus* $1/T$ for tempone in poly(phenylacetylene), was 296 K. The apparent activation enthalpy for the T_g relaxation process increased with increasing probe size, while the segmental size of the polymer appeared to be independent of the nitroxide used, and has a range of 898–922 Å^3. The segmental volume measured by the spin probe technique is in excellent agreement with the volume of 970 Å^3 of 10 repeat units on an average chain based on number-average molecular weight of 960. Thus our results showed that there are 17–20 backbone atoms in the segment of poly(phenylacetylene). Assuming the polymer segment to be of spherical shape, the diameter of the sphere was found to have a range of 11.7–12.4 Å.

(Keywords: e.p.r.; segmental volume; spin probe; poly(phenylacetylene))

INTRODUCTION

Several years ago we employed nitroxide spin probes to study lineshape changes in poly(phenylacetylene) in the fast[1] and slow[2] motional regions. In this investigation we are seeking a quantitative relationship between the glass transition temperature T_g and the e.p.r. parameter $T_{50\,G}$ with the segmental size of the polymer and we are examining the effect of nitroxide probe size on the parameters described above. In our analysis we used the equation[3] that relates $T_{50\,G}$ and T_g as shown below:

$$T_{50\,G} = \frac{T_g}{1 - 0.03T_g/\Delta H_a} \qquad (1)$$

where T_g is the glass transition temperature, $T_{50\,G}$ is the temperature at which the separation of the outermost peaks of the e.p.r. spectrum of the nitroxide probes in the polymer matrix is 50 G (gauss) and ΔH_a is the apparent activation energy for the T_g relaxation process. The equation that takes into consideration the volume of the probe and the segmental size of the polymer has been developed by Kusumoto[4,5] as follows:

$$T_{50\,G} - T_g = 52\left[2.9f\left(\ln\frac{1}{f} + 1\right) - 1\right] \qquad (2)$$

where f is the ratio of the volume of the probe to that of the segment. The experimental results are explained quantitatively on the basis of thermally activated motions of polymer segments. Using activation[6] volumes at T_g, we are able to obtain an independent estimate of the segmental volume of the polymer. Such data will allow a more quantitative examination of the effect of relative probe size for studying a particular transition in a particular polymer.

EXPERIMENTAL

E.p.r. measurements were carried out with poly(phenylacetylene) prepared as described earlier[1] and doped with nitroxide spin probes purchased from Molecular Probes. Thermogravimetric analysis on poly(phenylacetylene) samples used in this study showed that they are thermally stable up to 573 K. E.p.r. measurements were performed with a Varian E-109 X-band spectrometer using 100 kHz modulation. The spectrometer is interfaced with an E-935 data acquisition system, which employs the HP-9835B desktop computer for data processing. The spectra were digitized and stored on cassette tapes. The temperature was varied from 284 to 429 K using the Varian E-257 variable-temperature unit to within ±1°C, with thermal equilibrium for 10 min at each temperature before measurements. The microwave frequency was measured with a Hewlett-Packard model 5342A digital frequency counter. The magnetic field sweep was calibrated with a Varian E-500-2 self-tracking n.m.r. gaussmeter with an accuracy of ±0.2 mG. Microwave power and field modulation were carefully controlled so that power saturation and line broadening were absent. Four nitroxide spin probes of different size and shape were used (*Figure 1*). They are (a) 4-oxo-2,2,6,6-tetramethyl-piperidinyl-1-oxy (tempone), (b) doxylcyclohexane, (c) 4-hexadecanoyl-2,2,6,6-tetramethyl-piperidinyl-1-oxy (tempo palmitate) and (d) 4′,4′-dimethylspiro[5α-cholestane-3,2′-oxazolidin]-3-yloxy (doxylcholestane), as

---

* To whom correspondence should be addressed

0032-3861/91/0200231-04

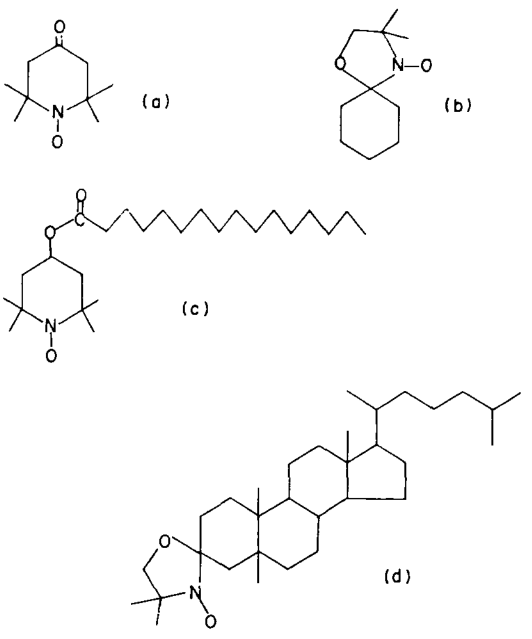

Figure 1 Molecular structures of spin probes used in this work. See text for names

shown in *Figures 1a–d*. The number-average molecular weight ($M_n = 960$) of the poly(phenylacetylene) prepared thermally was determined by vapour pressure osmometry (v.p.o.) in toluene using benzil as the standard.

RESULTS AND DISCUSSION

The signal of poly(phenylacetylene) in the presence of the four spin probes used in this investigation had an intensity that was stronger by 99% than that of pure (non-probed) poly(phenylacetylene). This suggests that the concentration of paramagnetic species in the poly(phenylacetylene) conjugated system was negligible (1%).

Figures 2–5 show the experimental e.p.r. spectra of four spin probes in poly(phenylacetylene) over a wide temperature range. The total lineshape is a function of the tumbling frequency and the anisotropy of rotation of the spin probes in the polymer matrix. This has been described elsewhere[1,2]. In this investigation, we focus our attention on $T_{50\,\mathrm{G}}$, which is the temperature at which the extrema separation is equal to 50 G. The value of $T_{50\,\mathrm{G}}$ can be directly determined from the extrema separation in the e.p.r. spectra, which is found to be in the region of the e.p.r. spectrum where rapid changes in the extrema separation take place. The extrema separation in gauss measured in the manner shown in *Figure 3* was plotted as a function of temperature, and is shown in *Figure 6*. From the plot in *Figure 6*, the $T_{50\,\mathrm{G}}$ values for the four spin probes in poly(phenylacetylene) were determined. Using equations (1) and (2), the values of ΔH_a and f were calculated and are listed in *Table 1*.

It was found that $T_{50\,\mathrm{G}}$ increases with increasing probe size and molar mass and reaches a maximum value of $T_{50\,\mathrm{G}} = 392$ K for doxylcholestane. One can explain this observation by assuming that increasing molar mass of the spin probes leads to increased intermolecular interactions between the spin probes and the polymer chains, resulting in a better coupling of rotational motions of spin probes with those of the polymer segments. This is reflected in the increasing values of $T_{50\,\mathrm{G}} - T_g$ and the apparent enthalpy of activation for larger spin probes. For example, $T_{50\,\mathrm{G}} - T_g = -15$°C for polystyrene when di-t-butyl nitroxide is used as spin probe and it is 43°C when tempone is used[5]. This behaviour is also predicted by the mathematical relationship between $T_{50\,\mathrm{G}} - T_g$ and probe size given in equation (2). The smaller the probe size, the lower the temperature at which it starts to tumble for a given polymer.

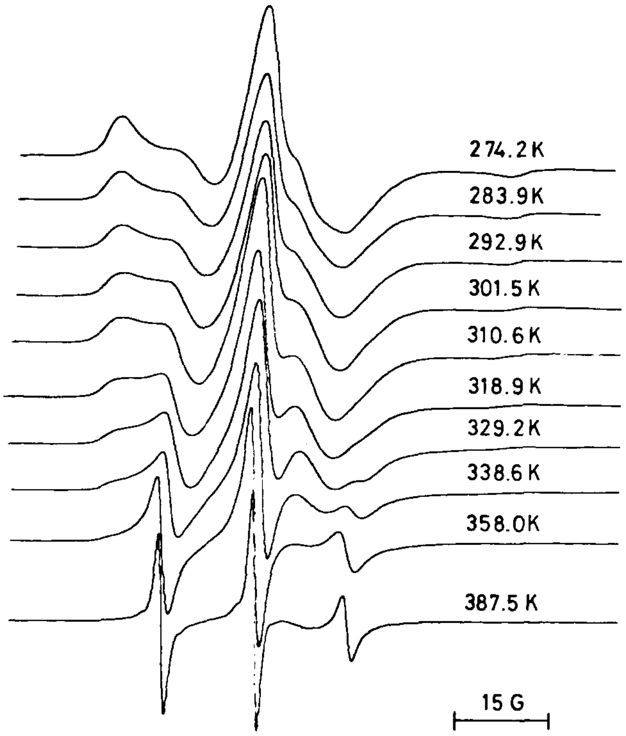

Figure 2 Experimental e.p.r. spectra of tempone in poly(phenylacetylene) in the temperature range 274.2 to 387.5 K

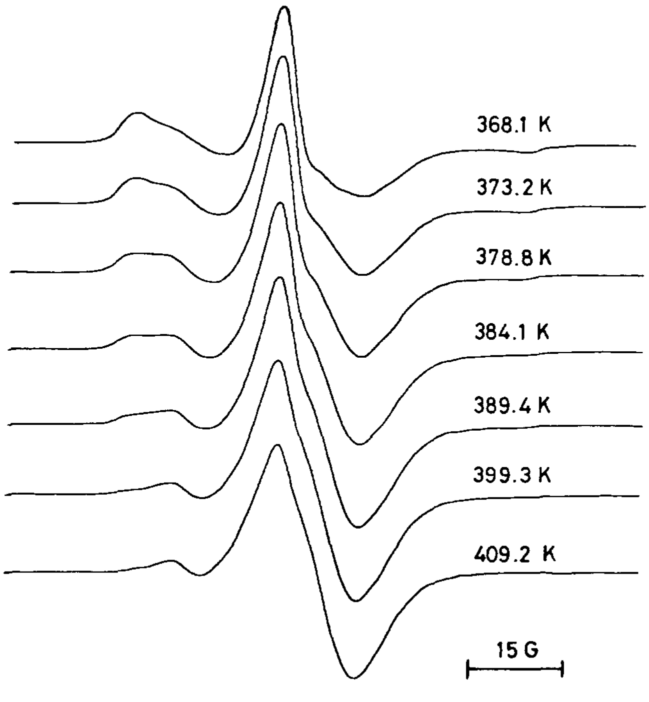

Figure 3 Experimental e.p.r. spectra of doxylcyclohexane in poly(phenylacetylene) in the temperature range 368.1 to 409.2 K

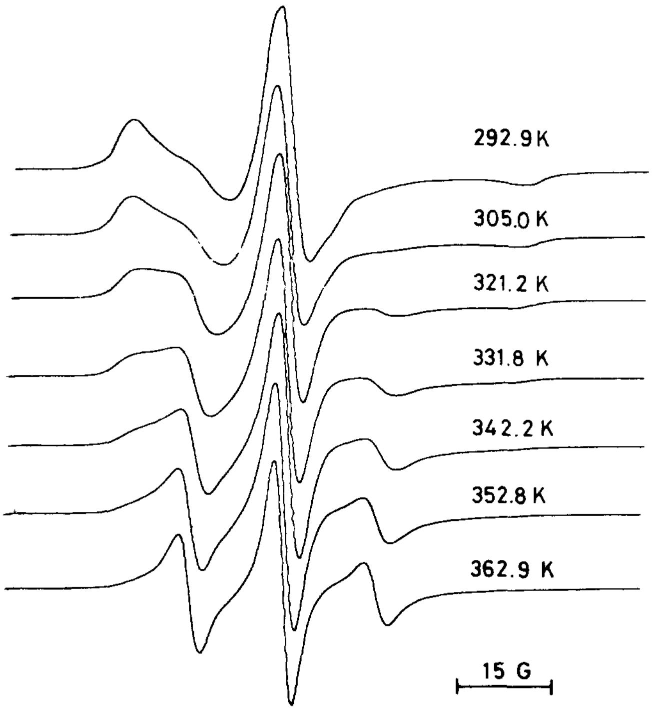

Figure 4 Experimental e.p.r. spectra of tempo palmitate in poly(phenylacetylene) in the temperature range 292.9 to 362.9 K

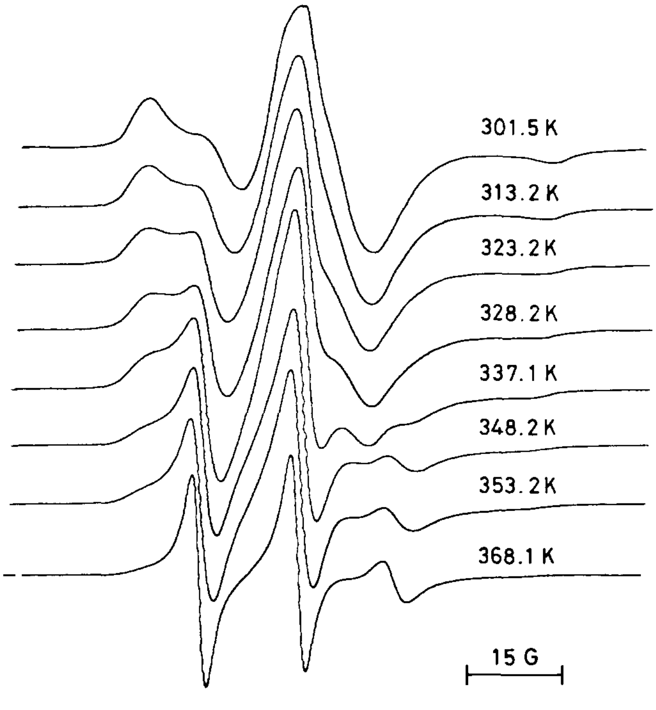

Figure 5 Experimental e.p.r. spectra of doxylcholestane in poly(phenylacetylene) in the temperature range 301.5 to 368.1 K

The f values were calculated by repeated iterations of equation (2) to fit the experimentally derived quantity $T_{50G} - T_g$. These values are listed in *Table 1*. It can be seen that f values increase with increasing probe size. Since f is defined as the ratio of probe volume (V_p) to the volume of the polymer segment experiencing motion (V_m), i.e. $f = V_p/V_m$, the segmental volume is given by V_p/f. The values of the segmental volume range from 834 to 992 Å^3 (*Table 1*). The fact that cholestane has a smaller segmental volume than the other spin probes may be due to a considerable variation in the structure, flexibility and polarity of this spin probe, and it is quite conceivable that these factors override the effect of probe volume in this case. If we consider the polymer segment to be of spherical shape, the diameter of the sphere would range from 11.7 to 12.4 Å.

As an independent estimate of the segmental volume, we used the activation volume data at T_g for 10 amorphous polymers (on figure 3 from a paper by Boyer and Kumler[6]) and obtained an activation volume corresponding to a spherical molecule with a diameter of 13 Å. This value is in good agreement with our results (12 Å). The number of backbone atoms of the segment was estimated by multiplying the number of backbone atoms of the repeat unit of the polymers by the excluded-volume ratio of the repeat unit to the segment. Thus, 17–20 backbone atoms are included in the segment of poly(phenylacetylene).

Since the tumbling behaviour of the nitroxide spin probe is related to the extrema separation[7], our study showed that the tumbling behaviour of nitroxide probes is qualitatively and even semiquantitatively related to the activation volumes. Thus, our study using nitroxide spin probes of different sizes and shape verified the correctness

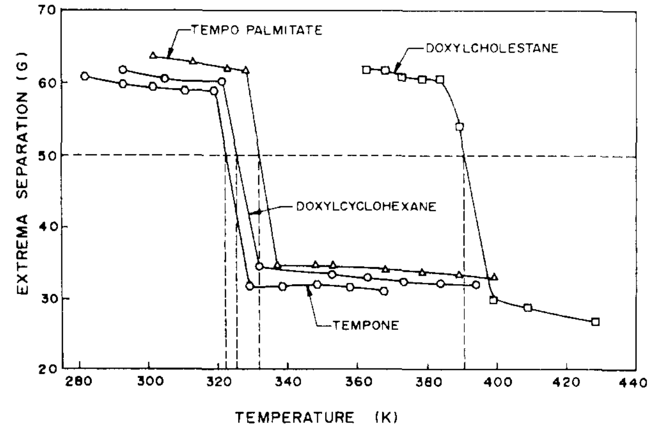

Figure 6 Temperature dependence of extrema separation for four spin probes in poly(phenylacetylene)

Table 1 Calculated segmental volume and diameter of the segment

Spin probe	Molar mass (g mol^{-1})	Size (Å^3)	T_{50G} (K)	$T_{50G} - T_g$ (K)	ΔH_a (kcal mol^{-1})	$f = V_p/V_a$	T_{50G}/T_g (from eq. (2))	Segmental volume, V_p/f (Å^3)	Diameter of segment (Å)
Tempone	170	177	322	26	110	0.197	25.97	898	12.0
Doxylcyclohexane	184	200	326	30	96.5	0.214	30.03	935	12.1
Tempo palmitate	412	239	332	36	81.9	0.241	36.06	992	12.4
Doxylcholestane	472	679	392	96	36.3	0.814	96.01	834	11.7

and applicability of Kusumoto's hole theory[5], a theory relating T_{50G} to the glass transition temperature of the host polymer in which the probe is supposed to diffuse through the polymer matrix as well as a polymer segment.

ACKNOWLEDGEMENT

This research was supported by King Fahd University of Petroleum and Minerals.

REFERENCES

1 Hwang, J. S. and Tsonis, C. P. *Macromolecules* 1983, **16**, 736
2 Hwang, J. S., Saleem, M. M. and Tsonis, C. P. *Macromolecules* 1985, **18**, 2051
3 Kumler, P. L. and Boyer, R. F. *Macromolecules* 1976, **9**, 903
4 Kusumoto, N., Sano, S., Zaitsu, N. and Motozato, Y. *Polymer* 1976, **17**, 448
5 Kusumoto, N., Sano, S. and Kujima, T. *Rep. Prog. Polym. Phys. (Japan)* 1977, **22**, 519
6 Boyer, R. F. and Kumler, P. L. *Macromolecules* 1977, **9**, 461
7 Goldman, S. A., Bruno, G. V. and Freed, J. H. *J. Phys. Chem.* 1972, **76**, 1858