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Comparative Study of the Chain Dynamics of Polymers Containing Group VIA Linkages

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Introduction

There is considerable current interest in the area of weak-link polymers, such as those containing peroxide, disulfide, tetrasulfide, diselenide, etc. linkages, of group VIA elements[1] for their technological importance as initiators,[2,3] fuels,[4] adhesives,[5] and semiconductors.[5] Although studies on the microstructure[6,7] and degradative behavior[1,8] of these polymers have been investigated, not much attention has been paid to their chain dynamics,[7] particularly comparative studies among the polymers of group VIA. Such a study will be extremely useful in understanding the physical properties and processability of this class of polymers. The effect of a heteroatom with respect to its hydrocarbon backbone analogue, because it is rare, is very attractive for studying chain dynamics behavior. In this paper, we report the chain dynamics of poly(styrene disulfide) (PSD) and poly(styrene tetrasulfide) (PST) in terms of spin-lattice relaxation (T_1) values. We have also attempted to make a comparative study of the effect of a heteroatom (O or S) on the chain dynamics of the backbone by also investigating other members of this group, namely, poly(styrene peroxide) (PSP) and poly(phenylthiirane) (PPT), as well as the parent polymer, polystyrene (PS). Stuctures of all of the polymers used in the present study are presented in Table 1. The T_1 values of PSP, PPT, and PS are available in the literature. In addition, variation in T_1 values with sulfur rank in these polysulfides has been investigated for the first time. We believe that the T_1 values of the polymers in group VIA may provide some insight into their relative flexibility. To further corroborate the trend, statistical calculations of their Kuhn length[9−11] have also been carried out. It may be noted that this type of group study, although common in simple organic compounds, is rare in polymers.

Experimental Section

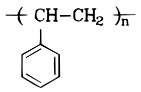
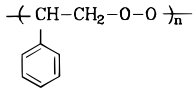
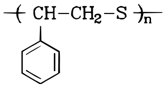
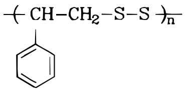
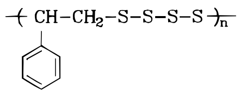
The NMR spectra were recorded in the pulsed Fourier transform mode using a Bruker AC 200 F spectrometer. Spin-lattice relaxation times were measured by the standard inversion recovery ($180-\tau-90-T$) pulse sequence, with a T of at least five times the longest T_1 of interest. The polymer solutions were not deoxygenated. All chemical shifts are referenced to internal tetramethylsilane (TMS). PSD and PST were synthesized as reported elsewhere.[1] It may be noted that $CHCl_3$ and $CDCl_3$ are good solvents for the polymers investigated here.

Calculation of Kuhn Statistical Segment Length *A*. The Kuhn statistical segment length A also known as the thermodynamic segment, is the most universal measure of estimating the equilibrium flexibility (rigidity) of a polymer chain.[9−11] The lower the value of A, the more flexible the chain will be. The calculation of Kuhn length is discussed in the following.

Let us consider a random flight polymer chain that is composed of N segments of length A. The mean-square end-to-end distance ($\langle R^2\rangle$) is given by

$$\langle R^2\rangle = NA^2 \tag{1}$$

Table 1. Structures of the Polymers

Polymer	Structure
PS	
PSP	
PPT	
PSD	
PST	

The end-to-end distance of the same chain (R_m) at full extension is given by

$$R_m = NA \tag{2}$$

From eqs 1 and 2, we get

$$A = \langle R^2\rangle / R_m \tag{3}$$

The real chain in bulk solution could be considered to exist under theta conditions. In a good solvent the chains expand, and their expansion factor (α) is the ratio between the end-to-end distance under expanded conditions and under theta conditions. The end-to-end distance for a real chain having n number of bonds of length a and angle θ between them is given by

$$\langle R^2\rangle = \{na^2(1 - \cos\theta)\alpha^2\}/(1 + \cos\theta) \tag{4}$$

Similarly, the R_m of a real chain is given by

$$R_m = na \sin\theta/2 \tag{5}$$

To compare the flexibility in real chains, they could be approximated as an equivalent freely jointed chain. The segment length A in eq 3 for real chains is called the Kuhn length, which is obtained by substituting eqs 4 and 5 into eq 3:

$$A = \{2a\alpha^2 \sin\theta/2\}/(1 + \cos\theta) \tag{6}$$

Equation 6 is applicable only for polymers containing one type of bond and one bond angle, for example, vinyl polymers. In the case of polymers that have heteroatoms in the backbone, due to the presence of different bonds and bond angles, a and θ can be replaced by the average values $\bar{a}$ and $\bar{\theta}$, so that

$$A = \{2\bar{a}\alpha^2 \sin\bar{\theta}/2\}/(1 + \cos\bar{\theta}) \tag{7}$$

In the present study, eq 7 was used to calculate the Kuhn length A. The required bond lengths and bond angles were taken from refs 12−14.

For vinyl polymers, which have one type of bond (C−C) and bond angle, their Kuhn length cannot be compared under theta conditions ($\alpha = 1$) as it will result in almost similar A values from eq 6. In such cases, it is necessary that we have α values

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Table 2. T_1 and Kuhn Length Values for the Polymers Investigated

polymer	solvent	concn (% w/w)	temp (°C)	T_1 (s) CH	T_1 (s) CH_2	Kuhn length (Å)	ref for T_1 values
PS	$CHCl_3$	22	33	0.10	0.055		7
PSP	$CHCl_3$	22	33	0.24	0.120	4.360	7
PSD	$CHCl_3$	22	33	0.51	0.253	4.175	this work
		22	40	0.56	0.28		this work
PSP	$CDCl_3$	22	45	0.30	0.155	4.360	7
PPT[a]	$CDCl_3$	20[b]	45	0.315	0.164	4.28	15
PPT	$CDCl_3$	20[b]	40	0.277	0.155	4.28	15
PSD	$CHCl_3$	22	40	0.56	0.28	4.175	this work
PST	$CHCl_3$	22	40	0.48	0.245	4.248	this work
		22	33	0.44	0.220		this work

[a] The CH and CH_2 T_1 values were calculated from a plot of T_1 values at different temperatures. [b] The unit is % w/v.

for individual polymers so that *A* can be compared. However, in those polymers that have heteroatoms in the backbone, such as the polymers containing group VIA linkages considered in the present investigation, a qualitative comparison of the trend in flexibility can be made under theta conditions due to substantial variation in their bond lengths and bond angles. Equation 7 was used to calculate the Kuhn length *A* for PSP, PPT, PSD, and PST in their bulk under theta conditions ($\alpha = 1$); results are given in Table 2.

Results and Discussion

The T_1 values for the backbone CH and CH_2 carbons of both PSD and PST are reported in Table 2. The 2:1 ratio of T_1 values for the CH and CH_2 carbons confirm the dipole−dipole nature of the backbone carbon relaxation. The fact that the T_1 values of CH and CH_2 carbons of both PSD and PST increase linearly with temperature indicates that the observations are on the high-frequency side of the T_1 minimum. Hence, it is clear that the higher the T_1 values, the more flexible the backbone.[7] It is to be noted here that the T_1 values of backbone carbons of other polymers, such as PS, PSP, and PPT used in the subequent discussion, also follow the above-mentioned behavior, i.e., T_1 increases with an increase in temperature. The T_1 values of PS,[7] PSP,[7] and PPT[15] have been taken from the literaure.

Effect of Heteroatom on Chain Dynamics. The polymers compared are PS, PSP, and PSD. The T_1 values (at 33 °C) show that PSD is the most flexible and PS is the least flexible. PSP, in terms of flexibility, lies in the middle since its T_1 values are twice that of PS, but half that of PSD. The flexibility difference between PS and PSP is corroborated from T_g data, which are much higher for the former.[16]

In the comparison of PSP with PSD, it was found from the literature (Table 2) that the PPT is slightly more flexible than PSP due to minor increases in their backbone T_1 values (at 45 °C) compared to that of PSP. The small difference in the amount of sample, i.e., 22% (w/w) for PSP and 20% (w/v) for PPT, we believe, will not affect the T_1 values to any significant extent. From softening temperature data, it is known that disulfide polymers are more flexible than their monosulfide counterparts.[17] Since PPT is slightly more flexible than PSP, it is clear that the disulfide linkage provides much more flexibility to the backbone than the peroxide linkage, which is reflected in the T_1 values (at 33 °C). The trend in flexibility of PSP, PPT, and PSD is consistent with the Kuhn length values (Table 2).

Effect of Length of Sulfide Linkages on Chain Dynamics. It is found from Table 2 that, with the increase in the length of the sulfide linkage from mono to tetra, we initially observe an increase in T_1 values (at 40 °C) upon going from PPT to PSD, followed by a decrease with PST. This means that flexibility decreases in the order PSD > PST > PPT. It has already been shown that PSD is more flexible than PPT. But the decrease in flexibility on further increasing the sulfide length, i.e., to tetrasulfide linkage (PST), can be explained by the T_g data. It is reported that the T_g's of the disulfide polymers are lower than those of their tetrasulfide counterparts,[5] which implies that tetrasulfide polymers are more rigid than their disulfide analogues; this is clearly reflected in the T_1 values of PSD and PST. The preceding trend in the flexibility of PSD, PST, and PPT is consistent with the trend in the flexibility predicted from Kuhn length data (Table 2).

Conclusions

A comparative study on the effect of group VIA linkages on the chain dynamics of the polymer backbone has been performed. On the basis of T_1 measurements and Kuhn length calculations, it was found that flexibility follows the order PSD > PSP > PS. It was also observed that, upon increasing the length of the sulfide linkage from mono to tetra in the backbone, the flexibility increases upon going from PPT to PSD, but from PSD to PST it decreases. PPT was found to be the least flexible.

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