An Experimental Study of the Dipole Moments of Isotactic and Atactic Poly(propylene sulfide)

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ABSTRACT: Poly(propylene sulfide) [$CH(CH_3)-S-CH_2-$] was synthesized in both the isotactic and atactic stereochemical forms. They were investigated by means of dielectric constant measurements in benzene and in carbon tetrachloride over the range 20–60 °C. The results in benzene indicate that the two polymers have essentially the same values of the dipole moment ratio and its temperature coefficient. These experimental values are, furthermore, in good agreement with values predicted from rotational isomeric state calculations. In carbon tetrachloride, the dipole moment ratio is approximately 15% lower than it is in benzene, and its temperature coefficient is somewhat larger. The observed differences are probably due to a specific solvent effect (long recognized with regard to chain dimensions), with possibly a small contribution from excluded volume effects arising from the fact that the group moment in poly(propylene sulfide) has a small component along the chain direction.

The poly(propylene sulfide) (PPS) chain [$CH(CH_3)-S-CH_2-$] is an unusually interesting molecule from the point of view of configurational analysis. It is obviously closely related to poly(ethylene sulfide) (PES) [CH_2-S-CH_2-], but it is much more tractable in experimental investigations since the melting point (52 °C)[1] of the crystallizable (isotactic) modification is well below that (210 °C)[2] of PES. Furthermore, the addition of the methyl group to the repeat unit gives the chain a stereochemically variable structure; in this regard, PPS is similar to polypropylene [$CH(CH_3)-CH_2-$] but the additional skeletal bond between the substituted carbon atoms would be expected to diminish the effect of stereochemical structure on some of the statistical properties of the chain.[3,4]

The polarity of PPS complicates the determination of reliable values of its dipole moments[5,6] because of "specific solvent effects" on chain conformations in the case of polar polymers. The methyl group in PPS also makes the repeat unit asymmetric in the sense that there is no longer a plane of symmetry through the sulfur atom, as there is in PES. It is thus a highly unusual chain molecule in not having this, or a related, element of symmetry.[5,6] In principle, this should give rise to an excluded volume effect on the dipole moment of the PPS chain, since the group dipole moment would have a component along the chain direction.[7-10] Although this component may be relatively small, it could be significant, particularly in the case of a very small quantity such as the temperature coefficient of the dipole moment.

The present study addresses some of the above issues. Specifically, it reports dipole moments and their temperature dependence for both isotactic and atactic PPS, in benzene and in carbon tetrachloride. The experimental results are compared with theoretical results based on a rotational isomeric state model of the polymer, and they are also scrutinized with regard to the dependence of the dipole moment on the solvent medium.

Experimental Section

Preparation of the Isotactic Polymer.[1,11] The monomer, racemic propylene sulfide, was distilled, dried over calcium hydride and sodium mirrors, and then checked for purity by gas chromatography. The initiator, cadmium thiolate ($Cd[SCH(CH_3)CH_2SC_2H_5]_2$), was prepared by reacting the required thiol with cadmium acetate in stoichiometric proportion. The monomer and initiator were sealed into a glass flask under high vacuum, and polymerization was allowed to proceed at 0 °C for 2 weeks. The polymer was obtained and purified by dissolution into tetrahydrofuran, precipitation into methanol, and drying under vacuum. It was crystalline in appearance and was obtained in essentially quantitative yield. According to its ^{13}C NMR spectrum, the chains were very highly isotactic (95–100% meso dyads). Light-scattering measurements indicated that its weight-average molecular weight was approximately 1.6×10^6.

Preparation of the Atactic Polymer.[12] The first stage in the polymerization consisted of adding a small amount of the purified monomer to a 2×10^{-5} M solution of carbazyl sodium in tetrahydrofuran. After 24 h at room temperature, the main charge of monomer was added, and the resulting solution was stirred at this temperature for 3 days. The "living" PPS thus prepared was terminated by adding a small amount of ethyl bromide. The polymer was recovered as described above, again in essentially quantitative yields. This atactic sample was a rubbery, amorphous material with a weight-average molecular weight of approximately 0.5×10^6.

Dielectric Constants and Refractive Indices.[13,14] The isotactic and atactic PPS samples were studied in benzene solutions at 20, 30, 40, 50, and 60 °C, and in carbon tetrachloride solutions at 20, 30, 40, and 50 °C. The dielectric constants ϵ of the solutions were determined by a standard capacitance bridge operating at a fixed frequency of 10 kHz. The three-terminal cell was calibrated at each of the above temperatures using benzene, toluene, and cyclohexane.[15,16] Values of the index of refraction n of the solutions were measured at 546 nm, using a Brice-Phoenix differential refractometer.

Results and Discussion

The dielectric constant and index of refraction for each PPS solution were expressed relative to the corresponding values for the pure solvent in the incremental quantities $(\epsilon - \epsilon_1)$ and $(n^2 - n_1^2)$. These quantities were then plotted against the weight fraction w of polymer in the solution; the slopes of these curves gave values of the derivatives $d(\epsilon - \epsilon_1)/dw$ and $d(n^2 - n_1^2)/dw$. Typical results are shown in Figure 1, and the values of the two derivatives for both polymers in both solvents at all of the temperatures are given in columns four and five of Table I. Values of the

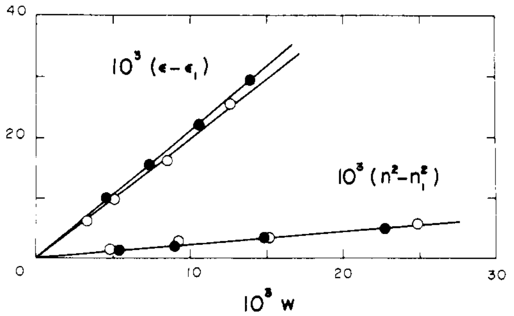

Figure 1. Typical data showing the concentration dependence of the increments in dielectric constant and squared index of refraction for isotactic (○) and atactic (●) poly(propylene sulfide) in benzene at 20 °C.

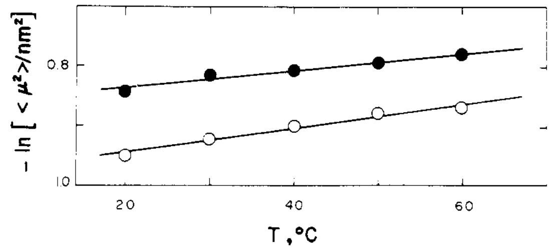

Figure 2. The temperature dependence of the natural logarithm of the dipole moment ratio for isotactic (○) and atactic (●) PPS in benzene.

Table I
Summary of Experimental Data and Results

solvent	polymer	T, °C	$d(\epsilon-\epsilon_1)/dw$	$d(n^2-n_1^2)/dw$	$\langle\mu\rangle/nm^2$
benzene	isotactic	20	1.94	0.23	0.386
		30	1.90	0.24	0.397
		40	1.86	0.25	0.406
		50	1.82	0.26	0.415
		60	1.74	0.27	0.420
	atactic	20	2.12	0.22	0.429
		30	2.08	0.23	0.442
		40	2.00	0.24	0.445
		50	1.94	0.25	0.452
		60	1.88	0.25	0.458
carbon tetrachloride	isotactic	20	3.20	0.65	0.325
		30	3.12	0.66	0.333
		40	3.05	0.67	0.338
		50	3.00	0.68	0.347
	atactic	20	3.52	0.68	0.362
		30	3.48	0.68	0.377
		40	3.44	0.68	0.393
		50	3.40	0.68	0.407

mean-square dipole moment $\langle\mu^2\rangle$ were then calculated from the standard equation of Guggenheim and Smith[17]

$$\langle\mu^2\rangle = \frac{27kTM}{4\pi N_A\rho_1(\epsilon_1+2)^2}\left[\frac{d(\epsilon-\epsilon_1)}{dw} - \frac{d(n^2-n_1^2)}{dw}\right] \quad (1)$$

in which k is the Boltzmann constant, T is the absolute temperature, M is the molecular weight, N_A is Avogadro's number, and ρ_1 is the density of the solvent. The results were expressed in terms of the ratio $\langle\mu^2\rangle/nm^2$, where n here is the number of skeletal bonds (and is equal to $3M/M_0$, where M_0 = 74.14 g mol^{-1}). The average m^2 of the skeletal bond moments was calculated from $m^2 = {}^1/_3(m^2_{C-S} + m^2_{S-C} + m^2_{C-C})$, in which m_{C-C} was taken to be 0.00 D.[18] Since the methyl group in the repeat unit should cause only a slight asymmetry in the electron distribution, it was tentatively assumed that $m_{C-S} = m_{S-C}$; both moments were assigned the value 1.21 D.[4,18]

Table II
Comparisons between Experimental and Theoretical Results (at 25 °C)

		isotactic	atactic
$\langle\mu^2\rangle/nm^2$	benzene	0.39	0.44
	CCl_4	0.33	0.37
	theoretical	0.41	0.39
10^3 d ln$\langle\mu^2\rangle$/dT	benzene	2.0	1.5
	CCl_4	2.1	4.0
	theoretical	2.2	2.2

All of the values of $\langle\mu^2\rangle/nm^2$ thus obtained are given in the final column of Table I. The values of both polymers in both solvents at the standard temperature of 25 °C are given in the first two rows of Table II. The values of this ratio for PPS are seen to be quite similar to those, 0.4–0.5, reported for poly(propylene oxide).[4,19] Comparisons between the statistical properties of these two polymers, and several others as well, and their interpretation in terms of rotational isomeric state theory will be reported elsewhere.[4] The theoretical values for PPS, predicted from preliminary calculations carried out on a rotational isomeric state model of the PPS chain,[4] are given in the third row. In the case of the results obtained in benzene, there is good agreement between experiment and theory in that the experimental values of $\langle\mu^2\rangle/nm^2$ show no significant dependence on stereochemical structure. This is presumably due to the fact that the unsymmetrically substituted carbon atoms are separated by three skeletal bonds rather than two, as in the case of the much-studied vinyl polymers.[20] The present result is thus consistent with the fact that the unperturbed dimensions and dipole moments of poly(propylene oxide) [$CH(CH_3)-O-CH_2$] show a similar insensitivity to stereochemical structure.[3,4,21,22] Furthermore, the experimental values of $\langle\mu^2\rangle/nm^2$ for the isotactic and atactic PPS are seen to be in very good agreement with the theoretical values. The values of this ratio obtained in carbon tetrachloride are also found to be independent of stereochemical structure but are approximately 15% below those obtained in benzene. This difference is most likely due to specific solvent interactions, which frequently have a very marked effect on the dimensions and dipole moments of polar polymer chains, for example poly(dimethylsiloxane).[5,20,23,24] There is, in fact, some semiquantitative evidence[25] for a specific solvent effect on the unperturbed dimensions of PPS. The effect apparently arises from the dependence of the coulombic part of the conformational energy on the dielectric constant of the medium and from changes in conformational distribution possibly arising from a weak complexation of the solvent molecules with the segments of the polymer chain. The observed difference could also be due to the fact that the group dipole in PPS has a component parallel to the chain direction. This component should be quite small judging from its value, 0.18 D,[10] in the case of poly(propylene oxide). In any case, this would give rise to an excluded volume effect on the dipole moment,[5-9] and the magnitude of this effect would of course depend on the "thermodynamic goodness" of the solvent medium. On the basis of the solubility parameters for PPS, benzene, and carbon tetrachloride (~9.6, 9.2, and 8.6, respectively),[25] benzene should be the better solvent for PPS. The fact that the dipole moments of PPS are larger in benzene than they are in carbon tetrachloride is thus consistent with the change to be expected from an excluded volume effect. Determination of the relative contributions of the two effects would require very careful measurements of the dipole moments as a function of chain length; the specific solvent effect is essentially insensitive to increase in chain length, whereas the excluded volume effect would increase without limit.[26]

The experimental and theoretical values of the temperature coefficient d ln $\langle\mu^2\rangle/\mathrm{d}T$ are given in the last three rows of Table II. Such coefficients are generally relatively small quantities, corresponding to changes of only a few tenths of a percent per degree.[20] Consequently, they are difficult to determine with accuracy. The fact that the average value of d ln $\langle\mu^2\rangle/\mathrm{d}T$ for the two polymers in carbon tetrachloride is somewhat larger than that in benzene may therefore be due to experimental error rather than to a specific solvent effect or excluded volume effect. In any case, the experimental results unambiguously indicate a moderately large increase in $\langle\mu^2\rangle$ with increase in temperature, which is in agreement with theory.

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A Numerical Solution for Sequence Distributions and Relative Rate Constants in Postpolymerization Reactions

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ABSTRACT: Postpolymerization reactions in which A units react to form B units are examined. Rate equations are set up for the triad fractions with the rate of reaction depending on whether 0, 1, or 2 B units surround the reacting A unit. Predictor–corrector methods are used to solve the equations. The predictor–corrector results are compared to analytical solutions and to Monte-Carlo results. The program is modified to calculate the relative rate constants necessary to produce a given set of A centered triad fractions. Experimental uncertainties in the measurements of the triads are propagated through the calculations to give uncertainties in the calculated rate constants.

Conventional copolymers are prepared by the polymerization of a mixture of two monomers. The composition and sequence distribution of these copolymers are dependent on the reactivity ratios and the monomer feed composition. Copolymers can also be produced from homopolymers by reacting the polymer chains with a reagent that effectively changes the monomer type. Polymeric reactions can produce copolymers with compositions and sequence distributions that are not possible to produce through conventional copolymerizations.

Conventional copolymerizations and their reactivity ratios have been studied extensively over the past 40 years. In polymeric reactions a model has been in existence for several years.[1] Relative rate constants take over the function that the reactivity ratios serve in conventional copolymerizations. That is, the sequence distribution of the copolymers produced through postpolymerization reactions is completely defined by the two relative rate constants and the degree of conversion. In conventional copolymers the sequence distribution is completely defined by the two reactivity ratios and the instantaneous monomer feeds, assuming that no penultimate effects are present.

The calculation of relative rate constants in these postpolymerization reactions is more difficult than the calculation of reactivity ratios. If a reliable method of calculating these relative rate constants could be found, the sequence distribution resulting from polymeric re-

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