Thermoelastic and Dielectric Properties of Poly(3-methyltetrahydrofuran): Correlation between Theory and Experiment

Evaristo Riande,* Julio Guzmán, and Leoncio Garrido

Instituto de Plásticos y Caucho (CSIC), Madrid-6, Spain. *Received June 1, 1983*

ABSTRACT: Poly(3-methyltetrahydrofuran) (PMTHF) was prepared by ring-opening polymerization of 3-methyltetrahydrofuran. The polymerization process yields an atactic polymer in which head-to-tail (or tail-to-head), head-to-head, and tail-to-tail structures appear along the chains. Mean-square dipole moments $\langle\mu^2\rangle$ of the chains were determined as a function of temperature by means of dielectric constant experiments carried out in the thermodynamically good solvent benzene. The values at 30 °C of the dipole moment ratio $\langle\mu^2\rangle/nm^2$ and its temperature coefficient $\mathrm{d}\ln\langle\mu^2\rangle/\mathrm{d}T$, where nm^2 is the mean-square dipole moment of the chains in the idealization that all of the skeletal bonds are freely jointed, were found to be 0.526 and 1.6×10^{-3} K^{-1}, respectively. The critical analysis of these configurational properties, in terms of the rotational isomeric state model, suggests that the cationic polymerization of 3-methyltetrahydrofuran proceeds preferentially by nucleophilic attack of the monomer oxygen atom onto the less hindered α carbon, relative to the oxonium ion. Polymer networks were also prepared by end-linking hydroxyl-terminated chains with an aromatic triisocyanate. From thermoelastic experiments, carried out on the networks, it was found that $10^3 \times \mathrm{d}\ln\langle r^2\rangle_0/\mathrm{d}T = 0.61 \pm 0.18$, in poor agreement with theory that predicts a negative dependence of the unperturbed dimensions on temperature.

Introduction

The transformation of tetrahydrofuran (THF) into 3-methyltetrahydrofuran (MTHF), by substituting a methyl group for a hydrogen atom, increases the free energy of polymerization of the resulting heterocycle.[1] The enthalpy of polymerization is similar in both monomers, but the entropy is lower in MTHF (−19.5 cal/(mol K)) than in THF (−12.5 in the same units). The ceiling temperature of MTHF lies in the vicinity of 4 °C and, as a consequence, its polymerization cannot be carried out above this temperature.[2]

From the microstructure of poly(3-methyltetrahydrofuran) (PMTHF), determined by ^{13}C NMR spectroscopy, it was concluded that the ring-opening polymerization occurs preferentially through one of the two bonds adjacent to the oxygen atom of the monomer ring.[3] Although no definitive conclusion was reached with regard to which carbon is preferentially attacked, it is obvious that head-to-tail (or tail-to-head), head-to-head, and tail-to-tail structures may appear along the chains. The structural heterogeneity and the additional steric congestion engendered by the methyl groups change drastically some of the physical properties of PMTHF in comparison with those of poly(tetrahydrofuran) (PTHF). Thus, PTHF is a crystalline polymer whereas PMTHF is an amorphous one; the glass transition temperature of the former polymer is also significantly lower than that of the latter.[4]

This investigation focuses on the study of the effects of the relatively bulky methyl groups on the configurational properties of PMTHF. It is well-known that the effect of stereochemical structure on statistical properties can be very pronounced in the case of vinyl chains, where only two bonds separate the substituted carbon atoms,[5-9] but it is much less pronounced in the case of chains like poly(propylene oxide) (PPO)[10-12] or poly(propylene sulfide) (PPS)[13-15] in which the substituted carbons are separated by three bonds. It can be expected that the stereochemical structure will have little effect on the configurational properties of PMTHF where the asymmetrical carbons are separated by four to six skeletal bonds. Simple scrutiny of structural characteristics of the chains indicates, however, that certain conformations which are accessible in PTHF are suppressed in PMTHF. It would be important, therefore, to investigate how the reduction in conformation phase space affects the statistical properties of poly(3-methyltetrahydrofuran).

In this study, the dipole moments of PMTHF and the temperature coefficients of both the dipole moments and the unperturbed dimensions are measured and the results are compared with those previously reported for PTHF. The experimental results are also interpreted in terms of the rotational isomeric state model, and information on the mechanism of ring-opening polymerization of 3-methyltetrahydrofuran is obtained.

Experimental Details

Poly(3-methyltetrahydrofuran) was obtained at 0 °C, in high vacuum, by cationic polymerization of purified 3-methyltetrahydrofuran, using acetylhexafluoroantimonate as initiator.[3] The polymerization was terminated with water and the products of the reaction were dissolved in benzene and precipitated with methanol. The acetyl-terminated end of the chains was hydrolyzed with a solution of sodium hydroxide in absolute ethanol at the refluxing temperature of the alcohol. The number-average molecular weight of the hydrolyzed sample was determined at 37 °C in chloroform solutions by using a Knauer vapor pressure osmometer.

The ^{13}C NMR spectrum of the polymer, shown in Figure 1, was recorded at 26 °C with a Bruker HX-90E Fourier spectrometer operating at 22.63 MHz, using deuterated chloroform as solvent and Me_4Si as internal reference. Long pulse delay times (>10 s) and inverse gated decoupling techniques were used in order to eliminate the nuclear Overhauser enhancement.

Dielectric constant measurements were carried out on solutions of PMTHF in benzene, at several temperatures, using a capacitance bridge (General Radio 1620 A) and a three-terminal cell (Foxboro Model 3HV35). The measurements were performed at 10 kHz. Values of the index of refraction of the solutions were determined at 546 nm with a Brice-Phoenix differential refractometer.

The hydroxyl-terminated PMTHF chains were cross-linked with 2,4-bis(*p*-isocyanobenzyl)phenyl isocyanate. Stoichiometric amounts of polymer and cross-linking agent were dissolved in a small amount of dried chloroform (ethanol free). The solvent was removed by evaporation and the mixture of polymer and aromatic isocyanate was molded at 70 °C for 12 h. Two networks (A and B) were prepared in this way with a fraction of M_n = 6700 g/mol. The networks were extracted with chloroform for 1 day, and the soluble fractions were 10 and 12% for networks A and B, respectively. Stress–strain isotherms were obtained on unswollen strips of cross-sectional area 4 mm^2, using standard techniques.[16,17] Thermoelastic measurements were carried out over the temperature interval 70–10 °C, with some inclusion of values out of order to test for reversibility. The networks exhibited poor ultimate mechanical properties; consequently thermoelastic experiments could only be performed at elongation ratios below 3. The ex-

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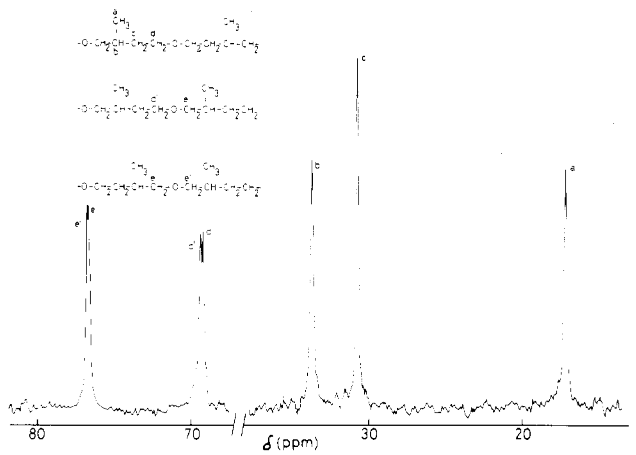


Figure 1. ^{13}C NMR spectrum of poly(3-methyltetrahydrofuran).

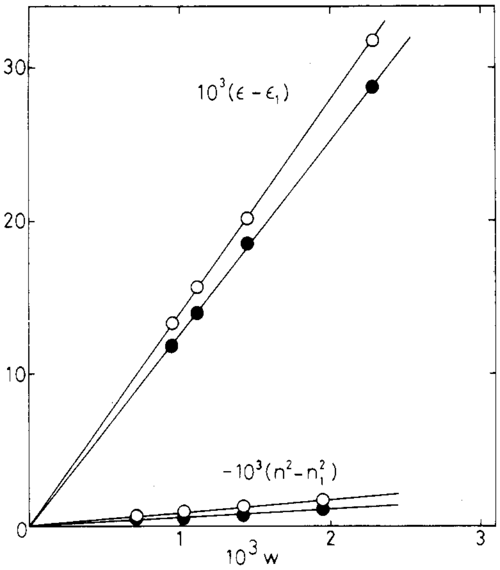


Figure 2. Increments in dielectric constant and squared index of refraction for solutions of poly(3-methyltetrahydrofuran) in benzene at 30 (○) and 60 °C (●).

pansion coefficient β was measured with a Perkin-Elmer thermoanalyzer and found to be 6.9×10^{-4} K^{-1}.

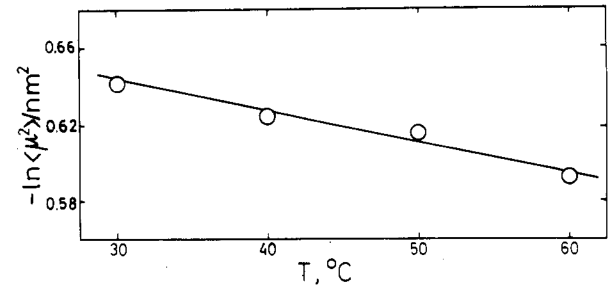


Figure 3. Natural logarithm of the dipole moment ratio against temperature.

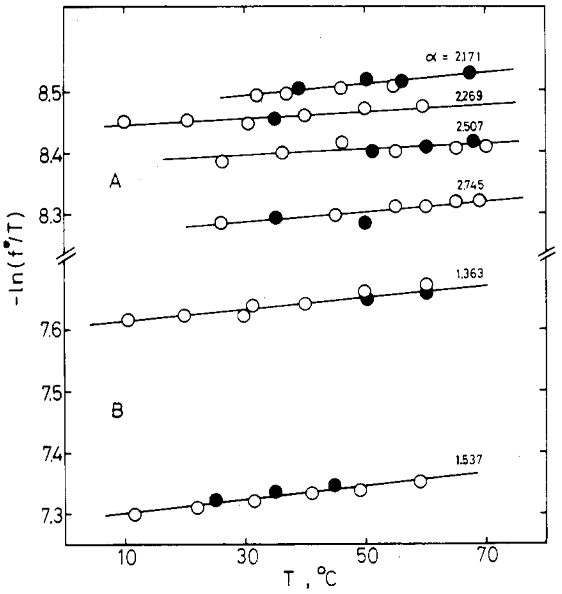


Figure 4. Thermoelastic results for networks A and B.

Table I
Summary of Dielectric Results

T, °C	$d(\epsilon - \epsilon_1)/dw$	$-d(n^2 - n_1^2)/dw$	$\langle\mu^2\rangle/nm^2$
30	1.392	0.089	0.526
40	1.347	0.080	0.535
50	1.294	0.071	0.540
60	1.263	0.062	0.553

Results and Discussion

Values of the dipole moment ratio $\langle\mu^2\rangle/nm^2$, where $\langle\mu^2\rangle$ is the mean-square dipole moment of a chain with n skeletal bonds and nm^2 is the same quantity in the idealization that all of the skeletal bonds are freely jointed, were determined at 30, 40, 50, and 60 °C by using the method of Guggenhein and Smith[16,17]

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

where k is the Boltzmann constant, T is the absolute temperature, N_A is the Avogadro number, M is the molecular weight of the polymer and ρ is the density of the solvent. The derivatives $d(\epsilon - \epsilon_1)/dw$ and $d(n^2 - n_1^2)/dw$ were obtained for each PMTHF solution from plots of the increments in dielectric constant and squared index of refraction against the weight fraction of polymer. Typical results are shown in Figure 2. The values of the derivatives at all four temperatures are given in columns two and three of Table I. Because of the very small effects of excluded-volume interactions on the dipole moments of such nearly symmetrical chains as PMTHF,[13,14,18-21] the values of $\langle\mu^2\rangle$ may be written as the unperturbed values $\langle\mu^2\rangle_0$.[5,18] The average m^2 of the skeletal bonds utilized in eq 1 was calculated from $m^2 = (1/5)(2m_{C-O}^2 + 3m_{C-C}^2)$ by using $m_{C-O} = 1.07$ D and $m_{C-C} = 0.00$ D.[23,24] The values of the dipole moment ratio thus obtained are listed in the last column of Table I. The value of the temperature coefficient $d \ln \langle\mu^2\rangle_0/dT$ was obtained by plotting the natural logarithm of the dipole moment ratio against temperature. As shown in Figure 3, the plot exhibits a positive slope, the value of $d \ln \langle\mu^2\rangle/dT$ being 1.6×10^{-3} K^{-1}.

Force–temperature results were obtained for different values of the elongation ratio α in the temperature range 20–70 °C. The thermoelastic data were represented in terms of $\ln (f^*/T)$ in Figure 4, where f^* is the elastic force referred to the undistorted cross-sectional area. It can be seen that the data are highly reversible as is required for subsequent conformational analysis of PMTHF chains. The temperature coefficient of the unperturbed dimensions of the polymer, $d \ln \langle r^2\rangle_0/dT$, was obtained from the slopes of the plots of Figure 4, by using the standard equation[25,26]

$$d \ln \langle r^2\rangle_0/dT = -[\partial \ln (f^*/T)/\partial T]_{p,L} - \beta/(\alpha^3 - 1) = f_e/fT \qquad (2)$$

Table II
Thermoelastic Results for Poly(3-methyltetrahydrofuran) Networks

network	α	fe/f	$10^3 \times \mathrm{d} \ln \langle r^2 \rangle_0/\mathrm{d}T$
A	1.363	0.133	0.44
	1.537	0.245	0.81
B	2.171	0.242	0.80
	2.269	0.118	0.39
	2.507	0.233	0.77
	2.745	0.139	0.46
			0.61 ± 0.18[a]

[a] Average.

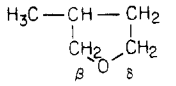
Table III
Comparison of Experimental Values of Some Configuration-Dependent Properties for Poly(tetrahydrofuran) and Poly(methyltetrahydrofuran)

property	PTHF[24]	PMTHF
$\langle \mu^2 \rangle / nm^2$	0.50, 0.52	0.526
$10^3 \times \mathrm{d} \ln \langle \mu^2 \rangle / \mathrm{d}T$	2.7	1.6
$\langle r^2 \rangle_0 / nl$	6.1	
$10^3 \times \mathrm{d} \ln \langle r^2 \rangle_0 / \mathrm{d}T$	−1.33	0.61

where f_e/fT is the internal energy component which serves as a measure of nonideality for elastomeric networks. Values of $\mathrm{d} \ln \langle r^2 \rangle_0/\mathrm{d}T$ at different elongation ratios are given in the third column of Table II and the average value of these quantities is 0.6×10^{-3} K^{-1}.

In Table III, and for comparative purposes, we have summarized the dielectric and thermoelastic results for PMTHF and PTHF. It can be seen that the value of the dipole moment ratio is similar for both polymers, but the dipole moments of PMTHF show a lower temperature dependence than those of PTHF. Moreover, the unperturbed dimensions of the former polymer are less sensitive to changes in temperature than those of the latter. The difference of the sign of this quantity in both polymers is surprising.

Before performing the theoretical analysis of the dipole moments and the temperature coefficients of both the dipole moments and the mean-square end-to-end distance of PMTHF chains, a few comments should be made on the polymerization mechanism of 3-methyltetrahydrofuran. The ring-opening polymerization of MTHF involves random scission of bonds β and δ in the monomer



and yields an atactic polymer in which HT (head-tail), TH, HH, and TT arrangements appear along the chains (see Figure 1). The analysis of the ^{13}C NMR spectrum of PMTHF suggests that 70% of the total scissions occur preferentially through one of the CH_2–O bonds.[3] However, although the steric hindrance of the methyl carbon presumably influences a preferential attack on the δ methylene carbon, no definitive conclusion can be reached with regard to which methylene carbon is preferentially attacked, because the steric factor is not predominant in all the cases.[27–29]

In order to carry out the theoretical calculations a three rotational state scheme was used. It was assumed as a first approximation that trans states are located at 0°; it was also assumed that gauche states about C–C bonds in the sequence C–C–C–C are situated at 112.5°, whereas gauche states about the remaining skeletal bonds were located according to the following assignments:[24] ±110° for C–O bonds and ±120° for the central C–C bond of the sequence C–C–C–O. The bond skeletal angles were assumed to be 110°, and the bond lengths used were $l_{\text{C–C}} = 1.53$ Å and $l_{\text{C–O}} = 1.43$ Å. Relevant to the theoretical analysis is the assignment of conformational energies to the rotational states associated with the skeletal bonds of the dyads that appear along the chains. For this purpose we have used statistical weight matrices similar to those utilized in PTHF[5,24] with the necessary modifications to take into account the hindrances of the methyl side groups. Two of the four possible isotactic dyads in planar all trans conformation are shown in Figure 5. As is represented there, the substituent CH_3 groups are alternating above and below the plane for an isotactic arrangement when the consecutive asymmetric centers are separated for an odd number of skeletal bonds; otherwise, the CH_3 groups are situated on the same side of the plane.

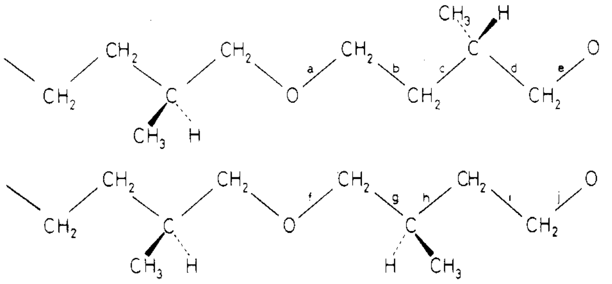


Figure 5. Isotactic ht and hh dyads in all trans conformation.

The conformations associated with the skeletal bonds listed in the dyads of Figure 5 are representative of most of the possible conformations that can appear in PMTHF chains. A brief summary of the conformational energies used in the calculations follows. Gauche states about skeletal bonds of type a and j have an energy[24] $E_{\sigma''} = 1.2$ kcal mol^{-1} higher than the alternative trans states. However, g$^+$ and g$^-$ rotations about C–O bonds of type e and f, respectively, cause steric overlap between a methylene and a methyl group separated by four bonds and, as the result, these conformations are excluded. Gauche rotations of positive sign about bonds of type b and g$^-$ rotations about bonds of type i give rise to first-order CH_2···O interactions with an attractive energy $E_{\sigma'}$ of[24] ca. −0.25 kcal mol^{-1}. Gauche negative and gauche positive conformations about bonds of type d and g, respectively, cause interactions between an oxygen atom and both a methylene and a methyl group separated by three bonds; an energy E_η lying in the range 0.5 to −0.25 was used for these states in the calculations, and the alternative gauche states were considered to have the same energy as the corresponding trans states. In the same way g$^-$ and g$^+$ states about bonds of type b and i, respectively, give rise to pentane-type interferences between an oxygen atom and a CH_2 group; the energy E_ω of this second-order interaction was considered to be[24] 0.6 kcal mol^{-1}. Finally, g$^-$ rotations about bonds of type c and g$^+$ rotations about bonds of type h have an energy similar to that of the corresponding trans states. The alternative gauche rotations about c and h bonds place a methylene group between a methyl and a methylene group and the energy associated with these states should be higher than 0.7 kcal mol^{-1}; in fact, values of E_σ lying in the range 0.6–2.1 kcal mol^{-1} were used in the calculations.

Pairs of gauche states of opposite sign g$^\pm$g$^\mp$ give rise to pentane-type interferences between groups and atoms separated by four bonds. In the cases in which the participating species are a CH_2 group and an oxygen atom, a repulsive energy E_ω of 0.6 kcal mol^{-1} appears.[24] For bond

Table IV
Variation of the Statistical Properties with the Structure of the Chains

W^a	$E_\sigma{}^b$	$E_\omega{}^b$	$\langle\mu^2\rangle/nm^2$	$\langle r^2\rangle_0/nl^2$	10^3d ln $\langle\mu^2\rangle/\mathrm{d}T$	-10^3d ln $\langle r^2\rangle_0/\mathrm{d}T$
0.30	0.69	0.6	0.615	5.6	0.6	1.2
	2.1	0.6	0.575	5.8	0.8	1.0
	0.69	2.1	0.630	7.6	0.8	0.7
	2.1	2.1	0.578	7.7	1.0	0.6
0.70	0.69	0.6	0.604	5.7	0.9	1.3
	2.1	0.6	0.553	5.8	1.1	1.2
	0.69	2.1	0.598	7.8	1.2	0.7
	2.1	2.1	0.524	7.9	1.6	0.6

[a] Fraction of bond scissions through bonds of type δ in the monomer ring. [b] The energies are given in kcal mol^{-1}.

pairs where the participating species are two CH_2 groups, the steric overlap causes the complete exclusion of these conformations.[5,24]

Monte Carlo techniques were used to generate chains that were representative with regard to bond scission of the monomer ring and atomic configuration (d vs. l).

Values of the dipole moment ratio, the characteristic ratio $\langle r^2\rangle_0/nl^2$, and the temperature coefficient of both the dipole moments and the unperturbed dimensions (d ln $\langle r^2\rangle_0/\mathrm{d}T$) were calculated at 30 °C by standard matrix multiplication methods.[5] Preliminary calculations showed that these properties are insensitive to the atomic configuration (d or l) of the asymmetric carbon. These results confirm previous ones according to which when the spacing between adjacent side groups is too large for such correlations, the stereochemical structure has little effect on statistical properties.[31] The set of energy parameters used was $E_{\sigma''} = 1.2$, $E_{\sigma'} = -0.25$, and $E_\eta = 0.14$, all in kcal mol^{-1}; the values of E_σ and E_ω were permitted to change in the range 0.6–2.1 kcal mol^{-1}. Values of the configurational properties are given in columns four through seven of Table IV for two extreme values of E_σ and E_ω shown in the same table. It can be seen that the dipole moments are moderately dependent on the values assigned to E_σ, but they are insensitive to the values chosen for E_ω. The unperturbed dimensions, on the contrary, are extremely sensitive to the value of E_ω, but they are almost independent on the value assigned to E_σ. It should be stressed that the configurational properties analyzed in this work are almost independent on the value of E_η, for values of this parameter lying in the interval 0.5 to −0.25 kcal mol^{-1}.

Very good agreement between theory and experiment is obtained for the dielectric properties assuming that 70% of bond scissions of the monomer ring occur through bonds of type δ and using a value of 2.1 kcal mol^{-1} for E_σ and E_ω. Actually, the values calculated for the dipole moment ratio and its temperature coefficient, given in the last row of Table IV, were 0.524 and 1.6×10^{-3} K^{-1}, respectively, in very good agreement with the experimental results shown in Table III. As can be seen in the fourth row of Table IV, these values are ca. 10% higher for $\langle\mu^2\rangle/nm^2$ and 38% lower for d ln $\langle\mu^2\rangle/\mathrm{d}T$ if it is assumed that bond scission occurs preferentially through bonds of type β in methyltetrahydrofuran. The critical interpretation of the dielectric results suggests, therefore, that the polymerization reaction of 3-methyltetrahydrofuran proceeds preferentially by nucleophilic attack of the monomer oxygen atom onto the less hindered α carbon relative to the oxonium ion.

As was stated above, the unperturbed dimensions are very sensitive to the value of E_ω. A decrease in the value of this parameter increases the probability that the chain folds back on itself and hence the chain dimensions decrease. For example, increasing the value of E_ω from 0.6 to 2.1 kcal mol^{-1} causes the characteristic ratio to increase from 5.8 to 7.8 as can be seen in the sixth and eighth rows of Table IV.

For PMTHF in the all trans conformation it holds that

$$\lim_{n\to\infty} \langle\mu^2\rangle/nm^2 = 0$$

$$\lim_{n\to\infty} \langle r^2\rangle_0/nl^2 = \infty$$

Since some of the skeletal bonds show a strong preference for trans states and the others are freely rotating or show a slight preference for gauche states, the response of the dipole moments and the unperturbed dimensions to changes in temperature should be opposite. Thus, whereas the dipole moments increase with increasing temperature, the unperturbed dimensions should decrease. The latter prediction is in sharp contrast with the experimental results according to which the temperature coefficient of the unperturbed dimensions, d ln $\langle r^2\rangle_0/\mathrm{d}T$, is positive. The theoretical results for d ln $\langle r^2\rangle_0/\mathrm{d}T$ are given in the last column of Table IV. It can be observed that increasing the value of E_ω from 0.6 to 2.1 kcal mol^{-1} changes the value of d ln $\langle r^2\rangle_0/\mathrm{d}T$ from -1.2×10^{-3} to -0.6×10^{-3} K^{-1}, still far from the experimental result (0.6×10^{-3} K^{-1}). Obviously, better agreement between theory and experiment can be reached by a proper adjustment of the remaining conformational energies; however, the modifications required would be unreasonably large.

The analysis carried out above indicates that the positive value obtained for the experimental temperature coefficient of the unperturbed dimensions cannot be interpreted in terms of the rotational isomeric state model. The use of eq 2 to determine d ln $\langle r^2\rangle_0/\mathrm{d}T$ has been criticized on the grounds that it often gives, unreasonably, strain dependent values of this quantity.[32-34] It has been suggested that the constant $2C_1$ of the Mooney–Rivlin plot should be used to obtain d ln $\langle r^2\rangle_0/\mathrm{d}T$, arguing that this method gives values of this property independent of strain. For example, application of this method to poly(1,4-butadiene) with high cis content (97.7%) gives[35] d ln $\langle r^2\rangle_0/\mathrm{d}T = -1.0 \times 10^{-3}$ K^{-1}, which contrasts with the positive value of 0.6 $\times 10^{-3}$ K^{-1} obtained for the coefficient using eq 2. The fact, however, that the results in Table III do not show strain dependence suggests that $2C_1$ and $2C_2$ have the same temperature dependence[26] and, therefore, eq 2 should be suitable to obtain d ln $\langle r^2\rangle_0/\mathrm{d}T$ for PMTHF chains. In any case, whether or not treatments based on $2C_1$ would give negative values for the temperature coefficient of the unperturbed dimensions of PMTHF is an open question that could not be tested owing to the poor mechanical properties exhibited by the networks thereby precluding elastic experiments at elongation ratios large enough to obtain reliable values of $2C_1$. The lack of agreement between theory and experiment should encourage further experimental work in which d ln $\langle r^2\rangle_0/\mathrm{d}T$ is determined by other methods as, for example, from changes of the intrinsic viscosity of the polymer with temperature in an athermal solvent.

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Theory of Light Scattering and Propagation in Dilute Polymer Solutions: Wormlike Chain Model with Intrinsic and Shape Optical Anisotropies

Mei Hsu Dung and Branka M. Ladanyi*,†

Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523.

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ABSTRACT: We present a continuum model for optical response of dilute solutions of polymer molecules. The solvent is represented as a uniform dielectric continuum. The polymer molecules are modeled as flexible cylinders of constant cross section with a locally axially symmetric anisotropic optical dielectric constant and thus have both permanent and "shape" optical anisotropy. The molecular conformation is represented by the wormlike chain model. Isotropic and depolarized light scattering intensities due to dissolved polymer molecules are evaluated approximately to quadratic order in the scattering wavevector. The refractive index increment of the solution is evaluated as well. The effects on these quantities of molecular shape, size, stiffness, and magnitudes of dielectric tensor components are studied. We show that the local field at a polymer molecule is dependent on the molecular size and conformation. As a consequence of this, familiar expressions, based on the independent scatterer approximation, which relate, for example, isotropic light scattering intensity to the polymer molecular weight and to its mean squared radius of gyration, become inaccurate for some systems. We suggest experiments that may further test the predicted local field effects on light scattering intensities and refractive index increments.

I. Introduction

Our primary goal in this paper is to construct a computationally simple and relatively physically realistic model for the optical response of polymers in dilute solution. Of special interest to us are the local field effects on light scattering (LS) and propagation in these solutions. In most of the treatments of LS from polymer solutions, polymer molecules have been modeled as a collection of independent scatterers.[1] In these models, the effective polarizabilities of the scatterers are scaled to yield the LS intensities close to those observed in a particular solvent, without recourse to a particular local field model. In order to investigate the breakdown of the independent scatterer approximation, it becomes necessary to develop a model for the local field experienced by a polymer molecule in solution. The present paper continues our investigation of models for optical properties of polymers in dilute solution. We have so far considered two types of models for this optical response. One of these is the continuum dielectric model for the polymer–solvent system;[2] the other treats the polymer and the solvent as collections of interacting induced dipoles.[3] This second model is more physically realistic and definitely preferable for solutions of small flexible molecules, but it is impractical for most polymer solutions, for which the model of ref 2 holds more promise. Here we present several improvements and extensions of the work of Ref 2 (from now on referred to as I). In I we developed the general theory of LS and propagation in polymer solutions, where the polymer molecule and the surrounding solvent were modeled as continuous dielectric media. We also presented numerical results for a model in which both the solvent and the polymer molecules were represented as uniform dielectrics with scalar dielectric constants. The polymer was modeled as a flexible cylinder of constant cross section whose conformation was described by the wormlike chain model.[4] We found that this model gave a physically realistic value of the refractive index increment but that the predicted depolarized scattering intensity was too low, since the only

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† Alfred P. Sloan Foundation Fellow.

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