values of x and z. The results for the POE chain with $N = 9$ show again high probabilities for x positive and z negative, in better accordance with the result obtained for PM.[9] For $N = 21$ the asymmetry is small and all octants have similar densities (not included in Table III). For the isotactic PMPS chain with $N = 20$ (considering fluctuations in the rotational angles), the results also show preference for the octants with z negative, especially when x is negative as well. Preferences are less noticeable in the syndiotactic chain, and the octants with x negative have the greater density. From all these results it can be concluded that the nature of the chain and the number of bonds have a complex influence on orientational preferences and only detailed numerical analysis can reveal these preferences in each given case. As a general and expected behavior, orientational preferences are smaller for higher values of R_0 and they are more significant for the stiffer chains with sharper distribution functions in the region close to $R = 0$ (PDMS and isotactic PMPS). In fact, the total cyclization probability (which can be estimated for each type of chain as the arithmetic mean of the results presented in Table III for the different octants) generally increases with increasing flexibility, being higher for longer chains of the same type and for the very flexible POE chains. A special case is constituted by rigid isotactic PDMS, for which the cyclization probabilities are high due to the presence of predominant almost cyclic conformations.

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Registry No. POE (SRU), 25322-68-3.

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Solvent and Temperature Influences on Polystyrene Unperturbed Dimensions

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ABSTRACT: The unperturbed chain dimensions of near-monodisperse atactic polystyrenes were evaluated from intrinsic viscosity measurements in 12 different solvents under Θ or near-Θ conditions over the temperature range 8.5–75.0 °C. In consonance with the indications of other workers, larger values of unperturbed dimensions were found in cyclic hydrocarbon solvents than in other ideal solvents at similar temperatures. Negative values for the temperature coefficient of chain dimensions were found within the three solvent series examined. Under conditions where specific solvent effects are eliminated or minimized, measurements yielded results in excellent agreement with the theoretical predictions for atactic polystyrene, i.e., $d \ln \langle r^2 \rangle_0 / dT = -1.1 \times 10^{-3}$ deg^{-1}.

Introduction

The success of the rotational isomeric state (RIS) approach[2,3] in evaluating the configurational statistics of macromolecules is now well established. Direct and circumstantial agreement exists between theoretical[4-18] and experimental values of the characteristic ratio[19-37] for a variety of polydiene and polyolefinic materials. Conversely, some disagreement exists between the RIS and experimental values for the temperature dependence of the unperturbed dimension, $d \ln \langle r^2 \rangle_0 / dT$ (κ); e.g., this parameter for polystyrene has been reported to have negative,[32,38-44] zero,[45,46] or positive[47-49] values. For many years an accepted experimental value of κ for atactic polystyrene was 0.4×10^{-3} deg^{-1}—a value derived from both thermoelasticity measurements and intrinsic viscosities under Θ conditions in chemically similar solvents.[49] These results, though, are unreconcilable with the RIS calculations, which led to a negative value of κ for various combinations of acceptable rotational energy parameters.[17,18]

Some recent studies[38-43] on atactic polystyrene have yielded values of κ in qualitative agreement with theory. Nevertheless, with one exception,[40] quantitative agreement with the theoretical predictions is lacking. A partial purpose of this paper is to adress this question via intrinsic viscosity results. A topic of additional investigation is the effect of solvent type on the unperturbed dimensions of polystyrene. A lack of recognition of the potential role of specific solvent influences on unperturbed chain dimensions is partially responsible for the diversity of values available for the temperature coefficient. To this latter end, three separate solvent series (cyclic aliphatic hydrocarbons, 1-chloro-*n*-alkanes, and diesters) were evaluated.

Experimental Section

The polystyrenes were prepared by Pressure Chemical Co. via polymerizations initiated by butyllithium. Molecular weight characterization was carried out in these laboratories through a

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Table I
Molecular Characteristics of Polystyrene[a]

sample	lot no.[b]	$\bar{M}_n \times 10^{-3}$	$\bar{M}_w \times 10^{-3}$	$\bar{M}_z/\bar{M}_w$[c]	$\bar{M}_w/\bar{M}_n$[c]
PS-37	7b	35.9	37.0	1.03	1.04
PS-50	60917	49.5	50.0	1.01	1.04
PS-111	4b	108.0	111.0	1.03	1.03
PS-254	50124	235.0	254.0	1.07	1.07
PS-392	3b	350.0	392.0	1.07	1.11
PS-950	61208		950.0	1.12	1.19

[a] The molecular weights are those determined for this work. [b] Pressure Chemical Co. designation. [c] SEC results.

combination of absolute molecular weight measurements and size exclusion chromatography (SEC).

The weight-average molecular weights were measured with a Chromatix KMX-6 low-angle laser light scattering photometer operating at 633 nm. The temperature of measurement was 23 °C. Toluene was the solvent and the dn/dc value was taken[50] as 0.108 mL g^{-1}. The number-average molecular weights were evaluated by using either the Wescan Model 232-A vapor pressure osmometer or the Wescan Model 230 membrane osmometer. Both instruments used toluene as the solvent at temperatures of 50 and 39 °C, respectively. Benzil and sucrose octaacetate were used as calibration standards for the vapor pressure osmometer. Table I lists the molecular weight values used in this work.

Cannon–Ubbelohde viscometers were used for the intrinsic viscosity measurements. Temperature control (via a Haake E-3 heater/circulator) was effective to within ±0.02 °C. Viscometers were chosen so that all solvent flow times ranged between 100 and 200 s. The reproducibility of solvent and solution flow times, when coupled with the random errors encountered in the concentration determinations, led to measured values of the intrinsic viscosity that were precise to about ±1%. The resulting unperturbed chain parameters are thus presented in light of these experimental uncertainties.

Conventional plots of η_{sp}/c vs. c were extrapolated to obtain the intrinsic viscosities. Relative viscosities for the highest concentration used in each run were about 1.3, a region well below C^* for the molecular weights investigated. Neither shear effects nor curvature in the η_{sp}/c vs. c plots was observed in these measurements. Linear regression analyses were used in evaluating the dilute solution viscosity data and the resulting unperturbed chain dimension parameters.

The solvents were obtained from Aldrich, Alfa, or CTC Organics. The three esters and 1-chloro-*n*-dodecane were found to be ca. 99% pure via gas chromatography. The remaining solvents were found to be at least 99.9% pure. The cyclopentane (CTC Organics) did not include any of the usual impurity (2,2-dimethylbutane).

The SEC measurements were made with a Waters 150C instrument equipped with six μ-Styragel columns having a porosity range of 10^5–10 nm. Tetrahydrofuran was the mobile phase at a flow rate of 1 mL min^{-1} at 30 °C. As a means of secondary characterization, an SEC calibration was used that was based on 15 polystyrene standards from Polymer Laboratories, Toya Soda, and Goodyear. The self-consistent character of the weight-average molecular weights used in this work is attested to by the plot (Figure 1) of log $\bar{M}_w$ vs. SEC elution volume. Therein, the $\bar{M}_w$ values of choice are shown relative to the calibration based on the aforementioned polystyrene standards. All SEC measurements used solutions of 6×10^{-3} g mL^{-1} and injection volumes of 0.20 mL.

The Θ and near-Θ temperatures used in this work are, in general, average values based on those reported in the literature. When values were not available, the Θ temperatures were estimated by phase equilibria studies. Table II lists the measurement temperatures used in this work.

Results and Discussion

The evaluation of unperturbed chain dimensions is most conveniently and accurately accomplished by measuring intrinsic viscosities of polymers under Θ or near-Θ conditions. We have followed this approach by using the same six polystyrene standards in all measurements. In this fashion the influence of random errors, generally not less than ±5%, on the molecular weight values is eliminated insofar as the *relative* comparison of the dual influences of temperature and solvent type on polystyrene unperturbed chain dimensions is concerned.

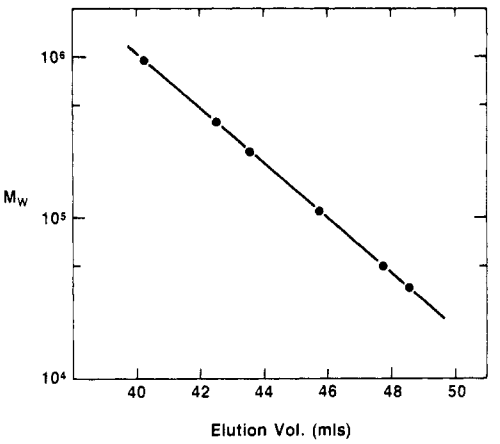

Figure 1. Plot of log $\bar{M}_w$ vs. SEC elution volumes of polystyrenes. The solid line is based on the behavior of 15 polystyrene standards. The solid circles denote the polystyrene samples used in this study.

Table II
Solvents and Measurement Temperatures for Polystyrene

solvent	temp, °C	solvent	temp, °C
1-chloro-*n*-decane	8.5	diethyl malonate	34.5
cycloheptane	19.0	diethyl oxalate	58.2
cyclooctane	20.5[a]	1-chloro-*n*-dodecane	58.6
cyclopentane	20.5	dimethyl succinate	67.6
1-chloro-*n*-undecane	32.8	methylcyclohexane	68.0
cyclohexane	34.5	ethylcyclohexane	75.0

[a] Approximately 7 °C above the freezing temperature.

Ideally, these measurements of intrinsic viscosities should be carried out under Θ conditions where the unperturbed chain dimensions are obtained directly from the well-known relation[51,52]

$$[\eta]_\Theta = K_\Theta \bar{M}_w^{1/2} = \Phi[\langle r^2\rangle_0/\bar{M}_w]^{3/2}\bar{M}_w^{1/2} \qquad (1)$$

where $[\eta]_\Theta$ is the intrinsic viscosity in deciliters per gram, Φ is the hydrodynamic constant,[53–55] $\langle r^2\rangle_0$ is the unperturbed mean-square end-to-end distance in square centimeters, and K_Θ denotes the unperturbed dimension (in dL g$^{-3/2}$ mol$^{1/2}$). The combined measurements of $[\eta]_\Theta$ and $\langle S^2\rangle_0$ for polymers of narrow molecular weight distribution give the hydrodynamic parameter, Φ. The systems used to experimentally determine this parameter are listed in Table III. The predominant value is 2.5×10^{21}—which was the value used in this work to calculate Flory's characteristic ratio.

The viscosity results and Huggins coefficients for the polystyrene samples are given in Table IV. These results, presented in terms of the Mark–Houwink–Sakurada (MHS) parameters K and α are given in Table V. Therein it can be seen that the viscosity measurements were done at or near the Θ state. The measurements carried out in cyclohexane at 34.5 °C lead to MHS parameters that are in good agreement with the results reported by other workers.[35–37,64–66]

For intrinsic viscosity measurements carried out under non-Θ conditions the use of the Burchard–Stockmayer–Fixman (BSF) extrapolation procedure[67,68] has proven to be a reliable means of evaluating K_Θ, at least for results obtained under near-Θ conditions. The BSF procedure was followed in determining K_Θ for *all* of the polystyrene–solvent systems listed in Table IV. Thus, the relative

Table III
Experimental Values of the Hydrodynamic Constant from Narrow Molecular Weight Distribution Polymers[a]

polymer	Θ solvent	Θ temp, °C	$\Phi \times 10^{-21}$ [b]	ref
poly(*p*-bromostyrene)	benzene	26.3	2.5	53
polychloroprene	methyl ethyl ketone	25	2.5	54
poly(dimethylsiloxane)	bromocyclohexane	28	2.5	55
polyisoprene	dioxane	34	2.5	56
poly(α-methylstyrene)	*trans*-decalin	9.5	2.0	57, 58
poly(α-methylstyrene)	cyclohexane	34.5	2.0	57, 58
poly(*p*-methylstyrene)	diethyl succinate	16.4	2.5	59
polystyrene	cyclohexane	34.5	2.5	36, 60–62
polystyrene	*trans*-decalin	20.4	2.5	63

[a] The narrow molecular weight distribution samples were obtained either by fractionation or via anionic polymerization. [b] Zimm (*Macromolecules* **1980**, *13*, 592) has calculated a value for a Φ of 2.51×10^{21} via a numerical simulation where the usual preaveraging approximation was not used.

comparisons of the unperturbed chain dimensions for the different solvent systems are based on K_Θ values (Table VI) obtained by the same procedure.

The determination of K_Θ then allows the evaluation of the characteristic ratio, C_∞:

$$C_\infty = \lim_{n\to\infty} \left[\frac{\langle r^2 \rangle_0 \bar{M}_w^{-1}}{(n'/M)l^2} \right]$$

where n is the number of chain bonds, n' is the number of bonds per monomer unit, M the monomer molecular weight, and l the mean-square average bond length (1.53 Å for polystyrene). The resulting values of C_∞ are given in Table VI.

In general, at a given temperature, higher characteristic ratios are observed for cyclic alkanes than for the other solvents used. This observation is in consonance with certain light scattering and intrinsic viscosity findings[35–37,61,63–66,70,71] for polystyrene and poly(α-methylstyrene); i.e., larger unperturbed chain dimensions were found in cyclohexane than in either the isomers of decalin or "linear" Θ solvents. Conversely, although polystyrene exhibits sensitivity to the type of Θ solvent, polyethylene unperturbed chain dimensions show virtually no similar dependency.[22,24,72]

Reasons for the more extended chain posture of polystyrene in cyclic hydrocarbon Θ solvents relative to corresponding 1-chloro-*n*-paraffins and diesters are unclear. Regarding the latter class of solvents, Munk, Abijaoude, and Halbrook[73] have reported that the Θ solvent ethyl acetate leads to diminished polystyrene unperturbed chain dimensions relative to cyclohexane. This they ascribed to the interaction of the carbonyl group with polystyrene.

In the case of certain biopolymers in aqueous media, specific solvent effects are well-known[74,75] and are attributed to hydrogen bonding and other polar interactions. With some cellulosics[76] and some polar synthetic polymers, e.g., poly(hexene 1-sulfone),[77] specific solvent effects are recognized to be quite strong. Also, with mixed Θ solvents, preferential solvations can lead to similar anomalies.[78–83] In one case, these effects were related to the cohesive energy densities of the polymer and solvents.[83]

Rotational isomeric state theory has not yet been developed to the point where specific solvent effects may be incorporated into models in a rigorous fashion, although suggestions regarding implementation of these effects have been registered.[84] It appears that certain solvents hinder internal rotation in macromolecules, which leads to more extended conformations.

Yoon, Sundararajan, and Flory[18] have noted that the proximity of the phenyl units in conformations such as tt of the meso diad limits access of solvent to the polymer and, in particular, to the phenyl groups. The consequence of this attenuated exposure of the phenyl groups to solvent is that the interaction energy between solvent and polystyrene becomes dependent on chain conformation. The effects of this dependence on conformational energy were taken into account by Yoon et al.[18] for polystyrene. Following this line, the influence of the 1-chloro-*n*-alkanes and diesters on unperturbed chain dimensions of polystyrene may be rationalized qualitatively on the grounds that their interactions with the polystyrene chain promote an increase in the overall average population of gauche conformers relative to that of the trans forms. However, without specific values for these interaction energies of solvent with specific conformers, it is currently not possible to address this subject in a quantitative fashion.

As was mentioned previously, the reported values of κ for polystyrene vary in magnitude and sign. A partial explanation for this has been a general lack of recognition of the potential role of specific solvent effects. The close chemical similarity of the solvents in a given homologous series used in this work would be expected to either eliminate[83,86] or minimize this influence on the temperature

Table IV
Polystyrene Intrinsic Viscosities and Huggins Coefficients[a]

sample	$[\eta]^{34.5}_{CHX}$, dL g^{-1}	k_H	$[\eta]^{68.0}_{MCH}$, dL g^{-1}	k_H	$[\eta]^{75.0}_{ECH}$, dL g^{-1}	k_H	$[\eta]^{19.0}_{CHP}$, dL g^{-1}	k_H	$[\eta]^{20.5}_{COC}$, dL g^{-1}	k_H	$[\eta]^{20.5}_{CPT}$, dL g^{-1}	k_H
PS-37	0.16_2	0.55	0.15_1	0.63	0.15_3	0.58	0.15_6	0.85	0.16_1	0.83	0.16_1	0.64
PS-50	0.18_7	0.50	0.16_7	0.54	0.17_3	0.62	0.17_6	0.79	0.18_8	0.69	0.18_7	0.53
PS-111	0.27_9	0.62	0.27_1	0.56	0.27_5	0.56	0.28_1	0.64	0.29_3	0.65	0.29_5	0.53
PS-254	0.42_4	0.63	0.39_9	0.60	0.42_1	0.56	0.42_0	0.69	0.44_5	0.65	0.44_3	0.55
PS-392	0.52_3	0.58	0.48_7	0.57	0.52_0	0.56	0.51_1	0.64	0.54_9	0.65	0.53_3	0.52
PS-950	0.82_3	0.71	0.75_5	0.52	0.82_8	0.53	0.80_1	0.66	0.92_5	0.64	0.86_2	0.60
sample	$[\eta]^{8.5}_{CDE}$, dL g^{-1}	k_H	$[\eta]^{32.8}_{CUD}$, dL g^{-1}	k_H	$[\eta]^{58.6}_{CDD}$, dL g^{-1}	k_H	$[\eta]^{34.5}_{DEM}$, dL g^{-1}	k_H	$[\eta]^{58.2}_{DEO}$, dL g^{-1}	k_H	$[\eta]^{67.6}_{DMS}$, dL g^{-1}	k_H
PS-37	0.15_4	0.86	0.14_8	0.82	0.14_4	0.77	0.14_3	0.75	0.14_2	0.66	0.13_8	0.66
PS-50	0.17_7	0.82	0.17_2	0.68	0.16_5	0.72	0.16_5	0.72	0.15_9	0.65	0.15_6	0.72
PS-111	0.26_9	0.73	0.25_7	0.85	0.24_7	0.92	0.25_6	0.64	0.24_6	0.67	0.24_4	0.64
PS-254	0.39_6	0.64	0.39_0	0.73	0.37_7	0.77	0.37_2	0.83	0.36_2	0.70	0.36_0	0.72
PS-392	0.48_0	0.67	0.47_5	0.67	0.46_3	0.69	0.44_9	0.92	0.44_3	0.71	0.42_7	0.81
PS-950	0.76_8	0.68	0.73_9	0.72	0.73_3	0.88	0.71_1	0.93	0.68_9	0.90	0.65_5	1.00

[a] Symbols for solvent identification: CHX = cyclohexane; MCH = methylcyclohexane; ECH = ethylcyclohexane; CHP = cycloheptane; COC = cyclooctane; CPT = cyclopentane; CDE = 1-chloro-*n*-decane; CUD = 1-chloro-*n*-undecane; CDD = 1-chloro-*n*-dodecane; DEM = diethyl malonate; DEO = diethyl oxalate; DMS = dimethyl succinate.

Table V
Mark-Houwink-Sakurada Parameters for Polystyrene under Θ or Near-Θ Conditions

solvent	$K \times 10^4$, dL g$^{-3/2}$ mol$^{1/2}$	α	temp, °C
1-chloro-*n*-decane	8.71	0.49_2	8.5
cycloheptane	7.45	0.50_8	19.0
cyclooctane	5.88	0.53_3	20.5
cyclopentane	7.26	0.51_4	20.5
1-chloro-*n*-undecane	8.10	0.49_5	32.8
cyclohexane	8.37	0.50_0	34.5
diethyl malonate	8.15	0.49_2	34.5
diethyl oxalate	8.15	0.49_0	58.2
1-chloro-*n*-dodecane	7.24	0.50_2	58.6
dimethyl succinate	8.65	0.48_3	67.6
methylcyclohexane	7.61	0.50_2	68.0
ethylcyclohexane	6.08	0.52_5	75.0

Table VI
Unperturbed Parameters for Polystyrene

solvent	$K_\Theta \times 10^4$,[a] dL g$^{-3/2}$ mol$^{1/2}$	C_∞	temp, °C
1-chloro-*n*-decane	8.01_5	10.4	8.5
cycloheptane	8.09_9	10.5	19.0
cyclooctane	8.16_4	10.5	20.5
cyclopentane	8.40_2	10.7	20.5
1-chloro-*n*-undecane	7.74_8	10.2	32.8
cyclohexane	8.37_1	10.7	34.5
diethyl malonate	7.53_5	10.0	34.5
diethyl oxalate	7.35_3	9.8	58.2
1-chloro-*n*-dodecane	7.40_2	9.9	58.6
dimethyl succinate	7.30_1	9.8	67.6
methylcyclohexane	7.82_1	10.2	68.0
ethylcyclohexane	7.80_6	10.2	75.0

Table VII
Temperature Coefficients for the Unperturbed Chain Dimensions of Polystyrene

solvents	temp range, °C	temp coeff $(\kappa) \times 10^3$, deg^{-1}
cyclohexane/3-methylcyclohexanol	34.5–98.5	-1.1_5[a]
cyclohexanes	34.5–75.0	-1.2_1
1-chloro-*n*-alkanes	8.5–58.6	-1.0_6
diesters	34.5–67.0	-0.6_6
1-chloro-*n*-alkanes/diesters	8.5–67.0	-1.0_5

[a] References 40 and 69. The temperature coefficient was recalculated from the K_Θ values obtained for the two Θ solvents via the BSF approach.

coefficient of chain dimensions. It should be stressed that our approach of determining the polystyrene K_Θ for each solvent by the use of a series of samples eliminates the potential errors inherent in the single-sample approach[39,44,49,70] There, slight deviations from the Θ temperatures can lead to erroneous trends for κ as a consequence of the strong temperature dependency intrinsic viscosity values can exhibit in the region of Θ.[87]

As shown in Table VII and Figure 2, κ is effectively independent of solvent type. The apparent lower value of κ found in the diester solvent series must be discounted as a consequence of the very limited temperature range of the evaluation.

It would be anticipated that the value of κ determined via viscosity measurements for polystyrene would agree with that from thermoelastic measurements. As was mentioned, this is not the case. A possible explanation for this discrepancy, insofar as thermoelastic measurements are concerned, is the suggestion of McCrum,[88] who emphasized the potential nonequilibrium character of thermoelastic measurements (reviews of this topic are available from Mark[89,90]). The general applicability of this proposal, though, remains to be tested, particularly in light of the current excellent agreement in the values of κ obtained by the two different measurement techniques for polyethylene,[20,22,24,91] polyisobutylene,[20,92,93] poly(ethylene oxide),[4,94,95] poly(*n*-butyl methacrylate),[86,96] and isotactic poly(*n*-pent-1-ene).[97]

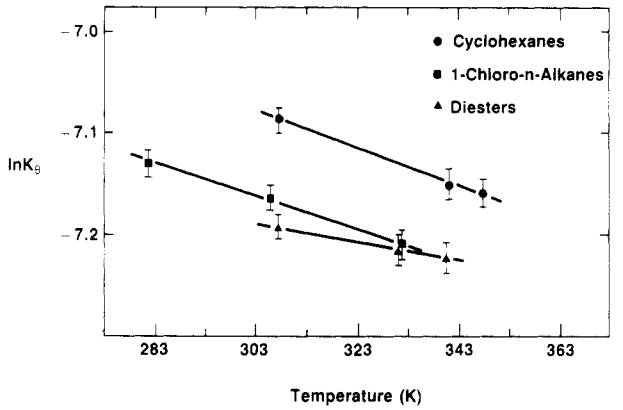

Figure 2. Plot of ln K_Θ vs. temperature for polystyrene in various solvents.

The temperature coefficient results of Table VII are in accord with the RIS model predictions of Yoon et al.[18] These values range between -0.28×10^{-3} and -1.52×10^{-3} deg^{-1}. These theoretical values are dependent upon tacticity ($P_r = 0.56$ for polystyrene prepared by lithium initiators,[98] which were used for the samples prepared in this study). The values for the characteristic ratio and temperature coefficient suggest that $E_{\omega''} = 2.4$–2.6 kcal mol^{-1} and $E_\eta = -0.8$ to -0.6 kcal mol^{-1} (where $E_{\omega''}$ and E_η are the conformational energy parameters given in Tables V and VI of ref 18).

The values of the Huggins coefficients in Table IV show a small dependence on solvent type—slightly higher values were found in "linear" Θ media than in the cyclic hydrocarbon solvents. The Huggins coefficients are also, to a first approximation, independent of molecular weight, a feature not shared by systems exhibiting lower or higher characteristic ratios relative to polystyrene.[99] In all instances values of k_H are in good agreement with the Peterson–Fixman theoretical predictions[100] for flexible polymers in Θ media.

Finally, we wish to comment on the claims[101-103] that viscosity "transitions" occur above the Θ temperature for poly(*p*-bromostyrene) and polystyrene. For polystyrene in cyclohexane the transition is purported[102,103] to lead to a K_Θ value at 40 °C, which is *lower* than that found under Θ conditions. Suffice it to state that these findings[103-105] are not supported by valid theory[2] nor by extensive data[36,41,44,53,54,57-59,61,63,65,104-113] for various solvent–polymer systems on the temperature dependence of intrinsic viscosity, second virial coefficient, chain dimensions, and diffusion coefficients near the Θ temperature.

Registry No. Polystyrene (homopolymer), 9003-53-6.

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The Multivariate Gaussian Distribution and the Dipole Moments of Perturbed Chains

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ABSTRACT: The behavior of the mean square dipole moment, $\langle\mu^2\rangle$, upon chain expansion was studied several years ago using a multivariate Gaussian distribution. A major conclusion was that $\langle\mu^2\rangle$ would be unaffected by expansion if the chain of infinite degree of polymerization has $\langle\mathbf{r}\cdot\boldsymbol{\mu}\rangle_0 = 0$. Here $\mathbf{r}$ and $\boldsymbol{\mu}$ denote the end-to-end and dipole moment vector, respectively, angle brackets denote the statistical mechanical average, and zero as a subscript denotes the ensemble unperturbed by long-range interactions. This prediction provides the basis for the interpretation of a large body of dipole moment data because many polymers have $\langle\mathbf{r}\cdot\boldsymbol{\mu}\rangle_0 = 0$. Recent simulations, including those reported here, find behavior in conflict with the earlier theory. For some chains with $\langle\mathbf{r}\cdot\boldsymbol{\mu}\rangle_0 = 0$, $\langle\mu^2\rangle$ increases upon chain expansion, and for others it decreases. The earlier theoretical work correctly describes the behavior of those chains for which $\boldsymbol{\mu}_t$ is proportional to $\mathbf{r}_t$, where the subscript denotes a subchain comprised of sufficient bonds so that the distribution of $\mathbf{r}_t$ is Gaussian.

Several years ago the mean square dipole moment, $\langle\mu^2\rangle$, was suggested to be independent of the chain expansion produced by long-range interactions if the resultant dipole moment vector for each repeat unit lies in a plane bisecting the bond angle at a chain atom.[1-3] A first-order perturbation treatment was presented by Nagai and Ishikawa.[4] Following Fixman's application[5] of the multivariate Gaussian distribution[6] for $\mathbf{r}$ and $\mathbf{r}_{ij}$ for the purpose of evaluating α_{r^2}, they employed the multivariate Gaussian distribution for $\boldsymbol{\mu}$ and $\mathbf{r}_{ij}$ to evaluate α_{μ^2}. Here $\mathbf{r}$ and $\boldsymbol{\mu}$ are the end-to-end vector and dipole moment vector for a specified configuration, $\mathbf{r}_{ij}$ is the vector from segment i to segment j in that configuration, $\alpha_{r^2} = \langle r^2\rangle/\langle r^2\rangle_0$, and $\alpha_{\mu^2} = \langle\mu^2\rangle/\langle\mu^2\rangle_0$. Angle brackets denote the statistical mechanical average of the enclosed physical property, and zero as a subscript denotes the ensemble unperturbed by long-range interactions. The result obtained by Nagai and Ishikawa is

$$\alpha_{\mu^2} - 1 = X(\alpha_{r^2} - 1) \tag{1}$$

$$X = \langle\mathbf{r}\cdot\boldsymbol{\mu}\rangle_0^2[\langle r^2\rangle_0\langle\mu^2\rangle_0]^{-1} \tag{2}$$

where X is evaluated for the unperturbed chain of infinite n. Nagai and Ishikawa call attention to two interesting consequences of eq 1 and 2:

A. α_{μ^2} must be one if $\langle\mathbf{r}\cdot\boldsymbol{\mu}\rangle_0$ is zero. Symmetry conditions (symmetry planes, twofold symmetry axes, and symmetry points) that produce $\langle\mathbf{r}\cdot\boldsymbol{\mu}\rangle_0 = 0$ are present in the majority of the polymers of commercial interest. Therefore $\langle\mu^2\rangle$ for such chains should be unaffected by chain expansion. The chains considered by Benoit[1,2] and Stockmayer[3] fall in this category.

B. If a chain has $\langle\mathbf{r}\cdot\boldsymbol{\mu}\rangle_0$ different from zero, it must have $\alpha_{\mu^2} > 1$ if $\alpha_{r^2} > 1$. No chain can have $\alpha_{\mu^2} < 1 < \alpha_{r^2}$ because X cannot be negative.

Soon after the appearance of the article by Nagai and Ishikawa, Doi[7] concluded that eq 1 and 2 are "... valid not only for any order of perturbation but also for any type of interaction...".

It might appear that there is nothing more to be said about the effect of excluded volume on $\langle\mu^2\rangle$ for chain molecules. Some curiousity might be aroused upon reading published accounts of experiments that find $\alpha_{\mu^2} \neq 1$ for certain homopolymers[8-10] and copolymers[11,12] that should have $\alpha_{\mu^2} = 1$ if they were to obey the predictions embodied in eq 1 and 2. Model chains also exhibit curious behavior.[13] A recent study of α_{μ^2} performed by the simulation of model chains perturbed by long-range interactions, finds results in severe conflict with eq 1 and 2 when $\langle\mu^2\rangle$ contains a contribution from an asymmetrically attached side chain:

A′. While it is true that some model chains with $\langle\mathbf{r}\cdot\boldsymbol{\mu}\rangle_0 = 0$ have α_{μ^2} indistinguishable from one, there are other model chains with $\langle\mathbf{r}\cdot\boldsymbol{\mu}\rangle_0 = 0$ and $\alpha_{\mu^2} \neq 1$. The latter chains are in conflict with the conclusion expressed above in A.

B′. A very simple model chain has $\alpha_{\mu^2} < 1 < \alpha_{r^2}$. It exhibits behavior in conflict with the conclusion expressed in B.

Here we report results of additional simulations that demonstrate the conflict with eq 1 and 2 is more general than suggested by the initial simulations. We also identify a heretofore unappreciated assumption in the earlier theoretical work[4,7] that restricts its validity to the case where $\boldsymbol{\mu}$ is proportional to $\mathbf{r}$. Consequently eq 1 and 2 apply only when $X = 1$ (or when $\alpha_{\mu^2} = \alpha_{r^2}$).

Simulations

The previous simulations[13] start with a simple unperturbed rotational isomeric state chain that has the geometry and statistical weights appropriate for unperturbed polyethylene.[14] Excluded volume is introduced via hard-sphere interactions between chain atoms i and $i + h$, with $h < 7$. A dipole moment vector, $\mathbf{m}_i$, was assigned to each bond in the chain. The local coordinate system in which $\mathbf{m}_i$ is simply expressed is depicted in Figure 1. The most interesting chain is the one where every $\mathbf{m}_i$ is $[0\ 0\ 1]^T$ when expressed in the local coordinate system for bond i. Generator matrix calculations then give $\langle\mathbf{r}\cdot\boldsymbol{\mu}\rangle_0 = 0$, but the

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