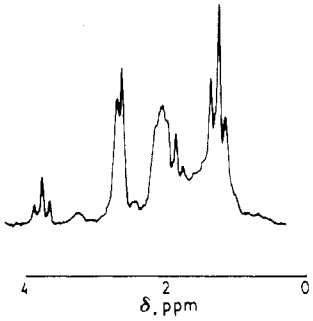

Figure 3. ^{1}H NMR spectrum of polymer B.

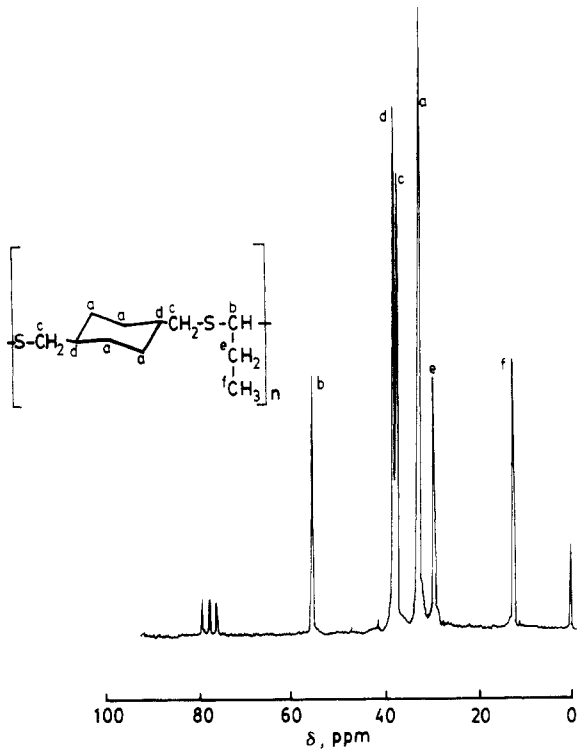

Figure 4. ^{13}C NMR spectrum of polymer B.

to the resonances of the six different carbons of the structural unit with the CH_2 substituents in 1,4-trans configuration. Therefore, isomerization is not apparently influenced by the reaction temperature.

Additional evidence that isomerization reactions take place in the polymerization of *cis*/*trans*-1,4-bis(mercaptomethyl)cyclohexane and paraformaldehyde is that polymer A is a crystalline material whose melting point (165 °C) is similar to that of the polymer obtained from 100% *trans*-1,4-bis(mercaptomethyl)cyclohexane and paraformaldehyde.[8]

Registry No. *cis*-1,4-Bis(bromomethyl)cyclohexane, 15898-77-8; *trans*-1,4-bis(bromomethyl)cyclohexane, 57702-84-8; thiourea, 62-56-6; *cis*-1,4-bis(mercaptomethyl)cyclohexane, 78307-98-9; *trans*-1,4-bis(mercaptomethyl)cyclohexane, 99113-60-7; (*cis*-1,4-bis(mercaptomethyl)cyclohexane)·(*trans*-1,4-bis(mercaptomethyl)cyclohexane)·(formaldehyde) (copolymer), 99559-85-0; (*cis*-1,4-bis(mercaptomethyl)cyclohexane)·(*trans*-1,4-bis(mercaptomethyl)cyclohexane)·(propionaldehyde) (copolymer), 99559-86-1.

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Determination of a Θ-Temperature Using Low-Angle Light Scattering

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The Flory Θ-temperature (T_Θ), where the excluded volume of the chain is just balanced by the attractive interactions and the polymer chain assumes its unperturbed dimensions, must be determined before measurements can be made at Θ conditions. The most common method of determination is extrapolation of cloud point temperatures to infinite molecular weight. Alternatively, the temperature where the second virial coefficient, A_2, vanishes can be determined by light scattering or osmotic measurements:[1]

$$Kc/R_{0,T} = (d\Pi_T/dc)/RT = 1/M + 2A_{2,T}c + 3A_{3,T}c^2 + \ldots \quad (1)$$

Here, c is the concentration, Π is the osmotic pressure, T is the absolute temperature, M is the molecular weight, and K is equal to $4\pi^2n^2(dn/dc)^2/\lambda^4N_A$, where n is the refractive index of the solution, dn/dc is the differential refractive index increment, λ is the wavelength of incident light, and N_A is Avogadro's number. The temperature dependence of n ($dn/dT = 0.00054$ °C^{-1} for cyclohexane in the range of T used here[2]) and dn/dc are considered in the determination of K at a given temperature. The Rayleigh factor (R_θ) measured at scattering angle θ extrapolated to $\theta = 0$ is indicated by R_0, and the temperature dependence of R_0, Π, and A_2 have been explicitly indicated by the subscript T. For polydisperse samples, the molecular weight M will be the weight-average molecular weight, M_w, and the number-average molecular weight, M_n, for light scattering and osmometry, respectively. The Rayleigh factor, R_0, where the subscript zero indicates zero scattering angle, must be determined by extrapolation of R_θ measured at higher scattering angles θ for polymers which are large enough ($>\lambda/20$) to have significant intramolecular interference at $\theta > 0$. The large sample volume used in most classical light scattering instruments increases the time required for equilibration at each temperature for scattering measurements. These constrainsts have made the determination of Θ-temperatures by light scattering time-consuming and subject to errors of extrapolation. We wish to report measurements on poly(α-methylstyrene) in cyclohexane where we have been able to measure the Θ-temperature very quickly using the technique of low-angle light scattering. This technique is more accurate than extrapolation of data from higher scattering angles and allows continuous monitoring of the scattering intensity as the temperature is raised or lowered. The time fluctuation of the scattered light intensity, which increases dramatically as the critical solution temperature is approached, can also be observed and studied simultaneously.

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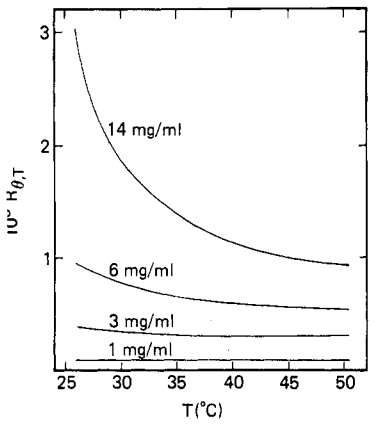

Figure 1. Reduced Rayleigh factor as a function of temperature, T, for several concentrations of poly(α-methylstyrene) in cyclohexane.

Materials and Methods

The polymer sample used was a narrow-distribution, anionically polymerized, essentially atactic sample obtained from Pressure Chemical Co. Detailed characterization of this sample was reported previously[3] and included M_w = 395 000 by light scattering, M_n = 314 000 by membrane osmometry, and tacticity by ^{1}H NMR.[4] The relative amounts of the different tactic forms were 0.051 isotactic, 0.424 heterotactic, and 0.525 syndiotactic. Spectroscopic-grade cyclohexane was used as received. Polymer solutions were prepared by weight and concentrations were calculated with literature values for the density of cyclohexane and partial specific volume of poly(α-methylstyrene) in cyclohexane.[5] Measurements of the excess Rayleigh factor, R_θ, at scattering angle θ = 4.55° were made with a Chromatix (LDC Milton Roy) low-angle light scattering photometer. Solutions were filtered directly into the cell through 0.2-μm Fluoropore membrane filters (Millipore Corp.). The temperature of the scattering cell was controlled by circulating thermostated fluid through the Teflon spacer containing the sample solution between two polished silica windows and was monitored at the sample. Each solution was introduced into the cell at ≃50 °C, and the scattering intensity of the nonflowing solution was recorded as the temperature was slowly lowered (0.5 °C/min) to 25 °C. For molecular weight determinations of polymers in good solvents at ambient temperature, where the temperature dependence is very small and scattering intensities are much lower, the solution is usually flowed slowly through the cell to facilitate identification of anomalous scattering due to dust or other large particles. In addition, the flowing of the solution reduces the fluctuation in the observed scattering intensity. The scattered intensity is recorded on a strip chart recorder as a fluctuating signal, and the average of this signal is used to calculate the Rayleigh factor at a given temperature. The curve of the average excess Rayleigh factor, $R_{\theta,T}$, at each concentration c was recorded as a function of temperature. The curves of the average reduced Rayleigh factor showed a smooth increase as the temperature T was reduced, as shown in Figure 1. Reheating the cell from 25 °C permitted observation of the decrease in R_θ, and the curves shown in Figure 1 were found to be completely reversible, which is evidence that the equilibrium state at each temperature T is attained very quickly for these small sample volumes. In one case, the temperature was lowered to the critical point, where the scattered intensity increased dramatically and the polymer began to precipitate. The average reduced Rayleigh factor was reproducible over the entire temperature range studied (25–50 °C) even when the solution was reheated from this point. As expected, the lower concentrations showed very little temperature dependence, since the higher order terms in eq 1 are very small. These concentrations provided a check on the M_w of the sample. The very small sample volume, 150 μL, which allows rapid temperature equilibration, permits the intensity to be continuously recorded as the temperature is slowly raised or lowered. Differential refractive index increments were determined at three temperatures with 632.8-nm incident light using a Chromatix KMX-16 differential refractometer that was calibrated with aqueous sodium chloride solutions. The results are 0.187, 0.191, and 0.195 mL/g at 30, 40, and 50 °C, respectively.

Table I
T_θ for Four Concentrations

c, mg/mL	T_θ, °C	c, mg/mL	T_θ, °C
3.1	34.6	6.5	34.4
5.9	33.8	14.3	33.6

Results and Discussion

The small scattering volume (5 μL) permits observation of the fluctuation in the intensity of the scattered light. As the temperature is lowered from 50 °C through the Θ-temperature and approaches the critical temperature, the amplitude of these fluctuations increases dramatically and is easily observed. Fluctuations were approximately 1% at 50 °C but increased to nearly 10% at 26 °C, just prior to precipitation. The fluctuations were recorded with a large (0.2 mm) pinhole since the total intensity was the parameter of interest. The amplitude of the fluctuations can be increased by reducing the number of coherence areas viewed by the detector, and the time correlation of these fluctuations can then be studied.

The Θ-temperature can be extracted directly from the scattering curves shown in Figure 1, provided the refractive index n, differential refractive index increment dn/dc, and the polymer concentration c are known at all temperatures T. When T equals the Θ-temperature, T_θ, the second virial coefficient A_2 vanishes, and

$$K^*(dn/dc)^2c/R_{\theta,T} = 1/M_w \qquad (2)$$

Here, K^* depends on T only through the refractive index n, and we have used R_θ determined at θ = 4.55° without correction to zero scattering angle. For this polymer sample, the difference between R_θ at θ = 4.55° and θ = 0 is less than 0.002% even when the coil is expanded in a very good solvent. Measurements at lower concentrations, where the second term in eq 1 above can be neglected, yielded a weight-average molecular weight of 390 000, in excellent agreement with the previously reported M_w[3]. Determinations of T_θ were made at each concentration c by substituting M_w = 390 000 in eq 2 and solving for R_θ. The temperature T at which this value for R_θ was measured was then determined from Figure 1, and results obtained for four concentrations are shown in Table I. The average value of 34.0 ± 0.5 °C is in excellent agreement with 34.5 ± 0.5 °C obtained by Kato and co-workers,[6,7] using the classical light scattering technique. Cowie and Bywater[8] reported that the Θ-temperature for poly(α-methylstyrene) is dependent on the tacticity of the sample, increasing from 32.5 °C for highly syndiotactic material to 37.0 °C for anionically polymerized samples. Although the sample used here was anionically polymerized, we obtained a somewhat lower value for T_θ than reported by Cowie, as did Kato and co-workers. The tacticity measurements reported above for the sample studied here are nearly identical with those reported by Cowie and Bywater for a sample polymerized at 6000 atm with azobis(isobutyronitrile) with T_θ = 35.6 °C.[8] Although this is still slightly higher than our result of 34.0 ± 0.5 °C, it is closer to our value and that of Kato and co-workers than the 37.0 °C reported for the anionic sample used by Cowie and Bywater. Thus it appears that small differences in tacticity obtained in anionic polymerizations can explain some of the differences in T_θ reported for poly(α-methylstyrene).

Values of the second virial coefficient, A_2, at any temperature between 26 and 50 °C can also be obtained by using eq 1. The third virial coefficient, A_3, is expected to

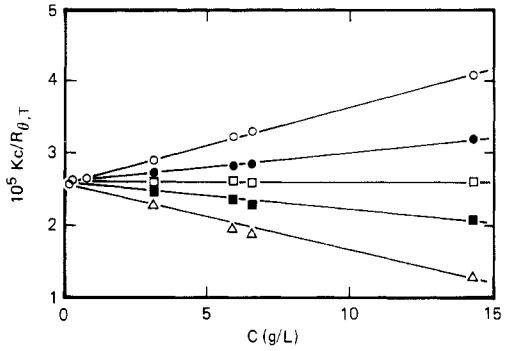

Figure 2. $Kc/R_{\theta,T}$ as a function of concentration c at five temperatures: (○) 50, (●) 38, (□) 34, (■) 30, and (△) 26 °C.

Table II
A_2 at Five Temperatures

T, °C	10^4A_2, mL/(g dalton)	T, °C	10^4A_2, mL/(g dalton)
50	0.49	30	−0.17
38	0.19	26	−0.51
34	0.01		

be related to the second virial coefficient A_2 as is the case for hard spheres:

$$A_3 = gA_2^2M \tag{3}$$

where g is a constant equal to $^5/_8$ for hard spheres but depends on the degree of expansion from the unperturbed dimensions for flexible-chain molecules. If $g = {}^1/_3$, then eq 1 may be rewritten[1,16]

$$(Kc/R_\theta)^{1/2} = (1/M_w)^{1/2} + A_2M^{1/2}c \tag{4}$$

neglecting terms c^3 and higher. This equation is often used instead of eq 1 to minimize extrapolation errors arising from contributions of the c^2 term when A_2 is large. The concentrations used here are quite large and the c^2 term in eq 1 may be significant despite a small A_2. The factor g is predicted to be near zero at the Θ-temperature[9] and to increase to an asymptotic value in good solvents which is near the hard-sphere value[10] or even larger.[11] Since the temperatures used here are near Θ, we expect $g \leq 0.2$, and use of eq 4 may underestimate A_2. Determination of A_2 was accomplished by linear regression of $Kc/R_{\theta,T}$ vs. c for five temperatures as shown in Figure 2, with results listed in Table II. Values of A_2 calculated with eq 4 were within 10% of those shown in Table II. The temperature dependence of A_2 is also in agreement with that obtained by Kato and co-workers[7] for an anionically polymerized sample of similar molecular weight. The temperature dependence is strong in the vicinity of T_θ and then decreases as athermal behavior is approached at higher temperatures.

A perturbation treatment of the McMillan–Mayer general theory of solutions[12] extended to flexible-chain polymers[13,14] which uses a random-flight model and neglects intramolecular interactions allows the second virial coefficient, A_2, for monodisperse linear polymers to be cast in the form

$$A_2 = 4\pi^{3/2}N_ABh(z) \tag{5}$$

where

$$B = (1/4\pi)^{3/2}(1/m)^2\beta \tag{6}$$

and the excluded volume parameter z is given by

$$z = B(R_{g,0}^2/M)^{-3/2}M^{1/2} \tag{7}$$

Here, m is the molecular weight of a segment, β is the intermolecular excluded volume, and $R_{g,0}$ is the unperturbed radius of gyration. For T near T_θ, the function $h(z)$ may be expanded in terms of z:[14,15]

$$h(z) = 1 - 2.865z + 9.202z^2 - \ldots \tag{8}$$

For T very near T_θ ($1 - T_\theta/T \leq \simeq 0.03$), the temperature dependence of B may be written[1,9,16]

$$B = B_0[1 - T_\theta/T] \tag{9}$$

so that B_0 and thus z can be estimated from the temperature dependence of A_2 near T_θ, if $R_{g,0}$ is known. Here, we use the iterative method of Berry[16] and use $R_{g,0}^2/M = 9.1 \times 10^{-18}$ cm^2, as obtained by Kato and co-workers.[7] Estimates of $h(z)$ may be made with one of the approximate closed expressions for $h(z)$.[9] Here we have used[17]

$$zh(z) = (1/5.73)[1 - \exp(-5.73z)] \tag{10}$$

which is based on a factored random-flight model, although various approximations based on other models yield similar results for B_0. The slope of $A_2/h(z)$ vs. the reduced temperature, $(1 - T_\theta/T)$, shown in Figure 3, yields $B_0 = 9.8 \times 10^{-29}$, in agreement with 10.1×10^{-29} obtained by Kato and co-workers.[7] This agreement provides additional evidence for the rapid temperature equilibration achieved with the small sample volumes used here.

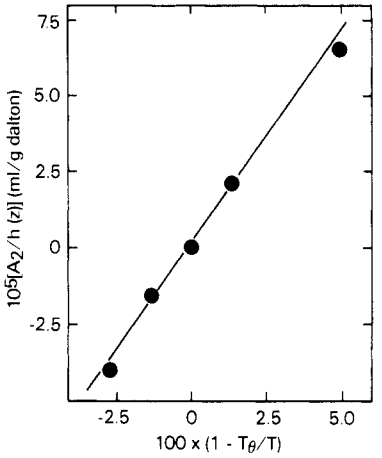

Figure 3. Reduced second virial coefficient $A_2/h(z)$, as a function of reduced temperature, $1 - T_\theta/T$.

Determination of Θ-temperatures with the technique of low-angle light scattering has been shown to give results at least as accurate as the more time-consuming methods of classical light scattering or cloud points. The Θ-temperature can be determined directly from the scattering curves as a function of concentration, eliminating the errors in determination of the second virial coefficient. The increase in amplitude of the fluctuations in scattering intensity as the critical point is approached is observed and enables investigation of the dynamic light scattering under identical conditions.

Registry No. Poly(α-methylstyrene) (homopolymer), 25014-31-7.

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Effects of Stereochemical Structure on Distribution Functions for Short Polypropylene and Poly(vinyl chloride) Chains

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The spatial configurations of low molecular weight polymers are of considerable interest, since short-chain molecules occur in a variety of materials, including thermosets,[1,2] bimodal elastomers,[3] adhesives,[1] and thickening agents.[2] Of foremost importance in characterizing chains of this type is the distribution $W(r)$ of their end-to-end separation r.[4-6] Such information would of course not be limited to short chains but would also be relevant to short sequences within long chains[7] and thus to radiation scattering by high molecular weight polymers.

Unlike long flexible chains, short chains do not have distributions that can be approximated by the Gaussian function.[4-9] Fortunately, better approximations[10-14] to $W(r)$ can now be obtained by using Monte Carlo simulations[7-9] based on very realistic rotational isomeric state (RIS) models[5] of the chain molecules of interest. In this way the calculated distributions reflect the geometric characteristics and conformational preferences of the particular chain structure of interest.

The purpose of the present investigation is to use the Monte Carlo–RIS technique[7-14] to obtain distributions for two important vinyl polymers, namely polypropylene (PP) $-[CHCH_3CH_2]-$,[5-15] and poly(vinyl chloride) (PVC) $-[CHClCH_2]-$.[5,16-18] Since these two chains contain chiral bonds, the effects of stereochemical structure on $W(r)$ are of considerable interest. Also of interest are comparisons among the distributions of polyethylene (PE) $-[CH_2CH_2]-$,[8-10] PP, and PVC since this will document the effects of replacing one hydrogen atom in the PE repeat unit by the relatively large methyl group or the somewhat smaller chlorine atom. Since one goal of the investigation was to characterize the effect of helicity on vinyl distribution functions, the simplest three-state scheme[5] was employed. In this approximation isotactic PP chains are predicted to have a preference for regular helical conformations. The more realistic five-state scheme[15] does not predict this preference, and in this sense the present calculations should probably be considered more illustrative than quantitative for the PP case.

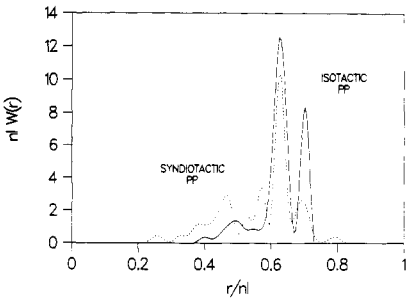

Figure 1. Distributions at 25 °C for the end-to-end separation r of polypropylene chains having n = 40 skeletal bonds and of length l. The two limiting stereochemical forms characterized are the syndiotactic (----) and the isotactic (—), with replication probabilities of 0.00 and 1.00, respectively.

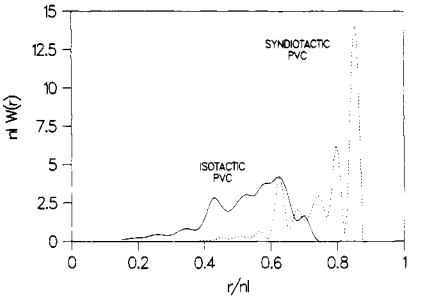

Figure 2. Distributions for poly(vinyl chloride) chains; see legend to preceding figure.

Theory

For all three polymers the bond length l was taken to be 0.153 nm and the bond angle supplement θ to be 68°.[5,15-18] Rotational states were located at values of the dihedral angle ϕ of 0, 120, and −120°, such states being termed trans (t), gauche positive (g^+), and gauche negative (g^-), respectively. Chains having n = 20 and 40 skeletal bonds were investigated.

In the case of PP and PVC, the stereochemical modifications studied were the syndiotactic, atactic, and isotactic, corresponding to replication probabilities P_m of 0.00, 0.50, and 1.00, respectively. For the atactic polymers, 80 000 chains having typical stereochemical structures were generated with a Monte Carlo technique,[17] with rejection of any chains having structures differing from that expected for P_m = 0.50 by more than ±0.10.

Characterization of conformations in PP and PVC requires three statistical weight factors which are described in detail by Flory.[5] The first, η, accounts for conformations in which the side group is syn (g^+ or g^-) to a CH group separated from it by three bonds, relative to a factor of unity for conformations in which a CH_2 group replaces the side group.[18] The second, τ, is for conformations in which both the side group and a CH_2 group are syn with respect to the CH. Interactions of second order, involving rotations about two consecutive skeletal bonds, were represented by a single average factor ω.

For PE, the factor σ is used for conformations in which a pair of CH_2 groups separated by three bonds are syn to one another and ω for the second-order interactions, as usual.[5,8,10]

Results and Discussion

Calculations were carried out for a temperature of 25 °C, using the following values for the statistical weight factors: For PP, η = 1.0, τ = 0.05, and ω = 0.010;[5] for PVC, η = 4.5, τ = 0.50, and ω = 0.050;[5,16-18] for PE, σ = 0.43, and ω = 0.034.[5,10] Each set of statistical weights were nor-

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