

Direct Measurement of the Three-Body Interaction Parameter in a Dilute Polymer Solution

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From measurements of the second virial coefficient by small-angle neutron scattering we have found that the theta temperature of linear polyethylene in dilute solution decreases with increasing molecular mass. This behavior supports polymer theories that incorporate both chain connectivity and three-body interactions. We calculate the three-body interaction parameter within the continuous-curve representation of a flexible polymer, and demonstrate from the same model that our value is consistent with the molecular-mass dependence of the critical precipitation temperature.

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The second virial coefficient A_2 of a flexible polymer in dilute solution represents the interaction energy between two polymer molecules. It can be expressed as the sum of effective 2-, 3-, . . . , n -body contacts between segments on the two chains [1]. In a good solvent the 2-body interactions are strong and repulsive, and so higher-order contacts can be neglected being, on average, much fewer in number. If the temperature is lowered the binary interaction decreases in strength, and eventually becomes attractive, while the ternary interaction remains repulsive and becomes relatively more important. At the theta temperature Θ_{A_2} , the second virial coefficient vanishes [2] because contributions from the 2- and 3-body interactions cancel. de Gennes has shown that the existence of 3-body interactions near Θ_{A_2} leads to tricritical behavior in polymer solutions [3], which can have measurable consequences [4]. The relative number of 2- and 3-body contacts depends on the length of the chain, so Θ_{A_2} is expected to depend weakly on molecular mass. This dependence has been seen with star-branched polymers [5], but quantitative analysis of such systems is complicated by the nonideal behavior associated with the branch point. Despite extensive light scattering investigations [6] no systematic dependence of Θ_{A_2} on molecular mass has been found before now in a linear-polymer-solvent system. We present the first observation of this effect, made by neutron scattering, and show how the 3-body coupling constant can be obtained from the measurements in a simple and direct way.

The system used was polyethylene in solution in deuterated biphenyl ($C_{12}D_{10}$). Structurally, polyethylene is the simplest flexible organic polymer, so it is a good model material for fundamental studies of long chain molecules. The polymer was prepared by hydrogenation of anionically polymerized polybutadiene, which yields essentially linear polymers with narrow molecular-mass distributions [7]. We have reported some of the physical properties of the polyethylene-biphenyl system earlier [8]. In the present investigation seven polymer samples were used, spanning a range in molecular mass from 4.4 to 100

kg mol⁻¹, and with polydispersity $M_w/M_n \leq 1.05$. We label them from A to G in order of ascending mass for convenience.

The neutron measurements were made on the diffractometer D17 at the Institut Laue-Langevin. We chose a neutron wavelength distribution that peaked at 1.1 nm and had a 30% spread (full width at half maximum). This, together with the choice of instrument geometry, gave a usable range of scattering vector of $0.10 \leq Q \leq 0.95$ nm⁻¹. The relaxed resolution resulted in high count rates and only slightly degraded the spectra compared with runs using more monochromatic neutrons. Resolution effects are of no significance in the relative changes measured in the present study.

The intensity of neutrons coherently scattered with small Q from a dilute solution of polymers depends on the second virial coefficient according to Zimm's equation [9]:

$$KcM_wP(Q)[d\Sigma(Q)/d\Omega]^{-1} \approx 1 + 2A_2cM_wP(Q), \quad (1)$$

where $d\Sigma(Q)/d\Omega$ is the coherent partial differential scattering cross section, $P(Q)$ is the single-molecule scattering function normalized so that $P(0)=1$, K is a constant equal to 9.3×10^{-4} mol m² kg⁻¹ for the polyethylene-biphenyl system [8], c is the solution concentration, and M_w is the weight-averaged molecular mass of the polymer. Equation (1) is exact in the limit of zero c and Q , so A_2 can be determined from the gradient of a plot of $Kc[d\Sigma(0)/d\Omega]^{-1}$ vs c . The intercept of such a plot gives M_w .

Neutron scattering has distinct advantages over alternative techniques, such as light scattering, for this experiment. First, the contrast for neutrons in a system of protonated polymer and deuterated solvent gives a better signal-to-noise ratio than an equivalent measurement with light, which is important at low M_w . Second, the measurements are made at Q values well matched to the size of the polymers, so $P(Q)$ varies strongly with Q . Curve fitting can then provide good estimates of $d\Sigma(0)/d\Omega$ from models for $P(Q)$. In the range of Q covered by

light scattering the signal is almost independent of angle, and so the discrimination against solvent background, which is fairly flat (and temperature dependent), is worse.

For each sample, we measured a number of solutions (between 5 and 7) of different concentrations up to a maximum of about 30 kg m^{-3} at several temperatures between 380 and 425 K. After subtracting the solvent background measured at the same temperature as the solution, and normalizing to the scattering from a sample of water, we fitted the spectra with the Debye model [10] for $P(Q)$, which we have found gives a good description of the coherent scattering from dilute solutions when A_2 is small. From these fits we extrapolated the cross sections to zero Q to give $d\Sigma(0)/d\Omega$, and used the concentrations appropriate to each temperature to determine A_2 . We note that there is a small correction due to multiple scattering [11] which causes the measured Θ_{A_2} to be too large. The correction was negligible for the samples with largest M_w , but for the smaller molecules it decreased Θ_{A_2} by up to 0.5 K.

The corrected values of A_2 are plotted as a function of temperature in Fig. 1. To a first approximation the data vary linearly with temperature, but a closer inspection reveals a small negative curvature which is most noticeable with the samples of higher molecular mass. This is to be expected, since in a good solvent A_2 decreases with molecular mass [1]. Although slight, this curvature must be allowed for if the values of Θ_{A_2} are to be reliable. Accordingly, we obtained Θ_{A_2} from the zero of a second-

order polynomial fitted to the data. For sample G only one measurement was made, but because the function $A_2(T)$ was so similar for each sample we could estimate Θ_{A_2} from that point with reasonable accuracy. The theta temperatures are indicated in Fig. 1 by the arrows. The uncertainty in the individual A_2 values is approximately $0.5 \times 10^{-4} \text{ mol m}^3 \text{ kg}^{-2}$, and from the fits we estimate the error in Θ_{A_2} to be approximately $\pm 0.5 \text{ K}$ for samples A to F , and $\pm 1 \text{ K}$ for G .

The dependence of Θ_{A_2} on chain length has been the subject of confusion and conflicting theoretical predictions for many years. Mean-field theories [12], such as Flory's smoothed-density model [2], assume that the segment-segment interaction energy of a flexible polymer is the same as that of a gas of disconnected segments having the same average spatial distribution as the polymer. Since the average segment density decreases as the length of the chain increases the effect of residual 3- and higher-body interactions at the theta temperature becomes less important as the molecular mass M increases [13]. Consequently, mean-field calculations lead to the conclusion that Θ_{A_2} increases with M .

In Fig. 1, on the other hand, Θ_{A_2} decreases with M . Such behavior has been found in computer simulations of linear chains [14], and arises from an inadequacy with mean-field theories first identified by Khokhlov [15]. He noted that because of connectivity the dominant term in A_2 due to 3-body interactions arises from instances where a pair of segments close together on one chain interacts with a third segment on a second chain, yielding an effective, repulsive, binary interaction. However, because of chain stiffness, two segments separated along the chain by a distance less than some cutoff cannot interact, so as M decreases the contribution to A_2 from these "coarse-grained" 2-body interactions becomes less important relative to that from genuine interchain 2-body interactions. Since the latter are attractive in poor solvents, Θ_{A_2} decreases with increasing M .

We discuss the results in the framework of the continuous-chain model, in which the trajectory of the polymer is represented by a smooth space curve, and segment-segment interactions by δ -function pseudopotentials [16] characterized by the dimensionless 2- and 3-body parameters, z_2 and z_3 , the latter of which is assumed to be independent of temperature in the theta region. Expressions for A_2 calculated by first-order perturbation theory [17] lead to

$$\Theta_{A_2}(N) - \Theta_{A_2}(\infty) = \frac{(8\pi)^{3/2} \Theta_0 z_3}{\kappa(Nl)^{1/2}}, \quad (2)$$

where N and l are the number and length of the statistical segments, Θ_0 is the temperature at which z_2 vanishes, and κ is defined by the dependence of z_2 on temperature close to Θ_0 ,

$$z_2 = \frac{\kappa(Nl)^{1/2}}{(2\pi)^{3/2}} \frac{T - \Theta_0}{\Theta_0}. \quad (3)$$

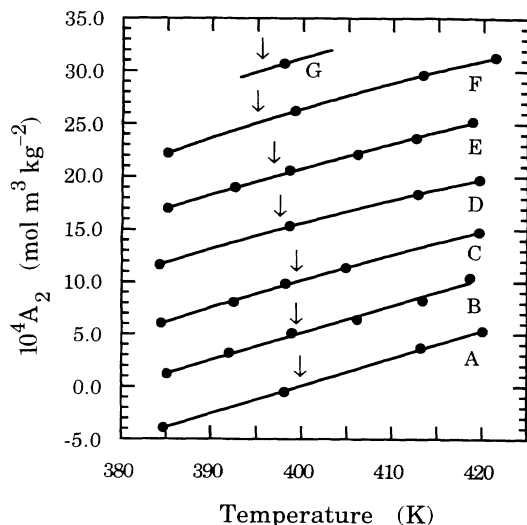


FIG. 1. Temperature dependence of the second virial coefficients of seven samples of polyethylene in d -biphenyl. The molecular masses (in kg mol^{-1}) are A , 4.4; B , 5.9; C , 9.7; D , 14.6; E , 32.8; F , 48; and G , 100. Each curve has been displaced upwards by $5 \times 10^{-4} \text{ mol m}^3 \text{ kg}^{-2}$ relative to the previous one. The lines are fits by a second-order polynomial, and the arrows indicate the Θ_{A_2} temperatures where the second virial coefficient vanishes.

Equation (3), together with the standard proportionality [1] of A_2 and z_2 , gives

$$\left(\frac{dA_2}{dT}\right)_\Theta = \frac{2^{1/2}N_A\langle S^2\rangle_0^{3/2}\kappa(Nl)^{1/2}}{M^2\Theta_0}, \quad (4)$$

where $\langle S^2\rangle_0$ is the mean-squared radius of gyration of the chain at the theta temperature. Combining Eqs. (2) and (4), we obtain

$$\Theta_{A_2}(M) - \Theta_{A_2}(\infty) = \frac{(16\pi)^{3/2}N_A}{2} \left(\frac{dA_2}{dT}\right)_\Theta^{-1} \times \left(\frac{\langle S^2\rangle_0}{M}\right)^{3/2} \frac{z_3}{M^{1/2}} \quad (5)$$

which is an expression for z_3 in terms of experimental quantities only [18]. Equation (5) has been derived by other methods based on finite-chain perturbation theory [19], and modifications to it have been calculated by renormalization-group theory [20].

Since $\langle S^2\rangle_0 \sim M$, and from Fig. 1 $(dA_2/dT)_\Theta$ is virtually independent of M , Eq. (5) predicts that $\Theta_{A_2}(M) - \Theta_{A_2}(\infty) \sim M^{-1/2}$. Figure 2(a) demonstrates that the measured Θ_{A_2} values are consistent with this relation, and we deduce the constant of proportionality $14 \pm 2 \text{ K kg}^{1/2} \text{ mol}^{-1/2}$ by linear regression. This, together with the average value of $(dA_2/dT)_\Theta = (0.25 \pm 0.01) \times 10^{-4} \text{ mol m}^3 \text{ kg}^{-2} \text{ K}^{-1}$ from Fig. 1, and the ratio $\langle S^2\rangle_0/M = (1.95 \pm 0.08) \times 10^{-18} \text{ m}^2 \text{ mol kg}^{-1}$ determined previously [8], yields

$$z_3 = (1.2 \pm 0.2) \times 10^{-3}.$$

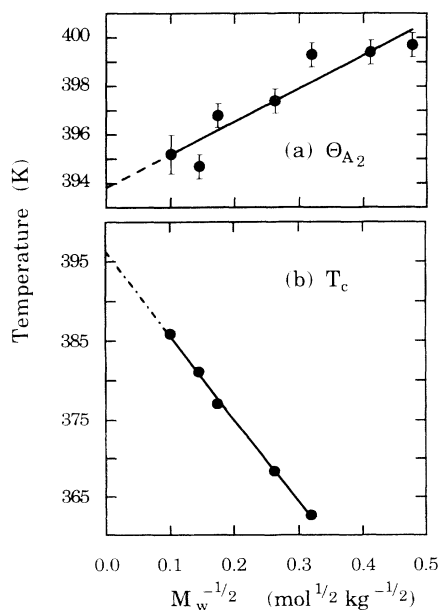


FIG. 2. Variation of (a) the theta temperature and (b) the critical precipitation temperature with molecular mass, plotted according to Eqs. (5) and (6). The temperature scale in (a) is enlarged 5 times compared to (b).

This value is comparable with estimates of z_3 in other polymer-solvent systems, for example from the third virial coefficient [17,21]. We stress, however, that the present experiment is the first to obtain z_3 directly in the limit of infinite dilution, and with a reliable value for z_3 it is now possible to test predictions for other solution properties at higher concentrations.

Recently, the continuous-curve model was used to calculate the critical point for phase separation of a polymer solution [22]. In the present notation, the critical temperature T_c varies according to

$$T_c(\infty) - T_c(M) = \frac{2^{1/2}N_A}{g_2^*(z_3)} \left(\frac{dA_2}{dT}\right)_\Theta^{-1} \left(\frac{\langle S^2\rangle_0}{M}\right)^{3/2} \frac{1}{M^{1/2}}, \quad (6)$$

where $g_2^*(z_3)$ is the reduced second cumulant evaluated on the mean-field critical isochore. From Eq. (6), $T_c(\infty) - T_c(M) \sim M^{-1/2}$. The theory in Ref. [22] with $z_3 = (1.2 \pm 0.2) \times 10^{-3}$ gives $g_2^*(z_3) = 0.85 \pm 0.05$, and so we predict $109 \pm 7 \text{ K kg}^{1/2} \text{ mol}^{-1/2}$ for the coefficient of $M^{-1/2}$. This is in good agreement with the value $105 \pm 3 \text{ K kg}^{1/2} \text{ mol}^{-1/2}$ obtained from the experimental T_c values [8] shown in Fig. 2(b), which is an important result from the theoretical point of view as it shows that the model can describe solution properties measured in different concentration regimes with a single set of parameters. Finally, let us note that the discrepancy between $\Theta_{A_2}(\infty) = 393.7 \pm 0.7 \text{ K}$ and $T_c(\infty) = 396.0 \pm 0.6 \text{ K}$ is not understood.

In conclusion, our experiments have exposed an inadequacy of mean-field theories of polymers and have shown that it requires the combined effects of chain connectivity and 3-body interactions to explain the behavior of polymers in theta solution. We have obtained the 3-body interaction parameter via a perturbation theory which is exact in the weak interaction limit, and have shown that the theory appears to be self-consistent over a range of solution concentrations.

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