The Interpretation of Viscosity–Temperature Coefficients for Poly(oxyethylene) Chains in a Thermodynamically Good Solvent

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ABSTRACT: Intrinsic viscosities $[\eta]$ of two samples of poly(oxyethylene) have been determined in benzene at a number of temperatures in the range 15–50°. Published values of the thermodynamic interaction parameter and the heats of dilution for this system are used to account for changes in the intrinsic viscosity due to polymer–solvent interactions and their temperature dependence, thereby permitting calculation of the temperature coefficient of the unperturbed dimensions $\langle r^2\rangle_0$ of poly(oxyethylene) chains from the measured values of d ln $[\eta]/\mathrm{d}T$. The result thus obtained, 10^3 d ln $\langle r^2\rangle_0/\mathrm{d}T = 0.2\ (\pm 0.2)\ K^{-1}$, is in good agreement with the previously reported value of 0.23 (±0.02) K^{-1} resulting from analysis of force–temperature measurements on elongated poly(oxyethylene) networks in the amorphous state. The present results confirm the previous suggestion that in the case of poly(oxyethylene), and other polymers as well, much of the confusion regarding values of d ln $\langle r^2\rangle_0/\mathrm{d}T$ obtained from viscosity–temperature experiments is simply due to the use of methods which do not properly account for polymer–solvent interactions and their variation with temperature.

As is now well known,[2] the temperature coefficient of a statistical property such as the unperturbed, random-coil dimension $\langle r^2\rangle_0$ assumes particular importance in the study of the configurations of chain molecules. In such configurational analyses, experimental values of the coefficient d ln $\langle r^2\rangle_0/\mathrm{d}T$ are interpreted using rotational isomeric state theory to yield chain conformational energies, which, in turn, may be used to interpret and even predict values of other configuration-dependent properties of the molecule.[2]

Poly(oxyethylene) (POE), H-$(\mathrm{CH_2}$-$\mathrm{CH_2}$-O-$)_x$H, is a chain molecule the configurations of which have been investigated particularly thoroughly.[3-6] The experimental result 10^3 d ln $\langle r^2\rangle_0/\mathrm{d}T = 0.23\ (\pm 0.02)\ K^{-1}$ was obtained for POE a number of years ago from force–temperature ("thermoelastic") measurements[7] on elongated networks of the polymer in the amorphous state and containing a constant amount of nonvolatile diluent.[3] This experimental result and previously reported experimental values of $\langle r^2\rangle_0$ itself were then interpreted using a rotational isomeric state model for the POE chain.[3] Conformational energies thus obtained were subsequently shown to give a good account of the dipole moments,[4] the temperature coefficients of the dipole moments,[5] and the optical anisotropies[6] of POE chains. Also successfully treated with these conformational energies are several statistical properties of two other polymers in the series $[-(\mathrm{CH_2})_m\text{-O-}]_x$ of which POE is a member, namely poly(trimethylene oxide)[8] and poly(tetramethylene oxide).[9]

De Candia and coworkers[10] have concluded recently that none of the presently available techniques for obtaining experimental values of d ln $\langle r^2\rangle_0/\mathrm{d}T$ are reliable in the case of POE chains and suggested that, in the case of this polymer, the presence of "supermolecular structures"[10] in both swollen and unswollen networks and in solution may cause anomalies. They base their criticism of these experimental methods largely on the fact that the thermoelasticity measurements they have carried out on POE networks in the unswollen state[11] and in equilibrium with diluent[10] yield the average value 0.1 (±0.3) K^{-1} for 10^3 d ln $\langle r^2\rangle_0/\mathrm{d}T$, whereas they obtain the result −1.0 (±0.2) K^{-1} from viscosity–temperature measurements on relatively short POE chains in the thermodynamically good solvents acetone and dioxane. As already has been pointed out,[12] their interpretation[10] of these viscosity–temperature data is subject to error for several reasons, the most important of which is the neglect of thermodynamic interactions between polymer and solvent molecules in the solutions thus investigated.

A definitive test of the suggestion that neglect of polymer–solvent interactions is the origin of the discrepancy found by de Candia and coworkers[10,11] is provided in the present study. We have carried out viscosity–temperature measurements on POE in benzene, a thermodynamically good solvent[13] for this polymer. There is sufficient published information[14] on the thermodynamics of mixing of POE with benzene to permit estimation of the contribution of polymer–solvent interactions to the viscosity–temperature coefficient d ln $[\eta]/\mathrm{d}T$, thereby permitting calculation of reliable values of d ln $\langle r^2\rangle_0/\mathrm{d}T$ for POE chains in solution.

Experimental Section

The polymers studied were two POE samples, hereinafter designated a and b;[15] their molecular weights are in a range sufficiently high for specific volumes and thermodynamic interaction parameters to have attained their limiting values for very long chains. The solvent employed for the viscosity–temperature measurements was Mallinckrodt reagent grade benzene. Values of the specific volume v of the benzene and high molecular weight POE at 35° are 1.171[16] and 0.893 $\mathrm{cm^3\ g^{-1}}$,[17] respectively; thermal expansion coefficients β = d ln $v/\mathrm{d}T$ are 1.24×10^{-3} [16] and $0.71 \times 10^{-3}\ K^{-1}$,[17] respectively.

Solutions of the polymer usually were prepared directly by dissolving a known weight of POE in benzene at approximately 40° and subsequently adding benzene to adjust the total volume to the desired value at 25°. For convenience, however, some solutions were obtained by quantitative dilution techniques. Concentrations c are expressed in g/dl of solution. Values of c at temperatures other than 25° are calculated using the appropriate values of v and β for the polymer and solvent; departures from perfect additivities of volumes are very small and of no consequence in the present context.

Viscosities of the benzene solvent and POE solutions were measured at 15, 25, 30, 35, 40, and 50° by means of a Cannon–Ubbelohde viscometer; the capillary size was so chosen that kinetic energy corrections were negligible. Temperatures were controlled to ±0.01° and efflux times were reproducible to ±0.1%. At least five concentrations were investigated for each polymer, with specific viscosities[18] $\eta_{\mathrm{sp}} = \eta_{\mathrm{rel}} - 1$ ranging from 0.3 to 1.1. Intrinsic viscosities $[\eta]$ were obtained in the usual manner[18] by extrapolation of both η_{sp}/c and ln $(\eta_{\mathrm{rel}})/c$ to infinite dilution. For the purpose of evaluating the effect of polymer–solvent interactions on the chain dimensions, intrinsic viscosities were likewise determined for the two POE samples in a Θ solvent, specifically, aqueous 0.45 M $\mathrm{K_2SO_4}$ solution at 35°.[19] Under these conditions, polymer–solvent interactions are known to be nullified by long-range interactions within the randomly coiled polymer chain.[18]

Results

The intrinsic viscosities in benzene at 25° were found to

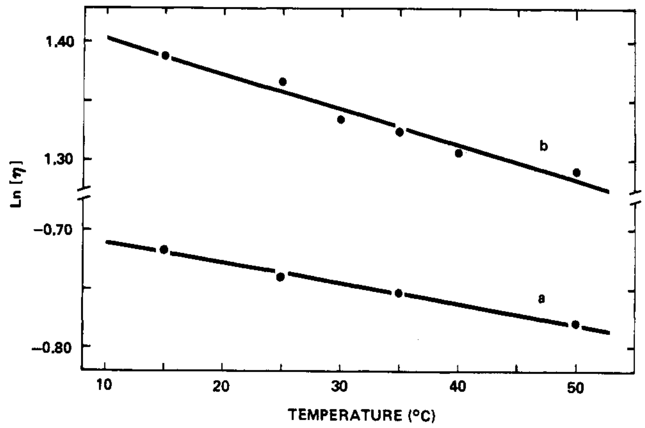

Figure 1. Intrinsic viscosity *vs.* temperature for poly(oxyethylene) in benzene; the molecular weights of the two samples are (a) 30.8 × 10³ and (b) 665 × 10³.

be 0.477 and 3.924 dl g^{-1} for the two POE samples a and b, respectively. These results indicate molecular weights of 30.8 × 10³ and 665 × 10³, respectively, according to the relationship

$$[\eta] = 3.97 \times 10^{-4}\, M^{0.686} \qquad (1)$$

reported for this system.[20] The dependence of ln [η] on temperature for the two samples in benzene is shown in Figure 1. The results for both are well represented by the straight lines shown, these having been located by the method of least squares. The slopes of the lines give 10^3 d ln $[\eta]/\mathrm{d}T = -1.71$ and -2.92 K^{-1} for samples a and b, respectively. These values are comparable in magnitude to the range of values −1.2 to −2.0 K^{-1} obtained by de Candia and coworkers[10] on four POE fractions having viscosity-average molecular weights M_v in the interval 400–4000, in the thermodynamically good solvents acetone and dioxane.

According to theory,[18,21] the intrinsic viscosity is given by the relationship

$$[\eta] = \Phi\langle r^2\rangle_0^{3/2}\alpha^{\gamma}M^{-1} \qquad (2)$$

which is applicable to POE chains having molecular weights greater than approximately 10⁴.[22] The factor $\alpha = (\langle r^2\rangle/\langle r^2\rangle_0)^{1/2}$ characterizes the extent to which polymer–solvent interactions expand the chain dimensions over their unperturbed values, and is thus unity in a Θ solvent. In the original theory,[18,21] the exponent γ was given as 3, but more recent calculations[23,24] suggest a value in the vicinity of 2.5 if Φ is treated as a constant. The temperature dependence of the expansion factor can be obtained from the theoretical expression[18,21,25]

$$\alpha^5 - \alpha^3 = (27/2)(2\pi)^{-3/2}N_a^{-1}v_2^{2}V_1^{-1} \times ((\langle r^2\rangle_0/M)^{-3/2}M^{1/2}(1/2 - \chi_1) \qquad (3)$$

where N_a is Avogadro's number, v_2 is the specific volume of the polymer, $V_1 = M_1v_1$ is the molar volume of the solvent, χ_1 is a parameter[18,21] characterizing the interaction between polymer and solvent, and the original value[18,21] of the numerical constant has been decreased by one-half as suggested by more recent theory.[25] Substitution of the temperature coefficient of α obtained from eq 3 into the expression for the temperature coefficient of [η] obtained from eq 2 gives the result[26]

$$\mathrm{d}\ln\langle r^2\rangle_0/\mathrm{d}T = 2(5\alpha^2/3 - 1)[(5-\gamma)\alpha^2 - (3-\gamma)]^{-1}\,\mathrm{d}\ln[\eta]/\mathrm{d}T - (2\gamma/3)(\alpha^2 - 1)[(5-\gamma)\alpha^2 - (3-\gamma)]^{-1}[(2\beta_2 - \beta_1) - (1/2 - \chi_1)^{-1}\mathrm{d}\chi_1/\mathrm{d}T] \qquad (4)$$

where β_1 and β_2 are the thermal expansion coefficients of solvent and polymer, respectively.

The values of χ_1 required in the present analysis were obtained from the recent vapor pressure measurements carried out by Booth and Devoy[14] on the POE–benzene system. For a narrow molecular weight fraction of POE having a viscosity-average molecular weight of approximately 8 × 10⁵, they report values of χ_1 which vary linearly with the volume fraction φ_2 of polymer in the system. Least-squares analysis of these data gives the result $\chi_1 = 0.258$ for high molecular weight POE at infinite dilution ($\varphi_2 = 0$) in benzene at 60.2°. The temperature coefficient of χ_1 was obtained from the heats of dilution $\Delta\bar{H}_1$ reported in the same study by Booth and Devoy.[14] Values of $\Delta\bar{H}_1/\varphi_2^2$ were also found to vary linearly with φ_2 for high molecular weight POE and, by least-squares analysis, gave $\Delta\bar{H}_1/\varphi_2^2 = -400$ cal mol^{-1} at infinite dilution. Use of the relationship[18,27]

$$\mathrm{d}\chi_1/\mathrm{d}T = -\Delta\bar{H}_1/\varphi_2^2RT^2 \qquad (5)$$

yields $\mathrm{d}\chi_1/\mathrm{d}T = 2.12 \times 10^{-3}\ K^{-1}$ at 35°; application of this coefficient to the experimental value of χ_1 at 60.2° gives $\chi_1 = 0.205$ at the same temperature, 35°. It follows that $(\frac{1}{2} - \chi_1)^{-1}\mathrm{d}\chi_1/\mathrm{d}T = 7.19 \times 10^{-3}\ K^{-1}$ for high molecular weight POE in benzene at 35°. (The same analysis applied to the data[14] reported for a low molecular weight fraction of POE (M_v = 6100) in benzene gives 7.34×10^{-3} K^{-1} for this ratio, thus confirming the expectation that $(\frac{1}{2} - \chi_1)^{-1}\mathrm{d}\chi_1/\mathrm{d}T$ is not markedly dependent on molecular weight.) This result, in conjunction with the values of the thermal expansion coefficients $\beta_1 = 1.24 \times 10^{-3}$ K^{-1} [16] and $\beta_2 = 0.71 \times 10^{-3}$ K^{-1} [17] yields -7.01×10^{-3} K^{-1} for the last factor $[(2\beta_2 - \beta_1) - (\frac{1}{2} - \chi_1)^{-1}\mathrm{d}\chi_1/\mathrm{d}T]$ appearing in eq 4.

Values of the expansion factor α for the POE samples in benzene were obtained in a number of ways based on eq 2 and 3. In the application of eq 2 to both Θ solvents and thermodynamically good solvents, $\langle r^2\rangle_0$ may be assumed to be independent of solvent according to the results of Beech and Booth[22] on eight POE fractions (M_v = 1.6 × 10³ to 1.0 × 10⁶) in the three Θ solvents, methyl isobutyl ketone at 50°, diethylene glycol diethyl ether at 50°, and 0.45 M aqueous K_2SO_4 solution at 35°. On this basis

$$\alpha^{\gamma} = ([\eta]/[\eta]_\Theta)(\Phi_\Theta/\Phi) \qquad (6)$$

where allowance has been made for the possibility that somewhat different values of Φ may be required for Θ solvents and thermodynamically good solvents.[28,29] Thus, α for samples a and b in benzene at 35° may be calculated directly from their intrinsic viscosities at 35° in benzene (0.471 and 3.760 dl g^{-1}, respectively) and in the Θ solvent 0.45 M K_2SO_4 (0.287 and 0.954 dl g^{-1}, respectively). If it is assumed that $\gamma = 3.0$ and $\Phi = \Phi_\Theta$, then the values obtained for α are 1.18 and 1.58, respectively; the corresponding values for the temperature coefficient 10^3 d ln $\langle r^2\rangle_0/\mathrm{d}T$ are 0.35 and 0.50 K^{-1}, respectively, thus giving a mean of 0.42 (±0.08) K^{-1}. Revision of γ to 2.5[23,24] lowers this result to 0.10 (±0.10) K^{-1}; alternatively, restoration of γ to 3.0 with choice of $\Phi_\Theta/\Phi = 2.5/2.1$[28,29] increases the coefficient to 0.73 (±0.05) K^{-1}. Since Beech and Booth[22] report values of the intrinsic viscosities of their POE fractions in benzene at 25° as well as in the Θ solvents cited, it is possible, as an alternative, to calculate the appropriate values of α directly from their viscometric results. Values of 10^3 d ln $\langle r^2\rangle_0/\mathrm{d}T$ obtained in this way are 0.25 (±0.15), −0.01 (±0.25), and 0.57 (±0.25) K^{-1}, respectively, for the three methods of calculation described above. Calculation of values of α directly from eq 3, with $(\langle r^2\rangle_0/M)^{1/2} = 0.879 \times 10^{-8}$ cm (g/mol)$^{-1/2}$,[22,30] gives results in good agreement with those already presented. The values of α thus obtained for samples a and b in benzene at 35° are 1.22 and 1.50, respectively. The choice $\gamma = 3.0$ then yields 10^3 d ln $\langle r^2\rangle_0/\mathrm{d}T = 0.45\ (\pm 0.13)\ K^{-1}$, and $\gamma = 2.5$ yields $-0.05\ (\pm 0.25)\ K^{-1}$. Taking account of the probable magnitudes of errors in the measurements and the relative uncertainties associated with the various methods used for estimating α, we conclude that 10^3 d ln $\langle r^2\rangle_0/\mathrm{d}T = 0.2\ (\pm 0.2)\ K^{-1}$ for POE chains in the vicinity of 35°.

Discussion

The foregoing value for 10^3 d ln $\langle r^2\rangle_0/\mathrm{d}T$ obtained from measurements in dilute solution is in good agreement with the result $0.23\ (\pm 0.02)\ K^{-1}$ obtained from the thermoelasticity study of Mark and Flory[3] and is also in satisfactory agreement with the value $0.1\ (\pm 0.3)\ K^{-1}$ deduced from the thermoelastic studies of de Candia and coworkers.[10,11] These results are irreconcilable with the suggestion[10] that "supermolecular structures" occur in POE or in its solutions. The substantial agreement between the results of these two experimental methods in this instance confirms, in fact, similar observations on a variety of other systems including polymethylene, poly(isobutylene), poly(dimethylsiloxane), and atactic polystyrene.[31]

There now have been a number of attempts to simplify the analysis of viscosity–temperature results described herein, by restricting such measurements to polymers of relatively short length.[10,32] Since the expansion factor α is known to decrease with decreasing molecular weight, as is indicated by eq 3, it is assumed[10,32] that for sufficiently short chains, α is very close to unity and its temperature dependence may be ignored. It would then follow directly from eq 2 that d ln $\langle r^2\rangle_0/\mathrm{d}T = (2/3)$ d ln $[\eta]/\mathrm{d}T$, and the use of the more complicated eq 4 should not be required. On the other hand, the chains must be of a length sufficient to assure the asymptotic hydrodynamic behavior required for eq 2 to hold. Although α may be near unity and its dependence on temperature small, it is necessary to bear in mind that the magnitude of d ln $\langle r^2\rangle_0/\mathrm{d}T$ generally is on the order of $10^{-3}\ K^{-1}$, or less. Even a relatively small change of α^2 with temperature is therefore likely to be significant.

In light of these general comments, it is instructive to consider briefly the use[10] of this approach in the analysis of viscosity–temperature results on short POE chains in thermodynamically good solvents. Of the samples studied by de Candia and coworkers,[10] we consider in detail their analysis for $M_\mathrm{v} = 4000$, since, for the range 400–4000 which they employ, results on this sample are the least likely to be invalidated by failure to meet the requirement[22] that the molecular weight of the POE chains be at least 10^4 for application of the theoretical equations for the intrinsic viscosity based on convergence to asymptotic hydrodynamic behavior. Beech and Booth[22] report values of the intrinsic viscosity of POE chains, including those of relatively short length, in one of the systems, acetone at 25°, studied by de Candia and coworkers.[10] Interpolation of the results of Beech and Booth in the range $M_\mathrm{v} =$ 1600–7400 gives values of the intrinsic viscosity in acetone and in a Θ solvent at $M_\mathrm{v} = 4000$, which, on the basis of eq 6, yield a value of $\alpha \cong 1.08$. A comparable result is obtained by direct calculation from eq 3, using a range of values of χ_1 likely to be appropriate for the POE–acetone system. The corresponding calculation for this sample in benzene yields $\alpha = 1.10$. It is also possible to estimate values of the temperature coefficient of α^2 from eq 3. Use of $(1/2 - \chi_1)^{-1}\mathrm{d}\chi_1/\mathrm{d}T = -7.3 \times 10^{-3}\ K^{-1}$, and other parameters cited above, gives d ln $\alpha^2/\mathrm{d}T = -0.8 \times 10^{-3}\ K^{-1}$ for the same sample in benzene at 35°. A stronger dependence of α^2 on temperature should be expected in acetone owing to its lower molar volume and the likelihood of a larger value of $\mathrm{d}\chi_1/\mathrm{d}T$. In any case, d ln $\alpha^2/\mathrm{d}T$ obviously is by no means negligible for POE chains of this molecular weight in acetone in the vicinity of room temperature.

For the samples of even lower molecular weight, ranging down to 400, α more closely approaches unity, and its temperature coefficient must diminish. However, as already has been pointed out,[12] such short chains fail to meet the conditions required for application of eq 2 to POE.[22] The values obtained for d ln $\langle r^2\rangle_0/\mathrm{d}T$ by de Candia and coworkers[10] from their viscometric data are thus subject to several sources of error. These sources include their use of an incorrect coefficient for d ln $[\eta]/\mathrm{d}T$ in eq 4, and, most importantly, their elimination of the last term in this equation by setting $\alpha = 1$. The same objections apply to the application of this procedure to other polymer chains.[32]

Many other discrepancies observed between values of d ln $\langle r^2\rangle_0/\mathrm{d}T$ reported for the same polymer but obtained by different methods probably also can be resolved by careful analysis of the methods employed, and recognition of their limitations. In this regard, it is particularly important to comment briefly on two additional procedures[33,34] frequently used to calculate values of d ln $\langle r^2\rangle_0/\mathrm{d}T$ from viscosity–temperature data. In the first of these, intrinsic viscosities in thermodynamically good solvents are plotted against a function of the chain length to give extrapolated values of $[\eta]$ thought to be characteristic of the chain at the Θ point;[35] these results are then used to calculate values of $\langle r^2\rangle_0$ from eq 2 on the assumption that $\alpha = 1.00$. Values of $\langle r^2\rangle_0$ thus obtained are, however, generally unreliable since the viscosity theories on which they are based are not applicable[36] in the region through which the extrapolation is performed. Values of the temperature coefficient of $\langle r^2\rangle_0$ obtained by carrying out such extrapolations on data taken at a number of temperatures[33] obviously are subject to even greater error.

The second of these procedures involves viscosity determinations in several different solvents, each at its Θ temperature, and, on the basis of eq 2, the slope of ln $[\eta]_\theta$ plotted against $T = \Theta$ for the various solvents is identified with (3/2) d ln $\langle r^2\rangle_0/\mathrm{d}T$. The intrinsic viscosity, however, is sensitively dependent on temperature near the Θ point. Results thus obtained may therefore be vitiated by cumulative errors in each separate determination of the Θ condition and the measurement of the intrinsic viscosity at the Θ point thus determined. Moreover, specific solvent effects on $\langle r^2\rangle_0$[37-39] may easily overshadow its temperature dependence; *e.g.*, a specific solvent effect amounting to 2% in $\langle r^2\rangle_0$ over a temperature interval of 40° will appear as a contribution amounting to $\pm 0.5 \times 10^{-3}\ K^{-1}$ in d ln $\langle r^2\rangle_0/\mathrm{d}T$. Unless the different solvents chosen are almost identical in chemical structure,[40] such complications can thus have a very marked effect on d ln $\langle r^2\rangle_0/\mathrm{d}T$ and their neglect[34] may lead to seriously erroneous results. Whereas the assertion[41] that "measurable" specific solvent effects occur only with polymers having either polar side groups, or groups that can form hydrogen bonds may be valid in another context, it is essential to recognize that polymer–solvent interactions having a scarcely discernible effect on $\langle r^2\rangle_0$ itself can lead to large errors in the relatively small temperature coefficient of $\langle r^2\rangle_0$ determined in this manner. Similarly, the implication[42] that specific solvent interactions generally can be ignored since they have a "random" effect on $\langle r^2\rangle_0$ is equally unconvincing since such studies seldom involve more than four or five solvents. Finally, it should also be pointed out that criticism[10,42] of the thermoelastic method in general, on the grounds that "ordering" in the amorphous state may cause the dimensions of the chain molecules to deviate from their unperturbed values is clearly without foundation. A variety of experimental results[31] has convincingly shown that such intermolecular ordering does *not* occur in the amorphous state, and the polymer chains under these conditions are, in fact, in their unperturbed states.

As demonstrated herein, the analysis employed in the present study to interpret viscosity–temperature data obtained in thermodynamically good solvents can be used to give reliable values of $\mathrm{d}\ln\langle r^2\rangle_0/\mathrm{d}T$. It suffers, of course, from the limitation that χ_1 and $\mathrm{d}\chi_1/\mathrm{d}T$ for the system must be known with a reasonably high degree of accuracy since the term $(\frac{1}{2} - \chi_1)^{-1}\mathrm{d}\chi_1/\mathrm{d}T$ in eq 4 is generally rather large in the case of thermodynamically good solvents. Much of this difficulty can be removed, however, by choice of a solvent sufficiently similar to the polymer in structure that the two will mix essentially athermally ($\Delta\bar{H}_1 = 0$); under these conditions, $\mathrm{d}\chi_1/\mathrm{d}T$ is zero. Examples of cases in which such an approach has been used to obtain reliable values of $\mathrm{d}\ln\langle r^2\rangle_0/\mathrm{d}T$ are a study of polyethylene in *n*-octacosane,[26] in which independent measurements showed $\mathrm{d}\chi_1/\mathrm{d}T$ to be of the order of only 10^{-4}, and another on poly(isobutylene) in *n*-hexadecane,[43] for which $\mathrm{d}\chi_1/\mathrm{d}T$ is known[44] to be the order of 10^{-5}.

In conclusion, reliable values of $\mathrm{d}\ln\langle r^2\rangle_0/\mathrm{d}T$ can be obtained from either viscosity–temperature measurements on polymer solutions or thermoelastic measurements on amorphous polymer networks. When properly carried out, the two methods give values of this important configurational characteristic which are in satisfactory agreement with one another. Alleged exceptions to these statements appear to be largely, if not entirely, due to neglect of important aspects of the now well-established theories of polymer chain configurations.

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