Some Properties of Low Molecular Weight Polybutadiene and Polytetrahydrofuran

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Synopsis

The proposition, that low molecular weight polymer fractions in good solvents behave as if they were under Θ conditions, has been examined experimentally. Series of monodisperse hydroxy-terminated polytetrahydrofuran (PTHF), 82% 1,4-polybutadiene (PBD), and 30% 1,4-PBD were prepared, and values of $\bar{M}_n$ obtained by vapor-pressure osmometry and endgroup analysis. The Mark-Houwink viscosity parameters K and ν were determined in a number of solvents. The general conclusion is that the proposition is invalid for these systems notwithstanding the fact that $\nu = 0.50$ for one of them [82% 1,4-PBD in methyl ethyl ketone (MEK) at 25°C]. For this particular case, the following evidence suggests that these are actually Θ conditions so that the apparent fulfilment of the proposition is fortuitous. (*1*) Cloud-point precipitation yields $\Theta = 26 \pm 3$°C in MEK. (*2*) The value of K is close to that of K_Θ found elsewhere for PBD in a different solvent at a similar temperature. (*3*) Application of the Kurata-Stockmayer iterative procedure for estimating K_Θ from data in good and bad solvents yields a reasonably small discrepancy (10%) between the K_Θ values from data in toluene and MEK at 25°C for this polymer and only a 3% difference in the unperturbed dimensions $(\langle r_0^2 \rangle / M)^{1/2}$ derived from them. Measured melting points T_m of PTHF ($\bar{M}_n = 1000$–13000), plotted as a function of chain length Z, viz., $1/T_m = 1/T_{m0} + 2R/Z\Delta H_f$, yield 43 ± 3°C and 1.6 kcal/submole, respectively, for the limiting melting point T_{m0} and the heat of fusion ΔH_f. The former is in good agreement with the value obtained dilatometrically for high molecular weight polymer, while the latter indicates a degree of crystallinity of ca. 54%.

INTRODUCTION

It is well substantiated that many physical and physicochemical properties of macromolecules are only characteristic of polymers which have attained a certain critical chain length. We may cite as typical examples density,[1] melting point,[2] specific refractive index increment in solution,[3] and refractive index.[4] The last of these has actually been utilized as a means of estimating the molecular weight of poly(ethylene glycols) in the molecular weight range of 300–20000.[5] In recent years, workers at the University of Genoa[6-12] in particular have studied the intrinsic viscosity–molecular weight relationships for fractionated low molecular weight polymers in good solvents, and proposed that the Mark-Houwink parameters K and ν possess the same values for them as those prevailing under Flory Θ

conditions, i.e., K_Θ and 0.5, respectively. There are, however, ample data in the literature[13-16] which refute this assertion, possible reasons being (1) failure to use monodisperse samples, (2) the difficulty of measuring molecular weights accurately within this range (particularly prior to the advent of vapor-pressure osmometry) and (3) the element of human nature whereby one is more likely to establish an effect if one is specifically looking for it.

In order to investigate the problem further we have prepared some low molecular weight polymers bearing terminal hydroxyl groups, thus affording a check on the molecular weight, which was obtained by vapor-pressure osmometry and by end group analysis assuming two hydroxyl groups per molecule. We have omitted the consistently implied abbreviation HT for hydroxy-terminated polymer. Elsewhere the following abbreviations are adopted: MEK, methyl ethyl ketone; THF tetrahydrofuran; BD, butadiene; PBD, polybutadiene; PTHF, polytetrahydrofuran, otherwise known as poly(tetramethylene oxide).

EXPERIMENTAL

Preparation of Polymers

Monodisperse PBD. Hydroxy-terminated PBD samples were obtained by a procedure involving a Szwarc catalyst according to the method of Hayashi and Marvel.[17] All operations were performed under high vacuum conditions. Such polymers possess a low degree of polydispersity, the range of $\bar{M}_n$ values being effected by varying the ratio [monomer]/[catalyst]. Ethylene oxide was refluxed over calcium hydride and stored *in vacuo* over fresh calcium hydride.

BD was purified as described by Hayashi and Marvel[17] and the THF was refluxed with sodium and stored in contact with the sodium–naphthalene complex under vacuum.

A solution of 1 g naphthalene in 500 ml THF was added under nitrogen to a sodium mirror and the solution stirred overnight, after which the decanted solution was sealed into ampules fitted with break seals. The ampules were attached to three-necked flasks (containing BD and the solvent, THF) on the vacuum line. The stirred monomer solution was cooled to $-78°C$ and the sodium–naphthalene catalyst admitted via the break seal. At the end of 2 hr polymerization the cooling bath was removed, the solution allowed to warm towards room temperature, and the ethylene oxide added. When destruction of the catalyst was evidenced by the disappearance of color, the polymer was isolated by precipitation in methanol and then purified by freeze-drying a solution in benzene. Analysis by nuclear magnetic resonance[18] revealed the composition to be 70% 1,2 and 30% 1,4-PBD.

Fractionated Commercial PBD. Polydisperse hydroxy-terminated PBD, designated as Sinclair R-45-M, was obtained from the Sinclair Chemical Corporation. Nuclear magnetic resonance analysis[18] revealed its composition as 18% 1,2 and 82% 1,4. Its specified functionality was 2.0

± 0.1. The sample was resolved into nine fractions by isothermal precipitation with methanol at 25°C from an initially 2% w/v solution in benzene.

Polydisperse PTHF. Diethyl ether was rendered peroxide-free by the procedure of Vogel.[19] Acetic anhydride (May & Baker Ltd.) was distilled and collected within the bp range of 138–140°C. A solution of perchloric acid (60% w/w) was utilized as supplied and THF was purified as described previously.[20] Using these materials we have followed the procedure of Hachihama and Shono,[21] obtaining similar polymer yields to them, viz., from 69% to 27% for the highest and lowest molecular weight products, respectively. Subsequent saponification to hydroxy-terminated PTHF was effected by boiling with 0.5N alcoholic KOH for 4 hr. The viscous oil remaining after decantation of the cooled alcoholic hydroxide solution was dissolved in ether, washed with water, and dried over sodium sulfate. A viscous oil which slowly solidified was finally obtained after removal of the ether by distillation, the yields being sensibly constant at ca. 91%. It was found possible to remove the yellow-orange colorations (imparted during saponification) by boiling the solutions with charcoal.

Fractionated PTHF. Attempts to fractionate each of the polydisperse PTHF samples by isothermal precipitation met with varying degrees of success. The system THF (solvent)–H_2O (precipitant) was the most satisfactory for this molecular weight range, but the precipitate, appearing as a floating yellow oil, seemed to consist of a solution of PTHF in THF more concentrated than the original. Furthermore, the volume of water required for initial turbidity was similar to that capable of precipitating the entire polymer. In abandoning this method in favor of the one to be described we should like to indicate that preliminary tests with pyridine–water at 25°C gave promising results, which may merit further investigation.

Fractional solution at 22°C with diethyl ether (solvent)–petroleum ether, bp 40–60°C (nonsolvent) was adopted successfully for each polydisperse sample and four fractions isolated in each case. Nonsolvent–solvent mixtures (ca. from 14:1 to 1:1 v/v) were added to the finely divided sample and the slurry stirred magnetically. During this high-speed stirring the polymer was rendered to an oily consistency. All the fractions were dried *in vacuo*.

Solution Properties

Viscosity. Solution viscosities were determined in an Ubbelohde suspended-level viscometer fitted with a built-in porosity 2 sinter. Measurements were conducted in MEK and toluene at 25°C for all PBD samples, and values of $[\eta]$ derived from a plot of η_{sp}/c versus c. For unfractionated and fractionated PTHF, measurements were made in benzene at 20°C and toluene at 30°C, respectively, and $[\eta]$ obtained from the common intercept of plots of η_{sp}/c and ln η_r/c versus c. The shallow slopes of the plots precluded an accurate assignment of the Huggins constant k'. Al-

though somewhat ill-defined, this parameter appears to be single-valued for PBD (0.41 ± 0.03 in toluene and 0.46 ± 0.03 in MEK) whereas a similar range to that already reported[22] obtains for PTHF in benzene and toluene. We have noted incidentally that $k' = 0.31$ for high molecular weight PTHF in benzene at 20°C.

Molecular Weights. Three methods have been utilized, viz.: (1) for samples of molecular weight >20,000, membrane osmometry (Mechrolab) in toluene at 30°C with the use of Sartorius feinst membranes, and for the remaining polymers, (2) vapor-pressure osmometry (Mechrolab) in carbon tetrachloride at 37°C with benzil as calibration standard, (3) endgroup analysis of terminal hydroxyl groups by acetylation with acetic anhydride in pyridine.[23]

Endgroup analysis applied in duplicate to a large number of PBD samples yielded agreement to within 5% of the results via the vapor-pressure osmometric method, which was employed for all the PBD samples. Molecular weights of PBD are quoted in terms of vapor-pressure osmometry measurements. The highest two molecular weight fractions of PTHF necessitated the use of membrane osmometry. For the remainder, results are quoted as the mean of duplicate determinations via vapor-pressure osmometry and endgroup analysis for the high and low molecular weights, respectively. The $\bar{M}_n$ values of unfractionated PTHF were obtained by endgroup analysis.

Theta Conditions of PBD in MEK. We have adopted the rapid turbidimetric procedure of Cornet and van Ballegooijen[24] in order to estimate the Θ temperature of Sinclair PBD in MEK. As no high molecular weight material was available, a commercial Sinclair sample (mol. wt. = 2320) was utilized as supplied, and the temperature of cloud formation T_{cp}
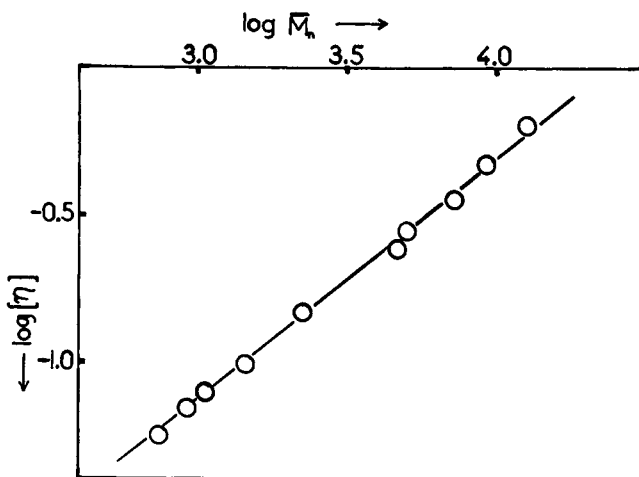

Fig. 1. Intrinsic viscosity–molecular weight relationship for unfractionated hydroxy-terminated PTHF in benzene at 20°C.
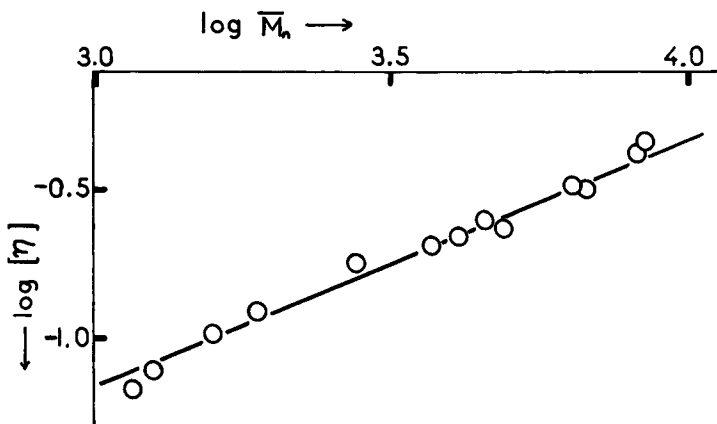
Fig. 2. Intrinsic viscosity–molecular weight relationship for fractionated hydroxy-terminated PTHF in toluene at 30°C.

observed visually with a sufficient degree of accuracy. The procedure was repeated with solutions of different concentration.

Melting Points. No determinations were made on either of the series of PBD as these low molecular weight materials are viscous liquids at room temperature. Melting points of unfractionated PTHF were obtained dilatometrically at heating rates of 1°C/hr, while those of fractions were observed visually in water-jacketed sample tubes.

RESULTS

Solution Viscosity

The intrinsic viscosity–number-average molecular weight relationships for all the systems are depicted in Figures 1–4, and the derived K and ν values are summarized in Table I.

TABLE I

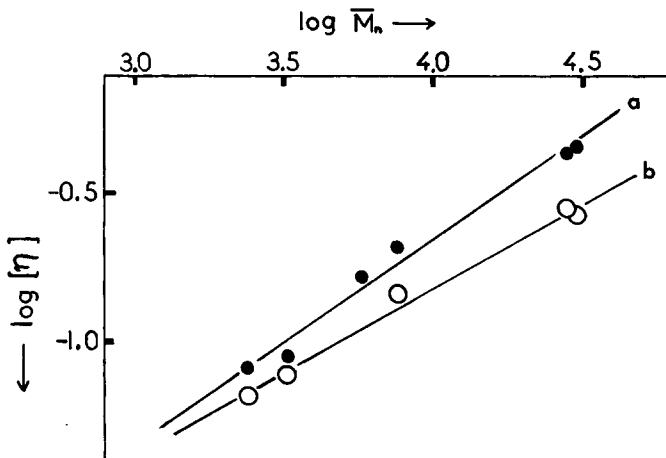| Polymer	Molecular weight range, $M \times 10^{-3}$	Solvent	Temp., °C	$10^4 \times K$, dl/g	ν
Unfractionated PTHF	0.75–12.8	Benzene	20	2.59	0.82
Fractionated PTHF	1.2 – 9.4	Toluene	30	2.73	0.81
Fractionated PBD (Sinclair)	1.2 – 7.1	Toluene	25	4.48	0.71
Fractionated PBD (Sinclair)	1.2 – 7.1	MEK	25	20.0	0.50
Monodisperse PBD	2.4 –28.0	Toluene	25	2.83	0.70
Monodisperse PBD	2.4 –28.0	MEK	25	8.51	0.56

Fig. 3. Intrinsic viscosity–molecular weight relationship for hydroxy-terminated mono-disperse PBD at 25°C in (a) toluene and (b) MEK.
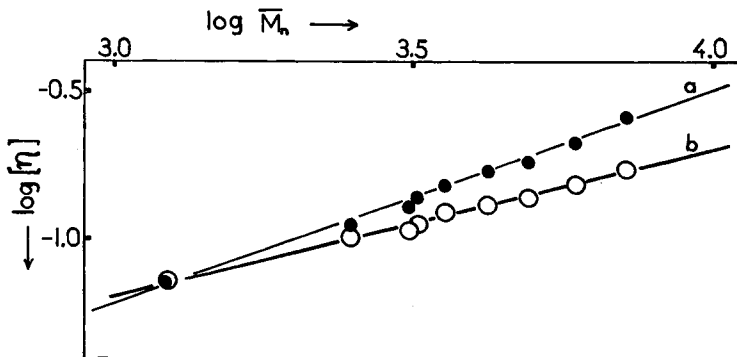

Fig. 4. Intrinsic viscosity–molecular weight relationship for fractionated hydroxy-terminated Sinclair PBD at 25°C in (a) toluene and (b) MEK..

Theta Temperature of Sinclair PBD in MEK

Cornet and van Ballegooijn[24] have demonstrated that the logarithm of the volume fraction of polymer ϕ_p in dilute solution at the onset of phase separation is related linearly to the reciprocal of the absolute temperature at this cloudpoint, T_{cp}. Extrapolation of the line to log $\phi_p = 0$, i.e., pure polymer, yields the θ temperature. The results for PBD in MEK within the polymer volume fraction range of 5.6×10^{-2}–1.1×10^{-3} are shown in Figure 5, from which the extrapolated value of θ is 26 ± 3°C.

Melting Behavior of PTHF

By analogy with the influence of diluents on melting point T_m, one may consider the depression in melting point arising from the concentration of chain ends, viz.:[2]
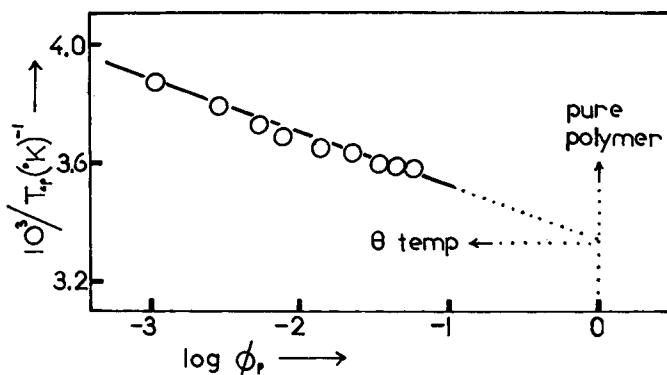
$$1/T_m = 1/T_{m0} + 2R/Z\Delta H_f \qquad (1)$$

Fig. 5. Turbidimetric determination of the Θ temperaure in MEK for hydroxy-terminated Sinclair PBD of $\bar{M}_n = 2320$.
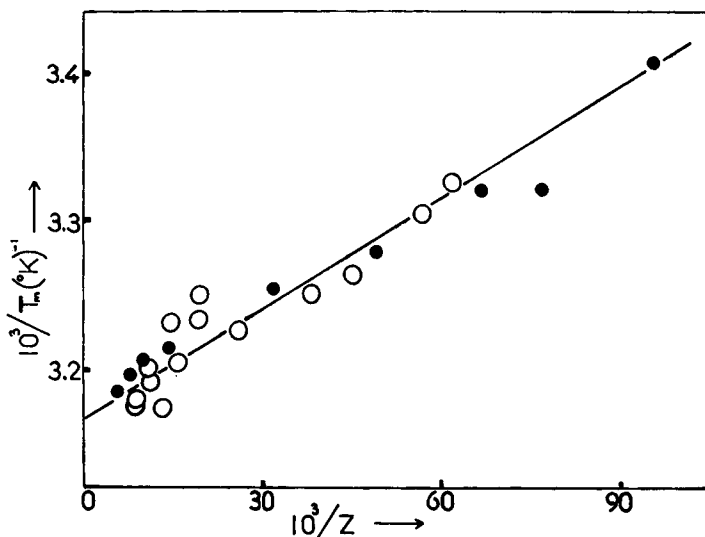

Fig. 6. Reciprocal of melting point vs. reciprocal of degree of polymerization for (●) unfractionated and (○) fractionated hydroxy-terminated PTHF.

In eq. (1), T_m is the absolute melting point of the polymer having a degree of polymerization Z; T_{m0} is the true limiting value of the melting point; R (cal/deg/mole) is the universal gas constant, and ΔH_f (cal/submole) is the latent heat of fusion. Hence $2/Z$ is essentially the mole fraction of chain ends. For PTHF, $Z = \bar{M}_n/72$. The validity of eq. (1) is demonstrated in Figure 6 from the intercept and slope of which, respectively are derived the values of $T_{m0} = 43 \pm 3°C$ and $\Delta H_f = 1.62$ kcal/submole.

DISCUSSION

Whether the exponent ν assumes a value of 0.5 constitutes the prime interest in the viscosity data. It is thus apparent that low molecular

weight PTHF does not fulfil this.   Furthermore, the value of K is smaller by a factor of ca. 10 than the K_Θ obtained independently by phase separation[25] and other studies.[26,27]   The two types of PBD remain to be considered.   They differ considerably in their 1,2/1,4 content and, as might be anticipated, possess different K values.   The data for the monodispersely prepared species (30% 1,4) are few and more dispersed (Fig. 3) than those for the fractionated Sinclair polymer (Fig. 4).   In view of the scatter it is unwise to accord absolute significance to the value of $\nu = 0.56$ in MEK, which is valid to ± 0.03.

The coherent results yielding $\nu = 0.50$ for well-fractionated Sinclair PBD are immediately suggestive that the proposition of Rossi et al.[6-12] is valid for this system.   However, it was deemed prudent to investigate if the effect could be accountable simply on the supposition that MEK is a Θ solvent at 25°C.   As already cited, the result of this investigation does in fact indicate Θ to lie in this region.   In this connection Cornet and van Ballegooijn[24] add a cautionary note that when a low molecular weight sample is used, the turbidimetrically determined Θ temperature is subject to a maximum error of ca. 10°C, as opposed to 1°C for a high molecular weight sample.   (No high molecular weight PBD of the same 1,2/1,4 ratio was available to us for cloud-point experiments.)   Our attention was next drawn to the case of fractionated carboxy-terminated PBD (molecular weight 1950–8600) studied by French et al.,[28] who obtained the relationship $[\eta]_{MEK}^{30°C}$ (dl/g) $= 1.54 \times 10^{-3} (\bar{M}_n)^{0.50}$, and concluded that MEK was a Θ solvent at 30°C primarily on the basis of ν and the rather dubiously significant proximity of k' to 0.50.   Abe and Fujita[29] have presented the values of Θ and of $K(=K_\Theta)$ for PBD in a series of pure and mixed ketones, among which MEK was not included. K_Θ varied from 1.81×10^{-3} to 1.57×10^{-3} dl/g, while the corresponding Θ temperatures were from 10.3 to 59.7°C, respectively.   Interpolation of our K (suggested as K_Θ) and that of French et al.[28] into this relationship would yield the equally unacceptable results of $\Theta = -21$ and $+66°C$, respectively.   The polymer used by Abe and Fujita[29] and a 95% cis-1,4 content, while that of
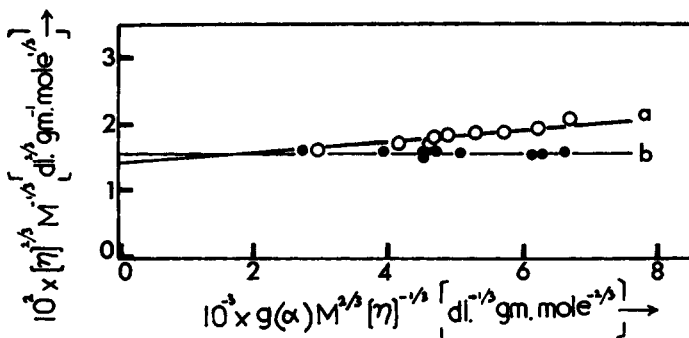

Fig. 7. Kurata-Stockmayer iterative procedure applied to solutions of fractionated hydroxy-terminated Sinclair PBD at 25°C in (a) toluene and (b) MEK.

French et al.[28] was not quoted.   It is significant that the reported value[30] of K_Θ, which is closest to our K in MEK ($= 2.00 \times 10^{-3}$ dl/g), also appertains to a temperature reasonably close to 25°C, viz. $K_\Theta = 1.85 \times 10^{-3}$ dl/g and $\nu = 0.50$ for 98% cis-PBD in isobutyl acetate at 20.5°C.

A final approach to resolving the issue was attempted by invoking the estimation of K_Θ from viscosity measurements in nonideal solvents. Several existing methods have been examined critically by Cowie,[31] who concluded that the most versatile remains the Stockmayer-Fixman relation:[32]

$$[\eta]/M^{1/2} = K_\Theta + 0.51\Phi BM^{1/2} \tag{2}$$

where Φ is the universal viscosity constant for chain polymers in Θ solvents and B is related to the Flory interaction parameter χ by eq. (3), where the other terms have their customary connotation:

$$B = \bar{v}^2(1 - 2\chi)/V_1 N_A \tag{3}$$

Viscosity data in good solvents should, therefore, extrapolate to the same intercept K_Θ as those for Θ solvents when plotted as $[\eta]/M^{1/2}$ versus $M^{1/2}$. However, in the case of Sinclair PBD in toluene and MEK at 25°C, the linear plots intersect and intercept to values of 1.41×10^{-3} and 2.00×10^{-3} dl/g, respectively.   Equation (4), based on the Kurata-Stockmayer theory,[33] is an improved form of eq. (2):

$$[\eta]^{2/3}/M^{1/3} = K_\Theta^{2/3} + 0.363\Phi B(g(\alpha)M^{2/3}/[\eta]^{1/3}) \tag{4}$$

Its use entails an initial approximate estimate of K_Θ as the intercept of $[\eta]^{2/3}/M^{1/3}$ versus $M^{2/3}/[\eta]^{1/3}$, i.e., by assuming the function $g(\alpha) = 1$. It is then possible, by using this value of K_Θ, to calculate $[\eta]_\Theta$, α, and $g(\alpha)$ via the following relationships:

$$[\eta]_\Theta = K_\Theta M^{1/2}$$
$$[\eta] = [\eta]_\Theta \alpha^3 \tag{5}$$
$$g(\alpha) = 8\alpha^3/(3\alpha^2 + 1)^{3/2}$$

The function $[\eta]^{2/3}/M^{1/3}$ is then plotted versus $g(\alpha)M^{2/3}/[\eta]^{1/3}$ to obtain an improved value of $K_\Theta^{2/3}$ and hence K_Θ.   We have adopted this procedure and have found one step sufficient to render $g(\alpha)$ insensitive to further iterations.   Plots of $[\eta]^{2/3}/M^{1/3}$ versus $g(\alpha)M^{2/3}/[\eta]^{1/3}$ for Sinclair PBD in toluene and MEK are given in Figure 7.   As $\nu = 0.50$ and $\alpha = 1$, the slope is of course zero for MEK and the intercept yields $K = 1.99 \times 10^{-3}$ dl/g.   Contrary to theoretical prediction the line for toluene does not converge to the same intercept, but intersects the plot for MEK and yields $K = 1.79 \times 10^{-3}$ dl/g.   This discrepancy results in a relatively small (ca. 3%) difference between the derived unperturbed dimensions $(\langle r_0^2 \rangle / M)^{1/2}$, which are 854×10^{-11} and 885×10^{-11} cm for toluene and MEK, respectively.   Such orders of discrepancy are not without precedent and have been reported, for instance, by Kinsinger and Ballard,[34] who examined

viscometric data for polyoctene-1 over a much wider range of molecular weight.

Although the situation has not been clarified to our complete satisfaction, there is sufficient evidence to point reasonably to (1) the exponent ν = 0.50 for low molecular weight Sinclair PBD in MEK at 25°C solely on account of the prevailing Θ conditions, and (2) for the other systems the original proposition is invalid.

With regard to the melting of PTHF, the value of T_{m0} is in good agreement with the previously reported result of 46°C for high molecular weight material measured by dilatometry.[35] Melting points of samples of $\bar{M}_n$ = 13000, 6760, and 6630 quoted by Trick and Ryan[36] fall satisfactorily on the plot in Figure 6. There is still disagreement[37] about the true value of ΔH_f for this polymer. Sims[35] has obtained a value of 4.8 ± 1.0 kcal/submole for Teracol 30 (Du Pont polymer of molecular weight 2520), which is presumably of high crystallinity. More recently,[38] calorimetric measurements on a sample of $\bar{M}_n$ = 25000 have yielded ΔH_f = 2.96 ± 1.0 kcal/submole. This figure includes a correction to 100% crystallinity utilizing the measured specific volume of the sample, 1.02 cc/g at 25°C for the specific volume of completely amorphous material and 0.917 cc/g as the currently accepted[36,39] specific volume of 100% crystalline PTHF. A value of ΔH_f = 3.03 kcal/submole may be interpolated from those for polyethylene and polyoxymethylene. On the basis of a value of ca. 3.0 kcal/submole for 100% crystalline polymer, the degree of crystallinity of our low molecular weight samples is ca. 1.62/3.0 = 54%.

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