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Excluded-Volume Effects in Dilute Polymer Solutions. VIII. Poly(D,L-β-methyl β-propiolactone) in Several Solvents and Reanalysis of Data on Poly(D-β-hydroxybutyrate)

Tatsumi HIROSYE, Yoshiyuki EINAGA, and Hiroshi FUJITA

Department of Polymer Science, Osaka University,
Toyonaka, Osaka 560, Japan.

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ABSTRACT: Samples of poly(D,L-β-methyl β-propiolactone) (PMPL) were prepared and studied in several solvents by light scattering and viscometry. No differences between PMPL and its isotactic homolog, poly(D-β-hydroxybutyrate) (PHB) could be observed in either the molecualr dimensions or thermodynamic properties. The values of the radius-expansion factor α_s for PMPL and PHB in TFE at 25°C were calculated on the basis of the characteristic ratio $\langle S^2\rangle_0/M_w$ estimated from $[\eta]_0$ of PMPL in butyl chloride at 13°C, a theta solvent for the polymer. These values increased in proportion to $M_w^{1/5}$, in accord with the fifth-power theories for flexible linear polymers. In contrast to the prediction from the current two-parameter theory, the values of $A_2M_w/[\eta]$ for PMPL in THF as a function of $\alpha_\eta^3 \equiv [\eta]/[\eta]_0$ showed a systematic deviation from literature data for $\alpha_\eta^3 < 5$ and continuously ascended as α_η^3 approached unity.

KEY WORDS Poly(D,L-β-methyl β-propiolactone) / Poly(D-β-hydroxybutyrate) / Light Scattering / Intrinsic Viscosity / Radius of Gyration / Second Virial Coefficient / Expansion Factor / Stockmayer–Fixman Plot / Binary Cluster Integral / Interpenetration Function /

In previous papers of this series,[1-3] we reported that a bacterium-produced poly(D-β-hydroxybutyrate) (PHB) undergoes an unusually large excluded-volume effect in trifluoroethanol (TFE). In fact, the data of $\langle S^2\rangle$ (mean-square radius of gyration), A_2 (second virial coefficient), and $[\eta]$ (intrinsic viscosity) as functions of weight-average molecular weight M_w approached the limiting asymptotes predicted by recent theories of dilute polymer solutions for very large values of the excluded-volume parameter z.[4-6] Unfortunately, we were unable to find any theta solvent for this polymer; and this situation remains unchanged even while the present paper is being prepared. Thus, for estimating characteristic quantities of unperturbed PHB, $\langle S^2\rangle_0$ and $[\eta]_0$, required for the computation of α_s (radius-expansion factor) and α_η (viscosity-expansion factor), we used an indirect method involving the analysis of the viscosity data in terms of the Stockmayer–Fixman plot.[4] However, the high molecular weights of the samples available, together with a very large volume-effect in the solvent studied, made it difficult to extrapolate the plots to zero molecular weight with accuracy. Following the failure of effort to extract lower molecular weight samples from the original material, we came to suspect that the isotactic structure of the PHB chain might not affect its conformation and average dimensions in dilute solution, since neighboring asymmetric carbons in the chain are separated by four single bonds apart. If this is correct, solution properties of PHB should not be substantially different from those of its atactic stereoisomer copoly(D,L-β-methyl β-propiolactone) (PMPL), which can be synthesized by a known method.[7]

The present paper reports the preparation of a series of PMPL fractions of relatively low molecular weights and their molecular characterizations by light scattering and viscosity measurements. Part of the results has been described elsewhere.[2,3] Here, we present additional data, the finding of a theta solvent, and the reanalysis of our previous data on PHB in terms of the $[\eta]_0$ values thatthave become available.

EXPERIMENTAL

Samples

Samples of PMPL were synthesized by ring-opening polymerization of an equimolar mixture of D- and L-β-methyl β-propiolactone with the system diethylzinc-water as a catalyst. This catalyst is known to produce a random copolyester.[7] In fact, the polymers obtained were amorphous pasty materials, differing from white powdery PHB. First, they were reprecipitated from dichloromethane solutions into methanol. However, this operation allowed about 1 wt% of zinc oxide to remain which is a degradation product of the catalyst. Hence the precipitated samples were further dissolved in acetylacetone, which is a chelating agent of zinc, and reprecipitation into methanol was carried out after the solution had been allowed to stand overnight at 30°C. This treatment reduced the content of zinc oxide to less than 0.001 wt%.

The purified samples were fractionated at 25°C by fractional precipitation with chloroform as a solvent and propylene glycol as a precipitant. The fractionation was iterated 3 to 6 times. Ten fractions were selected from a number of final fractions for the present physical measurements. Before use, they were dried in a vacuum oven for two to three weeks. Gel-permeation chromatography indicated that their molecular weight homogeneities were comparable to those of Pressure Chemical's standard polystyrene. In contrast with PHB, PMPL was found to dissolve in common organic solvents such as benzene, acetone, methyl ethyl ketone, TFE, chloroform, ethylene dichloride (EDC), buthyl chloride (BuCl), α-chloronaphthalene (α-Cl-N), tetrahydrofurane, ethyl acetate, etc. This feature can be attributed to its atactic structure preventing crystallization.

Light Scattering Measurement

Light scattering from the PMPL fractions in TFE at 25°C was investigated with a Fica 50 automatic light-scattering photogoniometer in the angular range from 30 to 150°, with vertically polarized incident light of 436 nm in wavelength. Additional measurements were made on one fraction in BuCl at temperatures from 12 to 25°C and on four fractions in α-Cl-N at 40°C.

The apparatus constant was calculated from the 90° scattering intensity of pure benzene and from a value of 46.5×10^{-6} cm^{-1} assumed for the absolute Rayleigh ratio of benzene at 25°C. Polymer solutions and solvents were made dust-free by 2 h centrifugation at 20000 rpm in a Sorvall RC2-B centrifuge and then directly pipeted into the measuring cells.

Specific refractive index increment $\partial n/\partial c$ of PMPL in THF at 25°C was determined with a differential refractometer of the Schulz–Cantow type. The values at 436 and 546 nm were 0.153_2 and 0.150_8 cm^3 g^{-1}, respectively, which agree with those for the system PHB–TFE within experimental errors.

Viscometry

Viscosities of the PMPL fractions were determined in TFE at 25°C, in chloroform and EDC at 30°C, in α-Cl-N at 40°C, and in BuCl at 130°C with conventional capillary viscometers of the Ubbelohde suspended-level type. The data were treated in the conventional way to determine $[\eta]$.

RESULTS

Light-Scattering Data

Figures 1 and 2 display, on Berry's square-root

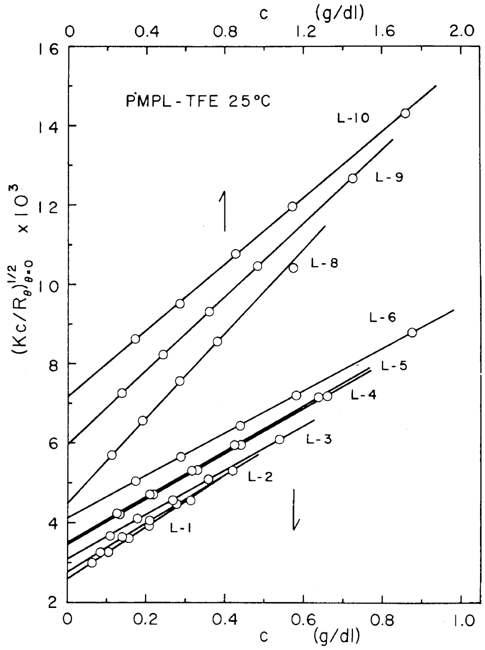

Figure 1. Square-root of reduced scattering intensity at zero angle $(Kc/R_\theta)^{1/2}_{\theta\to0}$ as a function of polymer concentration c for PMPL in TFE at 25°C.

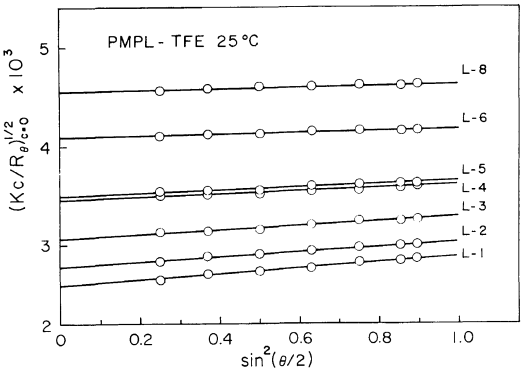

Figure 2. Square-root of reduced scattering intensity at zero concentration $(Kc/R_\theta)^{1/2}_{c=0}$ as a function of $\sin^2(\theta/2)$ (θ is scattering angle) for PMPL in TFE at 25°C.

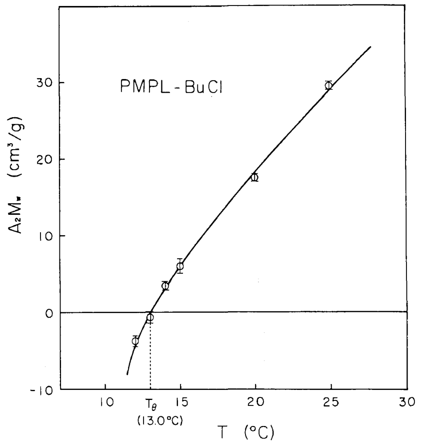

Figure 3. Temperature dependence of A_2M_w for fraction L-3 in BuCl.

plots,[8] the concentration dependence of zero-angle values of $(Kc/R_\theta)^{1/2}$ and the angular dependence of infinite-dilution values of $(Kc/R_\theta)^{1/2}$ for the PMPL fractions in TFE at 25°C, respectively. The values of weight-average molecular weight M_w, z-average root-mean-square radius of gyration $\langle S^2\rangle_z^{1/2}$, and second virial coefficient A_2 for each fraction were evaluated in the usual way from these data. Reliable values of $\langle S^2\rangle_z^{1/2}$ were obtained only for the highest three molecular weight fractions, because the angular dependence of $(Kc/R_\theta)^{1/2}$ for other fractions was too small. The values of M_w, $\langle S^2\rangle_z^{1/2}$, and A_2 are summarized in Table I, together with the A_2 values in α-Cl-N at 40°C.

The values of A_2M_w for fraction L-3 in BuCl, plotted against temperature T in Figure 3, show that A_2 vanishes at 13.0°C. Thus BuCl at this temperature is found to be a theta solvent of PMPL.

Intrinsic Viscosity

The values of $[\eta]$ for the PMPL fractions in five solvents are listed in Table II and plotted double-logarithmically against M_w in Figure 4. The points for each solvent follow a straight line, with the slope as indicated. From these straight lines, we obtain for $2 \times 10^4 < M_w < 15 \times 10^4$

$$[\eta] = 1.75 \times 10^{-1}\ M_w^{0.78} \quad \text{(TFE, 25°C)} \qquad (1)$$

Table I. Results from light scattering measurements on PMPL in THF at 25°C and in α-Cl-N at 40°C

Sample code	TFE 25°C			α-Cl-N 40°C
	$M_w \times 10^{-4}$	$A_2 \times 10^4$ cm³ mol g⁻¹	$\langle S^2\rangle_z^{1/2}$ nm	$A_2 \times 10^4$ cm³ mol g⁻¹
L-1	15.0±0.5	16.9±0.3	22±1	3.99±0.05
L-2	13.0±0.5	17.0±0.3	20±1	
L-3	10.7±0.5	17.2±0.3	18±1	
L-4	8.65±0.2	19.7±0.2	(15)	4.34±0.05
L-5	8.28±0.2	20.1±0.2		
L-6	5.89±0.2	22.0±0.5		
L-7	6.01±0.2	22.5±0.5		
L-8	4.91±0.1	24.1±0.5		4.75±0.05
L-9	2.85±0.1	27.9±1		5.79±0.05
L-10	1.96±0.05	30.3±1		

Table II. Intrinsic viscosities of PMPL in five solvents

Sample code	$[\eta]/10^2$ cm^3 g^{-1}				
	TFE 25°C	CHCl$_3$, 30°C	EDC, 30°C	α-Cl-N, 40°C	BuCl, 13°C
L-1	1.93	1.45	1.13	0.629	0.386
L-2	1.67	—	—	—	—
L-3	1.48	1.10	0.900	—	0.328
L-4	1.26	—	0.768	0.459	—
L-6	—	0.707	—	—	—
L-7	0.924	—	—	—	—
L-8	0.800	0.594	0.491	0.330	0.221
L-9	0.514	—	0.331	0.224	—
L-10	0.388	0.305	0.254	—	0.142

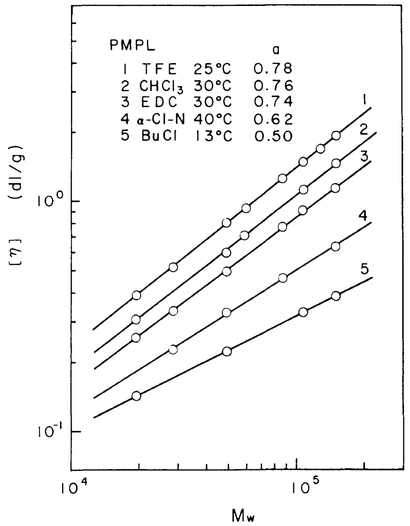

Figure 4. Molecular weight dependence of intrinsic viscosity $[\eta]$ for PMPL in five solvents.

$$[\eta]=1.66\times 10^{-1}\,M_w^{0.76} \quad \text{(chloroform, 30°C)} \qquad (2)$$

$$[\eta]=1.68\times 10^{-1}\,M_w^{0.74} \quad \text{(EDC, 30°C)} \qquad (3)$$

$$[\eta]=3.96\times 10^{-1}\,M_w^{0.62} \quad (\alpha\text{-Cl-N, 40°C}) \qquad (4)$$

$$[\eta]=1.00\times 10^{-1}\,M_w^{0.50} \quad \text{(BuCl, 13°C)} \qquad (5)$$

where $[\eta]$ are expressed in cm^3 g^{-1}. The exponent 0.5 in eq 5 is consistent with the finding that A_2 of PMPL vanishes in BuCl at 13°C.

DISCUSSION

Comparison with the PHB Data

The values of $[\eta]$ for PMPL and PHB in TFE at 25°C and those in chloroform at 30°C as functions of M_w are compared in Figure 5. The data points for both PMPL and PHB in either solvent can be fitted by a single straight line. Figure 6 compares the molecular weight dependence of $\langle S^2\rangle_z^{1/2}$ for PMPL and PHB in TFE at 25°C. As is the case with $[\eta]$, the data points for the two polymers are fitted by a single straight line with a slope of 0.60. These results confirm the starting idea of the present study that the average dimensions of PHB and PMPL in dilute solution should be essentially the same, although the two polymers differ in tacticity. We note that the slope 0.60 is the asymptotic limit predicted by the fifth-power theories for the expansion factor α_s for large values of the excluded-volume parameter z.[4–6]

In Figure 7, the values of A_2 for PMPL and PHB in TFE at 25°C are plotted double-logarithmically against M_w. It is seen that the PMPL data fall on a smooth extension of the data for PHB and that the single curve fitting all these data points has a slight upward curvature. This result implies that the distinct difference in tacticity between PHB and PMPL does not affect their thermodynamic behavior in TFE.

Estimation of the Characteristic Parameters

The unperturbed mean-square radii of gyration $\langle S^2\rangle_0$ of our PMPL samples were too small to be measured directly by light scattering measurements. Hence the characteristic ratio $\langle S^2\rangle_0/M_w$ of PMPL

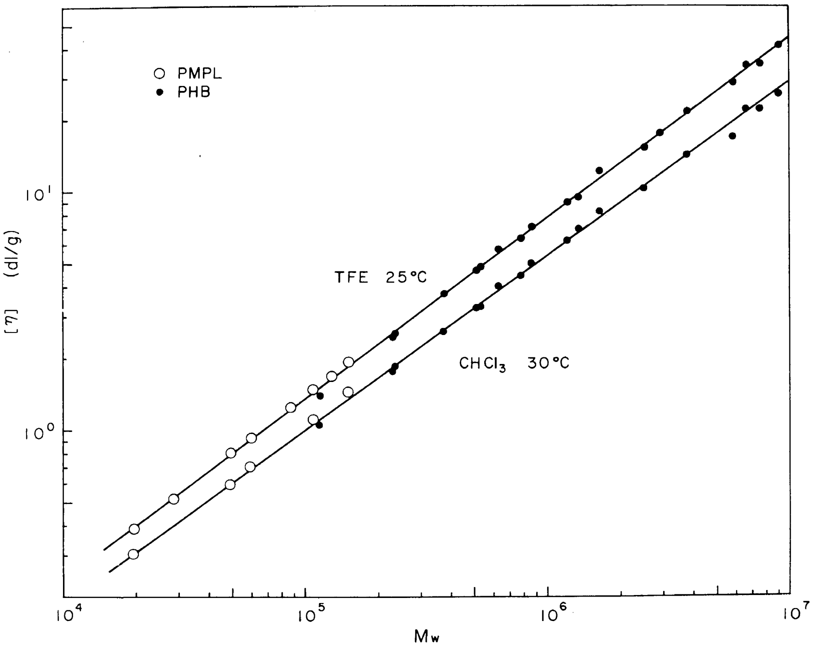

Figure 5. Molecular weight dependence of intrinsic viscosity $[\eta]$ for PMPL and PHB in TFE at 25°C and in chloroform at 30°C.

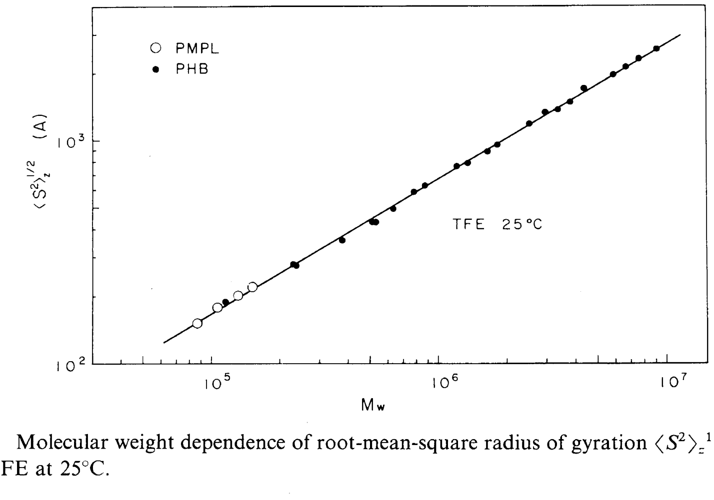

Figure 6. Molecular weight dependence of root-mean-square radius of gyration $\langle S^2\rangle_z^{1/2}$ for PMPL and PHB in TFE at 25°C.

was estimated from the intrinsic viscosity $[\eta]_0$ in the theta solvent, BuCl at 13°C, and the Flory–Fox equation:[9]

$$[\eta]_0=6^{3/2}\Phi_0(\langle S^2\rangle_0/M_w)^{3/2}M_w^{1/2} \qquad (6)$$

where Φ_0 is the Flory viscosity constant. Substitution of eq 5 into eq 6 gives

$$\langle S^2\rangle_0/M_w=1.05\times10^{-17}\,\mathrm{cm}^2 \qquad (7)$$

if Φ_0 is taken to be 2.0×10^{23}, as was done in our previous paper.[2] This value of $\langle S^2\rangle_0 M_w$ is about 20% smaller than 1.27×10^{-17} cm^2 as previously estimated from the Stockmayer–Fixman plots of $[\eta]$ in three nontheta solvents TFE, chloroform, and

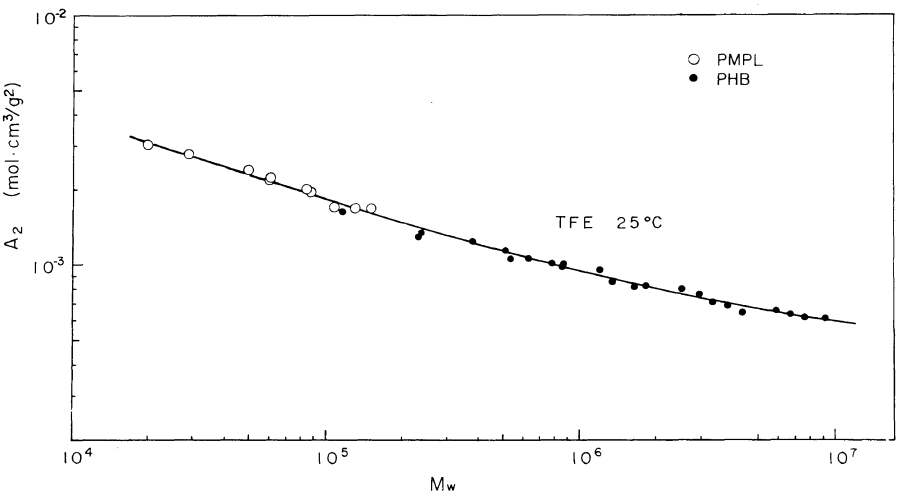

Figure 7. Molecular weight dependence of the second virial coefficient A_2 for PMPL and PHB in TFE at 25°C.

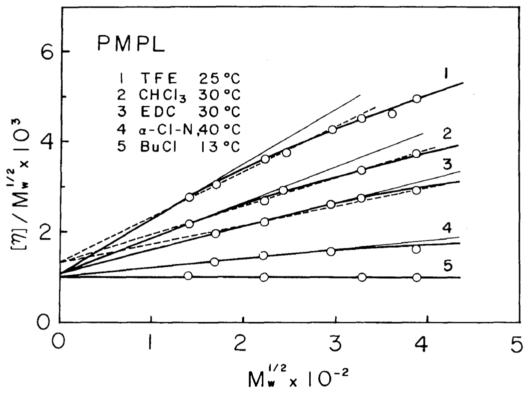

Figure 8. Stockmayer–Fixman plots of the viscosity data for PMPL in five solvents. The solid and dotted lines indicate the present and previous extrapolations of the plots to zero molecular weight, respectively.

EDC.[2] In Figure 8 are shown the Stockmayer–Fixman plots of the viscosity data for PMPL in these three solvents, BuCl, and α-Cl-N. It is seen that our previous extrapolations (indicated by the dotted lines) of the plots to zero molecular weight overestimated the interecept K. Yamakawa[4] has proposed empirical equations

$$[\eta]/M^{1/2}=1.05K+0.287\Phi_0 BM^{1/2} \qquad (1<\alpha_\eta^3<2.5) \tag{8}$$

$$[\eta]/M^{1/2}=K+0.346\Phi_0 BM^{1/2} \qquad (1<\alpha_\eta^3<1.6) \tag{9}$$

where B and α_η^3 are defined by

$$B=\beta/M_0^2 \tag{10}$$

$$\alpha_\eta^3=[\eta]/[\eta]_0 \tag{11}$$

whith β being the binary cluster integral for segment–segment interaction and M_0 the molar mass of a repeat unit of the polymer. With $K=1.00\times10^{-1}$ cm^3 g^{-1}, application of eq 8 and 9 to the data of Figure 8 gives the β values shown below.

Solvent	Temp/°C	$\beta\times10^{24}$/cm^3
TFE	25	159
Chloroform	30	104
EDC	30	71
α-Cl-N	40	22
BuCl	13	0

A marked variation of β with solvent is worth noting.

Expanision Factor $\alpha_s(z)$

Recent theories of flexible linear polymers[4] and computer calculations of nonintersecting lattice chains[10] have shown that the square of the expansion factor α_s, *i.e.*,

$$\alpha_s{}^2 = \langle S^2 \rangle / \langle S^2 \rangle_0 \qquad (12)$$

is asymptotically proportional to $z^{2/5}$ for large values of z, where the exluded-volume parameter z is defined by

$$z = (1/4\pi)^{3/2} (M/\langle S^2 \rangle_0)^{3/2} B M^{1/2} \qquad (13)$$

Domb and Barrett[6] have predicted 1.53 for the proportionality factor.

$A_2 M_w/[\eta]$.

In Figure 10, the values of $A_2 M_w/[\eta]$ for PMPL and PHB in THF at 25°C and those for PMPL in α-Cl-N at 40°C are plotted against $\alpha_\eta{}^3$. The points for PMPL in α-Cl-N are consistent with the solid curve which fits the literature data on a number of polymer–solvent systems. The points for PHB for $\alpha_\eta{}^3$ above 5 appear approximately on a smooth extension of the solid curve, whereas those for PMPL in THF and one point for PHB in the same solvent for $\alpha_\eta{}^3 < 5$ exhibit a systematic upward deviation from this curve. We note that $\alpha_\eta{}^3 = 5$ corresponds to a molecular weight of 10^5. The deviation is considered significant, though the literature data are scattered around the solid curve with deviations of ± 10% and our data are probably subjected to errors of about 5%. This result is not consistent with the two-parameter theory, according to which $A_2 M/[\eta]$ as well as $\alpha_\eta{}^3$ are functions of a single parameter z so that plots of $A_2 M/[\eta]$ *vs.* $\alpha_\eta{}^3$ for different polymer–solvent systems should give a single composite curve.[4] The upswing of $A_2 M_w/[\eta]$ at low $\alpha_\eta{}^3$ values is primarily assosiated with the upward

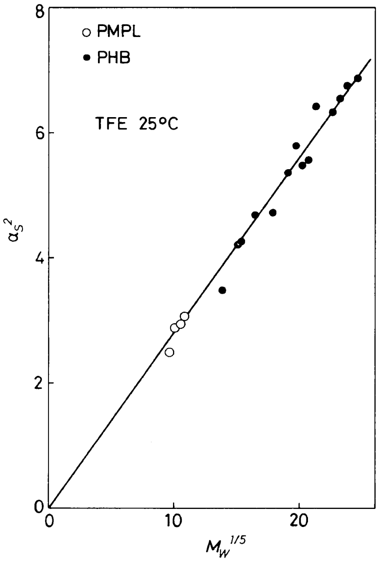

Figure 9. Plots of $\alpha_s{}^2$ *vs.* $M_w{}^{1/5}$ for PMPL and PHB in THF at 25°C.

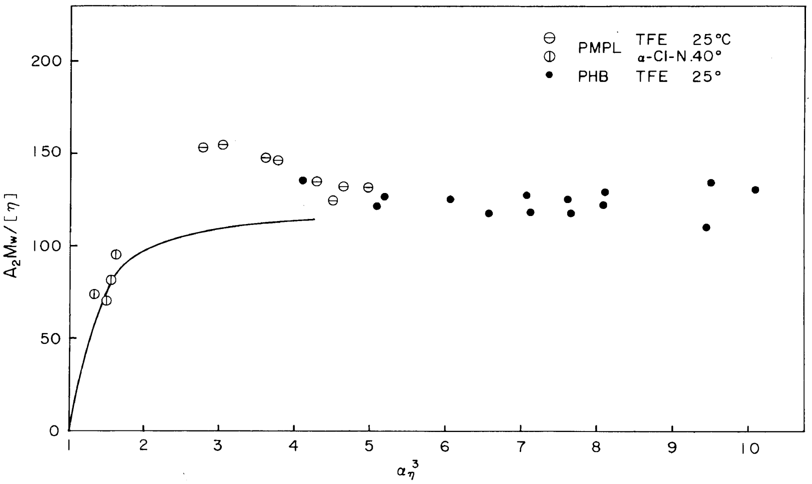

Figure 10. Plots of $A_2 M_w/[\eta]$ *vs.* $\alpha_\eta{}^3$ for PMPL in TFE at 25°C and in α-Cl-N at 40°C, and for PHB in TFE at 25°C. The solid curve is an empirical fit to the literature data for various polymer-solvent systems.

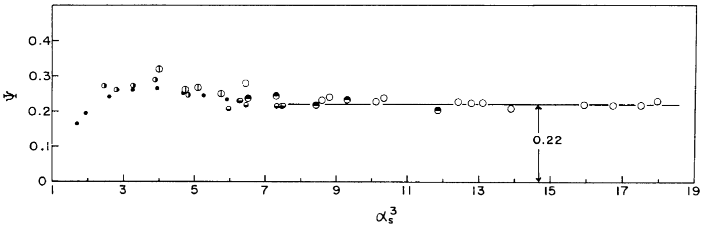

Figure 11. Interpenetration function ψ as a function of α_s^3: ⦶, PMPL in TFE at 25°C (present data); ○, PHB in TFE at 25°C (Miyaki *et al.*[2]); ◓, polystyrene in benzene at 25°C (Miyaki *et al.*[3]); ◒, polystyrene in benzene at 30°C (Fukuda *et al.*[12]); ◑, polystyrene in benzene at 30°C (Yamamoto *et al.*[13]). Filled circles are values calculated by Gobush *et al.*[14]

curvature of the molecular weight dependence of A_2 shown in Figure 7. In this context, it is worth noting that computer-calculated A_2 values of nonintersecting lattice chains show a sharp increase with a decrease in the number of steps.[11] As is illustrated in Figure 11, the interpetration function Ψ for PMPL and PHB in THF increases and passes through a broad maximum as α_s^3 is decreased to unity. The same behavior has been observed in the system polystyrene–benzene.[3] It is a future task to examine the generality of such behavior by accumulating data for Ψ at small α_s^3 values in good solvent systems. All we can say at the present is that no theory is yet available to account for these characteristic features of $A_2M_w/[\eta]$ and Ψ as functions of α_η^3 and α_s^3, respectively.

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