Wormlike Chain Parameters of Poly(hexyl isocyanate) in Dilute Solution

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ABSTRACT: Intrinsic viscosity-molecular weight relationships were determined for poly(hexyl isocyanate) in toluene and dichloromethane using a number of narrow-distribution samples covering a wide molecular weight range. The data were analyzed according to the Yamakawa–Fujii–Yoshizaki theory of viscosity of wormlike cylinders, yielding the following values for the persistence length q and molar mass M_L per unit contour length: $q = 41$—34 nm and $M_L = 730$—760 nm^{-1} in toluene between 10 and 40°C and $q = 21$ nm and $M_L = 750$ nm^{-1} in dichloromethane at 20°C. These parameter values are favorably compared with those reported for other solvent conditions for the same polymer.
KEY WORDS   Poly(hexyl isocyanate) / Wormlike Chain / Persistence Length / Yamakawa–Fujii–Yoshizaki Theory / Chain Stiffness / Stiff Chain / Intrinsic Viscosity /

It is well recognized that solution properties of a polymer are greatly influenced by its stiffness. In order to investigate this influence experimentally, we need polymer samples with varying degrees of stiffness defined explicitly. For this purpose, we have chosen poly(hexyl isocyanate) (PHIC) in this study because it is known as a typical semiflexible polymer, whose dilute solution properties can be well characterized in terms of the wormlike chain model originally due to Porod and Kratky.[1–6] It has been shown that the persistence length q of this polymer varies appreciably with the solvent conditions employed.[5–7] Indeed, Conio et al.[7] estimated q to be 40 and 20 nm in toluene at 25°C and dichloromethane (DCM) at 20°C, respectively, on the basis of Berger and Tidswell's intrinsic viscosity-molecular weight relationship in toluene at 25°C.[8] However it will be shown that this relationship differs from ours at low molecular weights, which is difficult to reconcile. Furthermore no information is available about the temperature dependence of q for any polyisocyanates. Therefore we performed another viscosity study on the same polymer-solvent systems with particular emphasis on temperature dependence. This paper describes preparation of narrow-distribution samples and their characterization by light scattering, sedimentation equilibrium and gel permeation chromatography (GPC). The data for intrinsic viscosity in toluene and DCM are analyzed according to the theory of Yamakawa, Fujii, and Yoshizaki[9,10] for intrinsic viscosity of wormlike cylinders to evaluate the wormlike chain parameters, q and M_L, the molar mass per unit contour length.

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EXPERIMENTAL

Poly(hexyl isocyanate) Samples

Poly(hexyl isocyanate) (PHIC) samples were prepared by polymerization of *n*-hexyl isocyanate according to the method reported by Shashoua *et al.*[11] and Aharoni.[12] Hexyl isocyanate purchased from Kanto Chemical Co., Ltd. was purified by vacuum distillation. Toluene and *N,N*-dimethylformamide were distilled one or two days before the polymerization.

About 10 g of purified hexyl isocyanate were mixed with a DMF+toluene (1:1) mixture (*ca.* 100 cm³) in the vessel cooled in a dry ice/acetone bath (−79°C). Well-dried sodium cyanide dissolved in toluene was used as a catalyst for the polymerization. The catalyst solution thus prepared was added to the hexyl isocyanate solution stirred by a magnetic bar in an argon atmosphere. Immediately the reaction mixture became turbid and viscous. After being kept for 5 h at −79°C, the reaction was terminated by adding about 100 cm³ of cold methanol, yielding white precipitates of PHIC. The precipitates were collected on a sintered glass filter and rinsed with cold methanol for several times. The polymer dried *in vacuo* for one day was dissolved in benzene and precipitated into methanol. In this way about 130 g of PHIC were obtained from 14 batches.

Each batch of PHIC sample was repeatedly fractionated with carbon tetrachloride as a solvent and methanol as a precipitant according to Rubingh and Yu.[4] Then fractions having nearly the same intrinsic viscosities (in 1-chlorobutane at 25°C) were combined and subjected to further fractionation. This process was repeated two to six times. Finally each fraction was reprecipitated from a benzene solution into methanol, freeze-dried from a benzene solution, dried *in vacuo* at room temperature, and stored at −20°C until use. Eventually 12 PHIC samples were obtained: W-70, W-5, W-4, W-3, Z-2, J2-2, L-2, K-2, NRX-12, Z-20, H-14, H-12.

Solution Preparation

All the reagent grade organic solvents used in the present work were distilled before use. Weighed amounts of a given PHIC fraction dried *in vacuo* overnight and a solvent were mixed in a stoppered flask at room temperature. Then the mixture was stirred by a magnetic bar for one day. However, mixtures containing higher molecular-weight samples (H-14, H-12) were stirred for three to five days at 40°C for complete dissolution.

Molecular Weight Determination

Seven PHIC fractions W-70, W-5, Z-2, L-2, K-2, NRX-12, and Z-20 were analyzed by sedimentation equilibrium with hexane of 25°C as a solvent. Use was made of a Beckman–Spinco model E analytical ultracentrifuge with a Kel-F 12 mm double sector cell and the interference optics with light of 546 nm wavelength. The length of the liquid column in the ultracentrifuge cell was adjusted to 1.5—3 mm and the rotor speed was varied from 6000 to 26000 rpm depending on the samples analyzed. Values for the weight-average molecular weight $\bar{M}_w$ and the second virial coefficient A_2 were evaluated using the equation:

$$M_{\text{app}}^{-1} = \bar{M}_w^{-1} + 2A_2\bar{c} + \cdots \qquad (1)$$

with

$$M_{\text{app}} = \frac{2RT}{\omega^2(r_b^2 - r_a^2)(1 - v_p\rho_o)} \cdot \frac{c_b - c_a}{c_0} \qquad (2)$$

where $\bar{c}$ is the average of the mass concentrations c_a and c_b (g cm⁻³) at the meniscus r_a and the bottom r_b, respectively, c_0 the initial polymer mass concentration, ω the angular velocity of the rotor, and ρ_o the density of the solvent. For PHIC in hexane of 25°C, the partial specific volume v_p was taken to be 0.950 cm³ g⁻¹ and the specific refractive index increment $\partial n/\partial c$ was taken to be 0.129 cm³ g⁻¹ at 546 nm and 0.134 cm³ g⁻¹ at 436 nm.[5] Fractions H-12 and H-14 were analyzed by

light scattering with hexane of 25°C as a solvent. A Fica 50 automatic photogoniometer was used to measure the Rayleigh ratio R_θ at scattering angles θ between 22.5 and 150° for vertically polarized light of 436 and 546 nm wavelengths with no analyzer. Following Murakami et al.,[5] we neglected optical anisotropy correction.

Osmotic pressures Π of fractions J2-2, K-2, and NRX-12 in toluene of 25°C were measured on a Knauer osmometer with a Sartorius SM11536 membrane. The cell part of the osmometer was covered with a jacket through which constant-temperature water was circulated and the temperature was controlled within ± 0.1°C.

Zero-shear viscosities of the samples investigated were measured in the following solvents: hexane at 25°C, 1-chlorobutane at 25°C, toluene at 10, 25, and 40°C, and dichloromethane (DCM) at 20°C. A low-shear four-bulb capillary viscometer was used for fractions Z-20, H-14, and H-12, whereas conventional capillary viscometers of the Ubbelohde type were used for the other fractions. Intrinsic viscosities $[\eta]$ were estimated by using Mead–Fuoss plots.

All the PHIC samples studied were analyzed by gel permeation chromatography (GPC) using a Toyo Soda 801A instrument equipped with a UV detector under the operating conditions: two TSK-Gel GMH columns connected in series; eluent, chloroform; polymer conc, 4×10^{-5} g cm^{-3}; injection volume, 0.5 cm^3; flow rate, 1 cm^3 min^{-1}; temperature, 40°C.

RESULTS AND DISCUSSION

Molecular Characterization

Figure 1 shows sedimentation equilibrium data for all the PHIC samples studied. The values for $\bar{M}_w$ and A_2 evaluated from the slopes and the intercepts of the indicated straight lines are summarized in Table I. Figure 2 displays plots of Q vs. $\bar{c}$ for the same

fractions, with Q defined by[13]

$$Q = \frac{(c_b - c_a)^2}{(r_b^2 - r_a^2)[(\partial c/\partial r^2)_{r=r_b} - (\partial c/\partial r^2)_{r=r_a}]} \quad (3)$$

$$Q = (\bar{M}_w/\bar{M}_z)(1 + 2A_2\bar{c} + \cdots) \quad (4)$$

In this figure the straight lines are drawn so that their slopes may be consistent with the A_2 values determined above. The $\bar{M}_z/\bar{M}_w$ ratios estimated from the intercepts of the lines are also given in Table I.

Figure 3 shows plots of Kc/R_0 vs. c for fractions H-14 and H-12, where K is the familiar optical constant and R_0 is the R_θ extrapolated to zero angle, yielding the values of $\bar{M}_w$ and A_2 given in Table I. Figure 4 shows osmotic pressure data, where $(\Pi/RTc)^{1/2}$ is
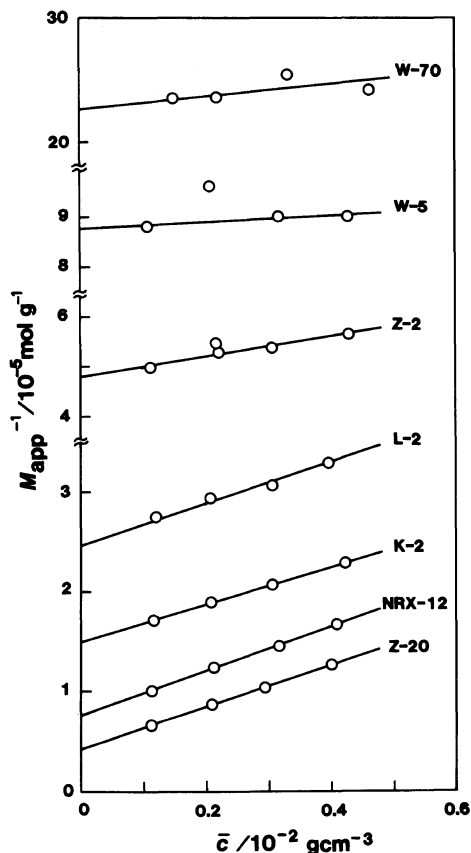

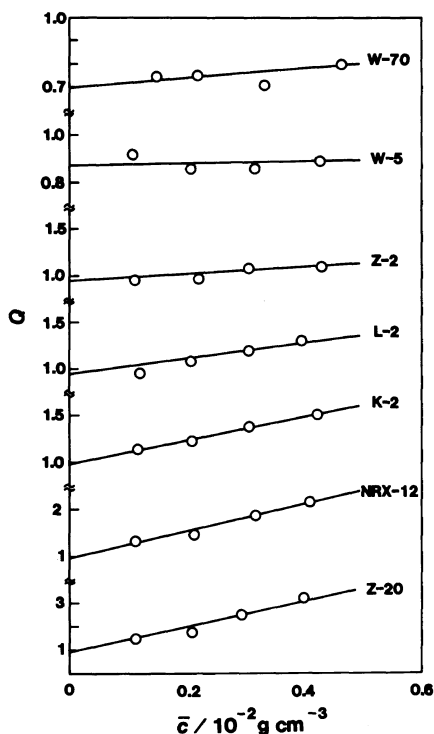**Figure 1.** Sedimentation equilibrium data for solutions of PHIC fractions in hexane of 25°C.

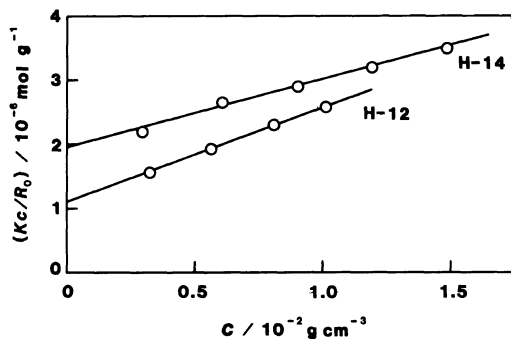**Figure 2.** Plots of Q vs. c for PHIC in hexane of 25°C.

Table I. Molecular parameters of the poly(hexyl isocyanate) samples investigated

Sample	$\bar{M}_w/10^3$	$\dfrac{A_2}{10^{-4} \mathrm{mol\,cm^3\,g^{-1}}}$	$\bar{M}_z/\bar{M}_w$	$(\bar{M}_z/\bar{M}_w)^{GPC}$
W-70	4.41	—	—	—
W-5	11.4	3.4	1.15	—
W-4	12.9[a]	—	—	1.045
W-3	15.2[a]	—	—	1.045
Z-2	20.9	10.0	1.06	1.06
J2-2	32.0[a]	—	—	1.1
	(30.8	6.2)[b]		
L-2	40.7	11.0	1.05	1.06
K-2	68	9.8	1.02	1.06
	(66.4	9.4)[b]		
NRX-12	133	11.2	1.05	1.05
	(122	9.7)[b]		
RX-2	162[a]	—	—	1.075
Z-20	244	10.7	1.05	1.07
H-14	510	5.3	—	1.17
H-12	910	7.4	—	—

[a] $\bar{M}_v$ calculated from $[\eta]$ in toluene of 25°C using the $[\eta]$ vs. $\bar{M}_w$ relationship established with the data for the other samples.

[b] Values in the parentheses: $\bar{M}_n$ and A_2 from osmotic pressure measurements with toluene of 25°C as the solvent.
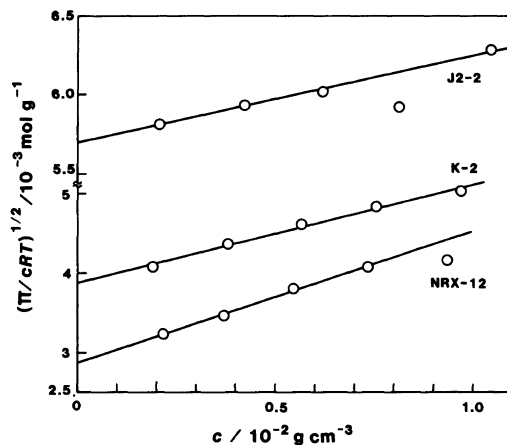

Figure 3. Plots of Kc/R_0 for PHIC fractions in hexane of 25°C.

Figure 4. Osmotic pressure data for PHIC fractions in toluene of 25°C.

plotted against concentration for three fractions. The results are also listed in Table I. It can be seen that the ratio $\bar{M}_w/\bar{M}_n$ is 1.02 for fraction K-2 and 1.09 for fraction NRX-12.

The elution volume V_e at the maximum of a GPC chromatogram was estimated for each of the nine samples whose $\bar{M}_w$ had been measured. Figure 5 shows a plot of $\log \bar{M}_w$ vs. V_e,

where all the data points except those for fractions W-70, H-12, and H-14 are seen to follow the indicated straight line. In the same figure are shown GPC curves for fractions W-5, Z-2, L-2, K-2, NRX-12, Z-20, and H-14
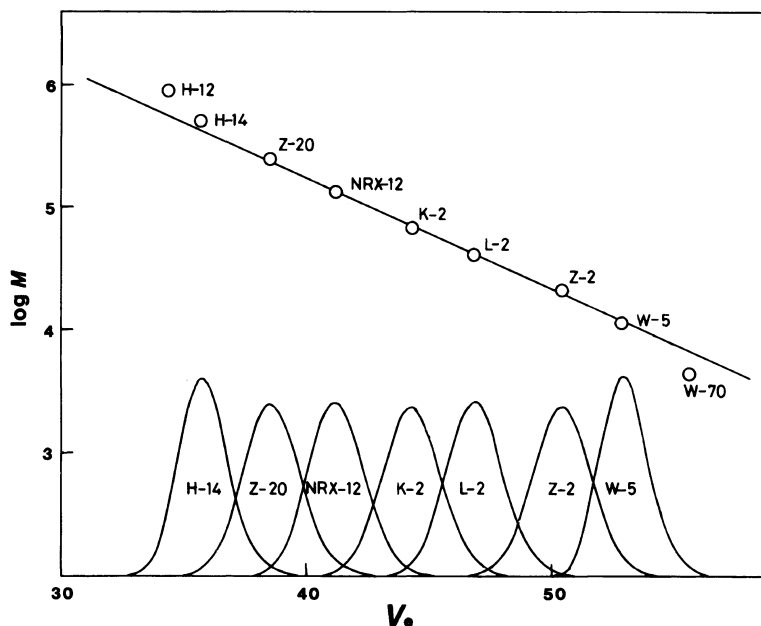
Figure 5. GPC calibration curve for PHIC. $M = \bar{M}_w$

each exhibiting a narrow and almost symmetric peak. Similar GPC curves were obtained for the other fractions. Therefore conversion of elution volume V_e to M was made by using

$$\log M = AV_e + B$$

where A is the slope of the indicated straight line and B was determined to give the best agreement between observed $\bar{M}_w$ and those calculated from the GPC curve.

Figure 6 shows the molecular weight distribution curves computed from the GPC curves for typical fractions using the calibration curve given above. $\bar{M}_w/\bar{M}_n$ and $\bar{M}_z/\bar{M}_w$ values evaluated from such distribution curves are designated as $(\bar{M}_w/\bar{M}_n)^{GPC}$ and $(\bar{M}_z/\bar{M}_w)^{GPC}$, respectively, and are summarized in Table I; in all the cases $(\bar{M}_w/\bar{M}_n)^{GPC} = (\bar{M}_z/\bar{M}_w)^{GPC}$ within experimental error. However, for fractions W-70, H-14, and H-12, this evaluation was impossible because the calibration curve did not cover their GPC curves completely. Whenever comparison can be made, $(\bar{M}_z/\bar{M}_w)^{GPC}$ is close
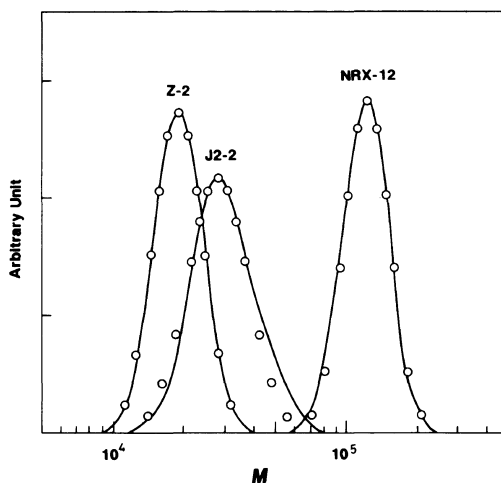

Figure 6. Molecular weight distribution curves for typical PHIC fractions. Solid curves, observed distribution functions; circles, logarithmic normal distributions calculated for the respective $\bar{M}_z/\bar{M}_w$ values.

to $\bar{M}_z/\bar{M}_w$ determined by sedimentation equilibrium, indicating that the GPC and sedimentation data are consistent with each other. The values for $\bar{M}_w/\bar{M}_n$, $\bar{M}_z/\bar{M}_w$, $(\bar{M}_w/\bar{M}_n)^{GPC}$, and $(\bar{M}_z/\bar{M}_w)^{GPC}$ are smaller than

1.05 except for a few sets of data, even for which they do not exceed 1.1. This shows that the molecular weight distributions of the PHIC samples examined are close to monodisperse. Incidentally, it is noted that the observed molecular weight distributions (solid curves) in Figure 6 are well approximated by the distributions (circles) of the logarithmic normal type with the corresponding $\bar{M}_z/\bar{M}_w$ values.

Viscosity Data

Table II gives the values of $[\eta]$ for the PHIC samples studied; the $\bar{M}_v$ values for fractions W-4, W-3, J2-2, and RX-2 determined using the $[\eta]$ *vs.* $\bar{M}_w$ relationship in toluene at 25°C established with the data for the other samples are given in the second column in Table I. It can be seen that $[\eta]$ in toluene decreases significantly with raising temperature. It is also noted that $[\eta]$ is much smaller in DCM than in toluene. This remarkable dependence of $[\eta]$ on solvent condition confirms the pre-

Table II. Intrinsic viscosities of the PHIC samples under various conditions[a]

| | $[\eta]/10^2\,\mathrm{cm}^3\,\mathrm{g}^{-1}$ | | | |
| | Toluene | | | Dichloromethane |
Sample	10°C	25°C	40°C	20°C
W-70	—	0.0767	—	—
W-6	—	0.11	—	—
W-5	—	0.181	—	0.156
W-4	—	0.214	—	—
W-3	—	0.268	—	—
Z-2	0.433	0.418	0.404	0.348
J2-2	0.802	0.778	0.746	—
L-2	1.14	1.10	1.04	0.838
S2-2	1.89	1.80	1.69	—
K-2	2.27	2.15	2.20	1.64
MO-2	3.85	3.59	3.33	—
NRX-12	5.14	4.78	4.40	3.32
RX-2	6.59	5.94	5.25	—
Z-20	9.97	9.10	8.27	5.84
H-14	21.9	18.9	16.9	10.2
H-12	35.5	32.2	28.6	17.6

[a] For all the cases examined, the Huggins viscosity constant k' was within 0.30—0.56.
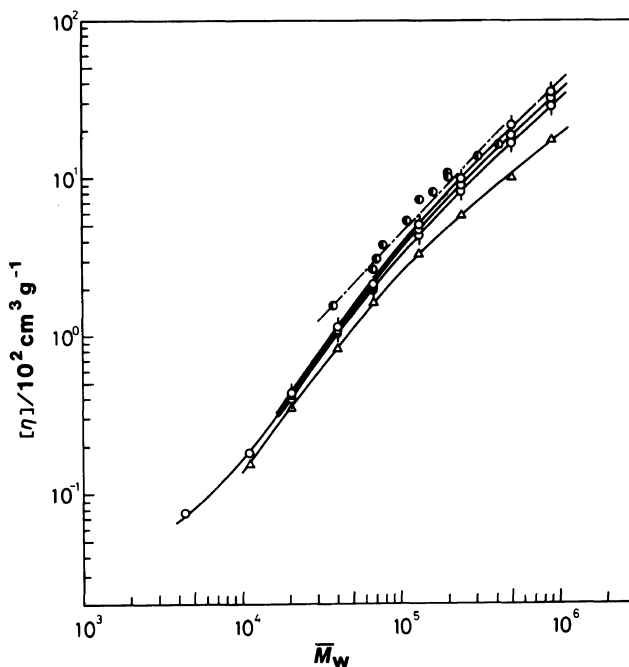
Figure 7. Double logarithmic plots of $[\eta]$ *vs.* $\bar{M}_w$ for PHIC. Solvents: △, DCM of 20°C; ○ (10°C), ○ (25°C), ○ (40°C), toluene; ●, toluene of 25°C by Berger and Tidswell.[8]

vious observations with this polymer by Berger and Tidswell[8] and Conio et al.[7]

The double-logarithmic plots of $[\eta]$ against $\bar{M}_w$ for the two solvents are shown in Figure 7. The data points are fitted by the indicated smooth curves convex upward. In this figure, half-filled circles represent the data of Berger and Tidswell[8] for PHIC in toluene at 25°C. They appear significantly above ours for the same system especially at lower molecular weights. This discrepancy may not be attributed to the polydispersity of these samples because their $\bar{M}_w/\bar{M}_n$ are reported to be smaller than 1.1.[8] It can be shown that our data in toluene at 25°C behave quite similarly to those in 1-chlorobutane at 25°C of Kuwata et al.[6] and those at 40°C are very close to the latter. Incidentally, our $[\eta]$ vs. $\bar{M}_w$ relationship in 1-chlorobutane at 25°C precisely confirms that reported by Kuwata et al.[6]

Analysis of Viscosity Data

Yamakawa and collaborators[9,10] developed theories of hydrodynamic properties of wormlike cylinders and indicated their applicability to real polymers. Recently, Bushin et

al.[14] and Bohdanecky[15] independently proposed a simple procedure based on the Yamakawa theory for determining the wormlike chain parameters: the molar mass M_L per unit contour length, persistence length q, and diameter d of the cylinder. It uses the equation

$$(M^2/[\eta])^{1/3} = I + SM^{1/2} \qquad (5)$$

with

$$I = 1.516 \times 10^{-8} A_0 M_L \quad (g^{1/3}\, cm^{-1}) \qquad (6)$$

$$S = 1.516 \times 10^{-8} B_0 (M_L/2q)^{1/2}$$
$$(g^{1/3}\, cm^{-1}) \qquad (7)$$

where M is the molecular weight of the polymer and A_0 and B_0 are known functions of $d/2q$. It has been shown that for $d/2q \sim 10^{-2}$ eq 5 is accurate in a wide range of $M/(2qM_L)$ from 0.4 to 300. Equations (5) through (7) contain the three wormlike chain parameters, M_L, q, and d. It is impossible to determine all these parameters independently from experimentally obtainable quantities I and S only when a plot of $(M^2/[\eta])^{1/3}$ vs. $M^{1/2}$ is linear.

Figure 8 shows plots of $(\bar{M}_w^2/[\eta])^{1/3}$ vs.
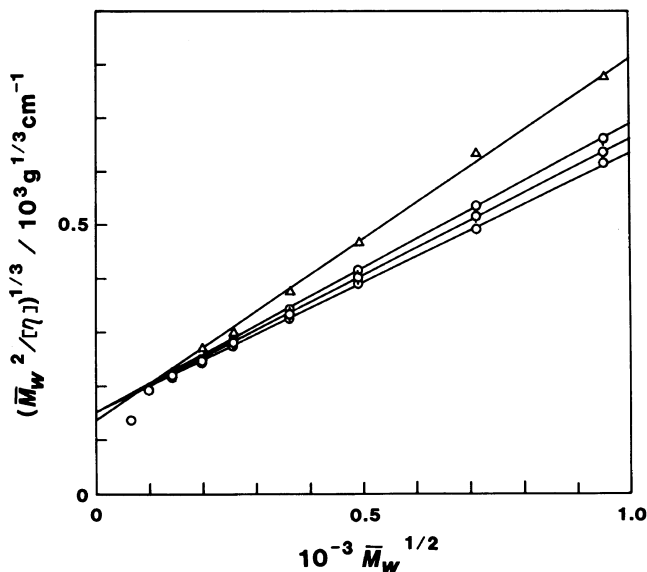
Figure 8. Plots of $(\bar{M}_w^2/[\eta])^{1/3}$ vs. $\bar{M}_w^{1/2}$ for PHIC under the specified solvent conditions. Symbols are the same as those in Figure 7.

goes remarkable solvent and temperature effects; it is nearly the same in hexane and in toluene but significantly smaller in DCM. It can be shown that in toluene q decreases with raising temperature T more rapidly than with T^{-1}.

A similar analysis of the $[\eta]$ data of Berger and Tidswell[8] for PHIC in toluene of 25°C gave considerably lower values for both M_L and q with any reasonable values assumed for d; M_L was found to be at most 550 nm^{-1} more than 20% lower than those shown above in Table III and those estimated by conformational analysis.[16] We take our values as correct, although we have no idea to reconcile this discrepancy. Conio et al.[7] reported q values of 38 and 19 nm for PHIC in toluene of 25°C and in DCM of 20°C, respectively, which were obtained by analyzing their $[\eta]$ data with $\bar{M}_v$ based on the Berger–Tidswell viscosity relationship for toluene solutions; they used a d value of 1.03 nm obtained from v_p of PHIC and with M_L assumed to be 635 nm^{-1}. However, the excellent agreement of their q values with ours is accidental, because the latter viscosity relationship does not agree with ours.

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