Dilute Solution Properties of Poly[*N*-(*n*-octadecyl)maleimide]. 2. Molecular Weight Dependence of the Intrinsic Viscosity in a Few Good Solvents

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ABSTRACT: The intrinsic viscosities of fractions of poly[*N*-(*n*-octadecyl)maleimide] (PMI-18) in the molecular weight range 1.25×10^3 to 1.9×10^5 have been measured at 25 °C in benzene, tetrahydrofuran, toluene, *o*-dichlorobenzene, and 1-chloronaphthalene. The intrinsic viscosity vs. molecular weight relationship exhibits in all cases two regimes. In the region of oligomers the intrinsic viscosities remain almost constant. In the high molecular weight region the data may be described by the usual Mark–Houwink equation. At low molecular weights the intrinsic viscosities approach a limiting value that is slightly dependent on solvent quality. Stockmayer–Fixman plots for the five solvents are used to determine the unperturbed dimensions, K_Θ, and the characteristic ratio, C_∞. For the highest molecular weights, the plots show a convergent trend, suggesting that the polymer should be treated as a stiff chain rather than as a perturbed random coil. In the oligomer region the plots are strongly curved upward, indicating the importance of thickness and rigidity in the chain. Calculation of molecular parameters such as statistical segment length and cross-sectional diameter of the present polymer–solvent systems has been performed by a procedure developed by Bohdanecký et al. based on the theory of Yamakawa and Fujii for wormlike cylinders. Huggins' constant k' values are considerably higher than those found in many other systems. Their dependencies on molecular weight and also on the solvent quality are shown.

Introduction

In the previous paper[1] (Part 1) on the behavior of poly[*N*-(*n*-octadecyl)maleimide] (PMI-18), a comblike polymer with a semistiff main chain and flexible side chains, we presented data on the synthesis, fractionation by coacervation and GPC analysis, number-average molecular weight and molecular weight distributions. The data, which covered a wide range in molecular weight, when analyzed by distribution functions provided satisfactory correlations among the results experimentally obtained by the two dissimilar methods of fractionation.

For a given pair of solute, composed of long-chain molecules, and solvent at a given temperature the intrinsic viscosity appears to be a unique function of the molecular weight, *M*. This function is generally expressed in the form of a simple power function

$$[\eta] = KM^a \qquad (1)$$

containing two empirical constants, *K* and *a*, which depend not only on the properties of the solute and solvent molecules but also on their interactions.

According to Huggins,[2] for extended, strictly rodlike solute molecules the exponent *a* should have the value 2. For the other extreme, solute molecules so tightly coiled that they can be considered as spherical, with no draining of solvent molecules through them, *a* should be equal to zero; in other words, the intrinsic viscosity should be independent of molecular weight. For molecules that are coiled in a purely random manner this exponent should have a value somewhat lower than unity, at least in the higher molecular weight range. When eq 1 is applied to polymer systems, it is usually taken for granted that the constants *K* and *a* must remain unaltered over a wide range of molecular weights. In fact, for linear polymers of high molecular weight at constant temperature in a particular solvent, the intrinsic viscosity–molecular weight relationship can generally be represented by a unique straight line in the double-logarithmic plot of intrinsic viscosity vs. molecular weight. However, there are a few cases where this simple general rule is not followed; i.e., deviations from linearity in the double-logarithmic plot may take place in the low molecular weight region, which means that either *K* or *a* may vary with *M*. In some of these cases the log–log plot of [η] vs. *M* can be represented roughly by two straight lines intersecting at some intermediate molecular weight.[3-7]

These apparent discrepancies have been explained from a semiquantitative point of view[8,9] in terms of (a) variation of specific thermodynamic interactions of solvent molecules with chain segments and especially with end groups of the polymer chain, (b) variations of conformational characteristics such as the ratio of the unperturbed mean square end-to-end distance of the chain to its molecular weight, which for low molecular weights deviates from its constant limiting value, (c) hydrodynamic properties of short chains, since the contribution of the individual chain hydrodynamic subunits to the intrinsic viscosity is not negligible, and (d) the partial draining effect of the coil.

The region in which such deviations may occur depends on both the polymer and the solvent.

With respect to comblike polymers, no particular attention has been given so far to the viscometric study of fractions in the low molecular weight range, namely, $M = 10^3$–10^4, corresponding to oligomers. According to the current literature and to the best of our knowledge, systematic studies are rather limited on the intrinsic viscosity [η] not only in Θ solvents but also in good solvents of these poly[*N*-(*n*-alkyl)maleimides]. One of the chain characteristics that makes PMI-18 especially attractive for the study of configurational properties is that it possesses a semistiff backbone and very long, flexible *n*-alkyl side chains.

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Table I

Number-Average Molecular Weight M_n, Polydispersity Factor Estimated from GPC Measurements $(M_w/M_n)_{GPC}$, and Intrinsic Viscosities $[\eta]$ (mL/g) and Huggins Constants k' of Poly[*N*-(*n*-octadecyl)maleimide] (PMI-18) Fractions in Five Good Solvents at 25 °C

fraction	$M_n \times 10^{-3}$	$(M_w/M_n)_{GPC}$	benzene		tetrahydrofuran		toluene		*o*-dichlorobenzene		1-chloronaphthalene	
			$[\eta]$	k'	$[\eta]$	k'	$[\eta]$	k'	$[\eta]$	k'	$[\eta]$	k'
F-1	190.0	1.74	28.6	1.7	32.0	0.1						
F-2	140.0	1.41	25.1	0.7	30.0	0.4						
F-3	118.0	1.41	23.4	1.5	24.9	0.5	22.0	0.6				
F-4	91.8	1.28	21.1	1.0	22.3	0.5			22.5	0.9	19.6	1.7
F-5	90.3	1.36	20.5	1.1	20.7	0.7						
F-6	73.6	1.31	15.8	1.5	18.8	0.6	15.8	0.8				
F-7	65.0	1.28	15.2	1.1	17.0	0.5			17.0	1.1	15.0	1.5
F-8	52.1	1.29	13.1	1.9	14.9	0.5	12.5	0.8	14.8	1.0	12.6	1.4
F-9	44.0	1.33	11.6	0.8	12.6	0.5						
F-10	40.0	1.40	9.6	2.9	12.4	0.5	10.0	0.9	11.3	0.7	10.5	1.1
F-11	33.7	1.32	8.8	3.8	11.0	0.4						
F-12	29.7	1.29	8.0	1.3	9.9	0.4	7.9	2.7	9.5	0.9	8.9	0.7
F-13	27.1	1.28	7.5	1.5	9.6	0.2						
F-14	23.0	1.27	6.3	2.5	8.2	0.8	7.0	3.3	8.0	0.8	7.0	0.8
F-15	17.8	1.26	5.6	3.5	6.8	1.3	5.5	5.7	6.9	2.2	5.2	1.8
F-16	13.5	1.25	5.5	2.4	6.4	3.5			6.6	0.7	5.5	5.2
F-17	12.2	1.23	4.6	5.9	6.2	6.1	4.7	3.5			5.2	1.8
F-18	10.0	1.25	4.7	2.2	5.8	4.0	4.7	4.2	6.4	1.3		
F-19	9.0	1.23	4.5	4.3	5.3	0.8			6.8	1.4	4.9	1.7
F-20	7.9	1.32	4.6	1.7	5.0	3.0	4.6	3.0	6.2	1.4		
F-21	5.4	1.21	4.5	1.0	4.8	1.3	4.5	1.1	6.3	1.4	4.6	1.6
F-22	3.7	1.20	4.3	0.6	4.2	1.7	4.5	1.3	6.2	1.5	4.7	2.3
F-23	2.3	1.25	4.7	1.0	4.0	1.5	4.6	1.4	6.0	1.6	4.5	4.4
F-24	1.25	1.27			3.7	4.5					4.3	3.5

In the range of low molecular weights it is to be expected that deviations from simple coil behavior should appear with this polymer, due both to its (partial) chain rigidity and to the importance of its chain thickness. The measurements of intrinsic viscosity of this polymer over a wide range of M down to the oligomer region are, therefore, of theoretical as well as practical significance. In the work described here we study the dilute solution viscometric properties in good solvents of the same PMI-18 fractionated samples prepared, characterized, and examined in the previous study.[1]

The results of our study show that, in fact, the Mark–Houwink representation of log $[\eta]$ vs. log M is far from linear and that two regions can be clearly distinguished, one for the oligomers and another for the higher M's. We analyze here these data by means of current theories that model the macromolecule either as a coil or as a wormlike cylinder. These theories depend on a few (usually two or three) adjustable parameters. It seems natural that such simplified treatment should not be satisfactory for the oligomer region, where a more detailed description taking into account the molecular geometry of the chain should be needed.

For this reason, in a subsequent paper we shall tackle the theoretical problem of giving a detailed hydrodynamic description of the molecular structure of PMI-18. This will allow for the direct calculation of its intrinsic viscosity without model fitting or any particular type of assumptions.

The low molecular weight region is more difficult not only from the theoretical point of view but also experimentally because of the very small values of the intrinsic viscosity that are being determined in some of the fractions of our comblike polymer.

Experimental Section

Samples. Poly[*N*-(*n*-octadecyl)maleimide] (PMI-18) fractions with M_n ranging from 1.25×10^3 to 1.9×10^5 measured by vapor pressure and membrane osmometry have been obtained from previously described fractionation and characterization.[1] Characteristics of the fractions are listed in Table I. The fractions, particularly those below 3.0×10^4, are quite narrow in distribution.

Solvents. Solvents were dried, redistilled, and stored over a suitable desiccant agent and freshly distilled before use. Generous head and tail fractions were discharged.

Viscometric Measurements. Viscosities of dilute polymer solutions were determined with typical Ubbelohde suspended-level dilution viscometers, the temperature being controlled to 25 ± 0.05 °C. Flow times exceeded 170 s. A minimum of three flow-time measurements was made on each solution and a mean deviation no more than ±0.1 s from the mean value of all measurements was required. Results at several concentrations determined in each instance from the weight of the sample and the density of the solvent at the temperature of the measurement were extrapolated in the usual manner to obtain $[\eta]$, i.e., using both the Huggins[10] and the Kraemer[11] equations. Linear least-squares fits of η_{sp}/c and ln $(\eta_{rel})/c$ vs. c data were used to obtain the intrinsic viscosities as a common intercept. Corrections for the effects of shear rate and kinetic energy on intrinsic viscosity were negligible.

Results and Discussion

The results of the intrinsic viscosities determined on dilute solutions of PMI-18 fractions are summarized in Table I, along with the number-average molecular weights. Also in Table I are included the heterogeneity indices determined by GPC.[1] The results are displayed in Figure 1 according to the double-logarithmic plot of the Mark–Houwink equation. As can be seen, the data deviate from the simple linear log $[\eta]$ vs. log M dependence usually found in most polymeric systems. The most striking feature of these plots if that their slope a decreases to a very small value in the region of low molecular weights. The phenomenon is quite general and not peculiar to any particular solvent since it is observed in all the solvents studied here.

This kind of behavior can be described empically by assigning two different sets of values of the Mark–Houwink parameters K and a, one for the high-M region (K_I and a_I) and another for the low-M region (K_{II} and a_{II}). The fitted values of these parameters are given in Table II. The transition to very small values of a observed here in the low-M region (a_{II}) is in agreement with similar observations

Table II

Parameters of the Mark-Houwink Equation, K and a, in the High Molecular Weight (K_{I} and a_{I}) and Oligomer (K_{II} and a_{II}) Regions, Molecular Weight at the Transition Point M_c, Flory Constant K_Θ, Characteristic Ratio C_∞, Characteristic Parameters of Chain Flexibility A_η and B_η, Statistical Segment Length l, and Chain Thickness d[a]

	high molecular weights			low molecular weights						eq 8-10		eq 11
solvent	a_{I}	10^3K_{I}	$10^{-3}M_c$	a_{II}	K_{II}	10^2K_Θ	C_∞	$10^{-3}A_\eta$	B_η	l, Å	d, Å	l, Å
benzene	0.71_4	5.38	11.5	0.007	4.26	2.8	16.6	2.30	8.0	81	11	30
tetrahydrofuran	0.67_4	9.61	12.5	0.202	0.84_2	3.7	20.0	1.35	9.5	73	19	36
toluene	0.70_1	6.04	12.0	0.015	4.03	2.4	15.0	1.90	10.0	70	14	27
o-dichlorobenzene	0.75_4	4.03	18.0	0.061	3.72	2.5	15.4	1.65	8.0	81	16	28
1-chloronaphthalene	0.77_3	2.89	14.5	0.089	2.23	2.7	16.2	2.15	8.5	78	12	29

[a] K_Θ is in units of $\mathrm{mL \cdot mol^{1/2} \cdot g^{-3/2}}$, A_η is in units of $\mathrm{mL^{-1} \cdot mol^{-1} \cdot g^2}$, and B_η is in units of $\mathrm{mL^{-1} \cdot mol^{-1/2} \cdot g^{3/2}}$ if $[\eta]$ is expressed in mL/g and M in g/mol. M_L (molecular weight per unit of contour length) = $141.5 \times 10^{-8}\ \mathrm{cm^{-1} \cdot mol^{-1} \cdot g}$.

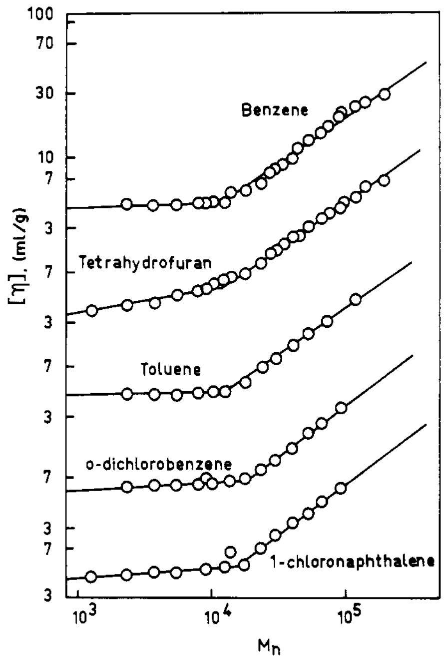

Figure 1. Intrinsic viscosity–number-average molecular weight double-logarithmic plot according to the Mark–Houwink equation for PMI-18 fractions at 25 °C in five good solvents.

made by other authors for different polymers.[3-7] The molecular weight at which the transition between a_{I} and a_{II} occurs in PMI-18 is around $M_n \simeq 1.2 \times 10^4$, which corresponds to a degree of polymerization, n, of about $n \approx 34$.

Deviations from the simple Mark–Houwink equation observed for oligomers[12] have been corrected by writting $[\eta] = B + KM^a$, with B being the value of $[\eta]$ for $M \rightarrow 0$. This type of equation is not adequate to describe our $[\eta]$–M data, because $[\eta]$ reaches an almost constant value at finite M (for $M \approx 1.2 \times 10^4$, approximately).

Before entering into the discussion of the chain characteristics of PMI-18 that can be deduced from the molecular weight variation of $[\eta]$, let us comment very briefly on the absolute values of $[\eta]$ in each of the solvents. The values of $[\eta]$ determined in the two more polar solvents, tetrahydrofuran and *o*-dichlorobenzene, are somewhat higher than the $[\eta]$'s in the other three solvents, benzene, toluene, and 1-chloronaphthalene. This is true both in the low-M and in the high-M regions. Presumably, the more polar tetrahydrofuran and *o*-dichlorobenzene molecules are able to solvate more extensively the polymer (oligomer) chains, producing their higher hydrodynamic volume. The strongest polarity is that of *o*-dichlorobenzene and the $[\eta]$ values of the oligomers are largest in this solvent.

For very low average degrees of polymerization the influence of the solvent on $[\eta]$ can, very likely, be due to changes in the cross section of the chain. The n-alkyl side chains may adopt more expanded configurations in response to increased solvation. For intermediate molecular weights, differences in $[\eta]$ can be due to this same effect and to changes in the stiffness of the backbone. Probably, both effects do not act independently but are coupled together because the flexibility of the backbone may depend of the configuration of its long side chains.

Let us consider now the molecular weight dependence of $[\eta]$, as expressed in the values of K and a. Several factors are recognized to contribute to the exponent a. Among them are the following: (i) chain stiffness; (ii) excluded volume; (iii) partial drainage; and (iv) chain thickness. The value of a that corresponds to a non-draining coil unperturbed by the excluded volume effect is $a = 0.5$. In the low-M region, the values found (a_{II}) are much smaller than $a = 0.5$. Of the four factors just mentioned as contributing to a, the only one that can act to reduce its value below $a = 0.5$ in good solvent systems is factor iv. In the limit of molecules having thickness equal to length (sphere), it is $a = 0$. As we can see, the experimental results of a_{II} are close to this limit. If we take the number of bonds as a measure of chain length, we have that each side chain contains 20 C–C (or C–N) bonds and that the backbone has a number of bonds which is of the same order of magnitude in the oligomer region, since the transition occurs around $n = 34$, corresponding to about 67 C–C bonds.

For the shortest chains, the thickness of the molecule becomes even larger than its length, and the overall molecular shape can be modeled as an equivalent ellipsoid. In such an instance, the anisometry of the molecule is reduced by increasing M and therefore, a decrease in $[\eta]$ followed by a constant value is predicted theoretically to take place when M increases.

In the region of high molecular weights, all the values found (a_{I}) are larger than $a = 0.5$. Factors i, ii, and iii, listed above may be operative in raising a up to the range experimentally observed: $a_{\mathrm{I}} = 0.67$–0.77. At present no theoretical framework is available that could allow for the splitting of a values into separate contributions, one for each of the individual factors cited.

The unperturbed dimensions may be obtained directly from $[\eta]$–M data under Θ temperature conditions or alternatively by using a number of plots based on theoretical or semitheoretical equations developed for this purpose, i.e., applications of the excluded volume equations between the molecular weight and intrinsic viscosities in good solvents.

The relationship proposed by Stockmayer and Fixman,[13] namely

$$[\eta]/M^{1/2} = K_\Theta + 0.51\phi BM^{1/2} \qquad (2)$$

is widely accepted because of its practical form as a basis

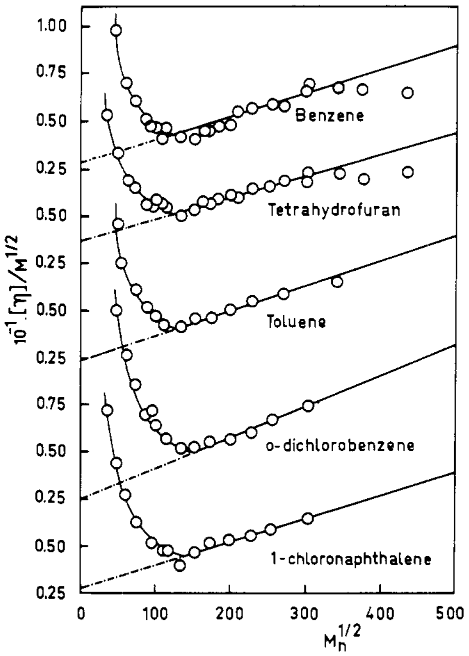

Figure 2. Stockmayer–Fixman plots for PMI-18 fractions at 25 °C in five good solvents.

for treating data covering the usual range of molecular weights encountered in experiments. Here, B is related to the second viral coefficient and ϕ is the Flory universal viscosity constant (theoretical value: $\phi = 2.87 \times 10^{23}$ mol^{-1}, with $[\eta]$ expressed in mL/g).[14] The constant K_Θ is related to the characteristic ratio C_∞ by the expression

$$C_\infty = \langle \bar{R}^2\rangle_0/2nb^2 = (M_0/2b^2)(K_\Theta/\phi)^{2/3} \quad (3)$$

Here, M_0 is the molecular weight of the repeating unit (349 g/mol) and b the length of a linkage, i.e., 1.54 Å for the C–C bond.[15] Actually the length of a C–C bond in the 2,5-dioxopyrrolidone-3,4-diyl residue of crystalline succinimide is 1.505 Å.[16] The difference lies in the limit of uncertainty in its experimental estimation.

In Figure 2 we have represented our viscosity data according to the Stockmayer–Fixman[13] plot. As we can see, eq 2 is not obeyed in the range of molecular weights studied. The lower fractions ($M_n \leq 1.2 \times 10^4$) determine a steep upturn, which produces a minimum in the plot. The occurrence of minima in the Stockmayer–Fixman plots at low molecular weights has been discussed previously in detail by Bohdanecký et al.[9]

In the intermediate range of molecular weight ($1.2 \times 10^4 < M_n < 8.0 \times 10^4$) the data can be fit by a linear variation with positive slope. If we regard the chains having M's in this intermediate range as flexible coils and attribute the positive slope of the plot in this range as due to excluded volume, then we can obtain K_Θ and C_∞ by the extrapolation $M^{1/2} \rightarrow 0$ (straight lines drawn in Figure 2). The values of K_Θ and C_∞ thus obtained are given in Table II. However, chain rigidity may be contributing to the slope in this intermediate range of M so that the results obtained for K_Θ and C_∞ could be inaccurate. An indication that the positive slope in this plot may include the effect of chain stiffness comes from the convergent trend observed in the curves at high molecular weights. The fractions with $M_n \geq 8.0 \times 10^4$ determine an almost horizontal course. This leveling of the slope cannot be accounted for by the theory of flexible coils perturbed by excluded volume but has been predicted by wormlike models of stiff chains.[17] Therefore, it seems more appropriate to interpret these results in terms of such models for chain stiffness.

A macromolecule such as PMI-18 may be represented by means of the theory of Yamakawa and Fujii[17] by a flexible cylinder of diameter d and contour length L. The flexibility of this cylinder is characterized by the length of its statistical segment, l, and the statistics of the wormlike chain. From this theoretical model, l and the unperturbed dimensions are related by

$$l/M_L = \lim_{M\rightarrow\infty} (\langle \bar{R}^2\rangle_0/M) \equiv (\langle \bar{R}^2\rangle_0/M)_\infty \quad (4)$$

Following Maeda, Saito, and Stockmayer,[18] M_L can be approximately estimated, very satisfactorily, by considering the length of the fully extended chain in the all-trans conformation as equivalent to the contour length L. This assumption has been used with success by some authors.[18,19] This parameter is related to L, the molecular weight M, or the molecular weight of the repeating unit M_0, and the degree of polymerization $n = M/M_0$ and may be written as

$$M_L = M/L = nM_0/L \quad (5)$$

When the backbone of a poly(N-maleimide) chain is extended to the all-trans conformation (i.e., threodisyndiotactic) by keeping the valence angle constant, we have the length

$$L = 2nb \sin (\theta/2) \sin (\varphi/2) \quad (6)$$

θ is the valence angle whose value is assumed to be 112°, the value determined from crystallographic data[18] and regarded to be more appropriate for carbon atoms in C–C chains. φ is defined as the angle between two successive $2nb \sin (\theta/2)$ virtual bonds in the threo-disyndiotactic conformation, i.e., by alternating free and fixed carbon–carbon bonds in the 2,5-dioxopyrrolidone-3,4-diyl residue of the backbone. In the numerical calculation φ has been put equal to 150° as estimated by direct measurement on the molecular model. Uncertainties in the measurement of this angle in the molecular model do not introduce large differences in the absolute value of the contour length L, and so in the final results of d.

In order to obtain the length of the statistical segment, l (eq 4), and the thickness or diameter of the chain, d, by means of the Yamakawa–Fujii theory, we treat the experimental $[\eta]$–M data according to the extrapolation ($M \rightarrow \infty$) procedure proposed by Kovář et al.[20] In this method the intrinsic viscosity of the flexible, thick cylinder is written as

$$M^{1/2}/[\eta] = B_\eta + A_\eta/M^{1/2} \quad (7)$$

where B_η and A_η are given by

$$B_\eta = \phi^{-1}(l/M_L)^{-3/2} \quad (8)$$

$$A_\eta = B_\eta(lM_L)^{1/2}A_0 \quad (9)$$

The parameter A_0 is related to the reduced thickness, d/l, by a theoretical function given by Yamakawa and Fujii,[17] which Kovář et al.[20] have approximated by

$$A_0 = -1.23 - 1.97 \ln (d/l) \quad (10)$$

For sufficiently long chains, the dependence of M on $[\eta]$ is well represented by eq 7 and a plot of $M^{1/2}/[\eta]$ vs. $M^{-1/2}$ yields l and d from the intercept and slope of the best straight line through the experimental points. Such a plot is given in Figure 3. The values of A_η and B_η derived by extrapolating to $M \rightarrow \infty$ the data in the high-M region are given in Table II. Also given are the values of l and d, obtained from A_η and B_η by means of eq 8–10.

The end-to-end distance ($\langle \bar{R}^2\rangle_0^{1/2}$) calculated for an unrestricted n-alkane chain of 20 C–C bonds is about 15

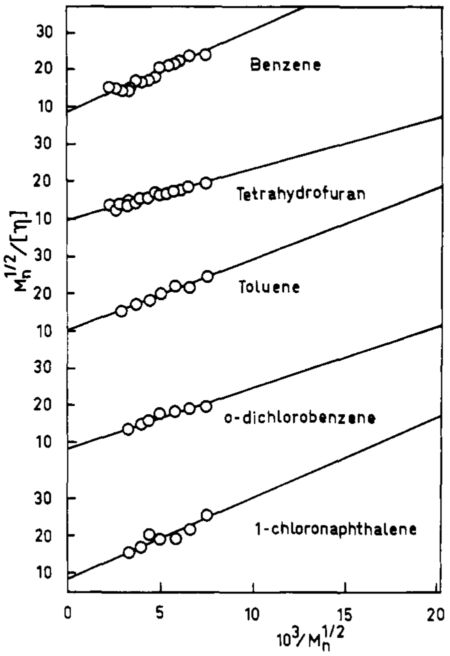

Figure 3. Treatment of viscosity–number-average molecular weight data using eq 7 for the PMI-18 fractions at 25 °C in five good solvents.

Å. Values around this figure are found for the diameter, d, of the PMI-18 molecule.

The length of a statistical segment, l, obtained now by extrapolating to $M \rightarrow \infty$ with the wormlike cylinder model of chain stiffness, can be compared with the unperturbed dimensions, K_Θ, obtained before from the extrapolation $M \rightarrow 0$, valid for flexible coils with excluded volume. From eq 3 and 4 it follows

$$l/M_L = (K_\Theta/\phi)^{2/3} \qquad (11)$$

Using the K_Θ's of Table II in eq 11, we get l values in the range l = 27–36 Å, much lower than the ones obtained from the wormlike model. We have already argued that the K_Θ values obtained from the Stockmayer–Fixman plot may be too low due to chain stiffness. Similarly, the values of l obtained from the wormlike cylinder formulas may be too high because the possible contribution from excluded volume is not considered separately. The l values may thus reflect both stiffness and excluded volume, and the real length of the statistical segment may be somewhat lower than the l's of Table II.

We could think of avoiding the influence of excluded volume by using data in the low-M region to calculate l. However, in that region, the simple extrapolation procedure of eq 7 ceases to be valid and, instead, the equation of Yamakawa and Fujii,[17] corresponding to the rod limiting behavior of the models, should be used. For the short chains belonging to that region, the details of the molecular structure are important in determining the hydrodynamic behavior. Consequently, a direct theoretical calculation of $[\eta]$ making use of the known geometry of the molecule is to be preferred over model fitting. Such a realistic calculation of $[\eta]$ for short chains will be described in the following paper.[21] There, we shall see that the experimental results of $[\eta]$ are well reproduced if we assume a chain rigidity equivalent to $l \simeq 79$ Å. Therefore, l's in the range 70–81 Å, determined here with the unperturbed cylinder model, are the ones to be preferred, since they are consistent with the realistic calculation for short chains.[21]

The values l = 70–81 Å correspond to average degrees of polymerization n = 28–33. That is, the transition from the low-M region ($K_{\rm II}$ and $a_{\rm II}$) to the high-M region ($K_{\rm I}$ and $a_{\rm I}$) occurs when the contour length of the chain becomes larger than one statistical segment.

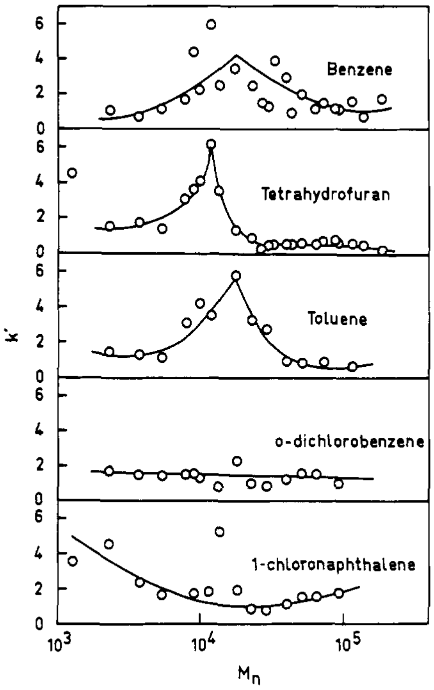

Figure 4. Huggins constant k' against number-average molecular weight, M_n, plotted on a semilogarithmic scale for PMI-18 fractions in five good solvents at 25 °C.

According to Weissberg et al.[22] the viscosity of a dilute solution is affected not only by the hydrodynamic interaction of chains but also by other types of interaction, fundamentally the thermodynamic ones. In addition, we believe that some of the typical features presented in conventional linear flexible macromolecules[23] may be quite different from those fulfilled by macromolecules with a semistiff backbone and flexible n-alkyl side chains.

Thus the value of the Huggins' constant k' can be used as an index to describe polymer–solvent and polymer–polymer interactions. Table I records the Huggins's constant k' determined for the PMI-18 fractions in the five solvents studied. They are considerably higher than would be expected, lying outside the limit established for conventional linear polymers, even when they possess effects[23] due to branching, molecular weight distribution, aggregation, aging,[24] chain entanglement,[25] etc.

The values have been plotted on Figure 4 as a function of the number-average molecular weight, M_n. It can be easily seen from this figure that the values of k' for the fractions in each solvent are rather scattered. A similar type of scattering has been observed with other families of polymers.[26,27]

They show that the k' values for PMI-18 fractions are very much greater than those found with many other conventional vinylic or acrylic polymers in dilute solution. For flexible, linear, nonpolar or not very polar polymers the value of k' usually lies between 0.3 and 0.4 in good solvents.[28] Values higher than 0.5 generally may indicate in some cases aggregation of polymer in solution.[28-30]

The interaction of the side chains, in many respects similar to the short-range forces exerted by the hydrogen bond in polypeptides, has been used to explain not only the crystallization of the long n-alkyl side chains from the melt state but also the gelation from very dilute or semidilute solutions in n-alkyl groups containing solvents.[31] This ability of intramolecular interaction between n-alkyl side chains may also account for the aggregation in dilute solution of solvents which do not include n-alkyl groups in their chemical structures and so for the high values found in the Huggins constant.

On the other hand, comblike polymers such as the PMI-18 considered here have some properties characteristic of linear polymers, some others of branched ones, and still others intermediate between those of branched and linear polymers. From this point of view and for some properties PMI-18 may be considered as a typical branched polymer. This fact can also explain the high values for the Huggins constant we have found. In fact, Simha[32,33] was also the first to point out that the value of the Huggins constant k' depends on the shape of the macromolecule. It ought to be increased by the presence of branching. Moreover, some experimental results have confirmed this prediction.[28]

From the present results, it is obvious that both aggregation and branching and some other physicochemical phenomena can be operative to raise the Huggins constant in dilute solution of comblike polymers.

In conclusion, we summarize the properties of the PMI-18 chain, as revealed by the analysis of the viscometric results, in the following way. The cross-sectional diameter (11–19 Å) and statistical segment length (70–81 Å) correspond to a thick and somewhat stiff chain. The intrinsic viscosity depends only slightly on molecular weight for chains shorter than one statistical segment. The *conformation of the chain* (backbone plus long side chains) is somewhat solvent dependent, its hydrodynamic volume being larger in more polar solvents. However, the transition from the low to the high molecular weight regimes is solvent independent. The long *n*-alkyl side chains seem to favor aggregation in dilute solution. More details about the conformation of this comblike polymer will be discussed in terms of the realistic hydrodynamic calculations described in the succeeding paper.[21]

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