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Dilute Solution Properties of Poly[*N*-(*n*-octadecyl)maleimide]. 4. Cloud Points, Θ Solvents, and Molecular Weight Dependence of Intrinsic Viscosity in *n*-Alkyl Alcohols as Θ Solvents

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ABSTRACT: Cloud point curves of poly[*N*-(*n*-octadecyl)maleimide] (PMI-18) in a homologous series of *n*-alkyl alcohols have been studied to determine Θ temperatures and thermodynamic interaction parameters. The solvents used are 1-butanol (Θ = 393.7 K), 1-hexanol (Θ = 352.1 K), 1-octanol (Θ = 326.8 K), and 1-decanol (Θ = 312.5 K). The intrinsic viscosity vs. molecular weight relationships in 1-hexanol, 1-octanol, and 1-decanol at their respective Θ temperatures have been determined (with 1-butanol, Θ is higher than the normal boiling point and $[\eta]_\Theta$ could not be determined). The $[\eta]$–M relationships present two regimes. In the region of oligomers, $[\eta]$ remains independent of molecular weight. In the high molecular weight region, the data follow a Mark–Houwink equation $[\eta] = K_\Theta M^{1/2}$, typical of unperturbed random coils. The characteristic ratio, C_∞, and the temperature coefficient of unperturbed dimensions, $\mathrm{d}\ln\langle R^2\rangle_0/\mathrm{d}T$, are obtained from K_Θ. The intrinsic viscosity is calculated theoretically by using a realistic hydrodynamic scheme previously developed for the comblike structure of PMI-18. Comparison between these theoretical $[\eta]$'s and experiment suggests that the conformation of the lateral *n*-octadecyl chains of PMI-18 is strongly solvent-temperature dependent. At the Θ temperatures of 1-decanol and 1-octanol the PMI-18 chains have a considerably lower hydrodynamic volume than at the Θ temperature of 1-hexanol.

Introduction

The preceding papers in this series deal with the fractionation[1] and the dilute solution properties[2] of poly[*N*-(*n*-octadecyl)maleimide] (subsequently referred to as PMI-18) in a number of thermodynamically good solvents, namely, benzene, tetrahydrofuran, toluene, *o*-dichlorobenzene, and 1-chloronaphthalene, all at 25 °C. The main purpose of the present paper is to determine Θ conditions for this polymer and to study its hydrodynamic behavior under such Θ conditions. Single-solvent media are chosen in the present study in order to obviate any effect arising from possible solvent–solvent interactions in ternary systems.

The theory of Shultz and Flory[3] allows for the determination of the Θ temperature, for a given polymer–solvent system, by studying the phase separation or the cloud point curve for several molecular weight fractions. The theory is known to describe adequately the behavior of flexible and moderately flexible linear polymers. It is of interest to test the same theory for branched structures such as our PMI-18, which is a comblike polymer, with a presumably semistiff backbone and flexible long *n*-alkyl side chains.

In fact, validity for comblike polymers has been tested by Chinai et al.[4-7] for poly(*n*-alkyl methacrylates) by studying Θ temperatures estimated from phase separation and second virial coefficients from osmotic measurements. Thus the values of the osmotic second virial coefficient for poly(*n*-octyl methacrylate)[4] in the ideal solvent 1-butanol (Θ = 16.8 °C determined from phase separation studies) were found to be zero or close to zero for all fractions,

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Table I
Number-Average Molecular Weight (M_n), Polydispersity Factor Estimated from GPC Measurements[2] [$(M_w/M_n)_{GPC}$], Intrinsic Viscosities ([η], mL/g), and Huggins' Constants (k') of Poly[*N*-(*n*-octadecyl)maleimide] (PMI-18) Fractions in Three Solvents at Their Respective Θ Temperatures and at a Common Temperature

			1-decanol (312.5 K)		1-octanol (326.8 K)		1-hexanol (352.1 K)		1-decanol (352.1 K)		1-octanol (352.1 K)	
fraction	$10^{-3}M_\eta$	$(M_w/M_n)_{GPC}$	$[\eta]_\Theta$	k'	$[\eta]_\Theta$	k'	$[\eta]_\Theta$	k'	$[\eta]$	k'	$[\eta]$	k'
1	190.0	1.74					13.8	0.7				
2	140.0	1.41	6.9	12.9								
3	118.0	1.41			7.9	3.8						
4	91.8	1.28										
5	90.3	1.36	5.5	19.2			11.0	0.8				
6	73.6	1.31	4.4	20.0			10.2	0.6				
7	65.0	1.28			7.1	4.5						
8	52.1	1.29					8.4	2.5				
9	44.0	1.33			5.0	5.3						
10	40.0	1.40	3.6	22.2								
11	33.7	1.32					6.8	4.1				
12	29.7	1.29	2.8	27.6	4.3	6.8						
13	27.1	1.28										
14	23.0	1.27										
15	17.8	1.26	2.6	39.8	3.1	7.1	5.5	1.4				
16	13.5	1.25			2.6	9.0						
17	12.2	1.23	2.5	18.0			4.4	3.7	4.0	2.6	4.4	5.0
18	10.0	1.25							4.3	4.1	4.5	3.2
19	9.0	1.23	2.5	11.0	2.8	6.9	4.4	3.1				
20	7.9	1.32	2.8	7.2								
21	5.4	1.21			2.5	6.4	4.5	1.3	4.1	3.6	4.6	6.2
22	3.7	1.20							3.6	1.8	4.3	2.1
23	2.3	1.25	2.5	8.4	2.5	6.7	4.5	3.3				
24	1.25	1.27										

regardless of their molecular weight. This also holds in the cases of poly(*n*-butyl,[5] *n*-hexyl,[6] and *n*-lauryl[7] methacrylates), which represent a wide range of methylene content of the *n*-alkyl side chain.

Apart from the extensive work developed on comb poly(*n*-alkyl methacrylates) by Chinai and co-workers,[4-7] only comparatively few studies have been reported on the dilute solution properties of comblike polymers with long *n*-alkyl chains under Θ conditions. At present, only very few experimental data have been reported about Θ solvents for comblike polymers.[8,9]

Here, we find suitable Θ solvents for our PMI-18, and, once these are found, we study the intrinsic viscosity of this polymer under Θ conditions.

Fractions of narrow molecular weight are used in this study and the determination of [η] is extended over a wide range of molecular weights in order to determine the [η] vs. M relationship. Previous results have shown[2] that in good solvents, the [η]–M relationship deviates from the Mark–Houwink equation in the range of low molecular weights. It is of interest to extend this study to Θ solvents to see what the differences in behavior are and how they can be interpreted in terms of the structure and conformation of the polymer chain.

In general, scarce data exist in the literature on the dilute solution behavior of low molecular weight fractions of polymers. We cover with our data the molecular weight range from $M_n = 2 \times 10^5$ down to $M_n = 10^3$. In the case of the PMI-18 comblike polymer, this means that our results go from long-chain high polymers down to short oligomers in which the thickness of the chain is comparable to its length. Two regions of behavior are encompassed by such a wide range of molecular weights, as is shown by the results.

As Θ solvents we have chosen long-chain aliphatic *n*-alkyl alcohols, namely, 1-butanol, 1-hexanol, 1-octanol, and 1-decanol, in consideration of their structural analogy with the side chains of the polymer. By using a homologous series it is possible to study the influence of increasing number of methylene groups in the solvent molecular chain. Since the influence may be different for members of the series having odd and even numbers of methylene groups, we have selected only the even members of the series. According to Nakajima et al.,[10] when homologous series of solvents are used, an additional conformational difference between contiguous odd and even members in the series may distort appreciably the interaction between polymer and solvent.

The use of homologous series of Θ solvents has been proposed as a convenient way of determining the temperature coefficient of the unperturbed dimensions, $\mathrm{d} \ln \langle R^2 \rangle_0/\mathrm{d}T$. By using solvents having the same chemical structure it is supposed that any possible influence of specific solvent effects on $\langle R^2 \rangle_0$ may remain constant on going from one solvent to another. This has been confirmed in the case of polystyrene by Orofino and Ciferri.[11] Here, we use the homologous series of aliphatic alcohols to determine $\mathrm{d} \ln \langle R^2 \rangle_0/\mathrm{d}T$ for PMI-18 and we study the importance of the comb structure in determining the change in dimensions with temperature.

Experimental Part

Materials. The preparation, fractionation, and characteristics of the 24 fractions of PMI-18 used, covering the number-average molecular weight range 1.25×10^3 to 1.90×10^5, were reported in two of the preceding papers of the series.[1,2] The number-average molecular weight and the polydispersity estimated from GPC of the fractions are shown in the second and third column in Table I, respectively.

1-Butanol (Carlo Erba, S.p.A.), 1-hexanol, 1-octanol, and 1-decanol (Merck, A. G.) were used as Θ solvents. They were purified and dried by standard and specific methods[12] in some of the cases and subjected to fractional distillation in an atmosphere of dry nitrogen at least 2 times before use. Generous head and tail fractions were discarded, only the middle cut being collected. The purity estimated by GLC was in all cases higher than 99.9%. Some physical constants such as density at 25 °C, index of refraction, boiling point, etc. agree with values given in the literature[13-15] for these compounds.

Cloud Point Curves. Exploratory tests done over a homologous series of *n*-alkyl alcohol solvents furnished only five that seemed to be Θ solvents within the range normally available for

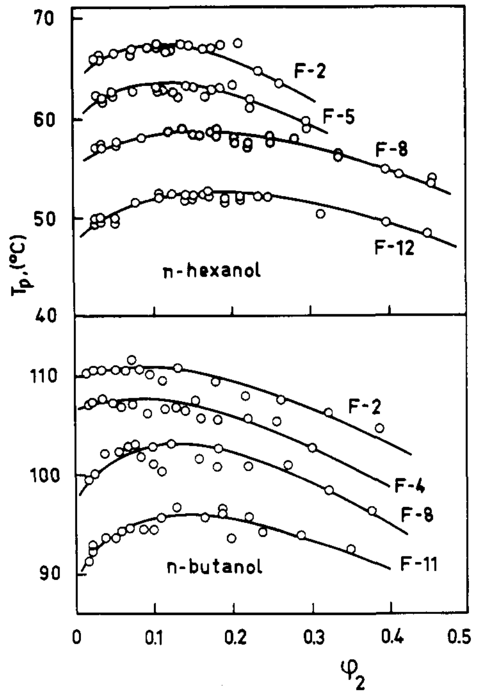

Figure 1. Cloud point curves for poly[*N*-(*n*-octadecyl)maleimide] fractions with *n*-alkyl alcohols in the region of high molecular weights. φ_2 represents the weight fraction of the *n*-alkyl alcohol.

this type of experiment, namely, from room temperature to about 100 °C.

Of these solvents, 1-dodecanol and higher homologues behaved anomalously during further precise phase separation experiments in the sense that gelation took place upon slow cooling of the solutions to room temperature. Keeping in mind the behavior observed in the $[\eta]$–M relationships in good solvents,[2] we studied the phase diagrams in the high and low molecular weight ranges separately. The phase diagrams were determined as follows: A weighed quantity of PMI-18 fraction in an amount of solvent to yield a concentration in the range 10–20% was heated in a small stoppered Pyrex test tube immersed in a water bath until the fraction completely dissolved. Then while the solution was continually stirred, the temperature was slowly lowered at a rate about 0.2–0.6 °C/min until turbidity appeared. At this point, the temperature was recorded by means of a Hewlett-Packard 2804 A quartz thermometer. Measurements of T_p were made in triplicate, and antioxidant (phenyl-2-naphthylamine) was incorporated in all solvents (~0.2% (w/v)). Values of T_p are average ones. Measured amounts of solvent were added to give the next concentration, the separated phase was redissolved by rewarming, and the new precipitation temperature for the dilute solution was determined by the same procedure. The T_p values determined under this thermal history were in agreement within the experimental error with the temperatures at which the turbidity disappears upon rewarming.

A few cloud point curves were determined for the low molecular weight fractions F-16, F-18, F-20, and F-22 in 1-decanol. In this case, hysteresis was found; the temperatures at which turbidity appears on cooling or disappears on rewarming are different, although both reproducible.

Intrinsic Viscosity. Intrinsic viscosities were determined as before,[2] making appropriate corrections for the thermal expansion of the *n*-alkyl alcohol[15] and unfractionated poly[*N*-(*n*-octadecyl)maleimide].[16] With 1-butanol, Θ is much higher than its boiling point. Hence intrinsic viscosities for this solvent at the Θ point cannot be determined.

Intrinsic viscosities of the chosen fractions of PMI-18 at each of the Θ temperatures were measured with an Ubbelohde capillary viscometer of the suspended-level dilution type. Flow times in each case exceed 170 s. Some other experimental conditions have been given elsewhere.[2] 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. Kinetic energy correction was found to be negligible.

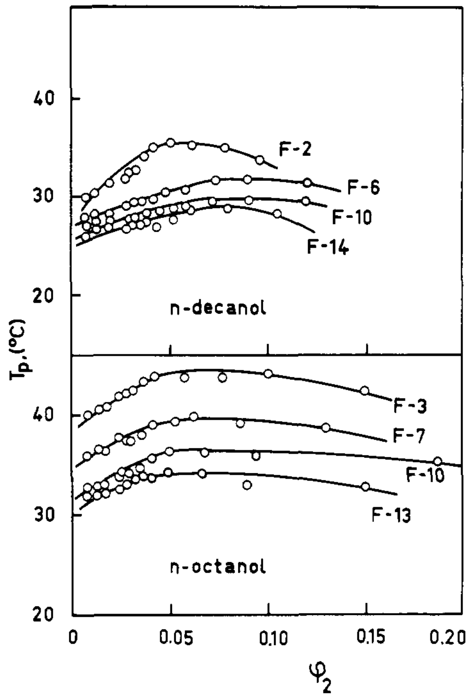

Figure 2. Cloud point curves for poly [*N*-(*n*-octadecyl)maleimide] fractions with *n*-alkyl alcohols in the region of high molecular weights. φ_2 represents the weight fraction of the *n*-alkyl alcohol.

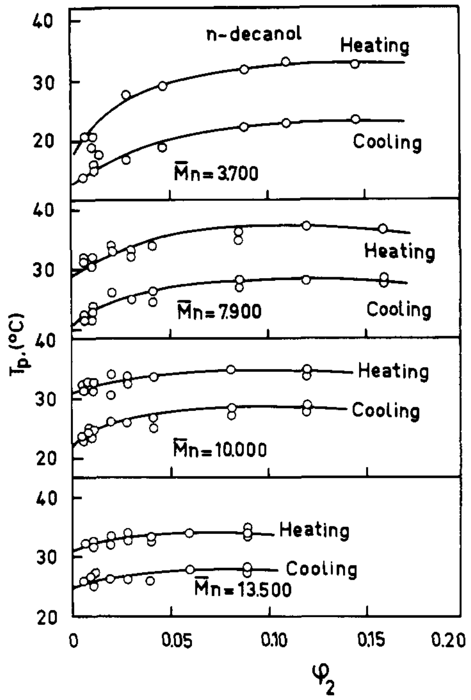

Figure 3. Cloud point curves for poly[*N*-(*n*-octadecyl)maleimide] fractions with 1-decanol in the region of low molecular weights. φ_2 represents the weight fraction of the 1-decanol.

Results and Discussion

Cloud Point Curves. The results obtained for the phase separation temperatures, T_p, are plotted as cloud point curves, namely, T_p vs. the weight fraction of polymer, φ_2, in Figures 1–3. Figures 1 and 2 show the curves for the high molecular weight fractions in 1-decanol, 1-octanol, 1-hexanol, and 1-butanol. Figure 3 shows the behavior for the low molecular weight fractions in 1-decanol. In all three figures we take as the critical temperature, T_c, for each fraction the highest T_p in its respective cloud point curve.

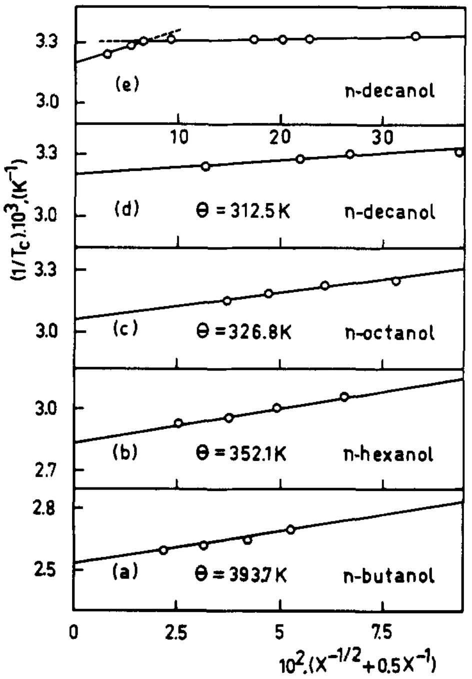

Figure 4. Reciprocal critical precipitation temperature ($1/T_c$) of poly[*N*-(*n*-octadecyl)maleimide] fractions in Θ solvents plotted against $X^{-1/2} + 0.5X^{-1}$.

Table II
Thermodynamic Parameters of Poly[*N*-(*n*-octadecyl)maleimide] (PMI-18)-Solvent Systems Derived from Cloud Point Measurements

solvent	Θ, K	ψ_1	χ_1 (300 K)
1-decanol	312.5	2.286	0.594
1-octanol	326.8	1.177	0.603
1-hexanol	352.1	0.835	0.645
1-butanol	393.7	0.794	0.746

Θ temperatures have been calculated from the T_c's corresponding to the high molecular weight fractions in each of the solvents employed, using Shultz and Flory's expression[3]

$$1/T_c = (1/\Theta)[1 + (1/\psi_1)(1/X^{1/2} + 1/2X)] \quad (1)$$

where X is the ratio of molar volumes of polymer and solvent, i.e., $X = M\bar{v}/V_1$ (M and $\bar{v}$ are molecular weight and partial specific volume of the polymer, respectively, and V_1 is the molar volume of the solvent), and ψ_1 is the entropy of dilution parameter.

The critical temperatures for the high molecular weight fractions are plotted in reciprocal form ($1/T_c$) against $X^{-1/2} + 0.5X^{-1}$ in Figure 4 for 1-butanol, 1-hexanol, 1-octanol, and 1-decanol (parts a–d, respectively). These plots follow a straight line, in agreement with the theory of Flory. From the intercept and slope, the Θ temperature and the entropy parameter ψ_1, respectively, are determined. From both Θ and ψ_1, the free energy or interaction parameter, χ_1, can be evaluated. The values of all these parameters are given in Table II.

The T_c's for the low molecular weight fractions show a different behavior. Neither the T_c's determined on cooling nor the ones determined on heating have any substantial molecular weight dependence. As can be seen in part e of Figure 4, the T_c's for the cooling cycle couple smoothly with those determined with the high molecular weight fractions. However, two different regimes are followed by the T_c–M variation: one for low M, where T_c is almost constant, and another for high M, where T_c varies with M as predicted by the theory of coiled molecules. This type of behavior is also followed by the $[\eta]$–M variation, as we shall see shortly (see also results in good solvents[2]).

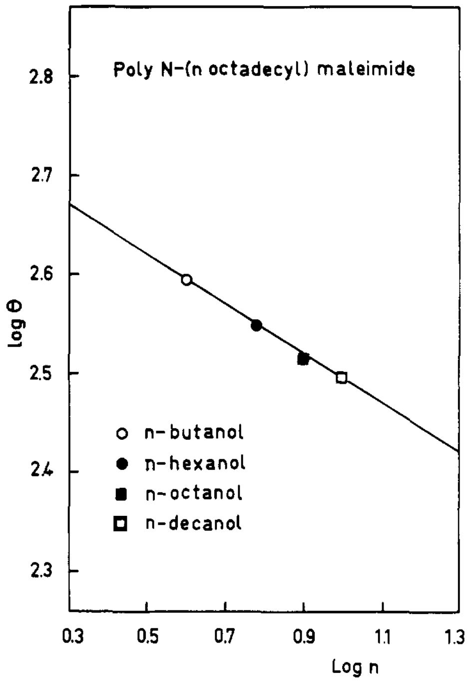

Figure 5. Double-logarithmic plot of the Θ temperature, Θ, as a function of the number of methylene groups, *n* (including the terminal methyl), in the *n*-alkyl alcohols employed as Θ solvents of poly[*N*-(*n*-octadecyl)maleimide].

The hysteresis between the heating and cooling cycles found with the low-*M* fractions, but not observed with the high-*M* ones, can, very likely, be attributed to the formation of gellike structures in the solution. Gels have been detected in comblike polymers of the type PMI-18 with *n*-alkyl alcohols.[8] The interaction between the long *n*-alkyl side chains of different molecules may be responsible for the formation of a network-like structure in the solution. This is more likely with the oligomers because the *n*-alkyl chains are then more dispersed in the solution since the polymer solute molecules are more subdivided into molecules of a lower molecular weight.

Let us now discuss the values of Θ and ψ_1 obtained from the results corresponding to the high molecular weight fractions. From the values in Table II we see that Θ decreases and ψ_1 increases as the number of methylene units in the *n*-alkyl chain of the solvent increases. The same behavior was found by Nakajima et al.[10] in the case of polyethylene and a series of *n*-alkyl alcohols. Also, Fox[17] found that the values of ψ_1 are proportional to the number of carbon atoms of *n*-alkyl derivatives for polyisobutylene and poly(methyl methacrylate).

Figure 5 shows a log–log plot of the Θ temperature vs. the number of carbon atoms, *n*, in the *n*-alkyl alcohols for the four Θ solvents used here with PMI-18. The straight line can be represented by the equation

$$\Theta = 5.61 \times 10^2 n^{-0.26} \quad (2)$$

The solubility of the polymer PMI-18 in this series of *n*-alkyl alcohols as measured by the value of Θ increases with the length of the methylene chain of the solvent. One of the reasons that alcohols are poor solvents of many polymers is the autoassociation by hydrogen bonding of these liquids. The importance of such autoassociation should diminish as the *n*-alkyl chain attached to the OH groups becomes less frequent in the liquid. This effect is quite general for many organic polymers. Another effect, which should be present in the particular case of our comb PMI-18, is the orientational correlation between the *n*-alkyl

Table III
Parameters of the Mark-Houwink Equation (K and a) in the Region of High Molecular Weights (K_I and a_I) and in the Oligomer Region (K_{II} and a_{II}), Molecular Weight at the Intersection Point of Both Regimes (M_c), Flory Constant (K_Θ), and Characteristic Ratio (C_∞) of Poly[*N*-(*n*-octadecyl)maleimide] (PMI-18) in the Three Θ Solvents 1-Decanol, 1-Octanol, and 1-Hexanol at Their Respective Θ Temperatures

		high MW			low MW		
solvent	θ, K	a_I	$10^2K_I = K_\Theta$	$10^{-3}M_c$	a_{II}	K_{II}	C_∞
1-decanol	312.5	0.50	1.83	20	≃0.0	2.5	11.7
1-octanol	326.8	0.50	2.35	11	≃0.0	2.5	13.8
1-hexanol	352.1	0.50	3.70	14	≃0.0	4.5	18.8

chains of polymer and solvent. This type of interaction can lead to a certain ordering of the solution. In some other polymer–solvent systems the stabilization of the solution by formation of order arising from correlation of orientations between methylene sequences of polymer and solvent has been detected.[18,19] Both effects, alcohol autoassociation and orientational correlations between polymer and solvent, should contribute in determining the decrease of the Θ temperature with n observed in the present system. In the case of long n-alkyl comb polymers such as PMI-18 the effect of orientational ordering is especially important among the n-alkyl chains pendant to the backbone.[8]

Intrinsic Viscosity. The intrinsic viscosities measured for the fractions of PMI-18 in 1-hexanol, 1-octanol, and 1-decanol at their respective Θ temperatures are given in Table I. Because of the various experimental measurements made, as reported in the different parts of this series, and the limited amount of samples available, it was in some cases impossible to obtain all data on the same fraction.

The Θ temperature of PMI-18 in 1-butanol is well above the normal boiling point of this liquid and hence $[\eta]_\Theta$ could not be determined in it. Figure 6 shows double-logarithmic plots of intrinsic viscosity against number-average molecular weight for PMI-18 fractions in 1-hexanol, 1-octanol, and 1-decanol at their respective Θ temperatures. The results over the entire range of molecular weights can be conveniently represented by two intersecting straight lines corresponding to two well-differentiated behaviors. In the range of high molecular weights the respective straight lines have been drawn through the experimental points with the theoretical slope of one-half. The slope $^1/_2$, typical of flexible-chain polymers in ideal solvents, shows that the PMI-18 chain behaves as a random coil in these three solvents in the high molecular weight region. This also confirms the adequacy of phase equilibrium studies to establish the Θ conditions for comblike polymers such as PMIs. The $[\eta]$–M relationships fitted to the data in this high molecular weight range are

$$[\eta]_\Theta = 3.70_0 \times 10^{-2}M^{1/2} \text{ (in 1-hexanol at 352.1 K)} \quad (3)$$

$$[\eta]_\Theta = 2.34_8 \times 10^{-2}M^{1/2} \text{ (in 1-octanol at 326.8 K)} \quad (4)$$

$$[\eta]_\Theta = 1.82_5 \times 10^{-2}M^{1/2} \text{ (in 1-decanol at 312.5 K)} \quad (5)$$

However, in the low molecular weight region the values of the exponent a and the constant K in the Mark–Houwink equation are quite different since $[\eta]_\Theta$ remains practically constant, independent of molecular weight, in each of the solvents. In this low molecular weight region, the value of the exponent is almost zero for all solvents studied. Values of a and K_Θ obtained in the three solvents in both the high (a_I and $K_{\Theta,I}$) and low (a_{II} and $K_{\Theta,II}$) molecular weight ranges are listed in Table III. Also listed in this table is the intersection point, M_c, at which the high and low molecular weight behaviors meet.

The Stockmayer–Fixman[20] plot of our data is presented in Figure 7. The unperturbed dimensions (K_Θ) for PMI-18 in each of the Θ solvents are deduced from data corresponding to the high molecular weight region (Table III).

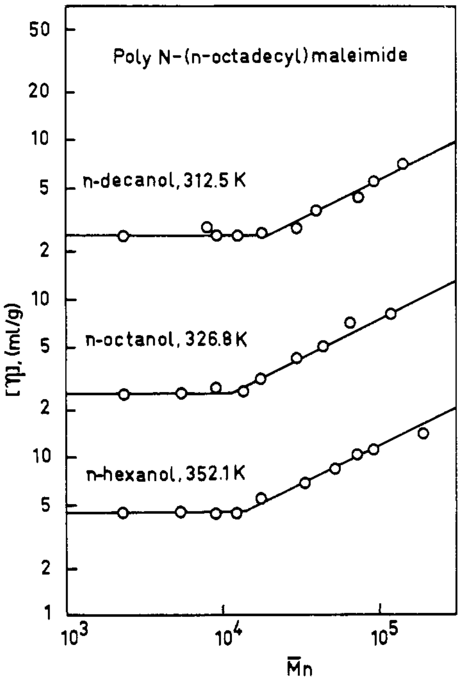

Figure 6. Double-logarithmic plots of the intrinsic viscosity–number-average molecular weight curves for poly[*N*-(*n*-octadecyl)maleimide] fractions in *n*-alkyl alcohols as Θ solvents at their respective Θ temperatures.

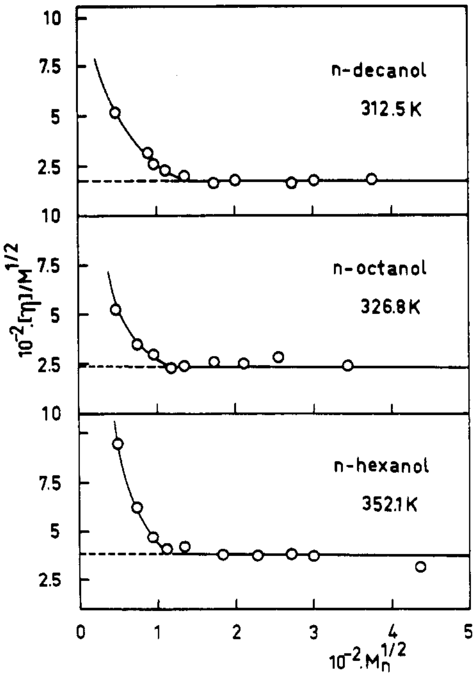

Figure 7. Stockmayer–Fixman plots for poly[*N*-(*n*-octadecyl)maleimide] fractions in three Θ solvents at their respective Θ temperatures.

From K_Θ we calculate the characteristic ratio, C_∞, according to

$$C_\infty = (M_0/2b^2)(K_\Theta/\Phi)^{2/3} \qquad (6)$$

using values of M_0 and b given before.[2] The values thus obtained for C_∞ in the three Θ solvents are shown in the last column of Table III. The value in 1-hexanol (C_∞ = 18.8) lies within the range of C_∞ values previously found for PMI-18 in good solvents (C_∞ = 15.0–20.0). The value in 1-octanol (C_∞ = 13.8) is lower but close to this range, and the value in 1-decanol (C_∞ = 11.7) is clearly below it. We shall discuss later the influence of the solvent on the conformation of PMI-18. For the moment, we note that all values of C_∞ for PMI-18, both in good and in Θ solvents, are larger than the ones for many atactic vinyl polymers, which are in the range C_∞ = 5–10 usually found in the literature.[21] The C_∞ values for PMI-18 are also larger than that for polyacenaphthylene[21,22] (C = 8.6), which has some similarity in structure of the chain backbone, i.e., alternating free and fixed bonds, and also larger than the value for maleic anhydride copolymers (C_∞ = 6.5 for poly(maleic anhydride-*co*-ethyl vinyl ether)).[23] It should also be remarked that the values of C_∞ for PMI-18 in good solvents probably have been underestimated, as they were obtained by extrapolating to $M = 0$ the high molecular weight region of the Stockmayer–Fixman plots in which the effect of stiffness is coupled with excluded volume (see Figure 2 of ref 2).

Two different factors may contribute in determining a high value of C_∞ for our comb PMI-18. One is the nature of the main chain, which is composed of maleimide rings. The other is the long *n*-alkyl side chains. These lateral chains occupy a large volume (thus posing steric hindrances) and, more importantly, they may hinder the backbone internal rotations by establishing orientational correlations between themselves. The stiffening of the polymer chain due to the presence of long *n*-alkyl pendant groups has already been reported for some other polymers.[8]

Since the values of K_Θ obtained here in the three Θ solvents correspond to different temperatures, we can attempt to determine the temperature coefficient of unperturbed dimensions from them. Chiang[24] in the case of polyethylene and Nakajima and Saijyo[25] in the case of polypropylene have found that specific solvent effects can be minimized, if not made negligibly small, by using homologous series of Θ solvents. The aliphatic alcohols employed in the present study fulfill this requisite for finding a reliable value of $\mathrm{d} \ln \langle R^2\rangle_0/\mathrm{d}T$. Using the relation

$$\mathrm{d} \ln \langle R^2\rangle_0/\mathrm{d}T = (2/3)\ \mathrm{d} \ln K_\Theta/\mathrm{d}T \qquad (7)$$

we obtain $\mathrm{d} \ln \langle R^2\rangle_0/\mathrm{d}T$ from the plot of log K_Θ vs. Θ shown in Figure 8. We see that the three K_Θ values fall on a single straight line. The value thus obtained is

$$\mathrm{d} \ln \langle R^2\rangle_0/\mathrm{d}T = 1.2 \times 10^{-2}\ (\mathrm{K}^{-1}) \qquad (8)$$

This is an unusually large value for the temperature coefficient of unperturbed dimensions—about 1 order of magnitude larger than the values usually found[26]—which probably reflects the influence of the solvent as well as that of temperature on the conformation of this comblike polymer. From the two factors mentioned above as giving rise to the large value of C_∞ found in PMI-18, the hindrances posed by the maleimide ring structure are probably much less sensitive to solvent–temperature effects than are the correlations between neighboring alkyl chains.

The main contribution to the large change in unperturbed dimensions observed on going from one Θ solvent to another is very likely the change in the conformation and correlation of the lateral chains of the comb. If this is the case, the effect should be noticeable also in the low molecular weight region (at M_n's below M_c), where the value of $[\eta]$ reflects mainly the cross-sectional characteristics of the polymer molecule. In fact, this is what actually happens, and we can see that the constant $[\eta]$ for $M_n < M_c$ follows a trend parallel fo C_∞; namely, the values in 1-hexanol are higher than in 1-octanol or 1-decanol. Also, the values of $[\eta]$ for oligomers in 1-hexanol are nearly equal to the ones found in good solvents ($[\eta] \simeq 4.5$ mL/g).[2] This constant $[\eta]$ indicates that the cross section of the molecule is very similar in 1-hexanol at Θ = 352.1 K and in good solvents at 298.2 K (and that the unperturbed dimensions obtained from $M_n > M_c$ are very similar in these two cases if one also accepts the extrapolated C_∞ in good solvents obtained previously[2]).

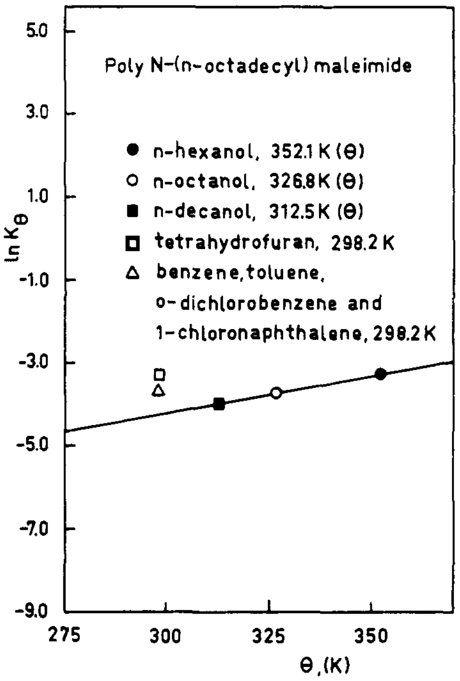

Figure 8. Plot of the logarithm of the Flory constants (ln K_Θ) as a function of their Θ temperatures of a series of *n*-alkyl alcohols employed as Θ solvents and those estimated from good solvents by means of the Stockmayer–Fixman plot.

A different situation holds in 1-octanol and 1-decanol at their respective Θ temperatures, where the constant $[\eta]$ for $M_n < M_c$ drops to a very low value of $[\eta] \simeq 2.5$ mL/g. This low value of $[\eta]$ means that in 1-octanol and 1-decanol, the hydrodynamic volume of the polymer units is shrunk compared to the one they have in 1-hexanol. This is probably due to a different conformation of the *n*-alkyl side chains.

Two variables differentiate the results $[\eta] \simeq 2.5$ mL/g (1-octanol and 1-decanol) and $[\eta] \simeq 4.5$ mL/g (1-hexanol). One is the nature of the solvent, which is a different alcohol in each case, and the other the temperature of the measurements, because Θ conditions are attained at different values of T in each case. To see what influence each variable has, we decided to meausre $[\eta]$ in the three solvents at the same temperature T = 352.1 K, which is the Θ temperature in 1-hexanol. Raising T above the Θ value in 1-octanol and 1-decanol should produce no perturbation of excluded volume in the low molecular weight region ($M_n < M_c$), so that the differences in $[\eta]$ in this region can be attributed solely to short-range interactions and to interactions of the lateral chains between themselves (orientational correlations) and with the solvent (solvation).

The results of $[\eta]$ in 1-octanol and 1-decanol at T = 352.1 K are given in the two last columns of Table I. They are

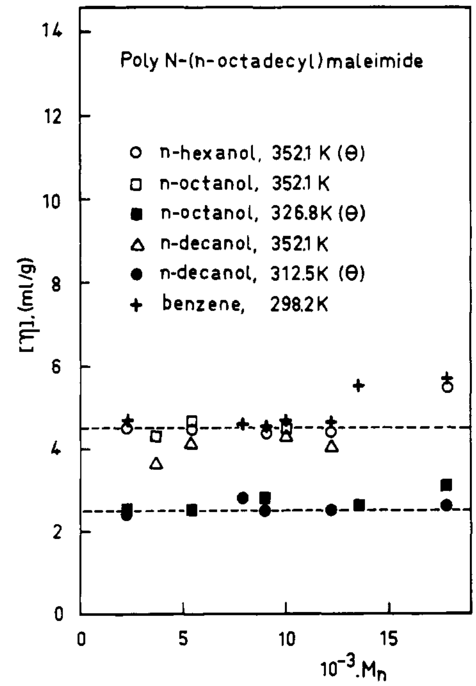

Figure 9. Comparison of [η] vs. number-average molecular weights (M_n) from values determined experimentally in good and Θ solvents at various temperatures in the region of low molecular weights.

compared in Figure 9 with those in 1-hexanol at the same temperature and with the ones determined previously in a typical good solvent, benzene, at 298.2 K, as it has been shown previously.[2] We see that no significant difference in [η] between the three alcohols exists when [η] is determined at the same temperature. No solvent effect seems to exist, but the hydrodynamic volume of the units in the polymer molecule changes strongly with temperature.

In our previous report on the hydrodynamic properties of PMI-18, we described this molecule by means of a realistic molecular model that takes into account the comblike geometry of the chain.[27] In this model the maleimide ring and the methylene units of the *n*-alkyl chains are represented by beads of different frictional resistance, which are placed at positions given by the bond lengths and bond angles appropriate for the chemical structure of the chain. The calculation of [η] with this realistic discrete model depends on one parameter, α, which measures the correlation between repeat units along the main chain. $\alpha = 1$ represents a completely rigid chain in the threo-disyndiotactic configuration, which is predominant in this type of polymer, and decreasing values of α represent more flexible backbones lacking such complete correlation. The lateral *n*-alkyl chains are represented in two possible conformations: one, the "all-trans", and the other, the equilibrium conformation of *n*-alkanes at 25 °C (to be called the "flexible" conformation).

In Figure 10 we present the theoretical curves obtained with this realistic hydrodynamic calculation with the two conformations of the *n*-alkyl side chains (curves a and b) for a value $\alpha = 0.87$. We can see that the experimental results of [η] for the alcohols at $T = 352.1$ K are well represented by these curves and that experiments lie between the two conformations assumed for the lateral chain (curve a, "all trans"; curve b, "flexible").

The values obtained with this realistic calculation extend to $n = 100$ or $M_n = 3.5 \times 10^4$ (here n means degree of polymerization). For sufficiently high M_n's, the details of the structure lose importance, and the molecule may be represented by the wormlike cylinder of Yamakawa and Fujii.[28] The parameters defining this model are l, the statistical segment length, and d, the cross-sectional diameter. l is related to α by the expression[29]

$$l/2 = b/(1 - \alpha) \qquad (9)$$

where b is the length of the repeating unit. For $\alpha = 0.87$, $l = 37$ Å. The value of d can be obtained by fitting the wormlike cylinder to the results at high molecular weights. In Figure 10 we show the theoretical results of the wormlike cylinder for $l = 37$ Å and $d = 18$ Å (curve c), which represent the best fit to the data in 1-hexanol. For low or intermediate M_n's the wormlike model does not describe the results of [η] at all.

The value $d = 18$ Å is within the range of cross-sectional diameters determined previously in good solvents ($d = 11$–19 Å).[2] It corresponds to a somewhat expanded conformation of the *n*-alkyl side chains. The value $l = 37$ Å is much lower than the statistical segment length found previously in good solvents ($l = 70$–81 Å).[2] While in this difference in l values is hidden some contribution from excluded volume—since our parameter α may represent long-range interactions as well as chain stiffness and the wormlike cylinder model does not take the excluded volume effect into account—it is, however, not altogether surprising that the rigidity of the chain may be influenced by the nature of the solvent and be different in 1-hexanol and in good solvents. The influence of the solvent on the stiffness of polymers having long *n*-alkyl side chains has been reported before.[8] Thus, Tsvetkov et al.[30] studying poly(*n*-decyl acrylate) found for the length of the statistical segment $l = 50$ Å in heptane and ethyl acetate and $l = 25$ Å in *n*-butyl alcohol. The solvent influence on the stiffness of the polymer can be understood if the solvent molecules are able to modify the orientational correlation among *n*-alkyl chains lateral to the backbone, which is one of the factors determining rigidity in this type of polymer.

The results of [η] obtained in 1-octanol and 1-decanol at their respective Θ temperatures lie well below the lower theoretical curve of the realistic calculation in which the lateral *n*-alkyl chains are represented as flexible *n*-alkane chains (curve b). A more compact or coiled conformation would be required to approach the experimental values in the two solvents at their Θ temperatures. For the highest molecular weights the wormlike cylinder fitted to the data in 1-decanol would give a diameter of $d \simeq 5$ Å, which corresponds to a very compact conformation of the lateral chains in this solvent (the equilibrium end-to-end distance for *n*-octadecane is around 15 Å). These results tend to indicate that PMI-18 in solution has a variable conformation of its lateral chains. In one case, it appears intermediate between the flexible and the "all-trans" alkane conformation (in alcohols at 352.1 K and in good solvents at 298.2 K), and in the other case, it appears to have a compact conformation, giving a smaller cross-sectional diameter for the macromolecule (in 1-octanol at 326.8 K and in 1-decanol at 312.5 K). When the temperature in these two alcohols is raised to 352.1 K, a transition from the more compact to the more expanded conformation occurs.

The realistic molecular model of PMI-18 used here in this interpretation is satisfactory in that it follows the experimental behavior, at least approximately, in the following features: (a) At low M, [η] remains fairly constant (or it grows slowly) over a range of molecular weights, and the absolute value of [η] is mainly given by the conformation assumed for the lateral chains. (b) At high M, [η] increases more steeply with M and the rate of this variation is gauged mainly by α, the parameter which

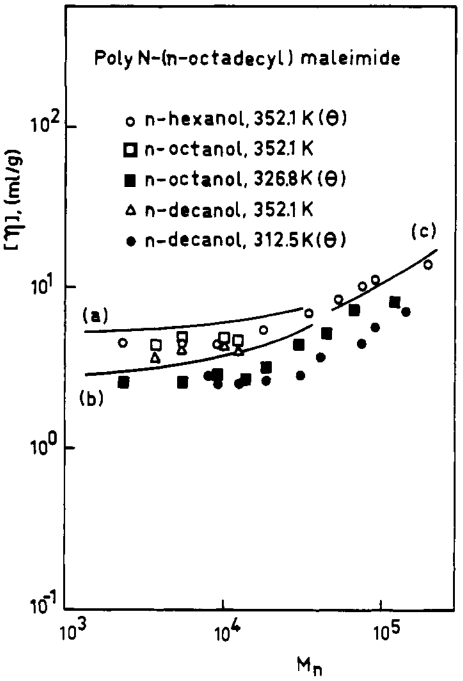

Figure 10. Double-logarithmic plot of the intrinsic viscosities for chains of varying lengths. The lower (b) and upper (a) curves describe the theoretical results obtained for the realistic model with the flexible and "all-trans" side-chain representations, respectively. The line (c) represents the theoretical results of the wormlike cylinder for l = 37 Å and d = 18 Å, which represent the best fit to the data in 1-hexanol.

measures the departure of the backbone from complete rigidity.

However, there is one detail of the experimental data that is not properly described by the theoretical curves. According to the interpretation in terms of the realistic calculation, the lateral chains are more coiled or compact in 1-decanol and 1-octanol at 326.8 and 312.5 K, respectively, than in 1-hexanol at 352.1 K. Hence, the polymer molecule should be thinner in the first two solvent–temperature cases. For short oligomers, the thickness and length of the molecule are comparable. As molecular weight increases, the molecule becomes more elongated and the intrinsic viscosity starts to rise with M. This effect of anisometry should become noticeable at lower molecular weights in the case of the thinner molecule. However, the results in 1-decanol at 312.5 K indicate that here $[\eta]$ remains constant over a wider range of molecular weights than in the case of 1-hexanol at 352.1 K, where the chain should be thicker. The theoretical results do not describe properly the extremely wide range of M over which $[\eta]$ remains constant when the molecule is supposed to be thin. Perhaps a theoretical model that considers a more coiled form as a fixed reference configuration for the backbone would be able to describe the very low values of $[\eta]$ in 1-decanol and 1-octanol without reducing the extension of the lateral chains.

The constant value $[\eta] \simeq 2.5$ mL/g found in 1-octanol and 1-decanol at their respective Θ temperatures is typical of unsolvated spheres and denotes a very low value of the hydrodynamic volume or a very compact conformation. It is difficult to understand how this value can remain constant over a tenfold increase of the degree of polymerization, as is the case with the experimental results in 1-decanol at Θ (Figure 9). Considering this fact alone, it would be reasonable to imagine that the polymer molecule is able to fill the space in a compact globular form, up to a certain degree of polymerization and then, for longer chains, to become a random coil. Perhaps some kind of association between the lateral chains is responsible for this apparent compact conformation.

In summary, we believe that orientation correlations between lateral chains and their interaction with solvent are mainly responsible for the configuration of the backbone. In good solvents the main chain adopts a partially rigid extended configuration and the n-alkyl chains are also expanded. In 1-hexanol, the interactions with solvent change the energetic balance of correlations between lateral chains, and the backbone is compelled to become considerably more coiled. This effect seems to be enhanced in 1-octanol and 1-decanol at their significantly lower Θ temperatures so that even short polymers adopt a very compact form. Simultaneous shrinkage of lateral chains may also occur. Perhaps the presence of intermolecular networks suggested by the hysteresis cycles found in the phase separation experiments could contribute to explain the low experimental values of $[\eta]$ obtained for oligomers in the latter cases.

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Registry No. Poly(N-stearylmaleimide) (homopolymer), 26714-93-2.

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