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Wholly Aromatic Polyamide Hydrazides. 2. Rheological Properties of Poly(4-(terephthaloylamino)benzoic acid hydrazide) in Moderately Concentrated *N*,*N*-Dimethylacetamide Solutions

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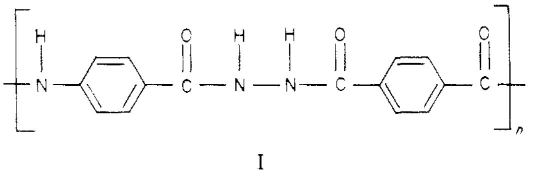
ABSTRACT: The steady state shear rheological properties of a semiflexible polyamide hydrazide, poly(4-(terephthaloylamino)benzoic acid hydrazide) (PTIPH), in moderately concentrated, 7% (w/v), *N*,*N*-dimethylacetamide (DMA) solutions were studied as a function of polymer molecular weight ($\bar{M}_w$), which ranged from 2×10^3 to 2.1×10^4, using the cone-and-plate geometry. The results obtained showed that within the investigated shear rate range, $1.8 \times 10^1 < \dot{\gamma} < 1.8 \times 10^3$ (s^{-1}), first indication of the non-Newtonian flow behavior could be observed for $\bar{M}_w \simeq 9 \times 10^3$ at $\dot{\gamma} > 1 \times 10^3$ s^{-1}. Comparison of the experimental results with the Graessley master curve (for $\bar{M}_w/\bar{M}_n = 2$) showed very good agreement with theory, but the ratio of the experimental and Rouse relaxation time (τ_0/τ_R) was found to be independent of the polymer molecular weight, probably because insufficiently high molecular weights were involved. No resemblance to the so-called "B. effect" earlier observed for the solutions of the same polymer in dimethyl sulfoxide (Me_2SO) could be observed. A plot of the zero-shear viscosity (η_0) vs. the Bueche contact parameter ($c\bar{M}_w$) revealed typical "entangled behavior", focusing further attention upon determination of the PTIPH chain length parameters critical for the onset of such behavior. To accomplish this, four different methods reported earlier in the literature were used. With the exception of the critical number of chain atoms (Z_{wc}) calculated from the critical value of the dimensionless chain length parameter χ_{wc}, proposed earlier by Fox and Allen, all of these methods led to the results which agreed within less than 10% of the average Z_{wc} value which was accepted for a critical number of chain atoms: $Z_{wc} = 253$ (corresponding to a critical entanglement molecular weight ($\bar{M}_{wc}$) of about 7000). Above these critical values, zero-shear viscosity (η_0) was found to be proportional to a polymer chain length parameter raised to the power of 4.0.

Introduction

Solution properties of wholly aromatic polyamide hydrazides, and among those in particular poly(4-(terephthaloylamino)benzoic acid hydrazide), I (PTIPH),[1] have attracted considerable research attention in recent years. The main reason for this originated from the discovery that these semiflexible polymers[2] could be successfully used for production of ultrahigh-modulus fibers when spun from organic solvents such as dimethyl sulfoxide (Me_2SO) or *N*,*N*′-dimethylacetamide (DMA),[3-5] similar to the well-known behavior of a number of rigid-rod aromatic polyamides, for example poly(*p*-benzamide) (PBA)[6-9] and poly(*p*-phenyleneterephthalamide) (PPTA).[10]



I

The molecular mechanism responsible for the development of high-modulus properties in polymer fibers has generally been associated with the ability of their macromolecules to achieve unusually high degrees of chain orientation, i.e., high degrees of long-range molecular order, during the spinning process.[11] Such chain orientation is greatly facilitated by processing polymer solutions which, even in unperturbed, or quiescent, state form a nematic mesophase, or in other words, which are liquid crystalline. In such cases spinning and stretching operations induce further orientation of the liquid crystals uniaxially aligning

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the macromolecular chains along the fiber axis, so that when the solvent is rapidly removed the high degree of orientation remains frozen in the fiber giving it ultrahigh-modulus properties in the stretching direction, which in some cases may become comparable to those of steel wire.[12]

In 1956 Flory[13] published a well-known theoretical examination of the behavior of rigid-rod polymers in solution, focusing attention on the conditions under which they would yield anisotropic phases and predicting a critical concentration point at which such anisotropic phase would be formed. Such behavior was experimentally observed in various systems, including a family of aromatic polyamides which among the others included PBA and PPTA. However, although Morgan[14] reported that PTIPH also formed an anisotropic solution in concentrated H_2SO_4 above the polymer concentration of approximately 10% by weight, such evidence could not be found for this polymer in quiescent solutions of the previously mentioned organic solvents[15,16] at usual spinning concentrations. Consequently, since a high degree of orientation along the fiber axis is responsible for the high modulus, it appeared that PTIPH did not behave like the structurally "similar" PBA and PPTA and that some other explanation was needed for the formation of high-modulus fibers which were obtained when this polymer was spun from Me_2SO or DMA solutions. A possible answer was offered by Ciferri and co-workers, who extensively investigated the PTIPH/Me_2SO system and published their findings in a series of papers.[16-19] They proposed that during the spinning operations the mechanical energy from flow contributes to the free energy for the isotropic–anisotropic phase transition, so that a mesomorphic phase will be formed at a solution concentration which is just below the critical concentration required for such transition in the unperturbed state. This theory thus implied that PTIPH is on the verge of forming a mesophase in Me_2SO solutions in quiescent state, but it is only through the action of the imposed flow field that such a transition can occur.

The theory arose as an explanation for the results of rheological investigation of PTIPH/Me_2SO solution which showed that the τ/γ ratio was very much a time-dependent property,[20] so that while at low shear rates it monotonically increased with concentration, at high shear rates it passed through a maximum at some critical concentration, followed by an abrupt decrease, similar to the well-known behavior of the zero-shear viscosity of the polymers which form a lyotropic mesophase in the quiescent state. The authors called this the "B. effect".

In a later study, Chapoy and la Cour[21] added to this information their observation of typical chain entanglement behavior at very low solution concentrations, showing that the concentration exponent in the viscosity vs. concentration relationship abruptly changed from 0.76 at lower to 3.2 at higher polymer concentrations. The critical solution concentration for this change was reported at about 0.6%, which was significantly below 3% which Ciferri and co-workers had related to the critical phase transition concentration on shearing.[20] This was in good agreement with the observations that for some rodlike polymer solutions, at concentration levels below those required for the onset of liquid crystalline transition, the steady-shear viscosity functions were very similar to those of the flexible chain systems, but the dependence of the zero-shear viscosity on molecular weight was somewhat higher than 3.4 usually found for the latter.[22-24]

Consequently, from this relatively large body of data, the situation at present seems at least explicable for the rheological behavior of PTIPH in Me_2SO. On the other hand, other than one published paper on the small-angle X-ray diffraction measurements,[25] it is not known to this author that anything similar to the already described rheological experiments was reported for PTIPH/DMA systems, although DMA represents another useful solvent for spinning operations, and perhaps more importantly, a usual solvent for PTIPH synthesis via condensation polymerization of *p*-aminobenzhydrazide and terephthaloyl chloride.[3-5,26] It was for this reason that an investigation of the flow behavior of semiconcentrated PTIPH/DMA solutions was undertaken in the present study, in an attempt to compare the results with those previously observed for PTIPH/Me_2SO systems and hopefully shed more light on the rheology of semiflexible macromolecules in solutions.

Experimental Section

Polymer Samples. Poly(4-(terephthaloylamino)benzoic acid hydrazide) samples were prepared by a low-temperature (0–4 °C) condensation polymerization reaction of *p*-aminobenzhydrazide (ABH) and terephthaloyl chloride (TCl) in *N*,*N*-dimethylacetamide (DMA) as solvent.[3,4] Desired polymer molecular weights were obtained by periodic isolation of the reaction products during the course of polymerization which was carefully followed by the recently described viscometric monitoring method.[26] Intrinsic viscosities were determined in DMA at 20 ± 0.5 °C with an Ubbelohde dilution viscometer. In all determinations the concentrations of original solutions ranged from 0.49 to 0.52 g/dL and flow times were measured at five different dilutions. Molecular weights were calculated using the Mark–Houwink relationship which was previously determined for this system:[26] $[\eta] = (5.16 \times 10^{-4})\bar{M}_w^{0.84}$.

Rheological Measurements. Steady state shear viscosities η were determined as a function of shear rate $\dot{\gamma}$ for 7% (w/v) solutions of polymer samples in DMA at 25 °C. In all cases this concentration was kept constant within 5×10^{-3}%. A Ferranti–Shirley cone-and-plate viscometer was used for this purpose. The plate diameter was 8.3 cm, the cone diameter was 3.5 cm, and the cone angle was 0.0057 rad. Shear rates in the range of 18.4 to 1.84×10^3 s^{-1} were applied. Zero-shear viscosities, η_0, were determined by a standard extrapolation procedure of the linear low-shear parts of the η vs. $\dot{\gamma}$ double-logarithmic plots.

Results and Discussion

Rheological Properties of PTIPH Solutions in DMA. Seventeen PTIPH samples of different molecular weights, which ranged from $\bar{M}_w = 2 \times 10^3$ to 2.1×10^4, were used in these investigations. Experimentally determined characteristic properties of these samples are shown in Table I, and the rheological flow curves obtained for their DMA solutions under the conditions of steady shear, as described in the Experimental Section, are shown in Figure 1.

It can be seen from this figure that for the low molecular weight samples, i.e., $\bar{M}_w < 6.2 \times 10^3$, the solutions appeared Newtonian over the entire range of investigated shear rates. Straight, horizontal lines drawn in Figure 1 for these samples represent the averages of the experimentally obtained points. However, as the molecular weight gradually increased, first indications of the non-Newtonian behavior were observed for samples 6 and 7 of Table I (molecular weights of 8.9×10^3 and 9.1×10^3, respectively) above the shear rate value of 1×10^3 s^{-1}. The onset of the non-Newtonian behavior shifted to lower shear rates as polymer molecular weight further increased, so that the viscosity vs. shear rate curves appeared typically non-Newtonian over the entire investigated shear rate range above the $\bar{M}_w$ value of about 1.4×10^4. As can also be seen from Figure 1, these curves did not intersect at any point, even at the highest shear rates applied in this work, indicating that

Table I
Rheological Parameters for Solutions of PTIPH in DMA[a]

sample number	$[\eta]$,[b] dL/g	$\bar{M}_w$[c]	η_0,[d] P	$10^5\tau_0$, s	$10^5\tau_R$, s	$c\bar{M}_w$	$\varphi_2\bar{M}_w$	τ_0/τ_R
1	0.307	2010	0.13		0.009	140.6	116.6	
2	0.389	2660	0.205		0.02	186.4	154.3	
3	0.514	3710	0.29		0.05	259.7	215.2	
4	0.578	4270	0.34		0.05	298.7	247.7	
5	0.735	5680	0.48		0.1	397.6	329.4	
6	1.071	8890	1.08	4.6	0.34	622.4	515.6	13.6
7	1.096	9140	1.29	5.5	0.41	639.7	530.1	13.2
8	1.577	14090	6.885	11.2	3.4	986.6	817.2	3.3
9	1.731	15750	9.55	15.8	5.3	1102.3	913.5	3.0
10	1.826	16780	13.805	20.3	8.1	1174.7	973.2	2.5
11	1.805	16880	14.79	27.5	8.8	1181.6	979	3.1
12	1.954	18190	19.055	33.7	12.2	1273.4	1055	2.8
13	2.018	18900	23.015	42.9	15.3	1323.1	1096.6	2.8
14	2.034	19080	24.775	50	16.6	1335.7	1106.6	3.0
15	2.055	19140	25.825	55.6	17.4	1339.4	1110.1	3.2
16	2.059	19360	27.165	63.2	18.5	1355.2	1122.9	3.4
17	2.224	21450	40.46	103.8	33.6	1501.4	1244.1	3.1

[a] Solution concentration $c = 7\%$ (w/v) in all cases. [b] In DMA at 20 °C. [c] As calculated from $[\eta] = (5.16 \times 10^{-4})[\bar{M}_w{}^{0.84}$, according to ref 26. [d] Zero-shear viscosities determined from the data of Figure 1.

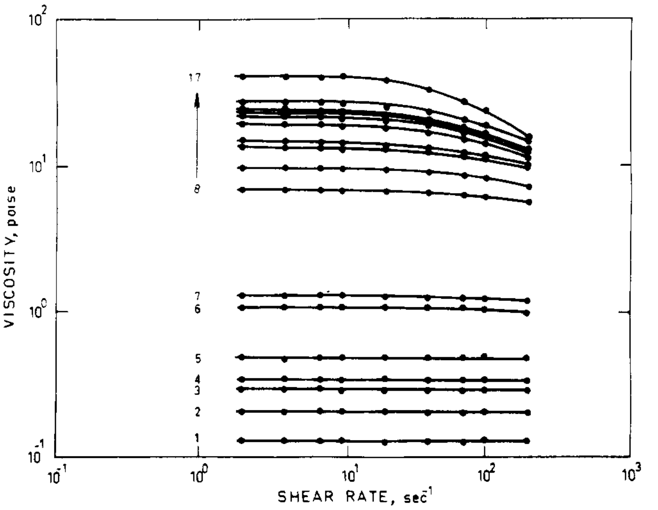

Figure 1. Viscosity vs. shear rate curves for DMA solutions of different molecular weight PTIPH samples at constant solution concentration of 7% (w/v) and constant temperature of 25 °C. Sample numeration is the same as in Table I.

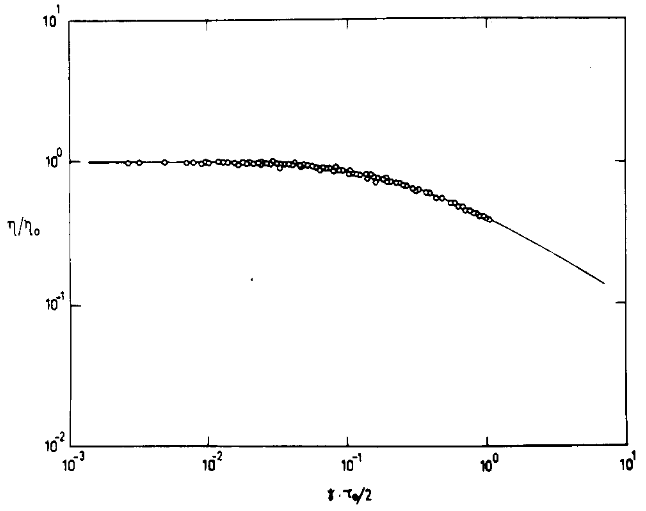

Figure 2. Viscosity data of Figure 1 shifted parallel to the coordinate axes to achieve a best fit with Graessley's theoretical master curve for polymers with $\bar{M}_w/\bar{M}_n = 2$. Molecular weights range from 2000 to 21 500 as shown in Table I. Solid line represents theory.

the investigated PTIPH/DMA solutions were too dilute or that polymer molecular weights were too low to exhibit behavior similar to the "B. effect" observed when Me_2SO was used as a solvent for the same polymer. This should be related to the critical concentrations found for the onset of "B. effect" in the PTIPH/Me_2SO system, which were reported to be about 3% (w/v) and 9% (w/v) for polymer samples having $\bar{M}_w$ of 41 400 and 16 600, respectively.[20]

Experimental rheological data shown in Figure 1 were next used to obtain the viscosity–shear rate master curve (η/η_0 vs. $\dot{\gamma}\tau_0/2$) and to compare it with that theoretically predicted earlier by Graessley.[27] This approach is based upon the often observed similarities in the shapes of η vs. γ flow curves for many different polymer systems, which could be explained by assuming that the processes involved in breaking up the intermolecular chain interactions in constant-shear field are also similar, regardless of the different polymer structures. However, since the shape of the master curve had been shown to depend upon the polymer molecular weight distribution, a theoretical master curve calculated for the polymers with $\bar{M}_w/\bar{M}_n = 2$ was selected for comparison, because it corresponded to the most probable molecular weight distribution usually found for step-growth polymerization products, a good representative of which is the investigated PTIPH. Consequently, according to the usual procedure, rheological flow curves of Figure 1 were shifted parallel to the coordinate axes to achieve the best fit with the theoretical master curve and using the relaxation times τ_0 thus obtained; points of the experimental master curve were determined as shown in Figure 2.

It can be seen from this figure that excellent agreement with the Graessley master curve was observed, and it should be mentioned that this was so not only for the respresentative data used for illustration but also for other solutions of differing $\bar{M}_w$.

Further, in Table I the values obtained[28] for relaxation times are compared with the Rouse relaxation times τ_R, calculated with the following well-known equation:[29,30]

$$\tau_R = \frac{6\eta_0\bar{M}_w}{\pi^2 cRT} \tag{1}$$

where $\bar{M}_w$ is the polymer weight-average molecular weight, c is the concentration of polymer in solution (weight per volume), R is the gas constant, and T is the absolute temperature.

It was reported earlier by Graessley and Segal[28] that for highly entangled polystyrene, τ_0 was related to τ_R through

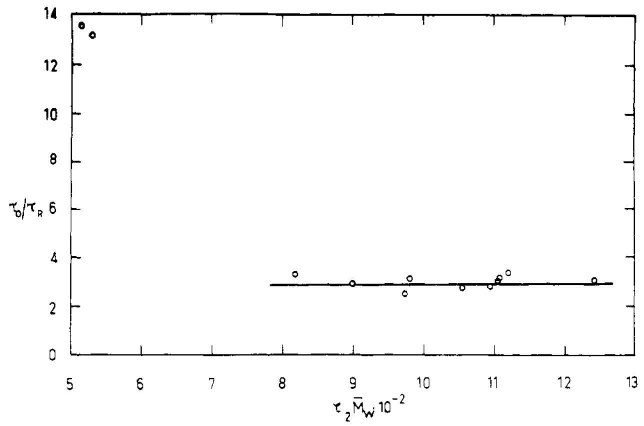

Figure 3. Viscosity relaxaton time constant ratio (τ_0/τ_R) vs. the product of the polymer volume fraction φ_2 and $\bar{M}_w$, from the data listed in Table I.

the correlating variable $\varphi_2\bar{M}_w$, and the equation expressing this relation was proposed to have the following form:

$$\frac{\tau_0}{\tau_R} = \frac{\alpha_1}{1 + \beta_1\varphi_2\bar{M}_w} \qquad (2)$$

where α_1 and β_1 are constants, φ_2 is the volume fraction of polymer in solution, and the product $\varphi_2\bar{M}_w$ is proportional to the entanglement density. Following the same procedure, values of τ_0/τ_R were plotted vs. $\varphi_2\bar{M}_w$ in Figure 3.

As can be seen from this figure, with the exception of the two points corresponding to very low values of $\varphi_2\bar{M}_w$, in spite of considerable scatter of data, the ratio of the relaxation times was almost constant, independent of the polymer molecular weight (since φ_2 was kept constant in all cases), and equal to about 3. A similar situation was reported for the solutions of PPTA in 100% H_2SO_4 by Baird and Ballman,[22] and the authors attributed such behavior to the relatively low molecular weights of their samples ($\bar{M}_w < 40000$) as compared to those previously used by Graessley and Segal ($\bar{M}_w$ as high as 3370000). Having at present no better explanation for the behavior of the PTIPH/DMA system, and since the molecular weights involved here were even lower than those reported for PPTA, it seems that present results support the above mentioned suggestion and that no significant deviation of the relaxation times ratio from constancy should be expected before considerably larger values of $\varphi_2\bar{M}_w$.

First Evidence for Entanglement Network Formation. The concept of entanglement coupling in polymers[31] proposes that in solutions of concentrations which are higher then some critical overlap concentration[32] the onset of entangled behavior corresponds to the point at which there is a transition in the time-dependent properties of polymer solutions as a function of polymer chain length. According to Frisch and Simha,[33] on the other hand, the product of solution concentration c and intrinsic viscosity $[\eta]$ could represent a measure of the degree of coil overlap in a solution, so that the onset of coil overlap corresponds to the situation in which $c[\eta] = 1$, while free draining behavior starts at about $c[\eta] = 100$. Consequently, since for the experiments described in this paper $2 < c[\eta] < 16$, the situation seemed just about right for a more detailed investigation of the onset of entanglement formation, so that the attention was further concentrated on the search for evidence for such behavior.

A good example and at the same time the most characteristic behavior cited as evidence for this is the steady-flow viscosity η, for which a sharp change in the slope of the log η vs. log of suitable measure of the chain length (like, for example, degree of polymerization ($\overline{DP}$), molecular weight ($\bar{M}_w$), number of backbone atoms (Z). etc.) has experimentally been found to occur at some critical chain length in a large number of different polymer–solvent systems.[34-36] Consequently, that critical chain length ($\overline{DP}_c$, $\bar{M}_{wc}$, Z_c, ...) has become customary to consider as the point at which entanglement couplings form, that is as the onset of the entangled behavior.

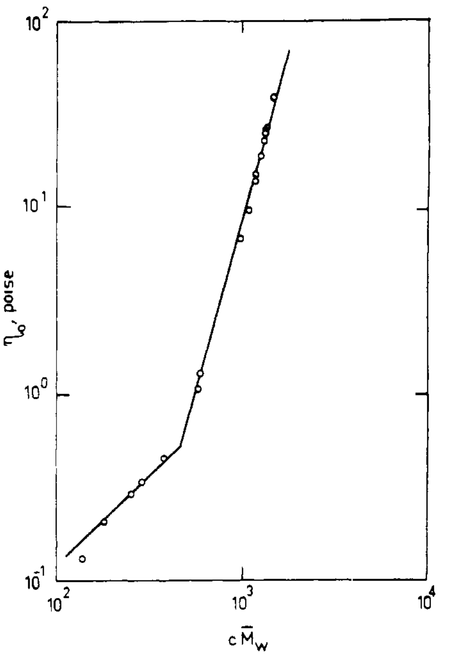

Figure 4. Zero-shear viscosity η_0 vs. the segment contact parameter $c\bar{M}_w$ for PTIPH/DMA solutions at 25 °C, from the data listed in Table I.

However, as Baird and Ballman pointed out,[22] the number of intermolecular contacts, as expressed by the Bueche contact parameter, $c\bar{M}_w$, could also be used as a measure of the chain length for determination of the critical macromolecular dimensions. Accordingly, log η_0 values were plotted vs. $c\bar{M}_w$ as shown in Figure 4.

From this figure it was estimated that the slope of the dependance of η_0 on $c\bar{M}_w$ was equal to unity for the low $c\bar{M}_w$ values while it changed to 3.7 above the $(c\bar{M}_w)_c$ which, in turn, was determined from the intercept of the two linear regions as 490, to yield the critical polymer molecular weight $\bar{M}_{wc}$ of about 7000. Starting from this information, in the following sections experimental data are analyzed in more detail according to the current understanding of the entanglement theory.

Onset of Entangled Behavior in Polymer Solutions. Summarizing it briefly, the concept of entanglement coupling in undiluted polymers or at constant concentration in concentrated polymer solutions predicts that at low molecular weights viscosity increases with polymer molecular weight, M, according to the Rouse theory;[29] i.e., η is approximately proportional to M, as follows:

$$\eta = (b^2\rho N_0/36M_0^2)\zeta M \qquad (3)$$

In this equation b is a characteristic length of the chain, ρ is density, N_0 is Avogadro's number, M_0 is molecular weight of a repeating unit, and ζ is the so-called friction coefficient. The ratio η/M in this molecular weight region depends on molecular weight alone, but through the friction coefficient ζ which asymptotically reaches a certain limiting value at high mulecular weights, so that if it is corrected to that limiting value, ζ_0, the product $\eta(\zeta_0/\zeta)$ becomes exactly proportional to M.[37] On the other hand, at even higher molecular weights, when entanglement effects become important, and where it seems that the reptation or tube model, originally proposed by de Gennes[38] and further developed by Doi and Edwards,[39,40] can successfully explain the viscoelastic behavior, η starts to increase with the 3.4 power of M and ceases to depend on ζ which has already reached its limiting value of ζ_0. The magnitude of M at which log η vs. log M exhibits the brake in slope (from unity to 3.4) represents a characteristic value, M_c, which according to Bueche[41,42] is related to the average molecular weight corresponding to the chain length between entanglement points, M_e, approximately by $M_c \simeq 2M_e$.

In order to investigate if PTIPH chains in DMA solutions behave accordingly and if so to evaluate the critical chain length at the onset of entangled behavior the following mathematical framework was utilized in this work to interpret the experimentally obtained data.

The viscosity of polymer solutions could be considered as the product of two factors, a structure sensitive factor $F(\chi)$, dependent primarily on number of atoms or atomic groups in the chain backbone Z, and a temperature, or density, dependent friction factor per chain atom, $\zeta(\rho)$,[34-36] as follows:

$$\eta = F(\chi)\zeta(\rho) \tag{4}$$

In this equation, the structural factor $F(\chi)$ can be defined by the following equation:

$$F(\chi) = (N_0/6)\chi_c(\chi/\chi_c)^\alpha \tag{5}$$

where, if appropriate weight averages are used, the chain length parameter χ_w could be expressed, according to Fox and Allen,[43] as follows:

$$\chi_w = Z_w(\langle s^2\rangle_0/\bar{M}_w)\varphi_2/v_2 \tag{6}$$

where

$$Z_w = Z_0(\bar{M}_w/M_0) \tag{7}$$

while v_2 is the polymer specific volume, $\langle s^2\rangle_0$ is the unperturbed radius of gyration, φ_2 is the volume fraction of polymer, $\bar{M}_w$ is the weight-average molecular weight of the polymer, M_0 is the molecular weight of its repeating unit, and Z_0 is the number of chain atoms per repeating unit.

Further, in accordance with the experimental evidence, exponent α in eq 5 could be defined as follows:

$$\alpha = 3.4 \qquad \text{for } \chi > \chi_c$$
$$\alpha = 1.0 \qquad \text{for } \chi < \chi_c \tag{8}$$

so that $\chi_{wc} = Z_{wc}\ (\langle s^2\rangle_0/\bar{M}_w)\varphi_2/v_2$ corresponds to the critical chain length at the point of changing slope in the viscosity vs. chain length plots.

Within this general mathematical framework, the values of $\langle s^2\rangle_0/\bar{M}_w$, which represents a measure of the polymer chain expansion per unit molecular weight, could be calculated from the intrinsic viscosity data by using the following equation:

$$[\langle s^2\rangle_0/\bar{M}_w]^{3/2} = [\eta]/\bar{M}_w^{1/2}\Phi \tag{9}$$

where Φ is a constant equal to 39.4×10^{21},[44,45] and where $[\eta]$ is in dL/g.

Parameter Z_w of eq 6 is usually defined as the number of atoms in a polymer chain of molecular weight M. However, this definition becomes quite ambiguous when one deals with polymers containing other than single bonds in the main-chain backbone, like for example p-phenylene rings in the macromolecules such as PTIPH. In such cases the question arises as to how many chain atoms one such group stands for. To answer this one can basically accept one of the following two ways to approach the matter. Either such groups can simply be regarded as extended interatomic bonds and as such not counted at all in calculation of the number of chain atoms, or they can be included in calculation of Z if the actual chain length is considered as a more fundamental property.[35] In this work, the latter of the above two views was accepted as more plausible, and although the caluclations were also performed neglecting the contribution of the p-phenylene groups to Z, only for illustrative purposes, it is believed that the results obtained by taking each $-C_6H_4-$ equivalent to two chain atoms are perhaps the most realistic, since each phenylene ring is then accounted for as a multiple unit giving thus definite physical meaning to its spatial dimensions. Consequently, the Z_w values were calculated using eq 7, for Z_0 of 6, 8, and 10, respectively, and taking $M_0 = 281$, while the corresponding χ_w values were calculated from eq 6, using $\varphi_2 = 5.8 \times 10^{-2}$ and $v_2 = 0.876$ cm^3/g. The value for v_2 was determined pycnometrically for solution concentrations ranging from 0.05 to 0.10 g/cm^3.[46]

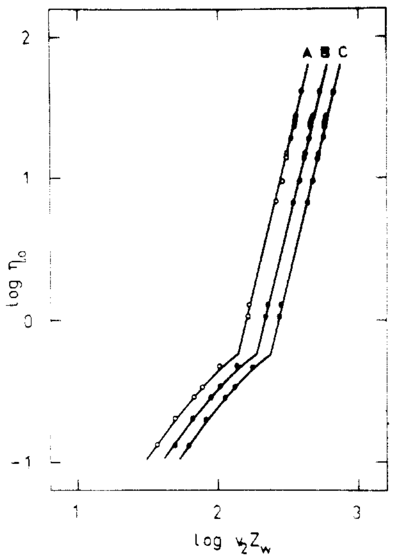

Figure 5. Log η_0 vs. log v_2Z_w for PTIPH/DMA solutions at constant concentration and temperature. c = 7% (w/v); T = 25 °C.

The results obtained in this manner for the investigated PTIPH samples are listed in Table II and plotted as log η_0 vs. log v_2Z_w and log η_0 vs. log $10^{17}\chi_w$ in Figures 5 and 6, respectively.

It can be seen from these figures that curved rather than straight lines were obtained in the low molecular weight region, indicating that the exponent α of eq 5 was some function of chain length, rather than a constant equal to unity as predicted by the Rouse theory.[29] This was not surprising, however, since such behavior had been observed for a number of previously investigated polymer systems,[35] and as already mentioned, it had been ascribed to a molecular weight dependence of $\zeta(\rho)$ at constant temperature. Generally, $\zeta(\rho)$ is understood, on the basis of the free volume theory, as an inherent friction factor exhibited by the chain segments as their resistance to flow which occurs through the corrdinated segmental motion. The magnitude of $\zeta(\rho)$ depends on local inter- and intramolecular forces between the neighboring segments in the flowing liquid, and hence it is dependent upon the length of a segment, asymptotically reaching some constant value which then remains constant with further increase in chain length. Consequently in order to analyze viscosity data as a function of chain length it follows that η_ζ should be examined at constant ζ rather than at constant temperature. Different methods have been worked out to deter-

Table II
Calculation of the Average Chain Dimensions

sample number	log η_0	$(\langle s^2\rangle_0/\bar{M}_w)\cdot 10^{17}$[a]	$Z_0 = 6$[b] Z_w[c]	log v_2Z_w[d]	$10^{17}\chi_w$[e]	log $10^{17}\chi_w$	$Z_0 = 8$[b] Z_w[c]	log v_2Z_w[d]	$10^{17}\chi_w$[e]	log $10^{17}\chi_w$	$Z_0 = 10$[b] Z_w[c]	log v_2Z_w[d]	$10^{17}\chi_w$[d]	log $10^{17}\chi_w$
1	−0.886	3.06	42.9	1.575	8.7	0.939	57.2	1.700	11.6	1.064	71.5	1.797	14.5	1.161
2	−0.688	3.26	56.8	1.697	12.3	1.090	75.7	1.822	16.3	1.212	94.7	1.919	20.4	1.31
3	−0.538	3.51	79.2	1.841	18.4	1.265	105:6	1.966	24.5	1.389	132	2.063	30.7	1.487
4	−0.468	3.62	91.2	1.902	21.9	1.34	121.6	2.027	29.1	1.464	152	2.124	36.4	1.561
5	−0.319	3.87	121.3	2.026	31.1	1.493	161.7	2.151	41.4	1.617	202.1	2.248	51.8	1.714
6	0.033	4.28	189.8	2.221	53.8	1.731	253.1	2.346	71.7	1.855	316.4	2.443	89.7	1.953
7	0.111	4.31	195.2	2.233	55.7	1.746	260.2	2.358	74.2	1.87	325.3	2.455	92.8	1.967
8	0.838	4.75	300.8	2.421	94.6	1.976	401.1	2.546	126.1	2.101	501.4	2.643	157.7	2.198
9	0.980	4.87	336.3	2.469	108.4	2.035	448.4	2.594	144.6	2.16	560.5	2.691	180.7	2.257
10	1.140	4.95	358.3	2.497	117.4	2.07	477.7	2.622	156.6	2.195	597.1	2.719	195.7	2.291
11	1.170	4.95	360.4	2.499	118.1	2.072	480.6	2.624	157.5	2.197	600.7	2.721	196.9	2.294
12	1.280	5.04	388.4	2.532	129.6	2.113	517.9	2.657	172.8	2.237	647.3	2.754	216	2.334
13	1.362	5.08	403.6	2.548	135.7	2.132	538.1	2.673	181	2.258	672.6	2.770	226.2	2.354
14	1.394	5.09	407.4	2.552	137.3	2.138	543.2	2.677	183.1	2.263	679	2.774	228.8	2.359
15	1.412	5.12	408.7	2.554	138.6	2.142	544.9	2.649	184.7	2.266	681.1	2.776	231	2.364
16	1.434	5.11	413.4	2.559	139.9	2.146	551.2	2.684	186.5	2.271	689	2.781	233.1	2.367
17	1.607	5.20	458	2.603	157.7	2.198	610.7	2.728	210.3	2.323	763.3	2.825	262.8	2.42

[a] Calculated from eq 9. [b] Number of backbone chain atoms per repeating unit (*I*) taking for phenylene ring values of 0, 1, 2, respectively. [c] Weight-average number of backbone atoms per chain for a polymer sample with weight-average molecular weight $\bar{M}_w$. ($M_0 = 281$). [d] Calculated using $v_2 = 0.876$ cm³/g experimentally determined as described in the text. [e] Calculated from eq 6.

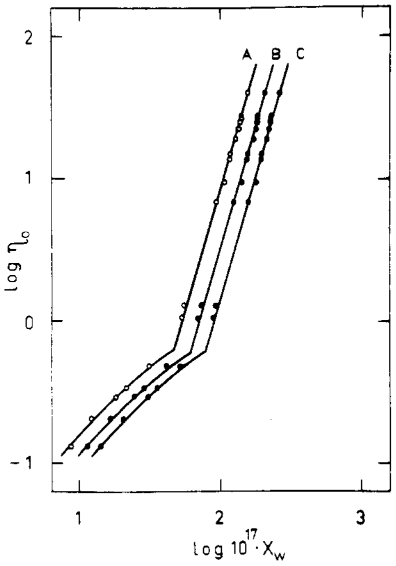

Figure 6. Log η_0 vs. log $10^{17}\chi_w$ for PTIPH/DMA solutions at constant concentration and temperature. $c = 7\%$ (w/v); $T = 25$ °C.

mine that critical value of ζ, after which it becomes independent of chain length, and then to use that value to correct the viscosity data at shorter chain lengths[35,37] to the corresponding viscosities at constant ζ. Such procedures yield log η_0 vs. log χ_w and log η_0 vs. log v_2Z_2 plots, which for many polymer systems were shown[35] to exhibit two regions with slopes equal to 1.0 and 3.4,[37] and from which chain dimensions critical for the onset of entangled behavior can be determined at the points of changing slopes.

Determination of the Critical PTIPH Chain Dimensions. Several different methods for determination of the polymer chain length critical for the onset of entangled behavior have been developed and described in the literature.[34-36] In order to evaluate the experimental data collected in this work the following three of these methods were selected.

First, critical number of chain atoms Z_{wc} and also the dimensionless χ_{wc} parameter were simply determined from the abscissae corresponding to the points of changing slopes in Figures 5 and 6. Their values are listed in columns 3 and 5 of Table III. Additionally, using these χ_{wc} values in eq 6 and accepting for $\langle s^2\rangle_0/\bar{M}_w$ the value of 3.87×10^{-17}, which was calculated for sample 5 (see Table II) laying just below Z_{wc} in Figure 5, another set of Z_{wc} values was obtained as shown in column 6 of Table III.

Table III
Determination of the Critical Chain Dimensions from the Data of Figures 5 and 6

Z_0	log v_2Z_{wc}	Z_{wc}	log $10^{17}\chi_{wc}$	$10^{17}\chi_{wc}$	Z_{wc}[a]
6	2.15	161	1.65	45	176
8	2.28	218	1.79	62	242
10	2.38	274	1.885	77	301

[a] Calculated by eq 6 using $\langle s^2\rangle_0/\bar{M}_w = 3.87 \times 10^{-17}$ and corresponding χ_{wc} values of column 5.

Second, Z_{wc} values were calculated by utilizing the approach of Fox and Allen[47] which is based upon the following equation:

$$3.4 \log Z_w^* - \log \eta^* + \log \eta/Z_w = 2.4 \log Z_{wc} - \log (\zeta^*/\zeta) \quad (10)$$

In this equation * stands for a "reference polymer" of $Z_w^* > Z_{wc}$ and of viscosity η^*, and Z_w for a polymer of $Z_w < Z_{wc}$ and of viscosity η. Since at the critical chain length and above it internal friction coefficient ζ^* becomes constant and independent of Z_w, it follows that at Z_{wc}, $\zeta = \zeta^*$, so that eq 10 reduces to

$$2.4 \log Z_{wc} = 3.4 \log Z_w^* - \log \eta^* + \log \eta - \log Z_w \quad (11)$$

When this is applied to samples 1–5 of Tables I and II, Z_{wc} values shown in Table IV were obtained. They were then used to construct the plots of Z_{wc} vs. log η_0, as shown in Figure 7, which yielded the critical Z_{wc} values as the asymptotes to the cruves at high viscosities.

Third, critical chain length parameters were also obtained from the general viscosity equations of the type originally proposed by Bueche.[11] By substitution of the χ_{wc} of Table III into eq 4 and 5 a set of numerical expressions could be obtained, such as the following one written here for $Z_0 = 10$:

$$\eta_0 = 7.7 \times 10^7(\chi_w/7.7 \times 10^{-16})^\alpha\zeta_0 \quad (12)$$

where

$$\alpha = 1.0 \quad \text{for } \chi_w < 7.7 \times 10^{-16}$$

$$\alpha = 3.4 \quad \text{for } \chi_w > 7.7 \times 10^{-16} \quad (13)$$

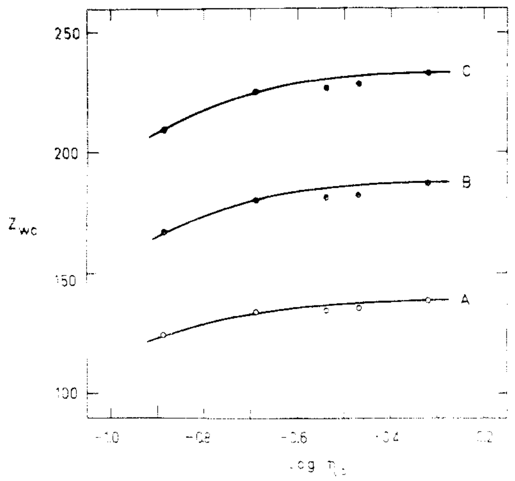

Figure 7. Determination of Z_{wc} values as the ordinates corresponding to the asymptotes in Z_{wc} vs. log η_0 plot.

Table IV
Determination of Z_{wc} Values from Eq 11[a]

sample number	log η_0	Z_0	log Z_w	2.4 log Z_{wc}	Z_{wc}
1	-0.886	6	1.632	5.026	124
		8	1.757	5.336	167
		10	1.854	5.569	209
2	-0.688	6	1.754	5.102	134
		8	1.879	5.412	180
		10	1.976	5.645	225
3	-0.538	6	1.899	5.107	134
		8	2.024	5.417	181
		10	2.121	5.650	226
4	-0.468	6	1.960	5.116	135
		8	2.085	5.426	182
		10	2.182	5.659	228
5	-0.319	6	2.084	5.141	139
		8	2.209	5.451	187
		10	2.306	5.684	233

[a] For the reference polymer, sample 11 of Tables I and II was selected. For that sample $\eta_0{}^* = 13.805$ P, and $Z_w{}^*$ values were 358.3, 480.6, and 600.7, for Z_0 values of 6, 8, and 10, respectively.

For $\alpha = 1.00$ and corresponding η_{0c} of Figure 6 these equations yielded the values for critical friction coefficients of 1.2×10^{-8}, 8.4×10^{-9}, and 6.8×10^{-9} for Z_0 of 6, 8, and 10, respectively, which were then used to correct the low molecular weight viscosity data as shown in Table V and to construct the log $\eta_{0\zeta}$ vs. log $v_2 Z_w$ and also log $\eta_{0\zeta}$ vs. log $10^{17}\chi_w$ plots corrected to constant ζ_0 shown in Figures 8 and 9.

It can be seen from these figures that when such corrections were utilized straight lines were obtained in the low molecular weight region, and also a new set of chain dimensions critical for the onset of entangled behavior was also obtained as listed below: for $Z_0 = 6$, $Z_{wc} = 150$ and $10^{17}\chi_{wc} = 44$; for $Z_0 = 8$ $Z_{wc} = 205$ and $10^{17}\chi_{wc} = 58$; for $Z_0 = 10$, $Z_{wc} = 250$ and $10^{17}\chi_{wc} = 74$.

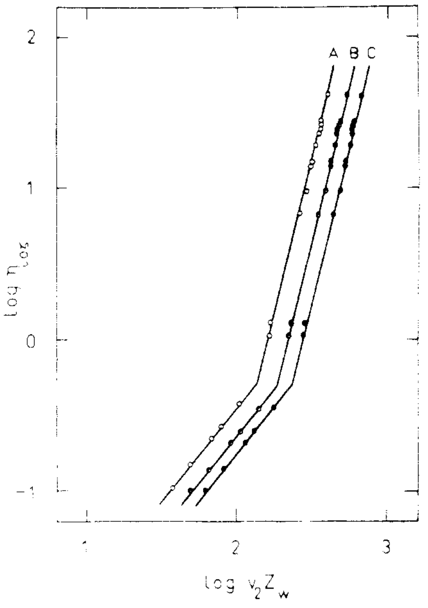

Figure 8. Log $\eta_{0\zeta}$ vs. log $v_2 Z_w$ for PTIPH/DMA solutions at constant concentration and temperature. The viscosity is corrected to constant friction factor ζ. $c = 7\%$ (w/v) $T = 25$ °C.

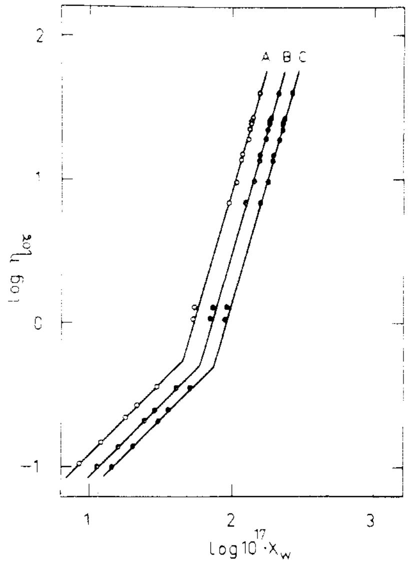

Figure 9. Log $\eta_{0\zeta}$ vs. log $10^{17}\chi_w$ for PTIPH/DMA solutions at constant concentration and temperature. The viscosity is corrected to constant friction factor ζ. χ_w is calculated according to $\chi_w = Z_w(\langle s^2\rangle_0/\bar{M}_w)\varphi_2/v_2$. $c = 7\%$ (w/v); $T = 25$ °C.

However, it can be also seen from Figure 9 that the slopes of the $\eta_{0\zeta}$ vs. $10^{17}\chi_w$ function were just equal to 1.0 and 3.4 in the low and high molecular weight regions, respectively; while, on the other hand, from Figure 8 their values were somewhat higher and equal to 1.2 and 4.0.

Finally, to summarize the results presented in this section all obtained critical PTIPH chain dimensions are listed in Table VI. It follows from this table that different methods led to different critical parameters. Concen-

Table V
Solution Viscosities Corrected to Constant ζ_0 for the Low Molecular Weight Samples of Table I

	$Z_0 = 6$			$Z_0 = 8$			$Z_0 = 10$		
sample number	$10^{17}\chi_w$	η_0, P	log η_0	$10^{17}\chi_w$	η_0, P	log η_0	$10^{17}\chi_w$	η_0, P	log η_0
1	8.7	0.105	-0.979	11.6	0.098	-1.009	14.5	0.099	-1.004
2	12.3	0.148	-0.830	16.3	0.137	-0.863	20.4	0.139	-0.857
3	18.4	0.222	-0.654	24.5	0.206	-0.686	30.7	0.209	-0.680
4	21.9	0.264	-0.578	29.1	0.245	-0.611	36.4	0.248	-0.605
5	31.1	0.375	-0.426	41.4	0.349	-0.457	51.8	0.354	-0.451

Table VI
Summary of the Critical Dimensions of the PTIPH Chains at the Onset of Entangled Behavior

determination method	$Z_0 = 6$	$Z_0 = 8$	$Z_0 = 10$
Critical Number of Chain Atoms, Z_{wc}			
from intercepts in log η_0 vs. log $\upsilon_2 Z_w$ plots of Figure 5	61	218	74
from eq 6	176	242	301
from eq 11 and Figure 7	139	188	233
from intercepts in the corrected log $\eta_{0\zeta}$ vs. log $z_2 Z_w$ plots of Figure 8	150	205	250
average of the values listed above	150.5	205	254
Critical Chain Length Parameters, $10^{17}\chi_{wc}$			
from intercepts in log η_0 vs. log $10^{17}\chi_w$ plots of Figure 6	45	62	77
from intercepts in the corrected log $\eta_{0\zeta}$ vs. log $10^{17}\chi_w$ plots of Figure 9	44	58	74
average of the values listed above	44.5	60	75.5

Table VII
Values for the K and a Constants of the Mark–Houwink Equation As Reported for PTIPH

K, dL/g	a	solvent	temp, °C	ref
1.05×10^{-3}	0.795	Me_2SO	25	16
2.90×10^{-4}	0.91	Me_2SO	25	17
6.15×10^{-5}	1.06	Me_2SO	25	53
5.16×10^{-4}	0.84	DMA	20	26

trating only upon the values for $Z_0 = 10$, for the reasons discussed in the previous section, it seems clear that with the exception of Z_{wc} values, obtained by means of eq 6, all others laid within less than 10% of the average Z_{wc} which equaled 253. When this is accepted for the critical number of PTIPH chain atoms at the onset of entangled behavior of this polymer in DMA solvent, critical degree of polymerization and corresponding polymer molecular weight were calculated by using the following equations:

$$\overline{DP}_{wc} = \bar{Z}_{wc}/Z_0 \tag{14}$$

and

$$\bar{M}_{wc} = \overline{DP}_{wc} M_0 \tag{15}$$

to yield $\overline{DP}_{wc}$ of 25 and $\bar{M}_{wc}$ of 7025. It should be noted at this point that this value of $\bar{M}_{wc}$ agreed very well with that estimated from Figure 4.

***K–a* Relationship.** It has been shown by a number of different authors[48-51] that a distinct relationship exists between the K and a constants of the well-known Mark–Houwink equation which, for a given linear polymer, solvent, and temperature, relates the intrinsic viscosity $[\eta]$ to the polymer molecular weight M, as follows:

$$[\eta] = KM^a \tag{16}$$

This K–a relationship was reported, for many different polymers, to be such that the higher is a, the lower is the value of K, so that these observations eventually led to establishment of a relatively simple form of its analytical expression which can be represented by the following equation:

$$\log K = C - Ba \tag{17}$$

where $C < 0$ and $B > 0$. It was also noted, first by Millich et al.,[50] that for a given polymer this relationship is independent of solvent and temperature (over a relatively wide temperature range), and for a number of rigid rod polymers (in the $0.53 < a < 1.8$ range), constants C and B in eq 17 were determined to have the values of −0.55 and 4.63, respectively, when K is expressed in dL/g.

According to this, and since for PTIPH, four different sets of K and a values were found in the literature, as shown in Table VII, these were plotted as a vs. −log K in Figure 10.

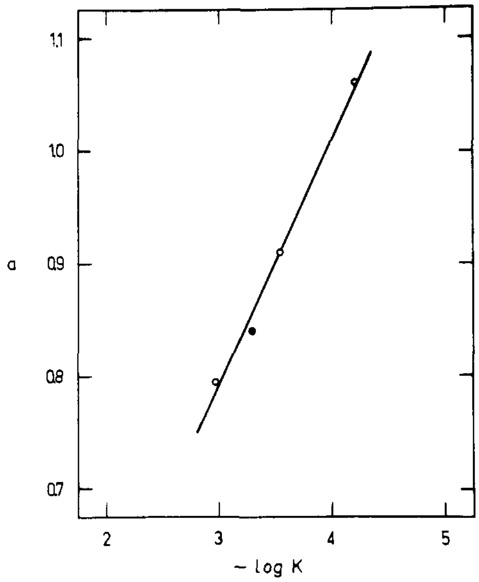

Figure 10. Relationship between the Mark–Houwink constants: a vs. log K plot for PTIPH.

It is clearly seen from this figure that all of the data points remarkably well fitted a straight line, as predicted by eq 17, and from the values obtained for its slope and intercept $C = -0.58$ and $B = 4.53$ were obtained. These were obviously in very good agreement with those earlier generalized for a large family of rigid macromolecules,[50] but in the first place with some particular examples like poly(γ-benzyl L-glutamate) where $C = -0.60$ and $B = 4.81$, polyisoprene where $C = -0.45$ and $B = 4.61$, or poly(ethylene oxide) where $C = -0.65$ and $B = 4.36$.[48]

Conclusions

Experimental results obtained in this work were primarily used to calculate the chain length parameters critical for the onset of entangled behavior in the investigated PTIPH/DMA solutions, and the following conclusions could be drawn from this study. Within the examined polymer molecular weight range ($2 \times 10^3 < \bar{M}_w < 2.1 \times 10^4$) these semiconcentrated (7% (w/v)) solutions did not exhibit the so called "B. effect" behavior earlier reported for Me_2SO solutions of the same polymer.[18-20] This may indicate that the main reason for different behavior of these systems most probably originates from their different structuralization, as it was proposed earlier by Krigbaum and Sasaki[25]—although these same authors also suggested that, on the basis of the intrinsic viscosity data, the polymer molecular conformation might be the same,[25] at least at very high dilutions.

Good agreement of the experimental master curve was observed with that theoretically predicted by Graessley. However, the ratio of the relaxation times τ_0/τ_R seemed independent of the polymer molecular weight, the reason for which may well be due to the relatively low molecular weights investigated.

The PTIPH chain length parameters critical for the onset of entangled behavior ($Z_{wc} = 253$ and $10^{17}\chi_{wc} = 75$) are undoubtedly lower than those typical for freely coiling macromolecules, where Z_{wc} is usually found about 350–650, and $10^{17}\chi_{wc}$ about 300–500,[35] but at the same time they are also significantly higher than those reported for the polymers of pronounced rigidity, like for example PBA[48] or PPTA,[22] for which Z_{wc} were determined as 38 and 30, respectively. When the literature data are reviewed, PTIPH values seem to come closest to those determined for the following polymers: poly(decamethylene adipate), $Z_c = 280$[34] to 320;[35] poly(decamethylene sebacate), $Z_c = 210$[35] to 290;[34] poly(tetrafluoroethylene), $Z_c = 264$;[34] polycarbonate of bisphenol A and ethylene, $Z_c = 251$;[48] polyester of bisphenol A and 1,1,3-trimethyl-3-phenylindan-4′,5-dicarboxylic acid, $Z_c = 203$.[48] Thus, PTIPH falls just in between the two groups of polymers which represent the extremes of the "macromolecular flexibility scale", which is in good agreement with the accepted understanding of the semiflexible nature of its chains.[2] Consequently, it follows that the effect of chain stiffnes of the semiflexible macromolecules on the rheological properties of their moderately concentrated solutions is to promote the onset of intermolecular interactions or entanglements at the intermediate values of Z, χ, or $\bar{M}_w$ as compared to those characteristic for flexible and rigid-rod chain polymers.

Polymer chain length parameters critical for the onset of entangled behavior were determined according to four different established and accepted methods. Of these, only the results obtained by calculating Z_{wc} from the points of changing slopes in log η_0 vs. log $10^{17}\chi_w$ functions (not corrected to constant ζ) deviated significantly, while at the same time all of the others fell within less than 10% of the average values. It is worth noting that excellent agreement of the result obtained by using the Bueche contact parameter as a measure of polymer chain length with that calculated from the average Z_{wc} was obtained. Practical importance of this conslusion lays in the possibility of avoiding long and sometimes tedious calculations if the $c\bar{M}_w$ path is adopted for similar investigations.

It should be noted that the dependence of η_0 on $(\upsilon_2 Z_w)^{4.0}$ was observed for these solutions in the high molecular weight region. This also distinguishes the DMA solutions of PTIPH not only from the solutions of linear flexible chain polymers, for which the exponent usually equals 3.4, but also from the solutions of rigid-rod macromolecules, for which values as high as 7–8 were reported.[22,24] Such an intermediate exponent value seems to be another property which corresponds to the semiflexible nature of PTIPH.

The exact nature of entanglements in the investigated PTIPH/DMA solutions does not seem completely clear yet. It is possible, however, especially considering very strong intermolecular interactions which exist in this system due to extensive hydrogen bonding, that a mechanism which is somewhere in between molecular looping and bending, invisioned to take place in the solutions of flexible polymers, and perhaps simple limitation of the number of paths available to the molecule during the flow by the action of the neighboring molecules, earlier proposed for the rigid-rod polymers, may be in operation. If such is the case, it could be expected that the latter influences early onset of entangled behavior, as indicated by the rleatively low critical chain length, while looping and bending become more pronounced at higher polymer molecular weights due to increased flexibility of these semiflexible molecules as compared to the more rigid, rodlike polymers.

Glossary

a	molecular weight exponent in the Mark–Houwink equation
b	constant in eq 3
B	constant in the Millich equation
C	constant in the Millich equation
c	concentration of polymer in a polymer–solvent mixture, g/dL
$\overline{\mathrm{DP}}$	average degree of polymerization
$\overline{\mathrm{DP}}_w$	weight-average degree of polymerization
$\overline{\mathrm{DP}}_{wc}$	critical entanglement weight-average degree of polymerization
K	constant in the Mark–Houwink equation
M	molecular weight
$\bar{M}_w$	polymer weight-average molecular weight
$(\bar{M}_w)_c$	critical entanglement weigth-average molecular weight
M_c	critical entanglement molecular weight
M_e	average molecular weight between entanglement loci
N_0	Avogadro's number
R	gas constant
$\langle s^2\rangle_0$	mean-square radius of gyration of the unperturbed chain
T	temperature
υ_2	specific volume of polymer
Z	number of chain atoms per molecule
Z_w	weight-average number of chain atoms per molecule
Z_{wc}	critical entanglement value of Z_w
α	$\partial \log \eta_0/\partial \log Z$
α_1	a constant in eq 2
β_1	a constant in eq 2
$\dot{\gamma}$	shear rate in s^{-1}
ζ_0	the friction factor per polymer segment
ζ_{0c}	limiting friction factor at which α becomes equal to 3.4
η	solution viscosity in poise
η_0	solution viscosity at zero-shear rate
η_{0c}	the value of η_0 when $Z_w = Z_{wc}$
η_s	solvent viscosity in poise
$[\eta]$	intrinsic viscosity, $[\eta] = \lim_{c\to 0} (\eta - \eta_s)/\eta_0 c$
φ_2	volume fraction of polymer in a polymer–solvent mixture
τ	shear stress
τ_0	relaxation time in seconds
τ_R	Rouse relaxation time defined by eq 1
ρ	density
Φ	Flory–Fox constant of eq 9
χ	dimensionless Fox–Allen chain length parameter
χ_w	the value of χ defined by $(\langle s^2\rangle_0/\bar{M}_w)Z_w\varphi_2/\upsilon_2$

Registry No. (*p*-Aminobenzhydrazide)(terephthaloyl chloride) (copolymer), 27102-68-7.

References and Notes

(1) In this paper poly(4-(terephthaloylamino)benzoic acid hydrazide) is referred to by the abbreviation PTIPH derived from its chemical name, rather than by the previously often used X-500 formulated earlier by Monsanto Co.

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Unified Description of Temperature and Concentration Crossover in the Excluded Volume Problem. 1. Osmotic Pressure and Correlation Lengths

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ABSTRACT: We use renormalization group theory to calculate all experimentally accessible correlation lengths and thermodynamic quantities for a dilute polymer solution. Our calculation covers the whole universal regime above the Θ-temperature ranging from single-chain to semidilute limits. Omitting the details of the calculations, we concentrate on the basic features of the method, and we carefully discuss the crossover diagram. Results of a consistent first-order calculation for all the above-mentioned quantities are given and are compared to experiment. In general, the agreement is very good. Discrepancies that occur in the semidilute Θ-limit are analyzed.

1. Introduction

Dilute solutions of long-chain molecules show two different types of crossover phenomena. In pure form the first type is observed if we increase the temperature T of a very dilute solution (i.e., number concentration c_p of chains almost zero) above the Θ-temperature. At $T = \Theta$ the effective interaction $\beta(T)$ of any two chain segments vanishes and therefore the long-range correlations within one chain are Gaussian. The radius of gyration R_g obeys a simple random walk law $R_g \sim N^{1/2}$ as a function of the number of monomers per chain N. Increasing T such that $\beta(T)N^{1/2} >> 1$, we reach the excluded volume limit. Here the long-range properties of the chains are dominated by the repulsive interaction $\beta(T)$. The correlations are non-

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