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Investigation of the Solution Behavior of Organosoluble Aromatic Polyimides

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Two high-molecular-weight organosoluble aromatic polyimides having the same diamine, 2,2′-(trifluoromethyl)-4,4′-diaminobiphenyl diamine (PFMB), but different dianhydrides, 2,2′-bis(trifluoromethyl)-4,4′,5,5′-biphenyltetracarboxylic dianhydride (HFBPDA) and 2,2′-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6FDA), were prepared *via* one-step polycondensation reactions. Molecular weight fractionation of these two polymers was carried out and the polyimide fractions possess successively lower weight-average molecular weights. Intrinsic viscosity data from both sets of polyimide fractions gave the Mark-Houwink-Sakurada constants of these two polyimides, which reflect differing chain rigidity in tetrahydrofuran (THF) solutions. The MHS relations are $[\eta] = 5.24 \times 10^{-4} M^{0.65}$ and $[\eta] = 3.77 \times 10^{-5} M^{0.97}$ for 6FDA-PFMB and HFBPDA-PFMB, respectively. The physical meanings of these constants are discussed using the intrinsic viscosity data of these two polyimides in varying solvents. The persistence lengths are calculated based on the viscosity and molecular weight results using Bohdanecky's approach and they were calculated to be 6.6 and 2.0 nm for HFBPDA-PFMB and 6FDA-PFMB, respectively. The experimental results indicate that the fully aromatic HFPBDA-PFMB is more rigid in THF solutions compared with 6FDA-PFMB. However, both of these polyimides are far from possessing true rigid-rod character. Plots of the weight-average molecular weight against the elution volume depict the differences in chain stiffness, and hence in hydrodynamic volume, between samples. Examination of the hydrodynamic volume of these polymers provides evidence that they both subscribe rather well to hydrodynamic theory at high molecular weights but that the stiffer HFBPDA-PFMB shows deviation at lower values.

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Keywords: Aromatic polyimide, intrinsic viscosity, persistence length

INTRODUCTION

Aromatic polyimides are well-known for their outstanding physical characteristics such as high thermal and thermo-oxidative stabilities, excellent mechanical and electrical properties and, more recently, for their interesting optical properties.[1] The insolubility of traditional polyimides required that their solution properties be determined from the precursor poly(amic acids). This posed several problems including polyelectrolyte effects and differing chain rigidity between the poly(amic acids) and corresponding polyimides.[2–4] Such complications made the already difficult task of the determination and interpretation of the solution behavior of these polymers even more challenging. For example, consider the most well-known polyimide Kapton™. This polymer is synthesized *via* the condensation of pyromellitic dianhydride (PMDA) and 4,4′-oxydianiline (ODA) and has been used in the electronics industries since the 1960s as insulating layers. Since the production of such dielectric films is typically carried out from the solution state, it is important to understand how these molecules behave in different solvents in order to optimize processing conditions. In addition, it is necessary to establish the molecular weight and molecular weight distributions to better understand and predict the physical properties. This importance is illustrated in the large number of publications examining such concerns.[2–12]

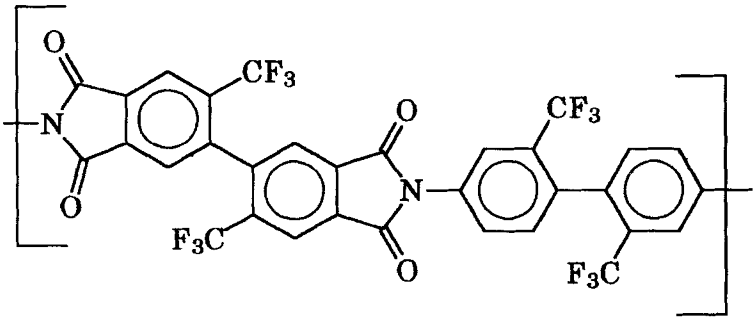
There have been many recent advancements at the University of Akron to develop single-step polycondensation reactions to synthesize fully imidized aromatic polyimides that are soluble in common organic solvents. The solvents in which they are soluble include tetrahydrofuran (THF), methyl ethyl ketone (MEK) and even acetone. The polyimides that have been developed are designed to be soluble while maintaining relatively stiff backbone structures.[13–17] This increased solubility provides the opportunity to directly examine the solution behavior of such polymers without having to rely on extrapolations from the corresponding poly(amic acid)s. Although conventional two-step polymerizations can also be used to prepare these polymers, the molecular weights are usually not as high due to the low reactivities of the substituted monomers at room temperature.[18–21] Obtaining high molecular weights in these polymers is not only important in practical applications but is also essential in the present study of their solution properties.

HFBPDA-PFMB was synthesized from 2,2′-bis(trifluoromethyl)-4,4′,5,5′-biphenyltetracarboxylic dianhydride (HFBPDA) and 2,2′-(trifluoromethyl)-4,4′-diaminobiphenyl diamine (PFMB). 6FDA-PFMB was prepared from 2,2′-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6FDA) and 2,2′-(trifluoromethyl)-4,4′-diaminobiphenyl diamine (PFMB). Both polyimides were polymerized *via* one-step polycondensations.[13–17] Their chemical structures are depicted in Figure 1. These specific polyimides were chosen since they are structurally and chemically similar with the exception of the hexafluoropropane linkage in the dianhydride portion of 6FDA-PFMB. This group acts to impart flexibility and decrease stiffness in the backbone. Both polymers are soluble in the same solvents and under the same conditions. This study uses size exclusion chromatography (SEC), multi-angle laser light scattering (MALLS) and viscometric analyses to arrive at the solution characteristics of these two soluble aromatic polyimides. By comparing the solution properties of this pair of polyimides, conclusions can be obtained concerning their chain rigidity and solution behavior. These results can be extended to achieve a general understanding of the solution behavior of this class of polymers.

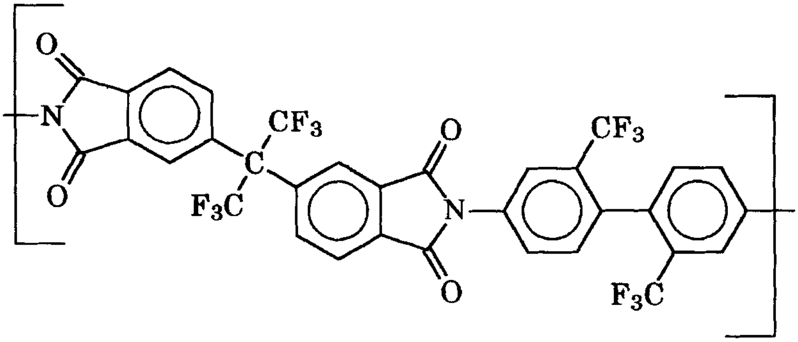
EXPERIMENTAL

Polymers and Sample Preparation

The synthesis of the HFBPDA-PFMB and 6FDA-PFMB polyimides were single-step polycondensation reactions carried out in *m*-cresol at elevated temperatures. The polymerizations are detailed elsewhere.[16,17] Molecular weight fractionation of the polymers was conducted through the use of a Waters fraction collector (part number WAT037040) in conjunction with a Waters 150 CV chromatography system (Waters Corporation, Milford, MA) at 30°C using ACS reagent grade THF as the mobile phase. The column set used to perform the molecular separation consisted of a series of four Waters Ultrastyragel analytical columns (7.8 mm i.d. × 300 mm each) in the order of 10^5, 10^4, 10^3, and 10^2 nm. Fractions were collected every 45 s at a flow rate of 1.0 mL/min. from



HFBPDA-PFMB



6FDA-PFMB

FIGURE 1 Chemical structures of HFBPDA-PFMB and 6FDA-PFMB.

successive 400 μL injections of an approximately 2 mg/mL solution. The fractions were recovered by transferring the solutions into pretared flasks and evaporating the solvent. The samples were all vacuum dried for 24 h at 125°C prior to any analysis.

Instruments and Experiments

Intrinsic viscosity [η] and molecular weight characterizations were performed using the Waters 150 CV chromatography system. Samples were prepared to be between 1–1.5 mg/mL and 400 μL injections were made using the instrument, columns and conditions described above. The single-

TABLE I SEC and MALLS Results for HFBPDA-PFMB Fractions in THF at 30°C

Fraction	*$M_w \times 10^4$ (g/mol) (MALLS)*	*M_w/M_n (SEC)*	*[η] (dL/g) (SEC)*
Fraction 8	6.03	2.06	1.64
Fraction 9	5.08	2.00	1.37
Fraction 10	4.57	1.83	1.22
Fraction 11	3.70	1.89	0.99
Fraction 12	2.91	1.86	0.81
Fraction 13	2.50	1.78	0.74
Fraction 14	2.08	1.84	0.55

capillary viscosity detector was used to obtain [η] values, while the differential refractometer (DRI) was used to calculate the molecular weight averages and distributions through the use of a universal calibration curve. In addition, a Wyatt Dawn™ F multi-angle laser light scattering detector (MALLS) (Wyatt Technology, Santa Barbara, CA) was placed between the viscosity and DRI detectors for on-line absolute molecular weight measurements. The data reported in Tables I and II are the overall average [η] values and molecular weights of the polyimide fractions. Fractions absent in Tables I and II were not characterized due to their negligible quantities. In addition to the overall [η] and MW results, the SEC and MALLS detectors also provide continuous output which furnish viscosity and weight-average molecular weight data at each elution volume, designated as $[\eta]_i$ and $M_{w,i}$. Since the fractions did not have narrow-molecular-weight distributions the determination of peak elution volumes was not straightforward. In circumstances where the elution volumes were needed, see Figures 4 and 5, the data used were the continuous slice results from the whole polymers and not the overall average values

TABLE II SEC and MALLS Results of 6FDA-PFMB Fractions in THF at 30°C

Fraction	*$M_w \times 10^4$ (g/mol) (MALLS)*	*M_w/M_n (SEC)*	*[η] (dL/g) (SEC)*
Fraction 5	9.37	2.18	0.84
Fraction 6	5.75	1.76	0.64
Fraction 7	3.81	1.54	0.47
Fraction 8	2.62	1.49	0.39
Fraction 9	2.19	1.49	0.33
Fraction 11	2.01	1.46	0.31

of the fractions. Table III contains the individual data slice results of the whole polymers that were used in the log M_w and log $[\eta]M_w$ *vs.* elution volume plots of Figures 4 and 5. The interdetector delays were found using narrow-molecular-weight distribution polystyrene standards. Polystyrene (PS) standards (Pressure Chemical Co., Pittsburgh, PA) were also used to develop a universal calibration curve for use in the Waters Expert Ease™ software calculations.

The Waters software calculates the MW averages utilizing the elution volumes v_e and intrinsic viscosities at any point along the chromatogram to determine the molecular weight at that point M_i, according to the previously determined universal calibration curve. These M_i values are then coupled with the concentration data c_i from the DRI detector at that v_e and summed over the entire chromatogram to calculate the MW averages.

The Wyatt Astra™ software package was used to analyze the MALLS data. This program plots the scattered light intensity at any point along the chromatogram as a function of the scattering angle in the form of a Debye plot. The weight-average molecular weight at that point $M_{w,i}$ is obtained from the intercept of the plot. This value is then combined with the DRI concentration data and averaged over the entire chromatogram to obtain the overall weight-average molecular weight values M_w. The instrument calibration constant was determined using pure THF SEC eluent and measuring the ratio of the solvent scattering at 90° to the laser output. The value was stable within ±1 mV over a 30 s time interval as suggested by the Astra software manual version 2.02. The detector normalization coefficients were found by using a 20,000 g/mol narrow MWD PS standard. The Dawn F-DRI delay volume was calculated from the chromatograms of 20,000 and 200,000 g/mol narrow MWD PS standards.

Intrinsic viscosities of these two polyimides in different solvents were measured using a Cannon-Ubblehode viscometer at 30°C to illustrate the varying interactions as a function of the solvent's solubility parameter. All the solvents were ACS reagent grade. The *n*-methyl pyrrolidinone (NMP) was distilled prior to use, all other solvents were used as received. They included THF, methyl ethyl ketone (MEK), 2-pentanone, 1,4-dioxane, propylene glycol methyl ether acetate (PGMEA), NMP, dimethylacetamide (DMAc), dimethylformamide (DMF), dimethylsulfoxide (DMSO), γ-butyrolactone, cyclohexanone, and cyclopentanone. Both the solvents and polymer solutions were filtered using 0.45-μm syringe filters prior to testing.

TABLE III Individual Data Slice SEC and MALLS Values for HFBPDA-PFMB, 6FDA-PFMB and NBS-PS-706 in THF at 30°C

v_e (mL)	*HFBPDA-PFMB*		*6FDA-PFMB*		*NBS PS-706*	
	$M_w \times 10^4$ (g/mol)	[η] (dL/g)	$M_w \times 10^4$ (g/mol)	[η] (dL/g)	$M_w \times 10^4$ (g/mol)	[η] (dL/g)
31.20	8.46	2.24	17.0	1.318	16.70	0.734
32.00	5.94	1.59	9.49	0.901	10.34	0.524
32.32	5.16	1.38	7.35	0.763	8.56	0.460
32.64	4.42	1.19	5.58	0.638	7.07	0.402
32.80	4.06	1.10	4.87	0.584	6.55	0.381
33.12	3.40	0.93	3.72	0.490	5.23	0.325
33.44	2.85	0.78	2.89	0.416	4.59	0.297
33.76	2.41	0.66	2.33	0.361	4.10	0.275
34.08	2.08	0.57	1.91	0.317	3.43	0.242
34.56	1.80	0.50	1.39	0.258	2.32	0.185
34.88	1.66	0.46	1.13	0.226	1.95	0.163
35.20	1.55	0.43	0.92	0.198	1.58	0.141
35.68	1.44	0.40	0.71	0.166	1.16	0.113
36.16	1.37	0.38	0.62	0.153	0.84	0.091
36.64	1.30	0.37	0.51	0.135	0.61	0.072

The specific refractive index increment (dn/dc) was determined using a Brice Phoenix differential refractometer modified to accept a HeNe laser light source ($\lambda = 632.8$ nm). A PS standard (NBS-PS-706) was used to determine the instrument constant. The dn/dc values were verified by integrating the area under the DRI detector response for the polyimides using NBS-PS-706 as a reference. The dn/dc values were determined in THF at 30°C to be 0.171 and 0.137 mL/g for 6FDA-PFMB and HFBPDA-PFMB, respectively.

Results and Discussion

Molecular Fractionation

Tables I and II show the SEC and MALLS results for the HFBPDA-PFMB and 6FDA-PFMB fractions. Figures 2 and 3 depict the SEC DRI tracings for the whole polymers and successive MW fractions for HFBPDA-PFMB and 6FDA-PFMB, respectively. It is first noticed that, although the polydispersities of the fractions are lower than the parent polymers, they certainly cannot be termed narrow ($M_w/M_n < 1.2$). Regardless, the fractionation does produce molecular weight fractions having successively lower weight average molecular weights. The application of SEC with the triple detector system described in the experimental section allows the acquisition of the Mark-Houwink-Sakurada (MHS) relationship, the persistence length estimation, and a measure of the appropriateness of the universal calibration to these polyimides.

SEC MW Calibration

Figure 4 is a plot of the molecular weight *vs.* elution volume v_e constructed from the SEC and MALLS data. The molecular weight data was obtained from the MALLS using the continuous output. Also included in this figure are the values of NBS-PS-706 for comparison. The results shown in Figure 4 and Table III indicate that the structurally more rigid HFBPDA-PFMB molecules that elute at the same v_e as the PS 706 have lower molecular weight. This is in accord with hydrodynamic theory which implies that the SEC technique separates molecules on the basis of their hydrodynamic volume and not merely by their molecular weight. As one would qualitatively expect, the structurally more rigid HFBPDA-PFMB would have a larger

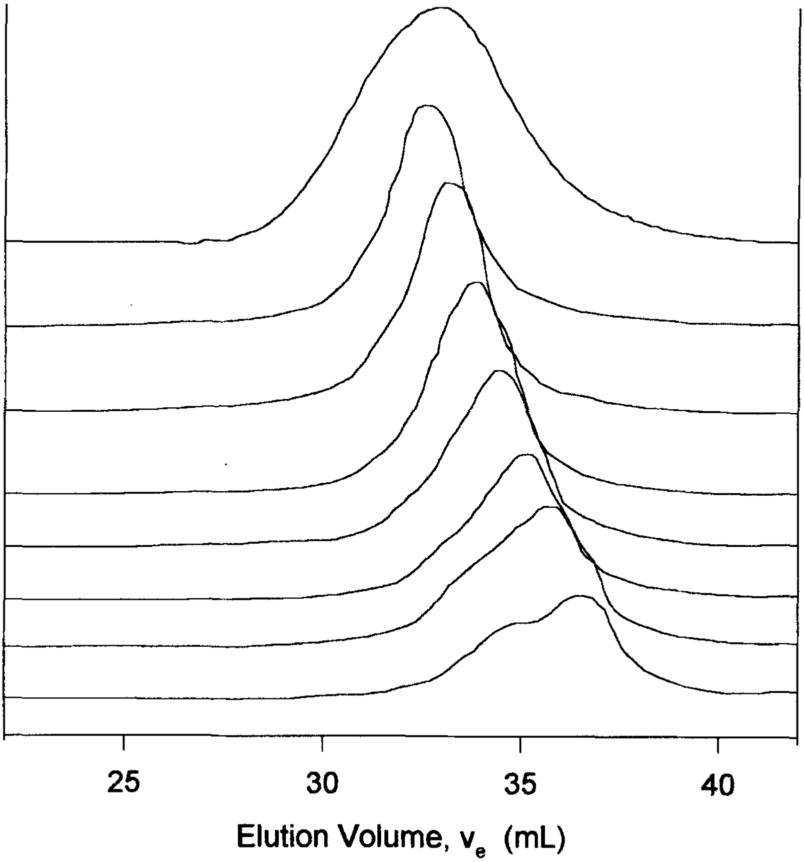


FIGURE 2 SEC DRI tracings for HFBPDA-PFMB whole polymer (top) and successive fractions.

hydrodynamic volume than a random coil of similar molecular weight. The chain conformation will approach that of a random coils as the MW increases and the contour length becomes much greater than the persistence length. Conversely, this means that the HFBPDA-PFMB chains become more rodlike at lower MWs where their hydrodynamic volume begins to increase. The curve for 6FDA-PFMB is in-between those of HFBPDA-PFMB and PS, as anticipated by comparison of their molecular structures. The errors in log M_w lie within the dimensions of the data symbols on the plot. The figure emphasizes the fact that using a SEC calibration based solely on the MW will lead to erroneous polyimide MW data.

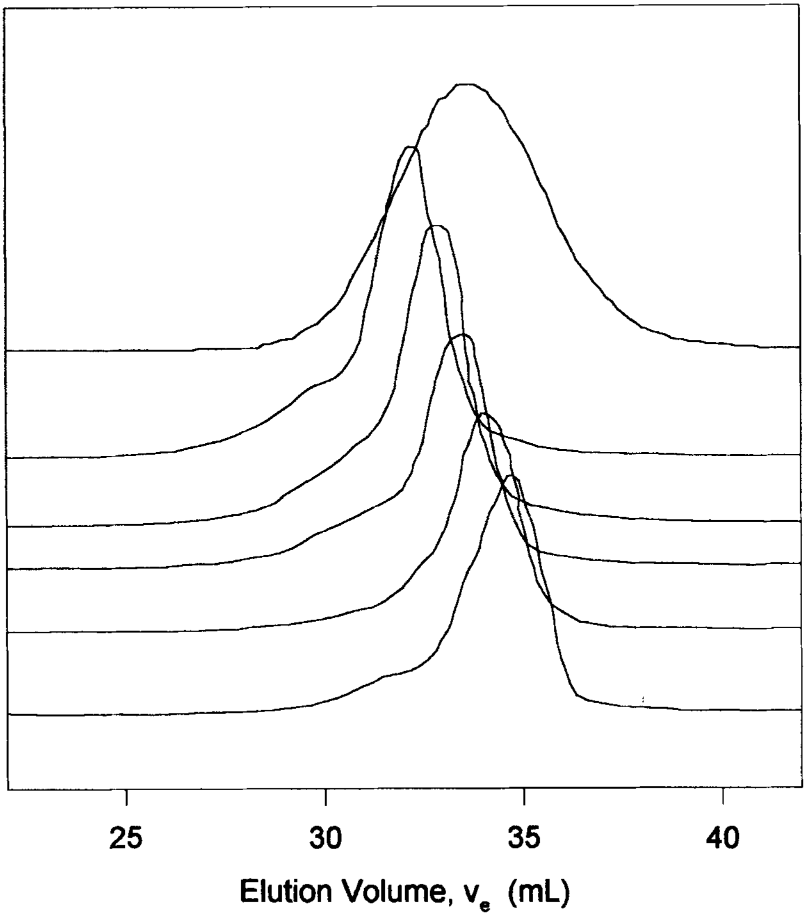


FIGURE 3 SEC DRI tracings for 6FDA-PFMB whole polymer (top) and successive fractions.

Universal Calibration

To avoid the problems associated with analyzing polymers having different chemical and configurational characteristics than the standard materials, Benoit[22] proposed a universal calibration based on the hydrodynamic volume, $[\eta]M_w$, which has been shown to be equivalent for most polymers. Figure 5 shows the plot of the log $[\eta]M_w$ *vs.* v_e for these polyimides and for NBS-PS-706. The results are obtained from the averages of five trials from the continuous $[\eta]$ and M_w output of the differential viscometer and MALLS detectors.

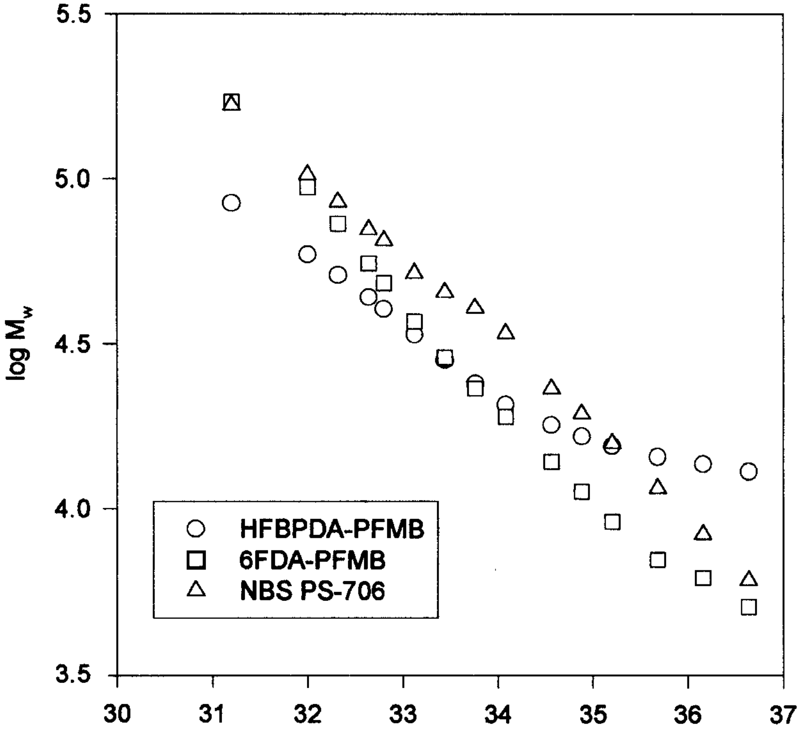


FIGURE 4 Weight-average molecular weight vs. elution volume for HFBPDA-PFMB, 6FDA-PFMB and NBS-PS-706 in THF at 30°C.

As Figure 5 indicates, both polyimides reasonably follow the universal calibration at higher MW but the more rigid HFBPDA-PFMB tends to fall off the relationship at lower MW. Again, this deviation is due to the hydrodynamic volume of the chains which tend to become more elliptical at lower MW. The errors in log $[\eta]M_w$ lie within the dimensions of the data symbols on the plot. These results indicate that the universal calibration can be used to analyze aromatic polyimide MWs but caution should be taken with samples containing a high degree of rigidity in the backbone.

Intrinsic Viscosities of Polyimides in Different Solvents

Figures 6 and 7 show the intrinsic viscosity and solubility parameter relationships of HFBPDA-PFMB and 6FDA-PFMB polyimides in different solvents. The better the solvent, the more expanded the chains and, conse-

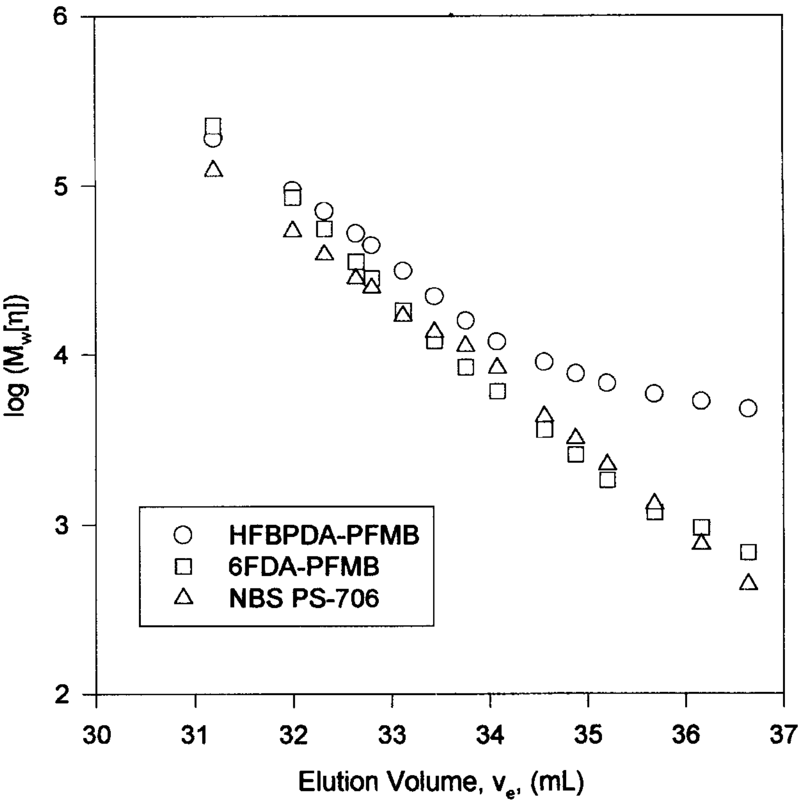


FIGURE 5 Hydrodynamic volume *vs.* elution volume for HFBPDA-PFMB, 6FDA-PFMB and NBS-PS-706 in THF at 30°C.

quently, the higher the [η]. The maximum [η] should result from the solvent whose solubility parameter is nearest that of the polymer. The calculated values for the solubility parameters of the polymers according to Van Krevelen's method[34] are 12.30 and 12.02 cal$^{1/2}$ cm$^{-3/2}$ for HFBPDA-PFMB and 6FDA-PFMB, respectively. In the case of 6FDA-PFMB, the maximum [η] is reached in DMAc which possesses a solubility parameter of 10.8 cal$^{1/2}$ cm$^{-3/2}$. HFBPDA-PFMB shows a maximum [η] in NMP which has a solubility parameter of 11.03 cal$^{1/2}$ cm$^{-3/2}$. Possible sources of deviation could be the effect of specific interactions such as hydrogen bonding, dipole interactions or dispersive forces. These results indicate that the interactions between the polymer segments and solvent molecules are the greatest in those sol-

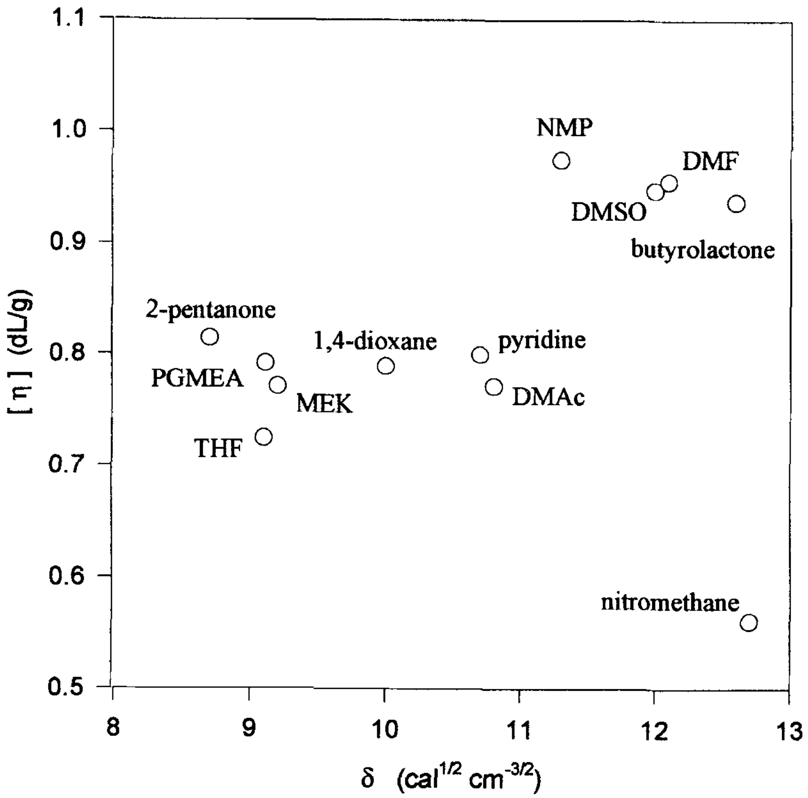


FIGURE 6 Plot of intrinsic viscosities of HFBPDA-PFMB against solubility parameter in different solvents at 30°C.

vents and that, as a result of the specific interactions, the persistence length and MHS constants may exhibit a solvent dependency.

Mark-Houwink-Sakurada (MHS) Constants

Despite the higher than desired polydispersities, the fractions do provide adequate data for determining MHS constants and estimating persistence lengths. Figure 8 shows a typical MHS plot constructed using the overall average MALLS M_w and SEC [η] values of the polyimide fractions. The

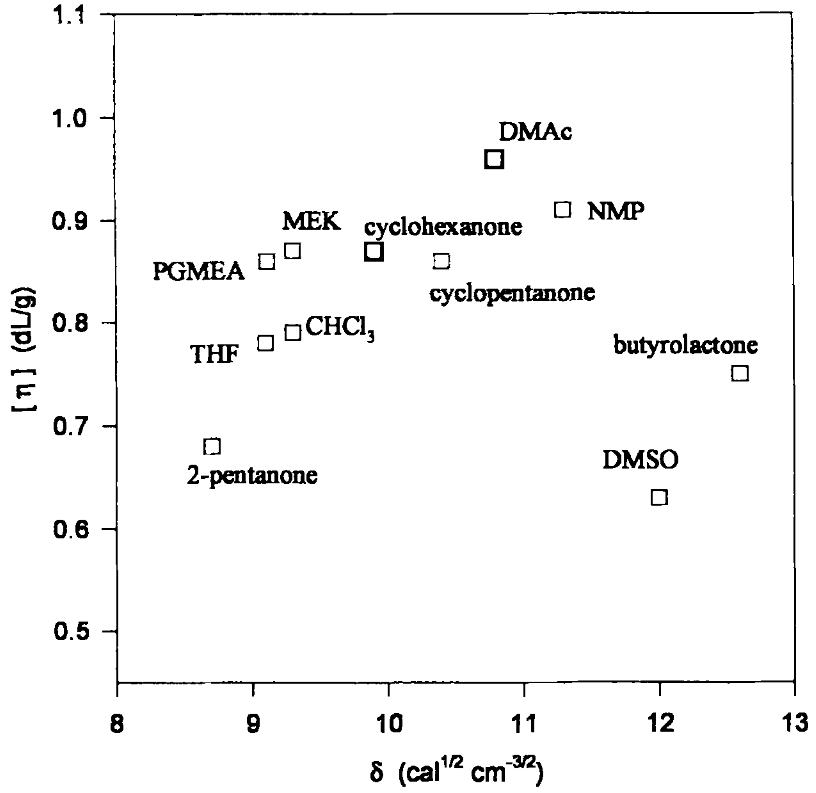


FIGURE 7 Plot of intrinsic viscosities of 6FDA-PFMB against solubility parameter in different solvents at 30°C.

slopes and intercepts of the plots provide the relationships between the molecular weights and [η]:

HFBPDA-PFMB $[\eta] = 3.77 \times 10^{-5} M^{0.97}$ (1)

6FDA-PFMB $[\eta] = 5.24 \times 10^{-4} M^{0.65}$ (2)

where [η] is in dL/g.

From the Mark-Houwink-Sakurada exponents, HFBPDA-PFMB is more rigid in THF than a typical random coil would be in a good solvent. Under those conditions, the random coil chain would be in its extended conformation and would yield an exponent of approximately 0.8. As indicated above

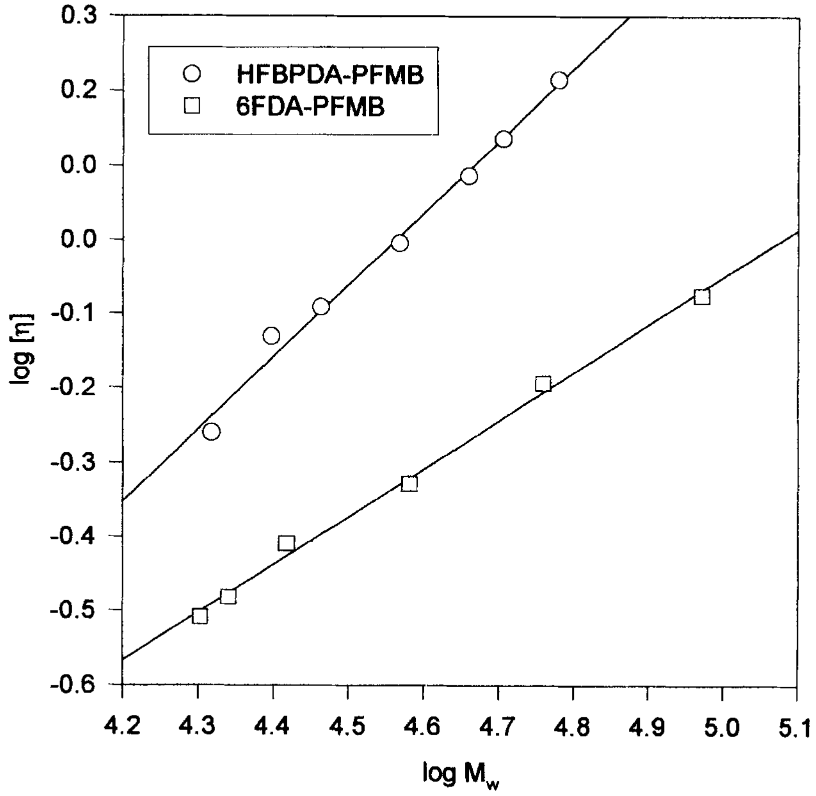


FIGURE 8 Mark-Houwink-Sakurada plot for the polyimide fractions of HFBPDA-PFMB and 6FDA-PFMB in THF at 30°C.

the chain dimensions in THF are smaller for HFBPDA-PFMB, as compared to NMP due to specific interactions (Fig. 6). Therefore, if NMP were used as the solvent, the MHS exponent would most likely be higher than 0.97. Regardless, HFBPDA-PFMB may not be considered to be a true rigid-rod polymer which would exhibit a theoretical value of 1.8.6 FDA-PFMB has an exponent of 0.65 and shows behavior in-between that of a random coil near the extended chain limit and the theta point value of 0.5. These values are consistent with those of the polyimide 6FDA-ODA reported by Young *et al.*[10] with constants of $a = 0.6$ and $K = 1.14 \times 10^{-3}$, and to the polyimide 6FDA-pPDA whose Mark-Houwink-Sakurada constants were found by Konas *et al.*[11] to be $a = 0.66$ and $K = 3.7 \times 10^{-2}$.[11] Note that 6FDA-ODA is structurally more flexible than 6FDA-PFMB due to the presence of the ether linkages in the diamine portion of the polyimide.

The trend of increasing chain flexibility and decreasing MHS exponent is illustrated by considering that 6FDA-ODA differs from 6FDA-PFMB only by the addition of flexible ether linkages in the diamine portion. This increase in flexibility yields a MHS exponent closer to that of a random coil than does 6FDA-PFMB. Supporting this trend in the MHS exponent and chain rigidity are the MW *vs.* V_e results of Figure 4. The extensive work done by Cotts *et al.*[8,9] on PMDA-ODA poly(amic acid) precursors in NMP yielded values of $a = 0.74$ and $K = 5.8 \times 10^{-2}$, indicating that the precursor conformation was similar to that of a random coil in a good solvent.

Persistence Lengths of the Polyimides in THF

Although these polyimides are aromatic in nature, they deviate from the conformation of true rigid-rod polymers like the *para* catenated heterocyclics. The dissimilarities come from the presence of asymmetric linkages, bridging atoms and bulky substituents along the backbone of most typical soluble aromatic polyimides. All of these factors contribute to nonlinearity within the chains. These polymers may thus be best classified as segmented rigid-rods. The treatment that describes such molecules is the Kratky-Porod worm-like chain model.[23] This model has been used to evaluate several classes of semirigid polymers including alkyl isocyanates,[24] aromatic polyesters,[25,26] polyamides[27] and poly(diisopropyl fumarate).[28] The works of Bohdanecky[29] and Yamakawa and Fuji[30] have provided methods of evaluating the worm-like chain parameters, such as the persistence length q, from experimentally determined $[\eta]$ and molecular weight measurements. Note that the extent to which a semirigid chain maintains its linear projection in solution is described as its persistence length. This quantity can be related to the length of the Kuhn link A by the relation of $A = 2q$. The persistence lengths of these polyimides are determined following the treatment proposed by Bohdanecky.[29]

The equations used to find q and the chain diameter d are

$$(M^2/[\eta])^{1/3} = A_\eta + B_\eta M^{1/2} \tag{3}$$

$$A_\eta = \Phi_\infty^{-(1/3)} A_0 M_L \tag{4}$$

$$B_\eta = \Phi_\infty^{-(1/3)} B_0 (M_L/2q)^{1/2} \tag{5}$$

where Φ_∞ is the Flory-Fox constant equal to 2.87×10^{23}. The functions A_0 and B_0 can be expressed in terms of d/2q as shown below:

$$A_0 = 0.46\text{-}0.53\log(d/2q) \tag{6}$$

$$B_0 = 1.00\text{-}0.0367\log(d/2q) \tag{7}$$

M_L, the molar mass per unit length (M/L), was obtained by taking the ratio between the mass of the polymeric repeat unit and its energy-minimized end-to-end distance. This distance was determined using the Insight II software package (Molecular Simulations, Inc., San Diego, CA). The lengths of the repeat units were calculated to be 1.9 and 2.1 nm for HFBPDA-PFMB and 6FDA-PFMB, respectively. By plotting $(M^2/[\eta])^{1/3}$ against $M^{1/2}$, as shown in Figure 9, a straight line is obtained whose intercept and slope yield values of A_η and B_η, respectively. For HFBPDA-PFMB, $A_\eta = 7.35 \times 10^{-6}$ and $B_\eta = 8.53 \times 10^{-8}$ while for 6FDA-PFMB $A_\eta = 3.09 \times 10^{-6}$ and $B_\eta = 1.43 \times 10^{-7}$. As one would expect from the chemical structures and MHS results, 6FDA-PFMB ($q = 2.0$ nm) is less persistent than HFBPDA-PFMB ($q = 6.6$ nm) in THF. These results are in the range indicated by Cotts[35] for similar aromatic polyimides such as PMDA-ODA ($q = 3.6$ nm), BPDA-PDA ($q = 3.0$ nm) and *p*-PMDA-Et_2/ODA ($q = 4.5$ nm). They are also on the same order of magnitude as an aromatic copolyester in phenol: 1,2,4-trichlorbenzene (50:50) studied by Cinquina *et al.*[26] ($q = 3.0$ nm) and a liquid-crystalline polyether in 4′-(pentyloxy)-4-biphenylcaronitrile ($q = 3.62$ nm) examined by Chen and Jamieson.[31] In terms of the persistence length, the values for HFBPDA-PFMB and 6FDA-PFMB do not place them in the category of true rigid-rod polymers. The estimates of $q = 6.6$ and 2.0 nm for these polymers are roughly an order of magnitude lower than would be expected for rigid-rod polymers.[32] The recently reported value of $q = 13$ nm for a soluble aromatic polyimide consisting entirely of *para* catenations[33] exemplifies the differences that symmetry makes in terms of the persistence length. This value is one order of magnitude greater than that determined for HFBPDA-PFMB whose backbone is entirely aromatic but is not completely para-catenated. HFBPDA-PFMB has nonsymmetrical linkages along its backbone which introduce nonlinearity and hence decrease the persistence length. The hexafluoropropane group in 6FDA-PFMB provides a sharp kink along the chain backbone as a result of the roughly 109° bond angle of the sp^3 hybridized carbon. This is in addition to the nonsym-

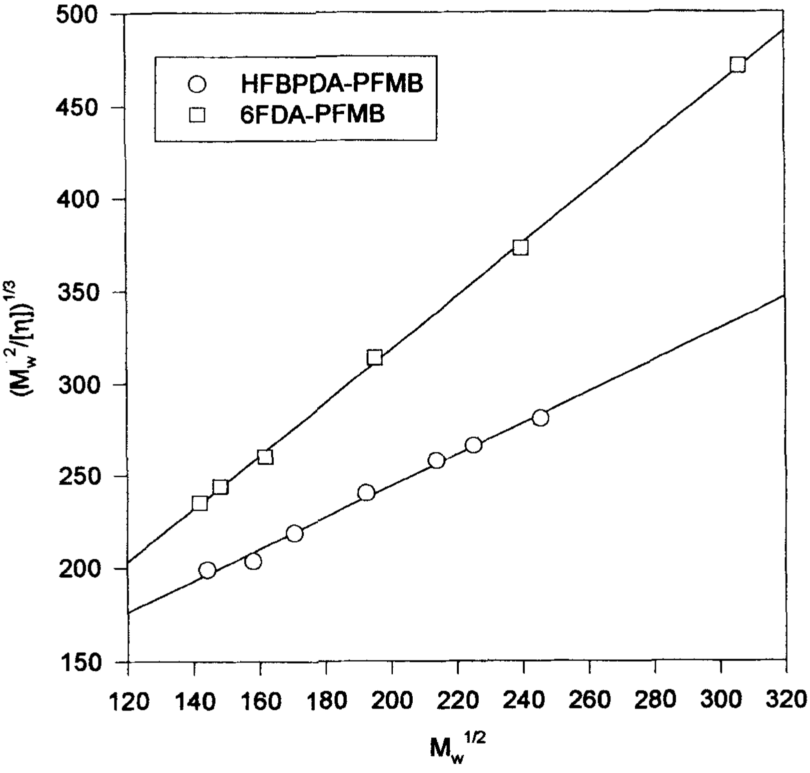


FIGURE 9 Persistence length determination using the Bohdanecky method for HFBPDA-PFMB and 6FDA-PFMB in THF at 30°C.

metry imposed by the catenation of the dianhydride. Therefore, the 6FDA-PFMB chains are even less persistent than HFBPDA-PFMB. Since persistence lengths are critically dependent upon the models assumed and on the molecular weight range of the samples, these calculated values are more meaningful when used to make internal qualitative comparisons rather than being viewed as absolute values.

CONCLUSION

Two high-molecular-weight soluble aromatic polyimides (HFBPDA-PFMB and 6FDA-PFMB) were fractionated and the molecular weight fractions were used to arrive at their MHS equations and persistence lengths in

THF at 30°C. From the MHS exponents and the persistence lengths for HFBPDA-PFMB and 6FDA-PFMB, HFBPDA-PFMB is more rigid as compared to 6FDA-PFMB. This data corresponds well with the molecular weight and elution volume relations in that, for a given v_e, the more rigid molecules possess smaller molecular weights than the more flexible molecules having similar hydrodynamic volumes. Both polyimides were shown to follow the universal calibration rather closely at high MW but the stiffer HFBPDA-PFMB tends to deviate at lower MWs where the hydrodynamic volumes become larger compared to the more flexible polymers. The intrinsic viscosity data in different solvents for these two aromatic polyimides shows that the best solvent for HFBPDA-PFMB is NMP while that for 6FDA-PFMB is DMAc.

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