Scalings of Fluorine-Containing Polyimides in Cyclopentanone

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ABSTRACT: Eight 2,2′-bis(3,4-dicarboxyphenyl) hexafluoropropane dianhydride-4,4′-diamino-3,3′-dimethylbiphenyl (6FDA-OTOL) fractions and seven 2,2′-bis[4-(3,4-dicarboxyphenoxy) phenyl] propane dianhydride-4,4′-diamino-3,3′-dimethylbiphenyl (BISADA-OTOL) fractions in cyclopentanone at 30 °C were characterized by a combination of viscometry and static and dynamic laser light scattering (LLS). In static LLS, the angular dependence of the absolute scattered intensity led to the weight-average molar mass (M_w), the z-average root mean square radius of gyration, and the second virial coefficient. In dynamic LLS, the Laplace inversion of each measured intensity–intensity time correlation function resulted in a corresponding translational diffusion coefficient distribution [$G(D)$]. The scalings of $\langle D\rangle$ (cm^2/s) = $8.13 \times 10^{-5} M_w^{-0.47}$ and [η] (dL/g) = $2.36 \times 10^{-3} M_w^{0.54}$ for 6FDA-OTOL and $\langle D\rangle$ (cm^2/s) = $3.02 \times 10^{-4} M_w^{-0.60}$ and [η] (dL/g) = $2.32 \times 10^{-3} M_w^{0.53}$ for BISADA-OTOL were established. With these scalings, we successfully converted each $G(D)$ value into a corresponding molar mass distribution. At 30 °C, cyclopentanone is a good solvent for BISADA-OTOL but a poor solvent for 6FDA-OTOL; this can be attributed to an ether linkage in BISADA-OTOL. Therefore, BISADA-OTOL has a more extended chain conformation than 6FDA-OTOL in cyclopentanone. © 2000 John Wiley & Sons, Inc. J Polym Sci B: Polym Phys 38: 2077–2080, 2000

Keywords: fluorine-containing polyimides; scaling relations; laser light scattering

INTRODUCTION

Aromatic polyimides are high-performance polymers with high thermal and chemical stability, good solvent resistance, and excellent electrical and mechanical properties.[1] They are widely used in industry as optical coatings, adhesives, dielectric insulators, and so forth. Molecular parameters are constantly required in their development and applications. However, because of a high content of aromatic rings, it is normally so difficult to dissolve polyimides in common organic solvents that the study of their solution properties, such as the chain conformation and molar mass distribution, has been hindered.[2] Often, the solution properties and molecular parameters of these insoluble polyimides have to be estimated from their precursors [e.g., poly(amic acid) formed in the

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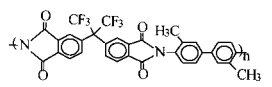
first-stage reaction of an aromatic diamine with an anhydride], leading to several serious problems,[3,4] such as unusual polyelectrolyte effects in a precursor solution and a large difference between the chain dimensions of the precursor and the polymer. Therefore, it is necessary to have a direct measurement of the physical properties of polyimides in solution.

Soluble high-performance polyimides have been developed.[2] One of the methods is to fluorinate a given monomer so that aromatic rings are twisted and the interactions between two polymer chains are suppressed. Moreover, these fluorinated polyimides have significantly reduced water adsorption, refractive index, and dielectric constant, which greatly enhances their electrical properties.[5,6] In this study, two sets of narrowly distributed high-performance polyimides, 2,2′-bis-(3,4-dicarboxyphenyl) hexafluoropropane dianhydride-4,4′-diamino-3,3′-dimethylbiphenyl (6FDA-OTOL) and 2,2′-bis[4-(3,4-dicarboxyphenoxy) phenyl] propane dianhydride-4,4′-diamino-3,3′-dimethylbiphenyl (BISADA-OTOL), were used to establish the scalings of these polyimides in cyclopentanone and to determine their chain conformation in solution.

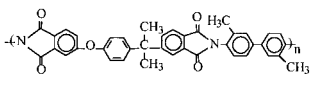
EXPERIMENTAL

Samples

The synthesis of 6FDA-OTOL and BISADA-OTOL can be found elsewhere.[7] Their chemical structures are as follows:



6FDA-OTOL



BISADA-OTOL

Eight fractions of 6FDAA-OTOL from one sample and seven fractions of BISADA-OTOL were used in this study. They were soluble in cyclopentanone at 30 °C. The concentrations used in this study ranged from 8×10^{-4} to 8×10^{-3} g/mL. Cyclopentanone was further purified by distillation. All the solutions used in laser light scattering (LLS) were clarified at room temperature with 0.5-μm Millipore filter to remove dust.

LLS

The LLS instrumentation has been detailed elsewhere.[8,9] The specific refractive index increment

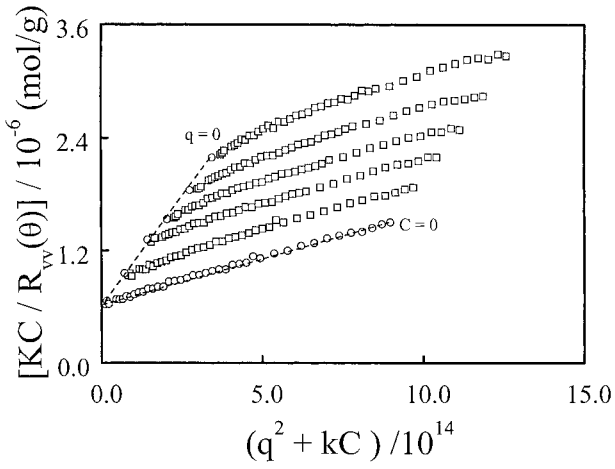


Figure 1. Typical Zimm plot of 6FDA-OTOL in cyclopentanone at 30 °C, where [η] is 1.01 dL/g and C ranges from 9.93×10^{-4} to 4.97×10^{-3} g/mL.

(dn/dC) was determined with a novel and precise differential refractometer.[10] In static LLS, the angular dependence of the absolute excess time-averaged scattered intensity, known as the Rayleigh ratio [$R_{vv}(q)$], can lead to the weight-average molar mass (M_w), the z-average root mean square radius of gyration ($\langle R_g^2 \rangle_z^{1/2}$, or $\langle R_g \rangle$), and the second virial coefficient (A_2),[11] where q is the scattering vector. In dynamic LLS, the cumulant analysis or Laplace inversion of the measured intensity–intensity time correlation function [$G^{(2)}(\tau,\theta)$] in the self-beating mode can result in an average line width ($\langle \Gamma \rangle$) or a line-width distribution [$G(\Gamma)$]. For a pure diffusive relaxation, $(\Gamma/q^2)_{q\to 0, C\to 0}$ equals the translational diffusion coefficient (D), which can be further related to the hydrodynamic radius (R_h) via the Stokes–Einstein equation: $R_h = k_B T/(6\pi\eta D)$, where k_B, T, and η are the Boltzmann constant, absolute temperature, and solvent viscosity, respectively.

RESULTS AND DISCUSSION

Figure 1 shows a typical Zimm plot of 6FDA-OTOL in cyclopentanone at 30 °C that incorporates both the angular and concentration dependencies on a single grid. The static LLS results of 6FDA-OTOL and BISADA-OTOL, that is, M_w and A_2, are summarized in Table I. For 6FDA-OTOL in cyclopentanone, larger positive A_2 values indicate that cyclopentanone at 30 °C is a good solvent for 6FDA-OTOL, whereas for BISADA-OTOL in cyclopentanone, $A_2 \sim 0$ suggests that

Table I. Static and Dynamic Laser Light Scattering Results

Fraction	$[\eta]$ (dL/g)	$M_w/10^4$ (g/mol)	$A_2/10^{-4}$ (mol · mL/g^2)	$\langle D\rangle/10^{-7}$ (cm^2/s)	$\langle R_h\rangle$ (nm)	M_w/M_n
			6FDA-OTOL			
1	1.95	35.8	2.9	1.85	11.4	1.5
2	1.85	16.0	3.8	3.14	6.7	1.4
3	1.54	14.7	3.5	3.21	6.6	1.6
4	0.98	5.2	2.5	4.43	4.8	1.7
5	0.69	3.2	4.1	6.34	3.3	1.3
6	0.57	2.7	5.2	7.61	2.8	1.2
7	0.47	1.8	4.4	8.20	2.6	1.9
8	0.37	1.4	2.8	8.37	2.5	1.5
			BISADA-OTOL			
1	1.01	14.6	0.2	2.70	7.8	1.3
2	0.91	7.0	0.1	3.92	5.4	1.4
3	0.72	5.5	0.1	4.15	5.1	1.5
4	0.61	3.2	0.2	6.30	3.4	1.5
5	0.56	2.3	−0.1	7.30	2.9	1.2
6	0.48	2.2	−0.5	7.78	2.7	1.2
7	0.33	1.3	0.1	10.5	2.0	1.2

cyclopentanone is a Θ or even a poor solvent for BISADA-OTOL. Table I shows that there is no clear molar mass dependence of A_2, which might be attributed to the relatively narrow range of molar masses studied. $\langle R_g{}^2\rangle^{1/2}$ is too small to be accurately measured.

Figure 2 shows a double logarithmic plot of the average translational diffusion coefficient ($\langle D\rangle$) versus the M_w, where the lines represent $\langle D\rangle$ (cm^2/s) = $8.13 \times 10^{-5}\ M_w{}^{-0.47}$ for 6FDA-OTOL and $\langle D\rangle$ (cm^2/s) = $3.02 \times 10^{-4}\ M_w{}^{-0.60}$ for BISADA-OTOL. Figure 3 shows a double logarithmic plot of the intrinsic viscosity ($[\eta]$) versus the M_w, where the lines represent $[\eta]$ (dL/g) = $2.36 \times 10^{-3}\ M_w{}^{0.54}$ for 6FDA-OTOL and $[\eta]$ (dL/g) = $2.32 \times 10^{-3}\ M_w{}^{0.53}$ for BISADA-OTOL.

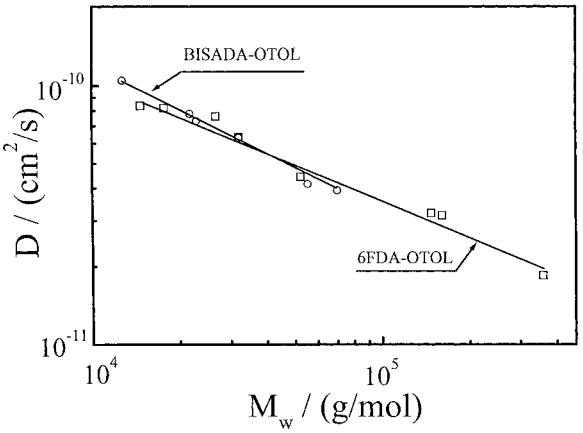


Figure 2. Double logarithmic plots of $\langle D\rangle$ versus M_w, where the lines represent the least-squares fittings of $\langle D\rangle$ (cm^2/s) = $8.13 \times 10^{-5}\ M_w{}^{-0.47}$ for 6FDA-OTOL and $\langle D\rangle$ (cm^2/s) = $3.02 \times 10^{-4}\ M_w{}^{-0.60}$ for BISADA-OTOL in cyclopentanone at 30 °C.

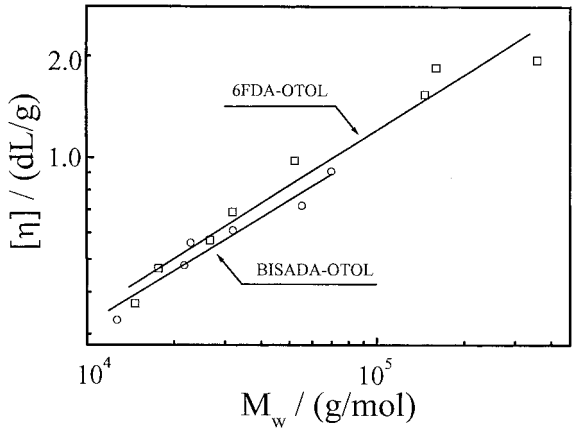


Figure 3. Double logarithmic plots of $[\eta]$ and M_w, where the lines represent the least-squares fittings of $[\eta]$ (dL/g) = $2.40 \times 10^{-3}\ M_w{}^{0.54}$ for 6FDA-OTOL and $[\eta]$ (dL/g) = $2.40 \times 10^{-3}\ M_w{}^{0.53}$ for BISADA-OTOL in cyclopentanone at 30 °C.

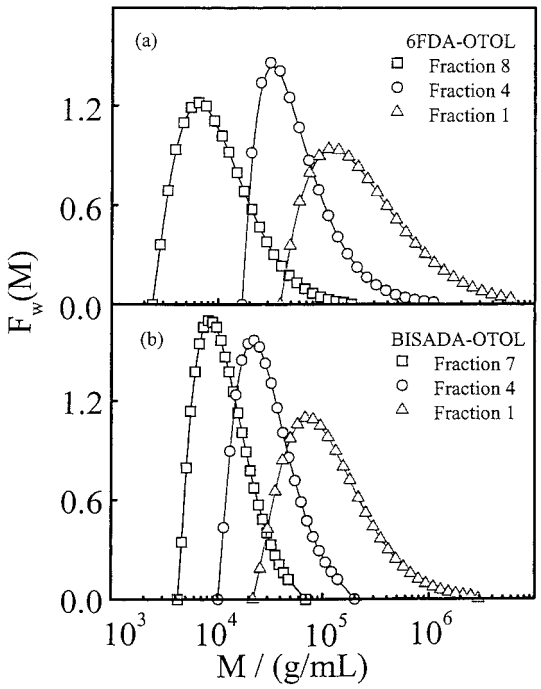


Figure 4. Typical $f_w(M)$ values of 6FDA-OTOL and BISADA-OTOL, where each $f_w(M)$ value was calculated from a corresponding $G(D)$ value with the scalings in Figure 2.

The scalings of $\langle D \rangle \sim M_w^{-0.47}$ and $[\eta] \sim M_w^{0.54}$ for 6FDA-OTOL in cyclopentanone indicates that the polyimide chains are more compact, whereas the scalings of $\langle D \rangle \sim M_w^{-0.60}$ and $[\eta] \sim M_w^{0.53}$ for BISADA-OTOL in cyclopentanone reveal a relatively extended chain conformation.

In Figure 4, each weight distribution of molar mass $[f_w(M)]$ was calculated from a corresponding translational diffusion coefficient distribution $[G(D)]$ with $\langle D \rangle = 8.13 \times 10^{-5} M_w^{-0.47}$ for 6FDA-OTOL and $\langle D \rangle = 3.02 \times 10^{-4} M_w^{-0.60}$ for BISADA-OTOL. The detail of the conversion from $G(D)$ to $f_w(M)$ can be found elsewhere.[12] These molar mass distributions reveal that all the fractions are narrowly distributed. The values of M_w/M_n (weight-average molar mass/number-average molar mass) for all the fractions are also listed in Table I. The scalings used in the conversion are independent of a particular LLS spectrometer as long as cyclopentanone is used as the solvent and the solution temperature is 30 °C. This is an advantage of using LLS to estimate a given polyimide's molar mass distribution over other analytical methods, such as GPC, because there is no need for calibration in LLS. Also, the scalings established in this study can be used in the future for a quick estimation of the molar mass distribution of soluble polyimides from LLS or the average molar mass from viscometry.

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