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PII: S0032-3861(97)10111-2

Polymer Vol. 39 No. 14, pp. 3193–3197, 1998

0032-3861/98/$19.00+0.00

Chain conformation of a high-performance polyimide in organic solution

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(Received 1 January 1997; revised 10 June 1997)

An organo-soluble polyimide based on 1,4-bis(3,4-dicarboxyphenoxy) benzene dianhydride (HQDPA) and 2,2′-dimethyl-4,4′-methylene dianiline (DMMDA), was synthesized via two-step polycondensation accompanied by chemical imidization. Five fractions were prepared by fractionation. The dilute solutions of the fractions were studied by LLS (Laser Light Scattering) and the intrinsic viscosities of the fractions were measured. The unperturbed dimension was determined by the intrinsic viscosity with the Stockmayer–Fox equation. The results indicate that the polyimide in this study has a flexible chain conformation in chloroform and *N,N*-dimethyl acetamide (DMAc). However, the degree of chain expansion differs in different solvents. © 1998 Published by Elsevier Science Ltd. All rights reserved.

(Keywords: organo-soluble polyimide; intrinsic viscosity; chain conformation)

INTRODUCTION

Aromatic polyimides have been used widely in applications such as thin films, adhesive and coating, etc.[1]. However, the insolubility of polyimides studied previously prevented them from being researched for their solution properties so the solution properties of insoluble polyimides were estimated from their precursor, polyamic acid. As a result, polyelectrolyte effects and the chain rigidity difference between a polyamic acid and its corresponding polyimide were dismissed[2,3].

Solution properties of polyimides are required, especially when they are used in microelectronics and optical applications. In practice, the correlation between chain flexibility and bulk properties is not known. To solve this problem, the development of soluble polyimides is necessary.

Up to now, a few organo-soluble polyimides have been synthesized via two-step polycondensation accompanied by chemical imidization. In this study, attempts at dilute solutions of an organo-soluble polyimide based on 1,4-bis(3,4-dicarboxyphenoxy) benzene dianhydride (HQDPA) and 2,2′-dimethyl-4,4′-methylene dianiline (DMMDA) were made to determine chain flexibility and degree of chain expansion in different organic solvents.

EXPERIMENTAL

Materials

Equimolar dianhydride and diamine were mixed in the medium of *N,N*-dimethylacetamide (DMAc) with stirring at room temperature for 48 h until a uniform solution, regarded as polyamic acid solution, was formed, and then triethylamine and acetic anhydride were added to imidize polyamic acid into polyimide. Finally, an organo-soluble polyimide solution was prepared. The procedure is outlined in *Scheme 1*. Then, 95% ethanol was poured into the solution with stirring so that polyimide can be precipitated. Washed for three times, white polyimide powders were obtained.

The polyimide powder is soluble in *N,N*-dimethylformamide (DMF), chloroform, *N*-methylpyrrolidone (NMP), *m*-cresol, epichlorohydrin (EPC), γ-butyrolactone (γ-but), in addition to DMAc. Five fractions were prepared by fractionation with chloroform as solvent and methanol as precipitant.

LLS measurements

Five solutions of the fractions with concentrations in the range of 4.0×10^{-4}–5.0×10^{-3} g/ml were prepared by dilution. All solutions were clarified at room temperature using a 0.22- or 0.1-μm Whatman filter according to the polymer size. A modified ALV/SP-125 Spectrometer equipped with an ALV-5000 multi-τ digital time correlator and a solid state laser (ADLAS DPY 425II with output power ≈ 400 mW at $\lambda_0 = 532$ nm) as the light source was used. The primary beam is vertically polarized with respect to the scattering plane. Toluene was used to calibrate the spectrometer so that it had no angular dependence in the angular range of 6~154°. The details of LLS instrumentation and theory can be found elsewhere[4,5]. All LLS measurements were carried out at 25.0°C. In static LLS, the angular dependence of the excess absolute time-averaged scattered intensity, known as the excess Rayleigh ratio, $R_{vv}(q)$, of a dilute polymer solution at the concentration C (g/ml) and a relatively low scattering angle can be related to the weight average molecular weight $\bar{M}_w$ as[6]

$$\frac{KC}{R_{vv}(q)} \approx \frac{1}{\bar{M}_w}\left(1 + \tfrac{1}{3}\langle \bar{R}_g^2 \rangle_z q^2\right) + 2A_2C \qquad (1)$$

where $K = 4\pi^2 n^2 (dn/dC)^2/(N_A \lambda_0^4)$ and $q = (4\pi n/\lambda_0)\sin(\theta/2)$ with N_A, dn/dC (in this case, it is 0.189 ± 0.002, in $CHCl_3$ at 25°C), n and λ_0 being Avogadro number, the specific

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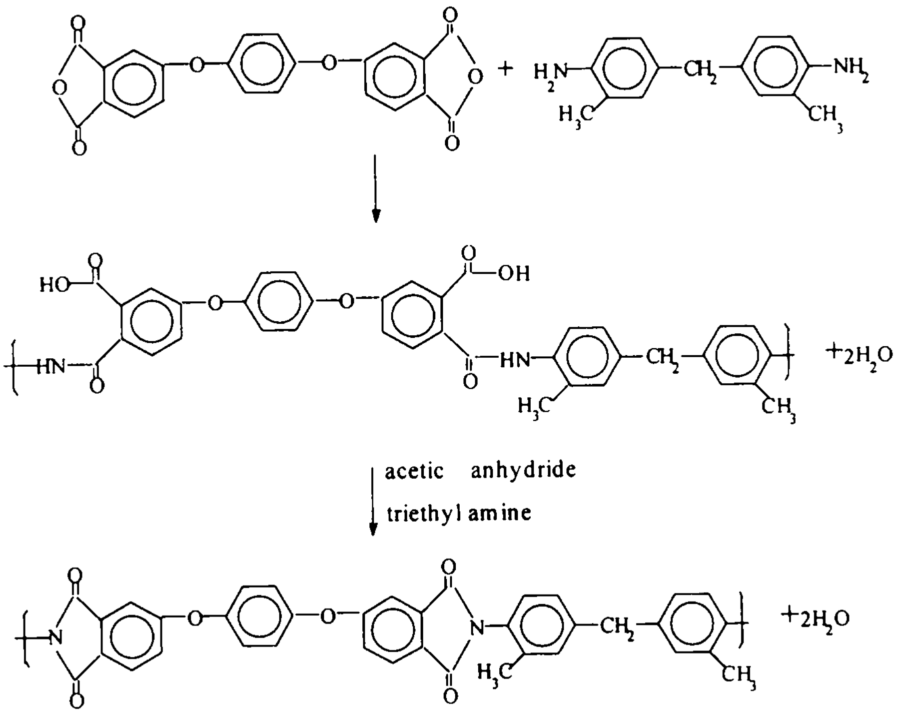

Scheme 1

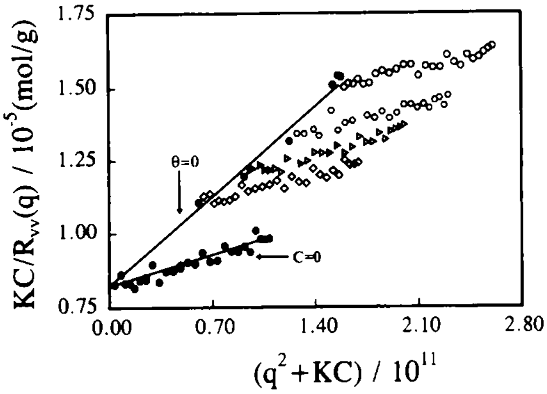

Figure 1 A typical Zimm plot for fraction 3 of the polyimide in $CHCl_3$ at 25°C, where *C* ranges from 4.06×10^{-4} to 2.03×10^{-3} g/ml

refractive index increment, the solvent refractive index and the wavelength of light *in vacuo*, respectively. A_2 is the second virial coefficient; and

$$(\bar{R}_g^2)_z^{\frac{1}{2}}$$

is the root-mean square z-average radius of gyration. Measuring $R_{vv}(q)$ at a set of C and q, we are able to determine $\bar{M}_w$,

$$(\bar{R}_g^2)_z^{\frac{1}{2}}$$

and A_2 from a Zimm plot which incorporates the extrapolation of $q \rightarrow 0$ and $C \rightarrow 0$ on a single grid[6]. *Figure 1* shows an example of a typical Zimm plot for fraction 3 of the polyimide in $CHCl_3$ at 25°C, where C ranges from 4.06×10^{-4} to 2.03×10^{-3} g/ml. On the basis of equation (1), we were able to determine the values of $\bar{M}_w$,

$$(\bar{R}_g^2)_z^{\frac{1}{2}}$$

and A_2 from the extrapolations of $[KC/R_{vv}(q)]_{q\rightarrow 0, c\rightarrow 0}$, $[KC/R_{vv}(q)]_{c\rightarrow 0}$ *versus* q^2 and $[KC/R_{vv}(q)]_{q\rightarrow 0}$ *versus* C, respectively.

According to the worm-like chain model[7], the following equation can be derived:

$$(\bar{R}_g^2)_z = l^2\left[\frac{L}{l} - 1 + \frac{2l}{L} - \frac{2l^2}{L^2}\left(1 - \exp\frac{-L}{l}\right)\right] \quad (2)$$

where l is persistent length; $L = nl_u$ (l_u is the projected length of the monomer unit;

$$n = \frac{\bar{M}_w}{M_0}$$

is the average number of monomer units on each chain), is the contour length. From equation (2), l can be calculated if

$$(\bar{R}_g^2)_z^{\frac{1}{2}}$$

has been obtained.

Intrinsic viscosities

Viscosity measurements were performed in an Ubbe capillary viscometer, and carried out in a water bath regulated at 25.0 and 30.0°C. The intrinsic viscosities were obtained from the intercept of the plots of

$$\frac{\eta_r - 1}{c}$$

and

$$\frac{\ln \eta_r}{c}$$

versus c in the limit $c \rightarrow 0$, where η_r is the relative viscosity. A representative plot of

$$\frac{\eta_r - 1}{c}$$

Table 1 The maximum excitation wavelengths of the polyimide solutions in different solvents

Solvent	DMAc	DMF	Chloroform	Dioxane	THF	EPC	γ-but
λ_{ex} (nm)[a]	378	387	391	368	367	392	394

[a] Maximum excitation wavelength

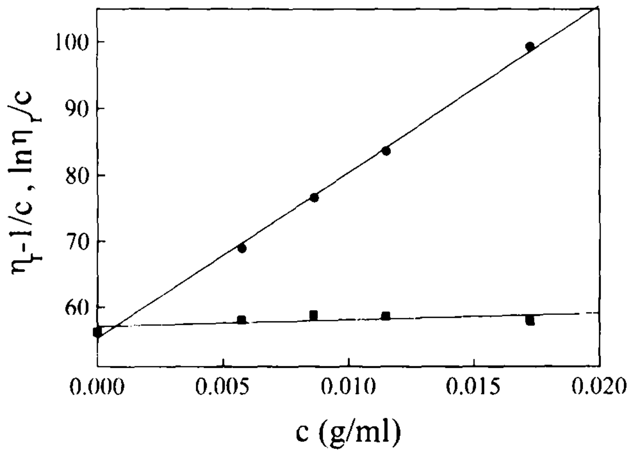

Figure 2 A representative plot of

$$\frac{\eta_r - 1}{c}$$

and

$$\frac{\ln \eta_r}{c}$$

versus c for the case of the polyimide in $CHCl_3$ at 30°C. (●, for

$$\frac{\eta_r - 1}{c}$$

versus c, ■, for

$$\frac{\ln \eta_r}{c}$$

versus c)

and

$$\frac{\ln \eta_r}{c}$$

versus c for the case of the polyimide in $CHCl_3$ at 30°C is illustrated in *Figure 2*.

Fluorescence spectroscopy

The polyimide was dissolved in different solvents at a concentration of 3–11 g/l. Fluorescence spectroscopy of the solutions above was conducted in a SPEX FL-2T2 spectrofluorometer at room temperature, and the fluorescence spectroscopy of the solvents was measured. Polyimide solutions and the relevant solvents contained in a standard quartz cell were excited in a front-face arrangement to minimize self-absorption at the same maximum excitation wavelength, where maximum absorptions occur respectively. *Table 1* lists the maximum excitation wavelengths for the solutions in different solvents. By subtracting the fluorescence spectroscopy of the solvents from that of the solutions respectively, the fluorescence spectra of the solutes in different solvents were obtained. The emission spectra are of interest in this study. The emission spectrum of the solute presented in a later section of this paper has been normalized as the concentration of the polyimide is 1 g/l.

Table 2 A few parameters determined by LLS and intrinsic viscosities in DMAc

Fraction	25°C in chloroform				25°C in DMAc
	$\bar{M}_w$ (g/mol)	$\bar{M}_w/\bar{M}_n$	$\bar{R}_g^2$ (nm)	l (nm)	$[\eta]$ (ml/g)
1	3.45×10^5	2.4	39	1.3	149.1
2	2.10×10^5	2.3	30	1.5	—
3	1.24×10^5	2.2	25	1.7	86.1
4	9.04×10^4	2.0	20	1.6	—
5	5.07×10^4	1.9	14	1.4	51.9

Relative errors: $\bar{M}_w$, $\pm$ 5%; $\bar{R}_g^2$, $\pm$ 10%; l, $\pm$ 15%; $\bar{M}_w/\bar{M}_n$, $\pm$ 10%

RESULTS AND DISCUSSION

A few solution parameters determined by LLS and intrinsic viscosities in chloroform and DMAc are listed in *Table 2*. Judging from the values of l (persistent length), it is concluded that the polymer has a flexible chain conformation in chloroform, compared with that of polystyrene ($l \cong 1.0$), which is a typical polymer.

By fitting

$$(\bar{R}_g^2)_z^{\frac{1}{2}}$$

as a function of $\bar{M}_w$, equation (3) can be obtained as follows:

$$(\bar{R}_g^2)_z^{\frac{1}{2}} = 4.95\times10^{-2}\bar{M}_w^{0.52} \quad (3)$$

The exponential factor falls into those of typical flexible polymers, indicating also that the chain has a flexible conformation in chloroform. In order to further discuss the chain conformation of the polyimide in organic solvents, the value of the unperturbed dimension was determined from the Stockmayer–Fixman equation[8].

$$\frac{[\eta]}{\bar{M}_w^{0.5}} = k_\theta + B\phi_0\bar{M}_w^{0.5} \quad (4)$$

where

$$k_\theta = \phi_0\left(\frac{\bar{R}_0^2)}{\bar{M}_w}\right)^{\frac{3}{2}}$$

is the intercept in the plot of

$$\frac{[\eta]}{\bar{M}_w^{0.5}}$$

versus $\bar{M}_w^{0.5}$ (as ploted in *Figure 3*), and

$$\left(\frac{\bar{R}_0^2)}{\bar{M}_w}\right)^{\frac{1}{2}}$$

,postulated from the value of k_θ, can characterize the unperturbed dimension.

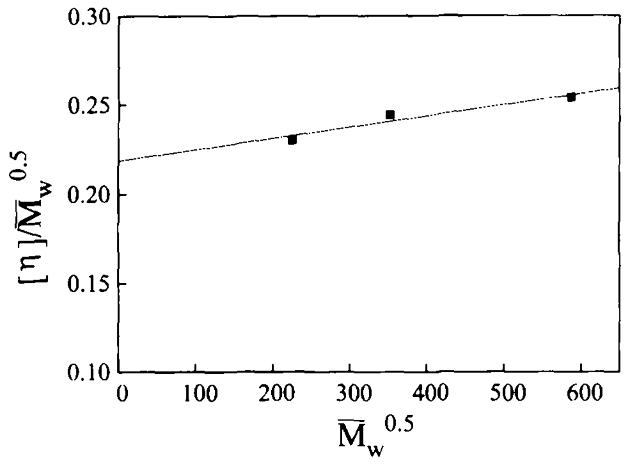

Figure 3 Plot of $\frac{[\eta]}{\bar{M}_w^{0.5}}$ *versus* $\bar{M}_w^{0.5}$

Table 3 The parameters k_θ and $\left(\frac{\bar{R}_0^2}{\bar{M}_w}\right)^{\frac{1}{2}}$ derived from solution in DMAc by the Stockmeyer–Fixman equation

	k_θ (ml/g)	$\left(\frac{\bar{R}_0^2}{\bar{M}_w}\right)^{\frac{1}{2}}$ $\times 10^4$ (nm)
DMAc	0.219 ± 0.007	956.8 ± 30.6

Table 3 lists the parameters k_θ and $\left(\frac{\bar{R}_0^2}{\bar{M}_w}\right)^{\frac{1}{2}}$ derived from the solutions of the fractions in DMAc at 25°C. It can be inferred that the polyimide chain has a flexible conformation in the solvent DMAc, based on the fact that the unperturbed dimension of the polymer is in the range of flexible chains[9].

Although the polyimide chain in DMAc and chloroform has a flexible conformation, the degree of expansion in the two solvents is not unique, postulated from the intrinsic viscosities in different solvents measured at 30°C.

Figure 4 shows the dependence of the intrinsic viscosity at 30°C on the solubility parameters of the solvents. It is easily seen that the polyimide chain in different solvents shows varying degrees of expansion, with the most expanded chain conformation in DMAc, resulting in the largest intrinsic viscosity.

The degree of chain expansion in different solvents can also be contrasted by fluorescence spectroscopy of the polyimide dilute solutions in different solvents (see *Figure 5*). According to previous studies[11], the broad and structureless emission spectrum of a dilute solution of polyimide is due to the intramolecular charge transfer of polyimide chains. In our case, the maximum wavelengths of the emission spectra of dilute solutions in different solvents, are in the range 485–515 nm, while their relative intensities show major differences as depicted in *Figure 6*, with the lowest intensity in DMAc, indicating that the chain in DMAc is most expanded, and least wavy, so that the intramolecular charge transfer takes much less effect, i.e. the relative intensity is the lowest.

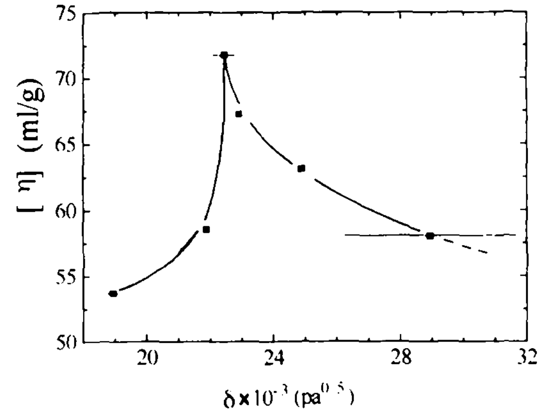

Figure 4 Dependence of the intrinsic viscosity at 30°C on the solubility parameter of solvents (the solubility parameters of the solvents are quoted from Ref [10])

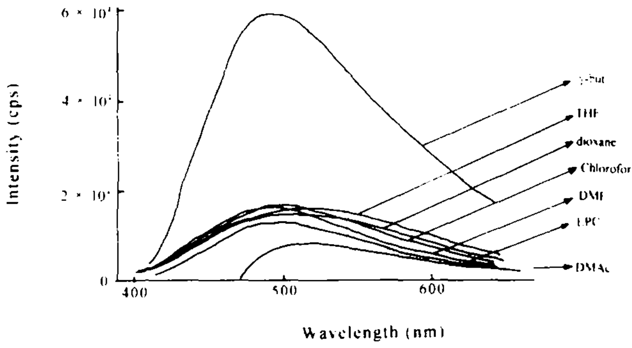

Figure 5 Fluorescence emission spectra of the polyimide solutions in different solvents

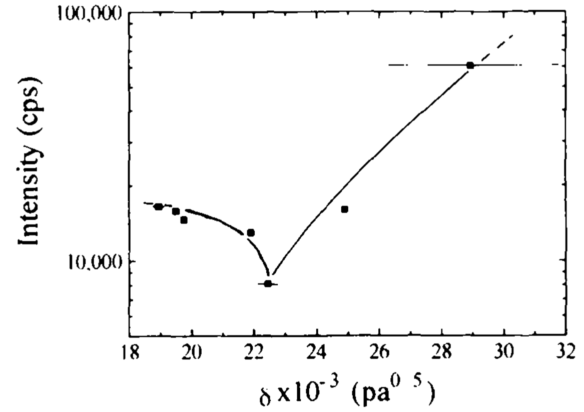

Figure 6 Fluorescence intensity of the emission spectra of the polyimide solutions in different solvents

ACKNOWLEDGEMENTS

Professor Tianbai He is greatly indebted to the Outstanding Young Scientist Foundation of the National Natural Science Foundation of China.

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