



Critical concentration and scaling exponents of one soluble polyimide—from dilute to semidilute entangled solutions



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ABSTRACT

A soluble polyimide (6FDA-TFDB) was synthesized and its properties in solution were investigated. The relationship between specific viscosity and concentration is established using rheometer and applying Zimm model (dilute solution), Rouse–Zimm model (semidilute unentangled solution), and Doi–Edwards model (semidilute entangled solution). In addition, the overlapped concentration (C^*) and semidilute entangled concentration (C_e) are determined. Results showed that all of the scaling exponents are higher than the theoretical values. The influence of factors, namely, electrostatic interaction, hydrogen bonding, dipole–dipole interaction and polydispersity index under different conditions (i.e., temperature, salt, and solvent) on critical concentration and scaling exponents are investigated extensively. In order to confirm the related conclusions, two soluble polyimides with different chemical structures are also synthesized and compared with the above results. The reasons for the deviation of scaling exponents are also discussed.

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1. Introduction

Polyimide (PI) is a high-performance polymer that exists in different forms, such as resin, film, fiber, and foam [1–8], which have been applied in microelectronics, aerospace, and other technologies. PI exhibits excellent chemical resistance and is normally insoluble in common organic solvents, which hinders investigation of its solution property for a variety of applications. Thus, soluble PIs have been designed and synthesized. In general, three approaches are available to obtain soluble PIs: (1) addition of $-\text{CH}_2-$ or $-\text{O}-$ groups between benzene ring to break the conjugation effect, and thus promoting chain flexibility; (2) addition of large volume pendent groups ($-\text{CH}_3$, $-\text{CF}_3$, etc.) on benzene ring to break the $\pi-\pi$ stacking, thereby facilitating solvent interaction with PI segments; (3) addition of strong electrophilic groups in chains to increase polarity, thereby increasing the interaction between polar solvent and PI segments. Some soluble PIs have been synthesized

successfully and their dilute solution properties have been studied. Wu and Siddiq used laser light scattering to study the relationship between z-average radius of gyration $\langle R_g \rangle$ and weight-average molecular weight M_w of two soluble PIs; using the wormlike chain model, they found that the two PIs have a slightly extended coil conformation in CHCl_3 [9]. Liu and coworkers studied two isomerized PIs, namely, poly(6FDA/3,3'-DMB) and poly(6FDA/2,2'-DMB), in DMF or THF with LiBr or tetrabutylammonium bromide (TBAB) using size exclusion chromatography (SEC) coupled with multi-detectors (RI-LLS-viscometer). In addition, the corresponding parameters related to conformations α and ν , which were evaluated from the scaling relationships $[\eta] = K_\eta M^\alpha$ and $R_g = K_g M^\nu$, are found to be 0.66–0.69 and 0.53–0.56, respectively [10,11]. Owing to the chain rigidity, the wormlike model is suitable to describe these PIs in dilute solution.

However, most studies for soluble PI focused on dilute solution because of lack of effective characterization techniques for high concentration solutions due to multi-light scattering, complicated inter-chain interaction, and unstable states. Fortunately, current rheometer can measure viscosity of polymer solution in a wide range of concentration with high precision, thereby providing a possibility to investigate the solution property at high

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concentrations.

In this study, one soluble PI was synthesized by 2,2'-bis(trifluoromethyl)-4,4'-diaminobiphenyl (TFDB) and 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6FDA). The soluble PI has good solubility, low water absorption rate, low dielectric constant, and high transparency [12], which are favorable for use as colorless film [13]. Based on rheological data and scaling theory, the scaling relationship between specific viscosity (η_{sp}) and concentration is established and the influence of factors on critical concentration and scaling exponents are discussed.

2. Theory

2.1. The intrinsic viscosity and its relationship between coil size and molar mass

The intrinsic viscosity is one of important parameters for polymer samples, which can be determined from the Huggins and Kraemer equations [14,15].

$$\frac{\eta_{sp}}{c} = [\eta] + k_H[\eta]^2 c \quad (1)$$

$$\frac{(\ln \eta_r)}{c} = [\eta] - k_K[\eta]^2 c \quad (2)$$

The k_H is the Huggins coefficient, k_K is the Kraemer coefficient, $\eta_r = \eta/\eta_s$ is the relative viscosity, $\eta_{sp} = (\eta - \eta_s)/\eta_s$ is the specific viscosity. Plots of η_{sp}/c and $\ln \eta_r/c$ versus c can get two straight lines, the intercept at $c = 0$ corresponds to the intrinsic viscosity. Based on the Flory-Fox equation, the relationship between intrinsic viscosity, coil size and molar mass can be determined [16]:

$$[\eta] = \phi \frac{R^3}{M} \quad (3)$$

where $\phi = 2.5 \times 10^{23} \text{ mol}^{-1}$ is a universal constant for all polymer-solvent system, R is the root-mean-square end-to-end distance, M is the molar mass of polymer.

3. Experimental

3.1. Chemicals

2,2'-Bis(trifluoromethyl)-4,4'-diaminobiphenyl (TFDB), 2,2-bis(3,4-dicarboxy-phenyl)hexafluoropropane dianhydride (6FDA), 4,4'-Diamino-2,2'-dimethylbiphenyl (DMB), 4,4'-Oxydiphthalic dianhydride (ODPA) were obtained from Beijing Multi Technology. Before reaction, all the materials were purified by sublimation. In order to reduce the effect of water, N,N-dimethylacetamide (DMAc) was dried in the presence of P_2O_5 overnight and the reaction was carried out at the room temperature with relative humidity less than 50%. Other chemicals were used without further purification.

3.2. Synthesis of polyamic acid (PAA)

2,2'-Bis(trifluoromethyl)-4,4'-diamino-biphenyl (TFDB) was added in N,N-dimethylacetamide (DMAc) solvent, stirred until TFDB was dissolved completely. Then the same molar amount of 2,2-bis(3,4-dicarboxyphenyl)hexafluoro-propane dianhydride (6FDA) was added and the mixture was stirred for 48 h at ambient temperature under nitrogen atmosphere.

3.3. Synthesis of polyimide (PI)

Triethylamine and 0.07wt% acetic anhydride were added into

the above PAA solution, the mixture reacted for 4 h to yield homogeneous PI solution. Then the solution was poured slowly into methanol for precipitation. Solid PI was washed thoroughly with methanol, and then redissolved in DMAc and precipitated in methanol again to obtain a purified sample. Finally, it was dried in a vacuum oven at 80 °C overnight. The synthetic procedure for 6FDA-TFDB, 6FDA-DMB, and ODP-A-TFDB polyimides was shown in Scheme 1.

3.4. Precipitation fractionation of PI sample

10.04 g PI sample (6FDA-TFDB) were solved in 1 L THF, then raise the temperature to 25 °C (5 °C higher than the room temperature) and kept at least 24 h to make sure that the solution was homogeneous. Then the water (precipitator) was dropped to PI solution. When 120 mL water was added in the solution, the precipitation appeared. Then another 40 mL water was added to make the solution turbid enough, and the temperature was kept at 25 °C at least 24 h to reach an equilibrium of dissolution-precipitation. Then the precipitated PI sample was collected by centrifugation (8000 rpm, 20 min), washed by water twice and dried in vacuum. The filtrate was repeated the previous step four times, and the volumes of water added were 25, 30, 40, and 100 mL, respectively. Five fractions were available finally.

3.5. Measurements

Fourier transform infrared (FTIR) spectra were recorded on a Bruker Vertex 70 spectrometer. ^1H NMR spectra were recorded using a Bruker AV400 NMR spectrometer in deuterated trichloromethane (CDCl_3 with 0.05% v/v TMS). Size exclusion chromatography (SEC) and multidetectors systems consist of a 515 pump (Waters Technologies), a 717 autosampler (Waters Technologies), two PL-gel 10 μm Mixed B-LS columns (Agilent Technologies), and a 2414 refractive index detector (RI) (Waters Technologies), Wyatt DAWN HELEOS II multi-angle laser light scattering detector (MALLS, 18 angles). The SEC system was operated at 35 °C using DMF with 3.1 mmol/L TBAB as the mobile phase at a flow rate of 1 mL/min. All rheological measurements were carried out with a TA instruments DHR-2 stress-controlled rheometer where a 40 mm, 2° cone plate geometry was used. Temperature-controlled Peliter plate was used to control the temperature. The sweep of frequency was chosen from 1 to 1000 rad/s. In order to prevent the evaporation of solvent, two semicircle 60 mm iron plates were covered around the plate geometry, and silicone grease was filled around the gap of the iron plates.

3.6. Basic characterization of PI samples

Fig. S1a, S1b, S1c, were the FT-IR spectra of 6FDA-TFDB, 6FDA-DMB, ODP-A-TFDB, respectively. For 6FDA-TFDB, the peak at 1786 cm^{-1} was assigned to C=O asymmetric stretching vibration, the peak at 1726 cm^{-1} came from C=O symmetric stretching vibration, and that at 1364 cm^{-1} was due to C–N stretching vibration. For 6FDA-DMB, the three peaks were at 1786 cm^{-1} , 1726 cm^{-1} and 1366 cm^{-1} . For ODP-A-TFDB, the three peaks were at 1782 cm^{-1} , 1722 cm^{-1} and 1360 cm^{-1} . These three peaks indicated the presence of imide ring. Moreover, for 6FDA-TFDB, 6FDA-DMB, the peak at 718 cm^{-1} and 719 cm^{-1} were a weak deformation of imide ring. Meanwhile, for three soluble PI samples, the vibration from –COOH and N–H groups cannot be found, which confirmed a complete imidization.

In our previous work, we found that addition of salts (LiBr or TBAB) was necessary to obtain a normal SEC elution curve [10,11]. Fig. S2 showed the SEC curve with a single peak, and the M_w was

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