A Method to Break Charge Transfer Complex of Polyimide: A Study on Solution Behavior

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ABSTRACT: Charge transfer complex strongly affects the optical transparency of polyimide film. Here, solution behavior of a polyimide derived from 3,3′,4,4′ biphenyltetracarboxylic dianhydride and 1,4-bis(3-aminopropyl)piperazine in acetic acid, chloroform, and their mixed solvents is investigated in detail by light scattering. It is found that the polyimide existed as single chains in acetic acid owing to the acid-base interaction. However, association is observed in chloroform solution because of the charge transfer complex and enhanced by increasing the solution concentration. To break the charge transfer interaction and clear the association, only a small amount of acetic acid is required to add into the chloroform solution owing to the protonation of the diamine groups, confirmed by the zeta potential measurements. Simultaneously, the associates disappear quickly after addition of acetic acid. This study will provide a novel method for preparation of high optical transparent polyimide film by simply tuning the solvent. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

INTRODUCTION

Aromatic polyimides are of a high performance polymer material, which have incredibly high thermal and chemical stability, flame resistance, radiation resistance, mechanical strength, low dielectric constant, and good flexibility.[1,2] Hence, aromatic polyimides have many applications ranging from aerospace to microelectronics, and so on.[3–8] However, their application is often limited by processing difficulties due to the high melting temperature and poor solubility. Many efforts have been spent on the synthesis of novel aromatic polyimides to improve the processability,[9] including the introduction of flexible linkages,[10–14] bulky substitutions,[15–17] and noncoplanar or asymmetric monomers into the backbone.[18–20]

Recently, how to improve effectively the optical transparency of polyimide film has attracted much attention owing to its optical and electric applications, such as optical waveguides.[21–23] However, most conventional polyimide films show considerable coloration, from pale yellow to deep brown. This is generally attributed to the formation of charge transfer complex owing to

intramolecular or intermolecular charge transfer interactions between alternating electron-donor (diamine) and electron-acceptor (dianhydride) moieties.[24] In other words, to obtain less colored or colorless polyimide film, one effective method is to inhibit the formation of charge transfer complex by weakening the charge transfer interaction. Thus, structural design of polyimide has been widely studied,[25–27] such as the trifluoromethyl-containing poly(ester imides)s.[28–30]

Besides synthesis of novel polyimides, an alternative method to inhibit formation of charge transfer complex or molecular association is to tune the solvent in the process of film formation[31] owing to the important influence of solvent on formation of molecular association. Because the process of film formation is usually very fast, the structure of initial solution cannot reorganize itself during the short time. Thus morphologies and properties of film depend on the conformation of polyimides in the initial solution at a certain extent. In other words, through adjusting the conformation or association of polyimides molecules in the initial solution in different organic solvents will
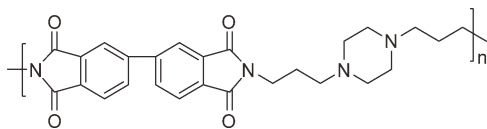
Figure 1. Chemical structure of BPPAP.

indirectly control the optical properties of polyimides films. Thus a detailed understanding of the relationships among molecular structure, molecular association in the solution/film and optical property of polyimide film is of great significance.[31–36] However, systematic studies on the solution behavior of polyimides, especially by laser light scattering (LLS) technique,[37] are rarely reported in literature.[38,39]

LLS is a very important technique to study the association of polymer in solution. Here, we investigated solution behavior of a polyimide derived from 3,3′,4,4′ biphenyltetracarboxylic dianhydride and 1,4-bis(3-aminopropyl)piperazine (BPPAP) in acetic acid, chloroform, and their mixed solvents by using this technique in detail. The chemical structure of BPPAP is shown in Figure 1. By combining the solution behavior and optical properties of BPPAP reported in the previous study,[12] an easy method to prepare colorless polyimide films by simply tuning the solvent was suggested.

EXPERIMENTAL

Material

Acetic acid and chloroform of analytical grade were purchased from Beijing chemical company. The samples were used as received without further purification. BPPAP was synthesized as reported in the previous study.[12] BPPAP (40.0 mg) was dissolved in organic solvents (acetic acid and chloroform) and diluted to precisely 10.00 mL in a volumetric flask to give stock solutions of concentration 4.0 mg mL^{-1}. The stock solutions were then diluted to a certain concentration used in the experiments with organic solvents. The tested concentration range is from 0.52 to 1.70 mg mL^{-1} for acetic acid solution, and from 0.020 to 1.57 mg mL^{-1} for chloroform solution. The solutions were filtered through a 0.22 μm PTFE membrane for dust free before light scattering experiments.

Laser Light Scattering

A commercialized spectrometer from Brookhaven Instruments Corporation (BI-200SM Goniometer, Holtsville, NY) was used to perform both static light scattering (SLS) and dynamic light scattering (DLS) over a scattering angular range of 15–155°. A 100 mW solid-state laser (GXC-III, CNI, Changchun, China) operating at 532 nm was used as the light source, and a BI-TurboCo Digital Correlator (Brookhaven Instruments Corporation) was used to collect and process data. In SLS, the angular dependence of the excess absolute time-averaged scattered intensity, known as the Rayleigh ratio $R_{vv}(\theta)$, was measured. For a very dilute solution, the weight-averaged molar mass (M_w) and the root mean-square radius of gyration (R_g) can be obtained on the basis of

$$HC/R_{vv}(\theta) = (1/M_w)\left[1 + (1/3)R_g^2 q^2\right] + 2A_2 C \quad (1)$$

where $H = 4\pi^2 n^2 (\mathrm{d}n/\mathrm{d}C)^2/(N_A\lambda^4)$ and $q = 4\pi n/\lambda \, \sin(\theta/2)$ with N_A, n, $\mathrm{d}n/\mathrm{d}C$, and λ being the Avogadro's number, the solvent refractive index, the specific refractive index increment, and the

wavelength of light in a vacuum, respectively. The $\mathrm{d}n/\mathrm{d}C$ values of BPPAP in acetic acid and chloroform were obtained according to the literature, being 0.17 and 0.10, respectively.[37] In dynamic LLS, the intensity–intensity time correlation function $G^{(2)}(\tau)$ in the self-beating mode was measured

$$G^{(2)}(\tau) = A\left[1 + \beta\left|g^{(1)}(\tau)\right|^2\right] \quad (2)$$

where A is the measured base line, β is a coherence factor, τ is the delay time, and $g(1)(\tau)$ is the normalized first-order electric field time correlation function. $g(1)(\tau)$ is related to the line width distribution $G(\Gamma)$ by

$$g^{(1)}(\tau) = \int_0^\infty G(\Gamma)e^{-\Gamma\tau}d\Gamma \quad (3)$$

By using a Laplace inversion program, CONTIN,[40] the normalized distribution function of the characteristic line width $G(\Gamma)$ was obtained. The average line width $\overline{\Gamma}$ was calculated according to $\overline{\Gamma} = \int \Gamma G(\Gamma)d\Gamma$. The polydispersity index, PDI, was defined as $\mathrm{PDI} = \mu_2/\overline{\Gamma}^2$ with $\mu_2 = \int (\Gamma - \overline{\Gamma})^2 G(\Gamma)d\Gamma$. $\overline{\Gamma}$ is a function of both C and q, which can be expressed as

$$\overline{\Gamma}/q^2 = D(1 + k_d C)\left[1 + f\left(R_g q\right)^2\right] \quad (4)$$

with D, k_d, and f being the translational diffusive coefficient, the diffusion second virial coefficient, and a dimensionless constant, respectively. D can be further converted into the hydrodynamic radius R_h by using the Stokes-Einstein equation:

$$D = k_B T/6\pi\eta R_h \quad (5)$$

where k_B, T, and η are the Boltzmann constant, the absolute temperature, and the viscosity of the solvent, respectively. The R_h values in this paper are determined according to eq. (5), but the translational diffusive coefficients D are obtained extrapolated at zero degree, but not at infinite dilution. The bimodal distribution of BPPAP in chloroform solution was determined according to Sato's method.[41] In brief, the static structure factors of the fast mode and the slow mode were obtained by

$$\widehat{S}_{\text{fast}}(q) = \widehat{S}(q) \times \frac{A_{\text{fast}}}{A_{\text{fast}} + A_{\text{slow}}}$$
$$\widehat{S}_{\text{slow}}(q) = \widehat{S}(q) \times \frac{A_{\text{slow}}}{A_{\text{fast}} + A_{\text{slow}}} \quad (6)$$

where $\widehat{S}(q)$, A_{fast}, and A_{slow} being the total static structure factor obtained by SLS, the integrated area in R_h distribution curves of the fast mode and the slow mode, respectively. Then the z-average mean-square radius of gyration of the fast mode and the slow mode can be calculated by

$$\widehat{S}_{\text{fast}}(q)^{-1} = \widehat{S}_{\text{fast}}(0)^{-1}\left[1 + \frac{1}{3}q^2 R_{g,\text{slow}}^2\right]$$
$$\widehat{S}_{\text{slow}}(q)^{-1} = \widehat{S}_{\text{slow}}(0)^{-1}\left[1 + \frac{1}{3}q^2 R_{g,\text{fast}}^2\right] \quad (7)$$

where $\widehat{S}(0)$ being the static structure factor at zero angle.

Zeta Potential Measurements

A Zeta potential analyzer from Brookhaven Instruments Corporation (ZetaPALS, Holtsville, NY) was used to measure the Zeta potential of BPPAP in organic solvents at 25°C. The Palladium electrode ensured the validation of the measurement in organic solvents. The mobility (μ_e) of BPPAP molecules was determined by the analyzer via phase analysis light scattering. The zeta potential ζ was calculated according to:

$$\mu_e = \zeta \varepsilon / \eta \qquad (8)$$

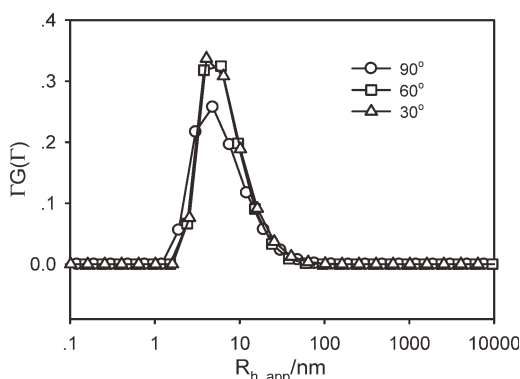with ε and η being the dielectric constant and the viscosity of the solvent, respectively.

RESULTS AND DISCUSSION

The polyimide BPAPP exhibited a unique solubility, as reported in previous work.[12] It was readily soluble in organic acids. As for neutral solvents, it is limited to chloroform and dichloromethane. However, the polyimide film casting from different kinds of solvents showed different optical properties, for example, transparent in organic acids and opaque in chloroform. To clarify the mechanism of the above phenomena at molecular level, acetic acid and chloroform were selected as the solvents, and the solution behavior of BPPAP was investigated.
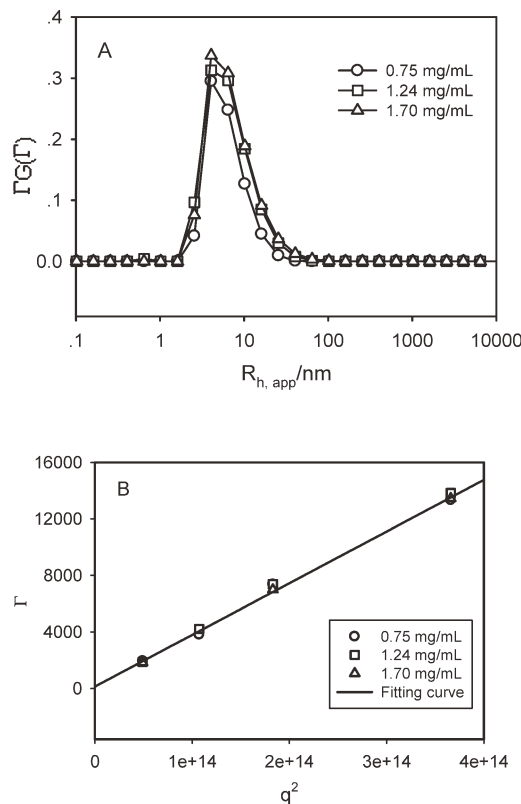
BPPAP in Acetic Acid

Figure 2 shows the angular dependence of hydrodynamic radius distribution of BPPAP in acetic acid at 1.70 mg mL^{-1}. There was only one diffusional model. The size was about 4.6 nm according to eq. (5). Considering the molecular weight of BPPAP, single chains existed in acetic acid. It had no angular dependence since the size was very small.

To investigate further whether there was any association for BPPAP in acetic acid, Figure 3(A) shows the concentration dependence of hydrodynamic radius distribution at 30°. As the concentration increased from 0.75 to 1.70 mg mL^{-1}, the size hardly changed. The Γ versus q^2 plot [Figure 3(B)] is linear and passes through the origin, indicating that the relaxation mode of BPPAP in acetic acid is diffusive. It was proposed that the conformation of BPPAP in acetic acid was stable in the studied concentration, confirming that single chains existed in acetic acid indeed. Because the size is very small ($<\lambda/20$), the light scattering
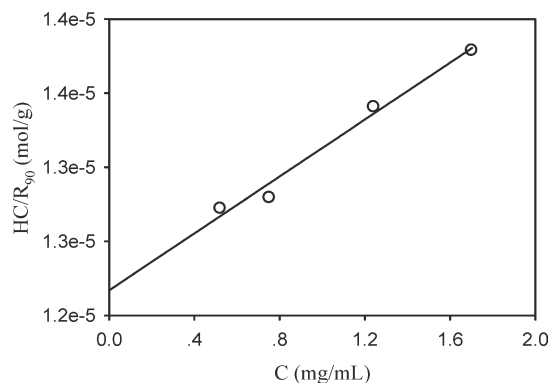

Figure 3. A: Concentration dependence (mg mL^{-1}) of hydrodynamic radius distribution of BPPAP in acetic acid at 30°; (B) Plot of Γ versus q^2.

intensity is angular independent. Thus, the second virial coefficient and the molecular weight were determined by the equation:

$$HC/R_{vv}(90) = (1/M_w) + 2A_2C \qquad (9)$$

using the light scattering intensity data at 90°. Figure 4 shows the SLS results of BPPAP in acetic acid. The second virial coefficient was calculated as 4.8×10^{-4} mL mol^{-1} g^{-2}, indicating that acetic acid was a good solvent for BPPAP. The molecular weight was calculated as 8.2×10^4 g mol^{-1}. Considering the molecular weight of the repeating unit is 458 g mol^{-1}, the degree of polymerization (n) is 179. The results are listed in Table I.

Figure 2. Angular dependence of hydrodynamic radius distribution of BPPAP in acetic acid. Concentration: 1.70 mg mL^{-1}.

Figure 4. SLS results of BPPAP in acetic acid.

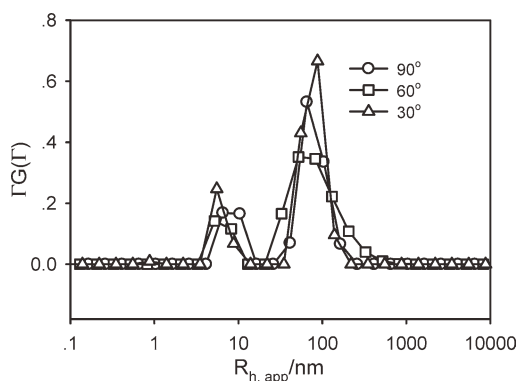**Table I.** The Results Obtained from SLS and DLS Measurements in Organic Solvents

Organic solvents	$R_{h,sing}$[a] (nm)	$R_{h,asso}$[a] (nm)	$R_{g,asso}$ (nm)	$R_{g,asso}/R_{h,asso}$	A_2 (10^{-4}mL mol g^{-2})	W_{asso}	$M_{w,sing}$ (10^4g mol^{-1})	$M_{w,asso}$ (10^4g mol^{-1})
Acetic acid	4.6	–	–	–	4.8	–	8.2	–
Chloroform[b]	5.1	61.3	68.2	1.1	−2.5	5%	8.2	920

[a]The subscripts of 'sing' and 'asso' represent the values of the single chains and the associates, respectively., [b]The solution concentration is 0.26 mg mL^{-1}.
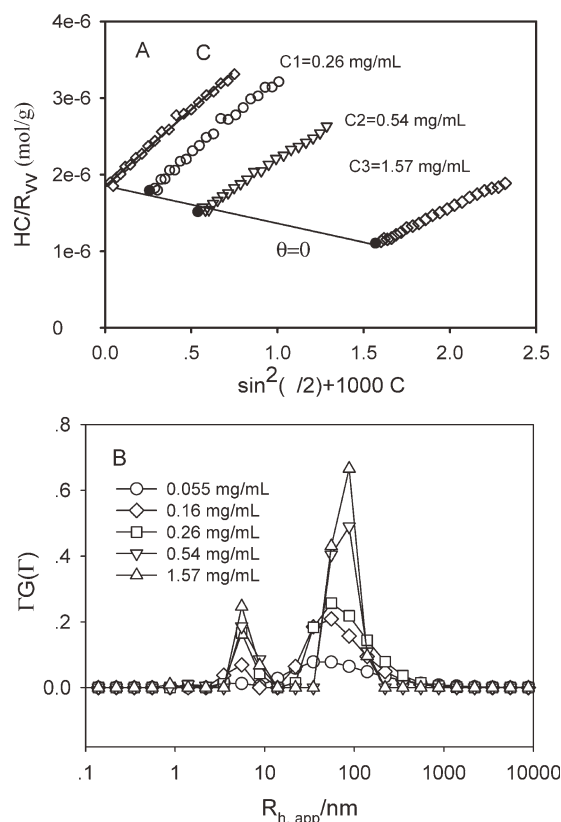
BPPAP in Chloroform

Different from that in acetic acid, BPPAP showed two diffusion modes in chloroform, as shown in Figure 5. The size of fast mode ($C = 1.57$ mg mL^{-1}) was 6.5 nm, slightly larger than that in acetic acid. The size of the slow mode was 71.7 nm, corresponding to the molecular associates of BPPAP. According to eqs. (2) and (3), the size distributions in Figure 5 were averaged by intensity. Because the scattered intensity was roughly proportional to the sixth power of the size, the number of the large associates in the system was much less than that of the individual chains. The strong angular dependence of light scattering intensity in SLS results also confirmed the association in chloroform solution [Figure 6(A)]. Taking C3 = 1.57 mg mL^{-1} as an example, the apparent root mean-square radius of gyration and molecular weight were 60.5 nm and 8.53 × 10^5 g mol^{-1}, respectively, much larger than that of single chains.

The concentration dependence of hydrodynamic radius distribution of BPPAP in chloroform at 30° was shown in Figure 6(B). As the concentration increased from 0.055 to 1.57 mg mL^{-1}, the size of the fast mode increases from 3.9 to 6.7 nm and the size of the slow mode increases from 43.0 to 71.7 nm, indicating that the association became stronger with increasing the concentration. To make it clear, Figure 7 shows concentration dependence on the size of the association. When the concentration of BPPAP increased from 0.020 to 0.38 mg mL^{-1}, the size increased from 32 to 70 nm. Then the size kept constant with further increasing concentration. Such critical concentrations were also observed in the previous study.[42] The apparent root mean-square radius of gyration and apparent molecular weight from SLS results showed the same trend [Figure 6(A)]. When

the concentration of BPPAP increases from 0.26 to 1.57 mg mL^{-1}, the apparent root mean-square radius of gyration hardly changes (C1: 64.2 nm; C2: 61.1 nm; C3: 60.5 nm). However, the apparent molecular weight increases (C1: 5.59 × 10^5 g mol^{-1}; C2: 6.62 × 10^5 g mol^{-1}; C3: 8.53 × 10^5 g mol^{-1}), owing to the increasing amount of the associates. The second virial coefficient of BPPAP in chloroform was calculated as −2.5 × 10^{-4} mL mol g^{-2}, indicating that chloroform was a poor solvent for BPPAP. Both DLS and SLS results proved that the association was enhanced by the increase of BPPAP concentration. The values of the apparent root mean-square radius of gyration and apparent molecular weight obtained in this approach are used only to indicate the degree of association; they do not have much physical meanings.

Figure 5. Angular dependence of hydrodynamic radius distribution of BPPAP in chloroform. Concentration: 1.57 mg mL^{-1}.

Figure 6. A: SLS results of BPPAP in chloroform; B: Concentration dependence (mg mL^{-1}) of hydrodynamic radius distribution of BPPAP in chloroform at 30°.
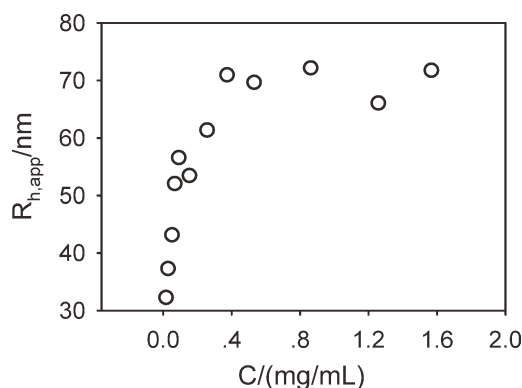
Figure 7. Concentration dependence of the association of BPPAP in chloroform.

According to Sato and coworkers,[41] the static structure factors $[S(q)]$ of the fast mode and the slow mode were able to be calculated separately, by the combination of the SLS and DLS data. The radius of gyration was then obtained from the S(q) by using the scattering data at 30°, 60°, and 90°. Taking C1 = 0.26 mg mL^{-1} as an example, the apparent root mean-square radius of gyration was 68.2 nm and independent on the concentration in this regime (C2: 66.2 nm; C3: 67.8 nm). The conformation of the associate was inferred from the R_g/R_h ratio. It was well established in literature that the R_g/R_h ratios were 0.775 and 1.5 for solid sphere and random coil, respectively.[43] The $R_{g,app}/R_{h,app}$ ratio of the associate formed by BPPAP in chloroform solution was ~ 1.1, much >0.775, indicating that the associate was in a loose conformation. In addition, the $\widehat{S}_{fast}(0)$ and $\widehat{S}_{slow}(0)$ is obtained according to eq. (7), being 7.75 × 10^4 and 4.63 × 10^5 g mol^{-1}, respectively. Assuming the fast mode were all single chains [there may be some oligomers, even at high concentration, see Figure 6(B)], with the known molecular weight of BPPAP single chains (8.2 × 10^4 g mol^{-1}), we can calculate the weight ratio and the $M_{w,app}$ of the associate according to the equation:

$$M_{w,fast} \times W_{fast} = \widehat{S}_{fast}(0)^{-1}$$
$$M_{w,slow} \times W_{slow} = \widehat{S}_{slow}(0)^{-1}$$

(10)

where W_{fast}, W_{slow}, $M_{w,fast}$, and $M_{w,slow}$ being the weight content of the fast mode and the slow mode, the molecular weight of the fast mode and the slow mode, respectively. The calculated results indicated that about 5% (weight ratio) of BPPAP chains formed the associate at 0.26 mg mL^{-1}. The apparent molecular

Table II. Zeta Potential Measurements of BPPAP in Organic Solvents

| Organic solvents	Mobility (μcm s^{-1} V^{-1})	Zeta potential (mV)
Acetic acid	0.103 ± 0.007	24.8 ± 1.7
Chloroform	−0.118 ± 0.097	−14.9 ± 12.3
Mixed solvent[a]	0.191 ± 0.042	26.2 ± 5.2

[a]The chloroform-acetic acid ratio (w/w) in mixed solvent is 96/4.

weight of the associate was about 9.2 × 10^6 g mol^{-1}, corresponding to an association number of ~ 110.

As reported in literature, the aggregation or association of polyimides in condensed state or in solution was attributed to the intermolecular charge transfer interaction between electron-donor (diamine) and electron-acceptor (dianhydride) units located on the chain backbone. Since the aggregate was in equilibrium with the single polymer chains, it was more proper to call it "associates," as suggested by Elias.[44] In our experiment, diamine of BPPAP has strong electron-donating ability and dianhydride has electron-withdrawing ability. Thus in chloroform solution, molecular chains were inclined to form strong charge transfer complex,[45] which corresponded to the slow mode in Figure 5. As expected, the association became strong when the concentration increased. However, when BPPAP was dissolved in the acetic acid, diamine would be protonated owing to acid-base interaction, and change from electron-donating unit to electron-withdrawing. Zeta potential measurements (Table II) demonstrated that the zeta potential of BPPAP in acetic acid was 24.8 ± 1.7 mV, indicating that the protonated process occurred, while BPPAP was neutralized in chloroform. As a result, intermolecular interaction via charge transfer complexes disappeared. The association thus dropped away and BPPAP existed as single chains.

The above results are closely correlated with the optical properties of BPPAP films. When the film was casted from acetic acid, BPPAP existed as single chains owing to the repulsive electrostatic interaction. Charge transfer complex was absent either in the solution or the film, thus the film was transparent. While in chloroform, charge transfer complex occurred, as a result, BPPAP film appeared opaque. It was proposed that the optical properties of BPPAP film significantly affected by the solution behavior. Just by simply tuning the solvent composition, we can control the properties of BPPAP film.

BPPAP in Acetic Acid and Chloroform Mixed Solvents
To get optical transparent films, one method is to weaken the association of BPPAP in chloroform. As discussed above, acid-base interaction between acetic acid and BPPAP can break the charge transfer complexes. However, the properties of polyimides films depend on the components of solvent, including
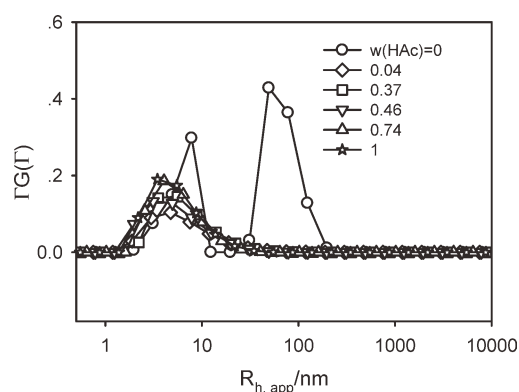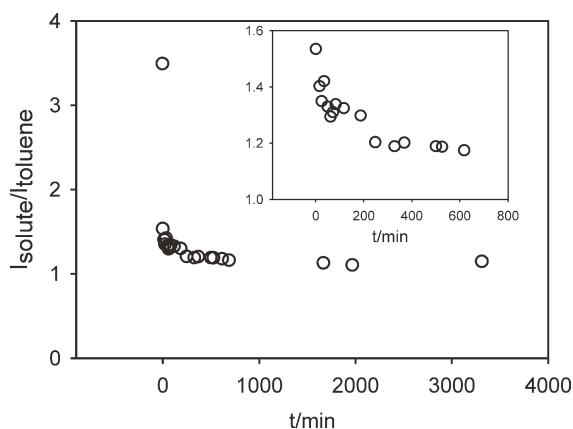

Figure 8. Hydrodynamic radius distribution of BPPAP in acetic acid and chloroform mixed solvents at 30°. Concentration: 0.50 mg mL^{-1}.
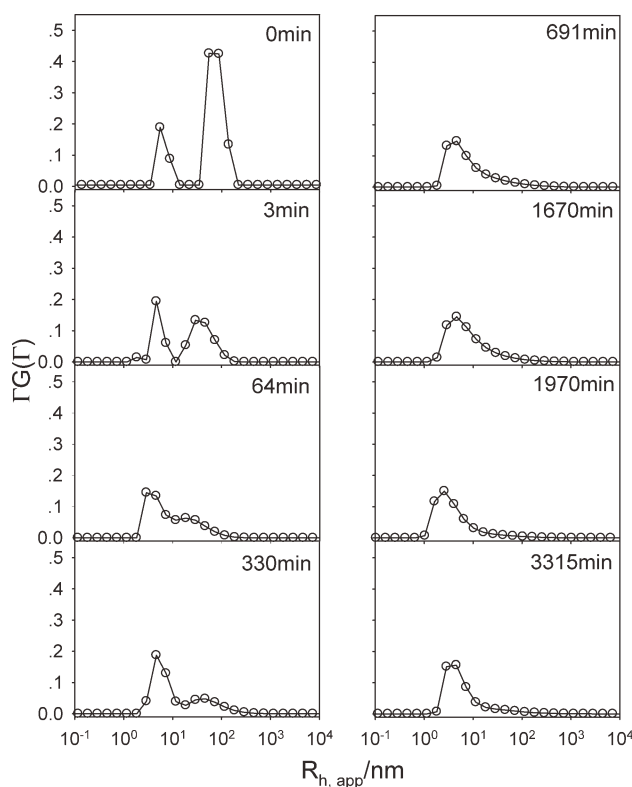
crystallization and melting properties.[12] Thus BPPAP in acetic acid and chloroform mixed solvents was investigated by using light scattering. In this experiment, the solutions were prepared in the mixed solvents and stayed overnight. In the following day, the solutions were filtered for LLS measurement. Figure 8 shows the acetic acid weight fraction dependence on the hydrodynamic radius distribution of BPPAP solution. When there was no acetic acid in the solution, an obvious association was observed. However, when the solvent comprised only 4% acetic acid, the association almost disappeared, only single chains existed in the solution. Then more acetic acid in the solvent had little effect on the conformation of BPPAP chains. It was suggested that a small amount of acetic acid was enough to break the charge transfer complexes, maybe an equivalent molar for the acid-base reaction.

To further investigate how fast acetic acid breaks the charge transfer complexes, we observed the dynamics of BPPAP associates in chloroform when 4% acetic acid was added to the solution, as shown in Figure 9. The curves can be divided into three parts. First, the light scattering intensity decreased sharply to a half in <3 min. Then it declined gradually in the following 300 min. After that, the intensity almost kept constant. This dynamical process was confirmed by the variation of hydrodynamic radius distribution with time, as shown in Figure 10. After acetic acid was added for 3 min, the amount of the associates decreased very quickly. Then the disassociation rate slowed down until the association almost disappeared. The above results indicated that the dynamics is very fast owing to the strong base-acid interaction. The protonation process is controlled by both the diffusion rate of acetic acid to each BPPAP and the rate of binding to BPPAP. The strong base-acid interaction causes the binding very fast, thus the diffusion of acid plays a critical role in this kinetics. When BPPAP is charged by the acid, the associates are unstable and disassociation occurs. Finally, BPPAP carries a large amount of positive charge. This was confirmed by the zeta potential measurements of BPPAP in the mixed solvents (Table II).

Thus, the work provides a novel and easy method to prepare optical transparent polyimide film by changing the solvent. Just

Figure 10. Hydrodynamic radius distribution of BPAPP with time at 30° in the mixed solvent. Chloroform/acetic acid (w/w) = 96/4.

by simply adding a small amount of acetic acid, association of BPPAP in chloroform solution disappeared quickly.

CONCLUSIONS

The solution behavior of BPPAP in different solvents was investigated. It is found that BPPAP existed as single chains in acetic acid, while association occurred in chloroform solution owing to charge transfer interaction. However, after adding a small amount of acetic acid to chloroform solution, associates disappeared quickly, which was attributed to strong base-acid interaction. The work hints that the association in solution significantly affects the optical transparency of BPPAP film, and can be inhibited by tuning the solvent. Thus, our study provides an important strategy for preparation of optical transparent polyimide film.

ACKNOWLEDGMENTS

Figure 9. Time dependence of light scattering intensity after 4% acetic acid was added to BPPAP/chloroform solution. Concentration: 0.50 mg mL^{-1}.

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