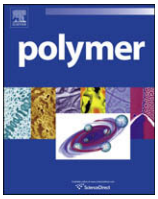
Polymer 50 (2009) 845–854

Contents lists available at ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer



The chemistry involved in the loading of silver(I) into poly(amic acid) via ion exchange: A metal-ion-induced crosslinking behavior

Shengli Qi, Zhanpeng Wu, Dezhen Wu*, Wantai Yang, Riguang Jin

State Key Laboratory of Chemical Resource Engineering, Beijing University of Chemical Technology, 15 Beisanhuan East Road, Beijing 100029, China

A R T I C L E I N F O

Article history:
Received 17 July 2008
Received in revised form
19 November 2008
Accepted 3 December 2008
Available online 10 December 2008

Keywords:
Ion exchange
Poly(amic acid)
Silver

ABSTRACT

Metal-ion-induced crosslinking of poly(amic acid) (PAA) was observed in the incorporation of silver ions into PAA through ion exchange. Studies on the interaction of silver ions with 3,3′,4,4′-benzophenonetetracarboxylic acid/4,4′-oxidianiline (BTDA/ODA)-based PAA suggest that the ion exchange reactions between poly(amic acid) and silver ions are not so simple as what we generally believed. It involves not only the formation of silver carboxylate but also the generation of diversified silver chemical entities arising from the strong chemical bonding of metal ions with the functional groups, such as carbonyl groups and amide groups, in the polymer chain, which are suggested to be responsible for the crosslinking behavior. Moreover, silver ions loaded into the film are readily self-reduced and provides us a convenient route to disperse very small metal nanoparticles into the polymeric matrix. Meanwhile, strong accelerating effect of silver ions was observed on the hydrolysis of PAA molecules and the characterization results indicate that about 14–16 wt% precursors were dissolved during the ion exchange in the aqueous silver ion solutions. Fortunately, it is found that the metal-ion-induced crosslinking structure formed in the silver-doped film has helped to prevent the damaging effect of silver ions and the essential structural features of PAA were retained in the remaining polymer matrix.

1. Introduction

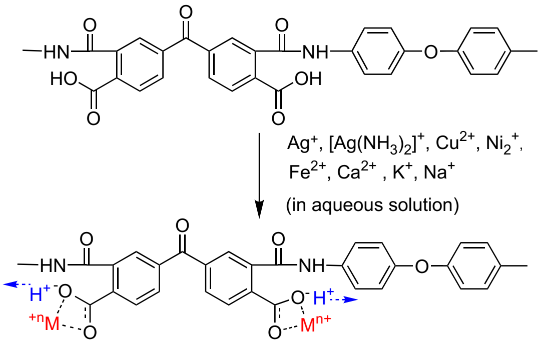
Polymeric matrices incorporated with metal nanoparticles have attracted great attention from both fundamental and applied research because of the potential applications in optics, catalysis, microelectronics, magnetic data storage and biosensors [1–8]. Ion exchange technique, which was increasingly employed in recent years, has been demonstrated to be a simple but highly effective approach in this area [9–13]. In our recent studies with the direct ion exchange self-metallization technique [14–16], by directly employing damp-dry poly(amic acid) (PAA) films to perform ion exchange reaction in aqueous silver solution (silver nitrate and silver fluoride) followed by thermal treatment under tension, silvered polyimide films with high reflectivity and conductivity on both film sides have been fabricated. And ahead of our works, relying on a simple alkali treatment of the bare polyimide resin to form PAA layer, subsequent loading of metal ions through ion exchange of PAA in aqueous metal solution, followed by metal ion reduction, Akamatsu has successfully formed patterned silver thin layers on polyimide surface [10] and has also successfully introduced Pt, Ni and Cu (<10 nm) nanoparticles with controlled interparticle spacing into the polyimide films via the ion exchange technique [13]. However, all these previous works were mainly concentrated on the polyimide metallization process, i.e. how to produce metal layers with preferable surface properties on the polyimide surface [10,14–16] or how to incorporate monodispersed metal nanoparticles into the polyimide matrix [13]. Up to now, studies regarding the interaction of metal ions with PAA as well as the structural variations of the polymer molecules during the ion exchange process are rather limited. What we could learn from literatures [9,17–19] is only limited to that metal ions would couple with carboxylic acid groups leading to the formation of metal-polycarboxylate and no other detailed information could be obtained. Currently, the chemistry involved in the ion exchange reaction is generally illustrated in Scheme 1.

In the present research, the ion exchange reactions of 3,3′,4,4′ benzophenonetetracarboxylic acid/4,4′-oxidianiline (BTDA/ODA)-based PAA with metal ions, especially Ag^+, are investigated with the purpose of getting a better understanding of the ion exchange process. The results with silver ions and PAA suggest that the ion exchange reactions are far beyond our general perception. It involves not only the simple formation of silver polycarboxylate (as depicted in many literatures) but also the possible generation of many other silver chemical entities. What is more, it is unexpected

---

* Corresponding author. Tel./fax: +86 6442 1693.
E-mail address: wdz@mail.buct.edu.cn (D. Wu).

0032-3861/$ – see front matter © 2008 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2008.12.010



Scheme 1. The generally-believed chemistry involved in the ion exchange of poly(amic acid) with metal ions.

to find that the silver-ion-exchanged PAA film could not be dissolved in its initial solvent and it is suggested that crosslinking structures are formed in the ion-doped films. And it is the formation of the crosslinking structure that inhibits the destructive effect of silver ions on the PAA chain that makes it possible to retain its basic macromolecular structures. Furthermore, we have established a method and quantitatively measured the destructive effect of metal ions on the poly(amic acid) during the ion exchange process. Films were characterized by ATR-FTIR, XPS, CA, ICP, TEM, EDS and DMTA.

2. Experimental

2.1. Reagents

3,3′,4,4′-Benzophenonetetracarboxylic dianhydride (BTDA) was purchased from Acros Organics and used without further purification. 4,4′-Oxydianiline (4,4′-ODA) was obtained from Shanghai Research Institute of Synthetic Resins and recrystallized in ethyl acetate prior to use. Dimethylacetamide (DMAc) (analytical pure, $\leq$0.1% water) was purchased by Tianjin Fu Chen Chemicals Reagent Factory and used after distillation. *N*,*N*-Dimethylformamide (DMF) (analytical pure, $\geq$99.5%) and *N*-methyl-2-ketopyrrolidine were obtained from Beijing Chemical Works and Beijing Chemical Reagents Company, respectively. Both were used as-received. Silver nitrate ($AgNO_3$) (analytic pure, $\geq$99.8% content) was produced by Beijing Chemical Works. Silver fluoride (AgF) (analytic pure, $\geq$98% content) was obtained from Zhejiang Dongyang Galt Fine Chemical Co., Ltd. Distilled water was used for all the aqueous solution preparation.

2.2. Synthesis of the damp-dry PAA films and their ion exchange with silver ions

The BTDA/ODA poly(amic acid) resin was synthesized by first dissolving the diamine in DMAc and then adding the dianhydride gradually. After stirring at room temperature for 2 or 3 h, a light yellow viscous solution was obtained. The resin employed in this study was prepared with a 1% (mol/mol) offset of dianhydride at 20 wt% solid content in DMAc. The inherent viscosity of the resulting solution applied in our present work was 1.77 $dL\,g^{-1}$ at 35 °C. Films were then cast on a clean and dust-free glass plate. After holding these wet films at ambient atmosphere or a vacuum oven for some time, most of the solvent was evaporated and damp-dry poly(amic acid) films were produced. Then, these films were peeled from the glass substrate and immersed into a 0.1 M aqueous silver fluoride solution or a 0.4 M silver nitrate solution to perform the ion exchange. Films with thicknesses of 40–45 μm and DMAc content in the range of 35–38 wt% were utilized in the present work. Following ion exchange, the silver(I)-containing films were rinsed with distilled water to remove the residual silver solution on the surface. For comparison, the surface of the damp-dry PAA film in contact with the glass substrate is referred to as the underside, while that exposed to the atmosphere is referred to as the upside. Since slight imidization was found to occur on the upside surface in previous study [16], to facilitate the discussion, the measurements in the present works are mainly performed on the underside surface, the molecule structures of which are supposed to be the same as that in the bulk.

2.3. Film characterization

Attenuated total reflection-Fourier transform infrared (ATR-FTIR) spectra of the films were collected using the Nicolet Nexus670 IR spectrometer.

X-ray photoelectron spectra (XPS) were collected using an ESCALAB 250 spectrometer (Thermo Electron Corporation) in the fixed analyzer transmission mode. The instrument is equipped with a monochromatic Al Kα X-ray source and a magnetic lens system that yields high spatial resolution and high sensitivity. A takeoff angle of 45° was used to obtain most of the spectra. The pressure in the analysis chamber was maintained at 2×10^{-10} mbar or lower during each measurement. Surface elemental compositions were calculated from the peak area ratios on the XPS spectra.

The cross-sectional morphology of the films was investigated using an HITACHI H-800 transmission electron microscope (TEM) with an operating voltage at 200 kV. Samples for TEM observations were prepared by adhering the film on a polyvinyl chloride plate followed by cutting it perpendicular to the film surface using an ultra-microtome. These thin sections floating on a water bath were mounted onto the carbon-coated TEM copper grids.

Contact angle measurements were performed on both sides of the films using an OCA contact angle system (Data physics instruments GmbH) with an input power of 55 W.

Elemental analysis was performed on an HITACHI S-4300 field emission scanning electron microscope (FE-SEM) equipped with an energy-dispersive spectrometer (EDS) produced by EDAX Inc. The samples were coated with ca. 10 nm gold prior to EDS measurements.

The incorporation of silver ions within the PAA films was quantified by a Seiko Instruments SPS 8000 inductively coupled plasma (ICP) atomic emission spectrometer. The measurements were performed after dissolving the ion-exchanged PAA films in a 5 wt% nitric acid solution.

The pH values of the aqueous solution were measured by a PHS-2C pH meter produced by Shanghai Kangyi Instrument Company (SHKY). The pH meter was calibrated using both aqueous potassium acid phthalate solution with a pH value of 4.00 and aqueous phosphate-mixture solution with a pH value of 6.86 prior to measurements.

Thermal mechanical behaviors of the films were characterized using a dynamic mechanical thermal analysis (DMTA) system of Rheometric Scientific, Inc. (RSI) with a heating rate of 5 $K\,min^{-1}$. Differential scanning calorimetry (DSC) spectra were collected using a Netasch4 differential scanning calorimeter with a heating rate at 5 $K\,min^{-1}$. Thermal gravimetric analysis (TGA) was performed with a Netzsch TG 209 system heating at 10 $K\,min^{-1}$.

2.4. Determination of the mass changes of PAA during ion exchange

Due to the existence of massive amide groups, poly(amic acid) molecules are substantially hydrolysable in aqueous solution, particularly when free reactive metal ions are involved. It is very probable that hydrolysis would break polymer chains and some of the polymer parts would be dissolved in the solution.

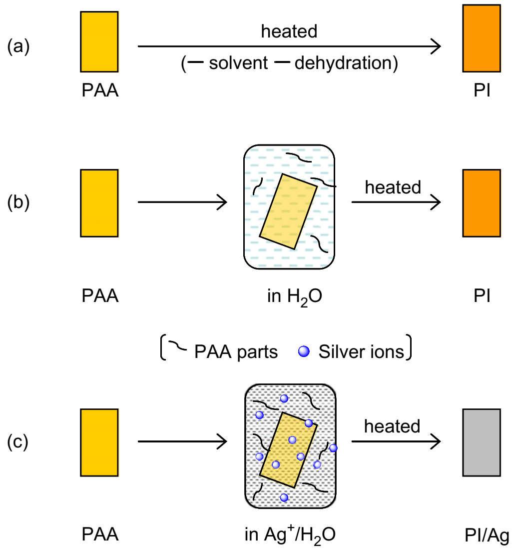
The mass losses of PAA during ion exchange could be measured and calculated by performing the experiments illustrated in Scheme 2. The first experiment (Scheme 2a) is the common conversion of the damp-dry PAA to polyimide upon thermal treatment, the chemistry of which is as that shown in Scheme 3. What occurs in this process are solvent evaporation and dehydration. If we assume that the solvent was completely removed from the system and the PAA was completely cyclized to polyimide after thermal curing, then the amount of the evaporated solvent and dehydration (wt% (DMAc + H2O)) and the content of pure PAA (wt% PAA) in the damp-dry PAA could be determined by Eq. (1):

$$\begin{aligned} \text{wt\%}(\text{DMAc}+\text{H}_2\text{O}) &= \frac{W_{\text{dampy-dry PAA-1}} - W_{\text{PI}}}{W_{\text{damp-dry PAA-1}}} \times 100 \\ \text{wt\% PAA} &= \frac{W_{\text{PI}} \times 522/(522-36)}{W_{\text{damp-dry PAA-1}}} \times 100 \end{aligned} \tag{1}$$

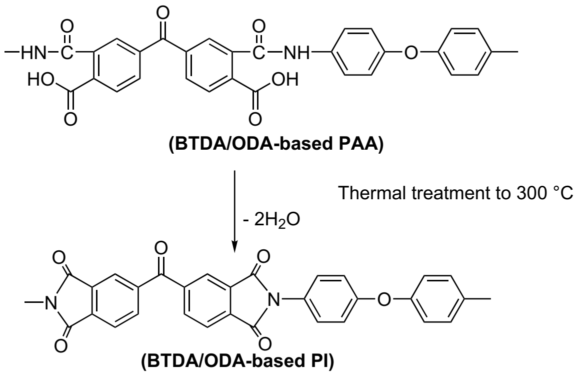
where $W_{\text{damp-dry PAA-1}}$ indicates the weight of the damp-dry PAA film used in the first experiment and W_{PI} indicates the sample mass after thermal cyclization, the factor 522 refers to the molecular weight of the repeating unit of the BTDA/ODA-based PAA, and the factor 36 refers to the molecular weights of the two water molecules eliminated during the thermal cycloimidization.

The second experiment (Scheme 2b) is designed to evaluate the hydrolysis of PAA in pure distilled water. In this experiment, the damp-dry PAA film was firstly immersed into the water for certain time followed by thermal cyclization to its final polyimide form. Mass changes of PAA in the whole process could be obtained by Eq. (2):

$$\begin{aligned} &\text{wt\% Mass changes after in H}_2\text{O}\,\&\,\text{cured} \\ &\quad = \frac{W_{\text{damp-dry PAA-2}} - W_{\text{PI in H}_2\text{O}}}{W_{\text{damp-dry PAA-2}}} \times 100 \end{aligned} \tag{2}$$



Scheme 2. Schematic diagrams for the experiments designed to determine the mass variations of poly(amic acid) during ion exchange.



Scheme 3. Thermal cycloimidization of BTDA/ODA-based poly(amic acid) to its polyimide form.

where $W_{\text{damp-dry PAA-2}}$ is the weight of the damp-dry PAA film employed in the second experiment and $W_{\text{PI in H}_2\text{O}}$ indicates the mass of the same PAA film after in pure distilled water and thermal treatment. Here we also assume that the PAA was completely cyclized to polyimide after thermal treatment.

By combining the results of the first and the second experiment, the amount of PAA dissolved in pure distilled water can be calculated by Eq. (3).

$$\text{wt\%PAA dissolved in H}_2\text{O} = \frac{\text{wt\% Mass changes after in H}_2\text{O}\,\&\,\text{cured} - \text{wt\%}(\text{DMAc}+\text{H}_2\text{O})}{\text{wt\% PAA}} \times 100 \tag{3}$$

The third experiment (Scheme 2c) is actually the process for preparing polyimide-silver composite film, including the ion exchange of PAA in aqueous silver ion solution and the thermal treatment of the silver-doped film to reduce the silver ions and to convert PAA into polyimide. In this process, the total mass changes of PAA could be easily determined by Eq. (4):

$$\begin{aligned} &\text{wt\%Mass changes after in Ag}^+\text{solution \& cured} \\ &\quad = \frac{W_{\text{damp-dry PAA-3}} - W_{\text{PI in Ag}^+\text{solution}}}{W_{\text{damp-dry PAA-3}}} \times 100 \end{aligned} \tag{4}$$

where $W_{\text{damp-dry PAA-3}}$ indicates the weight of the damp-dry PAA film used in the third experiment and $W_{\text{PI in Ag}^+\text{solution}}$ indicates the weight of the PAA film after ion exchange in silver ion solution followed by thermal cycloimidization. Silver ions loaded into the damp-dry PAA film are determined by ICP and it is assured that the total mass of silver remains constant in the whole thermal curing cycle. If we assume that only polyimide and silver are left in the final cured film and all other species have been decomposed or volatilized from the film, then the amount of PAA left after ion exchange in aqueous silver ion solution and the PAA dissolved could be given in respective by Eqs. (5) and (6):

$$\begin{aligned} &\text{wt\% PAA left after ion exchange} \\ &\quad = \Big(100 - \text{wt\%Mass changes after in Ag}^+\text{solution\,\&\,cured} \\ &\qquad - \text{wt\% Ag}^+\text{in PAA}\Big) \times 522/(522-36) \end{aligned} \tag{5}$$

$$\begin{aligned} &\text{wt\% PAA dissolved in Ag}^+\text{solution} \\ &\quad = \frac{\text{wt\% PAA} - \text{wt\% PAA left after ion exchange}}{\text{wt\% PAA}} \times 100 \end{aligned} \tag{6}$$

where (wt% Ag^+ in PAA) refers to the amount of silver ions loaded into the PAA film during ion exchange, as determined by ICP, the

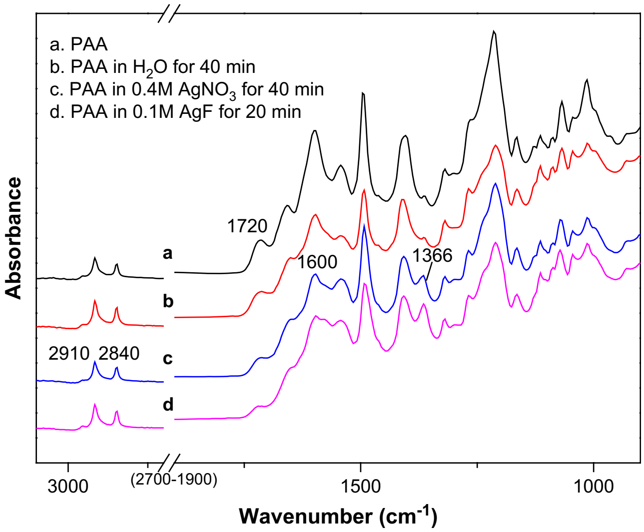


Fig. 1. ATR-FTIR spectra for (a) the pure poly(amic acid) film and its analogues (b) in distilled water, (c) in 0.4 M aqueous silver nitrate solution for 40 min as well as (d) in 0.1 M aqueous silver fluoride solution for 20 min.

factor 522 is the molecular weight of the repeating unit of the BTDA/ODA-based PAA, and the factor 36 is the molecular weights of the two water molecules released during the thermal treatment.

Experimental results suggest that some of the PAA were dissolved into the solution and the mass of PAA has been altered. Thus, the silver concentration in the ion-exchanged PAA film should be calibrated using Eq. (7):

$$\text{wt\% Ag}^{+}\text{in the left PAA after ion exchange} = \frac{\text{wt\% Ag}^{+}\text{in PAA}}{\text{wt\% PAA left after ion exchange}} \times 100 \qquad (7)$$

To convert the PAA film into polyimide, the cure cycles employed in these experiments are heating over 1 h to 135 °C and holding for 1 h, heating to 300 °C over 2 h, and remaining constant at 300 °C. For the pure PAA film and that immersed into pure distilled water for certain time, the films were heated at 300 °C for 4 h for cyclization. The films ion-exchanged in 0.4 M aqueous silver nitrate solution were cured at 300 °C for 3 h, while these ion-exchanged in 0.1 M silver fluoride solution were thermal treated at 300 °C for 2 h. A shorter thermal treatment time at 300 °C was selected for the silver-doped films since the silver metal could catalytically decompose the surface polyimide matrix at high temperature. Each

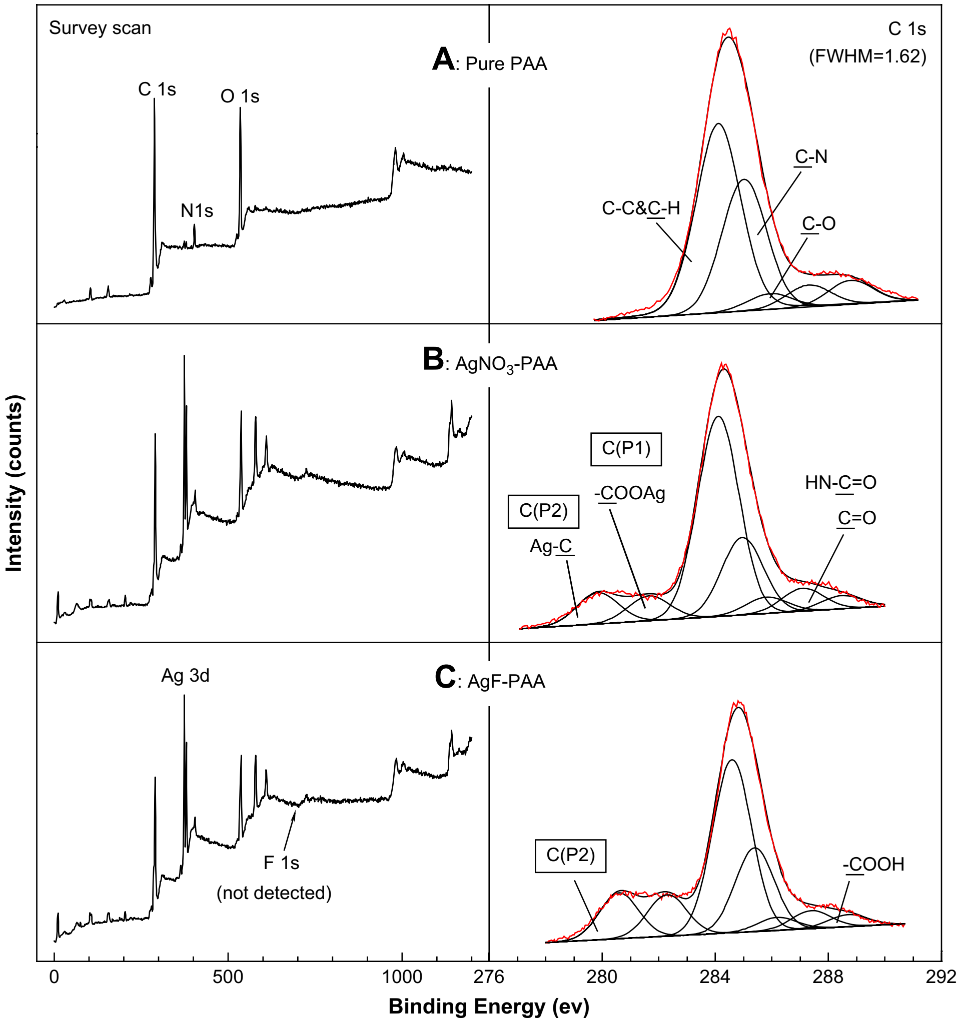


Fig. 2. XPS wide scan and C 1s core-level spectra of (A) pure poly(amic acid), and its corresponding analogues ion-exchanged in (B) 0.4 M aqueous silver nitrate solution for 40 min and (C) 0.1 M aqueous silver fluoride solution for 20 min.

value reported in the present work is the average of five parallel experiments.

3. Results and discussion

3.1. Ion exchange reaction of PAA with silver ions

ATR-FTIR characterization was carried out on the PAA films before and after ion exchange to investigate the reactions between PAA and silver ions, as shown in Fig. 1. It is clear that, after ion exchange in silver solution (see curve c and curve d), there is a strong peak at 1366 cm^{-1} and the band near 1600 cm^{-1} in IR spectra is broadened, reflecting that metal-carboxylate salt (poly-amate) has been formed in the PAA films [15,20–22]. Ion exchange reactions occurred and silver ions were incorporated. Meanwhile, an interesting phenomenon was observed. That is, after ion-exchanged in silver ion solution, the PAA films (curve c and curve d) cannot be dissolved in its initial good solvent such as dimethylacetamide (DMAc), dimethylformamide (DMF) or *N*-methyl-2-ketopyrrolidine (NMP). However, for the bare PAA film (curve a) and its analogues after in distilled water (curve b), re-dissolution could be easily achieved in few minutes in these solvent. Thus, it is reasonable to convince that it is the loaded metal ions that induce the crosslinking of the macromolecules resulting in the indissoluble silver-containing precursor films.

However, the changes in IR spectra are too limited to obtain enough information pertaining to the metal–polymer interaction. XPS measurements were performed to further clarify the interactions between silver ions and poly(amic acid), as displayed in Fig. 2. As a reference, the survey scan and C 1s core-level spectra of the pristine PAA film are shown in Fig. 2A. For the pure PAA films, the binding states of C 1s core-level electrons can be resolved into six contributions, characterized by the binding energies (BE) at 284.6 eV for the C–C (C–H) species, at 285.4 eV for the C–N species, at 286.2 eV for the C–O species, at 287.4 eV for the C=O species in the carbonyl and amide groups, and at 288.7 eV for the carboxylic species (–COOH) [23–29]. Fig. 2B and C exhibit the respective survey scan and C 1s spectra of the PAA films ion-exchanged for 40 min in 0.4 M aqueous silver nitrate solution and 20 min in 0.1 M aqueous silver fluoride solution. Intense Ag signals were detected in both survey scan spectra, confirming the incorporation of silver ions. And two additional peaks (CP1, CP2) are observed in the lower BE direction of C 1s core-level spectra. The lowered binding energy suggests an increase in electron density of the carbon atoms and should be attributed to the interaction with metal ions. The peak located at 282.3 eV (CP1) is suggested to correspond to the formation of silver polyamate. Whereas, another additional peak

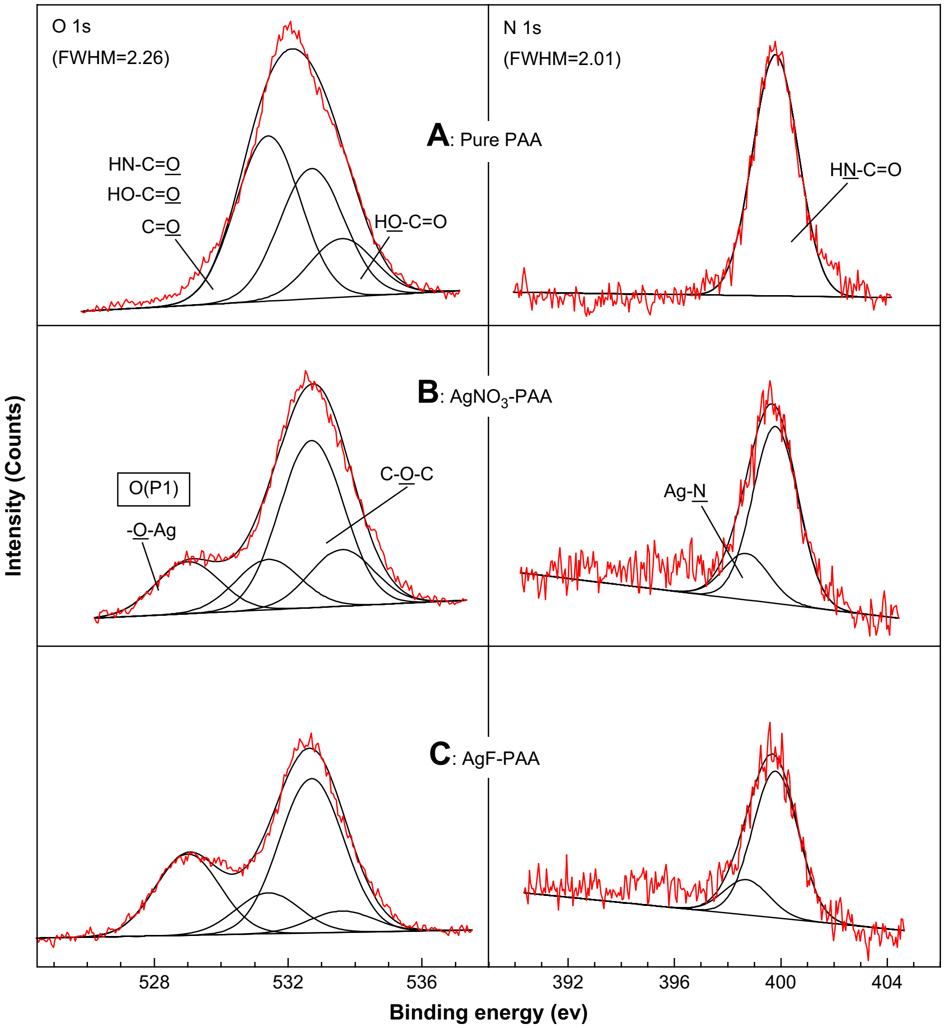
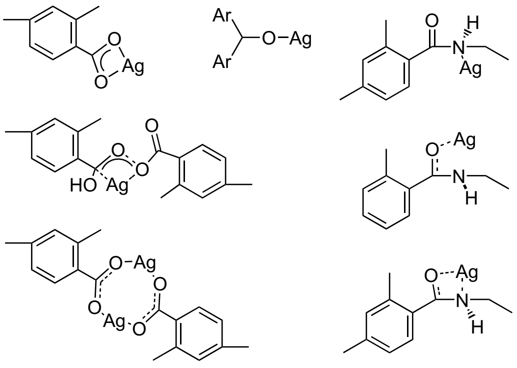


Fig. 3. High resolution XPS O 1s and N 1s core-level spectra of (A) pure poly(amic acid), and its analogues ion-exchanged in (B) 0.4 M aqueous silver nitrate solution for 40 min and (C) 0.1 M aqueous silver fluoride solution for 20 min.



Scheme 4. Possible complex species formed between silver ions and the functional groups of poly(amic acid) during ion exchange.

component with a binding energy of 280.6 eV (CP2) is supposed to originate from the direct bonding of C–Ag or the other type's coordination of silver ions with PAA [30]. The shape of the O 1s and N 1s core-level spectra also exhibit significant variations before and after ion exchange. Prior to ion exchange, the O 1s core-level spectrum can be curve-fitted with three peak components, as shown in Fig. 3A. The peak at 533.6 eV is pertaining to the CO$\underline{\text{O}}$H species; the peak at 532.7 eV is associated with the oxygen atoms in the C–O bonds; and the peak at 531.4 eV is corresponding to the oxygen atoms in all carbonyl groups (C═$\underline{\text{O}}$, C$\underline{\text{O}}$OH and C$\underline{\text{O}}$NH) [31–33]. However, following ion exchange, it can be clearly observed that an additional peak at 529.0 eV was present in the O 1s core-level spectra, as illustrated in Fig. 3B and C. This strong peak present in the lower binding energy side is suggested to be attributed to the interaction of silver ions with the carbonyl groups and the corresponding formation of C–O–Ag bond since the intensity of the carbonyl groups peak at 531.4 eV decreased substantially after ion exchange, while the C–O peak became predominant [34,35]. This is not unexpected since it is reasonable that the electrophilic silver cations covalently bond with the nucleophilic carbonyl groups forming the metal-oxygen species. The interaction of silver ions with nitrogen atoms was also observed from the N 1s spectra in Fig. 3. Besides the main peak centered around at a BE of 499.8 eV for the amide species (–$\underline{\text{N}}$H–C═O) [36], an additional peak was present at 498.7 eV after ion exchange in aqueous silver fluoride and silver nitrate solution. The appearance of this new peak in the lower BE side suggests that chemical bonds (Ag–N) have also been formed between silver ions and nitrogen atoms [35]. Discussions above indicate that ion exchange reactions between silver ions and poly(amic acid) are far more different from that illustrated in Scheme 1. It contains not only the formation of silver carboxylate but also the strong covalently bonding interactions between silver ions and the functional groups in PAA molecules. Scheme 4 shows what we believe (based on our FTIR, XPS data and literatures [31,36–39]) are the most probable chemical entities formed during the ion exchange of PAA in silver ion solutions. Some of them might promote the formation of inter- or intra-molecular hydrogen-bonding [40] or might function as crosslinking points joining the macromolecules together to form the extended network and therefore make the silver-ion-doped PAA film undissolved in its original good solvent.

Since XPS data only provide structural information on the surface with a depth no more than 10 nm, cross-sectional TEM images were recorded for the ion-doped films, as shown in Fig. 4. There are many spherical silver particles (ca. 5 nm or less in diameter) dispersing in the whole film depth, with greater amounts in the two near-surface layers and less in the inner bulk (Fig. 4A and C). The gradient distribution of silver nanoparticles suggests that the ion-exchange reaction occurring in the polymer matrix is a diffusion-controlled process and proceeds gradually from the outside layer of the PAA film to the inner bulk. However, the dispersion of silver nanoparticles in the whole film depth suggests that the ion exchange reactions not only occurred on the surface of the PAA film but have been extended to the whole film region. Correspondingly, the crosslinking structures were formed in the whole matrix and the ion-exchanged films exhibit an undissolved behavior. The cross-sectional TEM images in Fig. 4A and C were

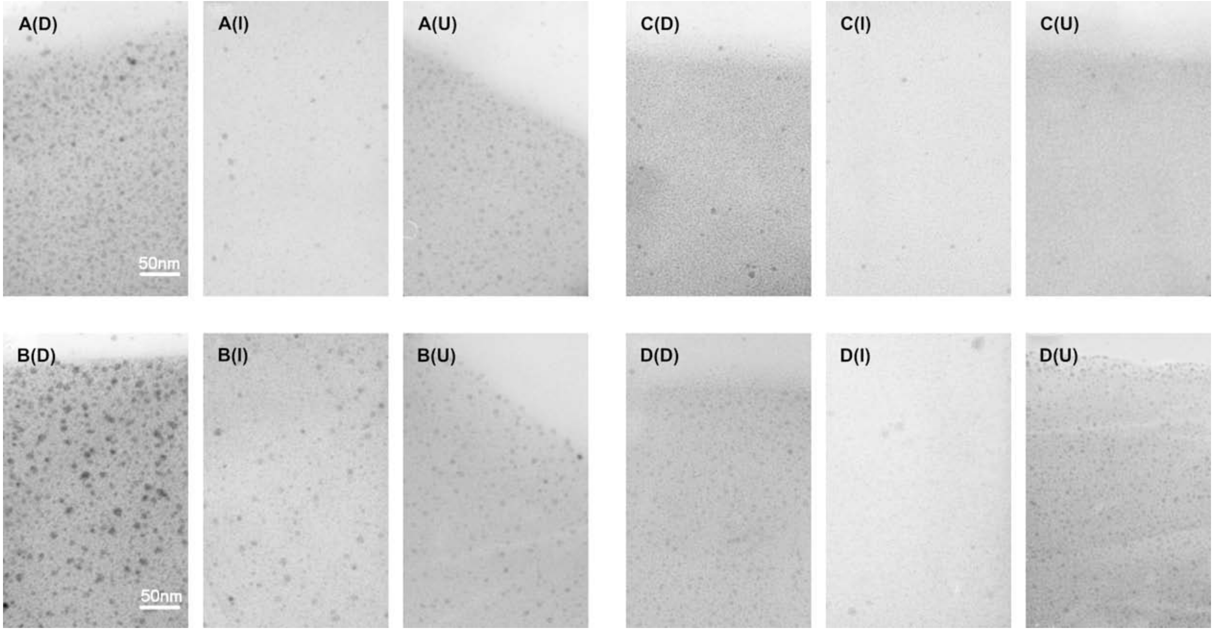


Fig. 4. Cross sectional TEM images for the BTDA/ODA-based poly(amic acid) films ion-exchanged in 0.1 M aqueous silver fluoride solution for 20 min (A and B) and in 0.4 M aqueous silver nitrate solution for 40 min (C and D). A and C were recorded after (45 ± 0.5) h of the ion exchange; B and D were recorded after (91 ± 0.5) h of the ion exchange. (D: underside of the film; I: inner of the film; U: upside of the film).

collected only 45 ± 0.5 h after ion exchange. The observation of so many reduced silver nanoparticles is unexpected and this has been attributed to the possible formation of a large number of electron donor–acceptor couples between silver ions and functional groups in PAA which are supposed to be very favorable for the silver reduction. However, herein we found a simple method for the incorporation of smaller silver nanoparticles into the poly(amic acid) film. This is important since Andreescu and his coworkers [41] once attempted to prepare poly(amic acid) composite films containing silver and gold nanoparticles for applications as electrode materials via an approach by thermal treatment of the gold- or silver-salt-containing PAA. Their efforts have been taken to producing the metal nanoparticles upon heating and to prevent the cyclization of PAA. As compared, our approach might possess potential advantages or applications in this aspect. And now it is found that the sizes of the silver nanoparticles in the ion-exchanged films are slightly increased with increasing time, as shown in Fig. 4B and D (<10 nm in diameter after 91 h). Efforts to prepare PAA composites with controlled silver nanoparticle size and to evaluate the factors influencing particle growth are currently under way.

Water contact angle measurements performed on the PAA films before and after in distilled water and aqueous silver ion solutions are shown in Fig. 5. After in distilled water, a slight decrease in contact angle was observed (curve a in Fig. 5). This is reasonable since carboxylic acid groups and amide groups in PAA molecules are all hydrophilic species and could be easily dissociated in aqueous solution to give more wettable surfaces. However, the precursor films exhibit highly promoted contact angles following ion exchange in silver ions solution, as shown in curve b and curve c in Fig. 5. Here, it is suggested that the greatly-enhanced contact angle was attributed to the successful loading of silver ions into the PAA matrix and the formation of silver-poly(amic acid) salts (might as in Scheme 4) which usually don't have good solubility in water. Meanwhile, the formation of crosslinking structures after the incorporation of silver ions would also be responsible for the more hydrophobic polyimide surfaces. However, the increase of contact angles mainly occurred in the first 20 min of the ion exchange. Further treatment doesn't enhance the contact angles further, as can be observed from curve b and curve c in Fig. 5. It is suggested that a silver-saturated surface layer is formed after 20 min ion exchange in silver ion solutions. XPS surface elemental composition measurements (see Table 1) indicate that the silver atomic concentration for the 20 min-ion-exchanged BTDA/ODA-AgF film was ca. 4.83 at% (29.5 wt%), while that for the 40 min-ion-exchanged BTDA/ODA-$AgNO_3$ film was 4.66 at% (28.7 wt%), the values of which are all close to the saturated silver concentration of 4.88 at% (30.0 wt%) [42]. As a result, the surfaces could not be more hydrophobic after that. However, this silver-saturated layer should only exist in the near-surface region since EDS measurements (probing depth ca. 100 nm) indicate that the silver concentrations were only ca. 2.8 at% (ca. 19 wt%) in a thicker film region, as shown in Fig. 6.

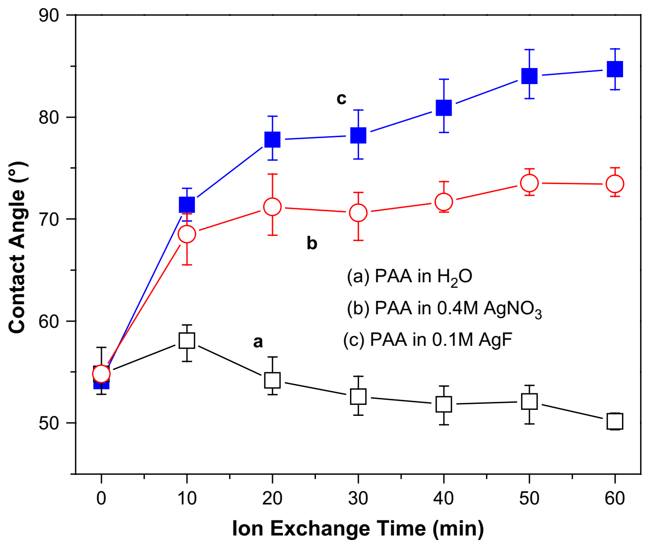


Fig. 5. Water contact angles as a function of the ion exchange time for the damp-dry poly(amic acid) films in (a) pure distilled water, (b) 0.4 M aqueous silver nitrate solution and (c) 0.1 M aqueous silver fluoride solution.

Table 1
XPS surface composition for the underside surfaces of the BTDA/ODA-based poly(amic acid) and that ion-exchanged in 0.1 M silver fluoride solution for 20 min and 0.4 M silver nitrate solution for 40 min.

Film samples	Relative atomic concentration (at %)			
	C1s	O1s	N1s	Ag3d
Bare PAA	71.83	22.66	5.51	0.00
PAA in 0.4 M $AgNO_3$ for 40 min	62.15	21.16	12.03	4.66 (28.7 wt%)
PAA in 0.1 M AgF for 20 min	63.30	19.62	12.25	4.83 (29.5 wt%)

3.2. Structural variation of PAA

Structural variations of poly(amic acid) molecules during the ion exchange process have always been the primary concern. Due to the existence of massive amide groups, poly(amic acid) molecules are substantially hydrolysable in aqueous solution, particularly when free reactive metal ions are involved [41]. The decrease in the intensity of the C–N species after ion exchange in silver solutions, as observed in the C 1s core-level spectra in Fig. 2, has demonstrated the breakage of C–N bond (hydrolysis of amide group). It is very probable that hydrolysis would generate many broken polymer chains and some of the polymer parts would be dissolved in the solution. The mass changes of PAA after ion exchange have been measured according to the method described in Section 2.4. Silver ion loadings in the ion-exchanged films were also quantified by inductively coupled plasma (ICP) atomic emission spectrometer. The results are shown in Fig. 7A and B, respectively. Fig. 7A (curve a) suggests that, after in distilled water, only ca. 1 wt% PAA macromolecules or its parts are lost into the solution. And the pure water only exhibits a slight decrease (0.4–0.7) in pH value after immersing the damp-dry PAA film for 60 min (1 g PAA in 50 ml water). All these indicate that the hydrolysis effect of water on PAA molecules is rather limited and what mainly occurred in pure distilled water should be the dissociation of carboxylic acid groups. However, great mass losses have been observed for the PAA films after ion exchange in silver ion solutions, as shown in Fig. 7A (curve b) with ca. 14 wt% lost in 0.4 M silver nitrate solution and Fig. 7A (curve c) with ca. 16 wt% lost in 0.1 M silver fluoride solution. This suggests that silver ions have strong accelerating effects on the hydrolysis of PAA molecules. The pH values of the silver solutions also display a significant decrease (ca. 2.2–2.8), consistent with the damaging effect of silver ions on the PAA microstructures. Fortunately, the dissolution of PAA was soon stopped in ca. 20 min and no significant mass loss was observed with increasing ion exchange time, as observed from curve b and curve c in Fig. 7A. This is similar with the variation of water contact angles in Fig. 5 and the formation of crosslinking structures in the polymer matrix should play a very significant role.

Fig. 7B shows the amount of silver ions loaded into the poly(amic acid) film as a function of ion exchange time, as measured by ICP and calibrated using Eq. (7) in Section 2.4. As can be observed, the loading of silver ions gradually increases with ion exchange

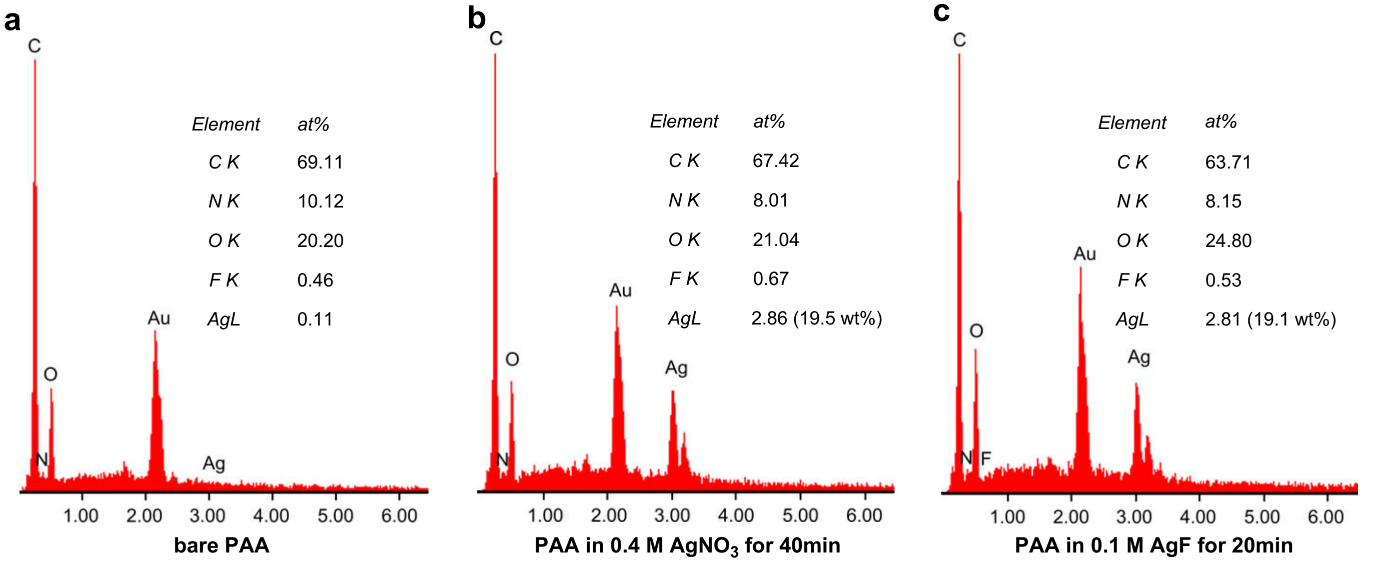


Fig. 6. EDS analysis of (a) the PAA film and its analogues ion-exchanged in (b) 0.4 M aqueous silver nitrate solution for 40 min and (c) 0.1 M aqueous silver fluoride solution for 20 min.

time but not in a linear fashion. In the first 20 min of the ion exchange, the increase of silver ion loading is almost proportional to the ion exchange time, indicating that the interaction between silver ions and poly(amic acid) occurs rather rapidly at this stage. This is consistent with the great mass loss of PAA observed at this stage in Fig. 7A, which has been suggested to be due to the strong accelerating effect of silver ions on the hydrolysis of PAA molecules. However, after 20 min, the loading of silver(I) was almost stopped and the amount of silver ions incorporated into the PAA film was only slightly increased from 20 to 40 min, as can be seen from Fig. 7B. This is suggested to be greatly associated with the metal-ion-induced cross-linking behavior of PAA molecules. The incorporation of metal ions will result in crosslinking and the formation of hydrophobic polymer matrix which would inversely impede the occurrence of ion exchange reactions between silver ions and PAA and consequently hinders the increase in silver loading. Meanwhile, it is suggested that the formation of crosslinking structure has helped to prevent the hydrolysis of poly(amic acid) and the subsequent dissolution into the aqueous solution, resulting in a nearly-stopped mass loss after 20 min, as can be seen from Fig. 7A. However, after 40 min, Fig. 7B suggests that silver loading continue to increase very significantly, indicating that extensive ion exchange reaction was proceeding again between silver ions and poly(amic acid), whereas the mass loss of PAA in Fig. 7A doesn't exhibit any distinct increase until 60 min. This is very strange but is not unreasonable. We interpret this further increase in silver loading as the result of the further hydrolysis of poly(amic acid) after a long period of ion exchange in silver ion solution. Although the metal-ion-induced crosslinking structure has effectively impeded the occurrence of the ion exchange reaction between silver ions and poly(amic acid) from 20 to 40 min, it is very probable that with an ion exchange time more than 40 min many hydrophilic amide groups (–CONH–) in the PAA chain would be broken (or hydrolyzed) under the catalysis of the silver ions in

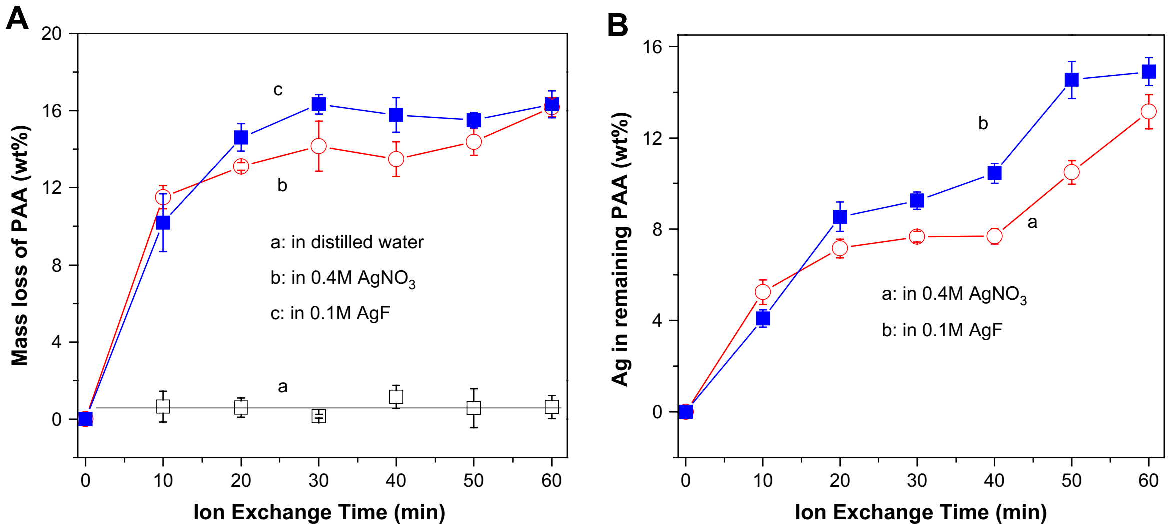


Fig. 7. (A) Mass losses as a function of treatment time for the poly(amic acid) films in (a) distilled water, (b) 0.4 M aqueous silver nitrate solution and (c) 0.1 M silver fluoride solution. (B) Silver ion loadings as a function of ion exchange time for the poly(amic acid) in (a) 0.4 M aqueous silver nitrate solution and (b) 0.1 M aqueous silver fluoride solution.

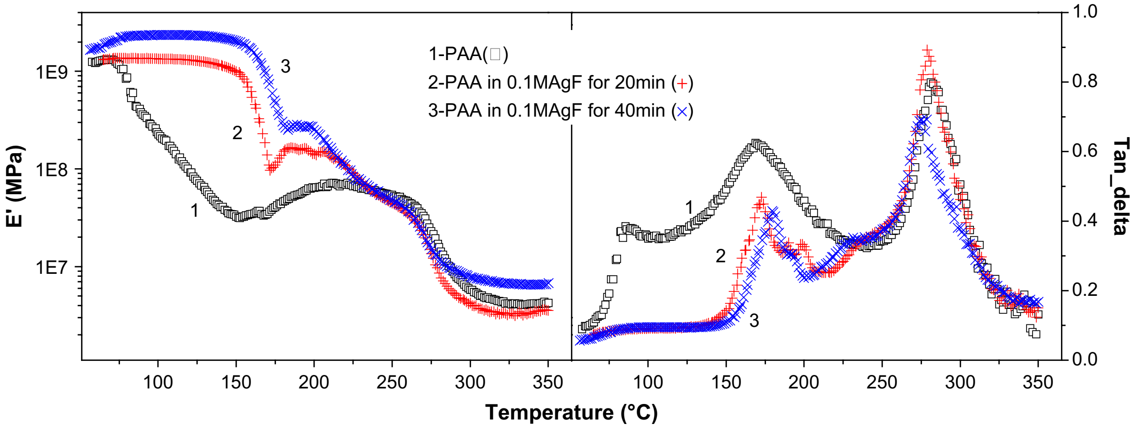


Fig. 8. Storage modulus and tan δ versus temperature of the thermal cure of the pure poly(amic acid) film and the films ion-exchanged in 0.1 M silver fluoride solution.

aqueous solution. The cleavage of the amide groups yields many new carboxylic acid groups (–COOH) in the PAA matrix and therefore results in a further increase in silver loading through the coupling of silver ions with these new carboxylic acid groups. Significant mass loss of PAA was not observed at this stage since the formation of the crosslinking structure would make it very hard for the hydrolyzed PAA or its part to dissolve into the aqueous solution.

Although a large amount of PAA has been dissolved in solution due to the silver-ion-accelerated hydrolysis, FTIR spectra in Fig. 1 suggests that the ion-exchanged films retained their basic structural and physical properties of the parent PAA film since the overall spectra before and after ion exchange were only slightly altered and no distinct changes were observed on the ion-doped films. To further clarify the structural variations, the thermal curing profiles of the silver-doped films were investigated by DMTA, as shown in Fig. 8. For the pristine film (curve 1 in Fig. 8), the storage modulus decreased gradually with increasing temperature, reflecting the continuous softening of PAA molecules. However, after ion exchange in 0.1 M aqueous silver fluoride solution, the films exhibit an almost constant storage modulus until a sharp drop was detected near 150 °C, as shown in curve 2 and curve 3 in Fig. 8. The maintenance of storage modulus here further confirmed the formation of crosslinking structures in the ion-exchanged films. And the modulus drop slightly shifts to a higher temperature with increasing ion exchange time, indicating an increase in crosslinking density with increasing ion-exchange time in silver solution. The sharp decrease in modulus at this time is mainly attributed to the glass transition of the PAA molecules. With the increasing of temperature, the modulus begins to increase after 150 °C due to the cycloimidization of PAA to polyimide [43]. Correspondingly, a distinct loss peak (175 °C) appears on the tan δ curves, indicating the occurrence of plasticization and cyclization of PAA. However, an additional loss peak (ca. 200 °C) was present for the ion-exchanged films, as can be seen on the tan δ curve 2 and curve 3 in Fig. 8. We suggest this might reflect the destruction of the metal-ion-induced physical crosslinking structure and the formation of the thermal-cyclization-induced chemical crosslinking structure in the metal-ion-doped films upon thermal treatment. A second major drop in modulus was observed at about 270 °C, which is consistent with the glass transition of polyimide chain. And the loss peak (ca. 270 °C) on the tan δ curves now suggests that the glass transition temperature of the ion-exchanged film is only slightly lowered than the pristine polyimide film. The nearly unaltered loss peaks at ca. 175 °C and 270 °C further demonstrate that both structural and chemical features of the PAA are maintained after ion exchange. And it has also been demonstrated that the silver-doped PAA films after thermal treatment maintained the essential structural features (see IR spectra in Fig. 9) and the basic mechanical properties of the parent polymer matrix [14–16]. Thus, it is very interesting to note that although silver ions have strong destructive effects on the PAA molecules, the crosslinking structures induced by silver ions inversely prevent the damaging effect spontaneously. And this self-preventing behavior has positively retained the essential characteristic structures in the PAA basic molecules.

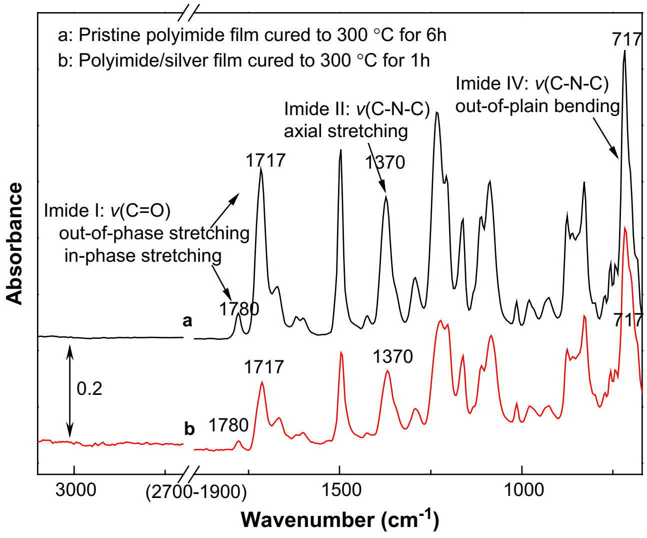


Fig. 9. FTIR-ATR spectra of (a) the pure PAA film cured at 300 °C for 6 h and (b) the PAA film ion-exchanged in 0.4 M aqueous silver nitrate solution for 40 min and cured at 300 °C for 1 h.

4. Conclusions

In summary, on the basis of these discussions, we have illuminated that the ion exchange between silver ions and poly(amic acid) molecules is not so simple as the ordinary formation of silver polycarboxylate, but involves the strong interaction of metal ions with all functional groups in the PAA chain which might generate diversified silver chemical entities. Furthermore, metal-ion-induced crosslinking structures have been formed in the ion-exchanged precursor films. And it is found that the silver ions loaded into the PAA film could be easily self-reduced which provides a convenient approach to the preparation of well-dispersed metal nanoparticle embedded polymer films. Efforts to control the silver nanoparticle size in poly(amic acid) are now under way. Silver ions have strong accelerated effect on the hydrolysis of poly(amic acid) molecules during ion exchange. However, the crosslinking structures induced by the incorporated silver ions positively prevented the destructive effect and retained the basic structural characteristics of the remaining polymer matrix. Crosslinking behavior of PAA was also found in our examination with other metal ions, including $Ag[(NH_3)_2]^+$, Cu^{2+}, Ni^{2+}, Fe^{2+}, Ca^{2+}, K^+ and Na^+. It seems this is a common phenomenon and detailed investigations regarding the mechanism and the potential applications have been in progress.

Acknowledgement

The authors greatly thank the financial support from the National Natural Science Foundation of China (NSFC, Project No. 50573007), the National High Technology Research and Development (Project No. 2007AA03Z537) and the program for New Century Excellent Talents in University (NCET-040118).

References

[1] Murdey R, Stuckless JT. J Am Chem Soc 2003;125:3995.
[2] Akamatsu K, Ikeda S, Nawafune H, Deki S. Chem Mater 2003;15:2488.
[3] Huang JC, Qian XF, Yin J, Zhu ZK, Xu HJ. Mater Chem Phys 2001;69:172.
[4] Breimer MA, Yevgeny G, Sy S, Sadik OA. Nano Lett 2001;1:305.
[5] Southward RE, Thompson DW. Adv Mater 1999;11:1043.
[6] Quaroni L, Chumanov G. J Am Chem Soc 1999;121:10642.
[7] Matsuda SI, Yasuda Y, Ando S. Adv Mater 2005;17:2221.
[8] Rifai S, Breen CA, Solis DJ, Swager TM. Chem Mater 2006;18:21.
[9] Akamatsu K, Ikeda S, Nawafune H. Langmuir 2003;19:10366.
[10] Akamatsu K, Ikeda S, Nawafune H, Yanagimoto H. J Am Chem Soc 2004;126:10822.
[11] Ho CH, Tobis J, Sprich C, Thomann R, Tiller JC. Adv Mater 2004;16:957.
[12] Li Y, Lu Q, Qian X, Zhu Z, Yin J. Appl Surf Sci 2004;233:299.
[13] Akamatsu K, Shinkai H, Ikeda S, Adachi S, Nawafune H, Tomita S. J Am Chem Soc 2005;127:7980.
[14] Qi SL, Wu DZ, Bai ZW, Wu ZP, Yang WT, Jin RG. Macromol Rapid Commun 2006;27:372.
[15] Qi SL, Wu ZP, Wu DZ, Wang WC, Jin RG. Chem Mater 2007;19:393.
[16] Qi SL, Wu ZP, Wu DZ, Wang WC, Jin RG. Langmuir 2007;23:4878.
[17] Thomas RR. Langmuir 2003;19:5673.
[18] Huang XD, Bhangale SM, Moran PM, Yakovlev NL, Pan J. Polym Int 2003;52:1064.
[19] Stoffel NC, Hsieh M, Chandra S, Kramer EJ. Chem Mater 1996;8:1035.
[20] Lee KW, Kowalcyzk SP, Shaw JM. Macromolecules 1990;23:2097.
[21] Lee KW, Kowalczyk SP, Shaw JM. Langmuir 1991;7:2450.
[22] Okumura H, Takahagi T, Nagai N, Shingubara S. J Polym Sci Part B Polym Phys 2003;41:2071.
[23] Tsai WH, Cave NG, Boerio FJ. Langmuir 1992;8:927.
[24] Fu GD, Wang WC, Li S, Kang ET, Neoh KG, Tseng WT, et al. J Mater Chem 2003;13:2150.
[25] Kang ET, Tan KL, Kato K, Uyama Y, Ikada Y. Macromolecules 1996;29:6872.
[26] Xiao Y, Chung TS, Chung ML. Langmuir 2004;20:8230.
[27] Xu FJ, Kang ET, Neoh KG. Macromolecules 2005;38:1573.
[28] Beamson G, Briggs D. High resolution XPS of organic polymers: the Scienta ESCA300 database. Chichester: John Wiley & Sons; 1992.
[29] Ward LJ, Schofield WCE, Badyal JPS. Chem Mater 2003;15:1466.
[30] Yang CY, Chen JS, Hsu SLC. J Vac Sci Technol 2005;A23:862.
[31] Serghini-Monim S, Norton PR, Puddephatt RJ. J Phys Chem B 1997;101:7808.
[32] Liu X, Neoh KG, Kang ET. Langmuir 2002;18:9041.
[33] Zhang F, Wolf GK, Wang X, Liu X. Surf Coat Technol 2001;148:65.
[34] Munoz-Rojas D, Subias G, Fraxedas J, Gomez-Romero P, Casan-Pastor N. J Phys Chem B 2005;109:6193.
[35] Lee WJ, Lee YS, Rha SK, Lee YJ, Lim KY, Chung YD, et al. Appl Surf Sci 2003;205:128.
[36] Serghini-Monim S, Norton PR, Puddephatt RJ, Puddephatt KD, Pollard KD, Rasmussen JR. J Phys Chem B 1998;102:1450.
[37] Olson LP, Whitcomb DR, Rajeswaran M, Blanton TN, Stwertka BJ. Chem Mater 2006;18:1667.
[38] Alexander MR, Beamson G, Blomfield CJ, Leggett G, Duc TM. J Electron Spectrosc 2001;121:19.
[39] Zabicky J, Grinberg S. Analytical aspects of organogold and organosilver compounds. In: Patai S, Rappoport Z, editors. The chemistry of organic derivatives of gold and silver. West Sussex: John Wiley & Sons, Ltd.; 1999. p. 131.
[40] Du X, Liang Y. Langmuir 2000;16:3422.
[41] Andreescu D, Wanekaya AK, Sadik OA, Wang J. Langmuir 2005;21:6891.
[42] The saturated silver atomic concentration is calculated on the hypothesis that at most two silver ions could be loaded per repeating unit of the PAA molecules (which is approximate, not true). That is, two molecules of -COO-Ag+ were formed in each polymer repeating unit. Atoms, except hydrogen, are all included in the calculation. According to this, the silver-saturated polymer repeating unit should be C29N2O8Ag2 for the BTDA/ODA-based PAA.
[43] Rubira AF, Rancourt JD, Taylor LT, Stoakley DM, Clair St AK. J Macromol Sci Pure Appl Chem 1998;A35:621.