

Synthesis of aromatic polyimides in DMAc containing large amount of water and the properties thereof

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Summary

A series of polyamic acids were prepared in N,N-dimethylactamide (DMAc) containing large amount of water, some of which contain the amount of water up to 25%. Their inherent viscosities decreased with the increase of water in DMAc, depending on the electronic properties of dianhydride and reaction condition. The molecular weights and mechanical properties of the polyimides thermally imidized from the polyamic acids were almost independent on the water content in solvent. The decomposition-resynthesis of polyamic acids during the curing was also investigated.

Introduction

Aromatic polyimides are well known for their excellent thermal, mechanical and electrical properties, and their outstanding chemical stability. These properties make them useful in many high-technology fields as high-performance polymeric materials¹⁾. Conventionally, polyimide is synthesized by the addition of a tetracarboxylic acid dianhydride to a diamine solution in a polar solvent such as N,N'-dimethylformamide (DMF), DMAc, and N-methylpyrrolidone (NMP) under stirring at 15 to 75 °C. The generated polyamic acid (PAA) is then cyclodehydrated to the corresponding polyimide by extended heating at elevated temperatures or by treatment with chemical dehydrating agents¹⁻⁵⁾.

It is generally accepted that dianhydride is sensitive to moisture. The hydrolysis stability of polyamic acid was studied and the effect of trace or small water on polyamic acid solution has been observed²⁻⁶⁾. However, little was known about the effect of large amount water in solvent on the formation of polyamic acid and the property of corresponding polyimide. In order to get high molecular weight of polymer, many attentions have been paid to keep reaction system from water by the use of anhydrous solvent in dry atmosphere. This may present many inconveniences for the synthesis and processing of polyimides. In fact, in many applications, such as in coating and in molding, moderate viscosity is required for the processing. Furthermore, sometimes water is essential in preparing polyimide material, such as in preparing inorganic-polymer hybrid⁷⁾. In this work, the effects of large amount water in solvent on the molecular weight and mechanical properties of polyamic acids and polyimides was investigated.

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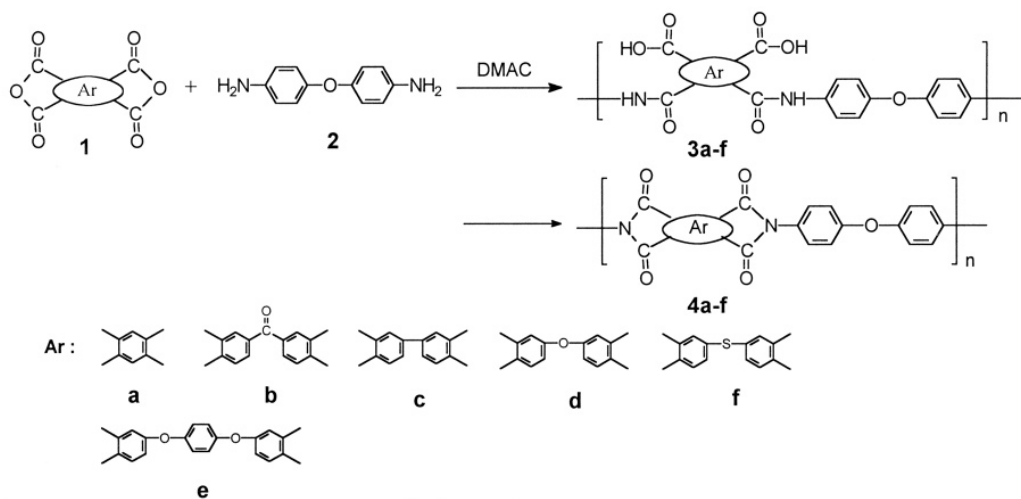
Experimental

Materials

3,3',4,4'-Biphenyltetracarboxylic dianhydride (BPDA), 3,3',4,4'-thiodipthalic dianhydride (TDPA), and 1,4-bis (dicarboxyphenoxy) benzene dianhydride (HQDPA) were prepared from 4-chlorophthalic anhydride in our laboratory⁸⁻¹⁰. Pyromellitic dianhydride (PMDA), 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA), 3,3',4,4'-oxydipthalic tetracarboxylic dianhydride (ODPA) and 4,4'-oxydianiline (ODA) were available commercially. Dianhydrides and diamine were purified by sublimation or recrystallization prior to use. Anhydrous grades of solvents such as DMAc were distilled under reduced pressure over calcium hydride and stored over 4Å molecular sieves and the other common reagents were used without further purification.

Synthesis of Polymers

The general procedure of polymerization is described as follows: To a mixture of the equivalent dianhydride and the diamine was added in one portion DMAc-H₂O binary solvent with the ratio of H₂O to DMAc from 0 to 30%, to make a 15% solid content. The slurry was stirred vigorously under ambient atmosphere at room temperature. Stirring was continued for 2h after the formation of a clear solution to ensure complete reaction. The polyamic acid solutions were filtered and cast onto glass plate. The plates were dried for 10h at 38 °C, then 2h at 100 °C in an air circulation oven followed by an additional hour at 200 °C and finally, at 300 °C for 10 minutes to complete the imidization reaction.



Characterization

FTIR spectra were obtained with a Bio-Rad Digilab Division FTS-80 spectrometer. Inherent viscosities were determined at 0.5g/dL in DMAc for polyamic acids and in m-cresol for polyimides with an Ostward viscometer at 30 °C ± 0.1 °C. The tensile measurements were carried out on an Instron Model 1121 testing machine at room temperature. Crosshead speed was 2.0 cm/min, corresponding to the relative strain rate of 1.0 cm/min.

Results and discussion

Synthesis of Polymers

Polyimides were synthesized by the two-step procedure as shown in Scheme I. The condensation reactions of the dianhydride and the diamine were carried out under room temperature except PMDA and ODA to which lower reaction temperature (0-5 °C) was

Table 1: Synthesis and properties of polymers^a

Poly(amic acid)s or Polyimides	H ₂ O wt% in solvent	η_i^{30} of PAA (dL/g)	Properties of polyimide films			
			η_i^{30} (dL/g)	Strength (MPa)	Elongation (%)	Modulus (GPa)
PMDA/ODA	0	1.99		119.27	54.12	1.43
PMDA/ODA	5	0.84		110.21	47.54	1.06
PMDA/ODA	10	0.46		99.19	28.52	1.02
PMDA/ODA	15	0.16				
BTDA/ODA	0	2.44		135.00	12.33	2.82
BTDA/ODA	5	1.09		132.55	13.10	2.62
BTDA/ODA	10	0.85		124.72	11.92	2.82
BTDA/ODA	15	0.79		140.13	14.74	2.77
BTDA/ODA	20	0.68		127.54	10.05	2.94
BTDA/ODA	25	0.59		131.62	10.71	2.30
BTDA/ODA	30	b				
BPDA/ODA	0	2.05		124.32	19.86	2.40
BPDA/ODA	5	1.37		114.59	22.51	2.03
BPDA/ODA	10	0.93		113.79	16.59	2.07
BPDA/ODA	15	0.85		111.72	11.15	2.06
BPDA/ODA	25	0.73		80.51	7.82	1.60
BPDA/ODA	30	b				
ODPA/ODA	0	0.97	1.09	107.25	18.86	2.02
ODPA/ODA	10	0.40	1.03	121.44	14.93	2.30
ODPA/ODA	15	0.36	1.02	109.93	9.47	2.05
ODPA/ODA	20	0.25	1.05	100.84	10.78	1.81
ODPA/ODA	25	0.22	0.99	105.51	10.18	1.78
ODPA/ODA	30	b				
TDPA/ODA	0	1.12	1.09	121.00	15.01	1.78
TDPA/ODA	5	0.85	1.02	108.94	8.97	2.26
TDPA/ODA	15	0.58	1.03	111.53	11.68	2.08
TDPA/ODA	20	0.44	1.12	95.54	7.73	2.02
TDPA/ODA	25	b				
HQDPA/ODA	0	1.02	1.15	104.00	12.20	1.48
HQDPA/ODA	5	0.91	1.11	105.10	17.26	2.10
HQDPA/ODA	10	0.83	1.01	106.74	22.77	2.16
HQDPA/ODA	15	0.69	1.01	111.53	11.68	2.03
HQDPA/ODA	20	b				

a Reaction temperature: 0-5 °C for PAA (PMDA/ODA); room temperature for other PAAs

b Phase separation

needed to obtain reasonable high molecular weight. The poor solubility of dianhydrides and polyamic acids in DMAc containing large amount of water caused much longer reaction time, e.g. up to 72 h in some case, to obtain homogeneous solution. The solubility of polyamic acids limited the amount of water which could be present in DMAc (usually 20-30%) depending on dianhydride used (Tab. 1). In the most cases, the homogeneous solution could be cast on the glass plate to form a film after thermal treatment except **3a** prepared in a solvent with water content more than 10%.

Properties of Polymers

As can be seen in Tab. 1, the values of inherent viscosity of **3a-f** decreased with the increase of water content. The hydrolysis of anhydride and polyamic acids would contribute to this result. The mechanism of hydrolysis has been investigated by several authors^{2,6)}. It is worth to point out that in our case the water was in large amount and the hydrolysis performed more seriously.

The nature of dianhydride may response to the extent of the decrease of the viscosity value. It was found that the hydrolysis stability of anhydride depends on the electrophilic properties of the carbonyl carbons of anhydride⁶⁾. An excellent measure of an anhydrides electron acceptor properties is provided by its electron affinity E_a ¹⁾. In this study, the rate of hydrolysis of dianhydride is proportional to the electron affinity of dianhydride and an approximately linear relationships between $\eta_{inh}(H_2O:0\%) / \eta_{inh}(H_2O:10\%)$ and E_a have been found to be existed (see Fig. 1). From this, electron affinity E_a of TDPA can be calculated and the value of E_a is 1.28.

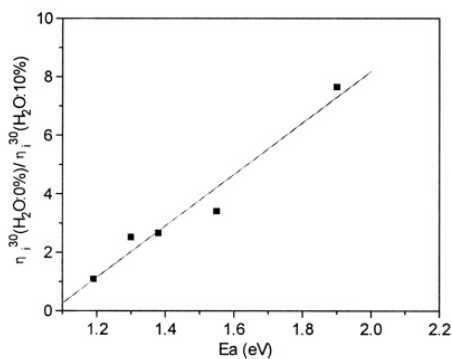


Figure 1. The dependence of relative viscosity of polyamic acids on the E_a of dianhydrides

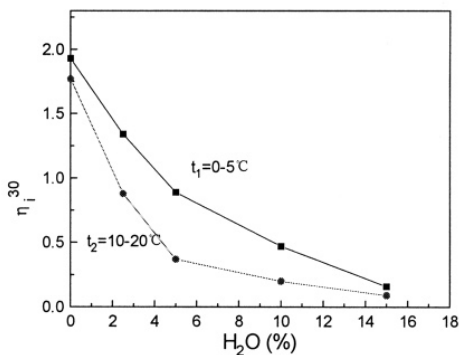


Figure 2. The effect of water content on viscosity of **3a**

Other conditions of reaction also contributed to the η_{inh} change of polyamic acid. The equimolarity of the reactive monomers is most important. The effect of purification of monomer on the polycondensation have been observed. The impurity in dianhydride and diamine can break down the equimolarity of the reactive monomers and affect molecular weight and, then, properties of polyamic acids and polyimides. As mentioned above, reaction temperature also affected the condensation reaction of diamine and dianhydride especially for the PMDA and ODA. The higher the reaction temperature, the more serious the extent of the decrease of viscosity (see Fig. 2). This result can be explained by the exothermal character of polycondensation equilibrium¹⁾.

However, Tab. 1 also shows that polyimides films **4a-f** can be prepared from **3a-f**, and their properties are as good as those of films obtained from high molecular weight prepolymers produced in the anhydrous solvent. The decomposition-resynthesis of polyamic acids in the curing would contribute to this result. The molecular weight of the polymer could increase as a result of the reaction of anhydride and amine groups. These considerations are confirmed by monitoring the anhydride end groups produced in the curing. Fig. 3 and Fig. 4 demonstrate that the anhydride groups gradually reappear during heat treatment. On the other hand, it is known that a depolymerization reaction at the amic acid units and a degradation of polyimides occur during thermal cyclization^{3,5}. Even if anhydrous solvent and condition were adopted, it is impossible to refrain from water producing in the thermal imidization. When a thick layer of solution was heated, extensive hydrolysis occurred before the water could escape, and the cured polymer was obtained as a powder or a brittle film of low molecular weight.

It is generally believed that we can take the advantages of high molecular weight of polyimide, especially to meet the need of good mechanical properties. However, high molecular weight, e.g. high apparent viscosity is usually not necessary for coating processing. Even in solution casting for preparing films, polyamic acid should be provided with moderate viscosity. Studies have shown that controlled molecular weight polyamic acid may be realized by employing end-cap addition such as phthalic anhydride or off-stoichiometry of anhydride and diamine^{2, 3,13}. In this study, the water-containing solvent has been used to control the molecular weight of polyamic acid and finally the high molecular weight of polyimide can still obtained after thermal imidization.

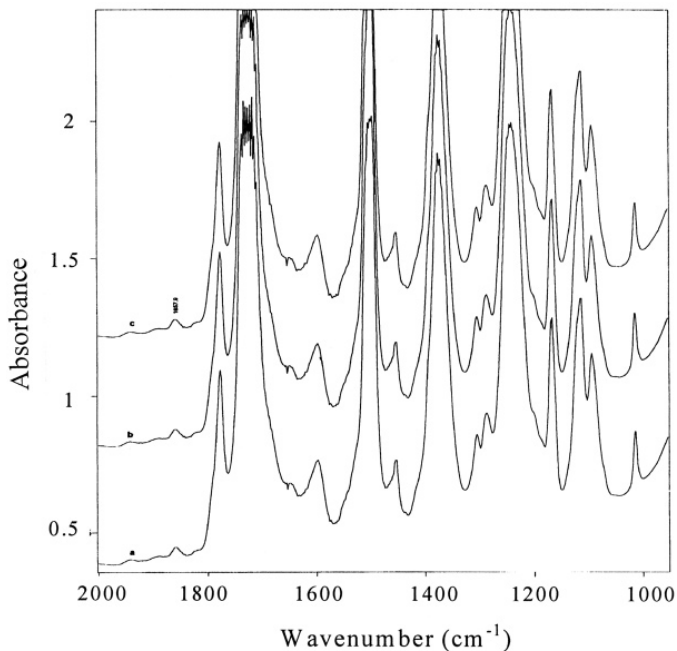


Figure 3. FTIR spectra of **3a** prepared in DMAc containing the amount of H₂O: (a) 0; (b) 5%; (c) 10%. All samples were heated at 180 °C for 5 min.

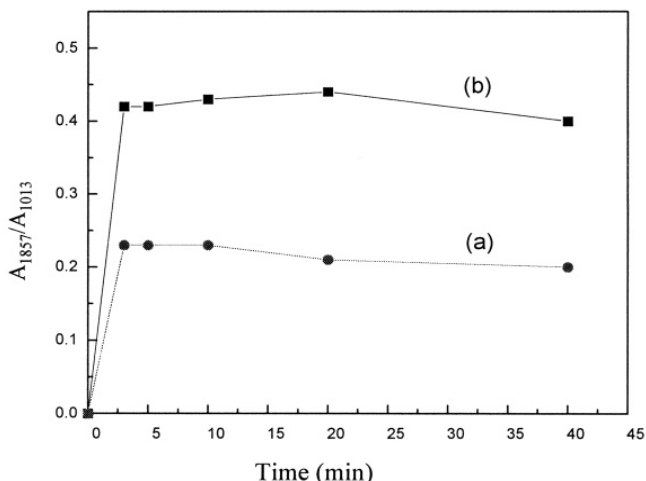


Figure 4. The accumulation of anhydride group at 180 °C in films of different poly (amic acid)s: (a) **3a**; (b) **3b**. Two samples were synthesised in DMAc containing the amount of 5% H₂O. (A_{1857} : absorbance of the band of anhydride group; A_{1013} : absorbance of the band of aromatic ring)

Nowadays polyimide-inorganic hybrids become a popular topic because of their unique properties. Water as reagent, solvent and by-product play an important role in sol-gel process⁷. It is certainly advantageous that the polyamic acids remain soluble in solvent containing water and have the ability to further processing even the water content up to 15-30%, varying with different dianhydrides. In fact, we have succeeded in preparing polyimide-SiO₂ hybrid by taking this advantage¹¹. In addition, some ultra-fine inorganic particles such as BaTiO₃ disperse in solvent containing water better than in anhydrous solvent¹².

Conclusion

A series of polyamic acids can be prepared in DMAc containing large amount of water. It was confirmed that a high molecular weight of the prepolymer is not an indispensable condition for obtaining polyimides with high molecular weight and good mechanical properties. However, the equimolarity of the reactive monomers (functional groups) in the synthesis is necessary. This approach can find some application in polyimide process and in the synthesis of polyimide-inorganic hybrid.

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