

Thermally stable imide oligomers from acridine yellow

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The synthesis and characterization of three new imide oligomers from acridine yellow, using pyromellitic dianhydride (PMDA), 3,3',4,4'-benzophenone tetracarboxylic acid dianhydride (BTDA) and 2,2'-bis(3,4-dicarboxyphenyl) hexafluoropropane dianhydride (6FDA), is reported in this paper. Due to the poor reactivity of acridine yellow, a two-step synthesis technique at lower temperature produced little or no product. The one-step, elevated temperature, solution imidization technique was deemed to be more efficient and was used to synthesize polyimides. Optimized reaction conditions were determined for all these polymers. Intrinsic viscosity values of poly(acridine yellow-co-PMDA) (AYPMDA), AYBTDA and AY6FDA polyimides were 0.11 in *N*-methyl-2-pyrrolidinone (NMP) and 0.10 and 0.13 dimethylformamide (DMF), respectively. The newly synthesized imide oligomers were thermally stable up to 400°C in a nitrogen atmosphere. AYBTDA and AY6FDA polyimides were soluble in DMF and dimethyl sulfoxide. AYPMDA polyimide was soluble in NMP. © 1997 Elsevier Science Ltd.

(Keywords: polyimides; acridine yellow; thermal stability)

Introduction

For the last two decades there has been an abundance of activity in the synthesis of new polymeric materials, as the need for advanced materials has been increasing. High temperature polymers are playing an increasingly important role in the protection and interconnection of a variety of electronic components. In recent years, their application has been extended to uses such as dielectrics in integrated circuits and as thin film multilayer electronic packaging^{1,2}. Polyimides are the leading group of polymers that have captured the attention of many scientists since they possess required properties for these applications. Aromatic polyimides are known for their excellent thermal and thermooxidative stability, chemical and solvent resistance and light stability. Due to these unique properties, they offer great promise for use in high technology applications. Aromatic polyimides have high demands in aerospace, automotive and chemical industries, and are extensively used in the electronic industry. Studies have shown that polyimides can also be used as a light guiding material with very low optical loss³. Polyimides can be patterned by selective irradiation using ultraviolet (u.v.) light. This type of photoreactive polyimides can be used in the fabrication of integrated circuits. Polyimides can also be used as an electrical insulating layer between devices and as protective layers in packaging against heat, mechanical damage or alpha-particles radiation. They can also be used as layers for selective ion implantation⁴.

Polyimides can be prepared from a variety of starting materials and by a variety of synthetic routes. Variations in properties like glass transition temperature, oxidative stability, toughness, adhesion, solubility and permeability can be achieved by altering or changing the starting materials. Most polyimides are insoluble in common organic solvents and decompose before melting. These

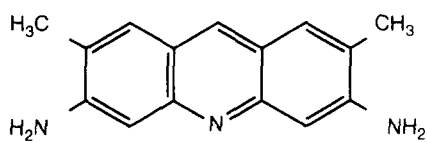
properties make the processing of polyimides very difficult. In order to achieve processability, polyimides are generally made by an expensive, two-step processable polyamic acid intermediate route, devised by Edwards and co-workers⁵⁻⁹. However, polyimides that are soluble in common organic solvents can often be prepared by a high temperature, one-step or single-stage method. The single-step method is very useful in the polymerization of unreactive dianhydrides and diamines. This single-step method yields polyimides with a higher degree of crystallinity compared to polyimides obtained by the two-step method of polymerization. This method also yields polyimides with a more favourable packing conformation of the polymeric chains.

Aromatic diamines give better thermal stability to polyimides than do aliphatic diamines due to resonance stabilization. Thermal stability of the polyimides can be increased further by using bicyclic or tricyclic aromatic diamines. However, by increasing the number of aromatic rings in the system, solubility and processability of the polyimides decreases. In the past, polymer chemists have improved processability of polyimides by incorporating flexible bridging units, bulky side groups or the more asymmetric *meta* catenation into the otherwise rigid backbone of these polymers¹⁰⁻¹⁴. Polyalicyclic structures have also been used to synthesize soluble polyimides¹⁵. The solubility of polyimides can also be increased by using heterocyclic diamines. In recent years, polyimides have been synthesized using heteroaromatic tricyclic diamines such as thionine and proflavine^{16,17}. These polyimides have shown better solubility and good thermal stability.

In this paper we describe the synthesis and characterization of new polyimides obtained from a tricyclic heteroaromatic dye, 2,7-dimethyl-3,6-diaminoacridine, commonly referred to as acridine yellow.

The presence of bulky methyl groups in acridine yellow is presumed to ease solvent penetration through

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ACRIDINE YELLOW
(2,7-dimethyl-3,6-diaminoacridine)

the polymeric chains and should yield solvent processable polyimides. In addition, due to the methyl groups, the polymeric chains will not stack up easily and this will impart better dielectric properties to the resulting polymer.

To determine the reactivity of acridine yellow towards dianhydrides, a computer simulation was performed using the Hyperchem simulation program. After determining the reactivity of acridine yellow theoretically, the preparation of the model compound was undertaken using acridine yellow and phthalic anhydride, as shown below.

Once the model compound was obtained, acridine yellow was reacted with various dianhydrides: pyromellitic dianhydride (PMDA), 3,3',4,4'-benzophenone tetracarboxylic acid dianhydride (BTDA) and 2,2'-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6FDA).

Experimental

Materials. Acridine yellow monohydrochloride (Eastman Kodak) was neutralized and purified before use. Phthalic anhydride (Fisher Scientific), PMDA (Eastman Kodak), BTDA (Eastman Kodak) and 6FDA (PCR Inc.) were used as received. Dimethylformamide (DMF) (Fisher Scientific) and dimethyl sulfoxide (DMSO) (Fisher Scientific) were vacuum distilled. *N*-Methyl-2-pyrrolidinone (NMP) (Fisher Scientific) was vacuum distilled after drying overnight over phosphorus pentoxide. Freshly distilled NMP was used for all reactions. Potassium bromide (IR grade, Fisher Scientific) was used as received.

Instrumentation. Infra-red (i.r.) spectra were obtained using a Fourier transform (FT) i.r. spectrometer (Analect fx-6260). Nuclear magnetic resonance (n.m.r.) spectra were obtained in solution using a FT n.m.r. spectrometer

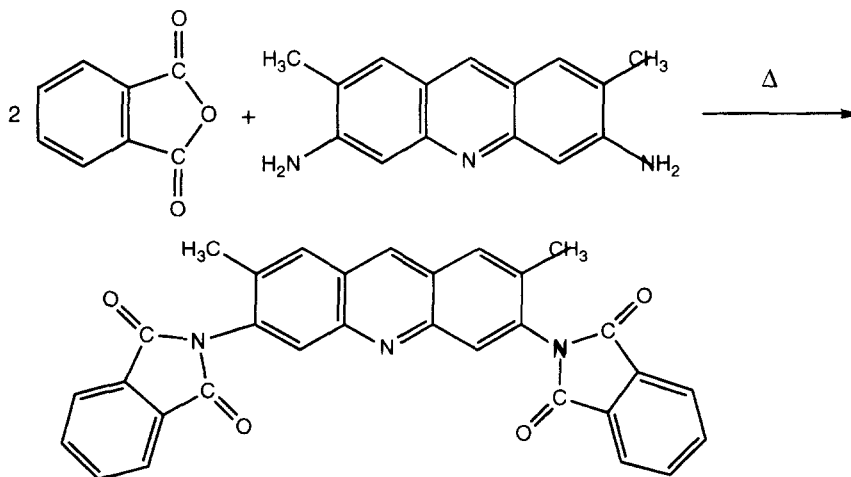
(General Electric QE-300), with ^1H frequency at 300.65 MHz and ^{13}C frequency at 75.6 MHz. Reduced specific viscosity measurements were performed using a Cannon-Fenske viscometer. Intrinsic viscosity measurements were performed using a Ubbelohde viscometer. U.v. spectra were obtained using a DU640 spectrometer (Beckman 600 series). Molecular weight measurements were performed using vapour pressure osmometry (VPO) (Wescan Instruments Model 233). A Melt-temp II (Laboratory Devices Inc.) was used to determine the melting point. Thermal stabilities of acridine yellow, the model compound and the polyimides were determined by using a thermogravimetric analyser (Perkin Elmer Series 7). Differential scanning calorimetry (d.s.c.) (DSC-4, Perkin Elmer) was used to examine glass transition temperatures. A wide angle X-ray spectrometer (Rigaku) with a wavelength of 1.54 Å was used for X-ray studies. Elemental analyses were performed by the Desert Analytics Laboratory (Tucson, AZ).

Purification of acridine yellow. Acridine yellow monohydrochloride (1 g) was dissolved in 100 ml of boiling distilled water. The solution was allowed to cool to room temperature. On cooling, 1 M sodium hydroxide was added, dropwise, until the precipitation of neutralized acridine yellow was complete. This solution was filtered and the precipitate was washed with 100 ml of distilled water. The neutralized acridine yellow was then vacuum dried at 25°C and recrystallized as long needles from DMF. The overall yield after recrystallization was 60%.

M.p: greater than 350°C; n.m.r. [in DMSO- d_6 with tetramethylsilane (TMS) as reference]: 2.26 (s), 5.57 (s, broad), 6.89 (s), 7.48 (s), 8.15 (s) ppm in a 6/4/2/2/1 ratio.

Synthesis of model compound. Acridine yellow (0.2 g) and phthalic anhydride (0.205 g) were dissolved in a 1/2 molar ratio in NMP (10% w/v), in a 25 ml round bottom flask and stirred continuously with a magnetic stirrer at different temperatures in a silicone oil bath. The model compound was precipitated, vacuum filtered and washed with distilled water. The product was dried in the vacuum oven at 60°C for 12 h. The structure of the model compound was confirmed by ^1H n.m.r. in DMSO- d_6 and i.r. spectroscopy. The reaction was optimized in terms of temperature and reaction time.

M.p: greater than 350°C with decomposition; i.r. (KBr



MODEL COMPOUND SYNTHESIS

pellet): 1724 and 1785 cm^{-1} ; n.m.r. (in DMSO- d_6 with TMS reference): 2.26 (s), 7.95 (d), 8.01 (d), 8.18 (s), 8.27 (s), 9.10 (s) ppm in 6/4/4/2/2/1 ratio.

Synthesis of polyamides. Polyimide poly(acridine yellow-co-PDMA) (AYPMDA) was obtained from acridine yellow and PMDA. Recrystallized acridine yellow (0.5 mmol, 0.1185 g) and PMDA (0.5 mmol, 0.1090 g) were mixed in a 25 ml round bottom flask. Freshly distilled NMP (2.3 ml) was added to this mixture to form a solution containing 10% solids. Nitrogen gas was bubbled into the solution, using a vent through the rubber septum, for 15 min, to remove the air from the flask. Optimum temperatures and reaction times were determined. The product was precipitated from the solution with 150 ml of methanol. The precipitate was vacuum filtered, washed with 100 ml of methanol and partially dried in a vacuum oven at 25°C for 4 h. The product was then crushed into a fine powder. Any adhered reaction solvent was continuously extracted for 24 h in a Soxhlet extractor using methanol as the solvent.

Polyimide AYBTDA was synthesized from acridine yellow and BTDA using the same technique as described above. Similarly, polyimide AY6FDA was synthesized using acridine yellow and 6FDA.

Results and discussion

Model compound synthesis. Initially, an attempt was made to synthesize the model compound using the two-step, low temperature synthesis technique. However, due to the poor reactivity of acridine yellow, the reaction at lower temperature was unsuccessful. Hence, the one-step, elevated temperature solution imidization technique was used. To ensure that acridine yellow does not decompose at the reaction temperature, the thermal stability of acridine yellow was determined. Acridine yellow was found to be stable up to 300°C, under a nitrogen atmosphere at a heating rate of 10°C min^{-1} . The small weight loss was observed at approximately 100°C in the thermogravimetric analysis (t.g.a.) of acridine yellow. This weight loss is interpreted as the evaporation of the absorbed moisture from the acridine yellow. The model compound was analysed by ^1H n.m.r. and i.r. The completely imidized model compound was obtained after 17 h of reaction time at 185°C. The i.r. spectrum of the model compound had characteristic imide peaks at 1724 and 1785 cm^{-1} . The model compound was dark brown in colour, with a melting point greater than 350°C. The t.g.a. of the model compound showed 10% weight loss at 350°C under nitrogen atmosphere at the heating rate of 10°C min^{-1} .

Synthesis of AYPMDA polyimide. AYPMDA polyimide was synthesized by reacting equal moles of acridine yellow with PMDA. Due to the poor reactivity of acridine yellow, the one-step, elevated temperature solution imidization technique was adopted for the synthesis of polyimides. Polymerization reactions were carried out at various temperatures in the polar aprotic solvents DMF, DMSO and NMP at 10% solid content. The results indicated that the incompletely imidized product precipitated from the DMF and DMSO solutions. Therefore, NMP was selected as the solvent. In NMP, the product did not precipitate from the solution throughout the reaction time.

Once the solvent was selected, optimization of

percentage solid content was undertaken at the reaction temperature of 185°C. At 5% solid content, i.r. spectroscopy and t.g.a. indicated incomplete imidization. At 15% solid content, premature polymer precipitation took place. Hence, both 5 and 15% solid content reactions did not yield the desired product.

At a high reaction temperature, the reaction time was the crucial factor for preparing the polymer of the highest molecular weight. The reaction was optimized in terms of reaction time, at the reaction temperature of 185 \pm 2°C, by carrying out reactions under identical conditions for different time periods. The extent of imidization was determined by i.r. spectroscopy and t.g.a. of the product. The presence of polyamic acid was determined by the broad peak of the hydroxyl group of polyamic acid in the range 3700–2500 cm^{-1} in the i.r. spectrum and weight loss in t.g.a. in the range 175–200°C. The presence of imide groups in the i.r. spectrum were identified by an asymmetric stretching band around 1720–1725 cm^{-1} and a symmetric stretching band around 1780–1785 cm^{-1} . Products of the reactions that gave completely imidized product were used to measure the reduced specific viscosity using a Cannon–Fenske viscometer, at 0.5% (w/v) concentration, in NMP at 30°C. Since the reduced specific viscosity and the molecular weight are directly proportional to each other, reduced specific viscosity values can be used to determine the optimum reaction time, the time at which the polymer with the highest molecular weight is obtained. A plot of reduced specific viscosities *versus* reaction time indicated an optimum reaction time of 4 h. After 4 h, the molecular weight decreases as indicated by the decrease in reduced specific viscosity.

Synthesis of AYBTDA polyimide. AYBTDA polyimide was synthesized by reacting an equal number of moles of acridine yellow and BTDA, using the techniques by which AYPMDA polyimide was synthesized. The reaction time was optimized at 185°C and 10% solids content in NMP. The reduced specific viscosities were measured at 0.5% concentration in DMF at 30°C and were plotted *versus* reaction time to identify the optimum time for the reaction. Viscosity results indicated that the molecular weight of the AYBTDA polymer increases with reaction time from 15 to 21 h and then decreases sharply. From the experimental results, it can be concluded that the maximum molecular weight of the AYBTDA polymer was obtained at 21 h of reaction time.

Synthesis of AY6FDA polyimide. AY6FDA polyimide was synthesized by reacting an equal number of moles of acridine yellow and 6FDA, using the previously described technique. The reaction was optimized in terms of reaction time at 185°C in NMP. The reduced specific viscosities were determined at 0.5% concentration in DMF at 30°C and were plotted *versus* reaction time to identify the optimum reaction time. There was no rapid change observed in the reduced specific viscosity of the AY6FDA polyimide, over the period of time. A comparison of reduced specific viscosity values of the products obtained at 18 and 21 h reaction time was identical.

Intrinsic viscosity. The intrinsic viscosities of all the three polyimides obtained under optimized conditions

were determined. All intrinsic viscosity measurements were performed by using an Ubbelohde viscometer at 30°C. The intrinsic viscosity of AYPMDA polyimide was measured in NMP and intrinsic viscosities of AYBTDA and AY6FDA were measured in DMF. The intrinsic viscosity results are shown in Table 1.

Solubility. In order to use these newly synthesized polyimides for commercial applications, they should be soluble in organic solvents. Therefore, solubility determination of these polyimides was carried out on a qualitative basis. Three observations were made. The first observation was made immediately after adding the solvent; the second observation was made 20 min after adding the solvent; the third observation was made after heating the solution. The results are shown in Table 2. The results showed that polyimides containing the benzophenone unit or fluorine possess better solubility characteristics and are completely soluble in common organic solvents. The polyimide containing PMDA is sparingly soluble in common organic solvents and dissolves in a strong acid such as sulphuric. The results obtained can be rationalized on the basis of the rigidity of the polymeric chains. AYPMDA has a rigid backbone, which makes it difficult for the solvent molecules to penetrate through the polymeric chains,

thus reducing the solubility of the polymer. In contrast, AYBTDA and AY6FDA polyimides contain flexible backbones. This permits the solvent molecule to penetrate easily through the polymeric chains, thereby making these polyimides more soluble in common organic solvents. Two methyl groups present on acridine yellow are also involved in imparting increased solubility characteristics to the polymers. The bulkiness of these groups increases the polymeric chain's separation, providing access for penetration of solvent molecules. Because of good chemical resistance of all these polyimides towards solvents like chloroform, methanol, tetrahydrofuran and *p*-dioxane, they can be used in the manufacture of chemical filters on suitable support.

Thermal stability. The thermal stability of a material is defined as its ability to retain certain properties for a stated period of time at elevated temperatures (> 230°C) under defined conditions. These conditions may include vacuum, air or inert atmosphere. Generally, the thermal stability of a polymer is reported as a temperature at which a specific weight loss occurs, typically 5 or 10%, under specified conditions. Thermal stabilities of these newly synthesized polyimides were investigated using a Perkin Elmer 7 Series thermogravimetric analyser under

Table 1 Results of acridine yellow polymerization reactions

Compound	Optimized reaction time (h)	Intrinsic viscosity	10% weight loss temp. under N ₂ (°C)	Weight remaining at 1000°C under N ₂ (%)	Elemental analysis			
					%C	%H	%N	
AYPMDA	4	0.11	460	55	Theor. ^a	71.6	3.12	10.02
					Theor. ^b	65.1	3.20	8.0
					Exp.	64.7	3.00	9.0
AYBTDA	21	0.10	450	57	Theor. ^a	73.4	3.2	8.0
					Theor. ^b	69.2	3.3	7.2
					Exp.	67.0	3.1	7.7
AY6FDA	18	0.13	380	57	Theor. ^a	63.2	2.6	6.5
					Theor. ^b	62.0	2.5	5.8
					Exp.	58.4	2.4	6.2

^a Assuming polymer of infinite molecular weight

^b Assuming polymer of finite molecular weight

Table 2 Solubility of different acridine yellow polyimides in different solvents

Polymer	Condition	CHCl ₃	Phenol	DMF	Cresol	NMP	DMSO	HCOOH	THF	TFA	<i>p</i> -Dioxane	H ₂ SO ₄
AYPMDA	R.T. (im)	-	-	-	-	-	-	-	-	-	-	+-
	R.T. (20)	-	-	+-	+-	+-	+-	+-	-	+-	-	+++
	Heat	-	+	++	+++	+++	+++	+++	-	+++	-	-
AYBTDA	R.T. (im)	-	-	-	-	-	-	-	-	-	-	+-
	R.T. (20)	-	+++	+++	+++	+++	+++	+++	-	+++	-	+++
	Heat	-	-	+++	+++	+++	+++	+++	-	+++	-	+++
AY6FDA	R.T. (im)	-	+++	+++	-	-	-	-	-	-	-	+-
	R.T. (20)	-	-	+-	+-	+++	+++	+++	+-	+++	-	+++
	Heat	-	-	+++	+++	+++	+++	+++	+-	+++	-	+++

R.T. (im) = room temperature, immediately after solvent addition; R.T. (20) = room temperature, 20 min after solvent addition; Heat = result after heating the solution

Solvents used: TFA = trifluoroacetic acid; DMF = dimethylformamide; DMAc = dimethylacetamide; NMP = 1-methyl-2-pyrrolidinone; DMSO = dimethyl sulfoxide

- = Insoluble; +- = slightly soluble; +++ = increased solubility; ++++ = completely soluble

nitrogen and air atmospheres. The results are summarized in Table 1. All three polyimides showed thermal stability in the range 370–460°C.

D.s.c. D.s.c. measurements were performed for these polyimides by using a Perkin Elmer DSC-4 under nitrogen atmosphere. None of the three polyimides showed a melting point and/or glass transition temperature in the experimentally feasible range.

Film formation. Using DMF as a solvent, films of these three polyimides were formed on a glass surface by placing two drops of polymer solution on a glass slide and drying in a vacuum oven at 60°C for 12 h. All three glass slides were inspected under a microscope. The films showed cracks at the edges. They could not be peeled from the glass surface. This may be due to the adhesive property of the polyimides. In order to peel the films from the polar glass surface, the polarity of the glass surface was altered by treating it with dimethyl-dichlorosilane. This was done to make the glass surface less polar and thereby avoid adhesion between the polymers and the glass surface. New films were formed on these less polar glass surfaces using the same technique. The slides were dipped into distilled water to remove the films from the surface. Due to the poor tensile strength of AYPMDA and AYBTDA films, they did not come off in one piece. However, the AY6FDA film was peeled off in one piece.

Molecular weight determination. The gel permeation technique was initially used to determine the molecular weight of the polyimides, using DMF as a solvent. It was impossible to use the u.v. detector, because the solvent, DMF, in which the polyimides were dissolved had a cut-off value for u.v. light above the absorption wavelength of the polyimides. In addition, the refractive index detector was not sensitive enough to measure the refractive index difference. VPO was then used to determine the molecular weights. The molecular weight of AYBTDA gave good correlation. The result indicated that the molecular weight of the AYBTDA polyimide was 2278 g mol⁻¹.

X-ray spectroscopy. To evaluate the crystallinity of the polyimides, X-ray spectra of the polyimides were obtained in the solid state, using wide angle X-ray scattering. The X-ray spectra of these polyimides indicated that they were partially crystalline. AYPMDA and AY6DA polyimides showed peaks at 18° corresponding to a *d* value of 4.92 Å. AYBTDA polyimide showed a peak at 17° corresponding to a *d* value of 5.53 Å.

Elemental analysis. Elemental analysis results are shown in Table 1. The expected values of the percentages of carbon, hydrogen and nitrogen for the polyimides of infinite molecular weight did not match with the results obtained. The observed deviation in the experimental values can be explained by one or both of the following facts:

1. Polyimides, in general, have low molecular weight. Thus, the end groups of the polymeric chain play an important role in determining the individual percentages. For example, a polyimide chain of limited size with anhydride end groups will show

different elemental analysis results compared to a polyimide chain with amine end groups.

2. Polyimides are obtained by a condensation reaction mechanism. All the polymeric chains are not of the same size. Thus, if the polyimide has limited molecular weight, any degree of polydispersity will affect the elemental analysis results.

Using the experimental values of the elemental analysis, one can predict the molecular weight of the small polymers to some extent. Therefore, an attempt was made to predict the molecular weight and the structure of these polyimides. For AYPMDA polyimide, the predicted structure contains three repeat units with hydrolysed PMDA as end groups. In addition, there are three water molecules for each polymeric chain. For AYBTDA polyimide, the predicted polymeric chain contains four repeat units with hydrolysed BTDA molecules as end groups. This structure gives the molecular weight of 2306 g mol⁻¹, which is close to the molecular weight obtained by VPO, i.e. 2278 g mol⁻¹. For AY6FDA polyimide, the predicted polymeric chain contains six repeat units with unhydrolysed 6FDA molecules as end groups.

Conclusion

Three new polyimides were synthesized from a tricyclic heteroaromatic diamine, acridine yellow and PMDA, BTDA and 6FDA as dianhydrides. The poor reactivity of acridine yellow, in a two-step synthesis technique at lower temperature produced little or no product. The one-step, elevated temperature solution imidization technique was deemed more efficient and was used to synthesize imide oligomers. Optimized reaction times for synthesis of AYPMDA, AYBTDA and AY6FDA polyimides at 185°C were 4, 21 and 18 h, respectively. Intrinsic viscosity values of AYPMDA, AYBTDA and AY6FDA polyimides were 0.11 in NMP and 0.10 and 0.13 in DMF, respectively. The newly synthesized polyimides were thermally stable up to 400°C in a nitrogen atmosphere. AYBTDA and AY6FDA polyimides were soluble in organic solvents DMF and DMSO. AYPMDA polyimide was soluble in NMP. On the basis of elemental analysis, the predicted structures of a polymeric chain of AYPMDA polyimide contains three repeat units with hydrolysed PMDA as end groups, a polymeric chain of AYBTDA polyimide contains four repeat units with hydrolysed BTDA molecules as end groups, and a polymeric chain of AY6FDA polyimide contains six repeat units with unhydrolysed 6FDA molecules as end groups. For AYBTDA polyimide, the predicted structure gives a molecular weight of 2306 g mol⁻¹, which is close to the molecular weight obtained by VPO, i.e. 2278 g mol⁻¹.

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