Synthesis and Imidization of Biphenylic Dianhydride–Oxydianiline-Based Isomeric Poly(amic methyl ester)s

WENXI HUANG, MENGXIAN DING

Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun, 130022, P.O. Box 1022, P. R. China

INTRODUCTION

Polyimides are generally synthesized in a two-step process, which involves soluble precursor polymers such as poly(amic acid)s and poly(amic ester)s as intermediates. The precursor polymers are then solvent cast to the desired form and thermally treated to cycloimidize the polymer, forming the final polyimides. Understanding the details of the imidization reaction is important to ensure optimal final properties and critical in the design of the processing window for good adhesion.

In the synthesis of the precursor polymer, the nucleophilic reaction on the dianhydride carbonyl may result in the addition of the diamine in the *meta* or *para* position, and the obtained poly(amic acid)s and poly(amic ester)s actually are copolymers containing several repeat units. For instance, in polymerizations involving pyromellitic dianhydride (PMDA), chain propagation results in both *meta* and *para* catenation; in the case of bridged dianhydrides, three different repeat unit isomers are formed during polymerization (for example, see Scheme 1). Theoretical considerations have led to the prediction that the isomerism of the repeat units has a effect on the cure behavior of the polymers and ultimately on the properties of the resulting polyimides.[1,2] This effect is predicted to arise from the relative difficulty of bringing the amide functionality into the correct geometry to react with the —OH group of the acid. In this regard, Volksen et al. had investigated the isomerism of PMDA–ODA based poly(amic ethyl ester)s and found that the *meta*-poly(amic ester)s have the advantage of having lower viscosity in concentrated solution and higher imidization temperatures than the randomized chain.[3] A similar observation on the *tert*-butyl esters of PMDA–ODA poly(amic acid) indicated that the isomerism of the repeat units does not appear to have any detectable effect on the cure behavior of the polymer, although *meta* isomerism appears to enhance solubility of the polymer in organic solvents.[4]
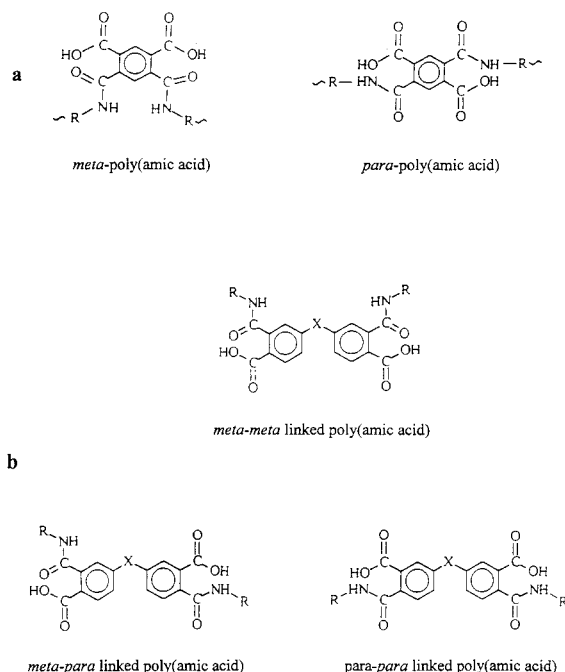
To gain a complete understanding of the imidization behavior of poly(amic ester) precursors and, in particular, the effect that difference in polymer chain architecture has on the ring-closing reaction, poly(amic methyl ester)s based on 3,3′,4,4′-biphenyl dianhydride (BPDA) and 4,4′-oxydianiline (ODA) were chosen for the present thermal imidization study because this system exists more commonly for three possible different repeat units in precursor form and the BPDA-based polyimides possess such attractive properties that they have been become increasingly important in industry.

EXPERIMENTAL

BPDA and ODA were purified by sublimation before use. *N,N*-Dimethylacetamide (DMAc) was distilled under vacuum over P_2O_5, and thionyl chloride ($SOCl_2$) was distilled under normal pressure and inert gas. Pyridine was used as received. Methanol was distilled under nitrogen from CaH_2. BPDA dimethyl ester-diacid (BPDE) was prepared by the reaction of BPDA

Correspondence to: W. Huang (present address: Department of Chemistry, New Mexico Highlands University, Las Vegas, NM 87701)

Scheme 1. Different repeat units of poly(amic acid) precursors (a) based on pyromellitic dianhydride and (b) based on bridged dianhydrides.

with methanol: BPDA was added to dry methanol and refluxed under dry nitrogen until all the solid had gone into solution, followed by distillation of excess methanol under pressure; the desired diester-diacid was obtained quantitatively. This is referred to as the mixed BPDE. Three isomers of BPDE were separated by fractional recrystallization.

Isomer Separation

The mixed BPDE (30.4 g) was suspended in ethyl acetate (500 mL) and refluxed with stirring for about 10 h. The resulting suspension was filtered. This procedure yielded (12.5 g) of hot ethyl acetate insoluble material corresponding mainly to the *meta–meta* attached isomer (*m,m*-BPDE). The isomeric purity was ∼ 80%. Recrystallization of the *meta–meta* isomer rich material from butyl acetate (∼ 100 mL) yielded 8.5 g of *m,m*-BPDE with an isomeric purity of more than 99%. The above ethyl acetate filtrate was concentrated to about 100 mL and was kept overnight with refrigeration to afford 6.5 g of white crystals, corresponding mainly to the *para–para* isomer (*p,p*-BPDE). The isomeric purity was ∼ 90%. Recrystallization of the *para–para* isomer rich material from ethyl acetate (30 mL) yielded 3.8 g of *p,p*-BPDE with an isomeric purity of more than 99%. The second filtrate was concentrated under vacuum until crystallization was initiated. After

overnight refrigeration the crystals were filtered off, and the filtrate was evaporated to afford 3.6 g of *meta–para*-attached isomer (*m,p*-BPDE) with an isomeric purity of 88%, which still contains 4% *m,m*-BPDE and 8% *p,p*-BPDE.
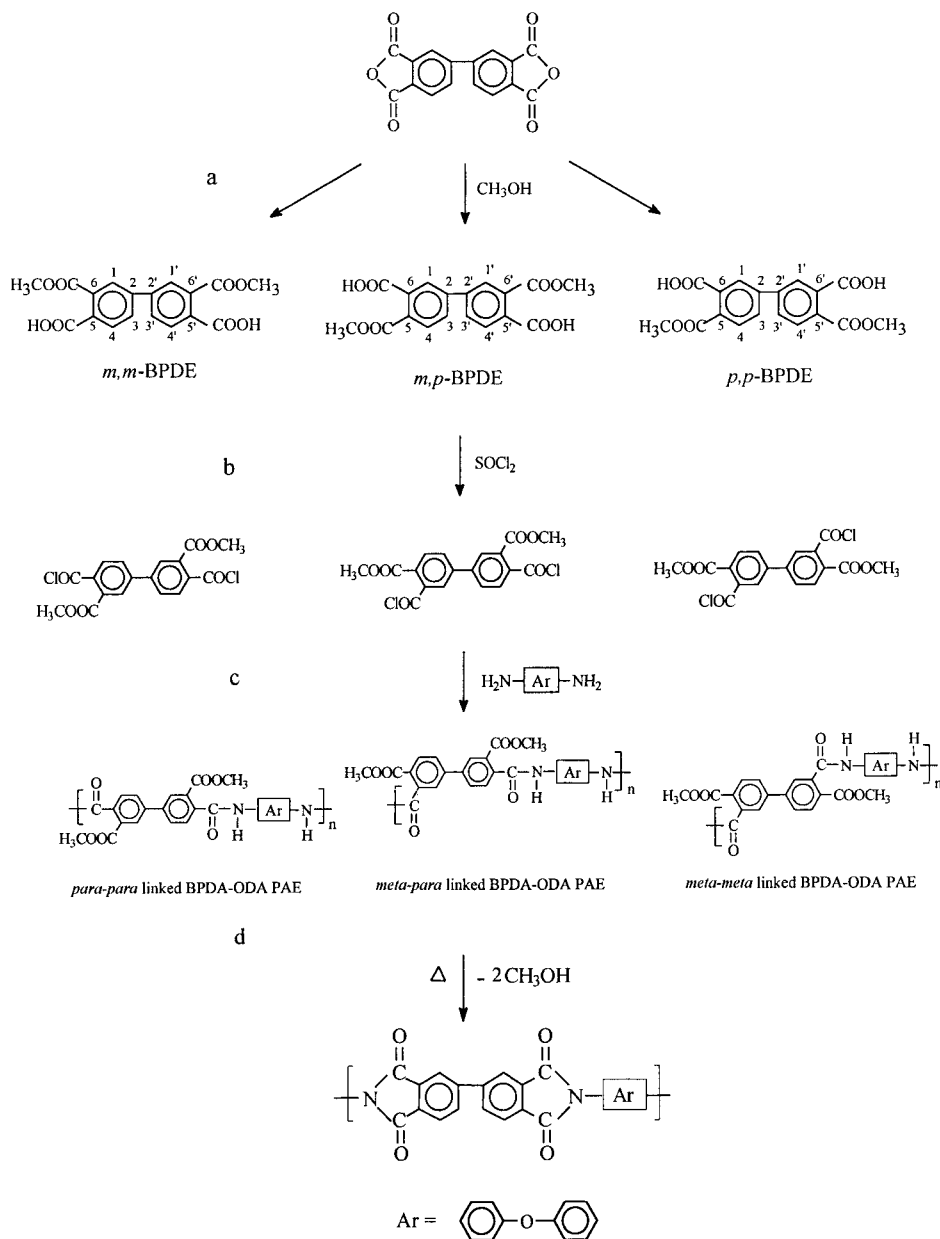
m,m-**BPDE** IR (KBr, cm^{-1}): 3437 (O—H, acid); 1730 (C=O, ester); 1698 (C=O, acid). ^{1}H-NMR (ppm; for assignments see Scheme 2a): 13.04 (br s, 2H, OH acid); 8.12 (d, 2H, CH-3, CH-3′); 8.11 (s, 2H, CH-1, CH-1′); 7.99 (d, 2H, CH-4, CH-4′); 3.90 (s, 6H, CH$_3$ ester). ^{13}C-NMR (ppm): 168.18 (C=O, acid); 167.69 (C=O, ester); 141.08 (C-2, C-2′); 133.94 (C-6, C-6′); 131.44 (C-3, C-3′); 130.18 (C-5, C-5′); 129.48 (C-4, C-4′); 126.80 (C-1, C-1′); 52.74 (CH$_3$ ester).

m,p-**BPDE** IR (KBr, cm^{-1}): 3435 (OH, acid); 1733 (C=O, ester); 1699 (C=O, acid). ^{1}H-NMR: 13.10 (br s, 2H, OH acid); 8.19 (s, 1H, CH-1′); 8.12 (d, 2H, CH-3, CH-3′); 8.11 (s, 1H, CH-1); 7.99 (d, 1H, CH-4); 7.87 (d, 1H, CH-4′), 3.90 (s, 6H, CH$_3$ ester). ^{13}C-NMR: 168.18, 168.09 (C=O, acid); 167.81, 167.69 (C=O, ester); 141.17 (C-2); 140.81 (C-2′); 133.95 (C-6); 133.58 (C-6′); 131.82 (C-3′); 131.40 (C-3); 130.18 (C-5); 129.82 (C-5′); 129.49 (C-4, C-4′); 127.38 (C-1′); 126.69 (C-1); 52.74 (CH$_3$ ester).

*pp,***BPDE** IR (KBr, cm^{-1}): 3446 (OH, acid); 1732 (C=O, ester); 1690 (C=O, acid). ^{1}H-NMR: 13.07 (br s, 2H, OH acid); 8.19 (s, 1H, CH-1, CH-1′); 8.12 (d, 2H, CH-3, CH-3′); 7.99 (d, 2H, CH-4, CH-4′), 3.90 (s, 6H, CH$_3$ ester). ^{13}C-NMR: 168.09 (C=O, acid); 169.81 (C=O, ester); 141.01 (C-2, C-2′); 133.65 (C-6, C-6′); 131.85 (C-3, C-3′); 129.84 (C-5, C-5′); 129.53 (C-4, C-4′); 127.39 (C-1, C-1′); 52.74 (CH$_3$ ester).

Mixed BPDE and its three pure isomers were converted to their respective diester-diacyl chlorides by reacting with thionyl chloride. Isomeric poly(amic methyl ester)s were prepared from corresponding isomeric diester-diacyl chlorides with ODA by low-temperature polymerization in DMAc.[5] The precursor solutions were precipitated in distilled water and washed several times with ethanol.

^{1}H- and ^{13}C-NMR spectra were recorded with a Varian Unity-400 spectrometer. All samples were dissolved in dimethyl sulfoxide-d_6 (DMSO-d_6). High-performance liquid chromatography (HPLC) was performed on the Gilson HPLC system with a Gilson model 306 pump. A 250 × 4.6 mm i.d. reverse phase column (Spherisorb ODS-2) was used. The wavelength of the detector was set to 254 nm. Thermo-

Scheme 2. Synthesis and imidization of BPDA–ODA-based isomeric poly(amic methyl ester)s.

gravimetric analysis (TGA) was performed on a Perkin-Elmer TGS-2 thermogravimetric analyzer. The heating rate was 10°C/min under nitrogen atmosphere. Dynamic mechanical thermal analysis (DMTA) was carried out with a Du Pont 982 DMA at a heating rate of 3°C/min from room temperature to 450°C. The specimens used for DMTA were prepared by supporting poly(amic ester) on a glass braid and then being dried at 80°C for 1 day under vacuum. The imidized samples were obtained by heating at 300°C for 1 h under vacuum.

RESULTS AND DISCUSSION

The initial step for the synthesis of poly(amic methyl ester)s involves the esterification of BPDA. Three diester-diacid isomers may appear as a result of the opening selectivity of anhydride groups toward the methanol (Scheme 2a). HPLC was used to separate the mixed BPDE, and three perfectly defined peaks confirmed the presence of three isomers.[6] The separation of three isomeric diester-diacids can be achieved by taking advantage of their different solu-
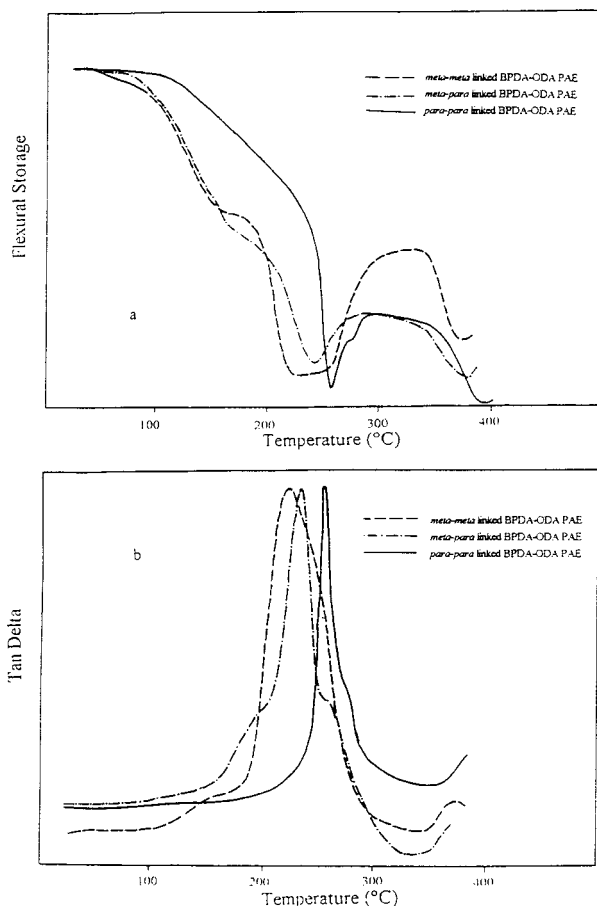
Figure 1. Typical DMTA trace of the thermal cure of three isomeric BPDA–ODA poly(amic methyl ester)s at 3°C/min: (a) flexural storage *vs* temperature (°C); (b) tan δ *vs* temperature (°C).

bility in organic solvents, and the pure isomers were obtained by fractional recrystallization. The structures of three isomeric diester-diacids were identified by ¹H- and ¹³C-NMR measurements, and the assignments of the NMR spectra were facilitated by comparing the spectrum of the isomer mixture to those of pure isomers.

The isomeric purity of the monomers, 100% for both *m,m*-isomer and *p,p*-isomer and 88% for the *m,p*-isomer, was verified by HPLC, while mixed BPDE contains three isomers with a isomer ratio of *m,m*-BPDE: *m,p*-BPDE: *p,p*-BPDE = 0.35 : 0.44 : 0.21. The aromatic diester-diacids were converted to the corresponding diester-diacyl chlorides by reacting with excess thionyl chloride (Scheme 2b). Consequently, the poly(amic methyl ester)s, mixed and three isomerically pure precursor polymers, were prepared by the low-temperature polymerization of ODA with the respective aromatic diester-diacyl chloride in DMAc (Scheme 2c). The molecular weight of these isomeric poly(amic ester)s lies within the medium molecular weight range. DMTA

has been particularly helpful for understanding the physical processes that accompany the imidization reaction (Scheme 2d). Figure 1a,b shows flexural storage modulus and tan δ traces of three isomeric poly(amic ester)s cured at 3°C/min from 50 to 400°C, respectively. Assignments regarding the processes occurring in each region of the thermogram are discussed below. There is a broad, weak peak in the tan δ curve between 110 and 180°C, which may be attributed to the β relaxation of the polymers; at a higher temperature the α relaxation is accompanied by a sharp drop in the storage modulus, corresponding to the glass transition of the partially imidized polymers and followed by a modulus increase due to the further imidization of the more flexible free poly(amic ester). Further heating causes apparent modulus drops due to shrinkage of the samples and softening of the curing polymers. It is clear from Figure 1 that different isomers of the precursors have a striking difference in the form of the DMTA trace. The *meta–meta*-linked polymer exhibits the earliest modulus drop, i.e., the lowest α relaxation temperature with peak at 222°C, while that for *meta–para*- and *para–para*-linked precursors is 232 and 256°C, respectively. The difference in the chain rigidity on the precursor backbone can be responsible for this observation. The *meta–meta*-linked precursor, due to the position of attachment, has the most bent conformation among the three isomers and, hence, yields the best flexibility on the precursor backbone, lowering its T_α. The order of stiffness for these materials would decrease as the polymer goes from all *para* catenation to all *meta*.

Table 1 compares some of the DMTA data from the polyimides obtained by thermal imidizing isomeric poly(amic ester)s at 300°C for 1 h. T_g values are obtained by the temperature at peak maximum of α relaxation in the loss modulus curves. It is found that the T_g values of the polyimides from different poly(amic ester) isomers have a distinct difference. The polyimide

Table I. Characteristics of the Relaxation Transitions of the Polyimides Obtained from BPDA–ODA Isomeric Poly(amic ester)s by Thermal Imidizing at 300°C for 1 h

Polymer	Glass Transition Temp T_g (°C)	
	Poly-(amic ester)	Polyimide
meta–meta-linked BPDA–ODA PAE	222	279
meta–para-linked BPDA–ODA PAE	232	274
para–para-linked BPDA–ODA PAE	256	295
mixed BPDA–ODA PAE	255	288

Table II. Thermogravimetric Analysis of BPDA–ODA Isomeric Poly(amic ester)s

Polymers	Imidization Onset Temp. (°C)	Max Rate of Imidization (°C)	Weight Loss During Imidization (%)		5% Degradation (%)
			Exp	Calc[a]	
meta–meta-linked BPDA–ODA PAE	218	235	13.4	12.3	562
meta–para-linked BPDA–ODA PAE	216	238	12.9	12.3	560
para–para-linked BPDA–ODA PAE	210	231	13.8	12.3	546
mixed BPDA–ODA PAE	217	240	13.3	12.3	570

[a] Calculated for loss of 2 methanol molecules/repeat unit.

obtained from its most extended *para–para*-linked precursor exhibits the highest T_g value among the three isomers. This difference cannot be attributed to the differences in molecular weight since the three isomeric precursors have similar molecular weight. Also, it cannot be accounted for by their possible differences in the imidization extent since, as confirmed TGA below, all precursor polymers had converted completely to the polyimides after imidizing at 300°C. This behavior is most possibly due to the difference in their molecular orientations of the polymer chains. It is obvious that the most extended and ordered *para–para*-linked poly-(amic methyl ester) precursor makes the obtained polyimide have more highly ordered main chain structure as compared to those of the polyimides obtained from other two isomeric precursors. The more ordered units favor chain–chain packing and therefore allow more interaction to occur, thereby resulting in the polymer having a higher T_g value.

The thermal imidization of isomeric poly(amic ester)s also was studied by TGA using a heating rate of 10°C/min from 50 to 650°C under nitrogen. All polymers showed two-step weight losses corresponding to the imidization process and thermal degradation. In the range 200–350°C, all the polymers showed a weight loss about 13% corresponding to the loss of methanol during imidization. The second step on the TGA curves starts at a temperature above 500°C (5% weight loss around 550°C) and corresponds to the thermal degradation of the polyimides. Table 2 compares some of the data for isomeric poly(amic ester)s from their TGA curves with calculated weight losses for imidization. It is clear that the three isomeric precursors do not appear to have any great differences in the imidization behavior, although the *para–para*-linked precursor exhibits a slightly earlier onset of imidization.

In conclusion, we have shown that BPDA–ODA-based poly(amic methyl ester)s can be prepared, as

pure *para–para*-, *para–meta*-, and *meta–meta*-linked polymers in good yield. TGA showed that these isomeric precursors do not appear to have any great difference in the imidization behavior. Further imidization studies by DMTA have found that the isomerism of the repeating units has a distict effect on the glass transition temperatures of the precursors and obtained polyimides. The *meta–meta*-linked polymer exhibits the lowest T_g, and the order of stiffness for three isomers is decreased as the polymer goes from all *para* catenation to all *meta* one. The difference for the obtained polyimides in T_g values was attributed to the difference in their molecular orientation of the polymer chains. Current work concentrates on a detailed investigation of the aggregation state of these materials by electronic spectroscopy.

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