Study on Isomerism in Esterification and Amidization of Dianhydrides and on the Behavior of Isomeric Polyamic Esters in Imidization Reaction

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ABSTRACT

The conventionally synthesized polyamic acid (PAA) and polyamic esters (PAE) actually are a copolymer containing several isomeric repeat units. Theoretical considerations have led to the prediction that the isomerism of the repeat units affect the cure behavior of the polymers and ultimately on the properties of the obtained polyimide. This effect is predicted to arise from the relative difficulty of conformational change required during the intramolecular cyclization. The isomerism of PAE studied so far was concentrated on pyromellitic dianhydride. A synthetic method has been developed in our laboratory that can create pure isomerically PAEs from a series of bridged dianhydrides, and the imidization behavior of these isomeric PAEs thus has been investigated in detail. In addition, the open selectivity of dianhydride towards alcohol and amine has also been investigated by HPLC and NMR, considering the position and chemical nature (donor or acceptor) of the bridged group.

INTRODUCTION

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, obtained poly(amic acid) and poly(amic ester) actually are copolymer containing several repeat units. In the case of bridged dianhydrides, three different repeat unit isomers are formed during polymerization (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 polyimide. 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.

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) was chosen for the present thermal imidization study because this system exists more commonly three possible different repeat units in precursor form and the BPDA based polyimides possess so attractive properties that have been considered becoming increasingly important in industry.

EXPERIMENTAL

BPDA dimethyl ester-diacid (BPDE) was prepared by the reaction of BPDA with methanol: BPDA was added to dry methanol, refluxed under dry nitrogen untill all solid has gone into solutions, and 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.

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. The precrusor solutions were precipitated in distilled water, washed several times with ethanol.

RESULTS AND DISCUSSION

The separation of three isomeric diester-diacids can be achieved by taking advantage of their different solubility in organic solvents and the pure isomers were obtained by fractional recrystallization. The ^{1}H NMR study enables structures to be attributed to these isomeric diether-diacids. The isomeric purity of the monomers, 100% for both *m, m*-isomer and *p, p*-isomer, and 88% for *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 an excess of thionyl chlorid. Consequently, the poly(amic methyl ester)s, mixed and three isomerically pure precursor polymers were prepared by the low temperature polymerization of ODA with respective aromatic diester-diacyl

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chloride in DMAc. The molecular weight of these isomeric poly(amic ester)s lies within the medium molecular weight range.

Table 1 compares some of the DMTA data from isomeric poly(amic ester)s and the resulting polyimides. T_α values were obtained by the temperature at peak maximum of the α relaxation in the loss modulus curves. It was found that the T_α values of the polyimides from different poly(amic ester) isomers have a distinct difference. The polyimide obtained from its most extended *para-para* linked precursor exhibits the highest T_α value among the three isomers. This difference can not be attributed to the differences in molecular weight since the three isomeric precursors have similar molecular weight. Also, it can not be accounted by their possible differences in the imidization extent since, as confirmed TGA, 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 orientation of 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 Tg value.
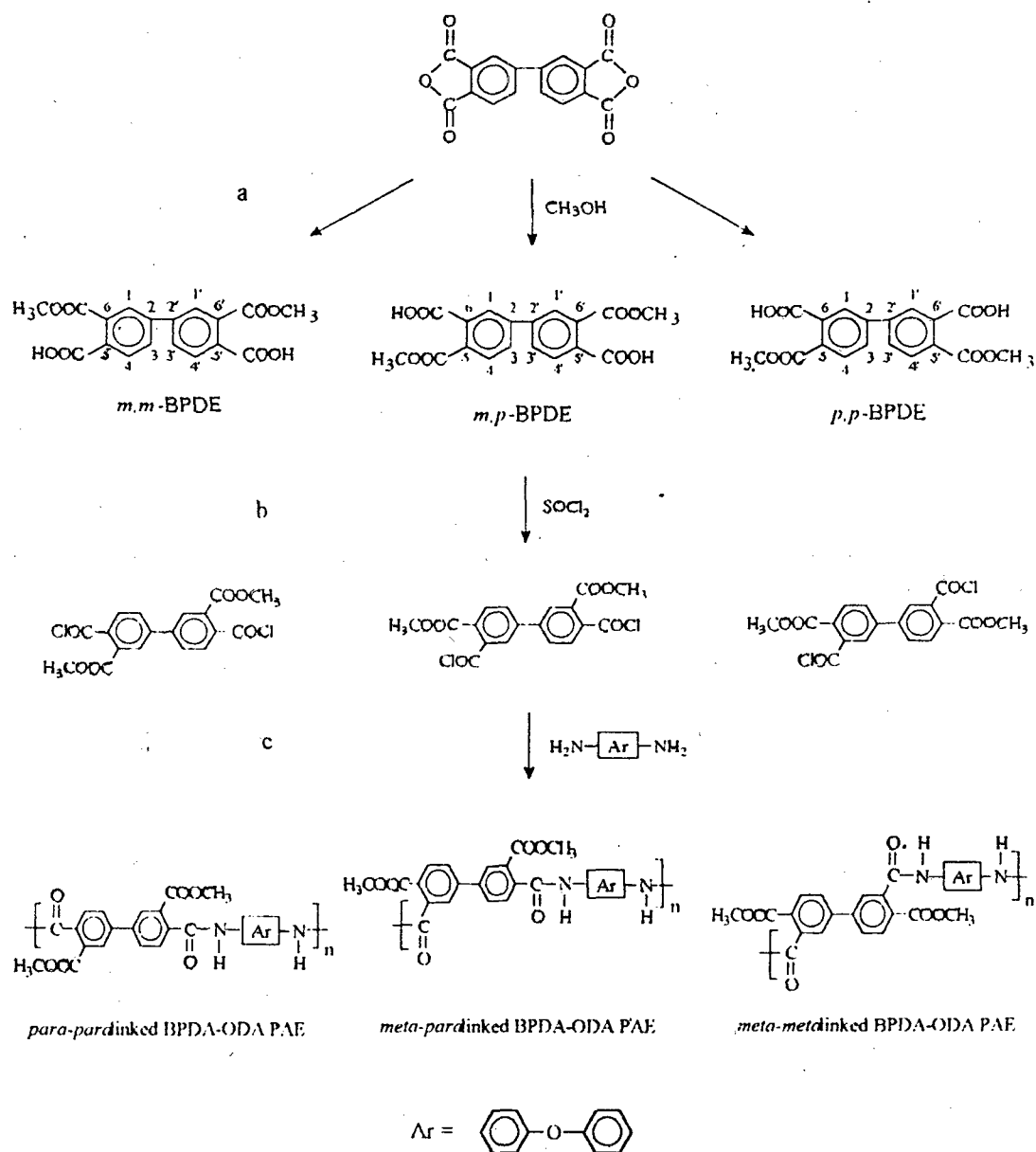
Table 1. Characteristics of the relaxation transitions of the polyimides obtained from BPDA-ODA poly(amic acid) and its esterified isomeric products

Polymer	Glass transition temperature Tg (°C)		T_d (PI 5%) (°C)
	Poly(amic ester)	Polyimide	
m-m (PAE) BPDA-ODA	222	279	562
m-p (PAE) BPDA-ODA	232	274	560
p-p (PAE) BPDA-ODA	256	295	546
mixed (PAE) BPDA-ODA	255	288	570

ª The polyimides obtained by imidizing the poly(amic acid) or poly(amic methyl ester)s at 300°C for 1 h.

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 of the precursors and obtained polyimides. The *meta-meta* linked polymer exhibits the lowest Tg, 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 Tg values was attributed to the difference

in their molecular orientation of polymer chains. Current work concentrates on a detailed investigation of the aggregation state of these materials by electronic spectroscopy.

Scheme 1. Synthesis of BPDA-ODA based isomeric poly(amic methyl ester)s