

Effect of Dianhydride Structures on Properties of Polyimides from Isomeric Diphenylsulfonetetracarboxylic Dianhydrides

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Introduction

Polyimides derived from isomeric dianhydrides have many different properties because of the various substitution positions of the anhydride group, and studies on polyimides from isomeric dianhydrides have attracted great interest for both fundamental research and practical applications. As part of continuing study of isomeric polyimides, we synthesized the novel asymmetric dianhydride, 3,4'-DSDA and two other symmetric dianhydride isomers, 3,3'-DSDA and 4,4'-DSDA. Based on the three DSDA isomers, a series of isomeric polyimides were prepared [Scheme 1]. In addition, the effect of dianhydride isomerism on the film-forming ability, solubility, thermal and mechanical properties as well as rheological behavior of the polyimides was investigated.

Results and Discussion

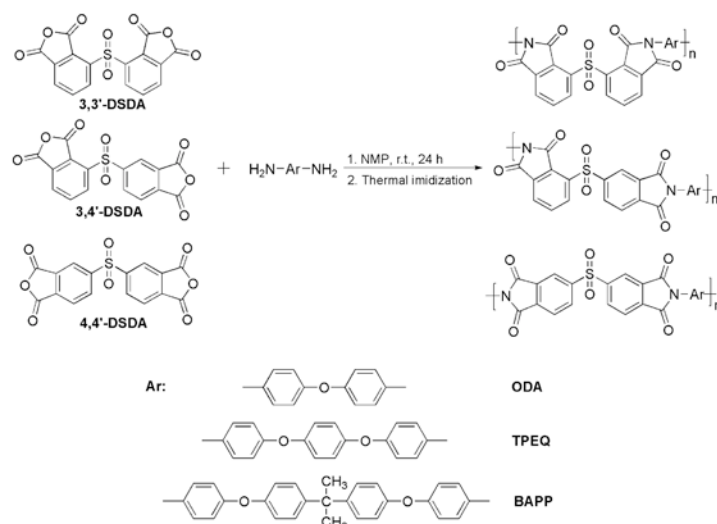
Poly(amic acid)s derived from the three DSDA isomers with 4,4'-oxydianiline (ODA), 4,4'-bis(4-aminophenoxy)benzene (TPEQ) and 2,2'-bis[4-(4-aminophenoxy)phenyl]propane (BAPP) had inherent viscosities of 0.84-1.22 dL/g and were converted into polyimide films by the conventional thermal imidization method [Table 1]. The resulting polyimide films derived from 4,4'-DSDA with the three kinds of diamines were flexible and tough, while the film of polyimide 3,4'-DSDA/ODA broke by folding up and the film of polyimide 3,3'-DSDA/ODA cracked during imidization. The polyimides 3,4'-DSDA/ODA and 3,4'-DSDA/TPEQ were soluble in NMP, DMAc, DMF, DMSO and *m*-cresol, whereas the corresponding polyimides synthesized from 3,3'-DSDA and 4,4'-DSDA were not soluble in the above solvents. Furthermore, for a given diamine, the T_g s of the polyimides from the three DSDA isomers decreased in the order: 3,3'-DSDA > 3,4'-DSDA > 4,4'-DSDA [Figure 1], while the 5% weight loss temperature in both air and nitrogen atmospheres of the polyimides from the three DSDA isomers mainly increased in the order of 3,3'-DSDA < 3,4'-DSDA < 4,4'-DSDA. Moreover, the complex viscosities of the 3,4'-DSDA and 4,4'-DSDA-based polyimides decreased with an increase in the temperature before 400 °C, while the complex viscosity of the 3,3'-DSDA-based polyimide increased when the processing temperature was over 320 °C [Figure 2].

Conclusions

Based on the three DSDA isomers, a series of isomeric polyimides were prepared. Several important conclusions are summarized as follows: (1) For a given diamine, the film-forming ability of the polyimides derived from the three DSDA isomers increased in the order of 3,3'-DSDA < 3,4'-DSDA < 4,4'-DSDA. A probable reason for this is that more bent dianhydride structure was more inclined to form undesired cyclic oligomers. (2) Polyimides from 3,4'-DSDA had better solubility than those from 4,4'-DSDA and 3,3'-DSDA, which could be ascribed to its looser molecular packing resulting from its asymmetric structure. (3) For a given diamine, the T_g s of the polyimides from the three DSDA isomers decreased in the order of 3,3'-DSDA > 3,4'-DSDA > 4,4'-DSDA. A possible explanation is that the internal rotation around the bond between the phthalimide and S was restricted according to the following order: 3,3'-DSDA-based polyimide > 3,4'-DSDA-based polyimide > 4,4'-DSDA-based polyimide. (4) For a given diamine, the 5% weight loss temperatures in both air and nitrogen atmospheres of the isomeric polyimides mainly increased in the order of 3,3'-DSDA < 3,4'-DSDA < 4,4'-DSDA. This could be because the ortho-substituted phthalimide unit had stronger electron-withdrawing effect to the SO₂ group than the meta-substituted phthalimide unit, and C_{Ar}-S bond attached to the ortho-position of phthalimide unit exhibited lower electron density and less double-bond character than the C_{Ar}-S bond attached to the meta-position of phthalimide unit. As a result, polyimides with more ortho-substituted phthalimide units on the sides of the SO₂ group exhibited worse thermal stability. (5) The melt of polyimide 3,3'-DSDA/BAPP was unstable at high temperature, which could also result from its weak C_{Ar}-S bond.

Reference

1. M. X. Ding, *Prog. Polym. Sci.*, **32**, 623(2007).
2. Q. X. Li, X. Z. Fang, Z. Wang, L. X. Gao, M. X. Ding, *J. Polym. Sci. Part A: Polym. Chem.*, **41**, 3249(2003).
3. J. L. Yan, Z. Wang, L. X. Gao, M. X. Ding, *Polymer*, **46**, 7678(2005).
4. H. B. Wei, X. L. Pei, X. Z. Fang, *J. Polym. Sci. Part A: Polym. Chem.*, **49**, 2484(2011).



Scheme 1. Synthesis of isomeric polyimides based on DSDA isomers.

Table 1. Film quality and thermal properties of the isomeric polyimides.

Polymer	η_{inh} (dL/g) ^a		Film quality	T_g (°C)		$T_{5\%}^g$ (°C)	
	PAA	PI		DSC ^c	DMTA ^d	N ₂	air
3,3'-DSDA/ODA	0.91	- ^b	Cracked	- ^e	- ^f	457	476
3,4'-DSDA/ODA	1.16	0.32	Brittle	311	- ^f	450	473
4,4'-DSDA/ODA	1.18	- ^b	Flexible	- ^e	305	462	492
3,3'-DSDA/TPEQ	0.99	- ^b	Flexible	309	303	451	470
3,4'-DSDA/TPEQ	0.97	0.52	Flexible	285	286	452	485
4,4'-DSDA/TPEQ	1.22	- ^b	Flexible	282	274	458	491
3,3'-DSDA/BAPP	1.07	0.38	Flexible	271	272	446	439
3,4'-DSDA/BAPP	0.84	0.50	Flexible	266	262	461	448
4,4'-DSDA/BAPP	0.98	- ^b	Flexible	255	257	473	458

^a Measured in NMP at a concentration of 0.5 g/dL at 30 °C. ^b The data were not measured because of poor solubility. ^c The data were obtained from DSC at a heating rate of 20 °C/min. ^d The data were obtained from DMTA at a heating rate of 3 °C/min. ^e Not detectable. ^f The data were not measured because the films were brittle. ^g 5% weight loss temperature.

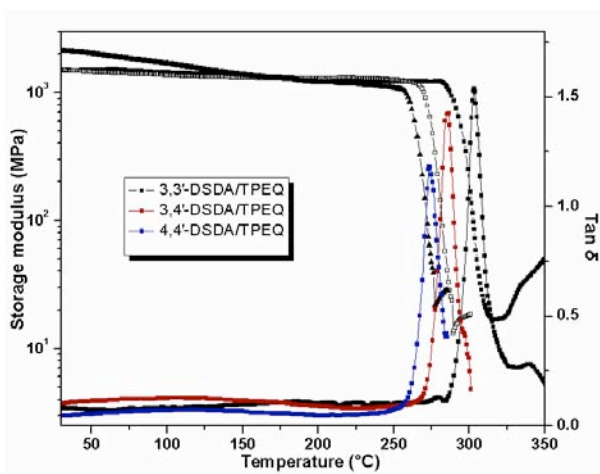


Figure 1. DMA curves of isomeric polyimide films from DSDA isomers with TPEQ.

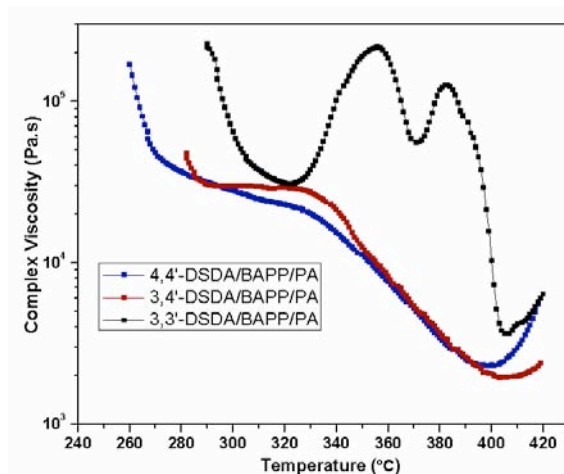


Figure 2. Rheological behavior of isomeric polyimide resins from DSDA isomers with similar Mw.