Comparative Study of Isomeric Polyimides

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Introduction

Aromatic polyimides are well known to show marked thermal stability and excellent mechanical, electrical and chemical resistant properties.[1-3] They are used as films, adhesives, plastics, coatings, matrix resins for advanced composites in many high-tech applications, such as automobile, aircraft, electrical and microelectronic industries. However, polyimide usually was difficult to fabricate because of high softening temperature and poor solubility resulted from their rigid structures. Therefore many efforts have been conducted to synthesize soluble and tractable polyimides without sacrificing their desired properties, the exploration and study on the isomeric polyimides is one of the approaches.

Isomeric polyimides from isomeric dianhydrides or diamines exhibit different properties because of the variety of substitution positions in benzene ring. Recently the study of the isomeric polyimides became one of the hotspot in the polyimide area.[4-26] Our group has presented the preparation and characterization of a series of polyimides from isomeric dianhydrides.[11-26] But at the present time, there are a few reports about the detailed study on the rheological and crystallization kinetic behavior of isomeric polyimides.

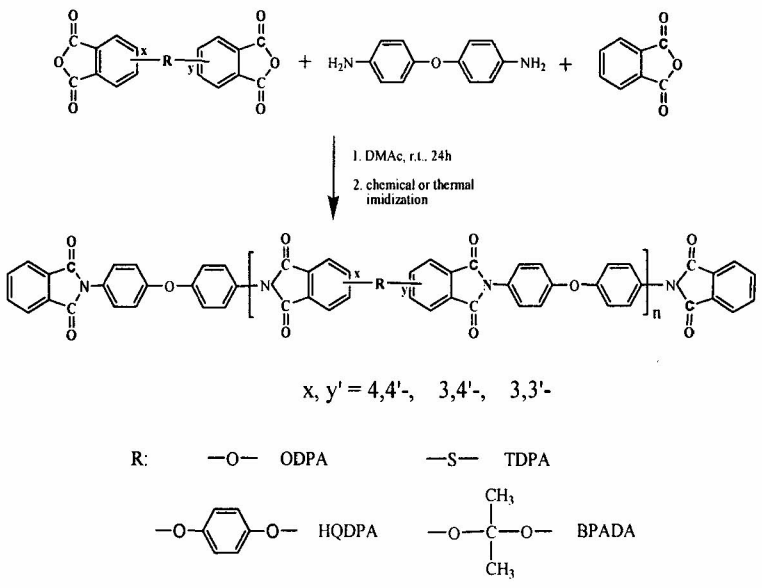
In this article, isomeric polyimides prepared from 4,4'-linked dianhydride, 3,4'-linked dianhydride and 3,3'-linked dianhydride were named as 4,4'-polyimides, 3,4'-polyimides and 3,3'-polyimides, respectively. The thermal and mechanical properties, rheological properties, and crystallization behavior of the polyimides from isomeric ODPAs, TDPAs, HQDPAs and BPADAs are compared and the isomeric effects on the polyimides are explained.

Thermal and Mechanical Properties

The thermal and mechanical properties of the isomeric polyimides are shown in Table 1. It is obvious that the 3,3'-polyimides showed the highest Tg, while the 4,4'-polyimides presented the lowest Tg, besides, the polyimides based on isomeric dianhydride showed close values in thermoxidative and mechanical properties.

Table 1: Thermal and mechanical properties of the isomeric polyimides

Polymer	Tg (°C)		Td (°C)	Tensile strength	Modulus	Elongation
	DSC	DMTA	$T_{5\%}$	(Mpa)	(Mpa)	(%)
4,4'-ODPA/ODA	262	269	493	105	1950	23
3,4'-ODPA/ODA	272	278	505	98	1860	10
3,3'-ODPA/ODA	290	295	500	98	1570	12
4,4'-TDPA/ODA	263	277	525	112	1743	22
3,4'-TDPA/ODA	269	287	514	123	2004	10
3,3'-TDPA/ODA	281	305	531	121	1962	9
4,4'-HQDPA/ODA	240	257	503	122	1453	64
3,3'-HQDPA/ODA	255	273	505	111	1574	32
4,4'-BPADA/ODA	221	226	476	90	1639	98
3,3'-BPADA/ODA	235	248	455	88	1648	8



Scheme 1: Synthesis of isomeric polyimides

Dynamic Mechanical Thermal Analysis

Figure 1, 2, 3, 4 showed the dynamic mechanical properties of the polyimides from isomeric ODPAs, TDPAs, HQDPAs and BPADAs. As can be seen that the 4,4'-polyimides have a broad and strong T_β transition than that of 3,4'-polyimides, 3,3'-polyimides showed almost no T_β transition. The absence of T_β for 3,3'-polyimides may result from the steric hindrance of the rotation around the bond to the benzene ring where the imide group vicinity located. Taking the peak temperature in the tan-delta or the turn pointing temperature of storage modulus as Tg, it is clear that Tg decreased in the order of 3,3'->3,4'-> 4,4'- as we reported previously. The polyimides from the same dianhydrides and diamine, such as that based on ODPAs/ODA and TDPAs/ODA showed the kindly similar original storage modulus.

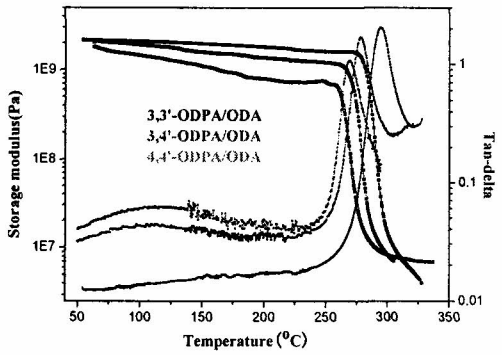


Figure 1: DMTA curves of isomeric polyimides from ODPAs/ODA

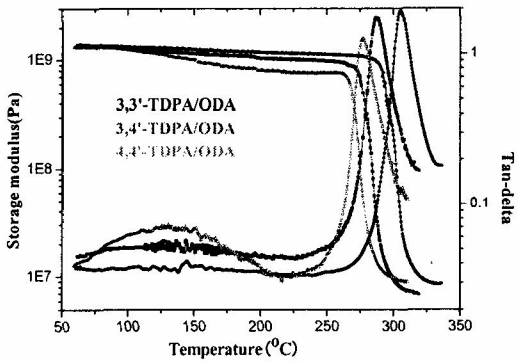


Figure 2: DMTA curves of isomeric polyimides from TDPAs/ODA

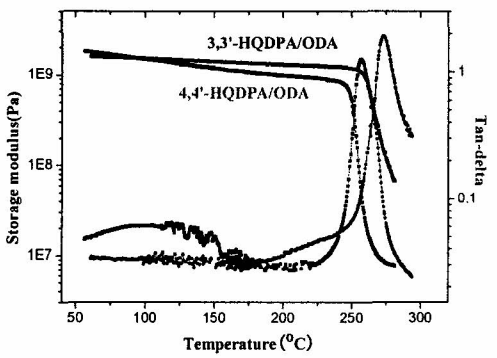


Figure 3: DMTA curves of isomeric polyimides from HQDPAs/ODA

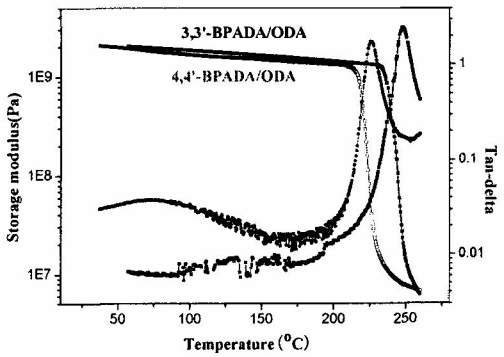


Figure 4: DMTA curves of isomeric polyimides from BPADAs/ODA

Rheological Properties

The rheological behaviors of isomeric polyimides were presented in Figure 5, 6, 7, 8. The samples of the same group have the comparable inherent viscosity. Figure 5 showed the rheological properties of isomeric polyimides based on ODPAs. As can be seen that the complex viscosity of 3,4'-ODPA appeared the lowest value about 700Pa.s at the range of 300-380°C, the 3,3'-ODPA/ODA showed the highest complex viscosity among the three isomeric polyimides over the whole tested temperature. The melt viscosities are determined by the intermolecular interaction and the rigidity of the polymer structure, 3,4'-ODPA-based polyimides showing the lowest melt viscosity mainly contribute to the asymmetrical structure of the main chain. Figure 6 summarized the rheological properties of isomeric polyimides from TDPAs/ODA. It is clear that the rheological behavior of polyimides from TDPAs/ODA was similar to that of ODPAs/ODA, 3,4'-TDPA/ODA also presented the lowest melt viscosity among TDPAs/ODA. Furthermore, as a whole, TDPAs/ODA series showed the lower melting viscosity than ODPAs/ODA series at the same temperature zone. Figure 7 showed the rheological properties of isomeric polyimides from HQDPAs/ODA. We can see from Figure 7 that the melt viscosity of HQDPAs/ODA dramatically decreased around 340°C. However, a big inflexion at 295°C appeared for 3,3'-HQDPA/ODA, the reason still remained unclear at present time, the further study is now in the progress. The complex viscosities of BPADAs/ODA were summarized in Figure 8. The melt viscosities decreased gently along with the process of raising temperature. 3,3'-BPADA/ODA showed a little higher complex viscosity than 4,4'-BPADA/ODA.

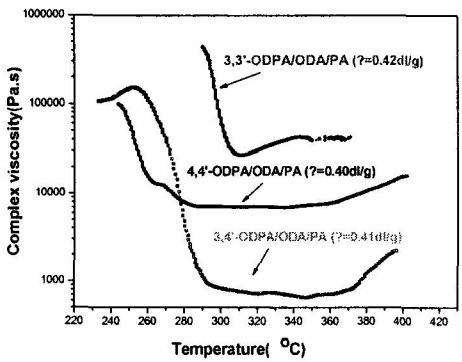


Figure 5: Rheological behavior of isomeric polyimides from ODPAs/ODA

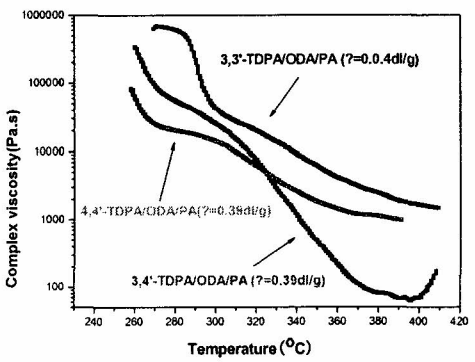


Figure 6: Rheological behavior of isomeric polyimides from TDPAs/ODA

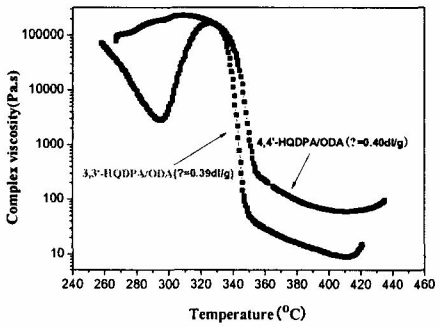


Figure 7: Rheological behavior of isomeric polyimides from ODPAs/ODA

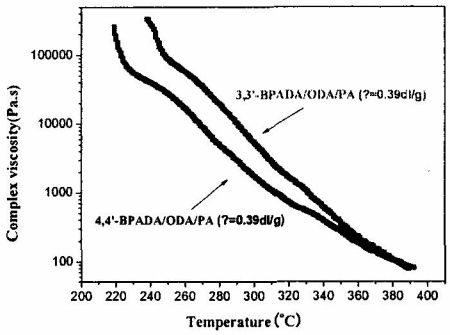


Figure 8: Rheological behavior of isomeric polyimides from BPADAs/ODA

Crystallization Behaviors

The crystallization behaviors of isomeric polyimides were detected by the wide angle X-ray diffraction (WAXD) and differential scanning calorimetry analysis (DSC). Figure 9, 10 showed the DSC curves of isomeric polyimides based on ODPAs and TDPAs. Among the polyimides from isomeric ODPA only 4,4'-ODPA-based polyimide exhibited a well-defined endothermic peak above the glass transition temperature, therefore, 4,4'-ODPA-based polyimides showed a great tendency to crystalline, while polyimides from isomeric TDPAs showed no obvious change of enthalpy after Tg. Figure 11 showed the WAXD curves of polyimides from 4,4'-TDPA and 3,4'-TDPA and 3,4'-ODPA annealed after heating at 260, 300, 330, 370 and 390°C for 50min each, the samples have typical Gaussian distribution curves, broad and structureless, suggesting that the samples were amorphous. Figure 12 showed the WAXD curves of 4,4'-ODPA-based polyimides with the heat treatment mentioned above. It can be seen that 4,4'-ODPA-based polyimide exhibited the well-defined long-range order or crystalline, and the crystal peaks became more clear and strong along with the raising of temperature, but the crystallization phenomena disappeared at 390°C. Figure 13 showed a set of DSC heating traces of 4,4'-ODPA-based polyimide annealed after heating at various temperature for 50min, the samples exhibited exothermic peaks above the glass transition temperature, the 370°C curve showed the highest exothermic enthalpy but at 390°C the peaks disappeared, which was agree with the WAXD. We also studied the effects of molecular weight on the crystallization of 4,4'-ODPA-based polyimide. Figure 14 and Figure 15 showed the

WAXD and DSC curves of 4,4'-ODPA-based polyimides with various inherent viscosities heated at 370°C for 50min. We can see the low molecular weight polyimides appeared the best crystallization, while the crystallization became more difficult along with the increasing of molecular weight.

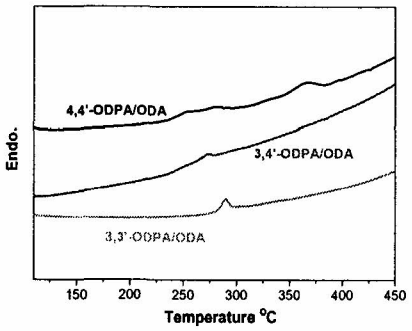


Figure 9: DSC of polyimides from isomeric ODPAs heated at 260°C for 50min.

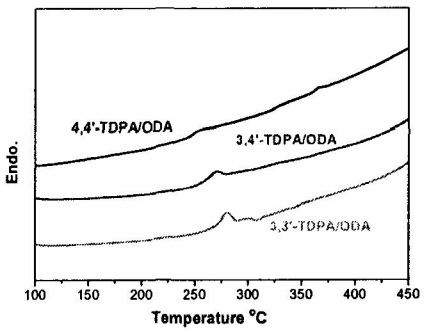


Figure 10: DSC of polyimides from isomeric TDPAs heated at 260°C for 50min.

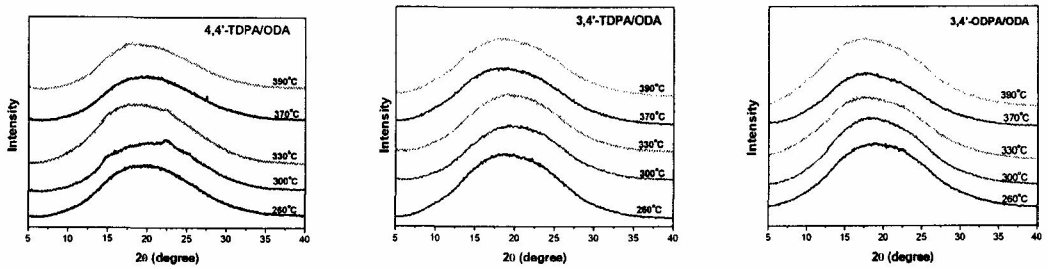


Figure 11: WAXD of polyimides from 4,4'-TDPA, 3,4'-TDPA and 3,4'-ODPA heated at various temperatures for 50min.

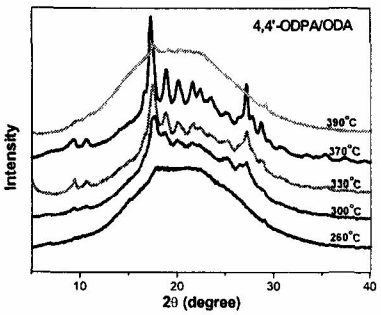


Figure 12: WAXD of 4,4'-ODPA-based polyimides heated at various temperatures for 50min.

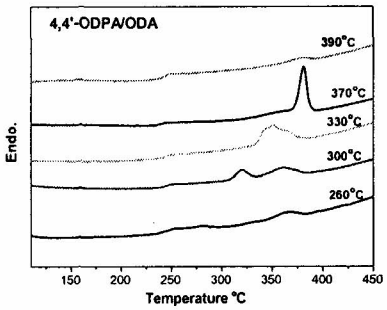


Figure 13: DSC of 4,4'-ODPA-based polyimides heated at various temperature for 50min.

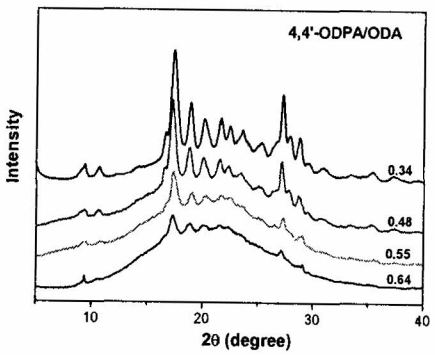


Figure 14: WAXD of 4,4'-ODPA-based-polyimides with different inherent viscosities heated at 370 °C

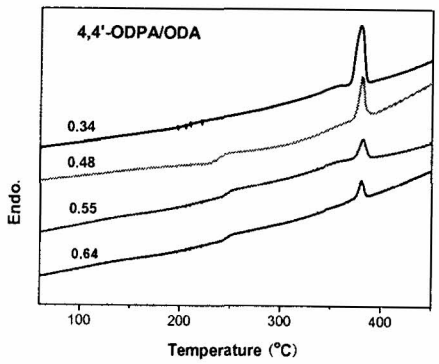


Figure 15: DSC of 4,4'-ODPA-based-polyimides with different inherent viscosities heated at 370 °C for

Conclusion

1. Four sets of isomeric polyimides based on ODA and the corresponding isomeric dianhydrides, ODPAs, TDPAs, HQDPAs and BPADAs were synthesized.
2. DMTA showed the Tg of the isomeric polyimides decreased in the order of 3,3'->3,4'-> 4,4'-polyimide.
3. The polyimide based on ODA and 3,4'-dianhydride for bridged dianhydride such as ODPA and TDPA and 3,3'-polyimide for HQDPA exhibited lower melt viscosity than the others.
4. From the WAXS and DSC study, the polyimide based on 4,4'-ODPA/ODA showed crystalline at 260-370°C, the Tm was at about 380-390°C, and the crystalline became obvious with the molecular weight decreasing. Neither the polyimides based on 3,4'-ODPA/ODA and 3,3'-OPDA/ODA nor isomeric TDPA/ODAs showed crystalline at whole temperature range studied.

Acknowledgements The authors express their thanks to the National Science Foundation of China (NO. 50333030 and 10577018) and the National 973 Project of China (NO.G2003CB615604 and 2003CB615704)) for their financial supports.

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