Study on Crystallization Behavior of Polyimides Based on Isomeric ODPAs and ODA

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Abstract: Aromatic polyimides are well accepted as highly thermally stable materials, such as films, engineering plastics, adhesives and matrices for high-performance composites etc. Most polyimides are considered as amorphous polymers, but in fact some polyimides do crystallized especially at relatively low molecular weight. Introducing crystalline in polyimide materials can offer the advantages of improving the thermal stability, increasing solvent resistance and radiation resistance, and partial retention of mechanical properties above the glass transition temperature (T_g). On the other hand, crystalline may cause problems for some materials, such as films and insulating covering materials for cables, because the crystalline may result in brittle and anisotropic property in different regions. Therefore, it is quite important to study the crystallization behavior of polyimides. A series of molecular-weight-controlled isomeric polyimides powders based on 4,4′-ODPA, 3,4′-ODPA and 3,3′-ODPA, and 4,4′-oxydianiline (ODA) were prepared by traditional two-step method in DMAc. The temperature-changed WAXD showed that the amorphous 4,4′-ODPA/ODA-based polyimide powder could crystallize during the heating process. The annealing temperature, annealing time, external force shearing and molecular weight effects on the crystallization of isomeric polyimides were studied. The results proved that the amorphous 4,4′-ODPA/ODA-based polyimide powder could crystallize during the annealing or shearing process above Tg, besides the crystallization of 4,4′-ODPA/ODA-based polyimide were enhanced by increasing the annealing temperature and time, decreasing molecular weight or pushing shearing above T_g. Two melting endotherms appeared evidently when annealing temperature was below 300°C. The two melting endotherms tended to close with the increase of annealing temperature, and only one melting endotherm was found when annealing temperature reached 370°C, however, this polyimide was difficult to recrystallize once melt. The polyimide with low molecular weight was easy to crystallization. It can be seen that the polyimide with η_{inh} of 0.34 dL/g showed the highest endotherm, the polyimide with the η_{inh} of 0.64 dL/g showed the smallest endotherm, while the polyimide with the η_{inh} of 1.1dL/g exhibited completely amorphous. DSC and WAXD results supported that the shearing process indeed enhanced the crystallization of polyimide above 260°C, although the effect was not so obvious. While in 250°C or lower temperature the shearing almost did not effect at all. The isomeric polyimides based on 3,4′-ODPA/ODA and 3,3′-ODPA/ODA were synthesized with the comparable inherent viscosity with 4,4′-ODPA/ODA, and suffered from the same treatment with 4,4′-ODPA/ODA, such as different annealing temperature, annealing time, shearing, etc., however, the two isomeric polyimides just as expected remained amorphous state as initial as-prepared whatever treatment subjected to.

Key words Polyimides, Crystallization, Isomeric dianhydride

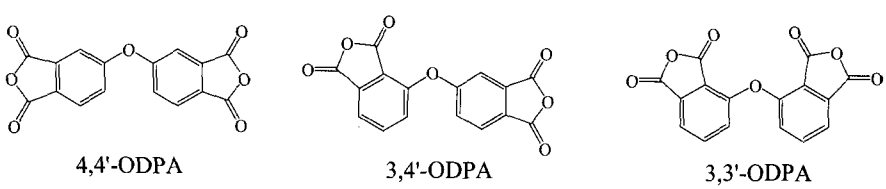

Figure 1: Chemical structure of dianhydride isomers

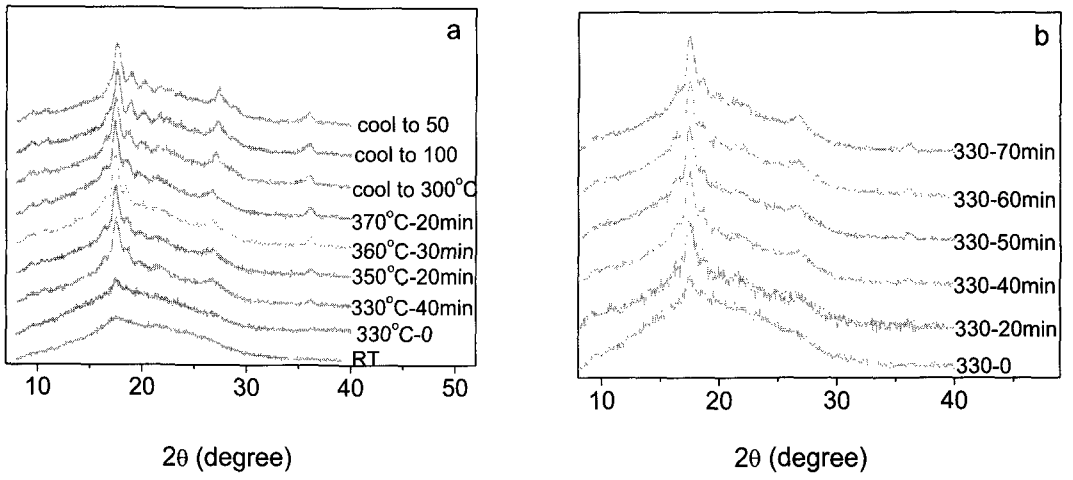

Figure 2: Temperature-changed WAXD of polyimide 4,4'-ODPA/ODA/PA (η_{inh}=0.40 dL/g)

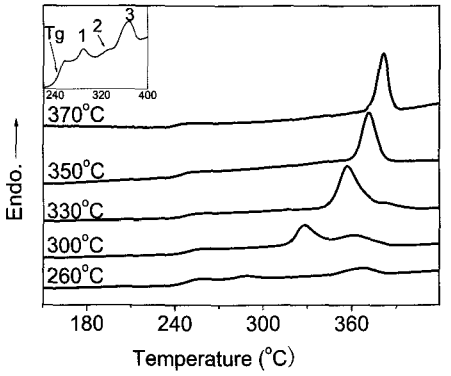

Figure 3: DSC comparison curves of 4,4'-ODPA/ODA/PA annealed for 50min at various temperatures

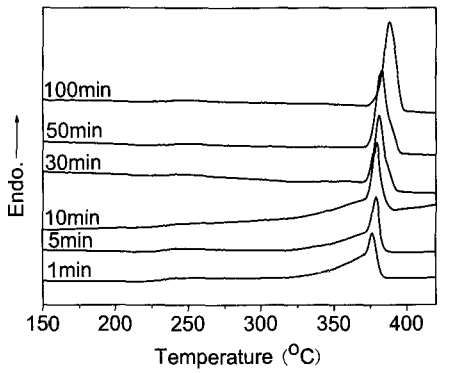

Figure 4: DSC scans for 4,4'-ODPA/ODA/PA annealed at 370°C for different time

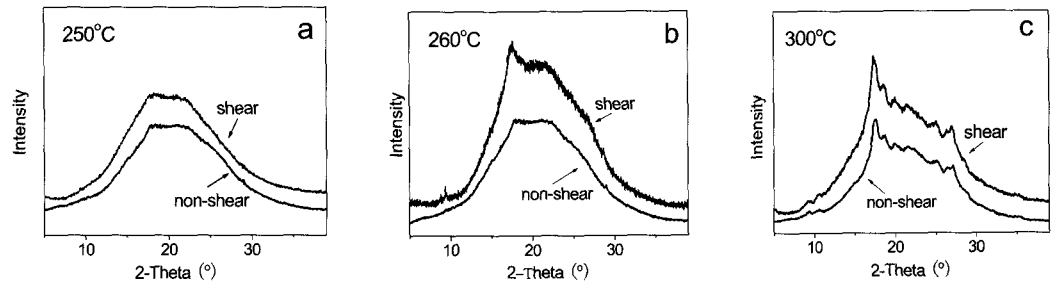

Figure 5: Comparative WAXD results of sheared and non-sheared 4,4′-ODPA/ODA/PA at (a)250°C, (b)260°C and (c)300°C for 100 min

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