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Synthesis and characterization of thermally stable semicrystalline polyimide based on 3,4′-oxydianiline and 3,3′,4,4′-biphenyltetracarboxylic dianhydride

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Abstract

The synthesis and characterization of a thermally stable semicrystalline polyimide based on 3,4′-oxydianiline (3,4′-ODA) and 3,3′,4,4′-biphenyltetracarboxylic dianhydride (BPDA), end capped with phthalic anhydride, were carried out. The glass transition temperature and the melting temperature of this polyimide (abbreviated as 3,4′-ODA polyimide) were detected at 251 and 402°C, respectively, by differential scanning colorimeter (DSC) measurement. The degree of crystallinity and heat of fusion for the annealed film of this polyimide, estimated by X-ray diffraction (XRD) and DSC measurements, were 28% and 32 J/g, respectively. The crystallization times of this polyimide under isothermal DSC measurement conditions were second order at below 300°C. This result showed the 3,4′-ODA polyimide to be a polymer having first crystallization kinetics. The thermal stability of the 3,4′-ODA polyimide was compared with that of a known semicrystalline polyimide based on 1,3-bis(4-aminophenoxy)benzene and BPDA (abbreviated as TPER polyimide). The 3,4′-ODA polyimide displayed excellent thermal stability, as evidenced by thermogravimetric analysis especially in air atmosphere and melt viscosity study during storage time. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Semicrystalline polyimide; Crystallization kinetics; Thermal stability

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1. Introduction

Aromatic polyimides [1–3] have marked thermal stability, and excellent mechanical, electrical and solvent-resistance properties. Therefore, they are being used in applications such as automobile and aircraft parts, electronic packaging, films, adhesives, and matrix materials for composites. The rigidity of aromatic polyimides arises from the stiff backbone structure, leading to glass transition and melting temperatures ranging from 200 to above 400°C. This has led to difficulties in melt processing of polyimides, since around 400°C is near the upper bound of stability for most polymers. Traditional processing has therefore often involved the solution casting of the poly-(amic acid) precursor into the desired shape, followed by thermal imidization into the polyimide. However, since melt processing is more desirable from both economical and environmental standpoint, the synthesis of melt processable, thermally stable resin is of prime interest. In the 1990s, melt-processable semicrystalline polyimide AURUM™ [4–11] having high glass transition temperature ($T_g = 250$°C) and high melting temperature ($T_m = 388$°C) was successfully developed and commercialized by scientists of Mitsui Chemicals, Inc. Semicrystalline polyimides offer further advantages of increased solvent resistance and retention of mechanical properties above the glass transition temperature. These features have made semicrystalline polyimides the focus of considerable research over the recent years [12–27].

In these recent research works, a semicrystalline polyimide based on 1,3-bis(4-aminophenoxy)benzene (TPER) and 3,3′,4,4′-biphenyltetracarboxylic dianhydride (BPDA), end capped with phthalic anhydride, was developed and its basic properties were reported [23–27]. The TPER/BPDA polyimide (abbreviated as TPER polyimide), which has a T_g of approximately 210°C and a T_m of 395°C, shows very fast crystallization kinetics. However, this polyimide shows poor thermal stability under melt condition. The melt viscosity of this polyimide increases by 1.65 times or higher compared to that of the initial viscosity on maintaining at 420°C for 30 min [26]. This viscosity change under melting condition made it difficult to apply the TPER polyimide for extrusion/injection moldings.

In this research work, the synthesis and characterization

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of high-thermally stable semicrystalline polyimide based on 3,4′-oxydianiline (3,4′-ODA) and 3,3′,4,4′-biphenyltetracarboxylic dianhydride (BPDA), end capped with phthalic anhydride (PA), are reported [28]. The properties of the synthesized 3,4′-ODA/BPDA polyimide (abbreviated as 3,4′-ODA polyimide) has also been compared with those of the TPER polyimide.

The basic thermal properties and crystallization study, including the bulk crystallization time, have been measured by differential scanning calorimetry (DSC). The crystallinity has been proved by X-ray diffraction (XRD) measurement. The thermal stability under harsh melting condition has been probed with two different analyses. One is the traditional analysis used in thermogravimetric analysis (TGA) to evaluate the degradation occurring via weight loss. However, the TGA technique by itself is inadequate for reflecting the thermal stability of polymers, since degradation reactions such as crosslinking or chain extension could occur with a small accompanying weight loss [22,26,29]. Another is the rheological analysis using a flow tester to evaluate via viscosity change, since melt viscosity is critically dependent on the molecular weight of the system.

The goal of this research work is to focus on the development of polyimide having good thermal stability and fast crystallization kinetics.

2. Experimental

2.1. Materials

3,4′-Oxydianiline (abbreviated as 3,4′-ODA) was synthesized according to the method described in a previous work [30]. 1,3-Bis(4-aminophenoxy)benzene (trivially termed triphenyl ether resorcinol diamine, referred to as TPER) was supplied by Wakayama Seika Co., Ltd. and was recrystallized from toluene before use. 3,3′,4,4′-Biphenyl tetracarboxylic dianhydride (BPDA) was obtained from Mitsubishi Chemicals, Inc. and was dried at 120°C prior to use. Phthalic anhydride (PA), 3-aminophenol and 4-nitrochlorobenzene are products of Mitsui Chemicals, Inc. 3-Methylphenol, used as a solvent for polymerization, was obtained from Tokyo Kasei Kogyo Co., Ltd. and used as received.

2.2. Polyimide synthesis

3,4′-ODA polyimide was synthesized with 28.10 g (95.5 mmol) of BPDA, 20.03 g (100 mmol) of 3,4′-ODA, 1.33 g (9 mmol) of PA, which was used for terminating the polymer chain end, according to the method described in a previous work [28]. A four-neck round-bottom flask equipped with a mechanical stirrer, nitrogen pad, thermometer and a condenser with a Dean–Stark trap was used as the reaction vessel. All monomers were added to a reaction vessel and then 3-methylphenol was added to achieve a 10% solids concentration. This solution was stirred and heated under nitrogen atmosphere for 12 h at 202°C, to afford the PA end-capped polyimide. During the reaction, the by-product, water, was removed by nitrogen flow. After cooling down, methylethyl ketone was added to the reaction mixture. The precipitated polyimide was collected by filtration, followed by thorough washing with methylethyl ketone and dried in a forced air oven at 300°C for 4 h under nitrogen atmosphere. The other polyimide obtained from TPER, BPDA and PA, was also prepared by almost the same method as mentioned above.

2.3. Preparation of polyimide films

The polyimides were used in the form of powder and quenched or annealed molded films for this study. The films were molded using a Toyo-Seiki Mini Test Press. The quenched polymer films were prepared by heating the polymer powder at 425°C for 10 min under 9.8 MPa load followed by quenching to liquid nitrogen temperature. The annealed films were prepared by heating the quenched films at 300°C for 10 min followed by quenching to liquid nitrogen temperature.

2.4. Characterization

The inherent viscosity (η_{inh}) of the polyimide was determined using an Ubbelohde viscometer at a concentration of 0.5% in a mixed solvent (*p*-chlorophenol/phenol = 9:1 w/w) at 35°C.

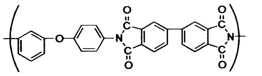
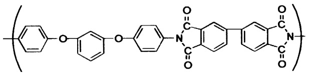
X-ray diffraction (XRD) measurement of the annealed film was carried out via an automated Philips diffractometer with Cu-Kα radiation. The data were collected in a fixed time mode with a step size of 0.02° (2θ) and run from $2\theta = 3$–$40°$.

Differential scanning calorimeter (DSC) measurement was conducted on a Perkin–Elmer DSC-7, on 6–7 mg of sample under a nitrogen purge, at a heating rate of 10°C/min. Temperature and heat flow were calibrated using indium and zinc standards. The DSC curves shown in this paper were normalized to 1 mg sample mass. The glass transition temperature (T_g) was taken at the inflection point of the ΔH versus temperature curve. The melting temperature (T_m) and crystallization temperature (T_c) were taken at the endothermic peak top temperature and exothermic peak top temperature from DSC curves, respectively.

DSC measurement for the 3,4′-ODA polyimide isothermally annealed at various temperatures was also carried out. In this study, powder samples heated at a rate of 10°C/min to 425°C and held for 10 min were cooled at a rate of 200°C/min to various temperatures and held for 90 min, and then cooled at a rate of 200°C/min to ambient temperatures. Then the samples were reheated at a rate of 10°C/min to 450°C.

Crystallization peak time study was also carried out. In this study, powder samples were heated at a rate of 10°C/min to 425°C, held for 10 min and were cooled at a rate of

Table 1
Chemical structures and inherent viscosity of synthesized polyimides

Name	Chemical structure	η_{inh} [a]
3,4′-ODA polyimide		0.62
TPER polyimide		1.05

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[a] Inherent viscosity (η_{inh}) was determined using an Ubbelohde viscometer at a concentration of 0.5% in a mixed solvent (*p*-chlorophenol/phenol = 9:1 w/w) at 35°C.

200°C/min to various temperatures. Then the samples were held at the temperature for getting the time of crystallization.

Thermogravimetric analysis (TGA) was carried out on a Shimadzu TGA-40 using the powder samples at a heating rate of 10°C/min under either nitrogen or air atmosphere.

The thermal stability of the polyimide under melting condition was probed by studying the melt viscosity change during storage time. The melt viscosity of the polyimide was measured by using a Shimadzu CFT-500 flow tester setting an orifice with 1 mm diameter and 10 mm length, under 9.8 MPa load at 425°C. Approximately 1.4 g of the polyimide powder was melted for the required time in the flow tester, which was held at 425°C, and then the measurement was carried out. For example, at the measurement temperature, the melt viscosity value increases to 1.5 times of its original value when the melt time was increased from 5 to 30 min, the thermal stability of the polyimide under melt condition was estimated as 1.5 times. Therefore, the estimated value nearer to 1.0 times indicates better thermal stability. This increase in the melt viscosity of the polyimide with increasing storage time in the melt arises as a result of changes in both nucleation density as well as chemical changes like chain extension/crosslinking occurring in the melt.

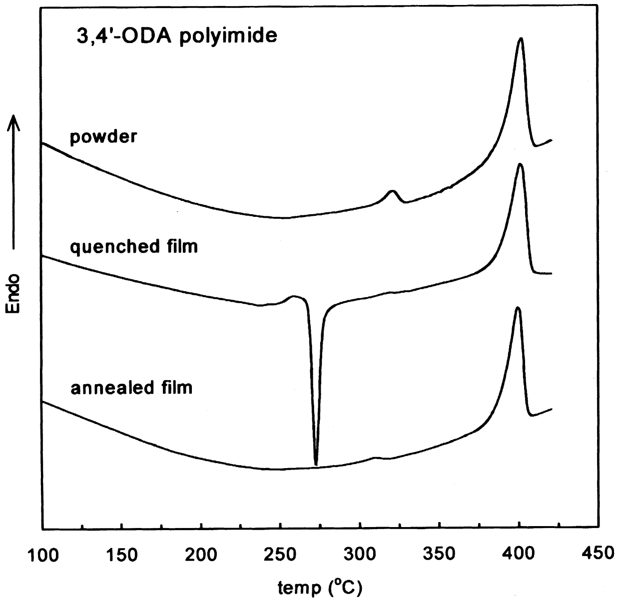

Fig. 1. DSC heat scans for the 3,4′-ODA polyimide.

3. Results and discussion

3,4′-ODA, a diamine monomer of 3,4′-ODA polyimide, was synthesized from 3-aminophenol and 4-nitrochlorobenzene followed by reduction, according to the method described in a previous work [30]. The yield of 3,4′-ODA based on 3-aminophenol was 88.6%.

3,4′-ODA polyimide was synthesized from 3,4′-ODA and BPDA, according to the method described in a previous work [28]. The polymer chain end was terminated by using PA as an end capper [28–31]. Referenced TPER polyimide obtained from TPER, BPDA and PA was also prepared by a method similar to the synthesis of 3,4′-ODA polyimide. The chemical structures of the synthesized polyimides and their η_{inh} values are summarized in Table 1.

The DSC heat scans for the as-made 3,4′-ODA polyimide powder, quenched and annealed films are shown in Fig. 1. The powder sample exhibited a weak endotherm and a prominent melting endotherm at 321 and 401°C, respectively. This weak endotherm can be attributed to the melting of the less perfect crystal formed at the final drying temperature. The additional discussion about this phenomenon is described later. The quenched film displayed a T_g and a T_m at 251 and 402°C, respectively. This quenched film also displayed an extremely narrow crystallization exothermic peak ($T_c = 272$°C) at just over the T_g. This heat flow phenomenon predicts this polyimide to be a polymer having first crystallization kinetics. The annealed film displayed a prominent melting endotherm at 400°C and the heat of fusion was estimated to be 32 J/g. Because of its prominent T_m peak without T_g transition and a T_c peak, this film is estimated to be crystallized.

The DSC heat scans for the as-made TPER polyimide powder, quenched and annealed films are shown in Fig. 2. The powder sample exhibited two weak endotherms at 322 and 343°C, followed by a sharp melting endotherm at 393°C. These multiple endothermic behaviors of the TPER polyimide have already been reported by Kreuz et al. and Srinivas et al. in their previous works [24–27]. They assigned these endotherms to the melting of less perfect crystals formed at the final drying temperature. The quenched film exhibited a weak specific heat transition corresponding to the T_g at ca. 192°C, followed immediately by a very weak crystallization exotherm at 218°C, and finally by a sharp melting endotherm at ca. 396°C. These T_g and T_m values are similar to the earlier reported values on

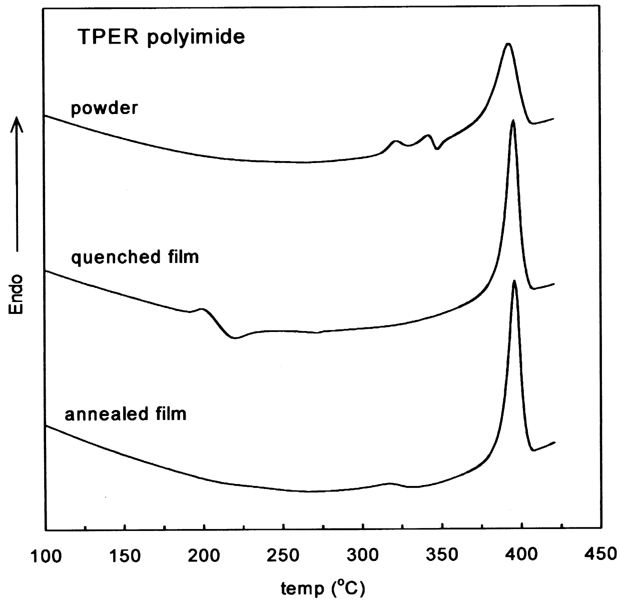

Fig. 2. DSC heat scans for the TPER polyimide.

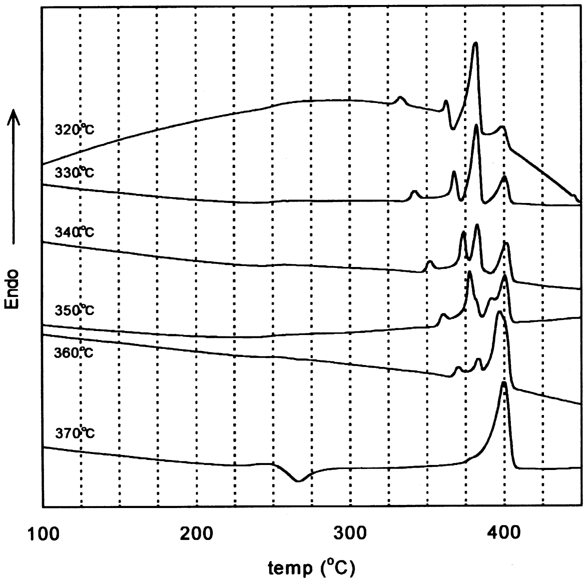

Fig. 4. DSC heat scans for the 3,4′-ODA polyimide isothermally annealed at various temperatures.

the same system [24–27]. The annealed film displayed a prominent melting endotherm at 396°C without T_g transition and a T_c peak, and the heat of fusion was estimated to be 42 J/g.

The crystallinity of the 3,4′-ODA polyimide was proved by XRD measurements. In this test, the powder and the annealed film exhibited obvious diffraction peaks that originated from crystal forms and the quenched film exhibited no diffraction peaks, as shown in Fig. 3. The degrees of crystallinity estimated from the diffractograms of the powder and the annealed film of the 3,4′-ODA polyimide were approximately 25 and 28%, respectively.

The DSC heating scans for 3,4′-ODA polyimide isothermally annealed at various temperatures after a melt treatment at 425°C for 10 min are shown in Fig. 4. Similarly to the case of the TPER polyimide reported earlier by Hsiao et al. [24–27], the 3,4′-ODA polyimide also exhibited multiple endotherms.

Isothermal DSC scans for the 3,4′-ODA polyimides at various temperatures are shown in Fig. 5. The samples were heated at a rate of 10°C/min to 425°C and held for 10 min, and they were then cooled at a rate of 200°C/min to different temperatures for the measurement, following which they were held at the measurement temperature for getting the time of crystallization at the temperature. All thermal scans were taken under nitrogen atmosphere. The

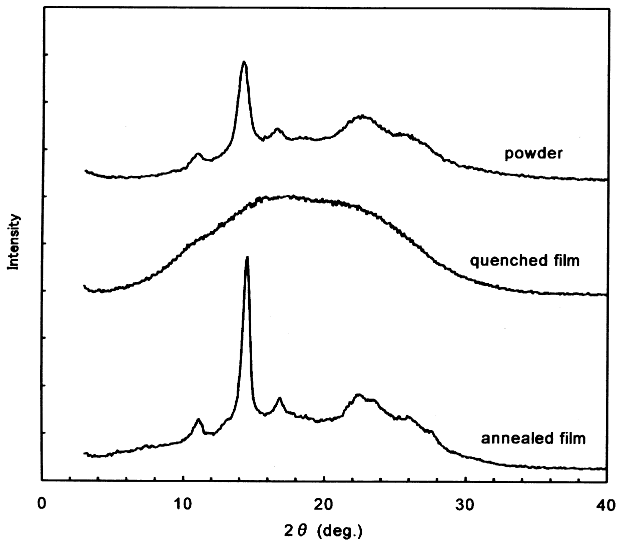

Fig. 3. XRD patterns of the 3,4′-ODA polyimide.

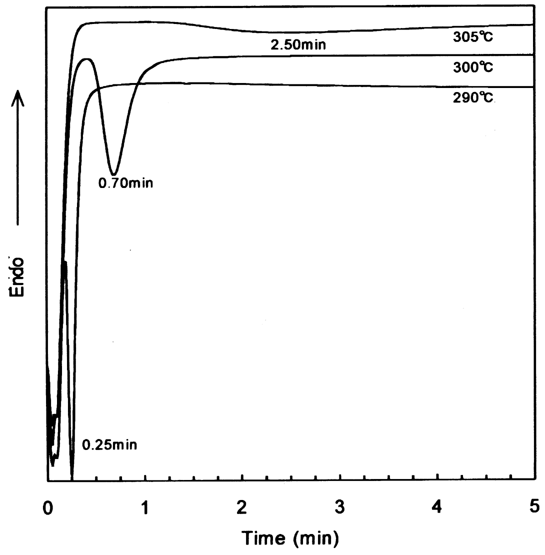

Fig. 5. Isothermal DSC scans for the 3,4′-ODA polyimide at various temperatures.

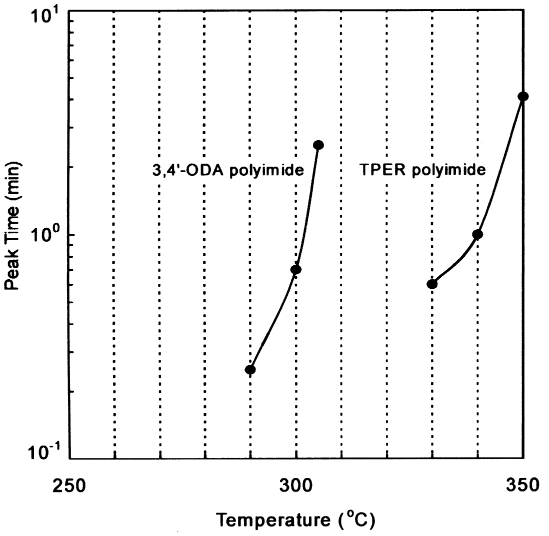

Fig. 6. Crystallization peak time vs. temperature plot of the 3,4′-ODA polyimide and the TPER polyimide.

isothermal crystallization peak time was recorded to characterize the crystallization rate (inversely proportional to the peak time). As shown in this figure, times of the isothermal crystallization peaks for the 3,4′-ODA polyimides at 290, 300 and 305°C were 0.25, 0.70 and 2.50 min, respectively.

The crystallization peak time vs. temperature plot for 3,4′-ODA polyimide and TPER polyimide is shown in Fig. 6. As shown in the figure, crystallization peak time for the 3,4′-ODA polyimide at 290°C was second order, and we estimate that this order is possible for crystallizing the polymer in a molding. The TPER polyimide showed the same order of crystallization peak time at 330°C. This temperature was higher than that of the 3,4′-ODA polyimide. As mentioned above, T_gs of the 3,4′-ODA polyimide and the TPER polyimide are 251 and ca. 192°C, respectively, and it can be said that crystallization could occur at temperatures above these T_gs. So, the crystallization temperature range of 3,4′-ODA was between 251 and 290°C, and that of the TPER polyimide was between 192 and 330°C. This result meant that the TPER polyimide could be crystallized in wider range of temperature than the 3,4′-ODA polyimide. On the other hand, comparing the DSC studies at the same condition of quenched films in Figs. 1 and 2, only the 3,4′-ODA polyimide showed a sharp crystallization exothermic peak. This peak meant that the quenched 3,4′-ODA polyimide film had not crystallized during the quenching treatment from 425°C to liquid nitrogen temperature, and conversely, the absence of the crystallization exothermic peak meant the TPER polyimide had crystallized during the quenching treatment. All things considered, the TPER polyimide can be said to be more easily crystallized than the 3,4′-ODA polyimide.

Table 2
Weight loss temperatures of the 3,4′-ODA polyimide and the TPER polyimide

Name	Atmosphere	Weight loss temperature[a] (°C)	
		1 wt.%	5 wt.%
3,4′-ODA polyimide	Nitrogen	548	580
	Air	550	580
TPER polyimide	Nitrogen	558	577
	Air	515	572

[a] Weight loss temperature was measured by the TGA method using the powder samples at a heating rate of 10°C/min under nitrogen or air atmosphere.

The thermal stability under harsh melting conditions has been probed with two different analyses. One is the traditional analysis used in thermogravimetric analysis (TGA) to evaluate the degradation occurring via weight loss. However, the TGA technique by itself is inadequate for reflecting the thermal stability of polymers, since degradation reactions such as crosslinking or chain extension could occur with a small accompanying weight loss [22,26,29]. Another is the rheological analysis using a flow tester to evaluate via viscosity change, since melt viscosity is critically dependent on the molecular weight of the system.

The weight loss temperatures of the polyimide powders under nitrogen and air measured by the TGA method are summarized in Table 2. The 3,4′-ODA polyimide and the TPER polyimide exhibited excellent thermal stability in nitrogen. In the case of the 3,4′-ODA polyimide, excellent thermal stability was also observed in air. The weight loss temperatures of the 3,4′-ODA polyimide in air were almost same as those in nitrogen. The TPER polyimide, however, exhibited relatively poor thermal stability in air, as evidenced by the fact that the 1% weight loss temperature in air was 43°C lower than that in nitrogen. This result suggests that the 3,4′-ODA polyimide had superior thermo-oxidative stability compared to the TPER polyimide.

Isothermal melt viscosity studies during storage time under a melting condition of 425°C were carried out on powder samples of the 3,4′-ODA polyimide and TPER polyimide. As shown in Fig. 7, the melt viscosity of both samples increased with time. This is speculated to occur due to chain extension/crosslinking reactions in the melt. In the case of the TPER polyimide, the melt viscosity after 60 min at 425°C was almost 6.4 times as large as that after 5 min at 425°C. At this time, the inherent viscosity (η_{inh}) after 60 min at 425°C was increased from 1.05 to 1.19 dl/g. However, in the case of the 3,4′-ODA polyimide, the melt viscosity did not show any appreciable increase for times up to 60 min at 425°C. Its melt viscosity after 60 min at 425°C is only 1.3 times as large as initial viscosity, and the η_{inh} was slightly increased from 0.62 to 0.63 dl/g.

From these results, it was found that the molecular weight change due to the chain extension/crosslinking reaction under melting condition was more prominent in the case

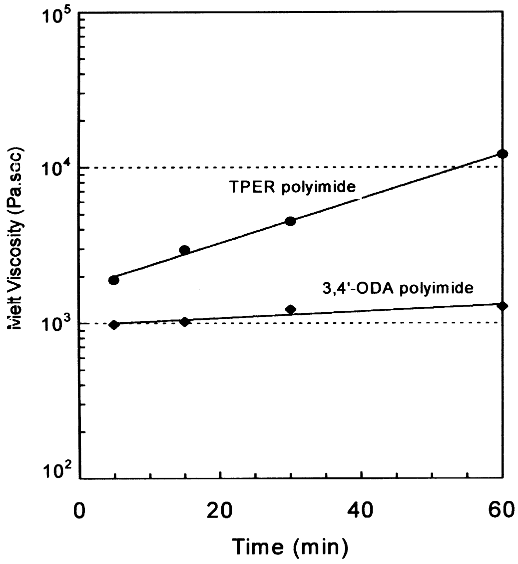

Fig. 7. Isothermal melt viscosity studies at 425°C for the 3,4′-ODA polyimide and the TPER polyimide.

of the TPER polyimide compared to the case of the 3,4′-ODA polyimide.

The excellent thermal stabilities (thermo-oxidative stability and melt viscosity stability mentioned above) of the 3,4′-ODA polyimide were estimated to be suitable for injection and extrusion molding.

4. Conclusions

The synthesis and characterization of high-thermally stable semicrystalline polyimide based on 3,4′-oxydianiline and 3,3′,4,4′-biphenyltetracarboxylic dianhydride, end capped with phthalic anhydride, have been reported. The quenched film of this polyimide displayed a glass transition temperature and a melting temperature at 251 and 402°C, respectively, by differential scanning colorimeter measurement. Isothermal differential scanning colorimeter studies ascertained this polyimide to be a polymer having first crystallization kinetics. Thermogravimetric analyses and isothermal melt viscosity studies evidenced excellent thermal stability (thermo-oxidative stability and melt viscosity stability) for this polyimide. By this research work, this polyimide was ascertained to be a high thermally stable semicrystalline polyimide and estimated to be a suitable polymer for injection and extrusion moldings.

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