Effects of the *o*-Aromatic Ring in the Molecular Chain on the Properties of Polyester Polyols

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ABSTRACT: A series of liquid polyester polyols from adipic acid (AA), phthalic anhydride (PA), ethylene glycol, propanediol-1,2, and trihydroxymethylpropane, varying in the molar ratio of PA to AA, were prepared. The effects of the *o*-aromatic ring in the molecular chain, which came from PA, on the viscosity, glass-transition temperature, and thermal degradation temperature of the polyester polyols were studied with viscometry, differential scanning calorimetry, and thermogravimetry. The intrinsic viscosity and glass-transition temperature increased with the concentration of the *o*-aromatic ring increasing. The temperature of the maximum thermal degradation rate for aliphatic polyester polyols was 434.20°C. Two steps of thermal degradation were found when there were *o*-aromatic rings in the molecular chain. One thermal degradation temperature was 358.36–360.48°C, and the other was 412.85–427.18°C. Polyester polyols with *o*-aromatic rings had higher stability at lower temperatures (<240.00°C). However, aliphatic polyester polyols had higher stability at higher temperatures (300.00–480.00°C). The activation energy and order of degradation were calculated from thermogravimetric curves. © 2002 John Wiley & Sons, Inc. J Appl Polym Sci 83: 1617–1624, 2002

Key words: polyester polyols; *o*-aromatic ring; thermal stability; viscosity; molecular chain

INTRODUCTION

Polyurethanes are used for a broad and varied range of applications at low cost from a wide variety of raw materials. With respect to the specific end use, chemists can design a material that is primarily either elastic or rigid in nature by merely varying the chemical constituents of the polymer. Most commercial polyurethanes are pre-

pared by a random, linear condensation of stoichiometric amounts of an aromatic or aliphatic diisocyanate, a low molecular weight glycol or diamine, and a polyether or polyester macroglycol. In rigid polyurethanes, the macroglycol of the polymer chain is above its glass-transition temperature (typically between −20.0 and −80.0°C) at its service temperature and forms the soft segment. The glass-transition temperature of the macroglycol depends on the molecular weight, structure, and so forth. The diisocyanate group coupled with a low molecular weight glycol or diamine chain extender has a glass-transition temperature (typically between 90.0 and 130.0°C) above its service temperature and forms the hard segment. Each polyurethane chain consists of al-

Table I   Properties of Polyester Polyols

Sample	PA/AA	Hydroxyl Value (mg of KOH/g)	Viscosity (mPa s 25°C)
1	0.0 : 100.0	253	1,270
2	20.0 : 80.0	251	1,400
3	40.0 : 60.0	247	3,100
4	60.0 : 40.0	257	15,000
5	80.0 : 20.0	250	> 100,000

ternating hard and soft segments that are joined end to end through covalent (urethane or urethane–urea) bonds. Polyurethanes are thus classified as multiblock copolymers. The character of the copolymer is determined to a large degree by the relative amounts of hard and soft segments and the nature of the domains they form.

The thermal stability of polyurethanes has been studied extensively because of the importance of this group of materials.[1–11] Polyurethanes are usually not very thermally stable polymers. The service temperature of polyurethane is generally 80.0°C. The degradation temperature of polyurethanes depends on the types of isocyanate and polyols used. Lee et al.[12] claimed that the decomposition temperatures of synthesized polyurethanes are relatively high because the soft-segment polyols of these polyurethanes have aromatic nuclei in their structure.

It is well known that the presence of aromatic rings in a polymer chain can increase the heat resistance of the polymer. In this investigation, a series of polyester polyols from adipic acid (AA), phthalic anhydride (PA), ethylene glycol (EG), propanediol-1,2 (1,2-PDO), and trihydroxymethylpropane (TMP), varying in the molar ratio of PA to AA, were synthesized, and the effects of o-aromatic rings in the chain on the properties of polyester polyols were explored. The experimental techniques we employed included rotation viscometry, differential scanning calorimetry (DSC), and thermogravimetry.

EXPERIMENTAL

Materials

Chemically pure-grade AA (Shanghai Agent Plant, P. R. China), PA (Chemistry Plant of Shanghai Chemical Agent Station, P. R. China), EG (Shandong Chemical Engineering College, P. R. China),

1,2-PDO (Shandong Chemical Engineering College), and TMP (Shandong Academy of Science, P. R. China) were used in this investigation.

Preparation of the Polyester Polyols

Polyester polyols were prepared by the reaction of EG, 1,2-PDO, and TMP with AA and PA at a fixed hydroxyl/carboxyl ratio of 2.4. By varying the molar ratio of PA to AA but keeping the total moles of carboxyl constant, we synthesized a series of polyester polyols (see Table I).

The polyesterification reaction was carried out in a 500-mL, round-bottom glass reactor with a stirring assembly, a thermometer, a nitrogen gas inlet tube, and a distillation condenser. The reactants were gradually heated from room temperature to 140.0°C for about 1.5 h and then from 140.0 to 180.0°C for 1.5 h. The reaction mixture was held at 180.0°C for 3.0 h and subsequently heated to 200.0°C slowly. The reaction was carried out at 200.0°C for 2.0 h at atmospheric pressure and continued under reduced pressure for removal of the water formed in the reaction. The extent of the reaction was controlled by the product's acid value. The acid value was measured throughout the course of the reaction every 0.5 h. The reaction was over when the acid value was less than 1.0 mg of KOH/g.

Thermal Measurements

For the measurement of thermal properties, a thermogravimetric analysis (TGA) was carried out with a Rheometric Scientific TGA1500 (Piscataway, NJ). The polyester polyols were heated from room temperature to 500.00°C at a rate of 10.00°C/min in an inert atmosphere of nitrogen. DSC (Rheometric Scientific DSC SP) was used to detect the glass-transition temperature at a rate of 25.00°C/min and the degradation temperature at a rate of 10.00°C/min in a dry nitrogen environment.
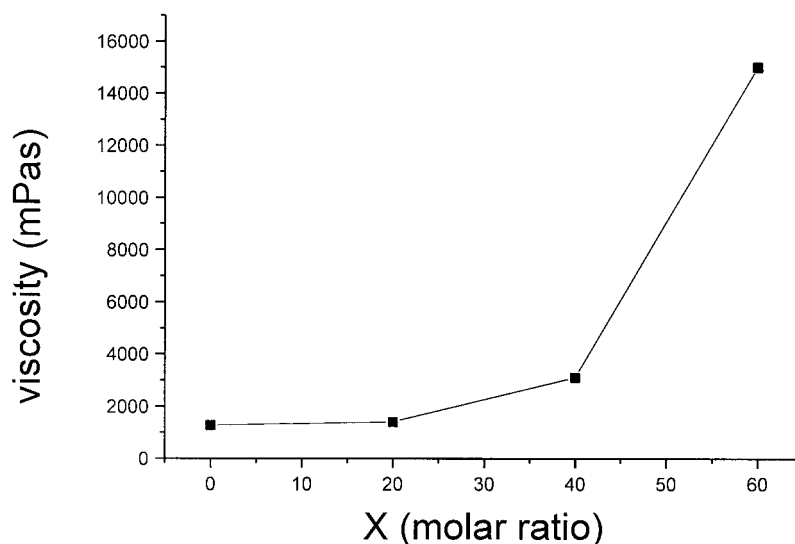
Figure 1 Viscosity of the polyester polyols versus the molar ratio of PA to (PA + AA) (*X*).

Viscosity

The viscosity values of the polyester polyols were measured at 25.0°C with a NDJ-79 rotational viscometer (Tongji University, P. R. China).

RESULTS AND DISCUSSION

Intrinsic Viscosity

The viscosity of a polymer is an involved function of many interaction variables, such as the molar mass, structure, and conformation of polymer molecules. We investigated the effect of o-aromatic rings in the chain on the intrinsic viscosity. The intrinsic viscosity of polyester polyols with almost the same weight-average molecular weight increases with the o-aromatic ring content in the chain increasing. This can be interpreted as the friction resistance increasing with the rigidity of the chain. The mean-square radius of gyration (R^2) can serve as an indication of the rigidity. We suggest the following relationship:

$$\eta = (\bar{M}n)^a R^b$$

(where η is the viscosity of polymer and $\bar{M}n$ is the number-average molecular weight).

According to the trend of the experimental data, the viscosity rises very sharply when the molar ratio of PA to (PA + AA) is greater than 40.0% (see Fig. 1). We think that there is also a critical radius of gyration that makes *b* have different values in different ranges.

Glass-Transition Temperature

The glass-transition temperatures of the polyester polyols, as determined by DSC, are illustrated in Figure 2. Chain stiffness has an important effect on the glass-transition temperatures of polymers. Gibbs and Di Marzio[13] suggested that chain stiffness is the dominant factor determining the glass-transition temperature and, consequently, depends on the conformational energy. With the o-aromatic ring content in the chain increasing, the chain becomes rigid, the chain segment mobility is reduced, and partial crystallinity of the polymer becomes possible. The glass-transition temperature of the polymer rises. Such behavior was seen with the polyester polyols (see Table II). The expected trend was seen of an increase in the glass-transition temperature with the proportion of o-aromatic ring in the chain increasing. The glass-transition temperatures of the polyols varied linearly with the increasing proportion of PA in the acid components (see Fig. 3). There is a close relationship between the glass-transition temperature (T_g) and the molar ratio of PA to (PA + AA) (*X*):
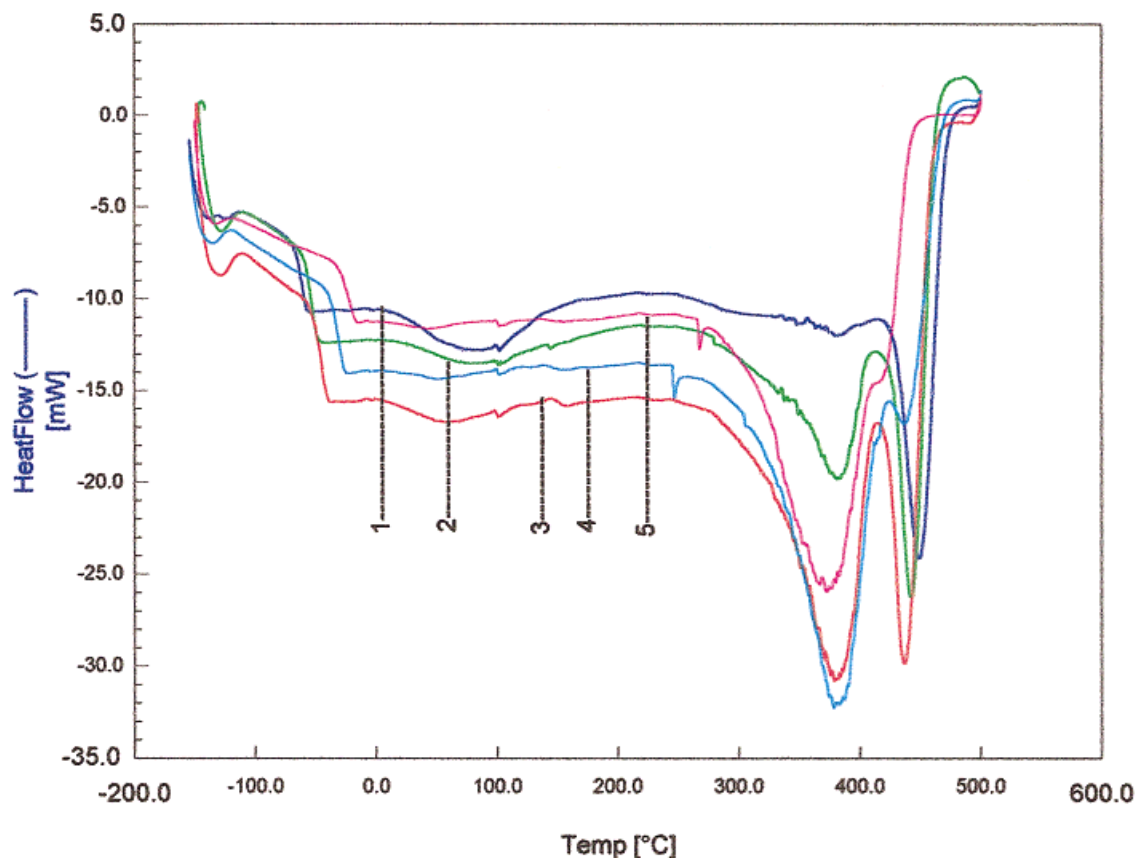
Figure 2   DSC curves of samples 1–5 (gas, N_2; ramp, 25°C/min). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

$$Tg = -63.95 + 0.50X$$

(where X is the molar ratio of PA/(PA + AA))

Thermal Stability

Thermogravimetry was used to investigate the degradation process in polyester polyols. The

TGA curves of the samples are shown in Figure 4. According to the TGA curves, samples 2–5 with o-aromatic rings in the chain clearly had higher thermal stability in the initial stages, and the stability increased with the o-aromatic ring content in the chain increasing. At higher temperatures (300.00–480.00°C), their thermal stability

Table II   DSC and TGA Data for Polyester Polyols

| Sample | DSC | | | TGA | | | | |
	T_g	T_{d1}	T_{d2}	T_{max1}	wt %	T_{max2}	E_a (kJ/mol)	n
1	−63.11		434.20			435.27	41.99	0.50
2	−54.23	359.58	427.18	359.56	50.00	420.17		
3	−46.48	360.48	412.85	363.55	57.00	409.01		
4	−32.34	358.36	414.35	358.62	64.00	404.51		
5	−24.52	356.34		369.81	67.00		72.07	1.38

T_g (°C) = glass-transition temperature (obtained at 25°C/min); T_{d1}, T_{d2} (°C) = degradation temperature (obtained at 10°C/min); T_{max1}, T_{max2} (°C) = temperature of the maximum rate of weight loss; wt % = weight loss before T_{max1}; E_a = energy of activation; n = order of degradation reaction.
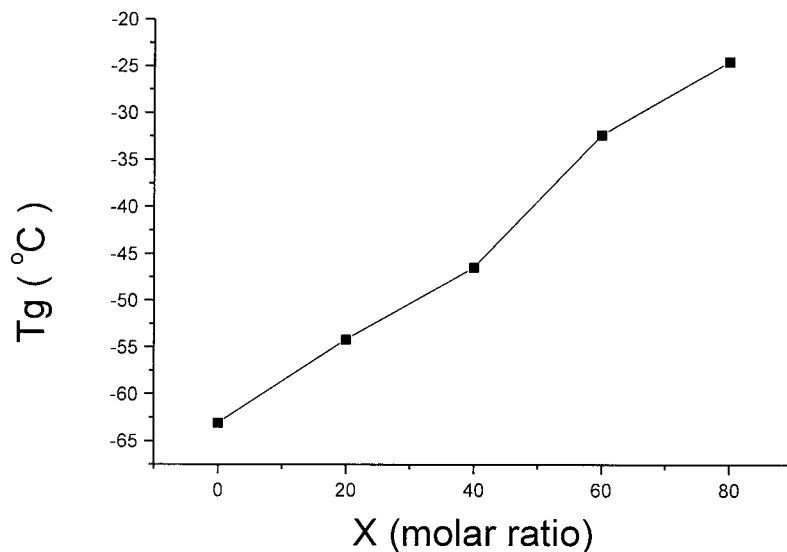
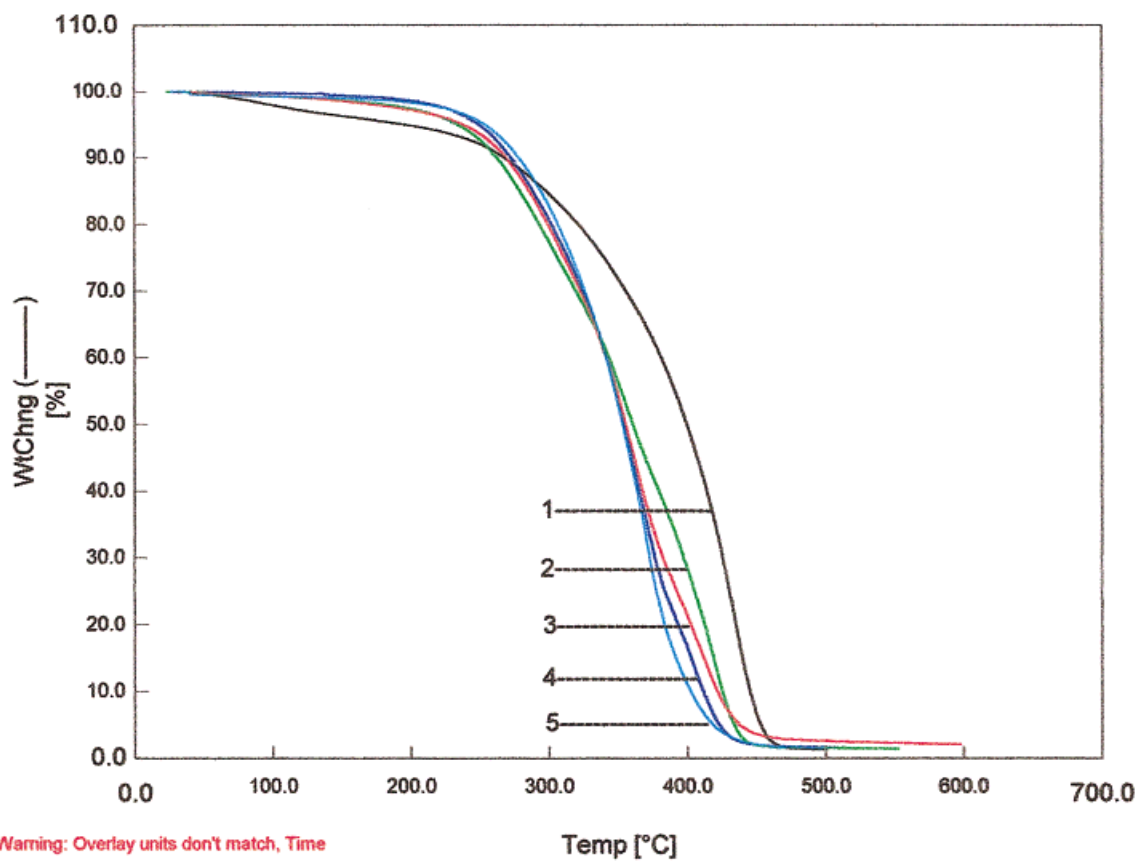**Figure 3**   Glass-transition temperature (T_g) versus the molar ratio of PA to (PA + AA) (*X*).

Figure 4   TGA curves of samples 1–5 (gas, N_2; ramp, 10°C/min). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Figure 5   DTG curves of samples 1–5 (gas, N$_2$; ramp, 10°C/min). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
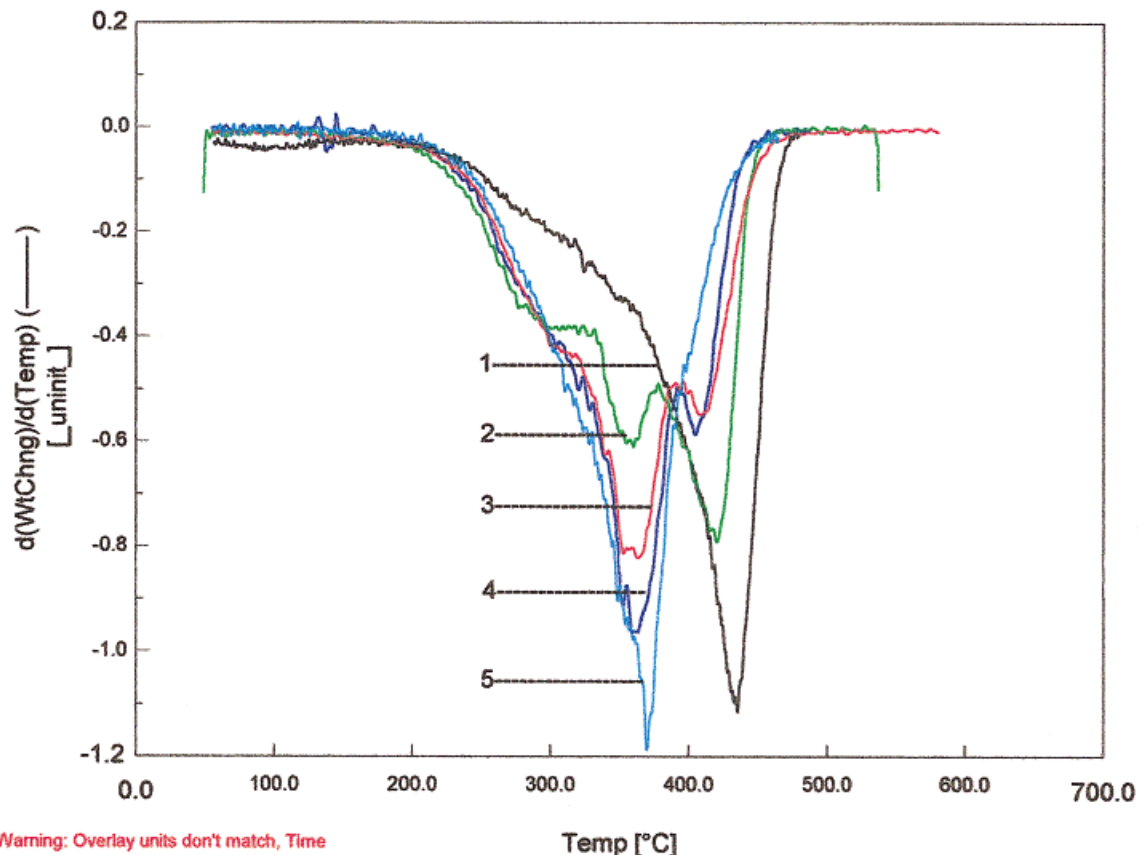
was lower than that of sample 1 without aromatic rings in its chains. The effect of the *o*-aromatic rings in the chain on the stability of the polyester polyols was distinct.

For the polyester polyols with *o*-aromatic rings, their TGA curves indicate that the rates of weight loss decreased with the increase in *o*-aromatic rings in the chains before 335.00°C. However, it was just the opposite after 335.00°C.

Derivative thermogravimetry (DTG) curves of the samples display different regions of weight loss (see Fig. 5). Sample 1 only had a maximum rate of degradation at 435.27°C. Samples 2–4 exhibited two steps of thermal degradation. One maximum rate of degradation was 420.17–404.51°C, and the other was 358.62–369.81°C. Moreover, with the *o*-aromatic ring content increasing, the size of the peak above 400.00°C decreased, and at the same time, the peak below 400.00°C increased. Sample 5 only had a maximum rate of degradation at 369.81. The results obtained here suggest that the *o*-aromatic rings in the chain are points of weakness through which degradation is initiated. The two ester groups attached to the aromatic ring are ortho. They are easily condensed into an acid anhydride ring:
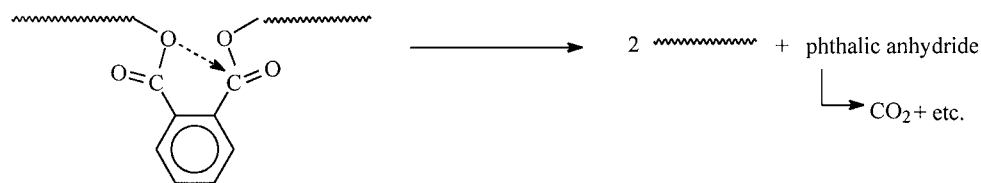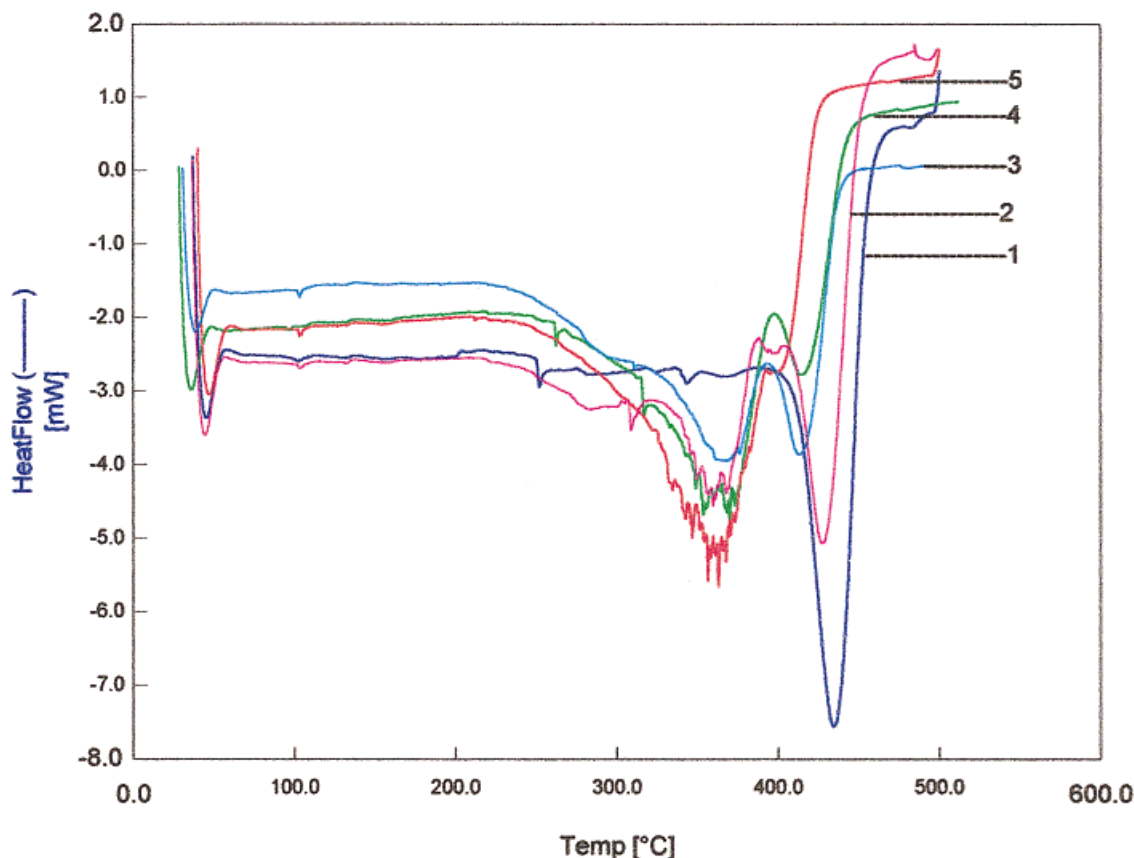
Figure 6   DSC curves of samples 1–5 (gas, N_2; ramp, 10°C/min). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

These samples were also studied with DSC (see Fig. 6). DSC exhibited a trend similar to that of DTG. Sample 1 only had a degradation peak at 434.20°C, whereas new degradation peaks between 358.36 and 360.48°C were found for samples 2–4, which contained *o*-aromatic rings in the chain (see Table II). Sample 5 only had an endotherm peak at 356.34°C ,just like the response of DTG. The size of the endotherm peaks changed in the same way as DTG showed.

Kinetic Analysis

The apparent activation energy and order of the degradation reaction were calculated with the Freeman–Carroll method[14] for samples 1 and 5 (see Table II). Although the temperature of the maximum degradation rate of sample 5 was lower than that of sample 1, sample 5 had a higher apparent activation energy. Sample 5 had higher stability at lower temperatures ($<240.00°C$). The order of the degradation reaction of sample 1 was less than 1.0. This resulted essentially in radical scission of random molecules.

CONCLUSION

With *o*-aromatic rings introduced into the chain, the intrinsic viscosity of polyester polyols rises. The glass-transition temperature of polyester polyols increases with the *o*-aromatic ring concentration in the chain increasing. Polyester polyols with *o*-aromatic rings have higher stability at lower temperatures ($<240.00°C$), but the *o*-aromatic rings in the chain are points of weakness through which degradation is initiated. Compared with aliphatic chains, the latter has higher stability at higher temperatures (300.00– 480.00°C).

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