

# Synthesis and Characterization of Copolyarylates Using Tin Octoate as a Catalyst

P. B. Waghmare, P. Pathak, S. A. Deshmukh, S. B. Idage, B. B. Idage

*Polymer Science and Engineering Division, National Chemical Laboratory, Pune-411 008, India*

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**ABSTRACT:** A series of copolyarylates of bisphenol A (BPA) with varying ratios of diphenyl terephthalate (DPT) and diphenyl isophthalate (DPI) were prepared by melt polymerization at a temperature ranging from 200 to 290°C under reduced pressure in the presence of tin octoate catalyst. Tin octoate catalyst has been extensively used for the preparation of biodegradable polymers namely, poly(lactic acid), poly(glycolic acid), and poly(lactide-glycolide) copolyesters. However, there are no reports on the preparation of copolyesters by melt polymerization using tin octoate catalyst. The effect of tin octoate catalyst was studied on the preparation of BPA/DPT/DPI copolyarylates. The copolyarylates were characterized by infrared and <sup>1</sup>H NMR spec-

troscopy, solution viscosity, thermogravimetric analysis, differential scanning calorimetry, and X-ray diffraction. The solution viscosities of copolyarylates were varied from 0.43 to 0.56 dL/g and the glass transition temperature ( $T_g$ ) of copolyarylates was varied from 155 to 222°C by varying the ratio of DPT and DPI. Most of the copolyarylates were found to be soluble in commonly used organic solvents and had film-forming properties. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 70–77, 2006

**Key words:** copolyarylates; tin octoate; melt polymerization; diphenyl terephthalate; diphenyl isophthalate

## INTRODUCTION

Polyarylates are polyesters derived from aromatic diols and dicarboxylic acid.<sup>1,2</sup> They belong to a class of engineering plastics and are characterized by their inherent flame retardance, resistance to UV, and relatively high glass-transition temperatures ( $T_g$ ). The copolyesters prepared from bisphenol A (BPA), terephthalic acid (TPA), and isophthalic acid (IPA) are the representative examples of polyarylates. These polyesters are expected to find applications in transportations (interior panels for buses and aircrafts), glazing parts (solar collectors and appliances), and other optical uses.

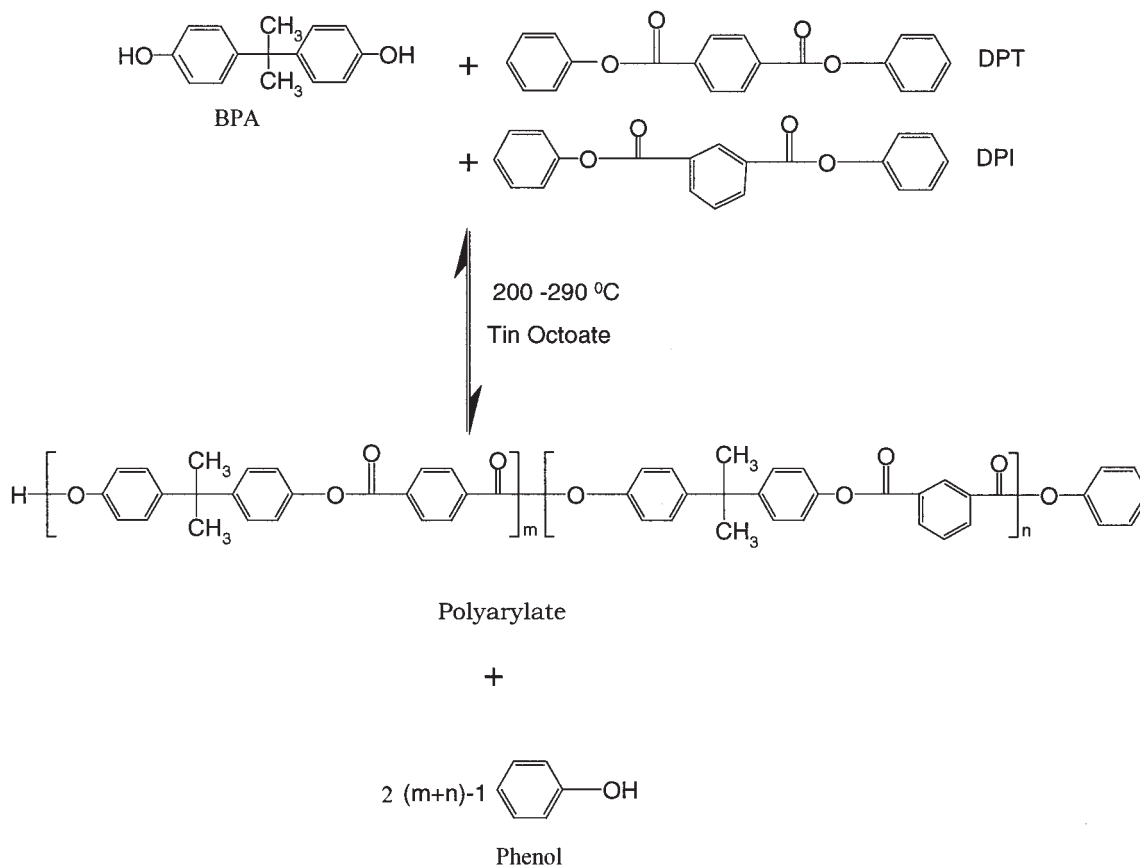
There are different methods for the synthesis of polyarylates namely, direct condensation between an aromatic diol(s) and an aromatic dicarboxylic acid(s) especially in the presence of a proper catalyst,<sup>3,4</sup> interfacial polycondensation of diacid dihalide(s) with diol(s), low temperature Schotten-Baumann<sup>5,6</sup> solution polycondensation between diacid dihalide(s) and a diol(s) in the presence of an acid acceptor, high temperature solution polycondensation<sup>7,8</sup> of a diacid dihalide(s) and a diol(s), transesterification<sup>9,10</sup> of an aromatic dicarboxylic acid(s) with a diacetate of an aromatic diol(s) at a high temperature and polymer-

ization of a diaryl (e.g., phenyl) ester<sup>11,12</sup> of an aromatic dicarboxylic acid(s) with an aromatic diol(s) via transesterification. All of the preparation methods possess certain advantages as well as disadvantages, and selection of a particular method is governed by factors such as economics, reliability of the process, and product quality.

The diacetate<sup>13</sup> and diphenate<sup>12</sup> routes are high temperature melt polymerization processes. The different types of catalysts are used to enhance the rate of the reaction. The high temperature of reaction and the presence of catalyst accelerate the rate of melt polymerization reaction. The sublimation of the diacid is a biggest problem in the diacetate process. This disrupts the stoichiometry of the reaction, and the high molecular weight polyarylate cannot be produced. The sublimation of diacid can be prevented by using large amounts of solvents together with a variety of catalysts and generally long reaction times in the polymerization process. The use of different catalysts and solvents produces the colored polyarylates, which have limited applications. However, the diphenate route is free from the above drawbacks and produces a polyarylate of acceptable color and molecular weight.

In the acid chloride route,<sup>14</sup> the dihydric phenol is reacted with a mixture of terephthalic and isophthalic acids by first converting acids to their diacid chlorides, isolating and purifying them, and then subjecting them to a solution polymerization or an interfacial polymerization with the dihydric phenol. The pol-

Correspondence to: B. B. Idage (bb.idage@ncl.res.in).



Scheme 1 Preparation of copolyarylates.

arylates of satisfactory quality are obtained by this route. However, the purification and isolation steps add to the cost of the final product, thus limiting their commercial exploitation.

The diphenate route has several advantages over the diacetate and interfacial condensation polymerization routes. A number of transition metal catalysts were reported to date for the preparation of polyarylates.<sup>15-21</sup> In the past, tin octoate has been extensively used for the preparation of biodegradable polymers namely, polylactic acid, polyglycolic acid, and copolyesters.<sup>22,23</sup> However, less attention has been paid towards the use of nontoxic and environment-friendly catalysts for the preparation of polyarylates.

In the present work, a transition metal catalyst, tin octoate, is used for the preparation of high molecular weight Bisphenol A/Terephthalic acid/Isophthalic acid polyarylates. Tin octoate catalyst has several advantages over the other catalysts reported in the literature for the preparation of polyarylates. The polyarylates prepared using this catalyst have several advantages e.g., reduction in the time of synthesis, quantitative yield of polymer, and high viscosity polymer. Furthermore, the catalyst is nontoxic and eco-friendly in nature.

## EXPERIMENTAL

### Materials

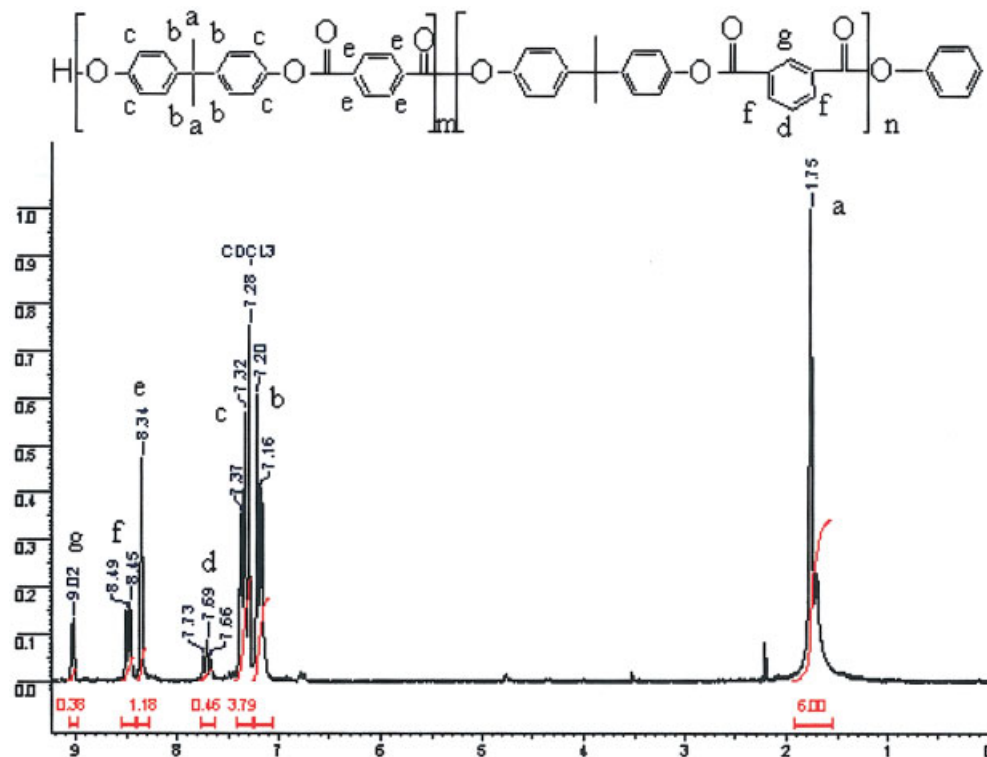
Bisphenol A (BPA) procured from Sigma Aldrich was used as such without further purification.

Diphenyl terephthalate (DPT) was prepared by the reaction of terephthaloyl chloride with sodium salt of phenol, using benzyltriethyl ammonium chloride

TABLE I  
Preparation of Copolyarylates

| Polymer code | BPA (%) | DPT (%) | DPI (%) | Yield (%) | $\eta_{inh}$ (dL/g) |
|--------------|---------|---------|---------|-----------|---------------------|
| PA 1         | 100     | 100     | 0       | 98        | —                   |
| PA 2         | 100     | 90      | 10      | 99        | —                   |
| PA 3         | 100     | 80      | 20      | 98        | 0.44                |
| PA 4         | 100     | 70      | 30      | 97        | 0.46                |
| PA 5         | 100     | 60      | 40      | 98        | 0.43                |
| PA 6         | 100     | 50      | 50      | 99        | 0.56                |
| PA 7         | 100     | 40      | 60      | 98        | 0.47                |
| PA 8         | 100     | 30      | 70      | 98        | 0.49                |
| PA 9         | 100     | 20      | 80      | 99        | 0.48                |
| PA10         | 100     | 10      | 90      | 97        | 0.48                |
| PA11         | 100     | 0       | 100     | 99        | —                   |

Catalyst, Tin octoate (0.5 wt %).



**Figure 1**  $^1\text{H}$  NMR spectrum of PA-6 in  $\text{CDCl}_3$ . [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

(BTEAC) as phase transfer catalyst and purified by recrystallization from methylene chloride. The crystallized product had a melting point of 197–199°C.

Diphenyl isophthalate (DPI) was prepared by the reaction of isophthaloyl chloride with sodium salt of phenol, using benzyltriethyl ammonium chloride (BTEAC) as phase transfer catalyst and purified by recrystallization from methylene chloride. The crystallized product had a melting point of 135–137°C.

Benzyltriethyl ammonium chloride (BTEAC) procured from Sigma Aldrich as used as such without further purification.

Tin octoate (tin-2-ethyl hexanoate) obtained from Sigma Aldrich Chemicals was used as such without further purification.

## Methods

Infrared spectra of polyarylate films were recorded on Perkin–Elmer 16 PC FTIR spectrophotometer.

Proton NMR spectroscopy was used for compositional and structural analysis of polymers. Proton NMR spectra were obtained using a Bruker 200 MHz spectrometer in deuterated chloroform. The chloroform reference peak at 7.28 ppm was used to ensure accuracy of peak assignments.

Ubbelohde viscometers were used to determine the inherent viscosities ( $\eta_{\text{inh}}$ ) at  $(30 \pm 0.1)^\circ\text{C}$  of polymer solutions having concentrations of 0.5 g/100 mL in chloroform.

Differential scanning calorimetry (DSC) thermograms were obtained with a Perkin–Elmer DSC-7. About 8–10 mg of polyarylate sample was crimped in an Aluminum pan. The samples were heated from 50 to 400°C at a heating rate of  $10^\circ\text{C min}^{-1}$ . The first and second heating run of the sample was recorded. The melting peak ( $T_m$ ) of the sample was recorded in the first run and the glass-transition temperature ( $T_g$ ) of the sample was recorded in the second run. The  $T_g$

**TABLE II**  
Composition of DPT and DPI in Copolyarylates

| Polymer code | Feed composition |         |         | Composition by $^1\text{H}$ NMR |         |         |
|--------------|------------------|---------|---------|---------------------------------|---------|---------|
|              | BPA (%)          | DPT (%) | DPI (%) | BPA (%)                         | DPT (%) | DPI (%) |
| PA 2         | 100              | 50      | 50      | 100                             | 51      | 49      |
| PA 6         | 100              | 30      | 70      | 100                             | 31      | 69      |
| PA 8         | 100              | 40      | 60      | 100                             | 42      | 58      |

was measured by taking the mid point between the onset and the endset of the DSC thermogram.

Thermogravimetric analysis (TGA) and derivative thermogravimetry (DTG) were carried out with a Perkin-Elmer TGA-7 thermogravimetric analyzer under nitrogen atmosphere at a heating rate of  $10^{\circ}\text{C min}^{-1}$ .

Wide angle X-ray diffractograms (WAXD) were obtained for powdered samples with a Phillips X-ray unit (Phillips generator, PW-1730), using nickel-filtered  $\text{CuK}\alpha$  radiation.

### Melt polymerization

All copolyarylates were prepared by the melt polymerization method. The preparation of copolyarylate (PA-6) is given here as a representative example.

A 100-mL three-necked cylindrical glass reactor was equipped with a mechanical stirrer, a nitrogen inlet, and a vacuum-jacketed Vigreux column and distillation head. The reactor was charged with 4.56 g (20 mmol) of bisphenol A, 3.18 g (10 mmol) of DPT and 3.18 g (10 mmol) of DPI, and 0.5 wt % of tin octoate catalyst. The melt polymerization was carried out at  $200^{\circ}\text{C}$  under nitrogen atmosphere for 3 h.

The temperature was then increased to  $220^{\circ}\text{C}$  and a vacuum of  $2 \times 10^4$  Pa was applied for 0.5 h; then, temperature was gradually increased and pressure was gradually decreased in the given manner as follows:  $240^{\circ}\text{C}$  at  $1.2 \times 10^4$  Pa 0.5 h;  $260^{\circ}\text{C}$  at 5000 Pa for 0.5 h;  $290^{\circ}\text{C}$  at 100 Pa for 0.5 h; and finally at  $290^{\circ}\text{C}$  at 1 Pa for 1 h. The reaction mixture was continuously stirred at constant speed through out the melt polymerization. A pale yellow-colored highly viscous product obtained was cooled to room temperature under the flow of nitrogen. Polyarylate was purified by the precipitation technique. The polyarylate was dissolved in chloroform (50 mL) and reprecipitated in methanol (400 mL). The colorless polymer obtained after the precipitation was separated by filtration. The polymer was dried at  $80^{\circ}\text{C}$  under reduced pressure and yield was recorded. The polyarylate was obtained in quantitative yield.

The same procedure was followed to prepare polyarylates with different mole ratios of DPT and DPI with Bisphenol A.

### Polymer solubility

The solubility of polyarylates and copolyarylates was checked at 5 wt % concentration in various polar and nonpolar solvents namely, chloroform, *m*-cresol, tetrahydrofuran (THF), dimethyl formamide (DMF), ethanol, and petroleum ether.

## RESULTS AND DISCUSSION

The copolyarylates of bisphenol A with varying ratios of DPT and DPI were prepared by melt polymeriza-

**TABLE III**  
Solubility Behavior of Copolyarylates

| Polymer code | Chloroform | DMF | <i>m</i> -Cresol | THF |
|--------------|------------|-----|------------------|-----|
| PA 1         | --         | --  | ++               | --  |
| PA 2         | +-         | --  | ++               | --  |
| PA 3         | ++         | --  | ++               | ++  |
| PA 4         | ++         | --  | ++               | ++  |
| PA 5         | ++         | --  | ++               | ++  |
| PA 6         | ++         | ++  | ++               | ++  |
| PA 7         | ++         | ++  | ++               | ++  |
| PA 8         | ++         | ++  | ++               | ++  |
| PA 9         | ++         | --  | ++               | ++  |
| PA 10        | ++         | --  | ++               | --  |
| PA 11        | --         | --  | ++               | --  |

+ +, Soluble, --, Insoluble; and + -, Equilibrium.

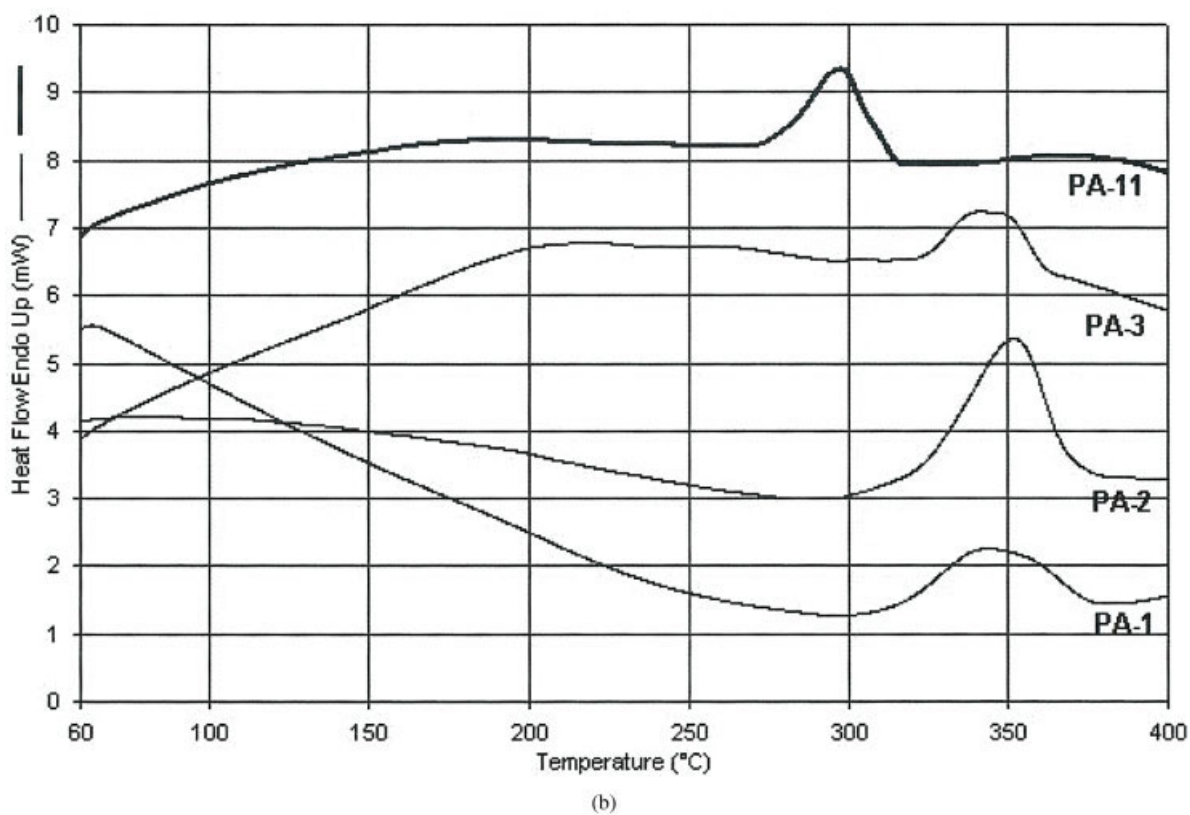
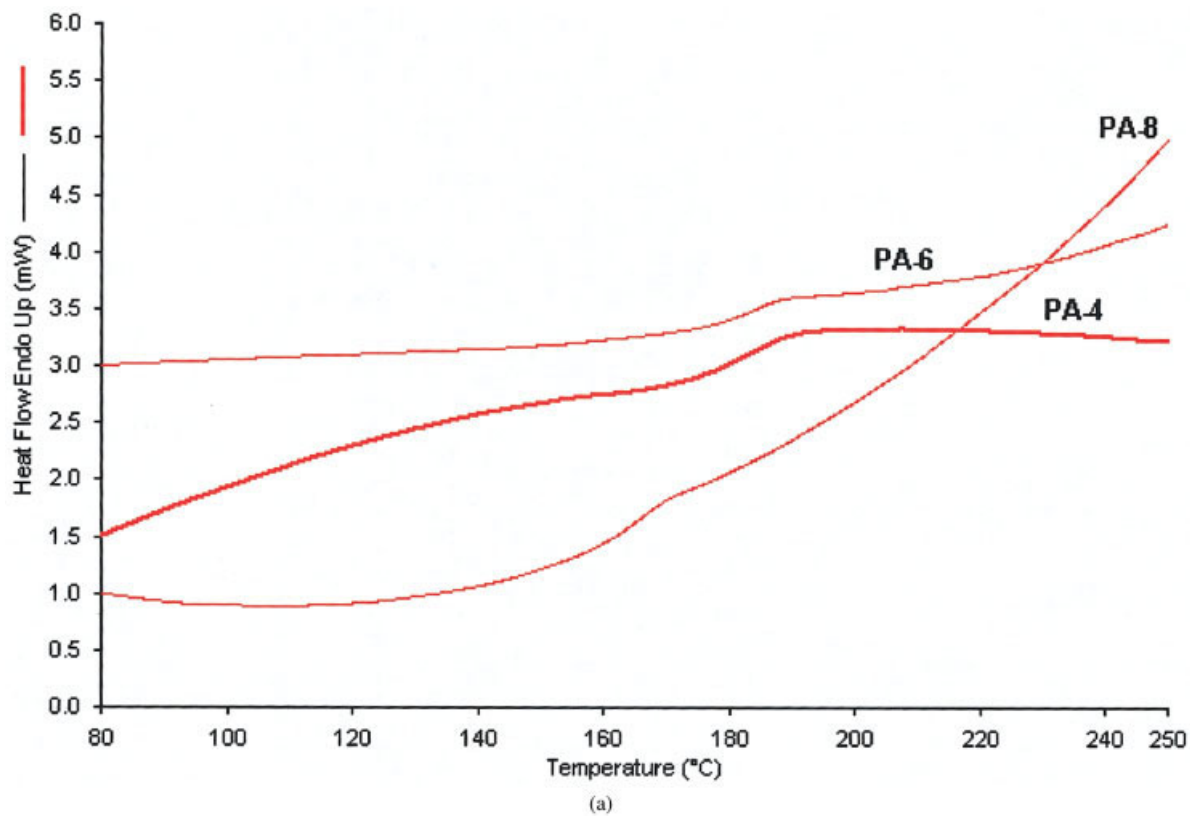
tion technique at a temperature ranging from 200 to  $290^{\circ}\text{C}$  under reduced pressure, using tin octoate as a catalyst. The tin octoate catalyst has been used for the first time for the preparation of BPA/DPI/DPT copolyarylates. The preparation of copolyarylates is shown in Scheme I.

The polyarylates were characterized by infrared spectra,  $^1\text{H}$  NMR spectra, solution viscosity, thermogravimetric analysis, differential scanning calorimetry, and X-ray diffraction. The properties of copolyarylates are summarized in Tables I-IV. The copolyarylates were obtained in quantitative yields.

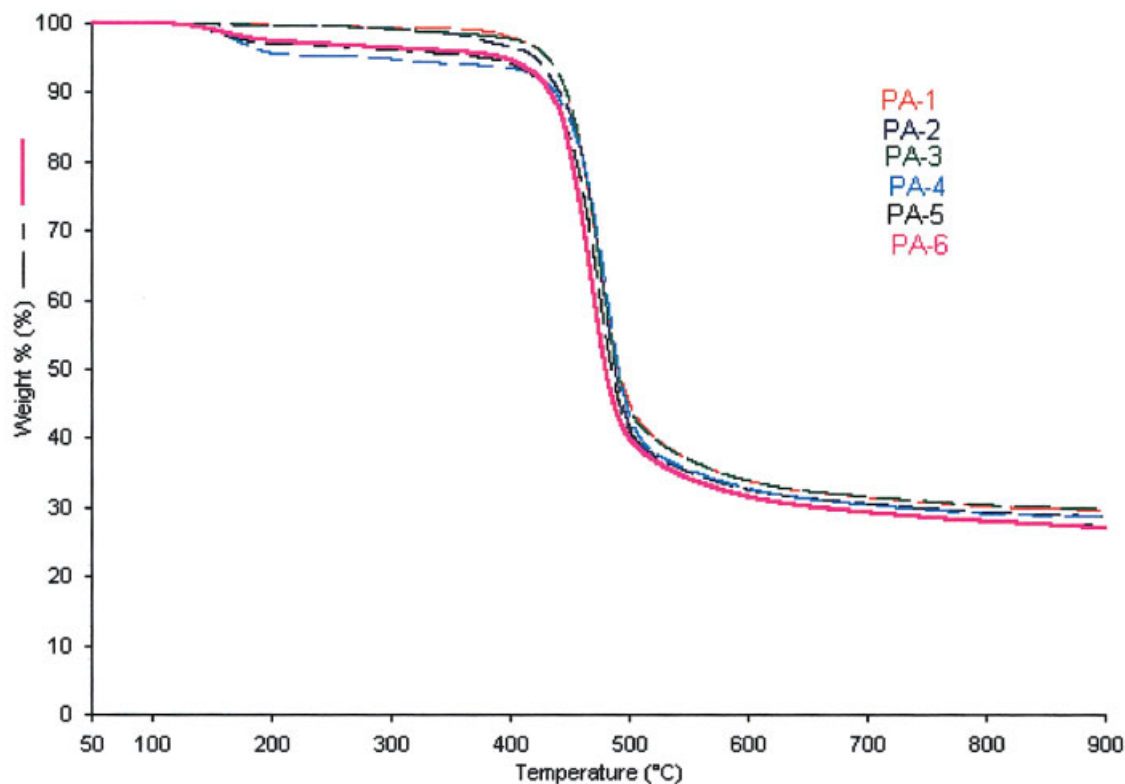
Inherent viscosities of the copolyarylates were determined in chloroform at  $30^{\circ}\text{C}$  (Table I) and were obtained from 0.43 to 0.56 dL/g. No particular trend in inherent viscosity was observed with respect to different ratios of DPT and DPI in the compositions studied.

The percentage composition of DPT and DPI in copolyarylates (PA-2, PA-6, and PA-8) was determined by  $^1\text{H}$  NMR spectroscopy. The  $^1\text{H}$  NMR spectrum of PA-6 copolyarylate is illustrated in Figure 1. The copolyarylate composition was determined using a singlet at 9.02  $\delta$  due to one proton ( $H_g$ ) of DPI and a singlet at 8.34  $\delta$  was obtained due to four protons ( $H_e$ ) of DPT. The percentage compositions of DPT and DPI comonomers in copolyarylates determined by  $^1\text{H}$  NMR spectroscopy are given in Table II.

The solubility behavior of copolyarylates was checked at 5 wt % concentrations in various polar and nonpolar solvents. The solubility behavior of copolyarylates in different solvents is summarized in Table III. It is observed from the results that the polyarylates prepared from BPA with DPT (100%) or DPI (100%) were found to be insoluble in chloroform, DMF, and THF. However, they were found to be soluble in only *m*-cresol. The polyarylates prepared from BPA with different ratios of DPT and DPI were found to be easily soluble in chloroform and tetrahydrofuran, and the solutions had film-forming properties. The transparent flexible films were prepared by dissolving the polyarylate in chloroform.



**Figure 2** (a) DSC thermograms of copolyarylates (PA-1, PA-2, PA-3, and PA-11) and (b) DSC thermograms of copolyarylates (PA-4, PA-6, and PA-8). [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]



**Figure 3** TGA thermograms of copolyarylates (PA 1–6). [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

The thermal behavior of copolyarylates was studied by differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and derivative thermogravimetry (DTG) by heating the polymers at a constant rate of  $10^{\circ}\text{C min}^{-1}$  under nitrogen atmosphere. The DSC thermograms of representative polyarylate samples are shown in Figure 2(a, b), respectively. The TGA thermograms of copolyarylates (PA 1–11) are illustrated in Figures 3 and 4. The thermal properties of copolyarylates are summarized in Table IV. The  $T_g$ 's of polyarylates prepared from BPA with DPT (100%) or DPI (100%) are very high. A decrease in  $T_g$  was observed by varying the ratios of DPT and DPI. However, no particular trend in  $T_g$  was observed with varying the ratios of DPT and DPI. The polyarylates PA-1, PA-2, PA-3, and PA-11 showed the melting endotherms in the DSC (Fig. 2(b)) due to crystalline behavior of the polyarylates.

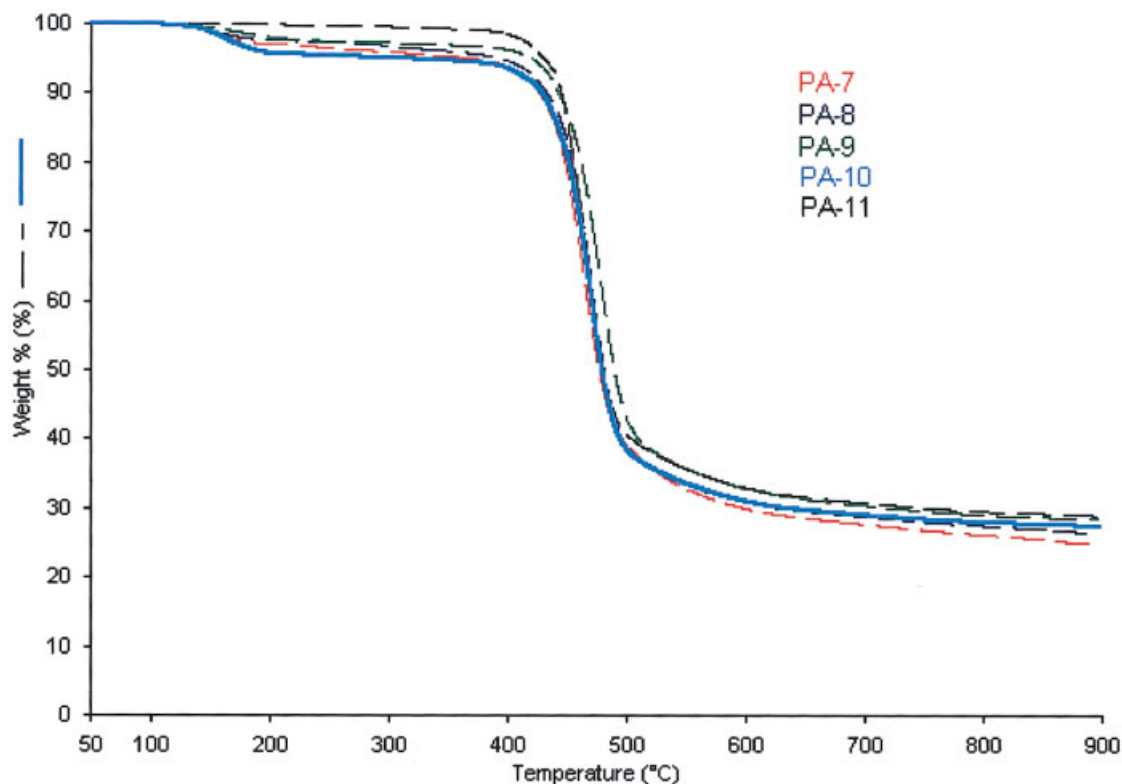
All polyarylates exhibit one-step degradation behavior by TGA and DTG. The initial decomposition temperature ranges from 420 to  $436^{\circ}\text{C}$  and  $T_{10}$  ranges from 428 to  $448^{\circ}\text{C}$ . The residue of nondegraded material at  $900^{\circ}\text{C}$  was determined from TGA curve and it ranges from 25 to 30%. The  $T_{\text{max}}$  varies from 463 to  $483^{\circ}\text{C}$ . The higher quantity of residue and  $T_{\text{max}}$  values indicate the high thermal stability of polyarylates. The high thermal stability of polyarylates is attributed to the presence of aromatic moieties in both bisphenol A

and diphenyl esters of isophthalic and terephthalic acid.

The crystalline/amorphous nature of the polyarylates was studied by wide angle X-ray diffraction (WAXD) spectroscopy. The X-ray diffractograms of different polyarylates are shown in Figure 5. The X-ray diffraction studies showed that the polyarylates prepared from BPA with DPT (100%) or DPI (100%) showed crystalline behavior; the same behavior was also observed in the DSC [Fig. 2(b)]. The crystallinity decreases with increase in the ratio of DPT and DPI. The polyarylate prepared by the melt polymerization of BPA with DPT (50%) and DPI (50%) showed completely amorphous behavior.

## CONCLUSIONS

High molecular weight polyarylates of bisphenol A (BPA) with varying ratios of diphenyl terephthalate (DPT) and diphenyl isophthalate (DPI) were prepared by melt polymerization using tin octoate as a catalyst. Tin octoate is a better transition metal catalyst for the preparation of polyarylates because of high reaction rates, high polymer yield, and low color. Furthermore, the tin octoate catalyst is nontoxic and ecofriendly in nature. The structure and composition of copolyarylates was confirmed by proton NMR spectroscopy. The compositions of DPT and DPI in copolyarylate



**Figure 4** TGA thermograms of copolyarylates (PA 7–11). [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

determined by  $^1\text{H}$  NMR spectroscopy are in good agreement with the feed compositions. The polyarylates prepared from BPA with different ratios of DPT and DPI were soluble in chloroform and tetrahydrofuran except the polyarylates derived from BPA with DPT (100%) or DPI (100%), and the solutions had film-forming properties. The  $T_g$ 's of polyarylate prepared from BPA with DPT (100%) or DPI (100%) is

very high. Furthermore, a decrease in  $T_g$  was observed with varying the ratios of DPT and DPI. All polyarylates exhibit one-step degradation behavior by TGA and DTG. No weight loss in polyarylates was observed up to 420°C, and the residue of nondegraded material at 900°C was up to 30% under nitrogen atmosphere. This indicates the high thermal stability of polyarylates. The polyarylates prepared from BPA

**TABLE IV**  
Thermal Behavior of Copolyarylates

| Polymer code | $T_g$ (°C) | $T_m$ (°C) | $\Delta H$ (J/g) | IDT (°C) | $T_{10}$ (°C) | $T_{\max}$ (°C) | Residue (%) |
|--------------|------------|------------|------------------|----------|---------------|-----------------|-------------|
| PA 1         | 222        | 343        | 36               | 432      | 448           | 474             | 30          |
| PA 2         | 198        | 353        | 55               | 436      | 441           | 476             | 29          |
| PA 3         | 181        | 348        | 31               | 434      | 446           | 475             | 30          |
| PA 4         | 185        | —          | —                | 434      | 441           | 481             | 29          |
| PA 5         | 181        | —          | —                | 433      | 434           | 474             | 28          |
| PA 6         | 187        | —          | —                | 427      | 432           | 471             | 27          |
| PA 7         | 166        | —          | —                | 420      | 428           | 463             | 25          |
| PA 8         | 167        | —          | —                | 434      | 436           | 470             | 26          |
| PA 9         | 179        | —          | —                | 436      | 442           | 477             | 29          |
| PA 10        | 155        | —          | —                | 434      | 429           | 472             | 27          |
| PA 11        | 203        | 298        | 34               | 436      | 444           | 467             | 29          |

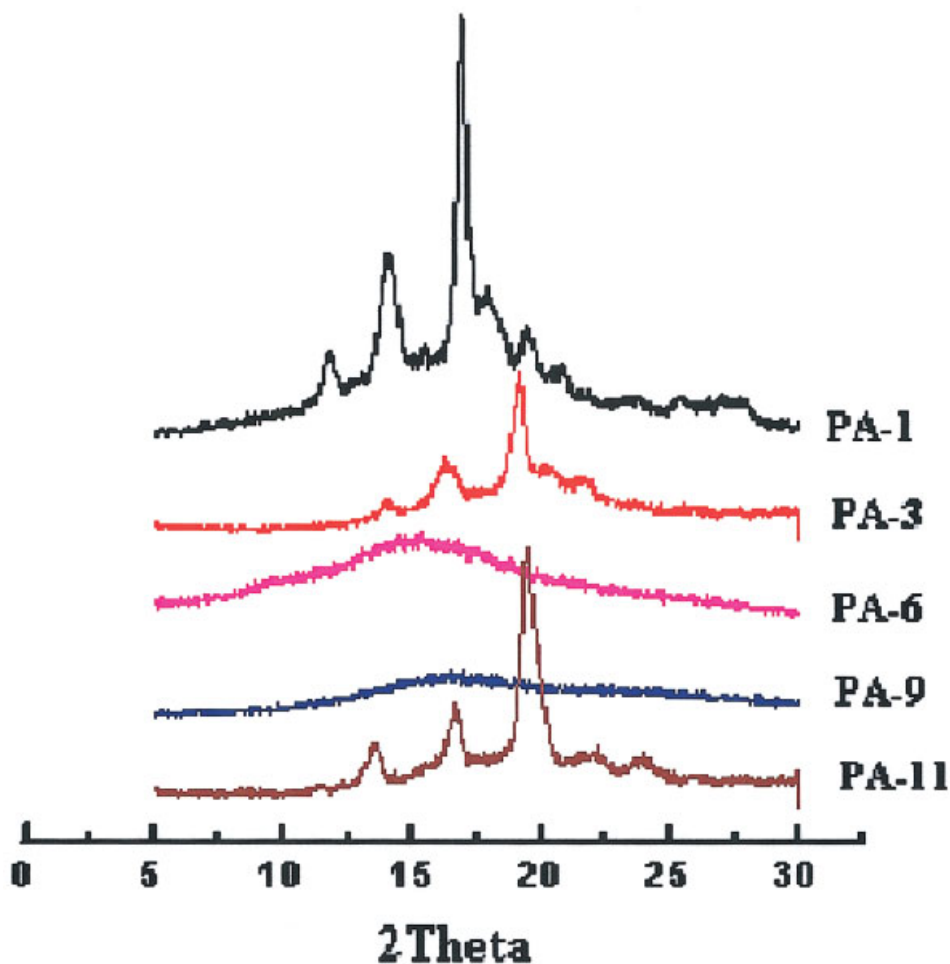
$T_g$ , Glass-transition temperature.

$T_m$ , Melting Temperature.

IDT, Initial decomposition temperature.

$T_{10}$ , Temperature of 10% weight loss.

$T_{\max}$ , Temperature of maximum weight loss.



**Figure 5** X-ray diffractograms of copolyarylates. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

with DPT (100%) or DPI (100%) showed crystalline behavior. The crystallinity increases with increase in the composition of DPT. The copolyarylate prepared by the melt polymerization of BPA with DPT (50%) and DPI (50%) showed completely amorphous behavior.

## References

- Korshak, V. V.; Vinogradova, S. V. *Polyesters*; Pergamon Press: Oxford, 1965.
- Korshak, V. V. *The Chemical Structure and Thermal Characterization of Polymers*; Israel Program for Scientific Translations, Keter: London, 1971.
- Morgan, P. W. *Polym Rev* 1965, 10, 366.
- Higashi, F.; Fujiwara, Y.; Yamada, Y. *J Polym Sci Polym Chem Ed* 1986, 24, 589.
- Hare, W. H. (to E. I. DuPont de Nemours and Co.). U.S. Pat. 3,234,168 (1966).
- Golberg, E. P.; Strause, S. F.; Munro, H. E. *Polym Preprints (ACS)* 1964, 5, 233.
- Matzner, M.; Barclay, R. J., Jr. *Appl Polym Sci* 1965, 9, 3321.
- Kantor, S. W.; Holub, F. F. (to General Electric Co.). U.S. Pat. 3,160,605 (1964).
- Yu, M. C. (to Phillips Petroleum Co.). U.S. Pat. 4,533,720 (1985).
- Calundann, G. W. (to Celanese Corp.). U.S. Pat. 4,067,852 (1978).
- Schnell, H. *Angew Chem* 1956, 68, 633.
- Uraski, T.; Hirabayoshi, Y.; Yoshida, T.; Inata, H. (to Teijin Ltd.). U.S. Pat. 4,436,894 (1984).
- Berger, M. H.; Gill, P. J.; Maresca, L. M. (to Union Carbide Corp.). U.S. Pat. 4,314,051 (1982).
- Gardner, H. C.; Matzner, M. (to Union Carbide Corp.). U.S. Pat. 4,229,565 (1980).
- Antic, V. V.; Govedarica, M. N.; Djonlagic, J. *Polym Int* 2003, 52, 1188.
- Schnell, H.; Boilert, V.; Fritz, G. (to Farbenfabriken Bayer AG). U.S. Pat. 3,553,167 (1971).
- Eise, K.; Friedrich, R.; Goemar, H.; Schade, G.; Wolfes, W. (to Dynamit Nobel AG). Ger. Pat. 2232877 (1974).
- Inata, H.; Kawase, S.; Shima, T. (to Teijin Ltd.). U.S. Pat. 3,972,852 (1974).
- Kosanovich, G. M.; Salee, G. (to Occidental Chemical Corp.). U.S. Pat. 4,465,819 (1984).
- Berger, M. H.; Matzner, M.; Tibbitt, J. M. (to Union Carbide Corp.). U.S. Pat. 4,314,051 (1982).
- Maresca, L. M.; Matzner, M.; See, B. (to Union Carbide Corp.). U.S. Pat. 4,321,355 (1982).
- Kowalski, A.; Duda, A.; Penczek, S. *Macromolecules* 2000, 33, 7359.
- Bero, M.; Czaplá, B.; Dobrzyn'ski, P.; Janeczek, H.; Kasperczyk, J. *Macromol Chem Phys* 1999, 200, 911.