

# Effects of the *t*-Butyl Substituent on the Miscibility of Polyarylates with Polyamides

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## SYNOPSIS

Amorphous polyarylates derived from 12–50 mol % of a *t*-butyl-substituted diacid, e.g., 5-*t*-butylisophthalic acid, exhibit miscibility with the amorphous phase of polyamides having aromatic and aliphatic character. Equally critical to blend miscibility is the aliphatic/aromatic carbon atom ratio (exclusive of the amide functionality) of the polyamide. An aliphatic/aromatic carbon atom ratio ( $\alpha$ ) greater than 1.4 but less than 2.5 is necessary.

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## INTRODUCTION

The contributions of the *t*-butyl substituent to the bulk properties of both polyarylates and polyamides have been reported.<sup>1–3</sup> The *t*-butyl group appears to have a pronounced effect on two properties in both polymer classes: increased thermal performance ( $T_g$ , HDT) and increased polymer solubility, which aids in polymer synthesis but detracts from end-use solvent resistance. The miscibility with amorphous and crystalline polyamides imparted by modifying the polyarylate backbone with the *t*-butyl substituent is the focal point of this article.

## EXPERIMENTAL

### Polyarylate Preparation

A 250-mL round-bottom flask was equipped with a 24/40 Claisen head adapter (supporting a thermocouple and nitrogen inlet), a 316 stainless steel paddle mechanical stirrer with sealed containment support, and a Barret trap topped with a condenser and nitrogen outlet. A 316 stainless steel thermocouple was used to monitor and control reaction mass temperature.

The reaction flask was charged on a volume basis to 70–75% of capacity. The diacetate derivative of the bisphenol was charged at 0.5 mol % excess to the diacids (Table I). Diphenylether was used to mediate reaction mass viscosity to achieve 50–60 wt % polymer solids. Under a nitrogen flow, the reaction mass was heated with stirring to 270°C (267–274°C) for 12–14 h. At the end of the reaction, dilution to 10% solids with chloroform was performed. The polymer was recovered as a powder by coagulation of the solution into isopropanol using a high-speed Waring blender.

### Polyamide Preparation

The polyamides (Table II) were prepared by standard interfacial or solution polycondensation procedures detailed elsewhere.<sup>4,5</sup>

### Analytical/Physical Property Measurement Procedures

#### Reduced Viscosity

Reduced viscosity (RV) for polyarylate samples was measured at 25°C in chloroform at 0.5 g/100 mL solvent. RV for polyamide samples was measured at 25°C in phenol/1,1,2,2-tetrachloroethane (60/40 w/w) at 0.5 g/100 mL solvent.

#### Glass Transition Temperature ( $T_g$ )

$T_g$  for polyarylate and polyamide samples was measured at a heating rate of 10°C/min and reported based upon the second heating cycle.

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**Table I** TBIA-Modified Polyarylates

| Composition                  | A    | B    | C    | D    | E    | F    | G    | H    |
|------------------------------|------|------|------|------|------|------|------|------|
| TA                           | 50   | 47.5 | 44   | 42.5 | 37.5 | 50   | 40   | —    |
| IA                           | 50   | 47.5 | 44   | 42.5 | 37.5 | —    | —    | —    |
| TBIA                         | —    | 5.5  | 12   | 15   | 25   | 50   | 60   | 100  |
| Bisphenol-A                  | 100  | 100  | 100  | 100  | 100  | 100  | 100  | 100  |
| RV (dL/g)                    | 0.62 | 0.97 | 0.99 | 0.87 | 0.83 | 1.03 | 1.01 | 1.12 |
| $T_g$ (°C)                   | 190  | 191  | 192  | 194  | 198  | 222  | 223  | 215  |
| %H <sub>2</sub> O absorption | 0.8  | 0.8  | 0.74 | 0.71 | 0.63 | 0.60 | 0.53 | 0.43 |

TA, terephthalic acid; IA, isophthalic acid; TBIA, 5-*t*-butylisophthalic acid.

### Physical Property Measurements

Samples were obtained by mixing a polyarylate and a polyamide in a Brabender mixing apparatus at 305–330°C under a nitrogen blanket at 60 rpm for 5 min. The polymer melt was compression molded into a plaque 0.125 × 4 × 4 in, from which test specimens were cut and physical properties measured.

## RESULTS AND DISCUSSION

Miscibility was first observed with the blends of polyarylate F [50 mol % 5-*t*-butyl isophthalic acid

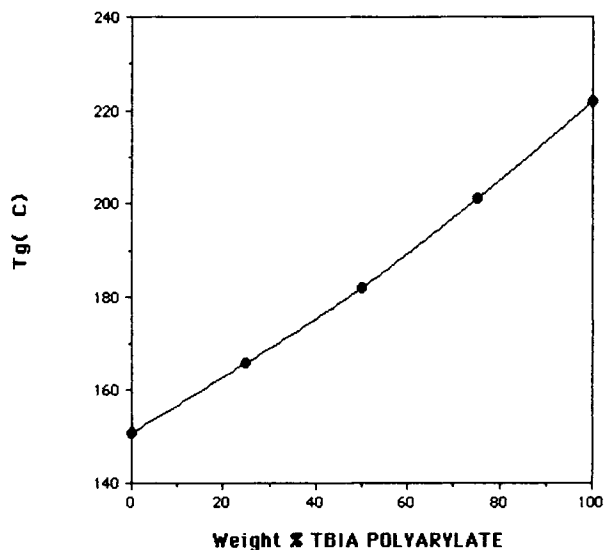
(TBIA)] and Trogamid T, an amorphous polyamide derived from terephthalic acid and 2,2,4-trimethylhexamethylene diamine. The polymer blends were transparent and exhibited a single glass transition temperature (Fig. 1) with the relationship between blend composition and  $T_g$  adhering closely to the Fox equation. At temperatures up to 330°C, no lower critical solution temperature (LCST) behavior was observed. Films of the 50/50 polyarylate F/Trogamid T were compression molded at 330°C and posttreated by either allowing the blend to cool to room temperature at 10°C/min or being quenched in liquid nitrogen. Fourier transform infrared (FTIR) analysis of the films relative to both Trogamid T and TBIA polyarylate controls showed no shift in either the amide carbonyl (1702 cm<sup>-1</sup>) or the ester carbonyl (1741 cm<sup>-1</sup>). This would suggest that the phenomenon responsible for the observed miscibility is not a specific interaction involving hy-

**Table II** Aliphatic/Aromatic Polyamides

| Composition                       |   | RV<br>(dL/g) | $T_g/T_m$<br>(°C) | $\alpha^a$ |
|-----------------------------------|---|--------------|-------------------|------------|
| TBIA/MPDA                         | I | 1.39         | 302/—             | 0.33       |
| 2,6-NDA/TMHMDA                    | J | 2.11         | 162/—             | 0.90       |
| PIDA/TMHMDA                       | K | 1.53         | 166/—             | 1.25       |
| T/I/AA/HMDA<br>(60/22/18//100)    | L | 1.14         | 107/294           | 1.36       |
| AA/MXD/HMDA<br>(100//80/20)       | M | 1.62         | 74/—              | 1.41       |
| TA/TMHMDA                         | N | 2.01         | 151/—             | 1.50       |
| TBIA/HMDA                         | O | 1.72         | 136/—             | 1.66       |
| TA/IA/AA/HMDA<br>(50/20/30//100)  | P | 1.57         | 98/281            | 1.76       |
| TA/IA/AA/HMDA<br>(65/5/30//100)   | Q | 1.41         | 101/302           | 1.76       |
| TBIA/TMHDA                        | R | 1.82         | 162/—             | 2.16       |
| TBIA/IA//1,2-DADD<br>(90/10//100) | S | 1.87         | 57/—              | 2.50       |
| TBIA/1,12-DADD                    | T | 2.13         | 62/—              | 2.66       |

MPDA, *m*-phenylenediamine; 2,6-NDA, naphthalene-2,6-dicarboxylic acid; TMHMDA, 2,2,4-trimethylhexamethylene diamine; PIDA, 1,1,3-trimethyl-3-phenylindan-4,5-dicarboxylic acid; AA, adipic acid; HMDA, hexamethylene diamine; MXD, meta-xylenediamine; DADD, 1,12-diaminododecane.

<sup>a</sup> Aliphatic/aromatic carbon atom ratio.



**Figure 1**  $T_g$  of Trogamid T/TBIA (50 mol %) polyarylate blends.

drogen bonding between the amide proton and the ester carbonyl. Comparatively, polyarylate lacking any *t*-butyl character was determined immiscible with Trogamid T over the blend composition range.

Extraction of 50/50 blends of polyarylate F/Trogamid T and polyarylate A/Trogamid T with chloroform resulted in > 98% of the polyarylate being recovered in the chloroform phase in both cases. This finding would eliminate the previously reported block polymer formation (resulting from aminolysis due to the terminal  $-\text{NH}_2$  groups present in the polyamides) as an explanation for miscibility.<sup>6,7</sup>

Determining the breadth of the miscibility profile in terms of mol % *t*-butyl functionality on the polyarylate and the polyamide character was addressed using statistically designed experiments. A  $2^3$  factorial design based upon mol % TBIA incorporated in the polyarylate and the ratio of aliphatic/aromatic carbons ( $\alpha$ , Table II) in the polyamide and Brabender melt temperature were the parameters varied with miscibility/immiscibility as the response factor (as determined by a single blend  $T_g$  or a dual  $T_g$  blend). Two overlapping  $2^3$  factorial designs were required to determine that the range of 5-*t*-butyl isophthalic acid needed was  $\geq 12$  but  $\leq 50$  mol % coupled with an aliphatic/aromatic carbon ratio ( $\alpha$ ) in the polyamide of  $1.4 \leq \alpha \leq 2.5$  to result in a miscible polymer pair. The upper limit melt temperature parameter of 330°C did not exhibit an interactive influence with the other two parameters. This miscibility window determined by the statistically designed experiments was tested (Table III) and found to be accurate. The importance of the aliphatic/ar-

**Table III Miscibility Window Validation (50/50 w/w Polymer Blend)**

| Polyarylate          | Polyamide             |                       |                       |                       |
|----------------------|-----------------------|-----------------------|-----------------------|-----------------------|
|                      | M (1.41) <sup>a</sup> | N (1.50) <sup>a</sup> | S (2.50) <sup>a</sup> | T (2.66) <sup>a</sup> |
| A (0) <sup>b</sup>   | —                     | —                     | —                     | —                     |
| B (5) <sup>b</sup>   | —                     | —                     | —                     | —                     |
| C (12) <sup>b</sup>  | —                     | +                     | +                     | —                     |
| D (15) <sup>b</sup>  | +                     | +                     | +                     | —                     |
| E (25) <sup>b</sup>  | +                     | +                     | +                     | —                     |
| F (50) <sup>b</sup>  | —                     | +                     | +                     | —                     |
| G (60) <sup>b</sup>  | —                     | —                     | —                     | —                     |
| H (100) <sup>b</sup> | —                     | —                     | —                     | —                     |

+, miscibility as determined by a single glass transition temperature (Fox eq.) and transparency; —, immiscibility as determined by dual  $T_g$  equivalent to blend components.

<sup>a</sup> Values ( ) represent  $\alpha$  from Table II.

<sup>b</sup> Mol % 5-TBIA in polyarylate.

**Table IV Properties of Polyarylate/Polyamide Blend**

| Polyarylate F (50 mol % TBIA)            | 100     | 50                | —       |
|--|---------|-------------------|---------|
| Polyamide P ( $\alpha = 1.76$ )          | —       | 50                | 100     |
| $T_g$ (°C)                               | 222     | 163               | 98      |
| $T_m$ (°C)                               | —       | 292 <sup>a</sup>  | 291     |
| $\Delta H_f$ (cal/g)                     | —       | 3.82 <sup>a</sup> | 7.9     |
| Tensile strength (psi)                   | 11,600  | 13,400            | 13,900  |
| Elongation at break (%)                  | 20      | 21                | 6.5     |
| Tensile modulus (psi)                    | 229,000 | 331,000           | 365,000 |
| Pendulum impact (ft-lb/in <sup>3</sup> ) | 104     | 162               | 47      |
| H <sub>2</sub> O absorption (%)          | 0.60    | 0.89              | 1.34    |

<sup>a</sup> Developed upon annealing at 150°C/8 h.

omatic carbon atom ratio ( $\alpha$ ) on the miscibility profile finds literature precedent in the segmental interaction parameter contribution to polyamide miscibility concept as advanced by Ellis.<sup>8,9</sup> Thus, in the case of the *t*-butyl-modified polyarylate and select aliphatic/aromatic polyamides intramolecular repulsive interactions would appear to dominate the interactional state of the polymer blend. It should also be pointed out that the difference in solubility parameter (as calculated from group contributions<sup>10</sup>) for the boundary compositions of the miscibility window exceed the accepted maximum  $\Delta\delta = 1.0$  mPa,  $\Delta\delta$  range =  $\delta_{\text{TBIA-PAR}} - \delta_{\text{PA}} = 2.8-3.6$ . Further work to develop a more rigorous treatment of the observed miscibility is required to resolve the apparent conflict with the solubility parameter difference.

Turning to a more applied perspective, an obvious advantage of this technology is in blending an amorphous polyarylate (heat resistance, toughness, dimensional stability) with a semicrystalline polyamide (solvent resistance, moldability) where the polyarylate is miscible with the amorphous phase of the polyamide. Fortunately, the critical  $\alpha$  value range includes semicrystalline polyamides, P and Q. Thus, blends were prepared using polyarylate F (having the highest  $T_g$  in the miscibility window) and polyamide P (Table IV).

It is evident from the data that the blend maintains the higher strength properties of the polyamide but with improved toughness and thermal performance. The one drawback is that the increase in  $T_g$  resulting from the *t*-butyl-containing polyarylate component slows the rate of crystallization, thereby requiring an annealing step to fully develop properties. Optimization of TBIA content in the poly-

arylate and the polyamide composition should allow for a blend composition that will develop properties without a separate annealing step.

## CONCLUSIONS

Bisphenol-A polyarylates derived from 12–50 mol % 5-*t*-butyl isophthalic acid are miscible with aliphatic/aromatic polyamides where the aliphatic/aromatic carbon ratio is  $\geq 1.4$  but  $\leq 2.5$ . Blends having good mechanical and thermal properties can be prepared up to 330°C without LCST behavior.

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