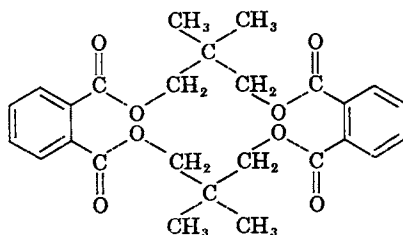


## ***Cyclization during Polyesterification: Isolation of an 18-Member Ring Compound from Reaction of Phthalic Anhydride with 2,2-Dimethyl-1,3-Propanediol***

It is generally accepted that cyclization reactions occur during condensation polymerization.<sup>1,2</sup> However, direct confirmation of their occurrence is rarely obtained.

Here we report isolation of 18-member ring compound **1** as a byproduct of oligomerization of phthalic anhydride (PA) and 2,2-dimethyl-1,3-propanediol (neopentyl glycol, NPG). Our findings provide direct evidence that cyclization occurs, and they also demonstrate a convenient method for synthesis of **1**, although yields are low (1.7%).



Existence of compound **1** has been postulated,<sup>3</sup> and we recently isolated it during attempts to synthesize monodisperse PA/NPG oligomers using monosilylated NPG.<sup>4</sup> To our knowledge, these are the first reported instances in which a cyclic byproduct of phthalic anhydride polycondensation has been isolated.

### **EXPERIMENTAL**

Complete experimental details are described in the Ph.D. dissertation of G.-F. Chen.<sup>5</sup> Materials were the best grades available from Aldrich Chemical Company and were used without further purification.

#### **Isolation of Compound 1 from Bulk Oligomerization of PA and NPG**

A melt of NPG (124.8 g, 1.2 mol), PA (118.4 g, 0.8 mol), and *p*-toluene sulfonic acid (0.25 g) in a 500-mL round-bottom flask was stirred under a slow N<sub>2</sub> purge as it was heated at the following temperature schedule: 100°C for 2 h, 140°C for 2 h, 160°C for 2 h, 220°C for 3 h, and 250°C for 4 h. The product was a viscous liquid; acid number: 3.2 mg KOH/g resin; GPC:  $M_n = 860$ ,  $M_w = 1360$ .

A solution of 12.8 g of the above liquid in 100 mL of methanol was kept for 2 days at room temperature. The white precipitate that formed was collected (3.84 g), washed with methanol, and dried. Acid number: 3.74 mg KOH/g resin; GPC:  $M_n = 1930$ ;  $M_w = 2210$ .

The filtrate was kept at room temperature for 2 more days; more white precipitate appeared. It was collected (0.40 g) and recrystallized from 60 mL of methanol to yield 0.166 g (1.3 wt % of 12.8 g) of crystalline **1**, mp 211–213°C.

#### **Isolation of Compound 1 from Solution Oligomerization of PA and NPG**

A solution of NPG (41.6 g, 0.40 mol), PA (39.4 g, 0.265 mol), and tris(2-ethylhexyl) phosphite (0.42 g) in xylene (189 g) in a 500 mL round-bottom flask was stirred at reflux under N<sub>2</sub> for 10 h. Xylene was removed by gradually heating to 240°C over 1 h to yield a viscous liquid having an acid number of 66 mg KOH/g resin, corresponding to 83% conversion of –COOH groups to ester groups. GPC:  $M_n = 560$ ;  $M_w = 780$ .

A solution of 45 g of this oligomer in 300 mL of methanol was kept at room temperature for 2 days. White precipitate appeared, but the amount was much smaller than was obtained (see above) from bulk oligomerization. The precipitate was collected (0.84 g) and was recrystallized from 150 mL of methanol to yield 0.78 g (1.7 wt %) of compound 1, mp 211–213°C.

### Characterization of Cyclic Compound 1

The white crystals, mp 211–213°C, had the following characteristics.

ANAL: Calcd for  $C_{26}H_{28}O_8$ : C, 66.67%; H, 5.98%; O, 27.35%. Found: C, 66.70, 66.56, 66.68%; H, 6.02, 5.92, 5.98%; O, 27.14, 26.81, 27.31.

$^1H$ -NMR( $CDCl_3$ ): 7.5–7.9 (m, 8H, aromatic H's), 4.15 (s, 8H,  $-CH_2-$ ), 1.1 (s, 12H,  $-CH_3$ ). FT-IR (KBr pellet, Fig. 1): 3446 and 3421 (suspected C=O overtones), 1738 and 1725 (C=O stretching), and 1595–1605  $cm^{-1}$  (aromatic C=C stretching). Acid number: < 1 mg KOH/g. Mass spectrum [m/e(relative intensity)]: 468 (0.1, molecular ion), 351 (0.6), 320 (1.0), 319 (0.8), 235 (65), 149 (100), 104 (36). GPC:  $M_n = 313$ ;  $M_w = 329$  / (Waters 100, 500,  $10^3$ , and,  $10^4$  Å columns in series, tetrahydrofuran solvent, polystyrene calibration standards).

### Characterization Methods

Elemental analyses were performed by Desert Analytics Co., Tucson, AZ.  $^1H$ -NMR spectra were determined using a Varian EM-390 90 MHz spectrometer using TMS as internal standard. Mass spectra were performed on MAT Model CH7 and CH5-DF instruments. FT-IR spectra were recorded using a Mattson Cygnus-25 instrument. Gel permeation chromatography (GPC) was performed in tetrahydrofuran solution using a Waters Model 510 pump, a Model R401 refractive index detector, a Model 730 data module, and 100, 500,  $10^3$ , and  $10^4$  Å columns in series. Accuracy of  $M_n$  and  $M_w$  values determined by GPC is, of course, subject to numerous sources of error.

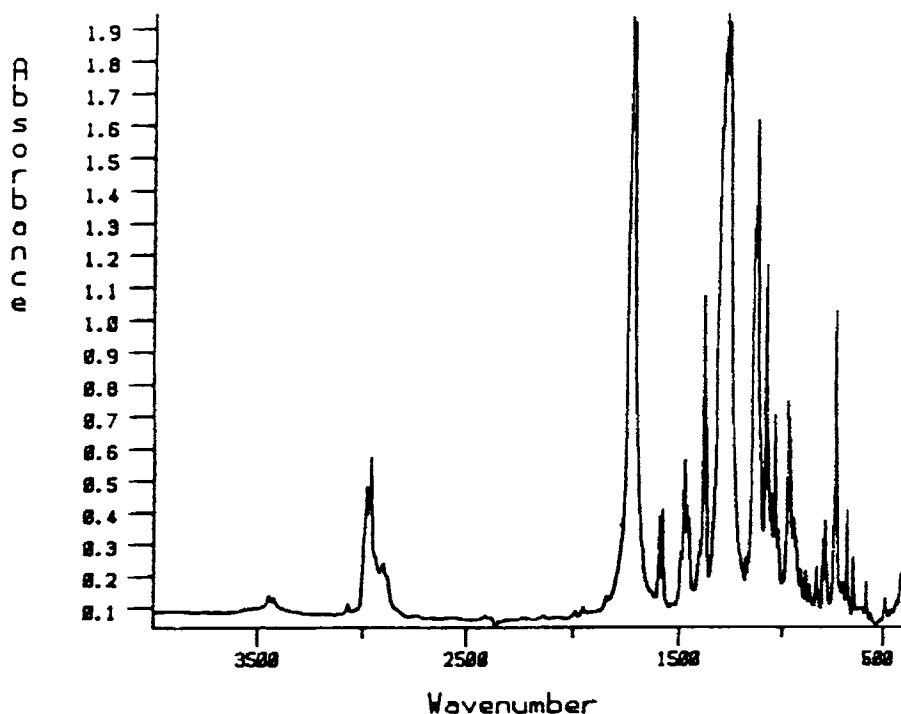


Fig. 1. FT-IR spectrum of cyclic compound 1.

## RESULTS AND DISCUSSION

As previously reported,<sup>4</sup> we isolated cyclic compound **1** in 7%–10% yields during attempts to synthesize monodisperse PA/NPG oligomers using monoprotected NPG. It formed during removal of the *t*-butyldimethylsilyl protecting groups. The facility with which compound **1** can be separated by crystallization led us to search for it in the products of conventional, high-temperature oligomerization of PA with NPG. As related above, this compound can indeed be isolated from such products.

Although the formation of compound **1** during alkyd resin synthesis has been postulated, a literature search did not uncover previous reports of its isolation or characterization.<sup>5</sup> Accordingly, the compound was characterized by a variety of methods. Proof of its structure rests mainly on elemental analysis, on <sup>1</sup>H-NMR and mass spectra, and on the fact that it contains no COOH groups detectable by titration.

Elemental analysis of the crystalline compound was very close to the theoretical values for **1** (C, 66.67%; H, 5.98%, and O, 27.35%) and were significantly different from theoretical values of PA/NPG noncyclic oligomers. For example, a  $\frac{2}{3}$  oligomer (C<sub>31</sub>H<sub>40</sub>O<sub>10</sub>) would contain C, 65.03%; H, 6.99%; and O, 27.97%.

The <sup>1</sup>H-NMR spectrum consisted simply of sharp singlets at 1.1 and at 4.2 ppm and a multiplet centered at about 7.65 ppm. This spectrum indicates that all methyl groups are magnetically equivalent, as are all methylene groups, and that none of the aliphatic hydrogens experiences detectable spin-spin splitting. These features are consistent with structure **1**. In contrast, acyclic PA/NPG oligomers have much more complex NMR spectra in which signals at about 3.35 ppm (–CH<sub>2</sub>OH end groups) are readily evident.<sup>5</sup>

The highest *m/e* peak in the mass spectrum is at 468, corresponding to the molecular ion for 18-member ring compound **1**. The peaks at *m/e* 383, 366, and 320 are attributable to loss of one NPG unit excluding water, from loss of one NPG unit, and from loss of one PA unit, respectively. The parent ion at *m/e* 149 is the mass of PA.

The IR spectrum (Fig. 1) is generally consistent with the assigned structure. Presence of small peaks at 3446 and 3421 cm<sup>-1</sup> was of concern because it suggested the possible presence of hydroxyl or other active hydrogen groups. These peaks are present in the photoacoustic FT-IR spectrum of compound **1** as well as in its transmission spectrum, indicating that they are not attributable to water. However, the spectra of many ketones, esters, and aldehydes have C=O overtones in this region.<sup>6</sup> For example, the IR spectrum of  $\gamma$ -butyrolactone has broad, relatively strong peaks at 3300–3650 cm<sup>-1</sup>. The frequencies of the 3446 and 3421 cm<sup>-1</sup> peaks are, within experimental error, twice those of the C=O peaks at 1738 and 1725 cm<sup>-1</sup>. Thus, it is reasonable to conclude that they are C=O overtones.

The fact that gel permeation chromatography indicates a lower than theoretical molecular weight for compound **1** is predictable in view of the molecules' compactness.

It is concluded that the overall evidence conclusively supports assignment of cyclic structure **1** to the crystalline compound isolated from condensation of phthalic anhydride and neopentyl glycol.

It is, of course, generally accepted that cyclization occurs to some extent during condensation polymerization. Cyclic oligomers have been isolated, for example, as byproducts of polyethylene terephthalate production. However, no reports of isolation of cyclic byproducts from oligomerization or polymerization of phthalic anhydride have been found. For years, partial cyclization has been strongly suspected to occur in the high-temperature polycondensation reactions used to produce alkyd and polyester resins.

Walz<sup>2</sup> and Kastanek and Podzimek<sup>7</sup> studied the relationships among acid number, hydroxyl number, and molecular weight during preparation of alkyd resins and of fractionated alkyds. Both found that molecular weights are lower than expected in view of the conversion of functional groups, and both attributed the discrepancy to "ring formation" during the alkyd resin preparation. Kastanek and Podzimek estimated the extent of intramolecular reaction at 4%–5%.

Although the previous studies are consistent with cyclization hypothesis, they do not prove it. Isolation of compound **1** in this study provides direct evidence for cyclization. The amount of **1** actually isolated was 1.3 wt % of the polyester prepared by the fusion process and 1.7 wt % of the polyester prepared by the solvent process. Of course, **1** is not the only cyclic structure that can form, and it is unlikely that all of it was isolated. Thus, the 1.3–1.7 wt % recoveries are not inconsistent with Kastanek and Podzimek's estimate of 4–5% total cyclization.

It is not surprising that the extent of the cyclization reaction is somewhat influenced by the method of preparation. Dilution effects would favor cyclization in solution processes relative to fusion (solvent-free) processes. Perhaps more important is the fact that the solution process was stopped at 83% conversion minimized formation of solid acyclic oligomers and facilitated isolation of cyclic compound **1**.

### CONCLUSIONS

Isolation of cyclic compound **1** provides direct evidence that cyclization occurs during polyesterification of phthalates. Oligomerization of phthalic anhydride and neopentyl glycol in xylene solution provides a convenient one-step synthetic route to cyclic compound **1**, although yields are low.

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