# Preparation and Properties of Copolyesters Polymerized in a Vented Extruder*

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## Synopsis

High molecular weight thermoplastic copolyesters from bisphenol A, neopentyl glycol, and terephthaloyl chloride have been prepared by a melt-polymerization technique carried out in a twin-screw, vacuum-vented extruder. Low molecular weight polymer, polymerized in a conventional melt reactor, was further polymerized to copolyesters with intrinsic viscosities, under the conditions investigated, of up to 0.76 dl/g. The optimum extruder reaction conditions with respect to temperature profile, vent configuration, and polymer throughput are described. A variety of properties for two representative copolyester compositions have been determined. Particular attention was given to melt viscosity and impact strength, two properties which depend markedly on whether the polymer is prepared by the subject melt process or, alternately, by a low temperature interfacial polycondensation. It is concluded, based on a study of deliberately branched, interfacially prepared copolyesters, that the property differences which depend on the polymerization method are attributable to the formation of branches in the copolyesters prepared by the high-temperature melt process.

## INTRODUCTION

Melt polymerization, carried out in the absence of a solvent, was investigated for the preparation of a high molecular weight thermoplastic polyester composed of bisphenol A (60–50 mole-%), neopentyl glycol (40–50 mole-%), and terephthaloyl chloride (100 mole-%). The polyester containing equimolar amounts of the bisphenol and the glycol would have the structure I.

I
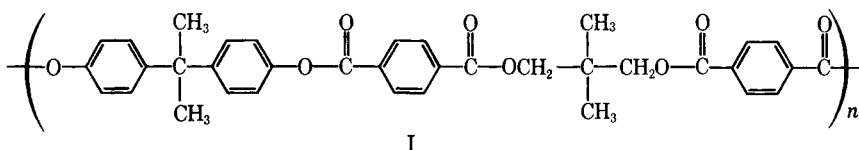
These copolyesters, when prepared by interfacial polymerization techniques, had been found to possess an interesting spectrum of properties which suggested utility as "engineering" thermoplastics. The melt method for carrying out the polycondensation was studied because of the economic advantages involved in the elimination of all processing solvents.

Since such an approach presents severe stirring and handling difficulties due to the high melt viscosities encountered, a continuous method employing an extruder was investigated. A machine with two (twin) counter-rotating screws was used in order to provide adequate agitation at the high polymerization temperatures required. A vacuum multivented barrel was also required in order to remove the hydrogen chloride produced in the polycondensation reaction. The fully polymerized product was extruded in a form, following drilling, which could be immediately fabricated without additional processing. A research size extruder was selected which was equipped with all the functions of commercial scale equipment and which also provided an adequate quantity of copolyesters for evaluation.

The extruder processing conditions required for the preparation of high molecular weight polyester are described. In addition, the properties of the resultant polyesters are discussed with particular reference to certain critical properties which depended on whether the polymer was prepared by the subject melt process or by a low temperature interfacial polycondensation. These property differences in the copolyesters prepared by the two methods are explained in terms of differences in their basic molecular structures.

## EXPERIMENTAL

### Reagents

The principal reagents employed were bisphenol A [2,2-bis(4-hydroxyphenyl)propane], a polymer-grade material used with and without subsequent vacuum distillation and recrystallization; neopentyl glycol (2,2-dimethyl-1,3-propanediol), either a commercial material obtained from the Eastman Tennessee Co. and fractionally distilled under vacuum after the removal of water by benzene azeotroping (mp 121–122°C) or a purified material obtained from Matheson, Coleman and Bell Co., code 7200, containing 0.05–0.06% water (mp 127.0–128.5°C); and terephthaloyl chloride (the diacid chloride of 1,4-benzenedicarboxylic acid), produced by the Hooker Chemical Corporation and subsequently distilled under vacuum.

### Vented Extruder

The extruder employed to carry out the melt polycondensations was a Point-Eight twin-screw multivented machine manufactured by Welding Engineers for research purposes. Its barrel diameter was 0.8 in. with a $L/D$ ratio of 37:1. It is depicted schematically in Figure 1. The extruder barrel was fitted with three vents which could be arranged either with the large vent (designated L) in the upstream position next to the hopper or in the extreme downstream position next to the nozzle. The two small vents (designated S) were adjacent to each other, either above or below the large vent. Each vent was either closed (C), provided with a nitrogen purge (N) or subjected to a vacuum of 2.0–2.5 mm Hg (V). Thus, the vent configuration indicated in Figure 1 would be designated $N_L$–$V_S$–$C_S$, indicating that the first vent (large) is under nitrogen, the second vent

(small) under vacuum, and the third vent (small) closed.  The screw assembly in the barrel was composed of interchangeable feed, compounding, milling and extruding segments selected to correspond to the particular vent configuration employed and to impart the desired amount of mechanical work to the feed.  Temperature was controlled in six separate stages along the barrel by means of six separate regulators.

The measured output rate and the corresponding residence time in the extruder, which were varied in conjunction with the screw speed, depended on the screw configuration used and on the extent to which the various screw flights were actually loaded.  The determination of the latter quantity was not practical.  However, approximate upper limits for the residence times were estimated for each screw speed by dividing a calculated extruder
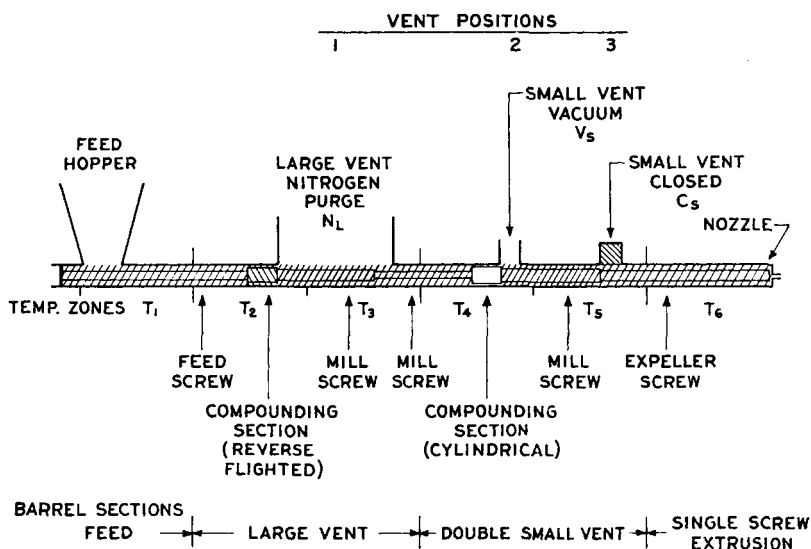


Fig. 1. Details of the ' point-eight" research extruder.

capacity of 145 g by the measured output rate.  Screw speed was varied from 50 to 100 rpm.  Over this range, the input rate (equal to the output rate) was increased from about 5 to about 10 g/min in order to maintain the extruder content at a workable level, an amount which necessarily fell somewhat below the calculated capacity.  In this manner, residence time could be changed in a known direction and its effects on the copolyester produced assessed in a qualitative way.  Calculated as described above, residence time varied from up to about 15 min at 100 rpm to up to about 30 min at 50 rpm screw speed.  Still longer residence times were obtained by making multiple passes through a given extruder configuration.

The feed material, generally ground to 10 mesh or smaller, was fed into the extruder hopper under anhydrous conditions from a motor-driven metering hopper.

### Stage I Copolyester (Extruder Feed)

The extruder feed material was a low molecular weight copolyester (designated stage I polymer) which was readily prepared in conventional reactors. In the first step, a so-called prepolymer was prepared from the neopentyl glycol and the terephthaloyl chloride, usually with slightly in excess of 100 mole-% of the latter, by heating at 100°C for several hours under a nitrogen flush. In a second step, this prepolymer was reacted with the required amount of bisphenol A under a nitrogen flush for about 3 hr up to a maximum temperature of about 155°C, followed by dumping of the resultant stage I polyester prior to the development of excessive viscosity. The stage I polymers were prepared under anhydrous conditions and kept dry prior to polymerization in the vented extruder.

### Reactivity Test for Stage I Copolyester

A "reactivity test" was employed to assess the polymerizability of stage I polymer under ideal conditions. It consisted in the further polymerization of the stage I feed in a glass flask by heating it at 275–300°C for 60–80 min under a vacuum of 0.1–0.5 mm Hg and the determination of the intrinsic viscosity of the product.

### Interfacial Polymerization

In common with the preparation of stage I feed, the interfacial technique consisted in the preparation of a prepolymer by the complete reaction of the neopentyl glycol with the terephthaloyl chloride at 100°C. The subsequent polymerization step in the interfacial method was carried out at room temperature by reacting the prepolymer dissolved in methylene chloride with an aqueous sodium hydroxide solution of the bisphenol A in the presence of a quaternary ammonium salt as catalyst.

A deliberately branched copolyester was also prepared in the same interfacial method by the inclusion of about 1 mole-% (based on bisphenol A) of the trifunctional phenolic compound II:



II
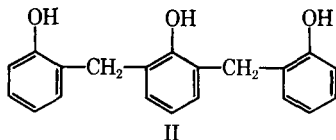
in order to introduce branch points into the copolyester structure. In addition, it was necessary to include 0.33 mole-% of a monofunctional phenol in order to avoid gelation. The latter presumably terminated the growing polyester chains prior to the formation of crosslinks.

### Copolyester Properties

Intrinsic viscosity was determined in *sym*-tetrachloroethane at 30°C by use of Cannon-Ubbelohde suspended-level solution viscometers.

Melt viscosity was determined in a capillary rheometer, the Tinius Olsen extrusion melt indexer, Model No. 3.

Additional properties, including the notched Izod impact strength, were determined by standard ASTM methods.

## RESULTS AND DISCUSSION

Copolyesters produced by the melt extrusion process were immediately evaluated by observation of the extrudate's color and its toughness when manually flexed. In addition, polyester intrinsic viscosity was also employed as an immediate indication of the degree of polymerization occurring in the vented extruder. These three criteria served as quick and reliable indications of the quality and mole weight of the polyesters produced.

### Polymerization Results in the Vented Extruder

The vented extruder was used to advance a low molecular weight copolyester (stage I), having an intrinsic viscosity of about 0.16 dl/g, to final high molecular weight polymer (stage II). As noted, the stage I feed was readily prepared in conventional reactors. The use of sufficiently reactive stage I feed, as judged by the reactivity test, was of primary importance for the attainment of stage II polyesters of maximum molecular weight.

Highly anhydrous monomers were required for the preparation of adequately reactive stage I feed. It was also necessary to employ strictly anhydrous conditions in the stage I polymerization and in the subsequent storage of the stage I polyester prior to its transfer to the extruder. Such materials were characterized by a proper balance of reactive end groups, in part determined by the precise stoichiometry of the reacting monomers, and a polymerizability in the reactivity test of at least an intrinsic viscosity of 0.72 dl/g.

Two basic vent configurations were examined: L-S-S (as depicted in Fig. 1) and S-S-L. The particular grouping used did not significantly influence the results, and the former configuration was generally preferred. Exploratory polymerizations of stage I feed also indicated that downstream temperatures in the range of 300–325°C were optimum for the development of maximum molecular weight, with the upstream temperatures being somewhat lower (in the regions corresponding to lower degrees of polymerization). An optimum temperature profile (stages $T_1$–$T_6$, Fig. 1) was found to be 75–250–275–300–325–325°C. The effects of the additional extruder variables studied are listed in Table I.

The conditions under which the vents operated were found to be critical. In the first place, it was observed that the application of vacuum to (upstream) vent 1 drastically reduced the final molecular weight of the extrudate (see lines 1 and 2, Table I), a result attributable to premature volatilization of monomer species prior to polycondensation. Thus, vent 1 was operated either closed or subjected to a nitrogen purge. Approximately the same results were obtained in either case (lines 4 and 5). Similarly,

TABLE I

Polymerization of Bisphenol A (60%)–Neopentyl Glycol (40%)–Terephthalate (100%) in a Vented Extruder

| Line | Run no. | Feed No. | Feed Intrinsic viscosity, dl/g | Reactivity test, intrinsic viscosity, dl/g | Triphenyl-phosphine, % | Extruder temp at $T_6$, °C | Screw speed, rpm[a] | Vents[b] 1 | 2 | 3 | Maximum extrudate intrinsic viscosity, dl/g |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | WE-4 | 52 | ca. 0.18 | 1.0 | None | 300 | 100 | $V_S$ | $C_S$ | $V_L$ | 0.53 |
| 2 | 29 | R-14 | 0.16 | 0.72 | None | 325 | 50 | $C_S$ | $C_S$ | $V_L$ | 0.76 |
| 3 |  | R-14 | 0.16 |  |  |  |  | $N_L$ | $V_S$ | $V_B$ | 0.68 |
| 4 |  | R-14 | 0.16 |  |  |  |  | $N_L$ | $V_S$ | $C_S$ | 0.66 |
| 5 | 31 | R-14 | 0.16 | 0.72 | None | 325 | 50 | $C_S$ | $C_S$ | $V_L$ | 0.66 |
| 6 | 29 | R-14 | 0.16 | 0.72 | None | 325 | 100 | $N_L$ | $V_S$ | $V_S$ | 0.55 |
| 7 |  |  |  |  |  |  |  | $N_L$ | $V_S$ | $C_S$ | 0.59 |
| 8 | 31 | R-14 | 0.16 | 0.72 | None | 325 | 150 | $C_S$ | $C_S$ | $V_L$ | 0.61 |
| 9 | 24 | R-13 | 0.16 | 1.09 | None | 325 | 100 | $N_L$ | $V_S$ | $C_S$ | 0.66 |
| 10 | 26 | R-13 | 0.16 | 1.09 | 0.63 | 300 | 100 |  | " |  | 0.62 |
| 11 |  |  |  |  | 1.25 | 300 | 100 |  | " |  | 0.69 |
| 12 | 24 | R-13 | 0.16 | 1.09 | 1.25 | 325 | 100 |  | " |  | 0.73 |
| 13 | 26 | R-13 | 0.16 | 1.09 | 1.75 | 300 | 100 |  | " |  | 0.64 |
| 14 | 30 | Run 29[c] | 0.65 | — | None | 325 | 50 | $N_L$ | $V_S$ | $V_S$ | 0.55 |
| 15 |  |  |  |  | 1.25 | 325 | 50 |  | " |  | 0.61 |
| Optimum |  |  | 0.16 | — | 1.25 | 300–325 | 50–100 | $N_L$ | $V_S$ | $C_S$ | ≤0.76 |

[a] As discussed in the experimental section, the throughput rates at 50 and 100 rpm were approximately 5 and 10 g/min, respectively, yielding residence times in the extruder of up to 30 and 15 min, respectively.

[b] See Fig. 1 for location of extruder vents.

[c] This feed is extrudate (stage II) copolyester from run No. 29, intrinsic viscosity = 0.65 dl/g.

equivalent results were obtained with (downstream) vent 3 either closed or under vacuum (lines 3 and 4, 6 and 7). The middle vent (number 2) was necessarily held under vacuum in order to achieve efficient removal of the hydrogen chloride released by the polycondensation reaction. Overall, then, the vent configuration $N_L-V_S-C_S$ was found to be optimum.

The remaining operating variable studied was screw speed. A speed of 50 rpm normally yielded higher molecular weight polyester than did higher screw speeds (compare lines 3 and 6, 4 and 7, and 5 and 8 in Table I) due to the longer extruder residence times associated with the lower speed. However, this factor was not critical, and a screw speed of 100 rpm was usually preferred in order to achieve higher output.

We may therefore summarize the optimum extruder operating conditions for the system studied as consisting in a maximum reaction temperature of 300–325°C, a vent configuration of $N_L-V_S-C_S$, and a screw speed of 50–100 rpm.

The question of whether or not a still longer residence time could be used to increase the molecular weight still further was examined in run 30 (lines 14 and 15, Table I). Stage II polyester prepared in run 29 and having an intrinsic viscosity of 0.65 dl/g was subjected to a second pass through the extruder. A slight degree of degradation accompanied by severe discoloration of the extrudate was observed.

It was found advantageous to incorporate a thermal stabilizer in the extruder feed in order to obtain the maximum final molecular weight. Triphenylphosphine was the most effective additive studied. As shown by the data in Table I, a 1.25% level was found to be optimum. This stabilizer was not effective in reducing the yellow-amber color normally found in the extrudates; in fact, it yielded green-brown colored extrudates possessing, if anything, even more intense color.

As indicated in Table I, stage I polyester was advanced in molecular weight in the extruder to yield products which typically had an intrinsic viscosity of 0.66–0.69 dl/g. The maximum extrudate viscosity obtained was in the range of 0.73–0.76 dl/g. Although these products clearly possessed substantial molecular weights, it is notable that higher degrees of polymerization were invariably obtained when the stage I feed was polymerized in glass by means of the reactivity test, as also indicated by the data in Table I. This is particularly true of the feeds which had the higher reactivity test polymerizabilities since each of the feeds listed in Table I, which had polymerizabilities in glass covering the range of 0.72–1.09 dl/g, nonetheless yielded very similar extrudate intrinsic viscosities (equal to or less than 0.76 dl/g, as noted above) when the polycondensations were carried out in the vented extruder.

In any melt polymerization conducted at elevated temperatures, thermal and oxidative degradation necessarily compete with polycondensation. In the vented extruder, degradation would also be enhanced by mechanical shear and the presence of metal surfaces. It is felt that these additional degradative factors were responsible for limiting the molecular weights

obtainable by the vented extruder process to values lower than those observed for polymerizations carried out in glass.

## Properties of the Copolyesters

**General Properties.** Copolyester compositions identical to those described above were also prepared by an interfacial polymerization technique. By this room temperature method, polymers with intrinsic viscosities in excess of 1 dl/g were readily obtained.

Table II lists a variety of mechanical, thermal, and electrical properties for the two copolyester compositions prepared by using the vented extruder. Included are properties observed for the same polymer compositions prepared by the interfacial process. Values identical within experimental uncertainty were observed for polyesters prepared by the two different processes for the properties listed in Table II with two minor exceptions.

TABLE II

Properties of Bisphenol A (60 or 50%)–Neopentyl Glycol (40 or 50%)–
Terephthalates (100%)

| Property, units | 40 mole-% glycol | | 50 mole-% glycol | |
|---|---|---|---|---|
| | Melt method[a] | Inter-facial method[b] | Melt method[c] | Inter-facial method[b] |
| Density, g/cm³ | 1.20 | | 1.20 | |
| Flexural modulus, psi | 3.0 ± 0.1 × 10⁵ | | 3.2–3.3 × 10⁵ | |
| Flexural strength, psi | 12,700–13,000 | | 12,700–13,700 | |
| Tensile yield strength, psi | 8,400–8,900 | | 8,000–9,200 | |
| Tensile elongation, % | | | | |
|   Yield | 8–10 | | 7–9 | |
|   Ultimate | 10–24 | | 47±7 | 31±2 |
| Rockwell hardness, M | 66–70 | 75–80 | 63–67 | 67–75 |
| Heat distortion temp, °C | | | | |
|   66 psi | 148 | | 128 | |
|   264 psi | 138 | | 118 | |
| Softening temp, °C[d] | 151 | | — | 138 |
| Dielectric constant | | | | |
|   60 cps | 3.28 | | 3.28 | |
|   10⁶ cps | 3.13 | | 3.13 | |
| Dissipation factor | | | | |
|   60 cps | 0.0025 | | 0.003 | |
|   10⁶ cps | 0.018 | | 0.018 | |
| Dielectric strength (0.125 in.), V/mil | | | | |
|   S/T | 430 | | 422 | |
|   S/S | 380 | | 366 | |
| Volume resistivity, ohm-cm | >10¹⁷ | | >10¹⁷ | |

[a] Intrinsic viscosity = 0.65–0.72 dl/g.

[b] Intrinsic viscosity ≥ 0.67 dl/g.

[c] Intrinsic viscosity = 0.73–0.75 dl/g.

[d] This is the temperature at which a film under a load of 170 g/mm² elongates abruptly when its temperature is raised at a rate of 3.5°C/min.[1]
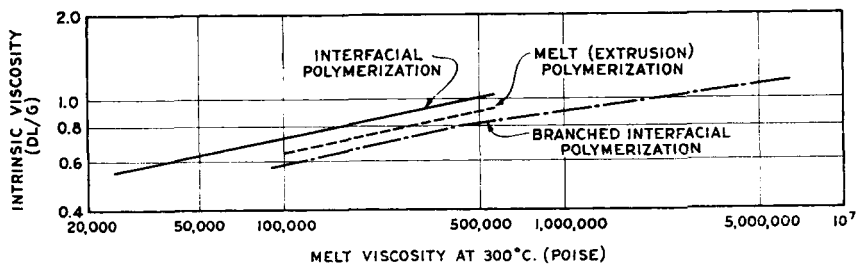
Fig. 2. Melt viscosity at 300°C vs. intrinsic viscosity for bisphenol A (60%)-neopentyl glycol (40%)-terephthalate (100%).
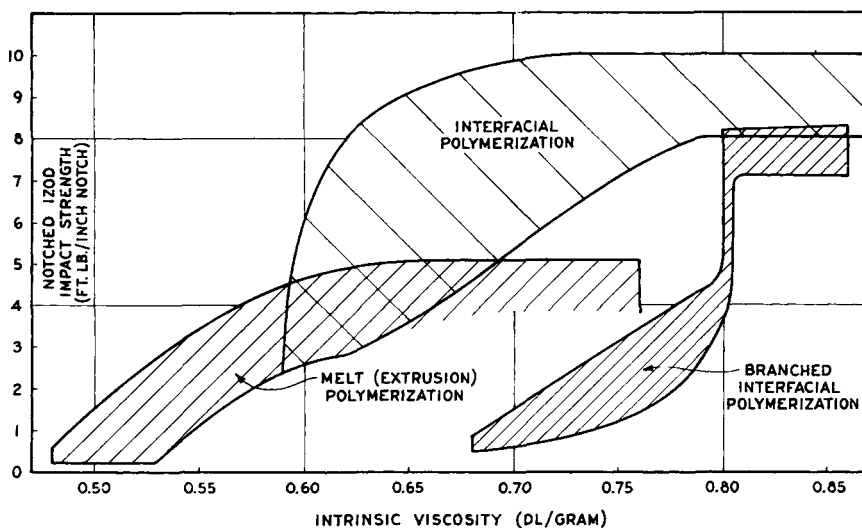


Fig. 3. Notched Izod impact strength vs. intrinsic viscosity for bisphenol A (60%)-neopentyl glycol (40%)-terephthalate (100%).

In particular, the melt-prepared copolyester containing 50% neopentyl glycol had a somewhat higher ultimate elongation, and in the case of both copolyester compositions, the melt-prepared polyesters were somewhat softer as indicated by their Rockwell M hardnesses.

**Melt Viscosity and Impact Strength.** Two properties of critical importance (not listed in Table II), the melt viscosity and the impact strength, differed very significantly for the two methods of preparation. This proved to be the case for melt-polymerized copolyesters prepared in glass with and without a solvent as well as for the materials prepared by the melt extrusion process.

Figure 2 is a log–log plot of intrinsic viscosity in deciliters per gram versus melt viscosity in poise at 300°C. The melt viscosity of the melt-prepared polyester differs from that for the interfacial polyester by a factor of nearly two over the entire intrinsic viscosity range studied. At a given intrinsic viscosity, the melt-polymerized polymer has the higher melt

viscosity, indicating a difference in molecular structure which is necessarily attributable to the method of polymerization.

Figure 3 is a plot of intrinsic viscosity versus notched Izod impact strength. The relationships for each of the copolyesters are indicated as partially overlapping areas. The impact strengths observed for the polyester prepared by the melt process fall significantly below the high values found for the interfacially prepared polymer, at least up to the maximum intrinsic viscosity level studied for the former, 0.76 dl/g.

**Study of Property Discrepancies.** Various possible explanations were considered for the melt viscosity and impact strength discrepancies observed for copolyesters prepared by the two methods, melt and interfacial polymerization. The copolyesters were examined for anhydride linkages in their backbones by study of their infrared spectra. Small amounts of this linkage were thereby detected in copolyesters prepared by the interfacial route; however, their levels appeared to be too low to account for the property differences observed.

It was considered that molecular weight distribution differences were also an unlikely explanation for the property discrepancies observed. In the first place, it appeared that a molecular weight distribution equilibration occurred by means of ester interchange on heating the polyesters for either the determination of melt viscosity or the molding of specimens for the determination of impact strength. In any case, the intrinsic viscosity–melt viscosity relationship, in particular, should be relatively insensitive to differences in molecular weight distribution since both quantities generally depend to a first approximation on the weight-average molecular weight.

A more likely explanation for the property differences was finally considered. Molecular chain branching could occur exclusively in the melt process, most probably by means of a Friedel-Crafts, hydrogen chloride–catalyzed acylation by terephthaloyl acid chloride groups of the bisphenol aromatic ring, rendering the latter residue trifunctional and thereby introducing a branch point. Such a reaction would not be expected to occur during polymerizations conducted at room temperature. In order to test this hypothesis, a deliberately branched copolyester was prepared interfacially.

The intrinsic viscosity–melt viscosity relationship for the branched interfacial copolyester is included in Figure 2. Its melt viscosity is about three times that of the normal, presumably unbranched interfacially prepared copolyester. Moreover, it is even greater than that of the polymer prepared by the melt process. These results are thus consistent with the hypothesis that chain branching occurs in the elevated temperature melt polymerizations. The finding that chain branching increases melt viscosity at a given intrinsic viscosity level is reasonable since the branched polymer would be expected to have the higher weight-average molecular weight, the molecular weight parameter which uniquely determines melt viscosity.

Falling projectile and notched Izod impact strengths, the latter included in Figure 3, were also determined for the chain-branched interfacially prepared copolyester. These results indicate that branching reduces this important property at intrinsic viscosities below about 0.80 dl/g. Thus, the impact strength discrepancies between the melt-prepared and normal interfacially prepared copolyesters can also be attributed to the occurrence of chain-branching in the polymer prepared by the melt route. Above an intrinsic viscosity of about 0.80 dl/g, the deliberately branched polyester exhibits strengths very nearly characteristic of the unbranched interfacial polymer (8–10 ft-lb/in. notch). Therefore, branching appears to increase the critical intrinsic viscosity level necessary for the attainment of optimum impact properties. Polyesters prepared in the melt extruder would presumably also exhibit high impact strength at intrinsic viscosity levels exceeding 0.80 dl/g; however, as noted above, such levels were not obtained experimentally.

## CONCLUSIONS

It may be concluded that bisphenol A, neopentyl glycol, and terephthaloyl chloride copolyesters of low molecular weight (stage I) may be further melt-polymerized on a continuous basis to high molecular weight polymers by means of a vented twin-screw extruder provided that optimum extruder operating conditions are employed. The resultant polyesters are darker in color and have significantly higher melt viscosities and lower impact strengths than identical polymer compositions prepared by a room temperature interfacial technique. Under the conditions investigated, the polyesters have a maximum intrinsic viscosity of about 0.76 dl/g. The melt viscosity and impact strength property differences are attributed to the occurrence of chain branching in the copolyesters prepared at elevated temperatures by the melt extrusion process.

### Reference

1. A. Conix, *Ind. Eng. Chem.*, **51**, 147 (1959).