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M. A. McCall^a; J. R. Caldwell^a; H. G. Moore^a; H. M. Beard^a

^a Research Laboratories, Tennessee Eastman Company Division of Eastman Kodak Company, Kingsport, Tennessee

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Polymer Intermediates and Polymers Derived from 5-t-Butyl-m-Xylene

M. A. McCALL, J. R. CALDWELL, H. G. MOORE, and H. M. BEARD

Research Laboratories

Tennessee Eastman Company

Division of Eastman Kodak Company

Kingsport, Tennessee

SUMMARY

A series of condensation polymer intermediates, which included several new compositions, was prepared from 5-t-butyl-m-xylene (I) so that the effect of the bulky t-butyl group on polymer properties could be determined. Compound (I) was oxidized with nitric acid to obtain 5-t-butyl-isophthalic acid (II), which was converted successively to the diacid chloride, the diamide, the dinitrile, and finally to 5-t-butyl-m-xylene- α,α' -diamine (VI); the overall yield was 80%. The dimethyl ester of (II) was prepared and converted to 5-t-butyl-m-xylene- α,α' -diol (VIII), a new composition, in 79.5% overall yield; the diphenyl ester was also prepared. The sodium salt of (II) was catalytically reduced to obtain 5-t-butyl-1,3-cyclohexanedicarboxylic acid (IIa) in 95% yield. (IIa) was converted successively to the diacid chloride, the diamide, the dinitrile, and finally to 5-t-butyl-1,3-cyclohexanebis(methylamine) (VIa), a new composition; the overall yield was 37%. (IIa) was also converted to the dimethyl ester and finally to 5-t-butyl-1,3-cyclohexanedimethanol (VIIIa), a new composition; the overall yield was 64%. Condensation polymers were prepared from the intermediates (II), (IIa), (VI), (VIa), (VIII), and (VIIIa). These polymers had higher glass transition temperatures (T_g) than corresponding polymers containing no t-butyl groups. This general effect of the t-butyl group to increase the T_g value of the polymer was noted in all polymers prepared, regardless of whether the intermediate carrying the t-butyl group

was a diacid, a diol, or a diamine, or whether the polymer was a polyamide, a polyester, or a polyurethane.

INTRODUCTION

The overall objective of this project was to obtain more information on the effect of monomer structure upon polymer properties. More specifically, it was to learn what effect certain bulky, substituted, difunctional monomers have upon the more important properties of molding or engineering plastics, especially the effect of the *t*-butyl group upon the glass transition temperature of the polymer.

Polyamides prepared from 5-*t*-butylisophthalic acid and diamines were reported by Carlston and Lum to have greater heat resistance than polyamides of isophthalic acid itself [1, 2]. They also reported that polyamides of 5-*t*-butyl-*m*-xylene- α,α' -diamine and aliphatic dicarboxylic acids are transparent, whereas those from *m*-xylene- α,α' -diamine and aliphatic dicarboxylic acids are opaque or translucent [3]. Therefore, it was of interest to us to prepare polymer intermediates containing a *t*-butyl group and to determine the effect of this group upon the glass transition temperature of the polymers. The glass transition temperature, which we shall refer to as T_g , is the temperature at which widespread, cooperative motion of chain segments occurs. Thus, polymers prepared from monomers containing bulky groups might be expected to require more thermal energy to bring about chain movement than less bulky polymers. Polymers with high T_g values have higher heat distortion temperatures and therefore higher use temperatures and wider application as engineering plastics than similar polymers having lower T_g values.

On the basis of these goals and as part of a continuing search for new, cheap polymer-building units, a series of condensation polymer intermediates and their precursors were synthesized from 5-*t*-butyl-*m*-xylene. The synthetic work deals first with the preparation of aromatic derivatives and then with the preparation of corresponding alicyclic derivatives. These aromatic and alicyclic compounds were obtained from the common starting material, 5-*t*-butyl-*m*-xylene. Polyamides, polyesters, and polyurethanes were prepared from these intermediates. The T_g values of these polymers were obtained and compared with T_g values of polymers containing no *t*-butyl group.

EXPERIMENTAL

Preparation of Polymer Intermediates

5-t-Butylisophthalic Acid (II). 5-t-Butyl-m-xylene (**I**, 200.0 g, 1.23 moles) obtained from Sinclair Petrochemicals, Inc., was oxidized with 30% HNO_3 at 160-180°C in a stainless-steel rocking autoclave. The autoclave was charged with 692.0 g of 70% nitric acid and 924.0 g of distilled water. The calculated nitric acid concentration was approximately 30%. This aqueous nitric acid was placed in a 1-gal autoclave and heated to 150-160°C. The heat was cut off and the 5-t-butyl-m-xylene was slowly pumped into the autoclave containing the hot nitric acid at such a rate as to maintain a temperature of 150-160°C. When the addition of 5-t-butyl-m-xylene was complete, the temperature of the autoclave was raised to 180°C and maintained for 2.5 hr. The reaction mixture was then cooled to room temperature. The solid product was isolated by filtration, washed with water several times, and then dried in a vacuum oven at 100°C at 0.1 mm. The amount of crude product from several runs ranged from 160.0 to 205.0 g. The crude product was heated to reflux in 300 ml of acetone, and the mixture was then cooled to 25°C. The product was collected on a filter and then dried in a vacuum oven at 110°C. The yields of purified diacid ranged from 134.0 to 190.0 g (60-72%), mp 341°C (reported [4] 343°C (sealed tube), and [5] 337-340°C). A total of 24 lb of 5-t-butyl-m-xylene were oxidized by this procedure. Neut Equiv: Calculated for $\text{C}_{12}\text{H}_{14}\text{O}_4$: 111. Found: 110-113.

An air oxidation procedure was also developed to give this diacid in 70% conversion and yields as high as 90%, but it was not used to prepare any of the 5-t-butylisophthalic acid used in this project.

5-t-Butylisophthaloyl Chloride (III). 5-t-Butylisophthalic acid (**II**, 308.0 g, 1.38 moles) and 300 ml of dry dioxane were placed in a 2-liter three-necked flask equipped with a sweep stirrer, thermometer, dropping funnel, and condenser. To this stirred slurry, 328.4 g (2.76 moles) of thionyl chloride was added. The mixture was then refluxed for 11.5 hr. A slight flow of dry nitrogen was maintained over the reaction mixture to aid in the removal of by-product HCl . The reaction mixture was then cooled, and the excess thionyl chloride, along with approximately 100 ml of dioxane, was removed at approximately 80°C under reduced pressure. The crude product, 5-t-butylisophthaloyl chloride, was used without purification for preparation of amide (**IV**). However, one batch was

distilled; bp 107°C at 0.4 mm. The distillate crystallized on cooling; mp 43°C. The NMR spectrum was consistent with the structure of (III).

Anal: Calculated for $C_{12}H_{12}Cl_2O_2$: C, 55.61; H, 4.68; Cl, 27.36.

Found: C, 55.53; H, 4.60; Cl, 27.45.

5-t-Butylisophthalamide (IV). Ammonium hydroxide (1226 ml 28% NH_3) was placed in a 2-liter flask equipped with a sweep stirrer, thermometer, and condenser. The ammonium hydroxide was then cooled to 10°C and 5-t-butylisophthaloyl chloride (III, 356 g, 1.38 moles) was added dropwise over 5 hr, keeping the reaction temperature below 15°C. The reaction mixture was then stirred for an additional hour while the mixture was allowed to warm to room temperature. The mixture was filtered and the residue was washed twice with ice water, then dried at 100°C in a vacuum oven. The yield was 293 g (96.4%); mp 248-253°C. The infrared spectrum was consistent with the structure of (IV).

5-t-Butylisophthalonitrile (V). 5-t-Butylisophthalamide (IV, 293.0 g, 1.33 moles) was mixed with 708 g (50% excess) of thionyl chloride in 550 ml of dioxane and heated to reflux for approximately 12 hr in a three-necked flask equipped with a sweep stirrer, thermometer, and condenser. The reaction mixture was allowed to stand overnight and then was poured into ice and water. The solid was collected on a filter, washed with ice water, then dried in an air oven at 80°C. The yield was 226 g (92.4%); mp 135-138°C. The infrared spectrum was consistent with the structure of (V). Anal: Calculated for $C_{12}H_{12}N_2$: N, 15.21. Found: N, 15.42.

5-t-Butyl-m-xylene- α,α' -diamine (VI). 5-t-Butylisophthalonitrile (V, 226 g, 1.22 moles) was mixed with 800 ml of benzene, and the solution was then treated with Darco activated carbon and filtered. The filtrate was placed in a stainless-steel autoclave, and 27.0 g of hydrogenation catalyst (G-67RS; zirconium-promoted catalyst on kieselguhr; Girdler Catalyst Dept., Louisville, Ky.) and 415.8 g of NH_3 were added. This mixture was then hydrogenated at 2500 psi for 5 hr at 130°C. The catalyst was removed by filtration, and the benzene was then removed by distillation under reduced pressure. The product was then distilled; bp 105-106°C (0.1 mm); n_D^{20} 1.5417. The yield was 210.7 g (90%). The infrared spectrum was consistent with the structure of (VI) [6]. Neut Equiv: Calculated: 96.2. Found: 101.7.

Dimethyl 5-t-Butylisophthalate (VII). 5-t-Butylisophthalic acid (II,

222.1 g, 1.0 mole) was dissolved in 800 ml of dry methanol, and the solution was heated for 4 hr in a stainless-steel autoclave at 200°C. The mixture was then cooled to 10°C and filtered. The solid product obtained was washed with cold methanol and then dried in a vacuum oven at 60°C. The yield was 171.5 g (90%); mp 93.5°C. More of this ester (55.4 g) was obtained by concentrating the filtrate. The first-crop product was recrystallized from 400 ml of methanol; mp 96-97°C. Sapon Equiv: Calculated for $C_{14}H_{18}O_4$: 125.2. Found: 125.4.

5-*t*-Butyl-*m*-xylene- α,α' -diol (VIII). Dimethyl 5-*t*-butylisophthalate (VII, 113.5 g, 0.455 mole) and 350 ml of methanol were placed in a stainless-steel autoclave to which 200 g of copper chromite hydrogenolysis catalyst was added. The autoclave was pressured with hydrogen to 5000 psi at 125°C and maintained at this temperature and pressure for approximately 12 hr. The contents of the autoclave were heated to reflux and filtered to remove the catalyst. The catalyst was washed with hot methanol, and the methanol extract was combined with the first filtrate, which contained the major portion of hydrogenolysis product. The methanol was then removed and the product was distilled; bp 140-145°C at 0.6 mm; mp 101-104°C. The yield was 70.2 g (79.5%). The infrared and NMR spectra were consistent with the structure of (VIII). Anal: Calculated for $C_{12}H_{18}O_2$: C, 74.17; H, 9.36. Found: C, 73.79; H, 9.29.

Diphenyl 5-*t*-Butylisophthalate (IX). 5-*t*-Butylisophthalic acid (II, 111.1 g, 0.5 mole) was dissolved in 150 ml of dry dioxane. Then 236 g of thionyl chloride was added dropwise to the solution, and the mixture was refluxed for 4 hr. The excess thionyl chloride was then removed under reduced pressure. The residue (236 g) was treated with a solution of 188.2 g of phenol in 75 ml of dry benzene. This mixture was heated at 110°C for 4 hr. A slight flow of dry nitrogen was maintained over the solution. The remaining HCl, excess phenol, and dioxane were removed under reduced pressure. The residue was recrystallized by dissolving it in ethylene chloride and then adding isopropanol until a precipitate formed. The yield was 150 g (80%); mp 135-137°C. Sapon Equiv: Calculated for $C_{24}H_{22}O_4$: 187.2. Found: 184.7.

5-*t*-Butyl-1,3-cyclohexanedicarboxylic Acid (IIa). 5-*t*-Butylisophthalic acid (II, 125 g, 0.56 mole) was converted into the sodium salt by treatment with a solution of 46.2 g (1.12 moles, 97.4%) of sodium hydroxide in 600 ml of distilled water. The pH of the solution was adjusted to 7.0 after the

acid had completely dissolved. This aqueous solution was placed in a stainless-steel autoclave with 42.3 g of aqueous Raney nickel, then pressurized with 4000 psi of hydrogen at 250°C. These conditions were maintained for 5 hr. The temperature was then raised to 275°C, and the pressure was increased to 4500 psi. These conditions were maintained for 6 hr or until hydrogen ceased to be absorbed. The reaction mixture was cooled and then filtered to remove the catalyst. The filtrate was poured into a mixture of 500 ml of water and 250 ml of 37% hydrochloric acid with vigorous stirring. The product was collected, washed with water, and stirred again in a mixture of 500 ml of water and 250 ml of concentrated hydrochloric acid. The product was collected by filtration, washed freely with water, and then dried at 110°C in a vacuum oven (1.0 mm). The yield was 118 g (87.5%). The aromaticity, as measured by ultraviolet absorption, was 0.143%. The melting point varied with different preparations (208-227°C). This variation was considered due to the presence of varying amounts of conformational isomers.

5-t-Butyl-1,3-Cyclohexanedicarbonyl Chloride (IIIa). 5-t-Butyl-1,3-cyclohexanedicarboxylic acid (IIa, 50.0 g, 0.22 mole) and 100 ml of dioxane were placed in a 500-ml three-necked flask equipped with a dropping funnel, magnetic stirrer, thermometer, and condenser. To this reaction mixture 104.2 g of thionyl chloride was added dropwise. The mixture was then refluxed for 11.5 hr. The excess thionyl chloride plus 50 ml of dioxane were removed by distillation under vacuum. The amber-colored residue was 5-t-butyl-1,3-cyclohexanedicarbonyl chloride dissolved in approximately 50 ml of dioxane. The diacid chloride could be isolated by removing all the solvent; however, isolation was found to be unnecessary, since this solution of diacid chloride could be used in the synthesis of amide (IVa) without further purification.

5-t-Butyl-1,3-Cyclohexanedicarboxamide (IVa). The dioxane solution containing approximately 58 g of 5-t-butyl-1,3-cyclohexanedicarbonyl chloride (IIIa) was added slowly to 200 ml of NH₄OH (28%) contained in a 1-liter three-necked flask, equipped with a sweep stirrer, thermometer, and condenser. The temperature was maintained at or slightly below 15°C during this addition. The mixture was stirred for 1 hr after the addition was complete. The solid product was filtered, washed with ice water, and then slurried in ice water and refiltered. The white product was dried in an air oven at 80°C. The yield of product was 34.7 g (70%); mp 232-237°C. The infrared spectrum was consistent with the structure of (IVa).

5-*t*-Butyl-1,3-Cyclohexanedicarbonitrile (Va). 5-*t*-Butyl-1,3-cyclohexanedicarboxamide (IVa, 29.0 g, 0.128 mole) and 100 ml of dioxane were placed in a 1-liter flask equipped with a magnetic stirrer, thermometer, and condenser. To this stirred mixture 68 g of thionyl chloride was added. The mixture was then refluxed for 5.5 hr. The diamide dissolved after heating for 30 min, giving a dark-brown solution. The reaction mixture was allowed to stand overnight and was then poured into ice water. The precipitate which formed was isolated by filtration and washed with ice water. The product was recrystallized from methanol and then dried in a vacuum oven at 75°C. The yield was 21.3 g (87.5%); mp 93-97°C. The infrared spectrum was consistent with the structure of (Va).

5-*t*-Butyl-1,3-Cyclohexanebis(methylamine) (VIa). 5-*t*-Butyl-1,3-cyclohexanedicarbonitrile (Va, 112 g, 0.58 mole) and 400 ml of benzene were placed in a stainless-steel autoclave with 13.5 g of a reduction catalyst. G-67RS and Raney nickel were used successfully. Approximately 200 g of NH₃ was used with either catalyst for this reduction. With G-67RS catalyst, a temperature of 145-150°C and a hydrogen pressure of 2500 psi were used. With Raney nickel, the reduction temperature was 125-135°C. The product and solvent were removed from the catalyst by filtration, and the solvent was then removed by vacuum stripping. The product was then distilled; bp 90-92°C (0.1 mm); n_D^{20} 1.4912. The yield was 72.7 g (63.3%). Neut Equiv: Calculated for C₁₂H₂₆N₂: 99.2. Found: 99.4.

Dimethyl 5-*t*-Butyl-1,3-Cyclohexanedicarboxylate (VIIa). 5-*t*-Butyl-1,3-cyclohexanedicarboxylic acid (IIa, 117 g, 0.513 mole) and 417 ml (10.3 moles) of methanol were placed in a stainless-steel autoclave and heated for 4 hr at 200°C. The reaction mixture was then distilled. The fraction boiling at 114°C (0.6 mm) was collected; 94.0 g (71.5%). The NMR and infrared spectra were consistent with the structure of (VIIa). Gas chromatographic analysis indicated that this product was composed of two isomeric materials in a ratio of approximately 15 to 85.

Attempts were made to obtain this dimethyl ester directly by reducing dimethyl 5-*t*-butylisophthalate catalytically with hydrogen in the presence of ruthenium-on-carbon catalyst. Absorption of hydrogen was slow and reduction was incomplete, even at temperatures as high as 180°C and at hydrogen pressures as high as 2000-3000 psi. When ruthenium-on-alumina was used, with small amounts of water added to activate this catalyst, the product was a 50/50 mixture of reduced free acid and reduced methyl ester.

5-t-Butyl-1,3-Cyclohexanedimethanol (VIIIa). Dimethyl 5-t-butyl-1,3-cyclohexanedicarboxylate (VIIa, 93.3 g, 0.36 mole) was mixed with 225 ml of methanol and 11.0 g of copper chromite hydrogenolysis catalyst in a stainless-steel autoclave. The mixture was heated to 250°C under hydrogen at 5000 psi for 3.5 hr. The catalyst was then removed by filtration and the product was distilled; 64.0 g (90% yield); bp 133-135°C at 0.5 mm. The distillate crystallized on cooling. Anal: Calculated for C₁₂H₂₄O₂: C, 72.23; H, 12.12. Found: C, 72.31; H, 12.16.

Preparation of Polymers Containing a t-Butyl Group

Polyamides from (II). Polyamides from 5-t-butylisophthalic acid (II) were prepared by heating equimolar quantities of (II) and the diamine in m-cresol under nitrogen at 200-280°C for 3 hr, and then finishing under vacuum.

From 1,6-hexanediamine: $\{\eta\}$ 0.60; T_g by DTA 163°C; sp (softening point) 225°C; mp 238-250°C.

From m-xylene- α,α' -diamine: $\{\eta\}$ 0.31; T_g by DTA 192°C; sp 250°C; mp 259-264°C.

From p-xylene- α,α' -diamine: $\{\eta\}$ 0.35; T_g by DTA 204°C; sp 265°C; mp 274-292°C.

From 1,4-cyclohexanebis(methylamine): $\{\eta\}$ 0.38; T_g by DTA 236°C; sp 300°C; mp 306-316°C.

Polyamides from (VI). Several attempts were made to prepare a polyamide from terephthalic acid and 5-t-butyl-m-xylene- α,α' -diamine (VI); however, all attempts to prepare a satisfactory polymer failed. The polymers were extremely high-melting; the products obtained did not melt below 320°C.

The polyamide from isophthalic acid and (VI) was prepared by heating equimolar amounts of the two reactants at 200-285°C for 2.5 hr and then finishing under vacuum; $\{\eta\}$ 0.79; T_g by DSC 188°C; sp 250°C; mp 264-281°C.

The polyamide from adipic acid and (VI) was prepared by first making the salt (5.0 g) and then heating this salt in 5 ml of m-cresol under nitrogen from 200 to 280°C for 7 hr. Vacuum was applied at about 280°C; $\{\eta\}$ 0.64; T_g by DTA 109°C; sp 170°C; mp 179-193°C.

Polyamides from (IX). Polyamides from diphenyl 5-t-butylisophthalate (IX) were prepared by heating equimolar quantities of (IX) and the diamine under nitrogen at 200-260°C for 4 hr and then finishing under vacuum.

From 3,4-dimethyl-1,6-hexanediamine: $\{\eta\}$ 0.83; T_g by DTA 173°C; sp 255°C; mp 264-273°C.

From 2,5-dimethyl-1,6-hexanediamine: $\{\eta\}$ 1.14; T_g by DTA 149°C; sp 215°C; mp 259-283°C.

From 1,3-cyclohexanebis(methylamine): $\{\eta\}$ 0.84; T_g by DTA 200°C; sp 260°C; mp 286-300°C.

Polyamides from (VIa). The polyamide from isophthalic acid and 5-*t*-butyl-1,3-cyclohexanebis(methylamine) (VIa) was prepared by a solid-phase method, but a polymer having a higher inherent viscosity was obtained from the diphenyl ester. The polymer was molded at 660°F; it had a heat distortion temperature of 220-224°C and a notched Izod impact value of 0.4 ft-lb/in.

This polymer was also prepared by heating a mixture of 19.8 g (0.1 mole) of (VIa) with 31.8 g (0.1 mole) of diphenyl isophthalate progressively from 200 to 290°C while slowly removing the by-product phenol. After about 30 min at 290°C, the mixture was placed under vacuum for about 40 min at 290°C to complete the reaction. The polyamide obtained was pale yellow; $\{\eta\}$ 1.4; T_g by DSC 209°C.

Polyurethane from (VIII). A polyurethane was prepared from 5-*t*-butyl-*m*-xylene- α,α' -diol (VIII) by a procedure similar to that described by Lyman [7]. A solution of (VIII) (9.71 g, 0.05 mole) in 50 ml of dimethyl sulfoxide was added dropwise with stirring to a suspension of 4,4'-methylene-*p*-phenylene diisocyanate (12.5 g, 0.05 mole) in about 50 ml of dimethyl sulfoxide, maintaining a temperature of 100-105°C. The addition required approximately 20 min, during which time the reaction mixture became homogeneous. Stirring and heating were continued for approximately 2 hr. The reaction mixture was allowed to cool to 25°C and was then added dropwise to 1 liter of distilled water with vigorous stirring. The polymer precipitated as a finely divided powder. It was dried at 120°C (0.1 mm) for 4 hr; $\{\eta\}$ 0.25; T_g by DTA 114°C; mp above 157°C.

Polyesters from (VIIIa). A polyester from 5-*t*-butyl-1,3-cyclohexane-dimethanol (VIIIa) and diphenyl terephthalate was obtained by heating 10.0 g of (VIIIa) with 15.9 g of diphenyl terephthalate at 200°C, slowly increasing the temperature to 240°C; $\{\eta\}$ 0.51; T_g by DSC 118°C; sp 180°C; mp 188-197°C.

An attempt to prepare the polyester from 5-*t*-butyl-*m*-xylene- α,α' -diol (VIII) and diphenyl terephthalate gave only a product having a low melt viscosity.

Table 1. Effect of the t-Butyl Group on the T_g of Condensation Polymers

Polyamide from:	$\{\eta\}$	$T_g, ^\circ\text{C}$	$\Delta T_g, ^\circ\text{C}$
1,6-Hexanediamine + 5-t-butylisophthalic acid (II)	0.60	163c	
Isophthalic acids ^a	0.75f	130	33
m-Xylene- α,α' -diamine + (II)	0.31	192c	
Isophthalic acids ^a	1.22	172d	20
1,4-Cyclohexanebis(methylamine) + (II)	0.38	236c	
Isophthalic acid	1.45	208d	28
3,4-Dimethyl-1,6-hexanediamine + diphenyl 5-t-butylisophthalate (IX)	0.83	173c	
Diphenyl isophthalate	1.75	125d	48
Isophthalic acid + 5-t-butyl-m-xylene- α,α' -diamine (VI)	0.79	188d	
m-Xylene- α,α' -diamine	1.22	172d	16
Adipic acid + (VI)	0.64	109c	
m-Xylene- α,α' -diamine ^b	—	73	36

Isophthalic acid + 5- <i>t</i> -butyl-1,3-cyclohexanebis(methyl- amine) (VIa) ^e	0.95	209d	
1,3-Cyclohexanebis(methylamine)	0.86	180d	29
<u>Polyurethane from:</u>			
4,4'-Methylenedi- <i>p</i> -phenylene diisocyanate + 5- <i>t</i> -butyl- <i>m</i> -xylene- α,α' -diol	0.25	114c	
<i>m</i> -Xylene- α,α' -diol	0.20	106d	8
<u>Polyester from:</u>			
Diphenyl terephthalate + 5- <i>t</i> -butyl-1,3-cyclohexane- dimethanol (VIIIa)	0.51	118d	
1,3-Cyclohexanedimethanol	0.47	75d	43

a Ref. [8].

b Ref. [9].

c By DTA.

d By DSC.

e Diphenyl ester used.

f η_{sp}/C for 0.5% solution in 90:10 phenol-ethanol at 25°C.

Preparation of Polymers Containing No *t*-Butyl Group

Polymers were prepared from isophthalic acid, diphenyl isophthalate, *m*-xylene- α,α' -diamine, 1,3-cyclohexanebis(methylamine), *m*-xylene- α,α' -diol, and 1,3-cyclohexanedimethanol by conventional methods for comparison with the polymers containing the *t*-butyl group. The comparison of T_g values is shown in Table 1. Where noted, the comparative reference data were taken from the literature [8, 9].

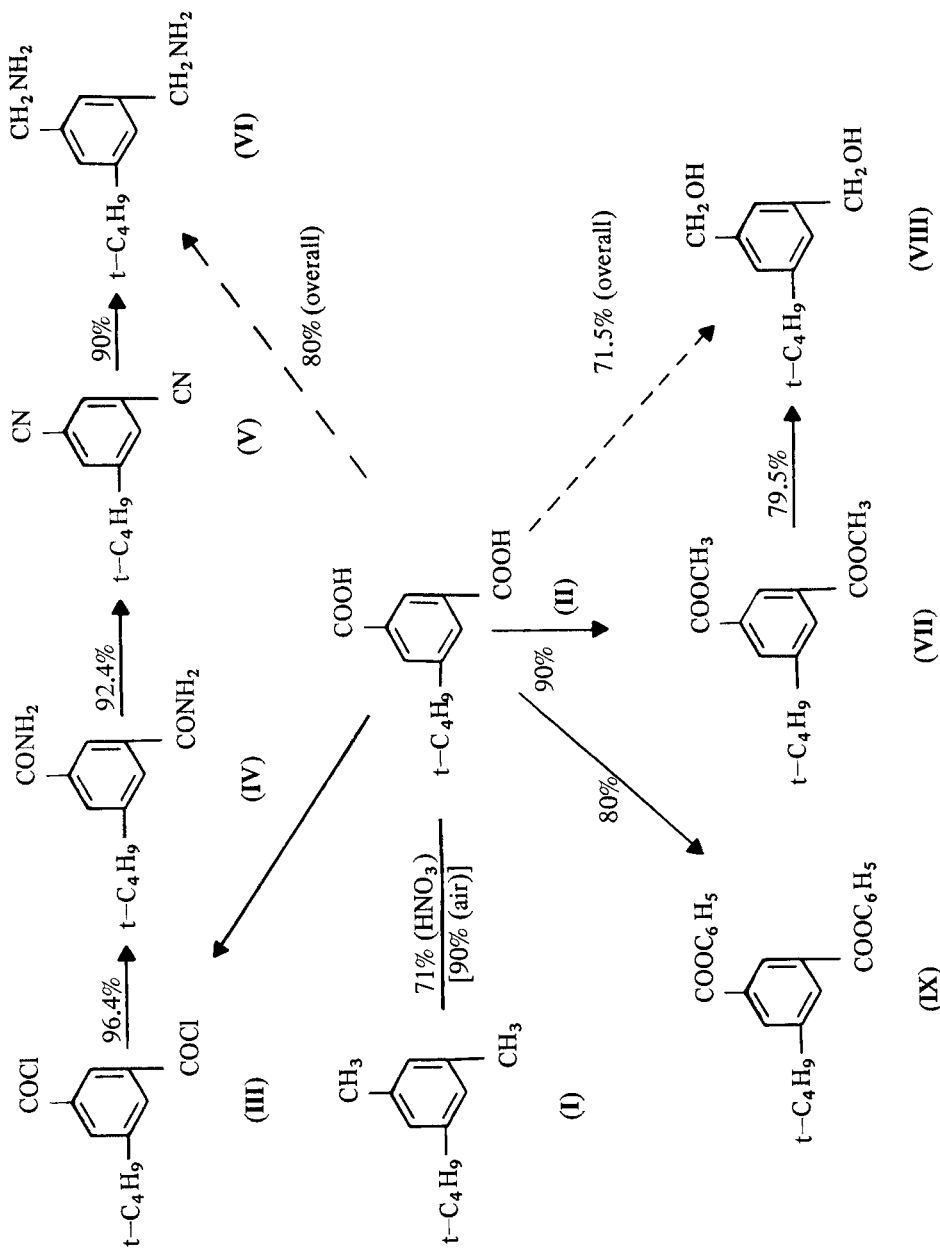
Physical Testing of Polymers

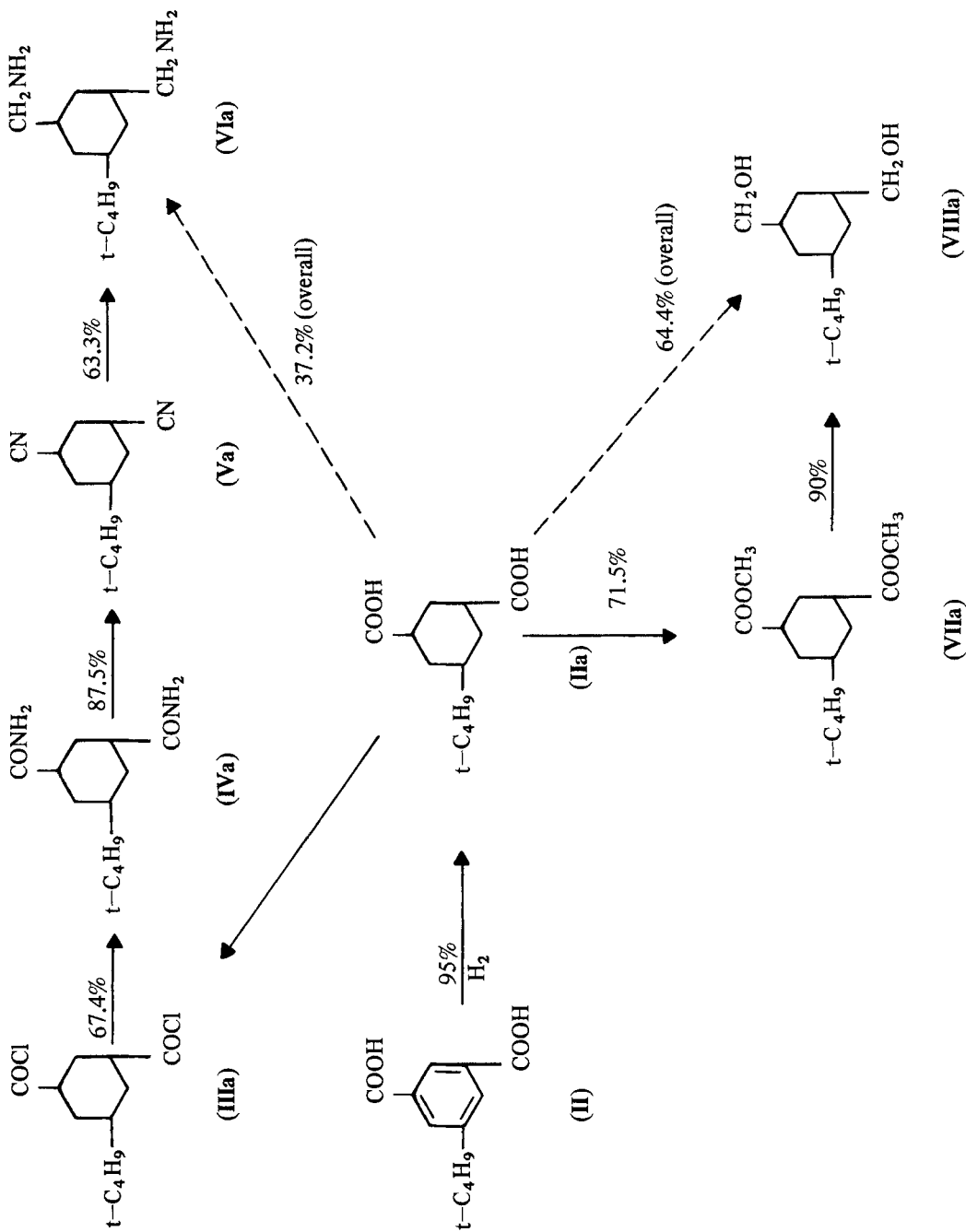
Inherent viscosities were determined using a 60/40 phenol/tetrachloroethane mixture as solvent and a polymer concentration of approximately 0.23 g/100 ml. Softening and melting points were determined by using capillary tubes that were sealed under nitrogen and heated on the hot stage of a microscope. The point at which the corners of the particles began to round off was noted as the softening point (sp) and the temperature at which the polymer began to flow was noted as the melting point (mp). Glass transition temperatures (T_g) were determined either by differential thermal analysis (DTA) or by differential scanning calorimetry (DSC). Within experimental error, the values obtained by the two methods were the same.

DISCUSSION AND CONCLUSIONS

The first step in the synthesis sequence was the oxidation of 5-*t*-butyl-*m*-xylene to 5-*t*-butylisophthalic acid (II). (II) was converted to the diacid chloride (III), diamine (IV), dinitrile (V), and then to the diamine (VI) in an 80% overall yield. Dimethyl 5-*t*-butylisophthalate (VII) was obtained in about 90% yield, and 5-*t*-butyl-*m*-xylene- α,α' -diol (VIII) was obtained from dimethyl ester (VII) in 79.5% yield. The diphenyl ester (IX) of (II) was obtained in 80% yield. (See diagram on following page.)

The first step in the synthesis of the corresponding alicyclic compounds was the reduction of 5-*t*-butylisophthalic acid (II) to 5-*t*-butyl-1,3-cyclohexanedicarboxylic acid (IIa). This reduction was carried out on an aqueous solution of disodium 5-*t*-butylisophthalate with Raney nickel catalyst. The yields were as high as 95%. An alternative reduction scheme starting with dimethyl 5-*t*-butylisophthalate with ruthenium-on-alumina catalyst was not satisfactory. With this catalyst, the ring was not reduced completely unless a small amount of water was present to activate the catalyst.





With water present, however, part of the ester groups were hydrolyzed, and therefore reesterification was necessary to convert the reduced, partially hydrolyzed product back to the dimethyl ester (VIIa). This reduced diacid, 5-*t*-butyl-1,3-cyclohexanedicarboxylic acid (IIa), was converted to the diacid chloride (IIIa), diamide (IVa), dinitrile (Va), and then to the diamine (VIa) in 37% overall yield.

The yields from these preparations were generally good. The yields of products in the aromatic series were slightly better than those of the corresponding products in the alicyclic series. The reason may be the lower solubility of the aromatic derivatives in the usual recrystallization solvents, thus reducing their loss in purification. Also, on reduction of the benzene ring, the possibilities for conformational isomers were introduced. None of these isomers was isolated; however, products in the alicyclic series had wider melting point and boiling point ranges, even though physical and chemical analyses indicated pure compositions. (See diagram on preceding page.)

All the polymer intermediates from 5-*t*-butyl-*m*-xylene were unusual in that the polymers produced from them had T_g values 8-48°C higher than those of corresponding polymers made from intermediates containing no *t*-butyl group (Table 1). The ΔT_g of 8 is probably a very conservative or minimum value because this difference was obtained from a comparison of polyurethanes which had unusually low inherent viscosities. Unlike all the other polymers, which had viscosities $\{\eta\}$ of at least 0.3 or above, these polyurethanes had $\{\eta\}$ values of only 0.20 and 0.25, which we consider borderline for fiber- and film-forming polymers. Probably the difference in T_g for these polymers would have been greater if the polymers had been of higher viscosity. These polyurethanes were prepared in dimethyl sulfoxide by a procedure described in the literature [7]. A high T_g is important in an engineering plastic, since polymers having high T_g values also have high heat distortion temperatures. The general effect of the *t*-butyl group is to increase the T_g value of the polymer, regardless of whether the intermediate carrying the *t*-butyl group is a diacid, a diol, or a diamine or whether the polymer is a polyester, a polyamide, or a polyurethane.

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