

Polymerization of Dialdehydes by Metal Alkyls

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INTRODUCTION

Mitin et al.¹ have recently described the polymerization of dialdehydes to polyesters by means of the Tischenko reaction with aluminum ethoxide as catalyst. They polymerized terephthalaldehyde, isophthalaldehyde, 2,5-dimethylterephthalaldehyde, and diphenyl-4,4'-dicarboxaldehyde. Saponification of the terephthalaldehyde polymer gave *p*-hydroxymethylbenzoic acid and terephthalic acid, but no further attempt to elucidate the structure of the polymer was made.

In a similar study, we have polymerized terephthalaldehyde and diphenyl-4,4'-dicarboxaldehyde with metal alkyls to obtain polymers apparently similar to those of the Russian workers.

RESULTS AND DISCUSSION

Terephthalaldehyde is readily available and easily purified; hence most of the work described was carried out with this intermediate.

Polymerization and Properties

Properties

Polymerization was effected by adding the metal alkyls to a suspension of terephthalaldehyde in a dry cycloalkane at 60–80°C. The polymer obtained, after purification, was almost colorless, had a polymer melt temperature² of ~140°C. (lit.,¹ 120°C.), and was soluble in hydrogen-bonding solvents such as trifluoroacetic acid and chloroform but insoluble in tetrahydrofuran, dimethylformamide, and acetone. Polymer inherent viscosities were in the range 0.2–0.4, measured in tetrachloroethane–phenol. Clear flexible films could be pressed at 140°C. from polymer of inherent viscosity higher than 0.35.

Diphenyl-4,4'-dicarboxaldehyde likewise yielded a polymer when treated with metal alkyls at 80°C. in dry decahydronaphthalene. The polymer was light yellow, had a melt temperature of 210°C. (lit.,¹ 250°C.), and was soluble in tetrachloroethane.

Two attempts to polymerize 4,6-dimethylisophthalaldehyde were not successful, perhaps because of steric hindrance; the dialdehyde was recovered almost quantitatively.

Catalysts

Catalysts (and yields of polymer) for the polymerization of terephthalaldehyde were triethylaluminum (>90%), triisobutylaluminum (>90%), triisopropylaluminum (>60%), diethylaluminum bromide (>60%), trimethylaluminum sesquibromide (>30%), and diethylzinc (>80%).

Highest inherent viscosity (0.3–0.4) was obtained in the presence of triethylaluminum or diethylaluminum bromide.

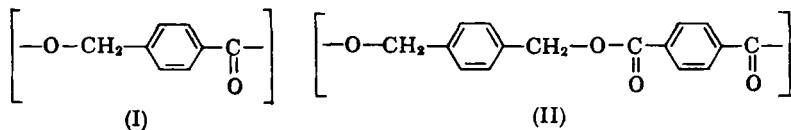
No polymerization occurred with ethylaluminum dichloride, tributylboron and potassium, and lithium *tert*-butoxides. Attempts to polymerize terephthalaldehyde to a polymer with aqueous base (Cannizzaro reaction) or aluminum isopropoxide under anhydrous conditions (Tischenko reaction) were likewise unsuccessful. Mitin et al.¹ also noted that aluminum isopropoxide is a noncatalyst for the polymerization, which is surprising since both triisopropylaluminum and aluminum ethoxide are effective catalysts.

Reaction Conditions

Trimethylaluminum as catalyst in cycloalkanes as reaction media gave the highest yields (>90%) of polymer at about 80°C.; at 0–20°C. the yield was ~15% and at 130°C. was ~20%. High yields of polymer were also obtained with *o*-dichlorobenzene as the solvent, but the polymers obtained had lower inherent viscosities (~0.2). Use of tetrahydrofuran as a reaction medium resulted in inhibition of polymerization. Bulk polymerization systems gave erratic results because of the exothermic nature of the polymerization.

Structure

From the hydrolysis results of the Russian workers and from interpretation of the infrared spectra, the polymer from terephthalaldehyde appeared to be a polyester. The product could be (a) poly(*p*-methylenbenzoate), structure (I), resulting from intramolecular disproportionation, (b) poly(*p*-xylyleneterephthalate), structure (II), from intermolecular disproportionation, (c) a random copolymer of structures (I) and (II), (d) a polymer mixture of (I) and (II), (e) a block copolymer of (I) and (II). These structures are given below:



X-Ray Diffraction Patterns

The freshly prepared and precipitated polyester from terephthalaldehyde was amorphous, as deduced from the x-ray diffraction pattern (Fig. 1). Concentrated solutions of the polyester in chloroform (20% solids) were

stable for several days at room temperature, but the polymer subsequently precipitated and then could no longer be redissolved in chloroform. This polymer was crystalline and its x-ray diffraction pattern (Fig. 2) showed crystallinity of intermediate amount and perfection.

The x-ray diffraction pattern of the terephthalaldehyde polymer was compared with those of compound (I), compound (II), and mixtures of (I) and (II) ranging in composition from 90% (I) to 90% (II). None of these polymers or mixtures of polymers were identical with the polyester from terephthalaldehyde in diffraction pattern spacings, although that of poly(*p*-methylenbenzoate) was similar in general appearance.

Infrared Absorption Spectra

Compounds (I) and (II) and the terephthalaldehyde polymers have similar infrared absorbance spectra except in the 13–15 μ region. The first shows selective absorbance maxima at 13.25 μ and 14.25 μ , and the second

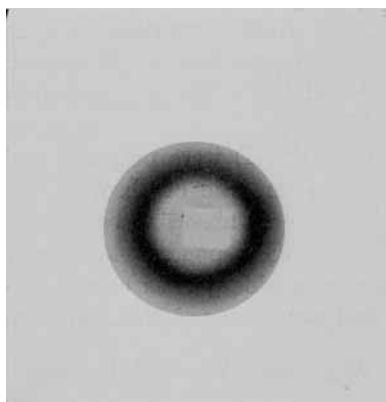


Fig. 1. X-ray diffraction pattern of freshly prepared and precipitated polyester from terephthalaldehyde.

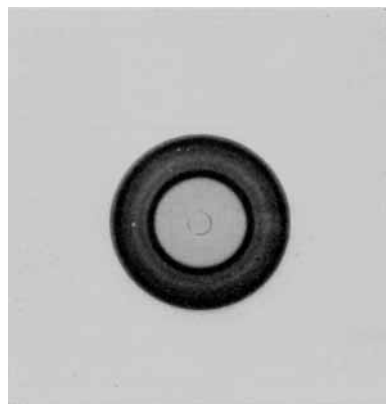


Fig. 2. X-ray diffraction pattern of polyester of Figure 1, which is separated from its solution in chloroform.

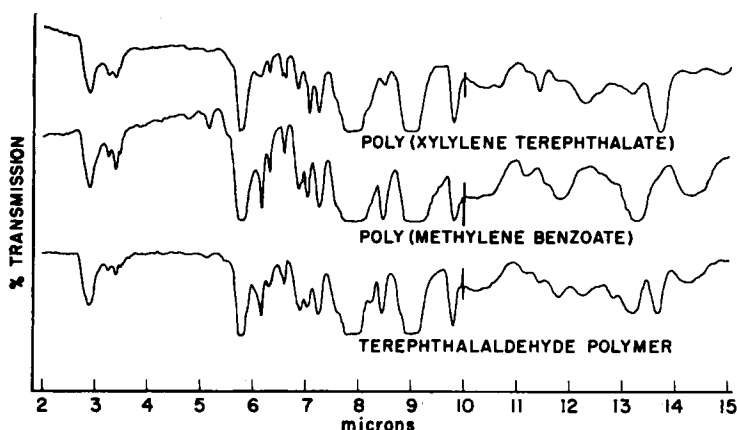


Fig. 3. Infrared absorption spectra of compounds (I), (II), and terephthalaldehyde polymer.

at $13.75\ \mu$. The polyester from terephthalaldehyde has absorbances at $13.25\ \mu$, $13.75\ \mu$, and $14.25\ \mu$, and thus would appear to have absorbances due to units of both (I) and (II). The infrared absorption spectra are reproduced in Figure 3.

Known mixture of (I) and (II) were prepared and a calibration graph of the weight ratio versus the ratio of absorbances ($14.25/13.75\ \mu$) was constructed. The ratio of these absorbances in the polyester from terephthalaldehyde was found to correspond to 45–55% of (I), indicating that the polyester from terephthalaldehyde is composed of equal amounts of *p*-methylenebenzoate and *p*-xylyleneterephthalate units.

Differential Thermal Analyses

Compounds (I) and (II), various mixtures of (I) and (II) ranging in composition from 20/80 to 85/15, and the polyester from terephthalal-

TABLE I
Differential Thermal Analysis Endotherms versus Polyester Composition

Polymer composition	Endotherms, °C. (maxima)
(I) ^a	250
85% (I)	245
70% (I)	245
50% (I)	240
40% (I)	240, 253
20% (I)	233, 250
(II)	240, 255
Polyester from terephthalaldehyde	158 ^b

^a This polymer exhibits an exotherm at 155°C . At this temperature, x-ray examination showed a change from one crystalline form to another.

^b No higher endotherm occurred.

dehyde were subjected to differential thermal analysis. The results are listed in Table I.

The above results show that (a) the terephthalaldehyde polymer is not a polymer mixture of (I) and (II) because in this case the differential thermal analysis endotherm would be higher and (b) the terephthalaldehyde polymer is not a block copolymer, i.e., it does not contain long units of structures (I) or (II), because in this case endotherms corresponding to each block of (I) or (II) would be observed and these occur at $\sim 200^{\circ}\text{C}$.

SUMMARY AND CONCLUSIONS

From the infrared data the polymer from terephthalaldehyde appears to be composed of equal amounts of *p*-methylenebenzoate and *p*-xylyleneterephthalate units. Comparative examination of x-ray diffraction patterns and differential thermal analyses exclude the possibility that the polymer is a block copolymer or a mixture of polymers. The polymer is, then, probably a crystallizable 50:50 random copolymer.

EXPERIMENTAL

Polymer melt temperature and inherent viscosities were obtained by standard methods of polymer characterization, recommended by Beaman and Cramer.² Inherent viscosities were measured at 0.5% concentration in tetrachloroethane/phenol (40/60 by weight) at 30°C .

Triisopropylaluminum

This was prepared by Dr. R. F. Tietz of this laboratory (b. p. $42\text{--}45^{\circ}\text{C}$. at 3 mm. Hg) devoid of the tri-*n*-propyl isomer, according to the procedures of Pitzer and Gutowsky³ and of Zakharkin and Okhlobystin.⁴

Poly(*p*-methylenebenzoate)

p-Hydroxymethylbenzoic acid (m.p. $178\text{--}180^{\circ}\text{C}$.) was polymerized without catalyst by heating under nitrogen at 197°C . for 4 hr. followed by further heating at 255°C . for 1.5 hr. and 255°C . at 0.1 mm. Hg for 66 hr. The polymer so obtained was a light-yellow glass which softened at and resolidified at $\sim 140^{\circ}\text{C}$. and then melted at $\sim 240^{\circ}\text{C}$. The inherent viscosity was 0.38.

Poly(*p*-xylyleneterephthalate)

This polymer was prepared by adding a solution of terephthaloyl chloride (10.15 g., 0.05 mole) in 100 ml. of dry chlorobenzene to a refluxing solution of *p*-bis(hydroxymethyl)benzene (6.91 g., 0.05 mole) in 100 ml. of dry chlorobenzene. Dry nitrogen was bled through the solution and refluxing was continued for 25 hr. The solution was cooled and added to 500 ml. of hexane, and the precipitated polymer was filtered and dried at

80°C. *in vacuo*. The polymer so obtained was a white powder melting at ~240°C. The inherent viscosity was 0.15.

Mixtures of Poly(*p*-methylenbenzoate) and Poly(*p*-xylyleneterephthalate)

Mixtures of these polymers were prepared by dissolving both polymers together in the desired ratio in hot *o*-dichlorobenzene to give a 3% solution. The solution was stirred to assure good mixing and then rapidly poured into 15 times its volume of hexane. In this way the polymers were instantly precipitated. This safeguarded against preferred precipitation or fractionation of one of the polymers. The precipitate was collected and dried at 80°C. *in vacuo*.

Polymerization of Terephthalaldehyde with Triethylaluminum Catalyst

Terephthalaldehyde (2.5 g.) was suspended in 50 ml. of dry cyclohexane under nitrogen. The suspension was warmed to 80°C. and 0.5 ml. of a solution (0.8*N*) of triethylaluminum in cyclohexane was added. After stirring overnight at 80°C. under nitrogen, a light-yellow suspension remained in the flask. Methanol (100 ml.) was added to the reaction mixture and the polymer was then filtered, washed with an additional 200 ml. of methanol, and air dried. The polymer was purified in the following manner. It was dissolved in 20 ml. of trifluoroacetic acid containing 1 ml. of tetrachloroethane, filtered, and reprecipitated by pouring the solution into a large excess of methanol. The polymer was then washed with excess methanol and dried at 60°C. under vacuum to give 1.9 g. of white polymer of 0.31 inherent viscosity measured in a 40–60 wt.-% mixture of tetrachloroethane and phenol at 30°C. This polyester could be melt pressed at 120°C. to give a flexible film.

References

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Synopsis

A variety of metal alkyls have been found to be catalysts for preparing a polyester from terephthalaldehyde via the Tischenko reaction. The polymer was examined by infrared spectra, x-ray diffraction patterns, and differential thermal analysis, and is apparently a crystallizable random 50:50 copolymer composed of *p*-methylenbenzoate and *p*-xylyleneterephthalate units. Diphenyl-4,4,-dicarboxaldehyde also underwent polymerization with the metal alkyls, but a hindered aldehyde, 4,6-dimethylisophthalaldehyde, did not and was recovered quantitatively.

Résumé

Une série de métaux-alcoyles peuvent être utilisés comme catalyseur dans la synthèse de polyesters au départ de téréphthalaldéhyde via la réaction de Tischenko. Les polymères

ont été examinés par analyse infrarouge, par diffraction des rayons-X et par analyse thermique différentielle. Ils sont apparemment composés de copolymères statistiques 50/50 cristallisables dont les unités sont le *p*-méthylène benzoat et le *p*-xylylène téréphtalate. La diphenyl-4,4,-dicarboxaldéhyde peut également être polymérisée à l'aide de métaux alcoyles, tandis que la 4,6-diméthyl-isophtaldéhyde, caractérisée par son empêchement stérique, ne peut être polymérisée et est récupérée quantitativement.

Zusammenfassung

Eine Reihe von Metallalkylen erwiesen sich als Katalysatoren bei der Darstellung ein Polyesters aus Terephthalaldehyd nach der Tischenko-Reaction. Infrarotabsorption, Röntgenstreuung und differentialthermoanalytisches Verhalten des Polymeren wurde gemessen; es ist offenbar ein kristallisierendes, statistisches 50/50-Copolymeres aus *p*-Methylenbenzoat- und *p*-Xylylnterephthalatbausteinen. Diphenyl-4,4,-dicarboxaldehyd polymerisierte ebenfalls mit den Metallalkylen, nicht aber ein sterisch gehinderter Aldehyd, 4,6-Dimethylisophtthalaldehyd, der quantitativ zurückgewonnen wurde

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