of this Laboratory, especially to Dr. J. R. Roland and Dr. S. L. Scott who assisted with the experimental work, to Mr. H. S. Young and his group who operated the pressure equipment, and to Dr. J. W. Stillman and his group who made the analytical determinations.

Summary

The free radical-initiated reaction of ethylene with several halomethanes under superatmospheric pressure has been studied. Series of products of the general formula $X(CH_2CH_2)_nY$ are obtained, in which X is hydrogen or halogen, and Y is the remainder of the halomethane molecule. The average chain length, n, varies inversely with the reactivity of the halomethane.

WILMINGTON, DEL. RECEIVED AUGUST 11, 1949

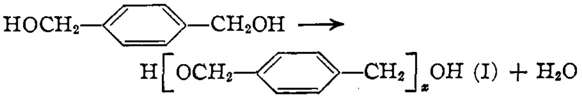
[CONTRIBUTION NO. 169 FROM THE GOODYEAR TIRE AND RUBBER CO., RESEARCH LABORATORY]

The Synthesis of Polymeric Ethers

BY MILTON J. RHOAD AND PAUL J. FLORY[1]

The investigation described in this paper has been concerned with the application of the familiar acid catalyzed etherification reaction of aliphatic alcohols to the preparation of polymeric ethers. While the etherification of ordinary aliphatic alcohols is extremely slow and is complicated by side reactions other than condensation, it has long been known[2] that benzyl alcohol in the presence of small amounts of acidic substances reacts rapidly at elevated temperatures with evolution of water to yield benzyl ether. The self-condensation of compounds in which two methylol groups are attached to an aromatic nucleus should result, therefore, in the formation of polymeric ethers.

We have found that *p*-xylylene glycol condenses readily above 150° in the presence of 0.1% by weight of sulfamic acid to yield the polymeric ether

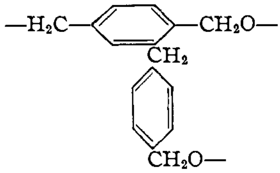


The only previous work done on such condensations is that of Hjelt[3] who reported that *o*-xylylene glycol condenses rapidly at 70° in dilute sulfuric acid to an insoluble, infusible, amorphous substance having the approximate composition C_8H_8O. While the polymer we obtained by the self-condensation of *p*-xylylene glycol contained appreciable quantities of gel, due presumably to a small proportion of condensation at ortho positions on the nucleus, further results have shown that suitably constituted glycols can be condensed to give linear high melting crystalline polyethers with molecular weights exceeding five thousand in some cases. To avoid nuclear condensation, the following substituted dimethylolbenzenes were used as monomers: dimethyloldurene, dimethylolisodurene and dimethylolmesitylene. The former two compounds, as well as the bis-(chloromethyl) intermediates from which they were prepared, have not been reported previously.

Discussion

Although the dimethylolbenzenes are stable compounds when heated under nitrogen at 50–75° above their melting points for periods as long as eight hours, the introduction of as little as 0.05% by weight of an acid or acid forming catalyst causes rapid evolution of water. *p*-Toluenesulfonic acid, sulfamic acid, ferric chloride, stannous chloride, zinc chloride, sodium bisulfate, calcium chloride, cadmium chloride, cobaltous chloride, magnesium chloride and various benzylic chlorides such as bis-(chloromethyl)-isodurene have proved effective in promoting polymerization. Sulfamic acid was chosen for most of the experiments as it induces rapid etherification with virtually no discoloration at the high temperatures of reaction employed.

At 200° with 0.1% by weight of sulfamic acid, *p*-xylylene glycol reacts rapidly, the viscosity of the melt increases, and after twenty minutes gelation occurs. The polymer obtained in this manner was semi-crystalline at room temperature and about 10% of it was soluble in benzene from which it could be crystallized, m. p. 120–122°. The gel was also semi-crystalline with a melting point of about 180°. Carbon–hydrogen analyses (see Table I) of both sol and gel were in close agreement with the values calculated for the linear polyether (I). A small proportion—too small to be detected by carbon–hydrogen analysis—of condensation at the ortho positions with the formation of branched units (II)



(II)

would account for the formation of network structure as indicated by the occurrence of gelation.[4]

When dimethyloldurene (III) similarly reacts at 340°, very rapid evolution of water occurs and the melt solidifies within five minutes. That

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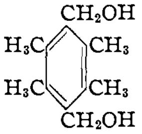
[2] S. Cannizarro, *Ann.*, **92**, 113 (1854).

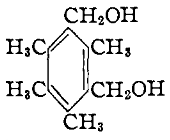
[3] E. Hjelt, *Ber.*, **19**, 1539 (1886).

[4] P. J. Flory, THIS JOURNAL, **63**, 3083 (1941).


(III)

this solidification is brought about by the advance of the melting point as polymerization progresses and not by network formation was shown by the solubility of the polymer in boiling phenylcyclohexane, from which it crystallized as a microcrystalline powder on cooling, m. p. 380–385° with decomposition. The crystallinity of the polymer was confirmed by X-ray diffraction.

Similar high melting crystalline polymers may be obtained by self-condensation of dimethylolisodurene (IV) and dimethylolmesitylene (V).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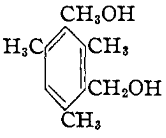
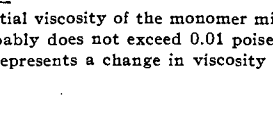

(V)

Both products are soluble in phenylcyclohexane indicating predominantly linear structures. Steric hindrance of adjacent methyl substituents in dimethylolmesitylene apparently discourages reaction at the unsubstituted nuclear position, thus preventing appreciable branching.

When the condensation of any of the compounds III, IV or V was carried out below the thermal degradation temperature of the polymer, solidification occurred at a relatively low degree of polymerization. When the reaction was conducted in solution in a refined paraffin oil (Nujol), the polymerization was interrupted at an intermediate stage by precipitation from the solution and the polymers thus produced were of lower molecular weight than those obtained without diluent, as evidenced by melting points and carbon–hydrogen analyses. In an effort to circumvent the difficulty of premature crystallization, a copolymer was prepared (without diluent) from dimethyloldurene (III) and dimethylolisodurene (IV) in the ratio of 1:2. The melt viscosity of this polymer rose steadily to over 60 poises[5] after twenty minutes at 255°. However, crystallization occurred after thirty minutes. On heating a portion of the polymer at 275°, it melted and the viscosity decreased as gradual decomposition set in.

Owing to the limited solubility of the above polyethers, conventional molecular weight determinations cannot be applied. Rough estimates of their degrees of polymerization may be made from their carbon analyses, however. In the case of dimethyloldurene, carbon–hydrogen analyses gave results (81.30% C and 9.06% H) which are consistent with the formula


(VI)

in which the average degree of polymerization $\bar{x}_n$ is taken as 19. (Calcd. for $x = \infty$, 81.77% C and 9.15% H.) A latitude of error of ±0.20 in the carbon analysis would allow a value of $\bar{x}_n$ in the range from 12 to 30; the hydrogen analysis is insensitive to the value of x. Such estimates as may be made from the melt viscosity obtained on the copolymer from dimethyloldurene and dimethylolisodurene suggest a degree of polymerization between 50 and 75. This value approximates the figure obtained from the carbon analysis (see Table I).

A few semi-quantitative observations have been made on the rate of esterification of benzyl alcohol compared with that for *p*-xylylene glycol under similar conditions (with 0.10% sulfamic acid at 200°), and the rate for 2,3,4,5,6-pentamethyl benzyl alcohol was similarly compared with that for dimethyloldurene. The bifunctional compounds appear to react somewhat more rapidly than their monofunctional analogs, as judged by the rate of water evolution. Fifteen minutes at 241° are required to give a 78% yield of bis-(2,3,4,5,6-pentamethylbenzyl) ether from 2,3,4,5,6-pentamethylbenzyl alcohol, while the reaction of dimethyloldurene at 250° is so rapid as to make accurate rate determination virtually impossible.

The ease with which polymers were obtained from the xylylene glycols encouraged an investigation of the similar reaction of aliphatic glycols. Diethylene, trimethylene, hexamethylene and decamethylene glycols were heated at 200° with catalytic quantities of sulfamic, *p*-toluenesulfonic and sulfuric acids, and with various acid reacting salts. All of these catalysts were ineffective, perhaps due to limited solubility, except sulfuric acid, 2.0% by weight of which induced polymerization of decamethylene glycol and caused decomposition of the other three glycols investigated. Decamethylene glycol reacted smoothly with steady evolution of water, though at a far slower rate than the xylylene glycols. The reaction rate slowly diminished and ceased altogether after four hours. The polymer obtained was a light brown waxy solid, soluble in hot acetone or alcohol from which it was crystallized, m. p. 72–75°. The polydecamethylene oxide structure

$$HO\left[-(CH_2)_{10}-O-\right]_x H \quad \text{(VII)}$$

is confirmed by carbon–hydrogen analyses which suggest a value for $\bar{x}_n$ in the vicinity of 25. Hill[6] reported the preparation of polydecamethylene oxide through the decomposition of polydecamethylene carbonate. His product, owing to its lower molecular weight (1200 by cryoscopic measurement in benzene), melted after recrystallization at 58–60°. We have obtained a similar polymer of lower molecular weight by condensing decamethylene glycol in Nujol.

The decompositions observed with the other aliphatic glycols investigated presumably are as-

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[5] The initial viscosity of the monomer mixture at reaction temperature probably does not exceed 0.01 poise, so that the viscosity value given represents a change in viscosity of 10^4 fold.

[6] J. W. Hill, THIS JOURNAL, **47**, 1131 (1935).

TABLE I

POLYMERIZATION OF GLYCOLS

Glycol	Catalyst (% by weight)	Reaction temp., °C.	Polymer anal. % C	% H	D. p. calcd. from analysis	M. p. of polymer, °C.
p-Xylylene glycol	NH_2SO_3H (0.1)	200	80.00[a] 78.60[b]	6.70[a] 6.62[b]	8[c]	135–137
p-Xylylene glycol	NH_2SO_3H (0.1)	200	80.00 80.10	6.70 6.52	50[d]	165–180
Dimethyloldurene	NH_2SO_3H (0.1)	340	81.77 81.30	9.15 9.06	19[e]	380–390
Dimethyloldurene (20% solution in Nujol)	Bis-(chloromethyl)-isodurene (0.2)	270	81.77 80.75	9.15 9.11	8[f]	230–235
Dimethylolisodurene	NH_2SO_3H (0.1)	241	81.77 81.24	9.15 9.02	19[g]	250–260
Dimethylolisodurene (20% solution in Nujol)	Bis-(chloromethyl)-isodurene (0.2)	241	81.77 80.54	9.15 9.05	7[h]	200–210
Dimethylolmesitylene	NH_2SO_3H (0.1)	241	81.48 81.30	8.64 8.59	30[i]	245–250
Dimethylolmesitylene (20% solution in Nujol)	Bis-(chloromethyl)-isodurene (0.2)	241	81.48 79.42	8.64 8.58	5[j]	235–237
Dimethyloldurene (1 pt.)-dimethylolisodurene (2 pts.) (copolymer)	NH_2SO_3H (0.05)	255	81.77 81.66	9.15 9.05	50[k]	250–255
Decamethylene glycol	25% H_2SO_4 (2.0)	200	76.92 76.55	12.82 12.72	24[l]	72–75

[a] Calculated C and H values for a polyether of infinite chain length. [b] Each figure represents the mean for two or more closely agreeing analyses. [c] The reaction was stopped at first sign of gelation (20 minutes); 90% soluble in hot benzene. [d] Polymer gelled after 30 minutes; highly cross-linked; only 10% soluble in organic solvents. [e] Polymer crystallized after three minutes reaction; soluble in boiling phenylcyclohexane. [f] Polymer precipitated from solution after one hour. Soluble in phenylcyclohexane. [g] Polymer reached maximum viscosity after ten minutes, then crystallized. Heating at 295° caused decomposition. [h] Polymer precipitated from solution after one and one-half hours; recrystallized from phenylcyclohexane. [i] Polymer crystallized after ten minutes; soluble in phenylcyclohexane. [j] Reaction quite slow. Polymer precipitated after two hours; soluble. [k] Molten polymer reached a viscosity of 62.4 poises after twenty minutes; crystallized after thirty minutes; soluble with difficulty. [l] Melt viscosity increased from 0.01 to 0.14 poise in four hours; soluble in hot ethanol.

sociated with cyclization reactions to which they are rendered susceptible by the lengths of their structural units. Aliphatic glycols above hexamethylene in the polymethylene glycol series might be expected to react in a fashion similar to decamethylene glycol.

Experimental

***p*-Xylylene Glycol.**—*p*-Xylylene dichloride was converted to the glycol by reaction with a 200% excess of a 10% aqueous sodium carbonate solution in an autoclave at 150° for eight hours. The reaction mixture was concentrated under reduced pressure and the crude product removed by filtration and washed with cold water. Recrystallization of this material from a 2:1 benzene–alcohol mixture yielded 40% of pure glycol, m. p. 117.5–118.5[7]; previously reported 115–116°.[8]

Bis-(chloromethyl)-durene.—Fifty grams (0.37 mole) of durene (m. p. 79–81°) dissolved in 200 ml. of a high boiling (175–190°) petroleum fraction, 113 ml. (1.5 moles) of 40% aqueous formaldehyde and 100 ml. of concentrated hydrochloric acid were heated with stirring on a steam-bath while a slow stream of hydrogen chloride gas was bubbled through the mixture.[9] After six hours, the oil layer was separated while hot and set aside to cool. The fine white needles of crude product which deposited were collected, leaving the intermediate monochloromethyldurene in solution. The liquor was treated with a fresh formaldehyde–hydrochloric acid mixture as described above, and an additional amount of crude product was obtained. A total of six such treatments of the original durene solution yielded 69 g. (80%) of crude bis-(chloromethyl)-durene. A single recrystallization from benzene gave 58 g. (67%), m. p. 193–194°.

Anal. Calcd. for $C_{12}H_{16}Cl_2$: Cl, 30.68. Found: Cl, 30.80.

Bis-(chloromethyl)-isodurene.—The chloromethylation of isodurene (b. p. 194–196°) proceeded more readily than in the case of durene. The same procedure was employed, but only two treatments of the isodurene solution with the chloromethylating mixture were required to obtain an 85% yield of the crude product. One recrystallization from hexane gave a product of m. p. 106–107° in 80% yield.

Anal. Calcd. for $C_{12}H_{16}Cl_2$: Cl, 30.68. Found: Cl, 30.68.

Bis-(chloromethyl)-mesitylene was prepared by the chloromethylation of mesitylene in a manner similar to that employed for the durenes. A single treatment with the chloromethylating agents gave an 85% yield of the bis-(chloromethyl) compound, b. p. 150–155° (10 mm.). Recrystallization from hexane yielded 80% of pure product, m. p. 105–106°.[10]

Dimethyloldurene.—Five grams of bis-(chloromethyl)-durene dissolved in 100 ml. of glacial acetic acid was added to a slurry of 10 g. (slight excess) of freshly prepared silver acetate in 100 ml. of acetic acid. The mixture was refluxed with stirring for two hours. Silver chloride was re-

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(7) All melting points and freezing points are uncorrected.

(8) E. Bourquelot and A. Ludwig, *Compt. rend.*, **159**, 213 (1914).

(9) See R. C. Fuson and C. H. McKeever, "Organic Reactions," edited by Roger Adams, Chapter 3, Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1942.

(10) W. T. Nauta and J. W. Dienske, *Rec. trav. chim.*, **55**, 1000 (1936), also report a m. p. of 105–106°.

moved by filtration, and the clear filtrate was poured onto ice. The precipitated bis-(acetoxymethyl)-durene was collected and recrystallized from alcohol to yield 5 g. (83%) of product, m. p. 181–183°.

The glycol diacetate (5 g.) was saponified by refluxing in 200 ml. of 15% alcoholic potassium hydroxide for two hours. The solution was poured onto ice, the precipitate collected and washed with cold water. The product was purified by recrystallizing twice from dioxane to give 3.3 g. of glycol; m. p. 245–247°, yield 80%, based on bis-(chloromethyl)-durene.

Anal. Calcd. for $C_{12}H_{18}O_2$: C, 74.18; H, 9.27. Found: C, 73.96; H, 9.24.

Dimethylolisodurene was obtained in 81% yield by conversion of the bis-(chloromethyl)-isodurene to the glycol diacetate and saponification to the glycol as described above; m. p. 216–218°.

Anal. Calcd. for $C_{12}H_{18}O_2$: C, 74.18; H, 9.27. Found: C, 74.10; H, 9.30.

Dimethylolmesitylene was obtained in 78% yield by the reactions applied to the durene derivatives; m. p. 185–187°, in agreement with the value previously reported.[10]

2,3,4,5,6-Pentamethylbenzyl Alcohol.—The chloromethylation procedure described above was employed for the conversion of pentamethylbenzene (Eastman Kodak Co. "practical grade," m. p. 51–55°) to chloromethylpentamethylbenzene. Recrystallization of the crude product gave a 60% yield of a white crystalline compound melting at 80–82°, the previously reported value being 99°.[11] However, chlorine analyses gave results in close agreement with the theoretical. Calcd. for $C_{12}H_{17}Cl$: Cl, 18.02. Found: Cl, 17.91. Reaction of the halide with silver acetate yielded the acetoxy derivative, m. p. 84–85°; and subsequent saponification gave the alcohol, m. p. 160–161°. The melting point values for the acetate and for the glycol are in agreement with those obtained in the earlier investigation.[11] The yield of the glycol after recrystallization from a 2:1 mixture of hexane–benzene was 60% based on the chloromethyl intermediate.

Bis-(2,3,4,5,6-pentamethylbenzyl) Ether.—0.49 g. of 2,3,4,5,6-pentamethylbenzyl alcohol and 0.001 g. of sulfamic acid were heated at 200° for thirty minutes in the polymerization apparatus described below. The removal of moisture was facilitated by blowing a stream of oxygen-free dry nitrogen through the melt and by heating under reduced pressure during the latter stages of reaction. Recrystallization of the residue from alcohol gave 0.38 g. (80%) of the ether, m. p. 171.5–173°; previously reported 168°.[12]

Aliphatic Glycols.—Decamethylene glycol was prepared by hydrogenating diethyl sebacate over copper chromite catalyst at 250°.[13] After recrystallizing twice from a 9:1 mixture of ethylene dichloride–ethyl alcohol, the material had a flat cooling curve at a f. p. of 71.3°.

Hexamethylene glycol, similarly prepared from diethyl adipate,[13] was purified by recrystallization from a 2:3 mixture of acetone–ether, f. p. 41.2°.

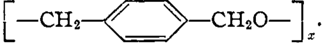
Diethylene glycol and trimethylene glycol (commercial grades) were purified by fractional distillation through an efficient column. Center cuts selected for the attempted polymerizations boiled at 130–131° (13 mm.) and 126–127° (30 mm.), respectively.

Polymerization Procedure.—The polymerizations were carried out in 14 mm. (o. d.) Pyrex tubes sealed at the lower end and 15 to 20 cm. in length. A side arm (6 mm. tubing) was attached about 5 cm. below the upper end. A small diameter glass tube (5 mm. o. d.) was inserted through the inner member of a $^{15}/_{35}$ taper joint connected to the upper end of the reaction tube. This small tube, extending to the bottom of the reaction tube, permitted flushing of the system with dry nitrogen prior to polymerization and passage of the inert gas through the molten polymer to facilitate the removal of water formed during reaction. The nitrogen inlet tube was replaced by a pipet viscometer in those experiments in which melt viscosities were measured.[14] The lower portion of the reaction tube was heated during a given polymerization experiment by the vapor of a refluxing liquid of suitable boiling point.

In carrying out a polymerization, from 0.5 to 2.0 g. of the glycol or glycols and the required amount of catalyst were placed in the bottom of the reaction tube and the system alternately evacuated and flushed with dry nitrogen to ensure an inert atmosphere. Heating was begun, and as soon thereafter as the system became liquid, a slow stream of nitrogen was passed through the melt. The polymerization was continued until there was no visible evidence of further evolution of water, or until the polymer gelled or solidified. The last traces of water were removed by heating at reduced pressure (1–2 mm.), after which the polymer was allowed to cool. The product was recrystallized (see Table I) whenever possible.

Acknowledgment.—The authors are indebted to C. R. Parks and W. C Hukari of this laboratory for the analytical work performed in the course of the investigation.

Summary

1. *p*-Xylylene glycol condenses readily at elevated temperatures in the presence of acidic catalysts to yield a crystalline polymer consisting predominantly of linear polyether chains,  $[-CH_2-C_6H_4-CH_2O-]_x$. Eventual gelation, with the formation of a product most of which is insoluble, indicates simultaneous condensation of the methylol groups at the unsubstituted ring positions to a minor degree.

2. The methyl substituted xylylene glycols, dimethylodurene, dimethylolisodurene and dimethylolmesitylene, condense rapidly above their melting points (*ca.* 250°) in the presence of traces of acid catalysts. Very high melting crystalline polymers are formed. The products are soluble, indicating that the methyl groups effectively inhibit branching side reactions.

3. 2,3,4,5,6-Pentamethylbenzyl alcohol condenses similarly under comparable conditions, though possibly somewhat less vigorously, to yield bis-(2,3,4,5,6-pentamethylbenzyl) ether.

4. Decamethylene glycol condenses much more slowly at 200° in the presence of a small amount of sulfuric acid to give crystalline polydecamethylene oxide having an average degree of polymerization of about 25.

5. The following hitherto unreported monomeric compounds have been prepared and characterized: bis-(chloromethyl)-durene, bis-(chloromethyl)-isodurene, dimethyloldurene and dimethylolisodurene.

AKRON 16, OHIO RECEIVED NOVEMBER 1, 1949

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[11] O. Jacobsen, *Ber.*, **22**, 1217 (1889).

[12] Willstätter and Kubli, *ibid.*, **42**, 4163 (1909).

[13] See H. Adkins, "Reactions of Hydrogen," University of Wisconsin Press, 1937, p. 99.

[14] P. J. Flory, THIS JOURNAL, **62**, 1057 (1940).