indicated two OH bands at 3.03 and 9.5 μ and the C=O band at 5.8 μ.

Infrared spectra of the products isolated from reduction of the dimers showed OH bands at 3.0 and 9.5 μ. The C=O band was absent in the spectra of these products.

Experimental[4]

Synthesis of Ketenes.—The ketenes employed in this study were synthesized by slight modification of the method reported previously.[2] Physical constants and analyses of the ketenes are shown in Table I.

Preparation of Derivatives of Ketenes.—Substituted hydrazides were prepared by treating samples of the ketene monomers with 2,4-dinitrophenylhydrazine reagent[1]; dihydrazones of the dimers were prepared similarly.

Physical constants and nitrogen analyses of the 2,4-dinitrophenylhydrazides of the ketene monomers and the 2,4-dinitrophenylhydrazones of the dimers are given in Table II.

Lithium Aluminum Hydride Reduction of Ketenes.—The procedure followed for reduction of the ketenes was essentially the same as that reported in an earlier study.[1] To a suspension of 2 g. (0.05 mole) lithium aluminum hydride in 800 ml. of dry diethyl ether was added *p*-*t*-butylphenoxy-*n*-butylketene monomer (17.4 g.). The reaction mixture was heated for 21 hours, cooled, hydrolyzed, and extracted with ether. Distillation of the dried extract gave two reaction products: *p*-*t*-butylphenol, b.p. 149–152° (9 mm.) (m.p. 95–96°); and 2-*n*-butyl-2-(*p*-*t*-butylphenoxy)-3-keto-1-octanol, b.p. 160–161° (9 mm.). Physical constants of the reduction products of the ketene monomers and dimers are described in Table III.

Preparation of Derivatives of Reduction Products.—A 1- to 2-g. sample of each reduction product obtained from the ketene monomers was treated, in the usual manner, with 2,4-dinitrophenylhydrazine reagent. Two of the reduction products formed substituted pyrazolines. Treatment of 1-g. samples of reduction products from the ketene dimers with 3,5-dinitrobenzoyl chloride gave, in three cases, the corresponding 3,5-dinitrobenzoates. Description of the physical constants of derivatives is shown in the footnotes to Table III.

Determination of Number of Hydroxyl Groups.—The number of hydroxyl groups in the several reduction products was determined by the procedure of Siggia.[5] By this procedure the reduction products from *p*-*t*-butylphenoxy-alkyl- and 2,4-dichlorophenoxyethylketene dimers showed 1.9 to 2.4 hydroxyl groups; the product from 2,4-dichlorophenoxyketene monomer indicated 0.9 hydroxyl group.

Acknowledgment.—The authors express appreciation to Professor David C. Gandy for assistance in the microanalysis work.

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[4] All melting points are corrected.

[5] S. Siggia, "Quantitative Organic Analysis via Functional Groups," John Wiley and Sons, Inc., New York, N. Y., 1949, p. 4.

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[CONTRIBUTION FROM THE CENTRAL RESEARCH LABORATORY, ALLIED CHEMICAL CORP.]

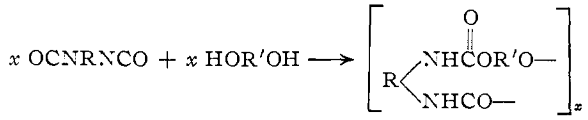
Terminal Unsaturation in Polypropylene Glycol

BY G. J. DEGE, R. L. HARRIS AND J. S. MACKENZIE

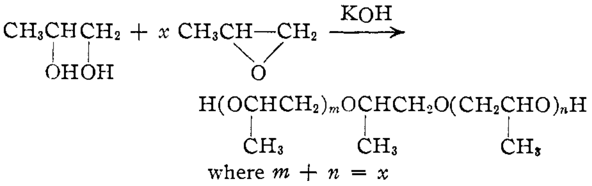
RECEIVED DECEMBER 4, 1958

Both allyl and *cis*-propenyl end groups are present in polypropylene glycol synthesized by the base-catalyzed addition of propylene oxide to propylene glycol initiator. The *cis*-propenyl group is readily identifiable from the characteristic 5.98 and 13.83 μ absorption bands in the infrared spectrum. Evidence for allyl unsaturation is provided by the periodate scission of the double bond and recovery of the released formaldehyde. The presence of terminal unsaturation in polypropylene glycol can seriously limit the length of the polymer chain in the reaction with diisocyanates to form polyurethans. The amount of *cis*-propenyl unsaturation formed in the synthesis of polypropylene glycol increases with increasing reaction temperature, catalyst concentration and extent of certain metallic surfaces. There is no simple relationship between any of the known reaction variables and the amount of allyl unsaturation produced.

There has been increasing interest in the synthesis of polyurethan flexible foams by the reaction of aromatic diisocyanates with polymeric glycols. Of considerable importance in this connection are the polypropylene glycols derived from the base-catalyzed addition of propylene oxide to propylene glycol initiator. Evidence that the base-catalyzed scission of the oxide ring yields primarily secondary hydroxyl groups has been obtained by a number of investigators;[1] although it should be noted that recent nuclear magnetic resonance measurements[2] on polypropylene glycol have indicated the proportion of primary hydroxyl groups to be higher than previously suspected. Polypropylene glycol in the 2000 molecular weight range is particularly well adapted to the synthesis of polyurethane foams. Of necessity this material must have a fairly high degree of bifunctionality in order not to seriously limit the polyurethan molecular weight. One of the important factors contributing to the generation of shortened polyurethan chains is the presence of terminal unsaturation in the polymeric glycol. Commercially available polypropylene glycol in the 2000 molecular weight range may contain anywhere from 4 to 20 terminal olefinic linkages per 100 polymer molecules. While it has not been possible to directly relate the properties of polyurethan foams to the polypropylene glycol



$$x\,\mathrm{OCNRNCO} + x\,\mathrm{HOR'OH} \longrightarrow \left[\mathrm{R}\begin{matrix}\diagup\mathrm{NH\overset{\overset{O}{\|}}{C}OR'O}-\\ \diagdown\mathrm{NHCO}-\end{matrix}\right]_x$$



$$\underset{\mathrm{OH\,OH}}{\mathrm{CH_3CHCH_2}} + x\,\mathrm{CH_3CH{-}CH_2}\ (\diagdown\!\underset{\mathrm{O}}{}\!\diagup) \xrightarrow{\mathrm{KOH}} \mathrm{H(O\underset{CH_3}{C}HCH_2)_{\mathit{m}}O\underset{CH_3}{C}HCH_2O(CH_2\underset{CH_3}{C}HO)_{\mathit{n}}H}$$

where $m + n = x$

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[1] A. A. Petrov, *J. Gen. Chem.* (*U.S.S.R*), **14**, 1038 (1944); *C. A.*, **40**, 7153 (1946); H. C. Chitwood and B. T. Freure, THIS JOURNAL, **68**, 680 (1946); P. D. Bartlett and S. D. Ross, *ibid.*, **70**, 926 (1948); A. R. Sexton and E. C. Britton, *ibid.*, **70**, 3606 (1948); W. Reeve and A. Sadle, *ibid.*, **72**, 1251 (1950); R. C. Elderfield, ed., "Heterocyclic Compounds," Vol. 1, John Wiley and Sons, Inc., New York, N. Y., 1950, p. 32; H. A. Pecorini, Doctoral Thesis, University of Michigan, 1954; Univ. Microfilms, Ann Arbor, Mich., Publ. No. 11337.

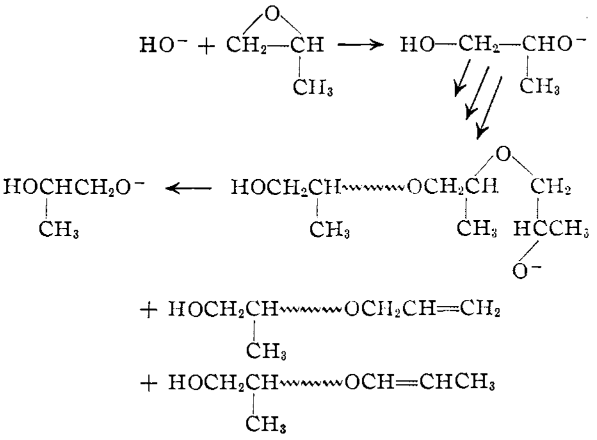
[2] A. J. Havlik and A. F. Hildebrandt, Abstracts of Papers, 134th Meeting, American Chemical Society, Chicago, Ill., September, 1958, p. 14-T.

unsaturation value, it has been shown in this Laboratory that the addition of a monofunctional polyether to 2000 molecular weight polypropylene glycol affects the formation of diisocyanate (pre)polymer in such a way that the rate of its viscosity buildup and final viscosity value decrease continuously with increasing monofunctional polyether concentration. Moreover, when the concentration of monofunctional polyether exceeds 25% the diisocyanate (pre)polymer cannot be foamed. A polyurethan foam prepared from 2000 molecular weight polypropylene glycol containing 25% monofunctional polyether showed reduced compression load relative to a "normal" foam.

Some insight into the nature of the olefinic linkages in polypropylene glycol was gained in the recent investigation of St. Pierre and Price.[3] Polymerizing propylene oxide over a solid potassium hydroxide catalyst at room temperature, they obtained products in the 3000–5000 molecular weight range. These products proved to be highly unsaturated, sometimes containing as many as 80 olefinic linkages per 100 polymer molecules. On the basis of the infrared spectra two types of terminal unsaturation were assumed to be present, allyl ether A (6.06 μ band) and propenyl ether B (6.27μ band)

$$\underset{\text{A}}{ROCH_2CH{=}CH_2} \qquad \underset{\text{B}}{ROCH{=}CHCH_3}$$

The propenyl peak disappeared on acid hydrolysis in agreement with the known properties of vinyl-type ethers.[4] The following reaction mechanism was proposed to explain the termination of the growing polypropylene glycol chain in an unsaturated group



While the foregoing facts and hypothesis provided a workable basis for understanding the nature and possible mechanism for the formation of unsaturation in polypropylene glycol, certain points in connection with the proposed propenyl structure remained obscure. Thus, examination in this Laboratory of the infrared spectra of commercial and laboratory prepared polypropylene glycols rarely showed a 6.27μ peak; and when this peak did appear it could be readily identified with the carboxylate ion. A prominent absorption band at 5.98μ, not mentioned by St. Pierre and Price, was observed in many laboratory prepared products before removal of the potassium hydroxide catalyst; this band was also observed in the finished product provided a strong acid was not employed in the catalyst removal step. This same band was frequently observed in a commercially available polypropylene glycol. The work of Hall, Philpotts, Stern and Thain[5] on the infrared spectra of *cis*- and *trans*-1-butenyl butyl ethers, closely related structurally to the propenyl group under discussion here, strongly suggested this band to be associated with propenyl unsaturation. Therefore, the main purpose of the present study was to provide positive identification of the types of unsaturation present in polypropylene glycol and to discuss several of the factors affecting their synthesis and removal.

Experimental

Materials.—Polypropylene glycols of the 2000 molecular weight range were purchased from the Union Carbide Chemicals Co. (NIAX Diol PPG 2025) and the Dow Chemical Co. (P-2000). Similar materials were synthesized in this Laboratory by the base-catalyzed addition of propylene oxide to propylene glycol initiator in batch and continuous reactors. The molecular weight distribution for the batch reactor product approximated the modified Poisson distribution suggested by Flory[6]; the distribution for the continuous reactor product was considerably broader. In most cases the catalyst was potassium hydroxide used at a 0.1 to 0.5% concentration level, based on final product weight. Reaction temperatures varied from 120 to 160°. The products were characterized by their hydroxyl number (acetylation), unsaturation, viscosity, moisture content, acidity, etc.

A sample of polypropylene oxide was also made by the method of St. Pierre and Price,[3] stirring liquid propylene oxide over finely divided solid KOH at about 33° for 40 hours. Comparison of reported properties and those found were: total unsaturation before catalyst removal 0.219 and 0.21 meq. C=C/g., after catalyst removal 0.198 and 0.18 meq. C=C/g., hydroxyl content 0.293 and 0.30 meq./g., respectively.

Infrared Spectra.—All infrared spectra were recorded on a Perkin–Elmer model 21 spectrophotometer using sodium chloride optics. In general the use of solvents was not necessary. Where required, carbon tetrachloride in 2–12 μ region and cyclohexane in the 12–15 μ region were used. The cell thickness was approximately 0.1 mm.

Unsaturation by Bromination.—A sample of from 1 to 5 g. of polypropylene glycol containing about 0.05 meq. C=C was added to a glass stoppered flask held in an ice-bath. Ten ml. of Br_2–CCl_4 solution (made by addition of 3 ml. of reagent grade bromine to 1 liter of carbon tetrachloride) was added and the flask allowed to stand in the ice-bath for 1 minute. Ten ml. of saturated KI solution and 100 ml. of methanol were added, and the liberated iodine was titrated with 0.1 *N* $Na_2S_2O_3$. To correct for possible bromine substitution, 10 ml. of 10% KIO_3 was added to convert HBr to bromine, and the equivalent released iodine was titrated. The procedure was repeated on a reagent blank prepared as above except for sample and addition of KIO_3 solution. The unsaturation of the sample was determined by difference.

Acid Hydrolysis.—The experimental technique employed was to add polypropylene glycol to 5% H_2SO_4 at a temperature of 100–105° and recover the propionaldehyde overhead through a distillation column. The propionaldehyde content of the distillate was determined by reaction with hydroxylamine hydrochloride. By fractionating known amounts of propionaldehyde away from a standard polypropylene glycol sample it was estimated that a propionaldehyde recovery correction factor of +0.009 meq./g. of

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[3] L. E. St. Pierre and C. C. Price, THIS JOURNAL, **78**, 3432 (1956).

[4] J. W. Copenhaver and M. H. Bigelow, "Acetylene and Carbon Monoxide Chemistry," Reinhold Publishing Corp., New York, N. Y., 1949, p. 46.

[5] R. H. Hall, A. R. Philpotts, E. S. Stern and W. Thain, *J. Chem. Soc.*, 3341 (1951).

[6] P. J. Flory, THIS JOURNAL, **62**, 1561 (1940).

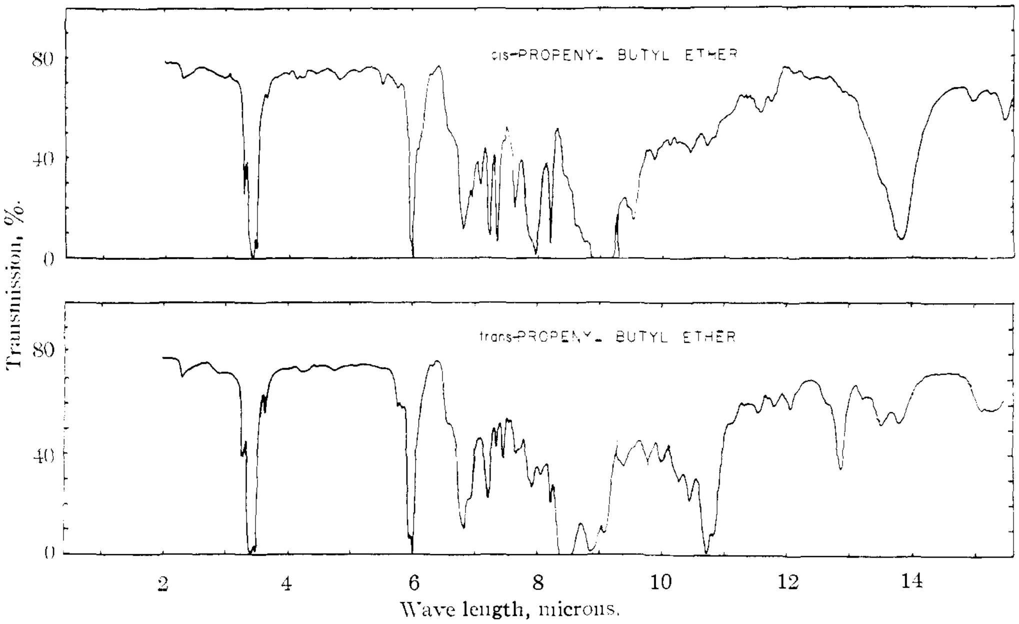

Fig. 1.—Infrared spectra of *cis-* and *trans*-propenyl butyl ether; carbon tetrachloride solvent for 2–12 μ region; cyclohexane solvent for 12–15 μ region; solute concentration 20% by volume.

polypropylene glycol should be used in all experiments. The hydrolyzed polypropylene glycol was recovered by solvent extraction using ethyl ether.

***cis*- and *trans*-propenyl butyl ethers** were prepared by the method of Hall, Philpotts, Stern and Thain[5] described for the preparation of *cis-* and *trans*-1-butenyl butyl ethers, *i.e.*, thermal cracking of propionaldehyde dibutyl acetal. Separation of the crude reaction mixture into the isomers was accomplished by means of 1 in. diameter, 4 ft. glass column filled with 0.16″ × 0.16″ protruded packing. Operating at 50–60 mm. pressure and 30:1 reflux ratio, the column was estimated to have approximately 35 theoretical plates. The *cis*-propenyl butyl ether, b.p. 50.0° (60 mm.), n^{25}_{D} 1.4134, had a purity of 95–96% according to analysis on the vapor fractometer. The *trans*-propenyl butyl ether, b.p. 56.5° (60 mm.), n^{25}_{D} 1.4147, had a purity of 94–95%. The major impurity in each case was the other isomer plus traces of *n*-butyl alcohol. The properties reported here agree quite closely with those reported for a mixture of *cis-* and *trans*-propenyl butyl ethers by Deschamps, Paty and Pineau.[7]

Results and Discussion

In view of the uncertainty regarding the infrared spectrum of the propenyl group, *cis-* and *trans*-propenyl butyl ethers were synthesized as described above. The spectra of these two materials, which strongly resemble those of the corresponding 1-butenyl butyl ethers, are shown in Fig. 1.

The *cis*-propenyl butyl ether has a strong C=C stretching band at 5.98 μ while the *trans*-propenyl butyl ether exhibits a double band in this region with peaks at 5.95 and 6.02μ. Positive identification of the geometrical isomers is provided by their out-of-plane C–H bending frequencies. Thus, the *cis*-propenyl butyl ether has a strong absorption band at 13.83μ and the *trans*-propenyl butyl ether at 10.72μ. These assignments agree remarkably well with those of Kitson[8] for a number of substituted *cis-* and *trans*-olefins. The boiling points of the two ether isomers served to confirm the spectral evidence.

The infrared spectra of NIAX Diol PPG 2025 containing 0.1 milli-equivalent per gram of added *cis*-propenyl butyl ether and of two laboratory prepared samples of polypropylene glycol from which the potassium hydroxide catalyst had not been removed are shown in Fig. 2.

The similarity of the known *cis*-propenyl sample and the 160° prepared product at 5.98 and 13.83μ strongly suggests the presence of *cis*-propenyl end groups in the polypropylene glycol. Similar peaks are frequently observed in a commercial polypropylene glycol. The spectrum of polypropylene oxide prepared at 33° according to the method of St. Pierre and Price[3] is seen to show the strong absorption at about 6.27μ which is weak or absent in the other spectra. As previously stated, these authors assigned the 6.27 μ absorption band to the propenyl C=C stretching vibration. A more likely assignment for the 6.27μ absorption band is the carboxylate ion vibration of by-product acids[9,10] (here neutralized by the alkaline catalyst). Acidification of a polypropylene glycol exhibiting the 6.27μ band produces the characteristic shift of this carboxylate band to the 5.75 μ carbonyl band.

In addition to the absorption peak at 5.98μ, a rather diffuse band at approximately 6.1μ is found in the spectra of many crude and finished polypropylene glycols (see Fig. 2). To check whether this band might be due to allyl unsaturation, the infrared spectra of NIAX Diol PPG 2025 samples containing several concentrations of allyl ether were

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(7) J. Deschamps, M. Paty and P. Pineau, *Compt. rend.*, **238**, 2006 (1954).

(8) R. E. Kitson, *Anal. Chem.*, **25**, 1470 (1953).

(9) L. J. Bellamy, "The Infrared-red Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1954, p. 150.

(10) The 6.27 μ carboxylate peak was calibrated by the addition of acetic acid to NIAX Diol PPG 2025 followed by neutralization with dry NaOH. The 6.27 μ peak of St. Pierre and Price type polyether showed 0.027 meq. acid per gram. Titration of the polyether after deionization with IR-120 resin showed 0.02 meq. acid per gram which was considered reasonable agreement. Polyethers made above 100° showed acid contents of 0.005–0.008 meq. per gram.

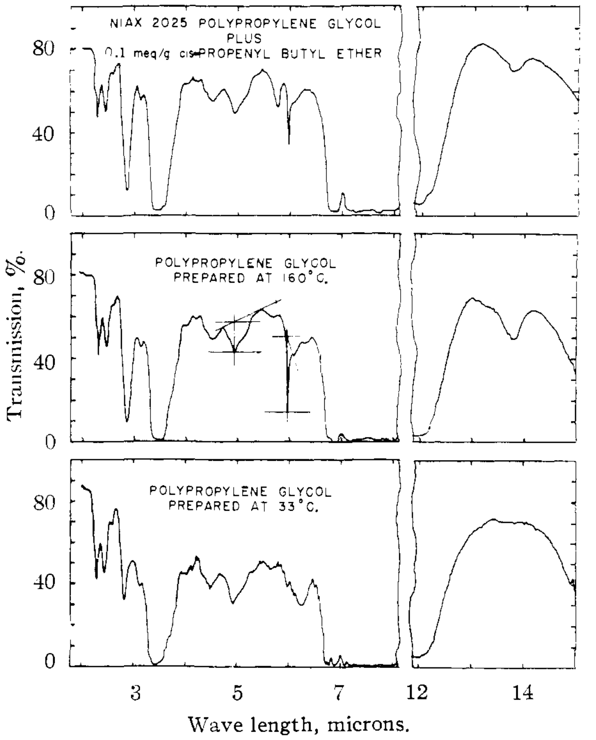


Fig. 2.—Infrared spectra of polypropylene glycol showing evidence for propenyl ether unsaturation at 5.98 μ: upper, NIAX polypropylene glycol with 0.1 meq. of *cis*-propenyl butyl ether added per gram; middle, polypropylene glycol prepared at 160° with potassium hydroxide catalyst; lower, polypropylene glycol prepared at 33° with potassium hydroxide catalyst by method of St. Pierre and Price.[3]

examined. In addition the spectrum of a laboratory product prepared by the reaction of propylene oxide with allyl alcohol initiator was also examined. In Fig. 3 the pertinent portions of these spectra around 6.0μ are shown. The C=C stretching vibration for the allyl structure is seen to be a weak but relatively sharp peak at 6.06μ, superimposed on the more diffuse 6.1μ band mentioned above. To the best of our knowledge the 6.1μ band is due to the presence of traces of water in the polypropylene glycol. It is known that hydrated salts absorb in this region[11]; also, in the preparation of potassium bromide disks for infrared work a similar diffuse band is observed unless moisture is rigorously excluded.

The addition of varying amounts of *cis*- and *trans*-propenyl butyl ether to NIAX Diol PPG 2025 permitted infrared calibration curves to be drawn for the quantitative estimation of these two isomers. Rather than depending on the precise adjustment of the cell thickness, absorbances were measured relative to a peak at 5.0μ, which appeared to remain substantially constant in polypropylene glycol samples of the 2000 molecular weight range. The procedure for determining the relative absorbance is indicated by the reference lines shown on the spectrum of Fig. 2.

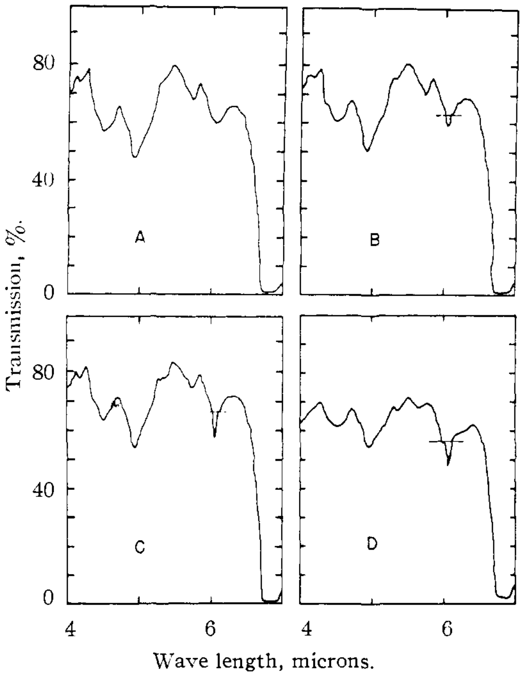
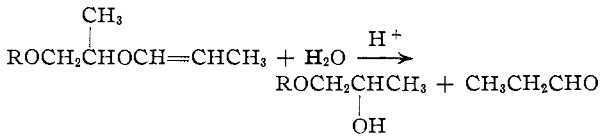


Fig. 3.—Infrared spectra in 6 mμ C=C stretching region: A, 0.0, B, 0.25, C, 0.5 meq. C=C as allyl ether added per g. NIAX polypropylene glycol; D, 2000 mol. wt. product of propylene oxide and allyl alcohol. Allyl ether absorption is below horizontal line in each spectrum.

To further confirm the infrared evidence for the existence of propenyl unsaturation in polypropylene glycol, a number of samples, most of which showed significant absorption at 5.98μ, were subjected to hydrolysis with dilute sulfuric acid at 100–105°. By analogy with vinyl ethers the hydrolysis products should be propionaldehyde and polypropylene glycol of three less carbon atoms. The results of



$$\mathrm{ROCH_2\overset{CH_3}{\overset{|}{C}}HOCH{=}CHCH_3 + H_2O \xrightarrow{H^+} ROCH_2\underset{\underset{OH}{|}}{C}HCH_3 + CH_3CH_2CHO}$$

a number of experiments are summarized in Table I. The fact that propionaldehyde was obtained was positively confirmed by the boiling point, 48–50°, and the methone derivative melting point, 154–156°. Of prime interest was the correspondence of the amount of propenyl unsaturation present and the amount of propionaldehyde released through hydrolysis. In several of the experiments these two quantities agreed quite closely. However, this agreement to a large extent must be regarded as fortuitous, since in other experiments the amount of propionaldehyde recovered both exceeded and fell below the expected value. The amount of recovered propionaldehyde can be affected by at least two factors, (1) secondary reactions of the propionaldehyde leading to low results and (2) the presence of propionaldehyde acetals in the polypropylene glycol leading to high results. In connection with the latter possibility, a recent patent[12] discloses an acid hydrolysis

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(11) A. Weissberger, Ed., "Technique of Organic Chemistry," Vol. IX, "Chemical Applications of Spectroscopy," Interscience Publishers, Inc., New York, N. Y., 1956, p. 430.

(12) E. J. Mills, Jr., and W. G. Tapp, U. S. Patent 2,812,360 (Nov. 5, 1957).

TABLE I

ACID HYDROLYSIS OF POLYPROPYLENE GLYCOL

Temp. 100–105°, reagent, 5% H_2SO_4, time, 4–8 hr.

Sample description	Unsaturation, meq. C=C/g. Before	After	Difference	Recovered propionaldehyde, meq./g.	Initial propenyl unsaturation (i.r.), meq. C=C/g.
Commercial sample A	0.041	0.011	0.030	0.026	0.008
Commercial sample B	.087	.045	.042	.027	.010
Commercial sample D	.046	.015	.031	.015	0
Laboratory, continuous process, 140°[a]	.048	.044	.004	.014	0
Laboratory, continuous process 140°, before KOH cat. removed	.085	.045	.040	.050	0.078
Same as above, dissolved in ether, extracted with water until neutral	.033[b]	.023	.009	.066	.064
Laboratory, continuous process, before KOH removed					
Stage 1				.013	0
Stage 2	...	...	...	.023	0.029
Stage 3				.041	.047
Stage 4				.043	.046
Laboratory, batch process with added steel wool surface	.470	.071	.399	.104	.180
NIAX 2025 with added *cis*-propenyl butyl ether, 0.048 meq./g.	...	...	...	.042[c]	.048

[a] In continuous process propylene oxide, KOH cat. and propylene glycol initiator fed into reactor stage 1; propylene oxide only fed into stages 2, 3 and 4. [b] Replicate of bromination analysis only confirmed this unexpectedly low value. [c] Corrected for small propionaldehyde blank of original NIAX 2025.

process very similar to the one employed here for the removal of acetals from polyethylene glycol. The infrared spectrum of the propionaldehyde acetal of NIAX Diol PPG 1025 polypropylene glycol was examined in an effort to find unique absorption bands suitable for analysis; no such bands could be discovered. It is entirely likely that the acetal and propenyl linkages have differing rates of hydrolysis, but no attempt was made to examine the kinetics of these two reactions. Other polypropylene glycol properties such as the hydroxyl number and viscosity were determined before and after hydrolysis but showed no significant variation. In all cases where a propenyl peak could be observed in the polypropylene glycol spectrum, it disappeared on acid hydrolysis. No other changes in the spectrum were observed.[13]

From Table I the total unsaturation, as determined by bromination, is seen to decrease on acid hydrolysis; however, the variation does not bear any exact relationship to the amount of propenyl unsaturation present. Such a result is not surprising in view of the complexity of the reaction of bromine with vinyl-type ethers.[14] Another factor contributing to the change of the unsaturation value is the partial hydrolysis of the allyl end groups under the experimental conditions employed. Studies with an allyl-terminated polypropylene oxide polymer indicated some 20 to 40% of the allyl unsaturation could be expected to undergo hydrolysis.

While the hydrolysis data do not unequivocally confirm the existence of propenyl unsaturation in polypropylene glycol, the weight of the evidence is strongly in favor of this possibility. It does appear likely, however, that propionaldehyde acetals are also present to some extent in polypropylene glycol.

Direct evidence for the presence of allyl unsaturation in polypropylene glycol was provided by scission of the double bond with periodic acid and recovery of the released formaldehyde.[15] The unsaturation value determined in this manner generally showed approximate agreement with the value found by bromination; the latter method was used in most instances for obtaining unsaturation values. Following the experimental technique of St. Pierre and Price[3] an attempt was made to observe the 6.06μ absorption band, corresponding to the C=C stretching vibration of the allyl group. However, the number of allyl groups in commercial polypropylene glycol and materials synthesized in the laboratory proved to be too few in number to permit this observation to be made. Unsaturation value limits for a number of commercial and laboratory-prepared polypropylene glycols, in which the amount of propenyl unsaturation was small or absent, are recorded in Table II.

TABLE II

ALLYL UNSATURATION IN 2000 MOLECULAR WEIGHT POLYPROPYLENE GLYCOLS

Sample	Reacn. temp., °C.	Unsaturation,[a] meq. C=C/g.
Commercial samples A	..	0.02–0.05
Commercial samples B	..	.04– .09
Laboratory, batch	120	.05– .08
	140	.05– .06
	160	.03– .08
Laboratory, continuous	120	.03– .05
	140	.05– .06
	160	.04– .08

[a] Range of values encountered in duplicate experiments or within an experiment. No significant dependence of the degree of allyl unsaturation on other reaction variables, such as the catalyst concentration or nature of the reactor surface, could be observed.

The variation within an experiment or between successive duplicate experiments was such that no simple relationship could be found between any of the known reaction variables and the amount of allyl unsaturation encountered. It should be emphasized the variation was not an analytical one since no difficulty arose in analyzing known amounts of allyl ethyl ether added to polypropylene glycol.

In Table III are recorded values of the pro-

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(13) One exception was noted for those samples exhibiting carboxylate absorption at 6.27μ. Here, neutralization of the samples entailed in their recovery from the acid hydrolysis reaction medium resulted in the characteristic shift of the 6.27 μ peak to the 5.75 μ carbonyl peak.

(14) A. E. Favorskii and M. F. Shostakovskii, *J. Gen. Chem. (U.S.S.R.)*, **13**, 1 (1943); *C. A.*, **38**, 330 (1944); A. E. Favorskii and M. F. Shostakovskii, *ibid.*, **15**, 385 (1945); *C. A.*, **40**, 4347 (1946); O. W. Cass, U. S. Patent 2,433,890 (Jan. 6, 1948); J. W. Copenhaver, U. S. Patent 2,555,637 (April 24, 1951).

(15) C. E. Bricker and K. H. Roberts, *Anal. Chem.*, **21**, 1331 (1949).

penyl unsaturation determined from infrared spectra, for several typical laboratory prepared products as well as some commercial samples. Here it is apparent that the amount of propenyl unsaturation increases with the preparation temperature, catalyst concentration and with certain surface conditions exemplified here by added steel wool. With regard to the catalytic effect of surfaces in the promotion of propenyl unsaturation it is seen that silicone oils apparently act as surface deactivators. The low propenyl unsaturation content of commercial samples is indication of mild preparatory conditions or acid hydrolysis during catalyst removal.

TABLE III

PROPENYL UNSATURATION IN POLYPROPYLENE GLYCOLS

	Preparatory conditions		Propenyl unsaturation
Temp., °C.	Final mol. wt. number avg.	Final cat. concn., % wt.	By infrared absorp., meq. C=C/g.
Laboratory products before catalyst removal			
120	2500	0.1	0.013
140	2400	.07	.042
160	2000	.18	.105
140	2000	.2	.023
140	2000	.3	.046
140	2000	.5	.130
160	1400	.5	
With added steel wool surface			.18
160	1600	0.5	
With added silicone oil			.028
Commercial samples containing no catalyst			
..	2000	..	
	Sample A		0.008
	Sample B		.010
	Sample C		.06
	Sample D		0

The reaction mechanism whereby the unsaturation arises is not known with any degree of certainty. Certain facts are suggestive, however. Work in this Laboratory on the thermal stability of polypropylene glycol in the presence of known dehydration catalysts, such as activated alumina, and under neutral and alkaline conditions, gave no indication that unsaturation develops by thermal degradation. The recent work of Price and his co-workers[16] on the stereospecific polymerization of ethylene oxide using mainly Lewis acid catalyst systems where a solid surface is present, showed the product to have one end completely unsaturated. It might be possible, therefore, that the solid surfaces present in the reactors in the synthesis of polypropylene glycol, even in alkaline medium, contribute to the generation of propenyl unsaturation. In any event, it is believed the unsaturation in polypropylene glycol arises from an alternate reaction path, competing with the polymerization step, whose velocity depends on the above-cited reaction variables, and not from thermal degradation of the product. The mechanism presented by St. Pierre and Price might well be operative, although it does not suggest why only the *cis*-propenyl isomer should be obtained.

Removal of propenyl unsaturation from polypropylene glycol is relatively easy by treatment with either a mineral acid or a strong acid ion exchanger. However, its occurrence is troublesome in that the loss of functionality limits the polymer molecular weight during synthesis and the formation of propylene glycol initiator engendered in its production starts new polymer chains throughout the course of the reaction. This latter phenomenon leads to a broad molecular weight distribution. Allyl unsaturation, although of a somewhat more permanent nature, can be corrected by hydroxylation[3] or severe acid hydrolysis.

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[16] C. C. Price, "Polyoxides," talk presented as part of North Jersey A.C.S. Lecture Series, Feb. 11, 1958.

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Preparation of Substituted 4-Pentenals

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Methods have been developed for the preparation of substituted 4-pentenals by the rearrangement of allyl alkenyl ethers, produced by the acid-catalyzed elimination of allyl alcohol from aldehyde diallyl acetals. Usually, the allyl alkenyl ethers are produced as transitory intermediates which are not isolated. Some of the reactions and derivatives of the substituted 4-pentenals are discussed.

The rearrangement of allyl vinyl ether to 4-pentenal at 252–255° was first reported in 1938 by Hurd and Pollack.[1] The kinetics of the rearrangement were studied later by Schuler and Murphy,[2] who found the reaction in the vapor phase to be homogeneous and first order, in accordance with a mechanism proposed by Hurd and Pollack.[3] Paul, *et al.*,[4] found that allyl vinyl ether rearranged to 4-pentenal to the extent of 20% after 96 hr. at 80° and 36% after 72 hr. at 100°. The rearrangement of a mixture of 2-pentenyl vinyl ether and 1-pentenyl vinyl ether at 220° was also reported by Hurd and Pollack.[3]

A method of producing 2-alkenylcrotonaldehydes by heating diallyl acetals of crotonaldehyde

[1] C. D. Hurd and M. A. Pollack, THIS JOURNAL, **60**, 1905 (1938).

[2] F. W. Schuler and G. W. Murphy, *ibid.*, **72**, 3155 (1950).

[3] C. D. Hurd and M. A. Pollack, *J. Org. Chem.*, **3**, 550 (1939).

[4] R. Paul, G. Roy, M. Fluchaire and G. Collardeau, *Bull. soc. chim France*, 121 (1950).