The Acid Hydrolyses of Poly-Oxymethylene Diisopropyl Ethers

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The acid-catalyzed solvolysis of compounds corresponding to R_1R_2C-$(OR_3R_4)_2$ has been reported in recent years for numerous acetals,[1] ketals,[1] and formals.[2] The data on formals originating from different workers[1-5] are of sufficient reproducibility to dispel any doubts as to the reliability of the methods employed. The mechanism of the reaction has been studied via acid dependence,[3] salt effect,[6] stereochemistry,[7] isotope location[8] and, recently, gas chromatography.[9] All agree that hydrolysis and solvolysis proceed via a unimolecular fission at the aldehydic carbon-oxygen bond following protonation of the acetal or ketal, forming the conjugate acid.

In two comprehensive papers Taft[1,10] has related the polar substituent and hyperconjugation effects of the substituents R_1, R_2, R_3, and R_4 to the rate constants of the hydrolysis reaction. The correlation is consistent for rate constants varying by several factors of 10, and one would accept that for alkyl substituents the rate is determined by the nature of the groups remaining after the initial bond cleavage,[9] i.e., of the remaining alkoxy group.

In the present investigation we have undertaken to study the variation of hydrolysis reaction rate with a change in the number of methylenic ether linkages in polyoxymethylene diisopropyl ethers. For the compounds of the type R—O—$(CH_2O)_n$—R, the rate constant could approach a constant value characteristic of the polyoxymethylene chain and independent of the endgroups R as n approaches large values, if there is a random scission of the —$(CH_2O)_n$— chain. The converse of this hypothesis would indicate that (a) the hydrolysis is specific at the endgroups, (b) the rate would not be independent of R, and (c) the rate would not necessarily be dependent on the remaining alkoxy group. If the last is correct, no information on the intrinsic rate of the polyoxymethylene chain would be obtained from our investigation. This rate would then have to be determined from compounds of the type R—O—$(CR_1HO)_n$—R. The proof or refutation of the hypothesis is of great importance in the interpretation of hydrolysis kinetics of formaldehyde-crosslinked cellulose polymers.[11]

EXPERIMENTAL

Preparation of Polyoxymethylene Diisopropyl Ethers

The method employed was based on the preparations described by Löbering and Fleischmann.[2] Isopropanol, 2 moles, containing 0.03 moles

of H_2SO_4, was stirred with 1 mole of formaldehyde (as paraformaldehyde) at reflux until two homogeneous liquid layers resulted. Both layers were extracted into benzene, and the resulting benzene solutions of the formals were freed from unreacted formaldehyde, alcohol, and acid by successive washes with water, 10% KOH solution, and water. After drying of the benzene solution over calcium chloride, the solvent and monomeric formal ($n = 1$) were distilled at atmospheric pressure. The remaining mixture of formals ($n = 2, 3, 4, 5$, and 6) were then separated by fractional distillation at 3 mm. Hg. All distillations were accomplished with a $7 \times {}^3/_8$ in. column packed with stainless-steel helices. With increasing distillation temperature some decomposition was noted; to remove dissolved formaldehyde from the products, the latter were washed with 3% Na_2SO_3 solution and redried.

Characterization

The products were characterized and examined for purity by the following techniques.

Gas Chromatography. Separations were made on a 5 ft. column packed with 10% Carbowax 1000/Chromosorb W, 60–80 mesh, at 80°C. Resolution was such that the formals were readily separated from each other, from isopropanol, and from diisopropyl ether; benzene was not resolved from the monomer and the packing retained free formaldehyde.

Figure 1 depicts the resolution obtained for the first five members of the series. Under fixed operating conditions it has been found that the log of adjusted retention times is, to a very close approximation, directly proportional to some increasing property of the homologous series members. A plot of the log of retention time versus number of (CH_2O) groups is shown in Figure 2.

Chemical Analyses. Since the gas chromatographic separations cannot indicate the presence of dissolved gaseous formaldehyde, the samples were analyzed for carbon/hydrogen content and for total (CH_2O) content. The latter was determined from hydrolyzed samples by the chromatotropic acid method.[12] The results are given in Table I.

TABLE I
Carbon-Hydrogen and Total CH_2O Analyses of Polyoxymethylene Diisopropyl Ethers

|	Analyses					
	Calculated, %			Found, %		
Compound	C	H	HCHO	C	H	HCHO
Isopropyl(OCH_2)O-isopropyl	63.64	12.12	22.72	63.72	12.12	23.15
Isopropyl(OCH_2)$_2$O-isopropyl	59.29	11.11	37.04	59.58	11.27	37.09
Isopropyl(OCH_2)$_3$O-isopropyl	56.25	10.42	46.88	56.60	10.67	47.29
Isopropyl(OCH_2)$_4$O-isopropyl	54.05	9.91	54.05	54.35	9.93	52.38
Isopropyl(OCH_2)$_5$O-isopropyl	52.38	9.52	59.52	52.68	9.10	57.84
Isopropyl(OCH_2)$_6$O-isopropyl	51.06	9.22	63.83	53.41	8.50	45.30
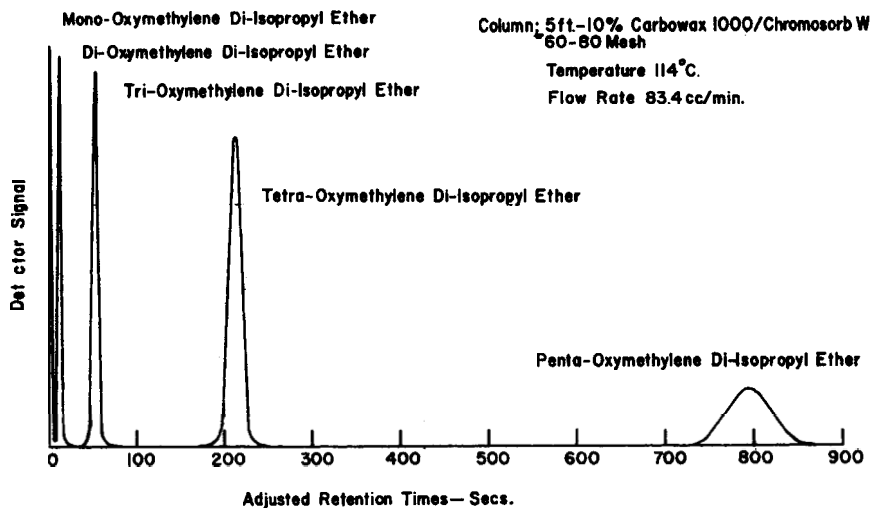
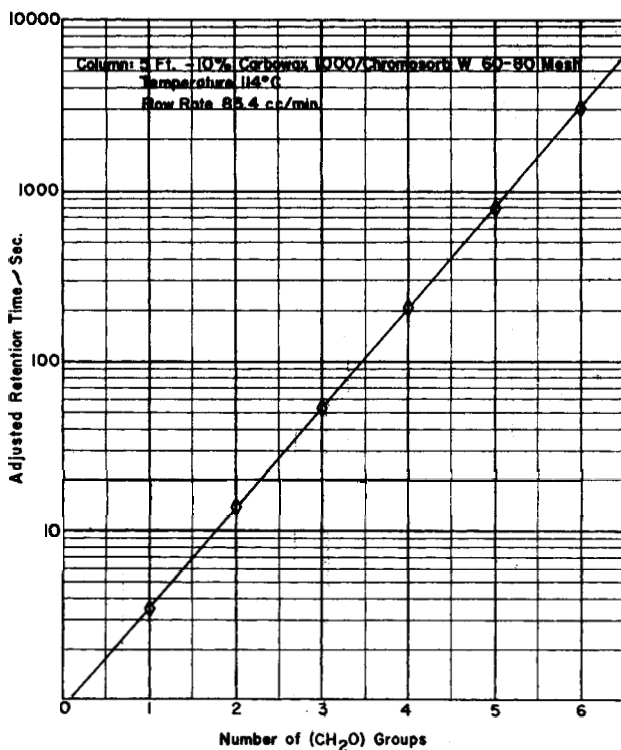Fig. 1. Resolution of polyoxymethylene di-isopropyl ethers.

Fig. 2. Log of retention time versus number of methylene groups.

Molar Refraction. Since the molar refractions of the higher homologues have never been reported, to our knowledge, these were determined. Refractive indices were found with an Abbe refractometer; densities were determined with pycnometers. These data are summarized in Table II.

TABLE II

Molar Refractions of Polyoxymethylene Diisopropyl Ethers

Compound	B.p., °C. at mm. Hg	n_D^{20}	d_{20}	Molar refraction	
				Calcd.	Found
Isopropyl(OCH$_2$)O-isopropyl	117–119/760	1.3864	0.8242	37.792	37.693
Isopropyl(OCH$_2$)$_2$O-isopropyl	39.5–41/23	1.3971	0.8897	44.053	43.918
Isopropyl(OCH$_2$)$_3$O-isopropyl	68.2–68.5/3	1.4035	0.9348	50.314	50.242
Isopropyl(OCH$_2$)$_4$O-isopropyl	93.5–94.5/3	1.4117	0.9751	56.575	56.684
Isopropyl(OCH$_2$)$_5$O-isopropyl	120–123/3.0	1.4235	1.0275	62.596	62.836
Isopropyl(OCH$_2$)$_6$O-isopropyl	159–163/3.7	1.4467 [a]	1.101 [a]	—	—

[a] At 26°C., m.p. 23.5–24.2°C.

Spectra. The infrared spectra of all of the formals reported were obtained with a Perkin-Elmer Model 21 recording spectrophotometer as
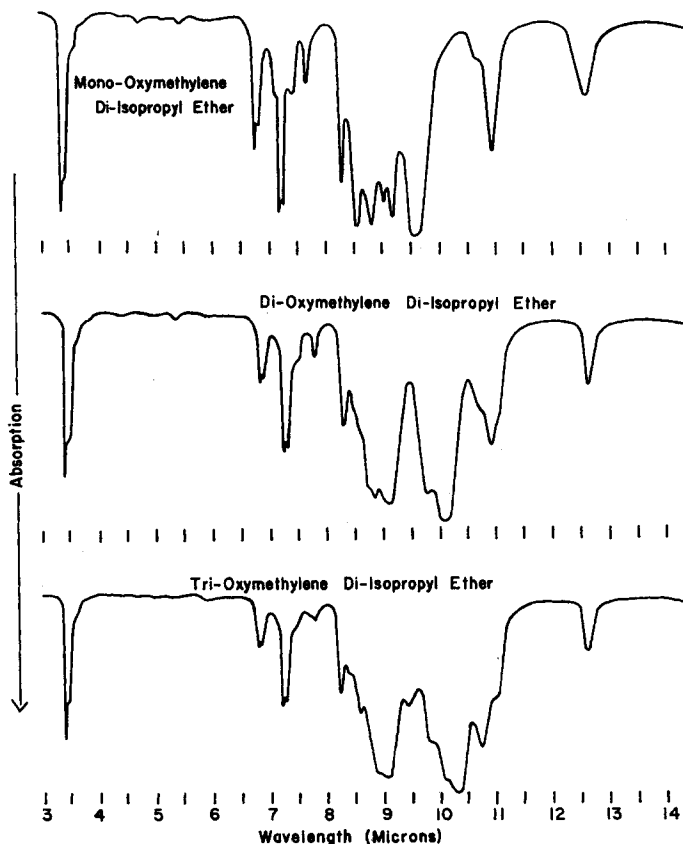

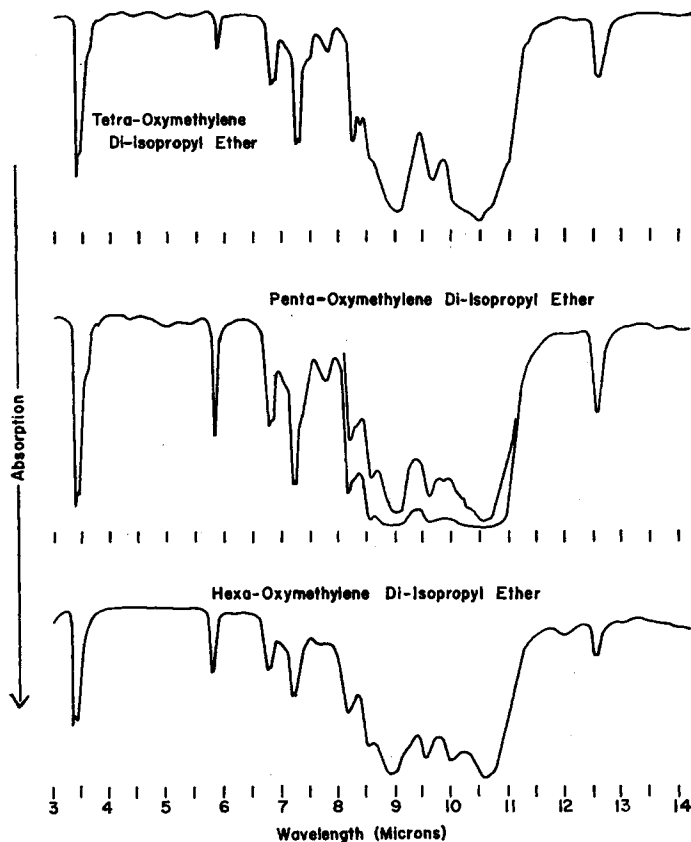Fig. 3. Infrared spectra of polyoxymethylene di-ethers

Fig. 4. Infrared spectra of polyoxymethylene di-ethers.

films on NaCl plates. Detailed analysis of these spectra will be given in a subsequent communication; however, the spectra as they appear, Figures 3 and 4, are useful for identification. It is to be noted that a band appears at 5.82 μ and becomes stronger in intensity with increasing chain length. To ascertain whether this band is due to some structural group associated with the formals, the tetramer and hexamer were collected as effluents from the gas chromatography column. The bands were still present, and it is concluded for the present that this 5.82 band, which is normally ascribed to a C=O vibration, is a real part of the spectra of the higher homologues of this series.

Kinetic Analyses

The liberation of formaldehyde as a function of time was followed by analysis of aliquots of the hydrolysis mixture, with acetylacetone as reagent.[13] Solutions ranging from 0.0025 to 0.005M with respect to formal in dioxane were prepared and thermostated. To initiate the reaction, equal volumes of the dioxane stock solution and 1.0 N HCl solution were

mixed. Periodic samples of 1.0 ml. were taken and quenched in the calculated equivalent concentration of NaOH. The neutralized samples were then developed with 4.00 cc. of the acetylacetone reagent and read at 412 mμ on a Beckman DU spectrophotometer, against a blank prepared from corresponding quantities of acid, base, dioxane, and unhydrolyzed formal. The use of a mixed dioxane–water system was dictated by the limited solubility of the formals in water. Previous reports[14] have shown that the mechanism in this solvent is identical with that in aqueous solutions.

The raw data were taken and plotted in such a manner as to facilitate determinations of rate constants by the Guggenheim method; i.e., samples were taken frequently over the first half-life period, then less frequently for two more half-life periods, and finally at the original frequency. After an elapsed period of over twenty-four hours an infinity sample was taken.

The acid-catalyzed reaction followed a pseudo first-order rate with good precision within a given run. The second-order rate constants obtained from these data are reproducible within ±5%.

RESULTS

The data were analyzed both by a graphical method, in which the log concentration of formal remaining was plotted against time, and by the method of Guggenheim. In the first of these methods, the best fit to the data was obtained by the method of least squares, and the rate constant was determined from the slope. However, because of the error involved in the determination of free formaldehyde present at the completion of the reaction, the Guggenheim method was used in the final calculation of all rate constants.

With this method, the concentration of formaldehyde was plotted against time, and the curve that best fit the experimental points was determined. The necessary data were taken from this curve for the application of the Guggenheim method. The method of least squares was then applied and the rate constant determined. These data are shown in Table III.

A comparison of our results with those of Löbering[2] reveals some marked differences, the most obvious being the variation in temperature dependence of the rate constant. This dissimilarity is pictured in Figure 5, where the log k (l. mole^{-1} sec.$^{-1}$) is plotted against $1/T$. It appears that the data of Löbering follow the Arrhenius equation, but our results indicate a slight deviation from the latter.

Löbering also reported a change in rate with variation in polymer chain length, in mixtures of polyoxymethylene–dimethyl ethers. Since such a mixture of polyoxymethylene linkages may exist in formaldehyde-treated cellulose, the hydrolysis kinetics of a mixture of monomer and dimer were followed. If the two rate constants k_1 and k_2 differ appreciably, a plot of log (CH_2O_t—CH_2O_0) versus time would show curvature,[15] and the use of such an analytical technique begs the question whether the rate constants differ. From the data in Table III we conclude that $k_1 = k_2$ and, as

TABLE III

Pseudo First Order Rate Constants k and Second Order Rate Constants k' for Polyoxymethylene Diisopropyl Ethers

|	At 20°C.		At 25°C.		At 30°C.	
	k, sec.$^{-1}$	k', l. mole^{-1} sec.$^{-1}$	k, sec.$^{-1}$	k', l. mole^{-1} sec.$^{-1}$	k, sec.$^{-1}$	k', l. mole^{-1} sec.$^{-1}$
Isopropyl(OCH₂)O-isopropyl	−1.185	−2.37	−2.040	−4.08	−3.245	−6.49
			−1.955	−3.91		
Isopropyl(OCH₂)₂O-isopropyl	−1.210	−2.42	−1.780	−3.56	−3.455	−6.91
			−1.945	−3.89	−3.315	−6.33
			−1.810	−3.62		
Isopropyl(OCH₂)₃O-isopropyl	−1.145	−2.29	−1.920	−3.84	−3.455	−6.91
	−1.185	−2.27				
Isopropyl(OCH₂)₄O-isopropyl	−1.120	−2.24	−1.895	−3.79	−3.410	−6.82
	−1.115	−2.23				
Isopropyl(OCH₂)₅O-isopropyl	−1.145	−2.29	−1.790	−3.58	−3.480	−6.96
Isopropyl(OCH₂)₆O-isopropyl	−1.190	−2.38	−1.880	−3.76	−3.200	−6.40
Average	—	−2.31	—	−3.78	—	−6.73

ᵃ All values × 10⁻².
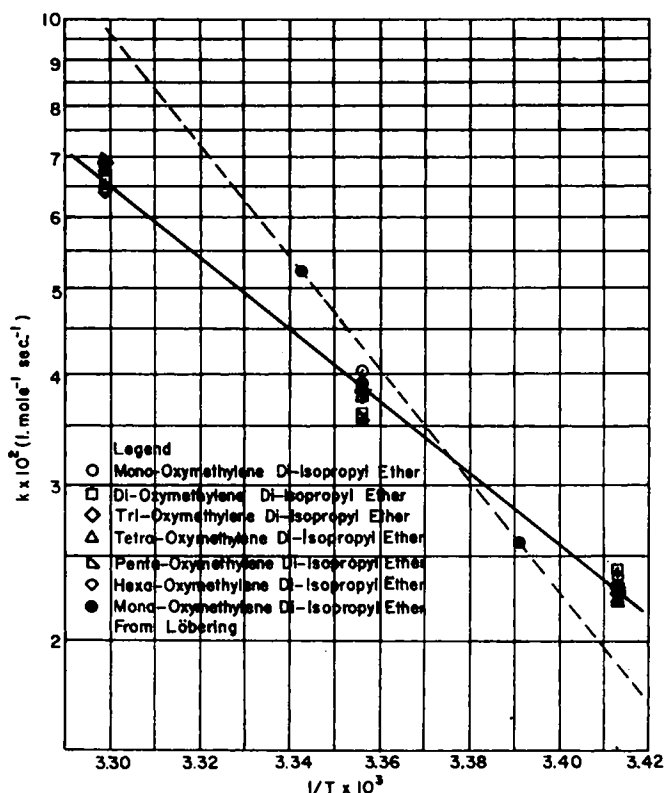
Fig. 5. Temperature dependence of the second-order rate constant.

would be expected, no curvature exceeding experimental error was found from the mixture data.

The energy of activation has been calculated by means of the Arrhenius equation, the slight deviation from linearity being neglected. The error involved in using this simplified form would not influence any conclusions.

From the data of Löbering, a comparison of calculated E_a values (see Table IV) leads to serious discrepancies. Within the set of cited data[2] there is a steady increase in activation energy with increasing endgroup complexity. In contrast, the present data, which we feel to be quite reliable in view of the techniques and replications applied, differ markedly from the cited values.

TABLE IV

Compound	E_a, kcal./mole	Ref.
Dimethyl formal	14.97	2
Dimethyl formal	24.55	2
Diisopropyl formal	29.19	2
Polyoxymethylene diisopropyl ether	18.91	This report

One fact, however, emerges quite convincingly: within a homologous series the change in activation energy is negligible compared with that experienced on changing endgroups. Further, from the isothermal data one is led to conclude that a change in the degree of polymerization of a polyoxymethylene dialkyl ether does not affect the rate of its hydrolysis; a change in alkyl endgroup, by contrast, leads to large changes. From these circumstances, the converse of the original hypothesis is established; i.e., the attack is specific at the endgroup, and is not necessarily dependent on the remaining alkyl group, since this latter functionality may be displaced from the site of reaction by several oxymethylene groups.

The conclusion, as applied to the study of —$(OCH_2)_n$— crosslinked cellulose, indicates that hydrolytic studies of the latter cannot yield any information on the value of n in the crosslinks.

References

1. Kreevoy, M. M., and R. W. Taft, Jr., *J. Am. Chem. Soc.*, **77**, 5590 (1955).
2. Löbering, J., and A. Fleischmann, *Ber. deut. chem. Ges.*, **70B**, 1713 (1937).
3. McIntyre, D., and F. A. Long, *J. Am. Chem. Soc.*, **76**, 3240 (1954).
4. Skrabal, A., and A. Schiffer, *Z. phys. Chem.*, **99**, 290 (1921).
5. Palomaa, M. H., and A. Salonen, *Ber. deut. chem. Ges.*, **67B**, 424 (1934).
6. Long, F. A., and D. McIntyre, *J. Am. Chem. Soc.*, **76**, 3243 (1954).
7. O'Gorman, J. M., and H. J. Lucas, *J. Am. Chem. Soc.*, **72**, 5489 (1951).
8. Stasiuk, F., W. A. Sheppard, and A. N. Bourns, *Can. J. Chem.*, **34**, 123 (1956).
9. Juvet, R. S., Jr., and J. Chiu, Am. Chem. Soc. Symposium on Gas Chromatography, March 21–25, 1961, Cleveland, Ohio.
10. Taft, R. W., Jr., *J. Am. Chem. Soc.*, **75**, 4231 (1953).

11. Dusenbury, J. H., 139th Meeting Am. Chem. Soc. Division of Cellulose Chemistry, Symposium on Cellulose Crosslinking, March 1961, St. Louis, Missouri.

12. Bricker, C. E., and W. A. Vail, *Anal. Chem.*, **22**, 720 (1950).

13. Daniel, J. W., and J. C. Gage, *Analyst*, **81**, 594 (1956).

14. Kreevoy, M. M., and R. W. Taft, Jr., *J. Am. Chem. Soc.*, **77**, 3146 (1955).

15. Frost, A. A., and R. G. Pearson, *Kinetics and Mechanism*, Wiley, New York, 1953.

Synopsis

A homologous series of polyoxymethylene di-isopropyl ethers [R—O(CH$_2$O)$_n$—R] from $n = 1$ through $n = 6$ has been prepared and characterized by gas/liquid partition chromatography, infrared spectroscopy, and other techniques. The acid hydrolyses of the series indicated no rate dependence on chain length between the endgroups, which suggests that the rate of hydrolysis is not dependent on the remaining intermediate group. The rate constants and activation energy are reported, as well as those from the literature. The conclusion is reached that hydrolytic degradation studies of formaldehyde-crosslinked cellulose cannot yield information on the chain lengths of the crosslinks.

Résumé

On a préparé et caractérisé une série homologue d'éthers poly-oxyméthylène di-isopropyliques depuis $n = 1$ iusqu'à $n = 6$ par chromatographie de partition gaz/liquide, spectroscopie infra-rouge et d'autres propriétés physiques. Les hydrolyses acides de séries n'indiquent aucune dépendance de vitesse en fonction de la longueur de chaîne entre les groupements terminaux, suggérant que la vitesse d'hydrolyse ne dépend pas du groupe intermédiaire restant. On décrit les constantes de vitesse et l'énergie d'activation, aussi bien que les valeurs prévues dans la littérature. Sur la base de ces travaux on conclut que les études de dégradation hydrolytiques de cellulose pontée au formaldéhyde ne permettent pas d'informer sur les longueurs des chaînes de pontage.

Zusammenfassung

Eine homologe Serie von Polyoxymethylen diisopropyl Äthern R—O(CH$_2$O)$_n$—R von $n = 1$ bis $n = 6$ wurde dargestellt und mittels Gas/Flüssigkeit Chromatographie, Infrarot Spektroskopie und anderen Methoden charakterisiert. Die Hydrolysen mit Säure liessen keineswegs auf Abhängigkeit von der Kettenlange zwischen den Endgruppen schliessen, was darauf hinweist, dass die Geschwindigkeit der Hydrolyse nicht von der übrigbleibenden Zwischengruppe abhängig ist. Die Geschwindigkeits Konstanten und die Anfangsaktivierungsenergie werden angeführt, sowie auch die in der Literatur vorhandenen Werte. Es folgt daher, dass hydrolytische Abbaustudien von mit Formaldehyd vernetzter Zellulose Aufschluss über die Kettenlänge der Zwischenglieder liefern kann.