Molecular Structure of High Molecular Weight Acetal Resins

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INTRODUCTION

High polymers of formaldehyde having sufficient stability to permit a study of their molecular structure have recently been made in this laboratory. The developments leading to these new polymers as well as the method of preparation for the polymer used in the present investigation are described in a companion paper.[1]

An important contribution to the understanding of the molecular structure of polyoxymethylenes was made by Staudinger and his co-workers.[2] The basic structures postulated in his early work are still essentially correct, but the investigations were limited by lack of stable polymer of high molecular weight and by the methods available at the time of his investigations.

The objective of the present work was to extend our knowledge of the structure of polyoxymethylenes to the stable high polymers now available. Polymer sample of $\bar{M}_n$ ranging from 20,000 to 98,000 were used. The study was directed toward describing the structure of esterified polymer, but samples of unesterified polymer were also used. The latter is referred to as "base" polymer.

COMPOSITION

The chemical composition of the base polymer was shown to be $(CH_2O)_n$ by analysis of the thermal degradation products. The conventional sodium sulfite method[3] was used, and a formaldehyde content of $99.6 \pm 0.3\%$ was obtained. The balance was accounted for as water by the standard Karl Fischer method.

ENDGROUPS

On esterification, the composition was altered by the introduction of acetate groups which replace the hydroxyl endgroups on the base polymer. This was shown by infrared absorption measurements. The base polymer showed an absorption
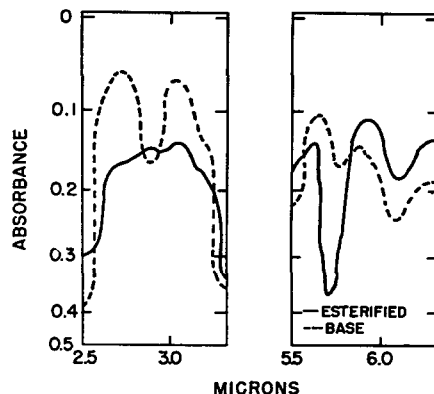

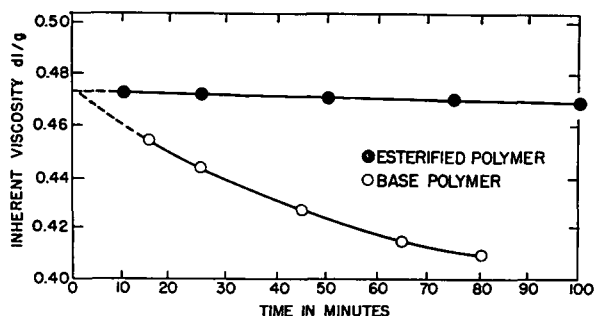Fig. 1. Change in infrared absorbance on esterification.

Fig. 2. Inherent viscosity vs. time.

at 2.9 microns, which was attributed to OH. On esterification of the polymer, this was replaced by absorption at 5.69 and 5.75 microns, which were attributed to the $C=O$ group. This shift in absorption is shown in the absorption spectra shown in Figure 1.

These samples were prepared by cold pressing the polymer into films of about 0.02 mm. in thickness. A Perkin-Elmer Model 21 infrared spectrometer operating on the double-beam null principle was used for making the measurements. Fluorite optics were used to study the region (2–8 μ) of interest.

Solution viscosity measurements were used to show that the molecular weight of the polymer was

not changed significantly during esterification. The equivalence of the inherent viscosities of a given polymer before and after esterification is shown in Figure 2, where the viscosities have been extrapolated to zero time to eliminate degradation effects. These solution viscosity measurements were carried out with a Cannon-Fenske viscometer. A 0.5% solution of polymer in dimethylformamide was used, and the measurements were made at 150°C.

Since there was a small amount of methanol present during the polymerization of the samples, the presence of some methoxyl endgroups was expected. Both methoxyl and acetate ends were found in the esterified polymer by chemical methods. In addition to identification of the endgroups, these analyses served as a measure of the molecular weight and will be discussed more fully under that heading.

CHAIN STRUCTURE

Two types of polymer chains can be formed by formaldehyde. One is sugarlike, with the repeating unit $(—CHOH—)_n$ obtained, for example, when formaldehyde is polymerized in the presence of a base. The other, which is the more common variety found in paraform, is the polyoxymethylene structure $(—CH_2O—)_n$. The stable, high molecular weight polymer studied in the present work was shown by the infrared absorption spectra to be of the polyoxymethylene type.

The spectrometer described previously was again used, but sodium chloride optics were substituted to cover the region of 8–15 μ. Samples were prepared by cold pressing polymer to make films about 0.02 mm. thick.
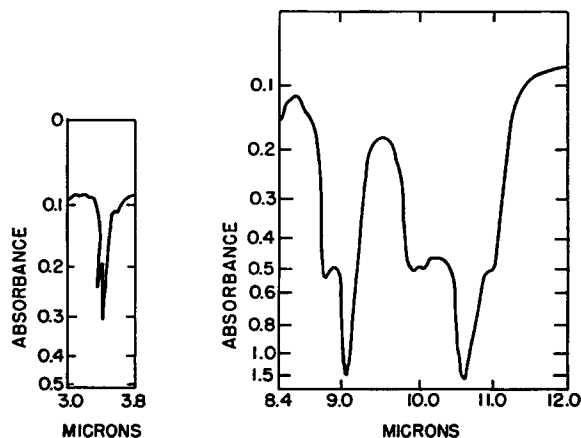

Fig. 3. Infrared absorbance indicating polyoxymethylene structure.

High absorption was obtained in the several regions, e.g., 3.4 μ, where C—H is known to absorb, and also in the 9.2 and 10.7 μ regions, where the C—O—C bonds absorb. Figure 3 shows a typical absorption spectrum. The reversibility of the polymerization reaction, i.e., the evolution of formaldehyde on heating of the base polymer, also suggests the polyoxymethylene structure. Polymers of the $(—CHOH—)_n$ structure are known to char on heating.

MOLECULAR WEIGHT

Determinations of number-average molecular weight were made both by osmometry and by endgroup analysis. As shown in the last column of Table I, the samples used in the present work ranged from 20,000 to 98,000 as measured by osmometry, although the methods used to prepare them do not limit the molecular weight to this range.

The osmotic-pressure measurements were carried out on phenol solutions at 90°C. in the type of osmometer described by Stabin and Immergut[4] with 0.45- and 0.60-mm. capillaries and gel cellophane membranes. The phenol was purified by distillation from solid potassium hydroxide. The membranes were conditioned from water to acetone to phenol, five equal increments for each solvent pair being used, and finally heated at 90°C. for four days to complete the shrinking and hardening process. The permeability of the membranes varied from 2×10^{-5} to 3.5×10^{-5} hr.$^{-1}$.

Both the static elevation and half-sum methods were used in determining the equilibrium height. With the same solution in the osmometer, the half-sum measurements were made, and then the capillary height was displaced and allowed to attain a static equilibrium height.

Measurements were carried out at four or more concentrations over a range of 0.05 to 0.65 g./dl., and a plot of reduced osmotic pressure versus concentration was extrapolated to zero concentration. The number-average molecular weight was calculated in the usual manner, a value of 1.015 g./cc. being used for the density of phenol at 90°C. The second virial coefficient, A_2, was in the range 1×10^{-4} to 2×10^{-4}. The density of the amorphous polymer was assumed to be 1.22 g./cc. at 90°C.

The molecular weight was also determined by chemical endgroup analysis. As shown in columns 2 and 3 of Table I, a preponderance of acetate end-

TABLE I
Comparison of Number-Average Molecular Weight Determined by Osmometry and Endgroup Analysis

Sample	Moles CH$_3$COO/mole CH$_2$O $\times$ 10^3	Moles CH$_3$O/Mole CH$_2$O $\times$ 10^3	$\bar{M}_n$ (by endgroup analysis) $\times$ 10^{-3}	$\bar{M}_n$ (by osmometry) $\times$ 10^{-3}
a	0.56	0.04	100	98
b	0.72	0.06	77	86
c	0.67	0.06	83.5	82
d	0.89	0.02	66	66
e	1.04		58	62
f	0.98	0.02	60	59
g	1.08		55.5	58
h	1.17		51	51
i	1.35		44.5	48
j	1.12		54	47
k	1.34	0.06	43	46
l	1.38		43.5	44
m	1.56		38.5	40
n	1.52	0.05	39.5	35
o	1.91		31.5	33
p	2.04		29.5	30.5
q	2.07	0.05	28	30
r	2.02		30	30
s	2.69	0.08	22	22
t	3.76	0.06	15.7	20

groups was found, but methoxyl endgroups were also found in low concentration.

The concentration of acetate ends was determined by a saponification method. The polymer was decomposed with methanolic HCl to convert the acetate end groups to methyl acetate. The excess acid was neutralized and the ester saponified with the sodium hydroxide. After complete saponification, the reaction mixture was reacidified to liberate acetic acid which, in turn, was titrated potentiometrically. The sensitivity of this method is about 0.3 moles of acetate/1000 moles of formaldehyde; the standard deviation is 0.05 moles of acetate/1000 moles of formaldehyde. The accuracy of the method was tested with mixtures of methyl acetate in base polymer, and recoveries of 95–100% were obtained.

A modified Zeisel method was used to determine the methoxyl groups. The sample was covered with about ten times its weight of phenol and cooled. Hydriodic acid was added and it was slowly brought to 145 $\pm$ 5°C., where it was held for one hour with a slow nitrogen sweep. The exit gases were scrubbed through a red phosphorous suspension, and the methyl iodide was removed by scrubbing through a solution of 1 M potassium acetate and 0.38 M bromine in acetic acid. The solution from the second scrubber was washed in 2.5 M potassium acetate, and formic acid was added to discharge the remaining bromine color. It was then acidified with dilute H$_2$SO$_4$, and 10%

potassium iodine solution was added. The solution was titrated with sodium thiosulfate using starch indicator.

This method gave 22.33% methoxyl for vanillin as the average of eight determinations with a standard deviation of 0.06, compared to a theoretical value of 22.40%. As an indication of the sensitivity of the test, values as low as 0.004% methoxyl were obtained for a 0.3 g. sample of polymer. Eight determinations on another polymer gave an average value of 0.043% methoxyl with a standard deviation of 0.0036.

$\bar{M}_n$ measured by the osmotic pressure method showed good agreement with the $\bar{M}_n$ calculated from the endgroup analysis, as shown by the values listed in the last two columns of Table I. The values based on endgroup analysis were calculated on the assumption that the polymer has two endgroups per molecule and by using the equation:

$$\bar{M}_n = \frac{60}{\text{moles endgroups/moles HCHO}}$$

BRANCHING

The high degree of crystallinity of polyoxymethylene polymers[5] indicates that this is a linear rather than a branched polymer, and this is borne out by all the experimental evidence obtained to date. The good agreement of $\bar{M}_n$ determined by osmometry with $\bar{M}_n$ calculated from chemical
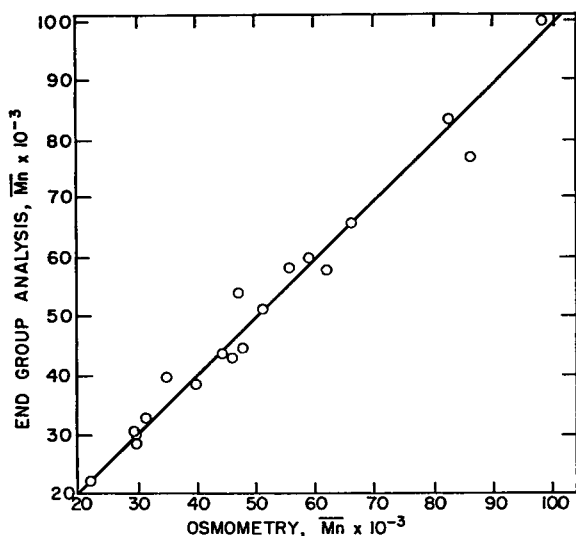
Fig. 4. Molecular weights by endgroup analysis vs. osmometry.

Fig. 5. Relationship of melt viscosity and $\bar{M}_n$ of polyoxymethylene.

analysis of endgroups was cited above in connection with molecular weight determinations. Since this agreement depends on the assumption of two endgroups per molecule, a strong indication that the polymer is essentially unbranched is obtained. This agreement is shown graphically in Figure 4.

In addition, chemical analysis for orthocarbonate and C—C structures as possible branch points gave negative results.

In testing for orthocarbonate structure, the polymer was degraded in methanolic HCl by refluxing, and then a slow stream of nitrogen was bled through the system and scrubbed through a solution of saturated barium hydroxide to precipitate any CO_2 which might have been released. None was detected.

In the analysis of C—C bonds, the polymer was again decomposed by refluxing with methanolic HCl. The methylal formed was carefully distilled off, and more methanol was added as required until testing of the distillate with chromatropic acid reagent gave a negative test for formaldehyde.[6] The residue was neutralized with potassium hydroxide, bromthymol blue being used as an indicator, and then 1% periodic acid solution was added and allowed to react for 10 to 20 minutes. Saturated lead acetate solution was added to the heated residue until no further precipitate formed. The precipitate was removed and the clear solution was treated with chromatropic acid reagent. After 25 minutes of heating at 100° C., the solution was cooled and diluted to a known volume. The adsorption of this solution at 570 mμ was
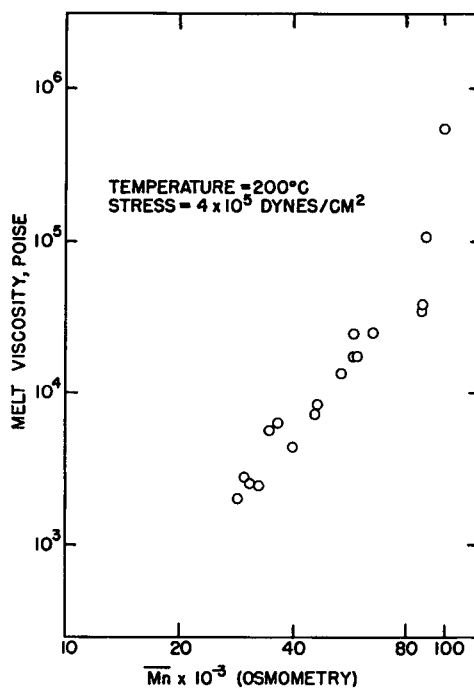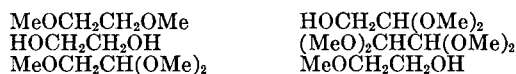
determined with a Beckman Model B spectrophotometer as a measure of formaldehyde formation.

This method assumes that, after digestion in methanolic HCl, such structures as the following would be present if there were C—C bonds in the polymer originally:

MeOCH₂CH₂OMe   HOCH₂CH(OMe)₂
HOCH₂CH₂OH   (MeO)₂CHCH(OMe)₂
MeOCH₂CH(OMe)₂   MeOCH₂CH₂OH

Tests run on model compounds showed that this method of analysis permitted detection of 20–40 ppm of the compound as ethylene glycol in the presence of polyformaldehyde.

A third structure, orthoformate, is theoretically possible, but was not fully investigated for lack of a reliable analytical procedure. However, the preponderance of evidence is in favor of a linear structure.

MOLECULAR WEIGHT DISTRIBUTION

A measure of $\bar{M}_w$ was desired to characterize the polymer further. Light scattering measurements are being made in this laboratory, but have not been completed as yet. Therefore, in the absence of a direct evaluation of $\bar{M}_w$, melt viscosity measurements have been used to obtain relative values on the basis that the general expression $\log \eta = K$
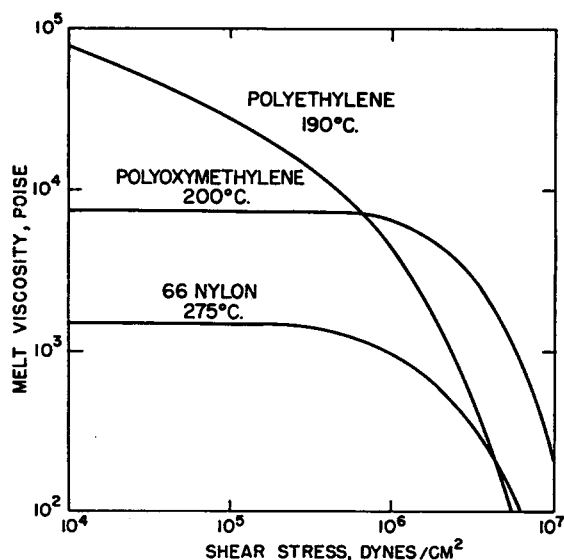
Fig. 6. Comparison of the rheological behavior of polyoxy-
methylene, nylon 66, and polyethylene.

log $\bar{M}_w + k$ is known to hold for a number of
linear polymers. Figure 5 shows the relationship
of melt viscosity and $\bar{M}_n$. The constancy of the
relation suggests a constant distribution over the
range of molecular weight investigated.

As a further indication of the molecular weight
distribution, the shear stress-shear rate behavior
of the polymer was compared with that of other
polymers of known distribution. The similarity of
polyoxymethylene polymer to a narrow distribu-
tion polymer (nylon 66) and dissimilarity to a broad
distribution polymer (polyethylene) is shown in
Figure 6.

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Synopsis

Stable, high molecular weight polymers of formaldehyde
have been studied to determine their molecular structure.
The polymer chain was shown to be a polyoxymethylene by
chemical analysis and infrared absorption spectra. Infrared
techniques also revealed hydroxyl end groups which were re-
placed by acetate groups on esterification. The endgroups,
which were also measured by chemical methods, were used
to determine the number-average molecular weight over
the range 20,000 to 98,000. Values obtained by assuming
two endgroups per molecule agreed with osmotic pressure
results, thus showing this to be an essentially unbranched
polymer. Two theoretically possible branch-point struc-
tures were investigated by chemical methods; none could
be detected, further indicating a linear polymer structure.
Indirect evidence of narrow molecular weight distribution
was obtained by comparing melt viscosity properties with
those of other polymers of known wide and narrow distribu-
tion.

Résumé

L'étude de polymères stables, de hauts poids moléculaires,
de formaldéhyde a été entreprise en vue de déterminer leur
structure moléculaire. On a montré que la chaîne polyméri-
que était du polyoxyméthylène, par l'analyse climique et par
les spectres d'absorption infra-rouge. Les techniques infra-
rouges ont également démontré la présence de groupes
terminaux hydroxyles qui, par estérification, sont remplacés
par des groupements acétates. Ces groupements terminaux
qui ont tét également mesurés par des méthodes chimiques,
ont été employés pour déterminer le poids moléculaire moyen
en nombre qui varie entre les valeurs de 20.000 à 98.000. Ces
valeurs, obtenues en plaçant deux groupements terminaux par
molécula sont en accord avec les résultats obtenus par pres-
sion osmotique; elles montrent donc que l'on est en présence
d'un polymère essentiellement non ramifié. On a recherché
deux structures ramifiés théoriquement possibles par des
méthodes chimques et aucune n'a été trouvée, ce qui indique
de nouveau une structure polymérique linéaire. Une évi-
dence indirecte d'une distribution faible de poids moléculaire
a été obtenue en comparant les propriétés viscosimétriques
avec celles d'autres polymères à grande et faible distribution
connue.

Zusammenfassung

Versuche zur Emittlung der Molekülstruktur stabiler,
hochmolekularer Formaldehydpolymerer wurden durchge-
führt. Die chemische Analyse und die Infrarotabsorp-
tionsspektren zeigten, dass das Polymere eine Polyoxy-
methylenkette besitzt. Die Infrarotmethode ergab auch
die Anwesenheit von Hydroxylendgruppen, die durch
Veresterung durch Acetatgruppen ersetzt wurden. Die
Endgruppen, deren Zahl auch nach chemischen Methoden
gemessen wurde, wurden zur Bestimmung des Zahlen-
mittelwerts des Molekulargewichts im Bereich von 20.000 bis
98.000 herangezogen. Werte, die unter der Annahme von
zwei Endgruppen pro Molekül erhalten wurden, stimmten
mit osmotischen Ergebnissen überein, was für ein im wesent-
lichen univerzweigtes polymeres spricht. Zwei theoretisch
mögliche Strukturen für Verzweigungspunkte wurden mit
chemischen Methoden nachzuweisen versucht, konnten aber
nicht gefunden werden; das liefert eine weitere Bestätigung
der linearen Struktur des Polymeren. Ein indirekter Hin-
weis auf eine enge Molekulargewichtsverteilung wurde durch
den Vergleich der Schmelzviskositätseigenschaften mit
denen anderer Polymerer von bekannter, sowohl weiter als
auch enger, Verteilung, erhalten.