Polymerization of Formaldehyde and the Physical Properties of the Polymerization Products. I

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Synopsis

Polymerization of formaldehyde carried out in the solution method and gas supply method using various initiators at various temperatures and characterization of the polyoxymethylene obtained are discussed. In both modes of polymerization, polyoxymethylenes with sufficient molecular weight ($\overline{M}_n$) and small $\overline{M}_w/\overline{M}_n$ were obtained. The toughness of polymer as determined by the $\overline{M}_w/\overline{M}_n$ of the polymer with sufficient M_n was confirmed.

The polymerization of formaldehyde has been known for many years. This paper deals with the basic knowledge concerning the polymerization of formaldehyde and the physical properties of the polymerization products.

Two principle methods for the polymerization of formaldehyde are known: Gas supply polymerization by continuous supply of gaseous formaldehyde onto a medium containing an initiator; and solution polymerization by adding an initiator to a solution containing absorbed formaldehyde gas. The former was first proposed by MacDonald[1] and the latter was first reported by Staudinger.[2]

With the Staudinger method (solution polymerization) one cannot obtain polyoxymethylene with enough thermal stability and toughness to produce useful plastics.

Schweitzer et al. reported that gas supply polymerization is a suitable method for making polyoxymethylene with excellent properties.[1,3]

MacDonald reported the following statement in his patent.[1] "The methods described in the prior art, such as those by Staudinger, produce formaldehyde polymers which are so unstable that they have never been considered to be suitable for conversion to molded articles commonly made from synthetic plastics."

On the other hand, "The formaldehyde polymers of this invention are obtained by continuously passing gaseous, substantially anhydrous, monomeric formaldehyde into a reaction zone containing a reaction medium which is inert to formaldehyde under the condition of reaction and permitting the formaldehyde to polymerize continuously as the monomer is introduced."

This invention produces high-molecular-weight polyoxymethylene, which in contradistinction to those of the prior art, can be made into articles having excellent physical properties.

The polymer by this invention is defined as either having a minimum of toughness retention, defined as a degree of toughness of at least 1, or having a minimum thermal stability, defined as a reaction rate constant for thermal degradation at 222°C of less than 1% by weight of the polymer per minute.

TABLE I
Monomer Purity

CH_2O	>99%
MeOH	<50 ppm
H_2O	<100 ppm
HCOOH	N.D.
HCOOMe	<300 ppm

To clarify the mechanism reported by MacDonald, we performed research on the essential problems of formaldehyde polymerization.

Thermal stability of polymer is not discussed in this paper, since we confirmed that the stability sufficient for molding is obtainable by the masking reaction of the polymer end groups, and removing impurities detrimental to thermal stability. This paper focuses on the polymerization and toughness of the polymer obtained.

EXPERIMENTAL

Monomer of constant purity is used as indicated (Table I). The apparatus used throughout our experimental work is shown in Figure 1. The same apparatus was used in gas supply polymerization and also in solution polymerization with minor modifications.

Number average molecular weight was determined by end-group analysis on acetylated polyoxymethylene. The weight average molecular weight was calculated from solution viscosity data.

Physical properties were observed on acetylated polyoxymethylene.

RESULTS AND DISCUSSION

Gas Supply Polymerization

The polymerization by various initiators and under various conditions was examined. Rate of polymerization is shown by the ratio of polymer obtained to feed monomer in weight percent. With triethylamine, a well-known initiator for formaldehyde, no polymer was obtained at 60°C (Table II).

With triethylamine, the $\overline{M}_w/\overline{M}_n$ ratio of the polymers obtained was very large. An example of the polymerization obtained with cobalt acetyl acetonate is shown in Table III. Results similar to those with the amine were obtained.
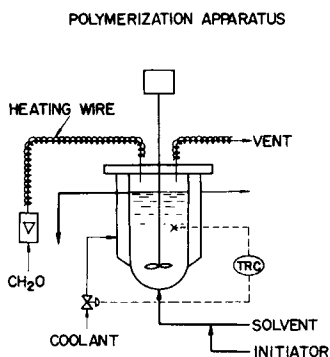
POLYMERIZATION APPARATUS

Fig. 1. Polymerization apparatus.

TABLE II
Polymerization of Gaseous Formaldehyde with Triethylamine

Temperature (°C)	Yield (%)	$\eta_{sp/c}$	$\overline{M}_n$	$\overline{M}_w/\overline{M}_n$
40	10	7.35	41,700	11.8
50	2	5.37	13,800	29.4
60		No polymerization occurred.		

Medium n-hexane
Initiator Concentration 2×10^{-4} mol/L

In Table IV, the results obtained with dimethyl distearyl ammonium acetate (DMDSAA) are shown. This initiator yields polymer having large $\overline{M}_n$ and small $\overline{M}_w/\overline{M}_n$ with no influence by temperature up to 60°C.

Table V shows the results with dibutyltin dilaurate (DBTDL). In this case, the temperature strongly influenced the ratio $\overline{M}_w/\overline{M}_n$ of the polymer obtained.

In all cases, the rate of polymerization was related to polymerization temperature and type of initiator. Using high boiling paraffin as solvent, at various temperatures, polymerizations with dibutyltindilaurate with strong initiating activity at a wide range of temperature was examined (Fig. 2).

Yield of polymer decreased markedly above 60°C, and at 105°C a very low yield of polymer was obtained. Enough monomer dissolves in the solvent at tem-

TABLE III
Polymerization of Gaseous Formaldehyde with Co(acac)$_3$

Temperature (°C)	Yield (%)	$\eta_{sp/c}$	$\overline{M}_n$	$\overline{M}_w/\overline{M}_n$
30	33	4.9	18,200	17.6
50	24	11.6	23,600	31.1
60		No polymerization occurred.		

Medium n-hexane
Initiator Concentration 3.3×10^{-5} mol/L

TABLE IV
Polymerization of Gaseous Formaldehyde with DMDSAA

Temperature (°C)	Polymer Yield (%)	$\eta_{sp/c}$	$\overline{M}_n$	$\overline{M}_w/\overline{M}_n$
40	90	1.90	29,700	2.90
50	85	1.60	30,500	2.22
60	70	1.99	44,800	2.15

Medium n-hexane
Initiator Concentration 1×10^{-4} mol/L

TABLE V
Polymerization of Gaseous Formaldehyde with DBTDL

Temperature (°C)	Yield (%)	$\eta_{sp/c}$	$\overline{M}_n$	$\overline{M}_w/\overline{M}_n$
40	90	7.11	27,700	18.3
50	85	2.30	28,000	4.1
60	70	1.88	28,600	3.0

Medium n-hexane
Initiator Concentration 1×10^{-2} mol/L

POLYMERIZATION TEMPERATURE vs POLYMERIZATION YIELD
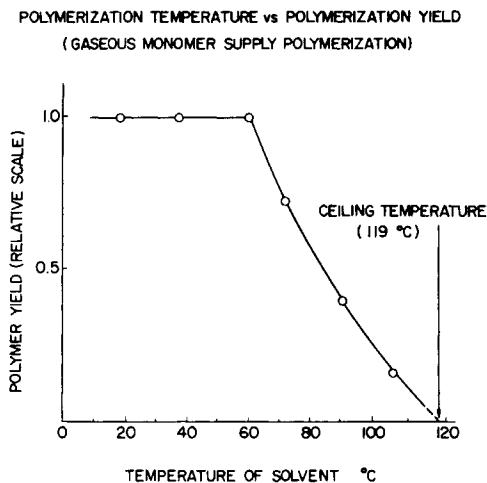(GASEOUS MONOMER SUPPLY POLYMERIZATION)

Fig. 2. Polymerization temperature vs. polymerization yield (gaseous monomer supply polymerization.

peratures below 60°C, but above 60°C monomer solubility decreases with temperture. No polymer would be obtained at 119°C. This coincides with the ceiling temperature of formaldehyde at normal pressure.

No polymerization occurs in boiling solvents, such as, in boiling diethylether in which formaldehyde dissolves easily. Below boiling temperature, even in the presence of a very active initiator, the gas supply polymerization method was examined. Hence, the rate determining factor in polymerization is the migration of monomers to initiator.

Table VI summarizes the results obtained in gas supply polymerization with various types of initiators. Polyoxymethylene having enough large $\overline{M}_n$ and sharp molecular weight distribution with some selected initiators, such as ammonium compounds or some tin compounds, were obtained by the gas supply method.

Solution Polymerization

In our laboratory, solution polymerization was conducted by one shot addition of a given amount of initiator into toluene solution containing absorbed purified formaldehyde. By this preparation method, excellent polyoxymethylene with high molecular weight was not obtainable. The polyoxymethylene obtained by the same method had a large $\overline{M}_n$ and a small $\overline{M}_w/\overline{M}_n$ ratio. Polymerization with triethylamine proceeded very slowly and yielded barely enough polymer for analysis; however, it proceeded more quickly with the addition of a small amount of water (Table VII).

TABLE VI
Summary of Gas Supply Polymerization with Various Initiators

No.	Initiator	Concentration (mol/L)	Temperature (°C)	Yield (%)	$\eta_{sp/c}$	$\overline{M}_n$	$\overline{M}_w/\overline{M}_n$
1	Et₃N	2×10^{-4}	40	10	7.35	41,700	11.8
2	DMDSAA	1×10^{-5}	50	85	1.92	36,700	2.2
3	DBTDL	1×10^{-4}	50	85	2.03	30,600	3.0
4	SnCl₄	2×10^{-4}	40	84	1.72	29,100	2.6
5	Co(acac)₃	3×10^{-5}	50	24	11.6	25,600	31.1

TABLE VII
Solution Polymerization in Toluene

No.	Initiator	Temperature (°C)	Yield (%)	$\eta_{sp/c}$	$\overline{M}_n$	$\overline{M}_w/\overline{M}_n$
1	Et$_3$N[a]	5	~100	1.37	23,100	2.4
2	DBTDL	−30	~100	2.55	33,500	3.9
3	TBAA[b]	−30	~100	1.80	31,900	2.5

[a] Addition of water of 2,000 ppm in toluene.
[b] Tetrabutylammonium acetate.

A polymer having only low $\overline{M}_n$ is obtained and film made from this polymer was fragile, but the $\overline{M}_w/\overline{M}_n$ ratios of the polymers were small, compared to those initiated by ammonium compounds. Polymerization with dibutyltindilaurate proceeded smoothly and gave a polymer with a large $\overline{M}_n$ and a moderately small $\overline{M}_w/\overline{M}_n$ ratio.

Polymerization with ammonium compounds proceeded smoothly yielding polymer at a high rate. Adding a chain transfer agent, such as water, allowed control of the $\overline{M}_n$. The ratio $\overline{M}_w/\overline{M}_n$ was small. Films made from polymers produced by the latter two initiators were tough enough to withstand the folding test described in MacDonald's patent.[1] The M_n and $\overline{M}_w/\overline{M}_n$ of these polymers indicate excellent qualities for use as industrial resins, and their mechanical properties were equal to those of current commercial plastics.

The polymers thus obtained were equal to those obtained by a gas supply polymerization in which monomer is fed continuously to permit polymerization of the monomer as it is introduced. This showed for the first time that, contrary to reports by Schweitzer and his co-workers,[3] polymers with excellent physical properties could be obtained by the method used by Staudinger, that is, by solution polymerization.

A primary condition for achieving this polymerization is purity of the monomer and the reaction medium. Although it proved difficult to obtain good polymer when an amine was used as initiator, selected initiators such as ammonium compounds or organotin compounds, yielded excellent polymer by solution polymerization, with solutions containing an excess of monomer over the rate of polymerization.

W. H. LINTON, AND H. H. GOODMAN,
J. APPL. POLYM. SCI 1 NO.2 183 (1959)

Fig. 3. Effect of molecular weight on elongation of tensile specimens at break.
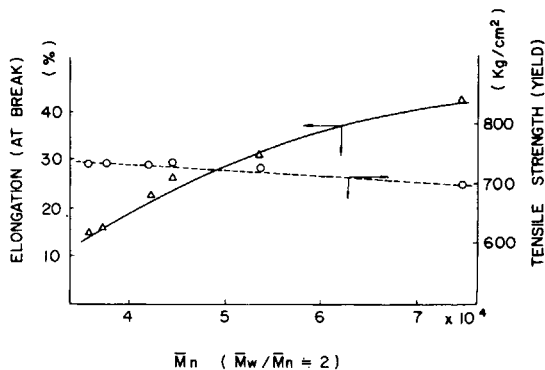
MOLECULAR WEIGHT vs TENSILE ELONGATION AND STRENGTH

Fig. 4. Molecular weight vs. tensile elongation and strength.

PHYSICAL PROPERTIES OF POLYOXYMETHYLENE

A great amount of work has been done on the physical properites of polyoxymethylene. Our experiments led us to the conclusion that the essential factors affecting the mechanical properties of polymer is the number average molecular weight and the molecular weight distribution. Linton[4] first reported the relationship between molecular weight and tensile elongation (Fig. 3). We made many polymers with the same $\overline{M}_w/\overline{M}_n$ ratio, but different $\overline{M}_n$ by gas supply polymerization, and plotted their tensile elongation and tensile strength as functions of $\overline{M}_n$ (Fig. 4). The tensile strength decreases linearly with the increase of $\overline{M}_n$, and the elongation increases with the increase of $\overline{M}_n$ (Fig. 4). The elastic and flexural modulus are affected very little by the $\overline{M}_n$.

The IZOD impact strength, which is a measure of toughness, increases markedly with $\overline{M}_n$ (Fig. 5). On the other hand, a peak in Dart impact strength was found at a certain value of $\overline{M}_n$. This curious behavior is caused by the morphology of the polymer in addition to the molecular weight effect. Very few reports refer to the relationship between physical properties and molecular weight distribution of polyoxymethylene.

Ackerman[5] compared the physical properties of two polyoxymethylenes having different $\overline{M}_v/\overline{M}_n$, and showed that the change in tensile strength and modulus with M_v/M_n appears small, but IZOD impact strength and elongation change greatly with changes in the M_v/M_n ratio.

MOLECULAR WEIGHT ($\overline{M}n$) vs IMPACT STRENGTH

Fig. 5. Molecular weight ($\overline{M}_n$) vs. impact strength.
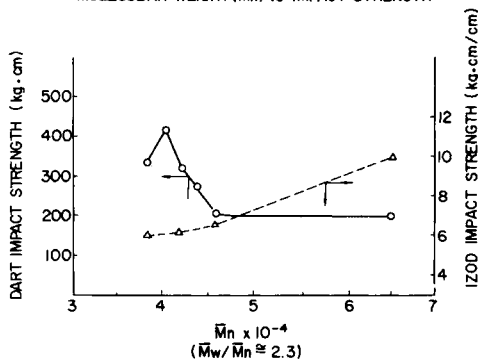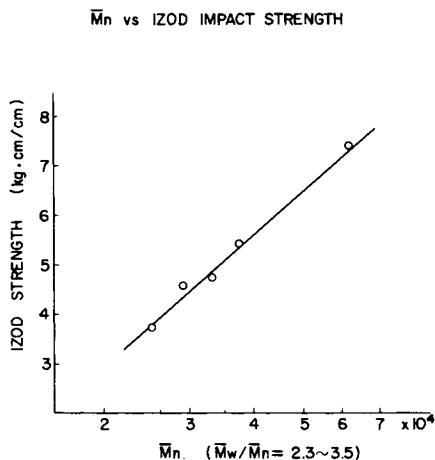
$\overline{M}_n$ vs IZOD IMPACT STRENGTH

Fig. 6. $\overline{M}_n$ vs. izod impact strength.

In studies of the Dart impact strength of polymers having $\overline{M}_w$ of about 83,000, but of various $\overline{M}_w/\overline{M}_n$ ratios in the range of 2.2–4.0, the lower the $\overline{M}_w/\overline{M}_n$ ratio is, the tougher the polymer (Table VIII).

Thus, at constant molecular weight, the $\overline{M}_w/\overline{M}_n$ ratio has a remarkably close relationship with the polymer toughness. On the other hand, by plotting the IZOD strength of polymers having different molecular weight and also different molecular weight distribution against their $\overline{M}_n$, the IZOD strength increases with an increase in $\overline{M}_n$; more precisely, the IZOD strength varies linearly with the log of the $\overline{M}_n$. In other words, in the $\overline{M}_w/\overline{M}_n$ range of 2.3–3.5, the exact relationship between the IZOD strength of the polymers and the log $\overline{M}_n$, regardless of their $\overline{M}_w/\overline{M}_n$ ratio, greatly affects the toughness of polymers having the same number average molecular weight; a larger number average molecular weight results in greater toughness (Fig. 6).

To obtain tough polyoxymethylene, it is essential to obtain polyoxymethylene as large as possible in $\overline{M}_n$, and as small as possible in $\overline{M}_w/\overline{M}_n$.

These two factors are determined primarily by the degree of purity of the polymerization system, and by selection of initiator.

SUMMARY

In this paper, the polymerization of formaldehyde under various conditions with various initiators was examined.

In gas supply polymerization (gaseous formaldehyde on the vehicle containing

TABLE VIII
Effect of $\overline{M}_w/\overline{M}_n$ on Falling Ball Impact Strength[a]

$\overline{M}_w/\overline{M}_n$	Dart Impact Strength (kg cm)
2.2	340
2.5	250
4.0	115

[a] $\overline{M}_w \doteqdot 83,000$.

initiator), polyoxymethylene with sufficient molecular weight $(\overline{M}_n)$ was obtained with many kinds of initiators; M_w/M_n was determined with one initiator.

Also, in solution polymerization, the method of adding initiator to the form-aldehyde solution, the polymer with sufficient molecular weight $(\overline{M}_n)$ and small M_w/M_n was obtained with some initiators.

Toughness of polymer, which appears to be the most important factor for engineering plastics, was determined by the $\overline{M}_w/\overline{M}_n$ of the polymer if the molecular weight $(\overline{M}_n)$ was high enough.

The $\overline{M}_w/\overline{M}_n$ of polymer is determined by the kind of initiator and polymerization temperature, rather than by the polymerization mode such as gas supply method or solution method.

References

1. R. N. MacDonald, U.S. Patent 2,768,994 to E. I. du Pont de Nemours and Company (1956).

2. H. Staudinger, *Die Hochmolekularen Organischen Verbindungen Kautschuk und Zellulose*, Springer, Berlin, 1932.

3. C. E. Schweitzer, R. N. MacDonald, and J. O. Punderson, *J. Appl. Polym. Sci.*, **1**, (2), 158 (1959).

4. W. H. Linton and H. H. Goodman, *J. Appl. Polym. Sci.*, **1**, (2), 179 (1959).

5. J. Ackerman, *Mater. Plast. Elastom.*, **35**, 1126 (1969).