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Anionic Oligomerization of Methyl Methacrylate by Alkali Metal Alkoxides

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ABSTRACT

The kinetics of the oligomerization of methyl methacrylate (MMA) by methoxide/methanol solutions was studied using gas chromatography techniques. The effects of the type of the alkali metal, $[CH_3OH]/[\text{monomer}]$ ratio, solvent, and initiator concentration were investigated. The rate of conversion using different alkali metal alkoxides was in the order $CH_3OLi > CH_3ONa > CH_3OK$, but no oligomers higher than the addition product, RO—MMA (n = 1), could be obtained by CH_3OLi. $\overline{DP}_n$ decreased with increasing the $[CH_3OH]/[\text{monomer}]$ ratio and with lowering of the initiator concentration. Using DMSO as solvent increased the yields of the higher oligomers. The formation of n = 1 was reversible, contrary to the formation of the higher oligomers. Some of the rate constants of the various steps of the oligomerization were estimated by taking into account the reversibility of the initiation reaction and assuming steady-state conditions in the concentration of the various anions present in the system.

INTRODUCTION

The oligomerization of methyl methacrylate by CH_3O^-/CH_3OH solutions has been previously studied [1]. Oligomers having $\overline{DP}$ up to six were isolated and characterized. Initiation was by addition of CH_3O^- to the double bond, and termination was by proton abstraction from the methanol. Accordingly $\overline{DP}$ decreased with an increase in the $[CH_3OH]/[\text{monomer}]$ ratio.

In the present work this general study was extended to deal with the kinetic aspects of oligomerization by CH_3O^-/CH_3OH. Use was made of the quantitative gas chromatography technique to follow the progress of the reaction, including the rates of disappearance of the reactants, monomer, and methanol, and of the formation of the various oligomers. A picture was thus obtained of what was going on at all times in the oligomerization mixture. From these rates an estimate was made of the rate constants of some of the various steps of the oligomerization. Such a detailed study was carried out in this laboratory in the case of the bulk oligomerization of methacrylonitrile by RO^-/ROH solutions [2].

Various factors affecting the rate of the oligomerization and $\overline{DP}$ of the oligomers, such as the ratio of reactants, $[CH_3OH]/[\text{monomer}]$, type of the alkali metal alkoxides, catalyst concentration, and solvent, were studied.

EXPERIMENTAL

Materials

Methyl methacrylate (B.D.H.) was refluxed over calcium hydride for 2-3 hr and distilled under argon. The fraction boiling at 94-96° was collected and kept under argon in a refrigerator for a period not longer than 48 hr. Methanol (B.D.H., maximum water 0.02%) was dried over magnesium. Argon was dried by passage through concentrated sulfuric acid followed by sodium hydroxide pellets. Dimethylsulfoxide was fractionally distilled in vacuo. The alkali metal alkoxide solutions were prepared by dissolving the alkali metal in methanol with exclusion of moisture. Their concentration was determined by titration. All the reagents were kept under argon and were transferred by syringes applying positive argon pressure.

Gas Chromatography

Quantitative analyses of the reactants and products were carried out by gas chromatography using a Perkin Elmer Model 820 and an

Aerograph Autoprep Model A-700 instruments. Helium was used as the carrier gas and 6 ft × 1/4 in. column was used to contain the packing of SE 30 [15% for the determination of methanol, monomer, and methyl β-methoxy α-methyl propionate ($n = 1$), and 5% for the higher oligomers]. The rate flow was 30-40 ml/min and the injector, oven, and detector temperatures were 170° (290°), 100° (190°), and 170° (270°), respectively, the numbers in parentheses being for the higher oligomers.

Oligomerization Procedure

The oligomerization was carried out as described previously [2] at 78°. Aliquots were removed from the homogeneous reaction mixture at various intervals and were analyzed by gas chromatography.

RESULTS

Effect of the Alkali Metal

The effect of the alkali metal on the rate of the oligomerization was studied using a relatively high [methanol]/[monomer] molar ratio (6/5) so that the reaction will stop mostly at the $n = 1$ stage. It was found (Fig. 1) that the rate of conversion was in the order $CH_3OLi > CH_3ONa > CH_3OK$. The yields after 180 min reaction were 55, 36, and 23%, respectively.

On the other hand, with the lithium catalyst, oligomers higher than $n = 1$ could not be obtained even on using low [methanol]/[monomer] ratios, contrary to the results with sodium and potassium.

It can be seen that the rate of reaction increased with increasing initiator concentration, and the $\overline{DP}$ of the oligomerization mixture also increased (Table 1), showing that $\overline{DP}$ was dependent on the initiator concentration.

Effect of Solvent

The effect of solvent was investigated using DMSO as solvent for the oligomerization. Methanolic sodium methoxide was added to the monomer in DMSO and the oligomerization was carried out as before (Table 2).

The important thing observed was that low methanol to monomer ratios, which in the bulk oligomerization led to the formation of only $n = 1$, here led to the formation of higher oligomers. With DMSO $\overline{DP}$ also increased with increasing initiator concentration (Table 3).

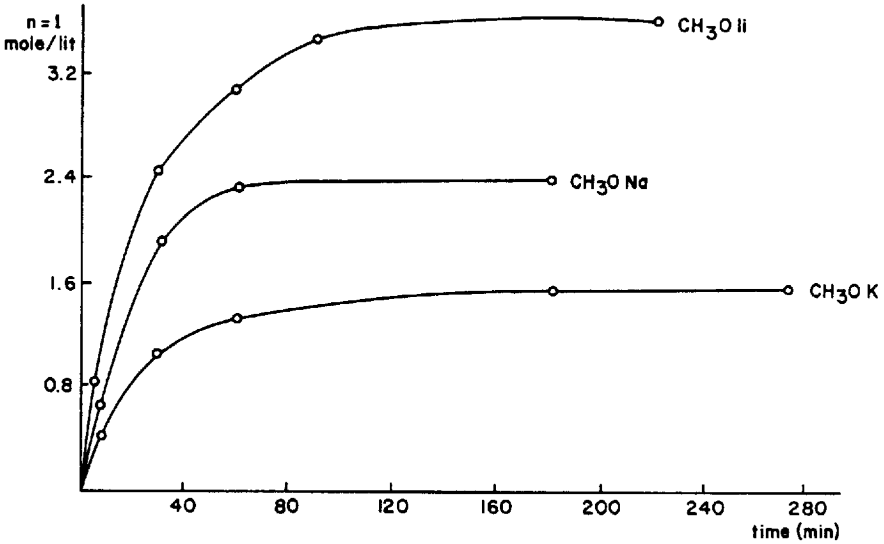


FIG. 1. Oliogomerization by alkali metal alkoxides. $[CH_3OH]/[MMA] = 6/5$ $[MMA] = 6.45$ mole/l. $[CH_3OLi] = [CH_3ONa] = [CH_3OK] = 4 \times 10^{-3}$ mole/l.

TABLE 1. Effect of Initiator Concentration[a]

Time (min)	[Monomer] (mole/l)	[n = 1] (mole/l)	[n = 2] (mole/l)	$\overline{DP}_n$	$[CH_3ONa]$ (mole/l)
0	8.39	-			
15	6.83	1.03	0.27	1.21	0.183
30	5.96	1.15	0.64	1.35	
60	5.11	1.24	1.01	1.45	
0	8.40	-	-		0.080
15	7.00	1.00	0.17	1.14	
30	6.70	1.18	0.25	1.18	
60	5.98	1.41	0.49	1.26	

[a] $[CH_3OH]/[Monomer] = 1/2$.

TABLE 2. Oligomerization in DMSO Solution

[Methanol] / [Monomer]	[n = 1] (mole/l)	[n = 2] (mole/l)	[n = 3] (mole/l)
1.20	0.18	0.85	0.13
1.60	0.36	0.96	
1.97	0.40	0.34	
2.38	0.42	0.16	
2.60	0.60	0.04	

TABLE 3. Dependence of $\overline{DP}_n$ on [CH_3ONa] in DMSO[a]

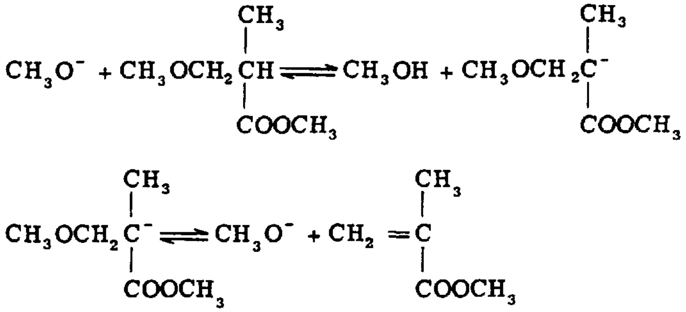
[CH_3ONa] mole/l	[n = 1] (mole/l)	[n = 2] (mole/l)	[n = 3] (mole/l)	[n = 4] (mole/l)	$\overline{DP}_n$
0.0022	0.076	-			
0.0044	0.042	0.056	0.009		1.69
0.0088	0.027	0.117	0.023		1.98
0.0176	0.0083	0.0082	0.017	0.0046	2.40

[a] [Methanol]/[Monomer] = 6/5; n = 4 was determined by distillation, bp 205°/0.1 mm.

Kinetics of the Oligomerization

Experiments were performed to follow the rate of disappearance of monomer and alcohol, as well as the rate of formation of the different oligomers. The results are given in Table 4.

An important observation was that in most of the reactions the amount of n = 1 increased to a maximum during the oligomerization and then decreased. The lowering in concentration of n = 1 during the reaction seems to be due to the reversibility of the reaction



$$CH_3O^- + CH_3OCH_2\underset{\displaystyle |\atop COOCH_3}{\overset{\displaystyle CH_3\atop |}{CH}} \rightleftharpoons CH_3OH + CH_3OCH_2\underset{\displaystyle |\atop COOCH_3}{\overset{\displaystyle CH_3\atop |}{C^-}}$$

$$CH_3OCH_2\underset{\displaystyle |\atop COOCH_3}{\overset{\displaystyle CH_3\atop |}{C^-}} \rightleftharpoons CH_3O^- + CH_2=\underset{\displaystyle |\atop COOCH_3}{\overset{\displaystyle CH_3\atop |}{C}}$$

To confirm this point, an experiment was carried out in which methanolic sodium methoxide was added to n = 1 under oligomerization conditions. The results (Table 5) showed that the n = 1 actually suffered elimination of methanol to give the monomer. No dimer (n = 2) was formed in the reaction, even after 3 hr.

To find out whether the formation of oligomers higher than n = 1 was also reversible under the general conditions of the oligomerization, an experiment similar to that carried out with n = 1 was conducted. The dimer, n = 2 (7 ml, 0.032 mole), was reacted with methanolic sodium methoxide (6 ml of 1.46 N solution), but no n = 1 or monomer was found. To determine the equilibrium constant, experiments using an excess of methanol were carried out, the system reached equilibrium, and the equilibrium concentrations in mole/l were [monomer] = 1.31; [n = 1] = 1.02, and $[CH_3OH] = 13.2$; $K_{eq} = 16.9$ mole/l. A similar experiment with lithium methoxide gave $K_{eq} = 1.88$ mole/l. This shows that there is a great dependence of the extent of the reversible reaction on the type of counterion.

DISCUSSION

It was shown that the only significantly reversible step of the oligomerization was that of the decomposition of n = 1 to monomer and methanol. The oligomerization system consists of a series of consecutive and competitive reactions which may be presented as follows:

$$M_1^- + CH_3OH \underset{k_1'}{\overset{k_1}{\rightleftharpoons}} M_1 + CH_3O^-$$

$$M_1^- + M \xrightarrow{k_3} M_2^-$$

$$M_2^- + CH_3OH \xrightarrow{k_4} M_2 + CH_3O^-$$

$$M_2^- + M \xrightarrow{k_5} M_3^-$$

$$M_3^- + CH_3OH \xrightarrow{k_6} M_3 + CH_3O^-, \text{ etc.}$$

TABLE 4. Oligomerization at Various [CH_3OH]/[MMA] Ratios[a]

Run No.	Time (min)	[CH_3OH] (mole/l)	[MMA] (mole/l)	[n = 1] (mole/l)	[n = 2] (mole/l)	[n = 3] (mole/l)	$\overline{DP}_n$
A	0	6.79	6.80				
	5	5.79	5.79	1.00			
	10	5.30	5.31	1.48			
	20	5.00	5.04	1.80			
	30	4.74	4.75	2.04			
	60	4.46	4.43	2.41			
	90	4.43	4.40	2.37			
	150	4.43	4.40	2.30	0.015		1.01
	180	4.29	4.25	2.30	0.12		1.05
	210	4.20	4.20	2.25	0.18		1.08
B	0	3.52	8.39				
	15	2.24	6.83	1.03	0.27		1.21
	30	1.73	5.96	1.15	0.64		1.35
	60	1.27	5.11	1.24	1.01		1.45
	90	1.11	4.80	1.20	1.10	0.07	1.52
	150	1.00	4.40	1.10	1.29	0.12	1.61
	180	0.85	4.11	1.01	1.46	0.18	1.72
C	0	4.77	7.60				
	20	3.80	6.60	0.90	0.08		1.08
	40	3.50	6.25	1.10	0.13		1.10
	60	3.10	5.80	1.42	0.21		1.13
	90	2.85	5.40	1.59	0.30		1.16
	120	2.85	5.31	1.50	0.36	0.04	1.23
	150	2.85	5.20	1.43	0.40	0.09	1.30

[a] Experimental conditions as follows. A: [CH_3ONa] = 0.134. B: [CH_3ONa] = 0.183. C: [CH_3ONa] = 0.134.

TABLE 5. Reversibility of the Addition Reaction[a]

Time (min)	$[CH_3OH]$ (mole/l)	[MMA] (mole/l)	[n = 1] (mole/l)
0	11.8	0	3.84
15	13.1	1.38	2.45
30	13.5	1.70	2.13
60	13.7	1.86	1.98
120	13.9	2.04	1.80
180	14.2	2.30	1.55

[a] Sodium methoxide, 0.13 mole/l, was added to methyl β-methoxy α-methyl propionate under the usual oligomerization conditions.

An exact kinetic treatment is very complex, but we have shown in the analogous oligomerization of methacrylonitrile by alcoholic solutions of alkoxide, which proceeds according to the same scheme, that it is possible to arrive to an estimation of the value of the rate constants of the various steps of the oligomerization taking into account the reversibility of the initiation reaction, and assuming steady-state conditions for the concentrations of the various anions present in the system. The rate equation derived was

$$\frac{-d[MMA]}{dt} = (k_1[CH_3O^-] + k_3[M_1^-] + k_5[M_2^-])[MMA]_t - k_1'[M_1^-]$$

The values of the rate constants and of the stationary concentrations of the anions in the present oligomerization system were calculated as in the case of methacrylonitrile [2] (Tables 6-8). The values obtained are not exact since the experiments have a certain error factor, and the various calculations lead to a possible error of 5 to 25%.

It can be seen that there is only a small difference between the values of k_1 and k_3, the rate constants of termination and of propagation of M_1^-, and these values are higher than the rate constant for the propagation of M_2^-. Internal association or complex formation of the anion of M_2^- with the oxygens of the first ester group in the chain can lower the activity of this anion for propagation. For this

TABLE 6. Pseudo rate Constants[a]

Run No.	$k_1[CH_3O^-]$	$k_3[M_1^-]$	$k_5[M_2^-]$	$k_4[M_2^-]$	$k_6[M_3^-]$
B	3.7×10^{-4}	19.0×10^{-4}	1.67×10^{-4}	7.2×10^{-3}	6.7×10^{-4}
C	3.06×10^{-3}	5.61×10^{-4}	0.74×10^{-4}	9×10^{-3}	1.4×10^{-4}

[a] The run numbers are as in Table 4. The rate constants are in liter mole^{-1} min^{-1}.

TABLE 7. Stationary Concentration of the Anions[a]

Run No.	$[CH_3O^-]$	$[M_1^-]$	$[M_2^-]$	$[M_3^-]$	$[CH_3O^-]_0$
B	0.0107	0.095	0.049	0.028	0.183
C	0.088	0.026	0.013	0.0058	0.134

[a] The concentrations are in mole/l.

TABLE 8. The Rate Constants[a]

Run No..	k_1	k_3	k_5	k_4	k_6
B	3.4×10^{-2}	2.06×10^{-2}	0.34×10^{-2}	14.7×10^{-2}	2.39×10^{-2}
C	3.4×10^{-2}	2.16×10^{-2}	0.57×10^{-2}	6.9×10^{-2}	2.4×10^{-2}

[a] The rate constants are in liter mole^{-1} min^{-1}.

reason the activities of the oligomeric anions higher than M_2^- are expected to be the same. An interesting observation is that the rate constants for termination k_4 and k_6 are only 2 to 7 times greater than the propagation rate constants.

With lithium methoxide the formation of n = 1 was faster than with the other alkali metal alkoxides. The fact that with lithium the extent of reversibility of the reaction was smaller, as seen from the K_{eq} value, may explain the higher yields obtained with the lithium alkoxide. High association of the lithium alkoxide as well as its more covalent character [3-5] may explain the inability of the $M_1^-Li^+$ to continue propagation.

No simple relationship between $\overline{DP}$ and initiator concentration could be derived, but $\overline{DP}$ increased with an increase of the initiator concentration. The effect of the initiator became more pronounced with a decrease of the [methanol]/[monomer] ratio.

DMSO has a high dielectric constant ($\epsilon = 46.4$) and a higher solvation for cations, so that in this solvent the ion-pairs of both the methoxide initiator and of the growing anions are expected to be more separated. This will lead to higher rates of reaction. The fact that higher oligomers were obtained in DMSO may point out that the influence on the propagation was more than on the initiation. It is also possible that DMSO will solvate the methanol present, and thus lower its effective concentration or the effective [methanol]/[monomer] ratio, and consequently higher oligomers are expected to be formed.

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