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Reactions Catalyzed by Soda Lime Glass. II. Polymerization of Methyl Methacrylate

A. B. MOUSTAFA and M. A. DIAB,* *Laboratory of Polymers and Pigments, National Research Centre, Dokki, Cairo, Egypt*

Synopsis

Rates of sodium bisulfite-initiated polymerization of methyl methacrylate (MMA) in water were determined in the presence and absence of colorless and colored soda lime glass (amber glass). The rate of polymerization increased in the presence of glass. For example, the rate of polymerization increased from 1.3×10^{-5} mole/(l. sec) to 3.9×10^{-5} mole/(l. sec) when amber glass (200 mesh) concentration was varied from 0 to 30 g/l. of the reaction mixture at 40°C. It was found that the finer the particle size of the soda lime glass, the higher was the conversion percentage of monomer to polymer. A glass–polymer combination containing 20 g glass was prepared and subjected to Soxhlet extraction with benzene; the insoluble polymer part was found to increase as initiator concentration was decreased.

INTRODUCTION

Very little is known about the initiation reaction at solid surfaces acting as catalysts and also about the propagation of the polymer chains in the surrounding media. A recent application has been the use of natural sand,[1] soda lime glass,[2] ferric oxide,[3] and graphite and silicon[4] in the manufacture of composite materials which can be used in the production of very useful articles by molding.

Although the kinetics of polymerization reaction of vinyl monomers have been studied both in bulk and in solution, yet a few studies on their polymerization in water medium have been reported using sulfur dioxide[1,5,6] or sodium bisulfite[2,3,4,7] as initiator.

The aim of this work is to find out the effect of colorless and colored soda lime glass (amber glass) on the kinetics of the polymerization reaction of methyl methacrylate in water medium using sodium bisulfite of various concentrations as initiator. However, the effect on the mechanical and electrical properties of the glass–polymer combination will be studied in a future work.[8]

EXPERIMENTAL

Materials

Methyl methacrylate monomer was obtained by the thermal degradation of scrap polymer; the monomer was then dried by anhydrous sodium sulfate and

* Present address: El Nasr Co. for Production of Glass and Crystal, Cairo, Egypt.

TABLE I
Chemical Analysis of the Used Substances

Substance	Chemical analysis, %									
	SiO_2	R_2O_3[a]	CaO	MgO	Fe_2O_3	Na_2O	Na_2CO_3	$NaHCO_3$	NaCl	Na_2SO_4
Sand	96.31	2.06	0.85	0.29	0.22	—	—	—	—	—
Limestone	0.19	0.38	55.20	0.37	—	—	—	—	—	—
Dolomite	1.19	0.31	30.55	20.53	—	—	—	—	—	—
Soda ash	0.18	—	—	—	—	—	98.90	—	0.90	0.12
Sulfate	1.37	—	—	—	—	—	11.74	4.65	0.70	81.76
Amber glass	71.81	1.90	8.81	3.02	0.17	14.35	—	—	—	—

[a] R = Trivalent metal.

fractionated by means of a fractionating column of about 15 theoretical plates and the fraction boiling between 100° and 100.5°C was collected.

Benzene and methanol were products of El Nasr Pharmaceutical Chemical Co., ARE; the nonvolatile matter in each did not exceed 0.005%.

Sodium bisulfite was a product of El Nasr Pharmaceutical Chemical Co. ARE, Laboratory Chemicals Division; assay (SO_2) not less than 60%.

Extraction cups were of the following specifications: fat extracted W&R. Balston Ltd., genuine Whatman extraction thimbles seamless (England).

Preparation of Colored Soda Lime Glass (Amber Glass)

Amber glass was a product of El Nasr Company for production of glass and crystal. It was made from the reaction of Maadi sand (900 parts), sodium carbonate (300 parts), limestone (63 parts), sodium sulfate (12 parts), dolomite (190 parts), and carbon (12 parts) by weight. The reaction mixture was melted at about 1500°C.

The chemical analysis of the used raw materials and glass is given in Table I.

Polymer Preparation

The polymerization of methyl methacrylate was carried out in water medium using sodium bisulfite as initiator at 40°C, in a 250-ml well-stoppered flask. All the calculations were carried out in the same way previously mentioned in part 1.[2] The polymerization was stopped at will by making the polymerization medium fairly alkaline by the addition of sodium hydroxide solution.[7] The sodium hydroxide proved to be an excellent inhibitor. At the end of the polymerization, the reaction mixture was filtered using a Buchner funnel. The precipitate was washed thoroughly with distilled water, methanol, and finally dried at 50°C.

RESULTS AND DISCUSSION

Polymerization of methyl methacrylate (4.7 g) in water (45 ml) was studied in the presence of different amounts of colored soda lime glass (amber glass) varying from 0 to 30 g/l. of the reaction mixture using 0.01 mole/l. sodium bisulfite at 40°C for 4 hr. The data are given in Table II and are represented in Figure 1.

From Table II, it is seen that the rate of polymerization of methyl methacrylate in this system increases with increase in amber soda lime glass up to a con-

TABLE II
Polymerization of Methyl Methacrylate Using Amber Glass

Amber glass weight, g	Glass–polymer combination weight, g	Monomer conversion, %	Polymerization rate × 10^5, mole/(l. sec)
0.00	0.84907	18.07	1.31
0.25	1.15300	24.53	1.78
0.50	1.48316	31.55	2.29
0.75	1.90371	40.50	2.94
1.00	2.31931	49.34	3.58
1.25	2.51829	53.49	3.88
1.50	2.53818	54.00	3.91

TABLE III
Polymer Weights

Run no.	$NaHSO_3$, mole/l.	Reaction time, hr	Weight of poly(methyl methacrylate) formed, g			
				In presence of amber glass		
			In absence	50 mesh	100 mesh	200 mesh
1	0.01	1	0.16059	0.91854	1.22973	1.79992
2	0.01	5	0.91191	2.00051	2.21260	2.76158
3	0.02	1	0.26448	0.98474	1.67644	3.76661
4	0.02	5	1.26802	3.88197	3.95167	4.00959
5	0.03	1	0.32745	1.28186	2.41777	3.82126
6	0.03	5	1.59717	4.06527	4.13528	4.15216
7	0.04	1	0.38849	1.49953	2.97893	3.86218
8	0.04	5	1.45997	4.15312	4.25723	4.24031
9	0.05	1	0.46296	2.01741	3.03043	3.90677
10	0.05	5	1.79192	4.25617	4.25911	4.26073

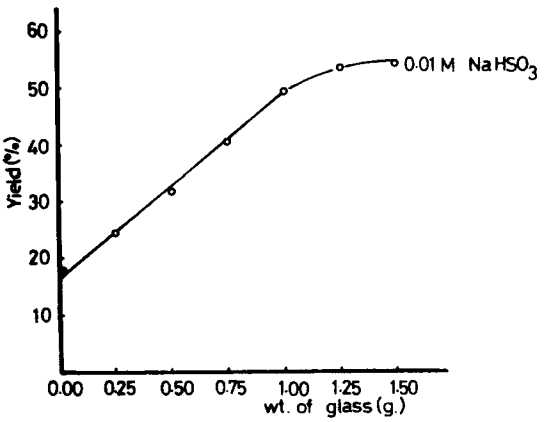

Fig. 1. Effect of amber glass (200 mesh) on conversion (%) of methylmethacrylate.

centration of 1.25 g/50 ml of MMA and water. Further increase of Ambar Glass resulted in a small effect on the rate of polymerization.

An amount (20 g) of amber glass was taken and the polymerization process was run with (4.7 g MMA) and 45 ml water at 40°C. The data are given in Table III.

TABLE IV
Polymerization Rate of Methyl Methacrylate (4.7 g) in Water (45 ml) at 40°C

Run no.	$NaHSO_3$, mole/l.	Rate of polymerization × 10^5, mole/(l. sec)			
			In presence of colorless soda lime glass		
		In absence	50 mesh	100 mesh	200 mesh
1	0.01	1.0	5.5	7.4	8.3
2	0.02	1.6	6.0	10.1	23.0
3	0.03	2.0	7.6	14.1	23.4
4	0.04	2.4	9.1	17.8	23.7
5	0.05	2.9	12.2	18.6	24.0

TABLE V
Rate of Polymerization of Methyl Methacrylate (4.7 g) in Water (45 ml) at 40°C in Presence of Amber Soda Lime Glass

Run no.	$NaHSO_3$, mole/l.	Rate of polymerization × 10^5 in presence of amber glass, mole/(l. sec)		
		50 mesh	100 mesh	200 mesh
1	0.01	5.7	7.5	11.1
2	0.02	6.1	10.3	23.2
3	0.03	7.9	14.9	23.6
4	0.04	9.2	18.3	23.9
5	0.05	12.4	18.6	24.1

The rate of polymerization of methyl methacrylate during the first hour was determined, and the values are given in Table IV, in which it is clear that the rate of polymerization of methyl methacrylate in the presence of colorless soda lime glass exceeded the rate of polymerization of MMA alone. Using an initiator concentration of 0.01 mole/l. sodium bisulfite, the rate of polymerization was 1×10^{-5} mole/(l. sec); it increased to 5.5×10^{-5} mole/(l. sec) when colourless soda lime glass of particle size (50 mesh) was used. Higher rates of polymerization such as 7.4×10^{-5} mole/(l. sec) and 8.3×10^{-5} mole/(l. sec) were obtained when colorless soda lime glass of finer particle size such as 100 and 200 mesh was used, respectively. In experiments 2, 3, and 4, it is visible that the catalytic effect of colorless soda lime glass having a particle size of 50 mesh increased the rate of polymerization by 3.8 times its value in the absence of glass, when an initiator concentration of 0.02, 0.03, and 0.04 mole/l. was used. Using a lower initiator concentration such 0.01 mole/l. resulted in a higher polymerization rate ratio (5.5 times its value when no glass is used). This may be attributed to the higher ions dissociated from the initiator–glass complex and consequently to the formed radicals which are responsible for the polymerization process.[1] Also, when using soda lime glass of particle size 100 mesh, the rate of polymerization increased to a mean value 6.92 times its value when no glass is used; while when using colorless soda lime glass of particle size 200 mesh, the ratio of increase in the rate amounted to 10.5 its value when no glass was used.

Polymerization of methyl methacrylate in the presence of amber soda lime glass was carried out under the same conditions as with colorless soda lime glass. It was found that when a low initiator concentration was used (0.01 mole/l.), the rate of reaction became 11 times greater than when no glass was used (Table V,

TABLE VI

Effect of Amber Soda Lime Glass on Polymerization of Methyl Methacrylate (4.7 g) in Water (45 ml) at 40°C

Run no.	$NaHSO_3$, mole/l.	Reaction time, hr	Monomer conversion, %			
				In presence of amber glass		
			In absence	50 mesh	100 mesh	200 mesh
1	0.01	1	3.42	19.54	26.16	38.29
2	0.01	5	19.83	42.54	47.08	58.75
3	0.02	1	5.63	20.95	35.67	80.14
4	0.02	5	26.97	82.57	84.08	85.31
5	0.03	1	6.96	27.27	51.48	81.32
6	0.03	5	33.98	86.49	87.98	88.34
7	0.04	1	8.18	31.90	63.38	82.17
8	0.04	5	31.06	88.36	90.58	90.22
9	0.05	1	9.85	42.93	64.26	83.12
10	0.05	5	38.10	90.13	90.62	90.66

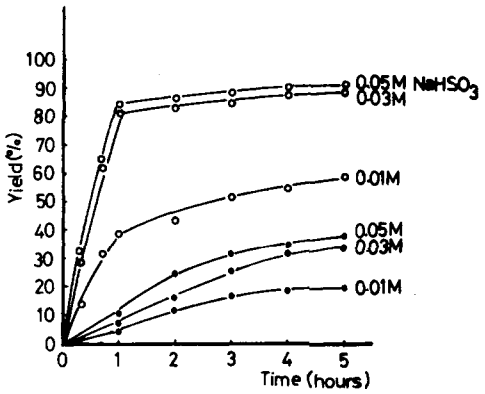

Fig. 2. Polymerization of methylmethacrylate using $NaHSO_3$ as initiator: (●) MMA alone; (○) MMA + amber glass (200 mesh).

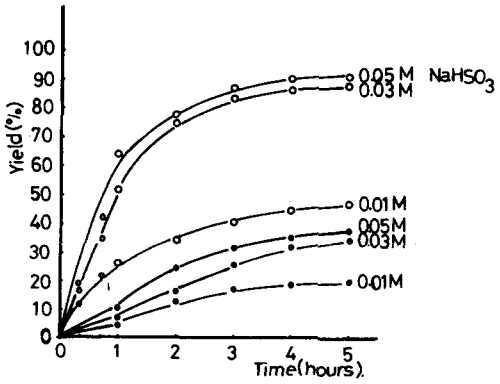

Fig. 3. Polymerization of methylmethacrylate using $NaHSO_3$ as initiator: (●) MMA alone; (○) MMA + amber glass (100 mesh).

TABLE VII
Soxhlet Extraction with Benzene for Glass–Polymer Combination[a]

Run no.	$NaHSO_3$, mole/l.	Amber glass mesh	Total polymer in GPC, %	Soluble polymer in GPC, %	Insoluble polymer in GPC, %
2	0.01	50	28.58	18.46	10.11
	0.01	100	30.68	14.56	16.12
	0.01	200	35.58	8.68	27.17
4	0.02	50	43.71	35.19	8.91
	0.02	100	44.14	33.92	10.21
	0.02	200	44.50	29.41	15.08
6	0.03	50	44.84	40.00	4.84
	0.03	100	45.27	39.70	5.56
	0.03	200	45.36	38.39	6.96
8	0.04	50	45.37	42.95	2.95
	0.04	100	45.99	42.07	3.91
	0.04	200	45.89	40.91	4.97
10	0.05	50	45.98	44.28	1.19
	0.05	100	46.00	44.51	1.73
	0.05	200	46.01	44.43	1.89

[a] GPC = Glass–polymer combination.

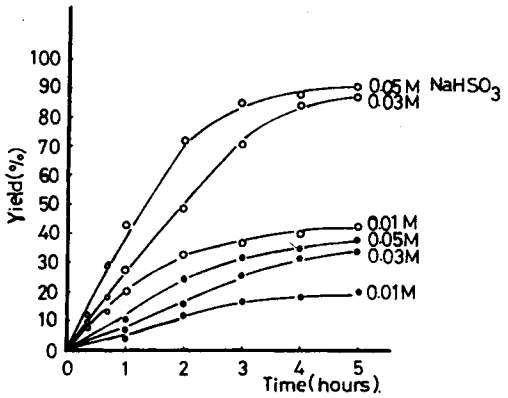

Fig. 4. Polymerization of methyl(methacrylate using $NaHSO_3$ as initiator: (●) MMA alone; (○) MMA + amber glass (50 mesh).

experiment 1). This may be explained in the same way as mentioned in case of colorless soda lime glass.

Comparing the data of Table V with those of Table IV, we deduce that the small change in the structure of soda lime glass by the addition of some carbon to the reaction mixture, which resulted in a partial reduction of some of the sodium sulfate present to sodium sulfide, lead to the formation of highly effective amber soda lime glass, especially when low initiator concentrations were taken into consideration (0.01 mole/l.) where the increase in the rate of polymerization is obvious.

The results of kinetic studies are presented in Figures 2, 3, 4, and 5. It has been noticed that the polymerization starts immediately with the addition of the sodium bisulfite. If the sodium bisulfite solution is left overnight and then used, no polymerization takes place. This is due to the oxidation of the bisulfite to the bisulfate.

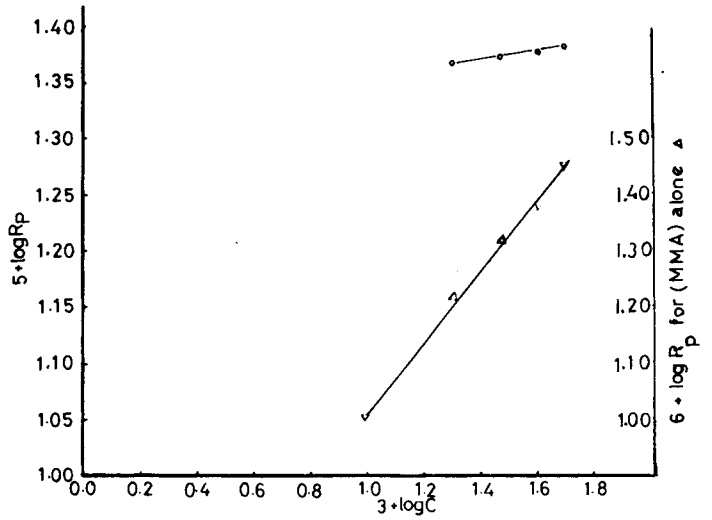

Fig. 5. Rate of polymerization (mole·l.$^{-1}$·sec^{-1}) vs. concentration of $NaHSO_3$ (mole·l.$^{-1}$) in presence of amber glass (200 mesh).

As previously observed in part 1, it has been found that the polymer yield increased greatly with increase of amber glass in the order 200 mesh > 100 mesh > 50 mesh, as shown in Table VI.

The glass–polymer combinations prepared by the polymerization of methyl methacrylate (4.7 g) in 45 ml water in the presence of 20 g soda lime glass for 5 hr at 40°C were subjected to Soxhlet extraction with benzene for 24 hr. The per cent of the soluble and the insoluble part of polymer were determined, and the data are given in Table VII. From Table VII, it is quite visible that the soluble polymer part increases with increase of initiator concentration. In run 2, we find relatively the insoluble part of the polymer is high, which will certainly find application in industry even after being subjected to Soxhlet extraction with benzene.

A little entrapped water causes a higher weight of soluble and insoluble polymer than the total polymer.

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