Iron (II) Chloride Catalyzed Emulsion Polymerization of Methyl Methacrylate Using Different Initiators

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ABSTRACT: The emulsifier and emulsifier-free emulsion polymerization of methyl methacrylate (MMA) using sodium bisulphite, acetaldehyde sodium bisulphite (ACSB), octyladehyde sodium bisulphite (OSB), benzaldehyde sodium bisulphite (BSB), and acetone sodium bisulphite (ASB) as different initiators, and dodecyl benzene sodium sulphonate (DBSS) as an emulsifier, were carried out at 30, 40, and 50°C. The effect of iron (II) chloride on the rate of polymerization and on the viscosity-average molecular weight was investigated. The effect of temperature, iron (II) chloride, and the type of initiator on the tacticity of the obtained polymers was investigated by means of nuclear magnetic resonance (NMR) spectroscopy. The effect of iron (II) chloride and the four carbonyl adducts (ACSB, OSB, BSB, and ASB) on the volume-average diameter and the number of polymer particles per unit volume was investigated. It was found that iron (II) chloride has a pronounced catalytic effect on the emulsion polymerization. The initiating powers of the four carbonyl adducts, ACSB, BSB, OSB, and ASB, were found to be 3.27, 0.6, 1.78, and 0.23, respectively. The rate of emulsion polymerization and viscosity-average molecular weight were found to be dependent on the emulsifier concentration, initiator type and concentration, temperature, and amount of the catalyst (FeCl$_2$). © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 68: 1725–1738, 1998

Key words: emulsifier-free emulsion polymerization; methyl methacrylate; different initiators

INTRODUCTION

The polymerization of methyl methacrylate (MMA) has been carried out in aqueous media by many scientists.[1–5] It was carried out in the absence and presence of some iron salts and complexes.[6] It has been found that the catalytic effect of the salts of some metals (copper, iron, nickel, cobalt, manganese, and sodium) on the aqueous polymerization of MMA initiated by NaHSO$_3$ is attributed to the cations as a major catalytic effect and to the anions as a minor catalytic effect.[7] The carbonyl adducts of NaHSO$_3$ with acetaldehyde, octylaldehyde, benzaldehyde, and acetone can be used as different initiators for the vinyl monomers.[8]

Poly(methyl methacrylate) (PMMA) prepared by the emulsion technique using the bisulphite radical led to the formation of a polymer, which is predominantly syndiotactic in structure.[9,10]

EXPERIMENTAL

The MMA monomer, a product of Merck Schuchardt (yield 99%) stabilized with 14 ppm hydroquinone and specific gravity at 20/4°C (0.942–0.944) was purified by being washed with a small amount of sodium hydroxide solution (3%) and then with distilled water until free from alkali. The MMA monomer was separated with a sepa-

rating funnel and then dried over anhydrous sodium sulphate. Chloroform, acetone, and octylaldehyde (2-ethylhexanal) are products from El Nasr Pharmaceutical Company, Cairo, Egypt. Sodium hydroxide, hydroquinone, and acetaldehyde (yield 99%) are products of Merck Schuchardt. Dodecyl benzene sodium sulphonate was distributed from Sigma Chemical Company.

Iron(II) chloride(technical) is a product Reidel de Haen. ACSB, OSB, BSB, and ASB were prepared by simple nucleophilic attack at the carbonyl carbon by the bisulphite ion.[11]

POLYMERIZATION PROCESS

All the polymerization processes were carried out in a round-bottomed three-necked Q.F. (250 mL) flask equipped with a mechanical stirrer, reflux condenser, and a thermometer for 2 h. The required amount of emulsifier (DBSS) was dissolved in distilled water (100 mL). In the case of using $FeCl_2$ as a catalyst, the calculated amount was dissolved in emulsified distilled water. This mixture was introduced into the flask under low rate of nitrogen bubbling. The next step is the addition of MMA monomer. Finally, the calculated amount of initiator, whatever sodium bisulphite or one of its carbonyl adducts (ACSB, OSB, BSB, and ASB), was introduced as one shot.

In the case of studying the effect of acetaldehyde additions on the polymerization process, acetaldehyde was the last additive to the reaction mixture. The polymerization was then carried out in an automatically controlled water bath at the required temperature with a stirring rate 300 rpm.

DETERMINATION OF INTRINSIC VISCOSITY AND VISCOSITY-AVERAGE MOLECULAR WEIGHTS FOR THE OBTAINED PMMA

PMMA was precipitated by methanol, filtered, and dried in an electric vacuum oven at 40°C for 48 h. The polymer was then soaked in a large amount of distilled water to remove the adsorbed emulsifier ions. The polymer was filtered and dried again in a vacuum oven at 40°C. The intrinsic viscosity (η) for the obtained polymers was determined by the usual method of extrapolation. The viscosity-average molecular weights for the respective polymers were calculated from the following equation[12]:

$$[\eta] = 0.485 \times 10^{-4} \, [\bar{M}_v]^{0.8}$$

The viscosity measurements were carried out in chloroform at 20°C.

RESULTS AND DISCUSSION

Effect of Initiator ($NaHSO_3$) on the Emulsion Polymerization of MMA

The emulsion polymerization of MMA (20 g) in water (100 mL) using $NaHSO_3$ of different concentrations (0.05, 0.075, 0.1, and 0.125 g mol L^{-1}) as an initiator in nitrogen atmosphere and (DBSS) as an emulsifying agent with continuous stirring, was carried out at 40 and 50°C. The data are given in Table I and represented in Figures 1 and 2. The rate of polymerization was determined between 40 and 50% conversion at high rate conditions and between 15 and 20% at low rate conditions. It was recognized that the rate of polymerization was found to increase with an increase of initiator concentration as it increased from 2.92 $\times 10^{-4}$ to 9.25 $\times 10^{-4}$ g mol L^{-1} s^{-1} at 40°C and from 11.11 $\times 10^{-4}$ to 27 $\times 10^{-4}$ g mol L^{-1} s^{-1} at 50°C with an increase of $NaHSO_3$ concentration from 0.075 to 0.125 g mol L^{-1}. As seen from figures 1 and 2, the conversion time plots are characterized by very short induction period approaching a maximum or an inflection point, after which the rate of polymerization becomes approximately constant, that is attributed to the dependence of the rate of polymerization on the monomer concentration; hence, after the inflection point, the monomer concentration becomes very small and approximately, gives, a constant polymerization rate.

As a consequence of increasing the polymerization rate due to the increase of $NaHSO_3$ concentration, the apparent activation energy E_a decreases. It decreased from 112.2 to 90 kJ/mol when the initiator concentration increased from 0.075 to 0.125 g mol L^{-1}. The data are given in Table I.

EFFECT OF THE EMULSIFIER (DBSS) ON THE EMULSION POLYMERIZATION OF METHYL METHACRYLATE

The emulsion polymerization of MMA (20 g) in water (100 mL) using $NaHSO_3$ as an initiator

Table I Polymerization of MMA (20 g) in water (100 mL) in the Absence and Presence of Emulsifier and Ferrous Chloride

Run No.	NaHSO$_3$ (g mol L^{-1})	FeCl$_2$ (g)	Emulsifier (g)	Rate at 40°C (g mol L^{-1} s^{-1} × 10^4)	M_v × 10^{-5}	Rate at 50°C (g mol L^{-1} s^{-1} × 10^4)	M_v (×10^{-5})	Apparent Activation Energy (kJ/mol)
1[a]	0.05	—	—	0.5	10.57	1	7.38	58.17
2[a]	0.05	—	1	3.47	6.25	13.8	3.42	116.40
3[a]	0.05	0.01	—	1.2	4.7	2.31	3.76	54.88
4	0.05	0.005	1	2.78	5.2	7.93	3.93	88
5	0.05	0.01	1	3.26	3.8	9.25	2.6	87.63
6	0.05	0.02	1	5.56	3.1	13.8	1.9	76.4
7	0.05	0.03	1	18.5	2.8	19.15	1.70	2.9
8	0.075	—	1	2.92	4.8	11.11	2.30	112.2
9	0.10	—	1	5.56	4.1	18.5	1.9	101
10	0.125	—	1	9.25	3.40	27	1.75	90

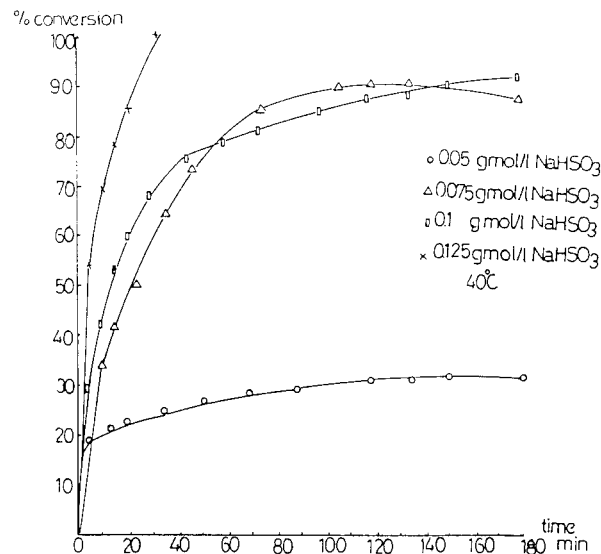[a] For runs 1, 2, and 3, the rate is measured from conversions (15–20%).

Figure 1 Effect of Initiator on polymerization rate at 40°C.

(0.05 g mol L^{-1}) in the presence and in absence of DBSS as an anionic emulsifier was carried out. The rate of polymerization was found to increase from 0.5×10^{-4} to 3.47×10^{-4} g mol L^{-1} s^{-1} when the emulsification with DBSS (1%) was carried out. The data are given in Table I. From Table I, it is clear that the emulsification resulted in decreasing the viscosity-average molecular weight. As it decreased from 10.57×10^5 to 6.25×10^5 at 40°C and from 7.38×10^5 to 3.42×10^5 g mol at 50°C, the emulsion polymerization of MMA (10 g) in water (100 mL) using ACSB, OSB, BSB, and ASB in the presence and absence of
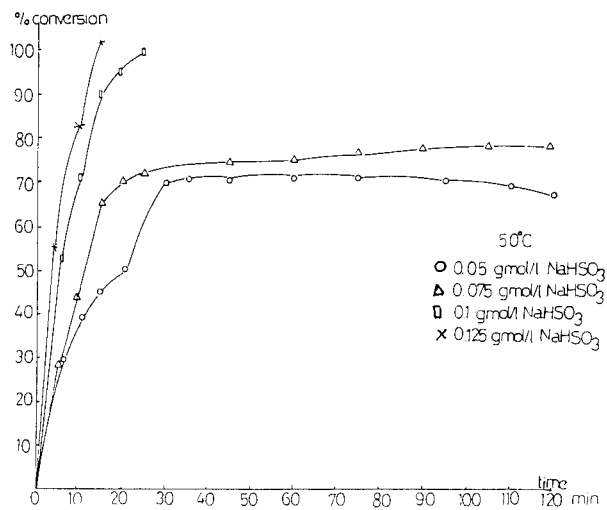

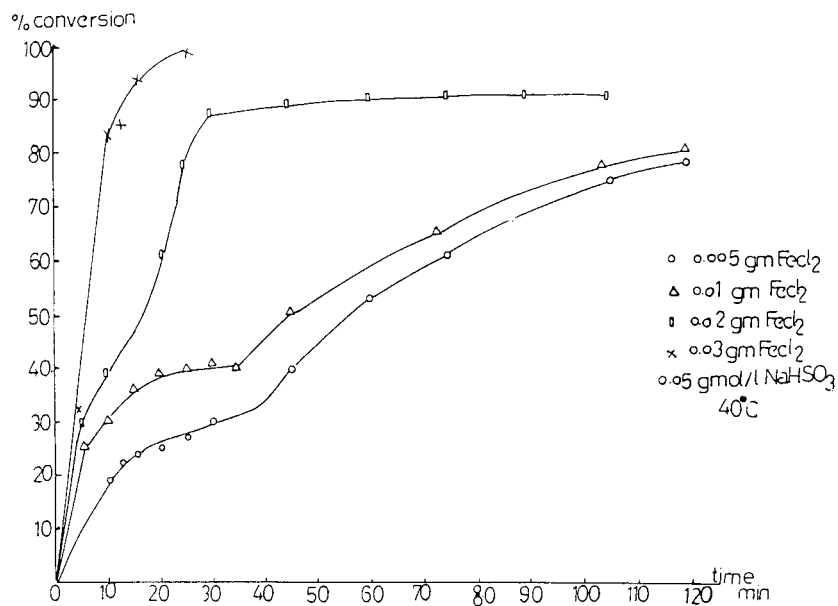**Figure 2** Effect of initiator on polymerization rate at 50°C.

Figure 3   Effect of ferrous chloride on polymerization at 40°C.

DBSS (0.1 and 0.5 g) as an emulsifier was carried out. The rate of polymerization was found to be higher than in case of the emulsifier-free emulsion polymerization under the same reaction conditions. The data are given in Table II. From Table II, the increase of the emulsifier concentration from 0.1 to 0.5 g/100 mL resulted in an increase in the rate of polymerization. It increased from

0.49×10^{-4} to 21×10^{-4} g mol L^{-1} s^{-1} at 30°C and from 1.9×10^{-4} to 43×10^{-4} g mol L^{-1} s^{-1} 40°C when BSB was used as an initiator (0.1 g mol L^{-1}).

The apparent activation energy decreased from 106.7 to 56.6 kJ/mol upon the increase of DBSS concentration from 0.1 to 0.5 g/100 mL water under the same reaction conditions. The viscosity-
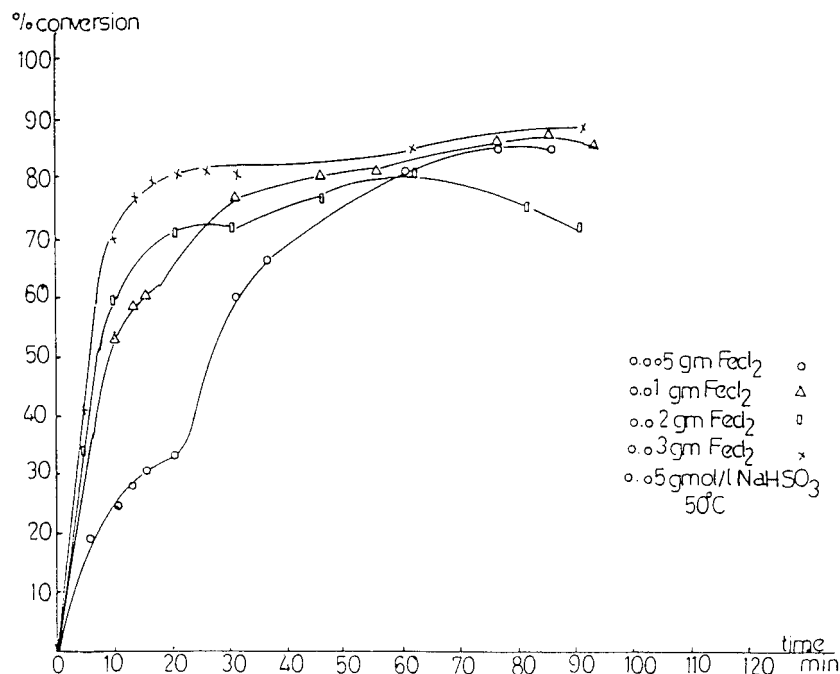

Figure 4   Effect of ferrous chloride on polymerization at 50°C.

Table II   Polymerization of MMA Using Different Initiators

No.	Initiator	Temperature (°C)	Initiator Concentration (g mol L^{-1})	Emulsifier (g)	Rate $\times 10^4$ g mol L^{-1} s^{-1}	$\bar{M}_v \times 10^{-6}$	Apparent Activation Energy (kJ/mol)
1	Acetaldhyde–sodium	30	1.25×10^{-5}	0.1	0.19	1.18	
2	–bisulphite	40	1.25×10^{-5}	0.1	0.95	0.99	126.7
3		30	$2.5\ \ \times 10^{-5}$	0.1	1.5	0.815	
4		40	$2.5\ \ \times 10^{-5}$	0.1	3.0	0.655	54.6
5	Octylaldhyde–sodium	30	0.018	0.1	0.4	0.776	
6	–bisulphite	40	0.018	0.1	1.89	0.497	122.3
7		30	0.027	0.1	2.5	0.313	
8		40	0.027	0.1	5	0.247	54.6
9	Acetone–sodium–	30	0.1	0.1	0.11	0.776	
10	bisulphite	40	0.1	0.1	0.5	0.681	119
11		30	0.15	0.1	0.9	0.41	
12		40	0.15	0.1	1.6	0.27	45
13	Benzaldhyde–sodium	30	0.1	0.1	0.49	0.831	
14	–bisulphite	40	0.10	0.1	1.9	0.776	106.7
15		30	0.15	0.1	1.5	0.601	
16		40	0.15	0.1	2.5	0.497	40.3
17	Benzaldhyde–sodium	30	0.05	0.5	2.1	0.278	
18	–bisulphite	40	0.05	0.5	10	0.137	123
19		30	0.1	0.5	21	0.479	
20		40	0.1	0.5	43	0.262	56.6

The reaction rates are measured from 15–20% conversion.

average molecular weights of the obtained polymers decreased from 0.83×10^6 to 0.479×10^6 g mol at 30°C and from 0.776×10^6 to 0.262×10^6 g mol at 40°C with an emulsifier concentration increase from 0.1 to 0.5 g/100 mL due to the larger number of the formed free radicals Figures 6–9 show the difference between the emulsifier and the emulsifier-free emulsion polymerization of MMA using the carbonyl adducts ACSB, ASB, OSB, and BSB as different initiators. The induction period in the case of emulsifier-free emulsion polymerization when using the initiator ACSB, OSB, and BSB was about 5 minutes, while it reached 20 minutes in the case of using ASB. It was found that the use of higher concentrations of DBSS than 0.5 g/100 mL resulted in complete monomer to polymer conversion and sometimes complete coagulation after a few seconds from the beginning of the reaction, especially in the case of using ACSB as an initiator, so that the concentration of emulsifier DBSS and the temperature were reduced to 0.1 g/100 mL and 30 and 40°C in order to facilitate the kinetic studies.

The polymerization of MMA using different mole proportions of sodium bisulphite to acetaldehyde (1 : 0, 1 : 0.5, 1 : 1, and 1 : 1.5) as separate additives did not succeed in the absence of emulsifier DBSS during the first 2 hours. When the reaction mixture was left for 24 h, the monomer appeared as an upper layer and the aqueous phase became turbid. This confirms the performance of a very low rate of polymerization reaction.

POLYMERIZATION OF METHYL METHACRYLATE USING DIFFERENT INITIATORS

The emulsifier and emulsifier-free emulsion polymerization of MMA using dodecyl benzene sodium sulphonate (0.1 and 0.5%) as an emulsifier and the carbonyl adducts of sodium bisulphite with acetaldehyde, octyladehyde, benzaldehyde, and acetone with continuous stirring (300 rpm) were carried out in a nitrogen atmosphere.

Acetaldehyde sodium bisulphite was found to be the best initiator used for the polymerization. It gave the highest polymerization rate and the highest viscosity-average molecular weight among the rest of the carbonyl adduct initiators. The data are given in Table II. From Table II, the rate of emulsion polymerization increased from
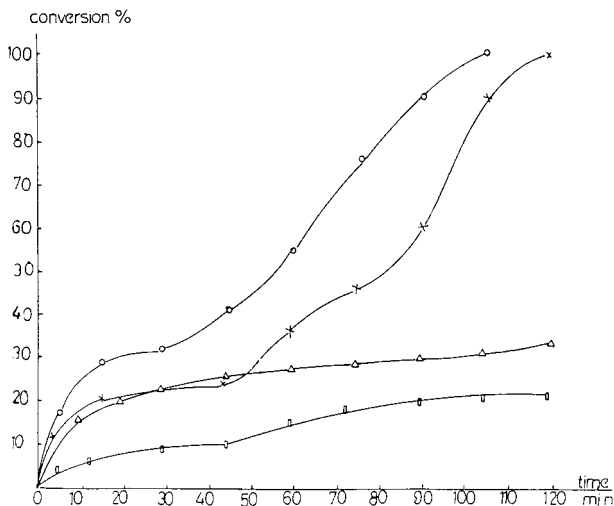
Figure 5 Conversion time curves. Effect of ferrous chloride on the emulsifier-free emulsion polymerization: ($\triangle$) 0.05 g mol L^{-1} NaHSO$_3$, 50°C; ($\bigcirc$) 0.05 g mol L^{-1} NaHSO$_3$, 50°C, 0.1 g FeCl$_2$; ($\square$) 0.05 g mol L^{-1} NaHSO$_3$, 40°C; ($\times$) 0.05 g mol L^{-1} NaHSO$_3$, 40°C, 0.01 g FeCl$_2$.

0.19×10^{-4} to 1.5×10^{-4} g mol L^{-1} s^{-1} at 30°C and from 0.95×10^{-4} to 3×10^{-4} g mol L^{-1} s^{-1} at 40°C when [ACSB] concentration was increased from 1.25×10^{-5} to 2.5×10^{-5} g mol L^{-1}, consequently, the apparent activation energy decreased

from 126.7 to 54.6 kJ/mol when determined between 30 and 40°C. The M_v was decreased from 1.18×10^6 to 0.815×10^6 g mol at 30°C and from 0.99×10^6 to 0.655×10^6 g mol at 40°C upon the same [ACSB] concentration increment. Octylaldehyde sodium bisulphite (2-ethyl hexanal) showed a similar behavior to that obtained by acetaldehyde sodium bisulphite but with lower degree of emulsion polymerization rate-enhancing effect. The rate of polymerization increased from 0.4×10^{-4} to 2.5×10^{-4} g mol L^{-1} s^{-1} at 30°C and from 1.89×10^{-4} to 5×10^{-4} g mol L^{-1} s^{-1} at 40°C when the [OSB] concentration was increased from 0.018 to 0.027 g mol L^{-1}. The apparent activation energy decreased from 122.3 to 54.6 kJ/mol when determined between 30 and 40°C, and M_v decreased from 0.776×10^6 to 0.247×10^6 g mol at 40°C. The chemical structure of the two carbonyl adducts (ACSB) and (OSB) played a catalytic role in the formation and stabilization of the formed free radicals; this is confirmed by carrying the polymerization reactions using the sodium bisulphite alone as initiator at the same [ACSB] and [OSB] concentrations, that is, 1.25×10^{-5} and 0.018 g mol L^{-1}, respectively. Using NaHSO$_3$ (1.25×10^{-5} g mol L^{-1}) failed to initiate the polymerization. While in the second case, NaHSO$_3$ (0.018 g mol L^{-1}) gave a lower polymerization rate compared with its carbonyl adduct. These results are shown in Figures 6 and 7.
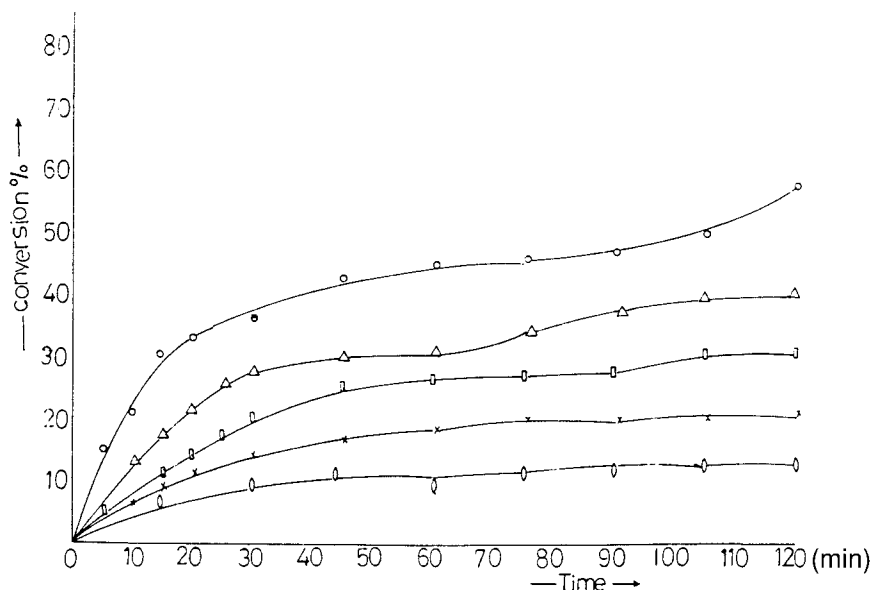

Figure 6 Conversion time curves. Effect of acetaldhyde sodium bisulphite as an initiator: ($\bigcirc$) 2.5×10^{-5} g mol L^{-1}, 40°C; ($\triangle$) 2.5×10^{-5} g mol L^{-1}, 30°C; ($\square$) 1.25×10^{-5} g mol L^{-1}, 40°C; ($\times$) 1.25×10^{-5} g mol L^{-1}, 30°C; and ($\diamond$) 1.25×10^{-5} g mol L^{-1} (emulsifier-free), 40°C.

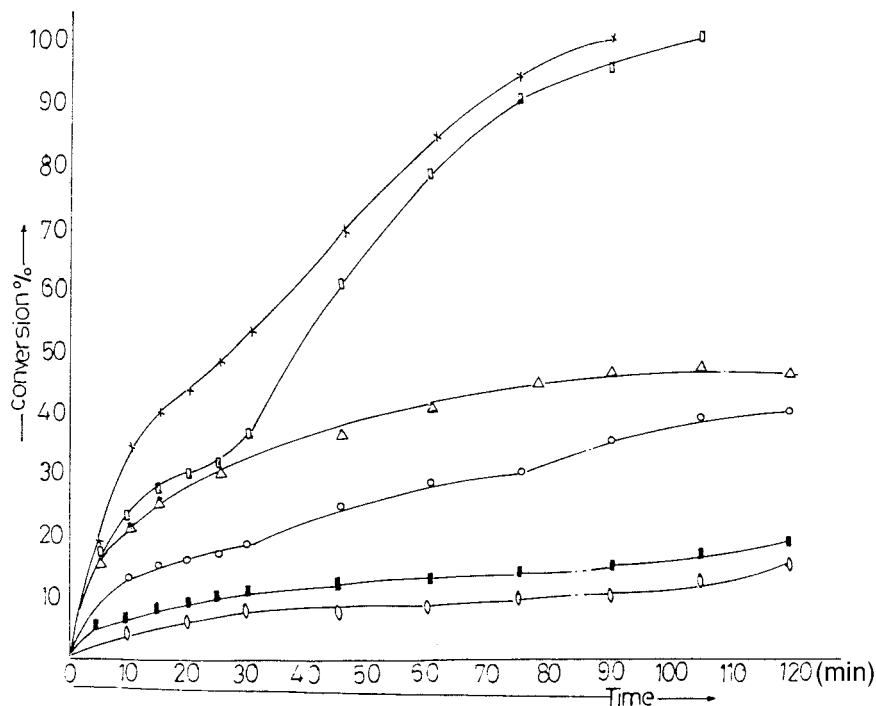**Figure 7** Conversion time curves. Effect of octylaldhyde sodium bisulphite as an initiator: ($\times$) 0.027 g mol L^{-1}, 40°C; ($\square$) 0.027 g mol L^{-1}, 30°C; ($\triangle$) 0.018 g mol L^{-1}, 40°C; ($\bigcirc$) 0.018 g mol L^{-1}, 30°C; ($\diamond$) 0.018 g mol L^{-1} NaHSO$_3$, 40°C; and ($\blacksquare$) 0.018 g mol L^{-1} (emulsifier-free), 40°C.

The rate of emulsion polymerization in the case of using benzaldehyde sodium bisulphite was found to increase with increasing [BSB] concentrations.

The rate of polymerization increased from 0.4 $\times 10^{-4}$ to 1.5 $\times 10^{-4}$ g mol L^{-1} s^{-1} at 30°C when the [BSB] concentration was increased from 0.1
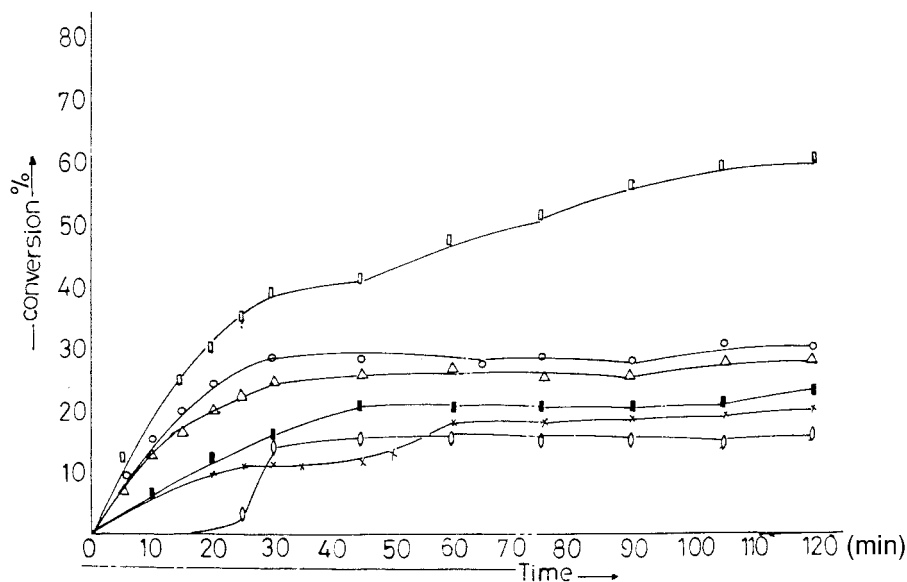

Figure 8 Conversion time curves. Effect of acetone sodium bisulphite as an initiator: ($\bigcirc$) 0.15 g mol L^{-1}, 40°C; ($\triangle$) 0.15 g mol L^{-1}, 30°C; ($\blacksquare$) 0.1 g mol L^{-1}, 40°C; ($\times$) 0.1 g mol L^{-1}, 30°C; ($\square$) 0.1 g mol L^{-1} NaHSO$_3$, 40°C; and ($\diamond$) 0.1 g mol L^{-1} (emulsifier-free), 40°C.
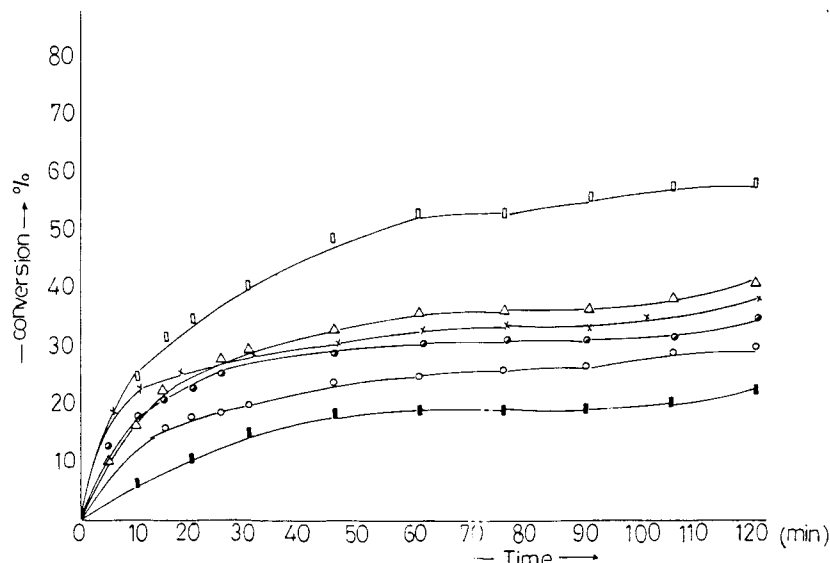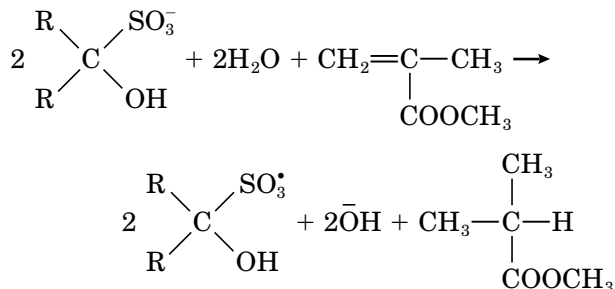
Figure 9 Conversion time curves. Effect of benzaldyde sodium bisulphite as an initiator: (△) 0.1 g mol L^{-1}, 40°C; (×) 0.15 g mol L^{-1}, 40°C; (◓) 0.15 g mol L^{-1}, 30°C; (○) 0.1 g mol L^{-1}, 30°C; (■) 0.1 g mol L^{-1}, 40°C (emulsifier-free); and (□) 0.1 g mol L^{-1} $NaHSO_3$, 40°C.

to 0.15 g mol L^{-1}. Using an equivalent concentration of sodium bisulphite (0.1 g mol L^{-1}) resulted in a higher rate of polymerization compared with that of [BSB]. The apparent energy of activation (E_a) decreased from 106.7 to 40.3 kJ/mol. The viscosity-average molecular weight decreased from 0.831×10^6 to 0.601×10^6 g mol at 30°C and from 0.776×10^6 to 0.497×10^6 g mol at 40°C. The data are given in Table II and represented in Figure 9.

The rate of emulsion polymerization in the case of using acetone sodium bisulphite as an initiator was found to increase with increasing the [ASB] concentration. The rate of polymerization increased from 0.11×10^{-4} to 0.9×10^{-4} g mol L^{-1} s^{-1} at 30°C and from 0.5×10^{-4} to 1.6×10^{-4} g mol L^{-1} s^{-1} 40°C when [ASB] was increased from 0.1 to 0.15 g mol L^{-1}. E_a decreased from 119 to 45 kJ/mol. The viscosity-average molecular weight decreased from 0.776×10^6 to 0.41×10^6 g mol at 30°C and from 0.681×10^6 to 0.27×10^6 g mol at 40°C. Acetone sodium bisulphite showed a similar effect to that of [BSB] such that sodium bisulphite alone (0.1 g mol L^{-1}) resulted in a higher rate of polymerization compared with its acetone adduct; this confirms that ASB and BSB have a rate-retarding effect on the polymerization process. The data are given in Table II and represented in Figure 8. The following illustrates the mechanism of free radical formation and initiation.

Mechanism of free radical formation:

Initiation:
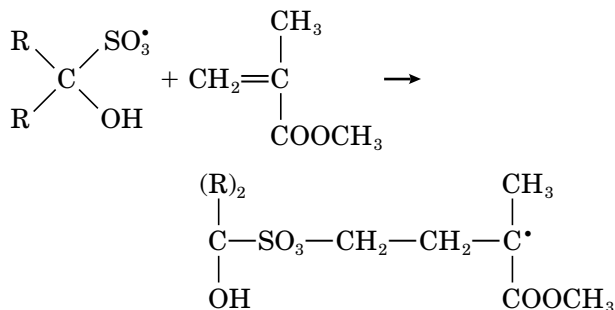
DETERMINATION OF THE INITIATING POWERS OF THE CARBONYL ADDUCTS

A logarithmic plot of the rate versus the concentration of the different initiators, acetaldehyde so-
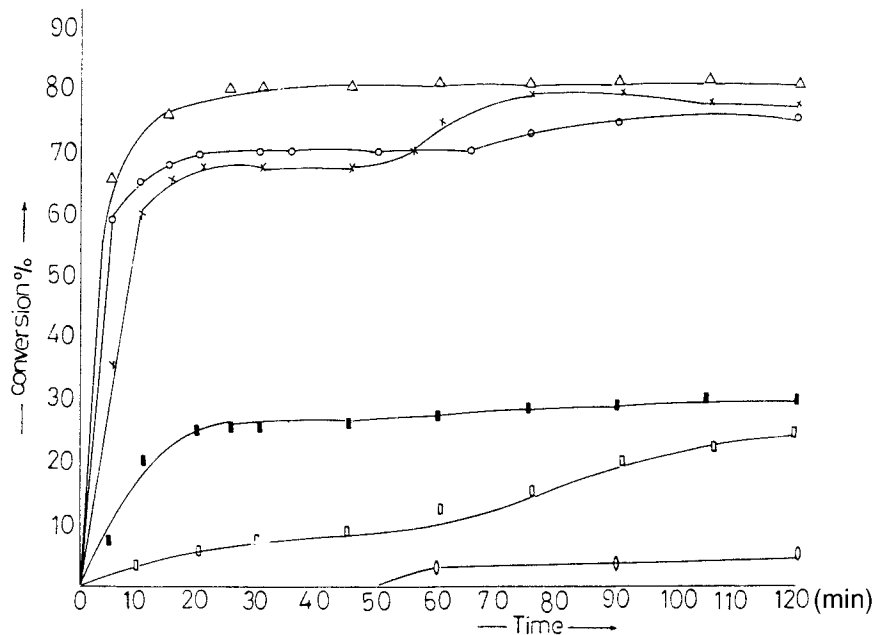
Figure 10 Conversion time curves. Effect of benzaldhyde sodium bisulphite as an initiator at a higher concentration of emulsifier (0.5 g): ($\triangle$) 0.1 g mol L^{-1}, 40°C; ($\times$) 0.1 g mol L^{-1}, 30°C; ($\bigcirc$) 0.05 g mol L^{-1}, 40°C; ($\blacksquare$) 0.05 g mol L^{-1}, 30°C; ($\square$) 0.05 g mol L^{-1} NaHSO$_3$, 40°C; and ($\diamond$) 0.1 g mol L^{-1} (emulsifier-free), 40°C.

dium bisulphite, octylaldehyde sodium bisulphite, benzaldehyde sodium bisulphite, and acetone sodium bisulphite, as represented in Figure 11, showed the initiating powers of 3.27, 1.78, 0.6, and 0.23, respectively. The data given in Table II show that the increase of the adduct chain length decreases the rate of emulsion polymerization.

The initiating power of octylaldehyde sodium bisulphite reached approximately half that of the acetaldehyde sodium bisulphite.

The effectiveness of the carbonyl adduct initiator is a counterplay of three main factors as follows: first, to what extent the emulsified solution of MMA (pH 6) can regenerate the carbonyl
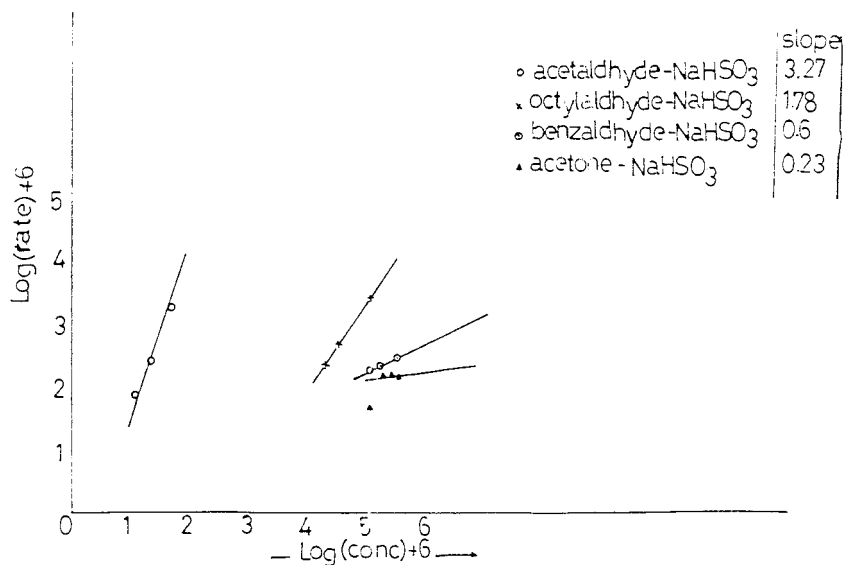

Figure 11 Plot of log (rate) versus log initiator concentration.

Table III   Effect of Acetaldehyde on the Emulsion Polymerization of MMA

No.	[NaHSO$_3$] g mol L^{-1}	Temperature (°C)	Acetaldhyde (g mol L^{-1})	Rate $\times 10^4$ g mol L^{-1} s^{-1}	Apparent Activation Energy (kJ/mol)
1	0.10	30	0.0	2.2[a]	42.6
2	0.10	40	0.0	3.78	—
3	0.10	30	0.05	1.16	93
4	0.10	40	0.05	3.78	—
5	0.10	30	0.10	0.75	95
6	0.10	40	0.10	2.5	—
7	0.10	30	0.15	0.22	164.6
8	0.10	40	0.15	1.78	—

[a] The reaction rates are measured from 5–10% conversion.

group[11]; second, to what extent the reaction between the free radical on the carbonyl adduct and the monomer molecule is sterically hindered[8]; and third, to what extent the formed free radical is stabilized by first- and/or second-order resonance.[13] The sum of the abovementioned three factors determines the initiating power of the carbonyl adducts.

EFFECT OF FERROUS CHLORIDE ON THE EMULSION POLYMERIZATION OF MMA

The emulsion polymerization of MMA (20 g) was studied using sodium bisulphite (0.05 g mol L^{-1}) as an initiator and dodecyl benzene sodium suphonate as an emulsifier in the absence and presence of ferrous chloride at 40 and 50°C. The data are given in Table I. From Table I, ferrous chloride was found to have a pronounced catalytic effect on the emulsion polymerization. The rate of polymerization increased from 2.78×10^{-4} to 18.5×10^{-4} g mol L^{-1} s^{-1} at 40°C and from 7.93×10^{-4} to 19.15×10^{-4} g mol L^{-1} s^{-1} at 50°C when the amount of FeCl$_2$ increased from 0.005 to 0.03 gm/100 mL. Figures 3 and 4 show the dramatic changes in the rate of emulsion polymerization upon the addition of small amounts of FeCl$_2$. The above results are attributed[6] to the redox reaction of FeCl$_2$ and NaHSO$_3$, which generates much more free radicals than NaHSO$_3$. Figure 3 shows that complete conversion at 40°C was reached using FeCl$_2$ (0.03 g/100 mL); this was not the case at 50°C using the same FeCl$_2$ concentration; the polymerization reaction was not able to reach 100% conversion. This may be attributed to the increase of the rate of termination, which is confirmed by the lower $\bar{M}_v$ values. The apparent activation energy is greatly affected. The data given in Table I show that the apparent activation energy between 40 and 50°C decreased from 88 to 2.9 kJ/mol with increasing FeCl$_2$ concentration from 0.005 to 0.03 g/100 mL water. The emulsion polymerization of MMA (10 g) was studied using DBSS (0.1 g) as an emulsifier and ACSB (2.5×10^{-5} g mol L^{-1}), ASB (0.1 g mol L^{-1}), OSB

Table IV   Effect of Concentration of Different Initiators on the Tacticity of PMMA

No.	Initiator	Concentration (g mol L^{-1})	Syndiotactic Percentage	Heterotactic Percentage	Isotactic Percentage
1	Benzaldhyde–sodium–bisulphite	0.1	59.2	36.2	4.5
2		0.15	71	25.5	3.4
3	Octylaldhyde–sodium–bisulphite	0.018	54.27	44.4	1.3
4		0.027	72.38	26.53	1.08
5	Acetone–sodium–bisulphite	0.1	65.12	31.4	3.4
6		0.15	61.2	33.15	5.65
7	Acetaldhyde–sodium–bisulphite	1.25×10^{-5}	75	22	3
8		2.5×10^{-5}	57.58	40	2.5

Table V   Effect of Temperature and FeCl$_2$ on the Tacticity of PMMA

Temperature (°C)	Syndiotactic (%)	Heterotactic (%)	Isotactic (%)	FeCl$_2$ (g)
40	50.1	36.8	13.1	0.01
50	59.0	32.9	8.1	0.01
40	62.38	34.45	2.7	—

(0.018 g mol L^{-1}), and BSB (0.1 g mol L^{-1}) as different initiators in the presence of 0.005 g FeCl$_2$. The four reactions were accompanied by partial and sometimes complete coagulation, which is attributed to the adsorption of positive Fe^{2+}, Fe^{3+}, and negative Cl$^-$ ions on the polymer particles leading to coalescence.

EFFECT OF FERROUS CHLORIDE ON THE EMULSIFIER-FREE EMULSION POLYMERIZATION

The emulsifier-free emulsion polymerization of methyl methacrylate at 40 and 50°C was studied using sodium bisulphite (0.05 g mol L^{-1}) as an initiator in nitrogen atmosphere, in the absence and presence of ferrous chloride (0.01 g/100 mL). The data are given in Table I. From Table I, ferrous chloride was found to have a pronounced catalytic effect on the emulsifier-free emulsion polymerization. The rate of polymerization increased from 0.5×10^{-4} to 1.2×10^{-4} g mol L^{-1} s^{-1} at 40°C and from 1×10^{-4} to 2.31×10^{-4} g mol L^{-1} s^{-1} at 50°C when FeCl$_2$ (0.01 g) was added to

Figure 12   Conversion time curves. Effect of acetaldehyde additions on the emulsion polymerization of MMA initiated by 0.1 g mol L^{-1} NaHSO$_3$, 30°C: ($\triangle$) 0.0, ($\square$) 0.05, ($\bigcirc$) 0.1, and ($\times$) 0.15 g mol L^{-1}.

the reaction mixture, and the apparent activation energy decreased from 58.17 to 54.88 kJ/mol upon the addition of FeCl$_2$ (0.01 g). Figure 5 shows the pronounced effect of FeCl$_2$ upon the rate of polymerization. As in the case of emulsified polymerization, FeCl$_2$ also decreased the viscosity-average molecular weights of the obtained polymers. Table I shows that FeCl$_2$ (0.01 g) decreased the $\bar{M}_v$ from 10.57×10^5 to 4.7×10^5 g mol at 40°C and from 7.38×10^5 to 3.76×10^5 g mol at 50°C.

EFFECT OF FERROUS CHLORIDE ON THE TACTICITY OF THE OBTAINED PMMA

The nuclear magnetic resonance (NMR) spectra of the polymer samples were carried out by using a Varian 200 MHz spectrometer. The polymer samples were dissolved in deuterated chloroform (8 wt %) containing a small amount of tetramethylsilane as an internal standard. The structure was determined from the areas under the peaks[9] and are reported in terms of percentages isotactic (I), heterotactic (H), and syndiotactic (S). Figures 21 and 22 show two NMR spectra of PMMA, with the second prepared in the presence of FeCl$_2$ (0.01 g/100 mL). Table V shows that FeCl$_2$ causes an increase in syndiotactic structure percentage from 50.1 to 62.38%; on the other hand, it decreased both the heterotactic and isotactic structures from 36.8 to 34.45% and from 13.1 to 2.7%, respectively.

EFFECT OF TEMPERATURE ON THE PREPARED PMMA

A typical NMR spectra of the PMMA samples prepared in the presence of ferrous chloride (0.005 g) as a catalyst and NaHSO$_3$ (0.05 g mol L^{-1}) as an initiator at 40 and 50°C are shown in Figure 22, and the data are given in Table V. From Table V, it is clear that rise of temperature from 40 to 50°C caused an increase in the syndiotactic structure percentage from 50.1 to 59.1% and decreased
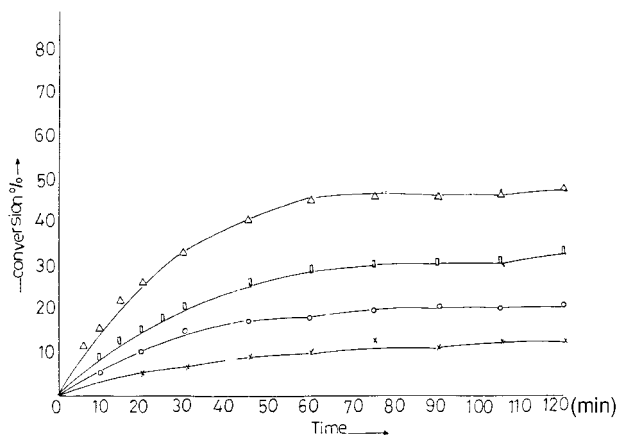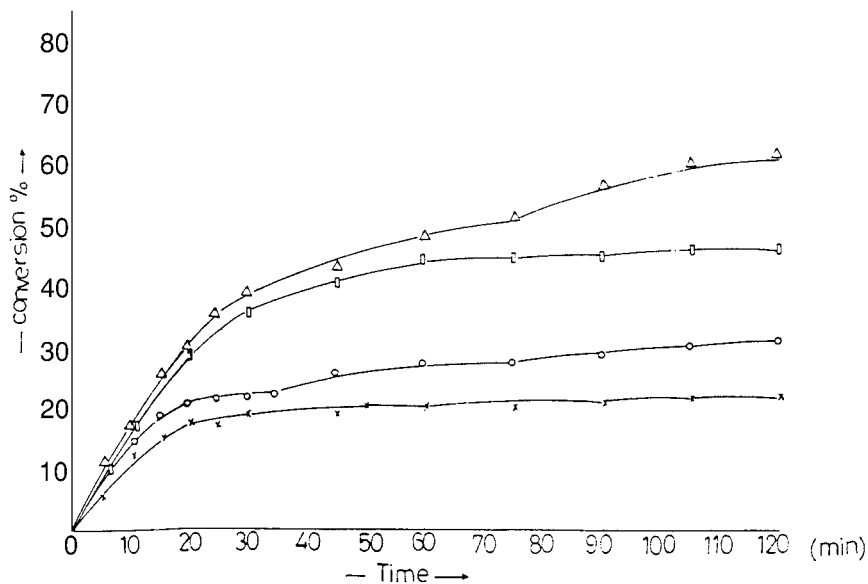
Figure 13   Conversion time curves. Effect of acetaldhyde additions on the emulsion polymerization of MMA initiated by 0.1 g mol L^{-1} NaHSO$_3$, 40°C: ($\triangle$) 0.0, ($\square$) 0.05, ($\bigcirc$) 0.1, and ($\times$) 0.15 g mol L^{-1}.

the heterotactic structure percentages from 36.8 to 32.9%, respectively.

EFFECT OF INITIATOR TYPE AND CONCENTRATION ON THE TACTICITY OF PMMA

The emulsion polymerization of methyl methacrylate using dodecyl benzene sodium sulphonate (0.1 g per 100 mL water) as an emulsifying agent at 40°C and the four carbonyl adducts, namely, acetaldehyde, octylaldehyde, benzaldehyde, and

acetone sodium bisulphite, as different initiators was carried out in nitrogen atmosphere. The tacticity of the obtained polymers was determined with a Varian 200 MHz spectrometer. The data are given in Table IV. From Table IV, acetaldehyde sodium bisulphite gave the best stereoregular structure of the PMMA as it yielded 75% syndiotactic structure. However, octylaldehyde sodium bisulphite gave an undesirable stereoregularity as it yielded the highest heterotactic structure percentage (44.4%). The NMR spectra are shown in figures 23 to 30. From Table IV, it was found that the increase of both the initiator con-
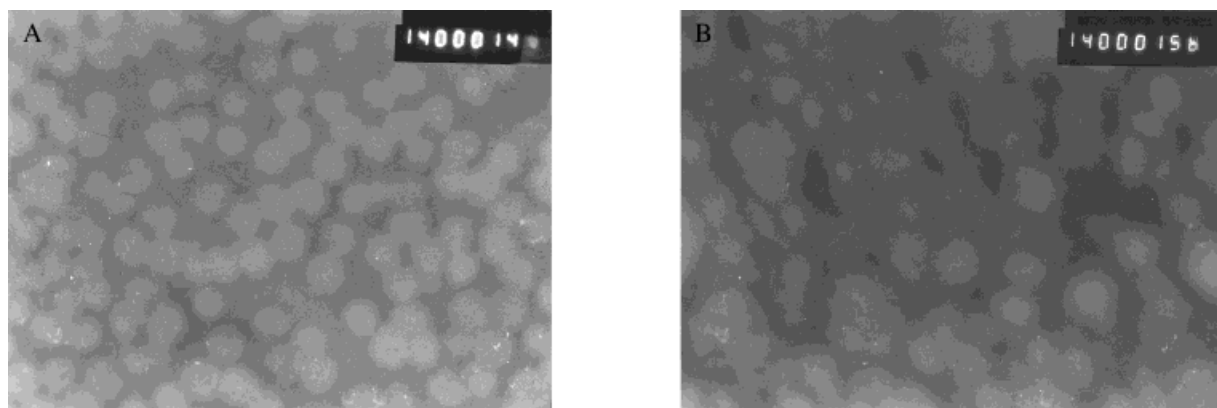
Photographs A–B.   Effect of FeCl$_2$ on the morphological characteristics of polymer particles (Magnification power 14 × 10^4). A: 0.05 g mol L^{-1} NaHSO$_3$. B: 0.05 g mol L^{-1} NaHSO$_3$ + 0.005 g/100 mL water FeCl$_2$.

**Table VI   Number of Particles per cm^3 (N_t) and Volume-Average Diameter (D_v) of PMMA Latex**

Sample Property	A	C	D
N_t	2.58×10^{19}	7.75×10^{18}	1.2×10^{18}
D_v (nm)	1.88	2.3	4.13

centrations of [BSB] and [OSB] from 0.1 to 0.15 g mol L^{-1} and from 0.018 to 0.027 g mol L^{-1}, respectively, resulted in an increase in both the heterotactic and isotactic structure percentages.

On the other hand, the increase in the [ASB] and [ACSB] concentration from 0.1 to 0.15 g mol L^{-1} and from 1.25×10^{-5} to 2.5×10^{-5} g mol L^{-1}, respectively, led to a decrease in the syndiotactic and an increase in both the heterotactic and the isotactic structures.

EFFECT OF ACETALDEHYDE ADDITION ON THE EMULSION POLYMERIZATION OF METHYL METHACRYLATE

The data for the emulsion polymerization of MMA using dodecyl benzene sodium sulphonate (0.1 g) as an emulsifying agent and sodium bisulphite (0.1 g mol L^{-1}) as an initiator in both the absence and presence of different mole proportions of NaHSO$_3$ to acetaldehyde (1 : 0, 1 : 0.5, 1 : 1, and 1 : 1.5) are given in Table III. From Table III, the polymerization rate was found to decrease with an increase of acetaldehyde addition. It decreased from 3.78 to 1.78 g mol L^{-1} s^{-1} at 40°C and from 2.2 to 0.22 g mol L^{-1} s^{-1} at 30°C as a consequence of the rate retardation effect. The apparent activation energy was increased from 42.6 to 164.6 kJ/mol. Figures 12 and 13 represent the conversion time curves at 30 and 40°C. With regard to Figures 12 and 13, it was found that the polymeriza-
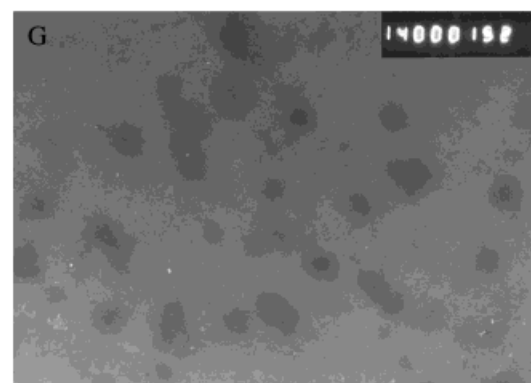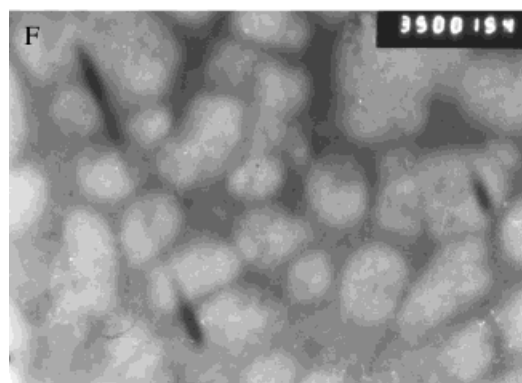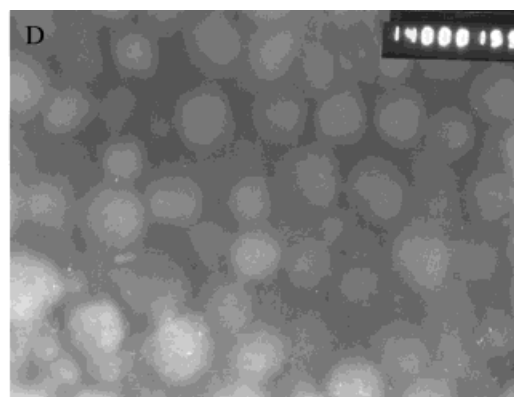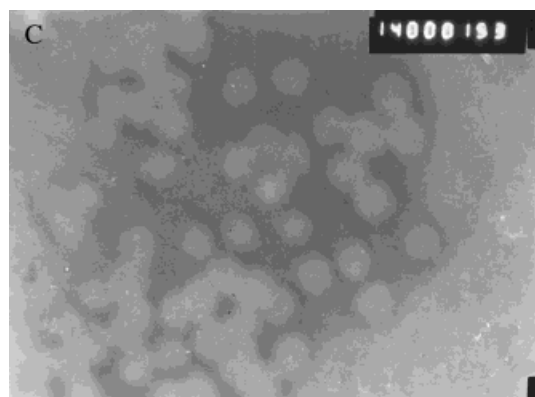
Photographs C, D, F, and G.   Effect of bisulphite adducts of different chain lengths on the morphological characteristics of polymer particles: C (ACSB), D (OSB), F (BSB), G (ASB).

tion reaction curve reaches an inflection point after 20 min at 40°C and after 60 min at 30°C. Beyond this point, no monomer was polymerized. This is attributed to the presence of acetaldehyde, which acts as a strong transfer agent. The transfer constant[9] of acetaldehyde was found to be 6.5 $\times$ 10^4 at 60°C.

These results diminished the probability of acetaldehyde sodium bisulphite formation during the reaction because its presence in very low concentration, up to 10^{-5} g mol L^{-1}, affects the polymerization reaction rate dramatically.

EFFECT OF FERROUS CHLORIDE AND THE FOUR CARBONYL ADDUCTS ON THE PARTICLE SIZE AND THE PARTICLE SIZE DISTRIBUTION OF PMMA

Two samples (A and B) of PMMA emulsion were prepared using NaHSO$_3$ (0.05 g mol L^{-1}), MMA (20 g), and DBSS (1.0 g/100 mL water) as an emulsifier at 40°C. Sample B was catalyzed by 0.005 g FeCl$_2$.

The two samples were imaged by the transmission electron microscopy (TEM) via a magnification power of 140,000. Photographs (A and B) show that FeCl$_2$ (0.005 g) result in the formation of irregularly shaped particles and in an ununiformity in the shape of the particle size.

Four samples of PMMA were prepared using MMA (10 g) and DBSS (0.1 g/100 mL water) as an emulsifier, ACBB (2.5 $\times$ 10^{-5} g mol L^{-1}), OSB (0.018 g mol L^{-1}), BSB (0.1 g mol L^{-1}), and ASB (0.1 g mol L^{-1}) as different initiators at 40°C.

The four samples, photographs C, D, F, and G of ACSB, OSB, BSB, and ASB, respectively were imaged by TEM via a magnification power 140,000, except sample F, which was magnified at 35,000 due to its coarse particle nature. It was found that, the use of the initiators NaHSO$_3$, ACSB, and OSB produce regular emulsion latex particles, while BSB and ASB produce irregular emulsion latex particles.

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