Heterogeneous Polymerization of Some Methacrylate Monomers

ABDALLA B. MOUSTAFA, JOHN R. EBDON,* and BARRY J. HUNT,*
Laboratory of Polymers and Pigments, National Research Centre, Dokki, Cairo, Egypt

Synopsis

It has been found that sodium metabisulphite failed to initiate the polymerization of methyl and butyl acrylates but succeeded in polymerizing methyl, ethyl, and hydroxy propyl methacrylates. All the samples of the poly(hydroxypropyl methacrylates) were crosslinked, even those prepared at low conversions. Gel permeation chromatographic analysis indicated a multinodal molecular weight distribution, suggesting the existence of more than one mechanism occurring in such a heterogeneous system. It has also been proved by electron spin resonance that the polymerization process, using sodium bisulphite as the initiator in such a system, is a radical mechanism. The use of substances such as quartz, glass powder, and kaoline powder enabled the detection of the bisulphite radicals by trapping them. Using ^{13}C NMR spectroscopy, the estimated triad fractions from α-methyl peaks and from quaternary carbon peaks of the poly(methyl methacrylates) and poly(ethyl methacrylates) showed that the polymers obtained were all predominantly syndiotactic in structure, as expected. The poly(ethyl methacrylate) samples were found to have a slightly higher syndiotacticity than the poly(methyl methacrylates), also as expected. The greater bulk of the ethyl ester group relative to that of the methyl ester group probably leads to greater steric hindrance in the isotactic and heterotactic triad (i.e., in a mesodyad).

INTRODUCTION

Although many publications dealing with the polymerization of some vinyl monomers in water using sulphur dioxide or sodium bisulphite as initiator have recently appeared,[1–13] very little work on the tacticity of the polymers prepared by this method has been published.[14]

In this work, ^{13}C spectroscopy was used to determine the tacticity of the polymers obtained. Gel permeation chromatography (GPC) was used to determine their average molecular weights and electron spin resonance (ESR) and to prove that the polymerization process in such a system takes place according to a radical mechanism.

EXPERIMENTAL

Materials

Methyl methacrylate, supplied by BDH Laboratory Chemicals Ltd., Poole, England, was stabilized with 0.1% hydroquinone; the minimum assay was 99.5%.

Ethyl methacrylate, a product of Koch-Light Laboratories Ltd., Coinbrook, Bucks, England, was stabilized with 0.1% hydroquinone.

---

* Also at Department of Chemistry, University of Lancaster, Lancaster, England.

Hydroxy propylmethacrylate, a product of the Imperial Chemical Industries Ltd., Mond Division, Research Department, Widnes, had a weight per ml at 20°C (0.953–0.955 g); the boiling range of 95% is 79°–81°C and was stabilized with 0.02% 4-methoxy phenol.

Sodium metabisulphite, a BDH Laboratory Chemicals reagent, had a minimum assay iodometric 90% $Na_2S_2O_5$; maximum limits of impurities, chloride [Cl, 0.1%; iron (Fe), 0.01%].

Sodium hydroxide pellets, a product of May and Baker Co. Ltd., Dagenham, England, had an assay not less than 96% NaOH.

Kaoline was a laboratory reagent purified product from Hopkin and Williams, Chadwell Heath, Essex, England.

Titanium dioxide was a BDH Laboratory reagent, with an assay (ex Ti not less than 98%); the loss on ignition is not more than 0.5%, and the iron content is not more than 0.05%.   ex ≡ extracted or determined from gravimetric analysis

Soda lime glass a product of Ballotini Manufacturing Co. Ltd., 5000, Barnsley, Yorkshire, England; had a particle size less than 10 μm.

Polymer Preparation

The polymerizations were carried out in either 250 or 1000 ml conical flasks equipped with well-fitting stoppers.   The monomer was added to the water in the absence or presence of the inorganic substance under consideration (glass, Kaoline, titanium dioxide); finally, the initiator (sodium metabisulphite) was added.   The reaction flasks were put in a thermostatically controlled water bath at 40°C.   In some of the experiments, the reaction mixture was shaken for 1 sec every 10 min for a total of 1 hr.   In low-conversion experiments, the 1 sec shaking was carried out every 15 min for a total of 45 min, and for high conversions, every 15 min for a total of 16 hr.   The polymerization reaction was stopped by the addition of a few drops of a 10% sodium hydroxide solution.   The reaction mixture was poured into a beaker containing methanol (500 ml), stirred for 15 min, and filtered through a sintered glass funnel (G3).   The polymer was washed thoroughly with distilled water, until the filtrate was neutral, then washed with methanol (100 ml), and finally dried under vacuum at room temperature.   The conversions were calculated as described in a previous publication.[3]

Preparation of Polymer Solution for Gel Permeation Chromatography

A solution of the polymer in pure chloroform (AR) (0.5%) was prepared, filtered under pressure using a sartorius membrane filter (GmbH 34 Göttingen, West Germany) having a pore size of 0.8 μm.

Determination of Average Molecular Weights by Gel Permeation Chromatography

The average molecular weights were determined by gel permeation chromatography (GPC) using a Waters Associates Liquid Chromatograph ALC/GPC 502.

The instrument was equipped with columns 16 ft long by ³⁄₈ in. diameter packed with Styragel having a linear pore-size distribution up to 10^5 Å.   The

eluent was monitored by a differential refractometer (Waters Associates, Model 401) and an infrared detector (Wilks Miran I variable filter infrared Analyzer; Techmation Ltd., 58 Edgware Way, Edgware, Middlesex). The refractometer was used at an attenuation setting of 4. The IR detector gave a linear absorbance scale (0.25 absorbance units for full-scale deflection). The wavelength was set at 5.8 μm in order to monitor the carbonyl band. A slit width of 2 mm was used. The instrument was operated with chloroform as solvent at a flow rate of 1 ml min^{-1}.

The gel permeation chromatographic runs were carried out on a 0.5% W/V polymer solution in chloroform. The chromatograms were analyzed by measuring the curve heights at half count (2.5 ml) intervals after construction of the suitable base line.

The average molecular weights for the first set of experiments[1–12] were calculated using a polystyrene calibration and a Q factor of 39, where Q is the effective molecular weight per Å chain length. The number average molecular weight is $\overline{M}_n = \overline{A}_n Q$; the weight average molecular weight is $\overline{M}_w = \overline{A}_w Q$, where

$$\overline{A}_n = \frac{\sum H_i}{\sum (H_i/A_i)} \text{Å}, \quad \overline{A}_w = \frac{\sum (H_i \cdot A_i)}{\sum H_i} \text{Å}$$

H_i is the height under the peak and A_i is the chain length of the calibration sample (polystyrene) at the same elution volume.

The ESR apparatus used was a Varian E3 with a variable temperature accessory. Since the spectra were recorded in aqueous solution, it was necessary to record the spectra at $-10°$C. Since the spectra were generally of low intensity, the instrument was operated at a relatively high modulation amplitude and receiver gain. The operating conditions used for ESR spectra were: scan range, $\pm 0.5 \times 10^3$ G; time constant, 3 sec; modulation amplitude, 10 G; receiver gain, 8×10^5; microwave power, 10 mW; field, 3400 G; scan time, 2 min; and microwave frequency, 9.29 GHz.

The ^{13}C NMR spectra were recorded on 10% W/V solutions in CDCl$_3$ on a Varian CFT 20, 20 MHz ^{13}C NMR spectrometer. The relevant operating conditions were: sweep width, 4000 Hz (equivalent to 200 ppm); acquisition time (for 4096 data points), 0.511 sec; pulse width, 12 μsec (equivalent to a tip angle of approximately 50°); and number of transients, minimum: 50,000, maximum: 100,000.

RESULTS AND DISCUSSION

The polymerization of methyl methacrylate (MMA), ethyl methacrylate (EMA), hydroxy propyl methacrylate (HPMA), methyl acrylate (MA), and butyl acrylate (BA) were carried out at 40°C in water using sodium metabisulphite as the initiator for different periods of time. The data are given in Table I.

From Table I, we find that the conversion of the monomer in run 4 is the highest, and that the average molecular weight of the poly(methyl methacrylate) obtained was found to be higher than that of the polymer obtained in run 3 as expected. This is due to the fact that sodium metabisulphite ionizes in water saturated with a monomer to a lesser degree than in pure water, and so the number of radicals produced from the bisulphite ions will be small; consequently,

TABLE I
Polymerization of Some Vinyl Monomers at 40°C Using Sodium Bisulphite (0.05 mol/l) as Initiator

Run no.	Reaction time, min.	Reaction flask capacity, ml	Water volume, ml	Monomer Type	Monomer wt. g	Con-version, %	Average molecular weights × 10^{-5} $\overline{M}_w$	$\overline{M}_n$	Molecular weight distribution, $\overline{M}_w/\overline{M}_n$
1	60	250	100	MMA	4.7000	21.6	—	—	—
2	60	250	100	MMA	9.4000	9.4	—	—	—
3	60	1000	100	MMA	9.4000	14.5	4.90	1.54	3.2
4	60	1000	672	MMA	9.4000	31.5	6.53	1.89	3.2
5	45	250	100	MMA	4.700	5.9	4.00	3.10	1.3
6	45	250	100	MMA	9.4000	7.7	5.05	0.97	5.2
7	60	250	100	HPMA	5.7210	3.9	—	—	—
8	45	250	100	EMA	7.4660	5.2	2.88	0.09	3.2
9	60	250	100	HPMA	7.4360	7.5	—	—	—
10	60	250	100	EMA	5.6860	6.6	—	—	—
11	60	250	100	MA	4.3110	Nil	—	—	—
12	60	250	100	BA	6.408	Nil	—	—	—

the number of monomer molecules initiated by the radicals produced will be small and this will result in larger average molecular weights. The formation of radicals can be expressed in the same way as given in a previous publication.[3]

The molecular weight distribution of the polymers obtained, with the exception of that in run 8, lie between 1.3 and 5.2; in run 8, it amounts to 32. This is due to the long low molecular weight tail obtained in the GPC trace, which decreases the number of average molecular weight and, consequently, increases the molecular weight distribution. We also noted that the sodium metabisulphite initiator failed to initiate the polymerization of methyl acrylate and butyl acrylate since no polymer was obtained.

A polymerization reaction of the same type also takes place in the monomer phase; the only difference is that the monomer concentration is much higher and the radical concentration is lower. This will result in very high average molecular weight that may not be completely resolved by the columns used. These very high average molecular weights are shown in Figure 1 by the shoulder of the trace.

Polymerization of MMA in Presence of Inorganic Substances

The polymerization of different amounts of MMA in water using sodium metabisulphite as an initiator in the absence and presence of some other materials such as soda lime glass powder, kaoline, or titanium dioxide, was carried out at 40°C for a period of 16 hr. The conical reaction flasks were shaken for 1 sec every 15 min. The reaction mixture was poured into a beaker containing methanol (500 ml), stirred for 15 min, and filtered through a G3 sintered glass funnel. The precipitate was washed thoroughly with distilled water and then with methanol, and finally dried under vacuum at room temperature.

The average molecular weights of the second set of experiments were calculated using a computer program described by Pickett et al.[15] using an ICL 1905 computer. The results were obtained from both the refractive index and the infrared chromatograms and are given in Table II.
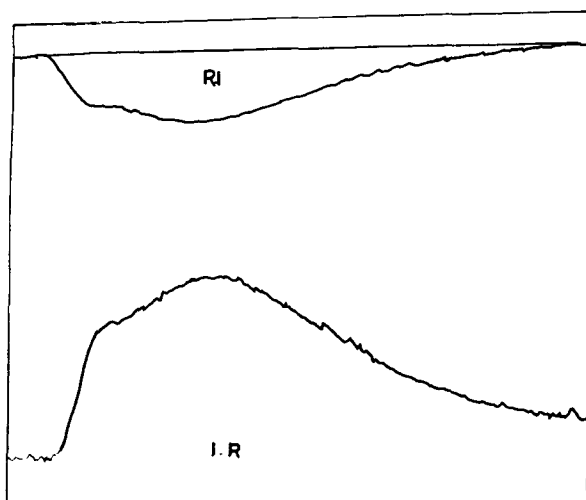

Fig. 1. Refractive index (RI) and infrared (IR) absorbance traces of poly(methyl methacrylate) (sample 3).

TABLE II

Polymerization of MMA in Absence and in Presence of Glass (G), Kaoline (K), or Titanium Dioxide (T) in Water at 40°C Using Sodium Metabisulphite as Initiator

Run no.	Substance used		Water vol., ml	Monomer, wt. g	$Na_2S_2O_5$, wt. g	Monomer convn., %	Average molecular weights			Mol. wt. distribution		Trace used for calculations
	Type	wt. g					$\bar{M}_w \times 10^{-5}$	$\bar{M}_z \times 10^{-6}$	$\bar{M}_{z+1} \times 10^{-6}$	$\bar{M}_z/\bar{M}_w$	$\bar{M}_{z+1}/\bar{M}_z$	
13	G	0.9482	100	9.400	0.0950	73.8	2.759	1.254	1.863	4.5	1.5	RI
							2.473	1.154	1.807	4.7	1.6	IR
14	G	1.9000	100	9.400	0.0950	72.1	7.663	1.710	2.142	2.2	1.2	RI
							7.272	1.630	2.038	2.2	1.2	IR
15	—	—	200	37.600	0.3800	68.4	11.12	1.75	2.041	1.6	1.2	RI
							11.88	1.85	2.169	1.6	1.2	IR
16	K	1.0000	100	9.400	0.1900	95.3	10.84	1.822	2.029	1.7	1.1	RI
							11.26	1.906	2.206	1.7	1.1	IR
17	T	1.997	100	9.400	0.1900	79.4	8.986	1.588	1.946	1.767	1.2	RI
							8.892	1.522	1.861	1.711	1.2	IR

The weight average and the centrifuge average molecular weights in Table II calculated either from infrared or from refractive-index trace were found to be comparable.

On the one hand, the weight average molecular weights in runs 13, 14, and 17, calculated from infrared trace, are found to be lower than the weight average molecular weight values calculated from the refractive-index trace, by about 8%, 5%, and 1%, while the centrifuge average molecular weights are found to be lower by 7%, 4.7%, and 4.1%, respectively.

On the other hand, the weight average molecular weights in runs 15 and 16, calculated from infrared trace, were found to be higher than the average values calculated from the refractive-index trace by 6.8% and 3.9%, while the centrifuge average molecular weights were found to be higher by about 5.7% and 4.6%, respectively.

It was also found that the use of micronized soda lime glass (≤ 10 μm) beyond a certain limit (10 g/l) increased the average molecular weights. This is a new addition to the existing literature.[6] It may be explained in the following way: Grinding the soda lime glass to ≤ 10 μm leads to alkaline solutions with a pH of 9. In this case it will suppress the ionization of the sodium metabisulphite, and the number of bisulphite ions will be smaller, resulting in a smaller number of bisulphite radicals; this, in turn, gives rise to higher average molecular weights.

In such a heterogeneous polymerization, we obtained a multinodal molecular weight distribution. The nodes were detected in both the refractive index and infrared absorbance traces (Fig. 2) indicating that polymerization occurs in the monomer phase, in the water phase, at the interfacial layer between the water and the monomer, and on the surface of substances such as soda lime glass powder.

ESR spectra were recorded on a variety of different solutions, for example, on solutions of initiator and monomer only and on a solution of initiator and monomer containing added quartz or kaoline. The intensity of the spectra obtained varied from one sample to another.
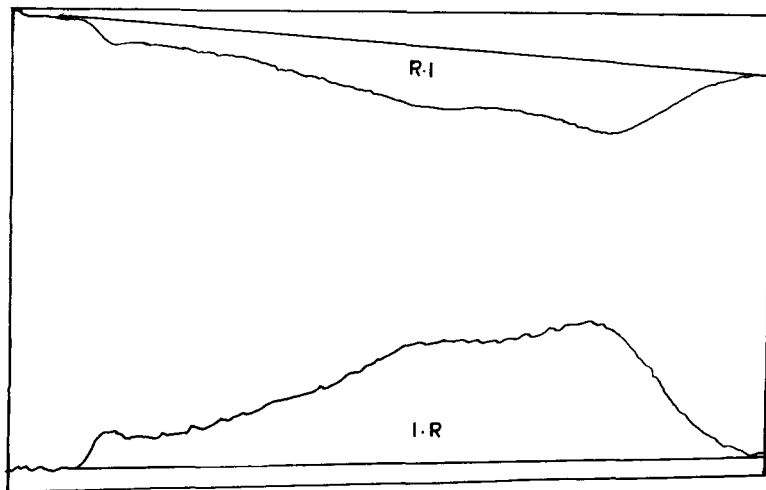

Fig. 2. Refractive index (RI) and infrared (IR) absorbance traces of poly(methyl methacrylate) (sample 14), showing the multinodal distribution. Heterogeneous polymerization of methyl methacrylate (9.4 g) in water 100 ml using sodium metabisulphite (0.095 g) as initiator (for 16 hr).

For those solutions containing kaoline in addition to the monomer and initiator, a reasonably strong ESR spectrum was obtained. However, a further investigation of this system showed that the same spectrum was present in a sample of the kaoline used in these experiments. Since the position of this spectrum in the magnetic field coincided with that of the free radicals obtained during the polymerization; it was not possible to record spectra of the free radicals formed in this particular set of solutions.

For solutions containing initiator and monomer only, the ESR spectra obtained were of low intensity but could be detected above the general level of the typical background noise.

The concentration of the free radicals in this system, however, was small. However, a larger concentration of free radicals was detected in those solutions where quartz was added to the reacting mixture. A typical spectrum obtained for this system is shown in Figure 3. The g value is $h\nu/\mu_B B$, where h is Planck's constant, ν is the microwave frequency, μ_B is the Bohr magneton, and B is the magnetic field (mT).

The g value for the free radicals obtained in these experiments was measured by comparison with a standard sample and was found to be 2.00 ± 0.01. In the same way, the concentration of the free radicals was estimated to be in the region of 4×10^{-8} mol l^{-1}.
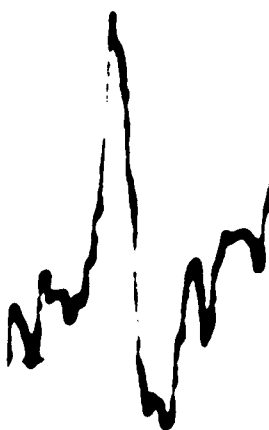
Fig. 3. Typical ESR spectrum obtained for the heterogeneous polymerization of MMA (9.4 g) in water 100 ml using sodium metabisulphite (2.375 g) as initiator for 1 hr in presence of quartz glass powder 10 g l^{-1} which had been heated for 1 hr at room temperature.

^{13}C NMR Spectroscopy

Triad and pentad tacticities for some of the poly(methyl methacrylates) and poly(ethyl methacrylate) have been evaluated from α-methyl, quaternary carbon, and carbonyl peaks. The α-methyl and quaternary carbon peaks were each split into three components which were assigned to isotactic, heterotactic, and syndiotactic triads in order of increasing field. The carbonyl carbon peaks showed more complicated splitting. The assignments made for the components of these peaks are indicated in Figure 4. These assignments are similar to those proposed by Inoue et al.[16]

All the relevent peak assignments are listed:

|	Triad	Chemical shift
(1) α-methyl assignments for poly(methyl methacrylate)		(related to TMS)
	isotactic (mm)	21.0 ppm
	heterotactic (mr)	18.7 ppm
	syndiotactic (rr)	16.5 ppm
for poly(ethyl methacrylate)	isotactic	21.0 ppm
	heterotactic	18.6 ppm
	syndiotactic	16.7 ppm
(2) Quaternary carbon assignments for poly(methyl methacrylate)	isotactic	45.5 ppm
	heterotactic	44.8 ppm
	syndiotactic	44.5 ppm
for poly(ethyl methacrylate)	isotactic	45.6 ppm
	heterotactic	45.1 ppm
	syndiotactic	44.8 ppm
(3) Carbonyl assignment for	Pentad	Chemical shift
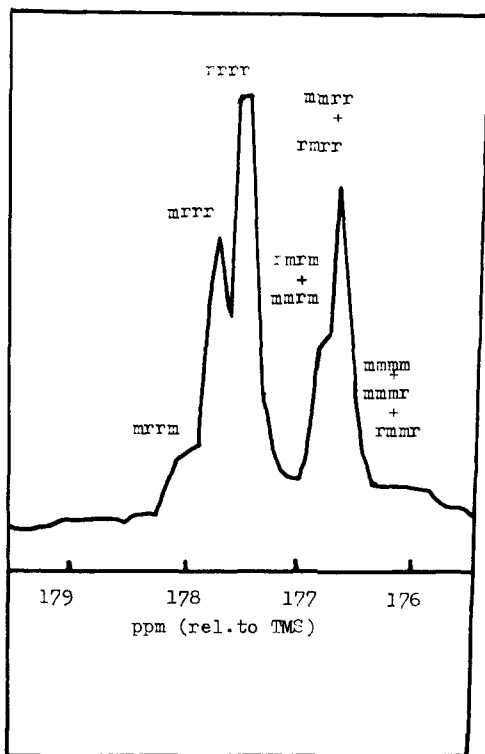
Fig. 4. Carbonyl peaks in the ^{13}C NMR spectrum of poly(methyl methacrylate) (sample 4) showing pentad peak assignments (r is the racemic dyad, m is the mesodyad).

poly(methyl methacrylate)   *mrrm*   178.2 ppm
                                 mrrr   177.9 ppm
                                 rrrr   177.5 ppm
                                 rmrm ⎫   176.9 ppm
                                 mmrm ⎰
                                 mmmm ⎫
                                 mmmr ⎬   175.5 ppm
                                 rmmr ⎭
for poly(ethyl methacrylate)   Pentad   Chemical shift
                                 mrrm   177.9 ppm
                                 mrrr   177.6 ppm
                                 rrrr   177.3 ppm
                                 rmrm ⎫   176.8 ppm
                                 mmrm ⎰
                                 mmrr ⎫   176.6 ppm
                                 rmrr ⎰
                                 mmmm ⎫
                                 mmmr ⎬   175.4 ppm
                                 rmmr ⎭

(where m is the mesodyad and r is the racemic dyad).

Estimated Triad and Pentad Fractions

Overlapped peaks were deconvoluted with the aid of a Dupont curve resolver using generated peaks of Lorentzian shape. Triad fractions from α-methyl peaks are given in Table III. Triad fractions from quaternary peaks are given in Table IV. The pentad fractions were estimated from the carbonyl peak analysis and the data are given in Table V.

From the triad analysis, it is clear that the poly(methyl methacrylate) and poly(ethyl methacrylate) polymers are all predominantly syndiotactic in structure as expected. The poly(ethyl methacrylate) samples have a slightly higher syndiotacticity than poly(methyl methacrylate) samples, again as expected. The greater bulk of the ethyl ester group relative to that of the methyl ester group probably leads to greater steric hindrance in the isotactic and heterotactic triad (i.e., in a mesodyad).

There are no significant differences in tacticity between the various poly(methyl methacrylate) polymers.

In addition, from the carbonyl peak analysis and determination of pentad fractions, it has been noted that there is no indication of any significant differences between the poly(methyl methacrylate) polymers. The poly(ethyl methacrylate) polymers are slightly more syndiotactic, reflected here in the slight increase (relative to PMMA) in the proportion of the long syndiotactic sequence *rrrr*.

Triad fractions from α-methyl and quaternary carbon peaks are roughly consistent with polymerization following Bernoullian trial statistics with a probability of mesoplacement (m) of 0.20 for poly(methyl methacrylate) polymers and 0.18 for poly(ethyl methacrylate) polymers. Pentad fractions are also roughly consistent with these statistics, although, for example, proportions of *rrrr* are slightly smaller than expected. One would expect *rrrr* = 47% for poly(ethyl methacrylate) polymers if m = 0.18 and *rrrr* = 40% for poly(ethyl methacrylate) polymers if m = 0.2.

TABLE III
Triad Fractions from α-Methyl Peaks

Sample no.	Reaction time hr	Conical reaction flask capacity, ml	Water volume, ml	Monomer Type	Monomer wt. g	Initiator Na₂S₂O₅, wt. g	Conversion, %	Triad Isotactic	Triad Heterotactic	Triad Syndiotactic
1	45	250	100	MMA	4.7	0.475	5.9	4 ± 1	36 ± 2	60 ± 2
2	45	250	100	MMA	9.4	0.475	7.7	4 ± 1	35 ± 2	61 ± 2
3	60	1000	100	MMA	9.4	0.475	14.5	5 ± 1	35 ± 2	60 ± 2
4	60	1000	672	MMA	9.4	3.192	31.5	5 ± 1	33 ± 2	62 ± 2
5	60	250	100	EMA	5.6856	0.475	6.6	4 ± 1	29 ± 2	67 ± 2
6	45	250	100	EMA	7.4663	0.475	5.2	6 ± 1	31 ± 2	63 ± 2

The initiator column header reads $Na_2S_2O_5$.

TABLE IV
Triad Fractions from Quaternary Carbon Peaks

Sample no.	Polymer type	Triad, %		
		Isotactic	Heterotactic	Syndiotactic
1	PMMA	7 ± 1	31 ± 2	62 ± 3
2	PMMA	7 ± 1	31 ± 2	62 ± 3
3	PMMA	7 ± 1	34 ± 2	59 ± 3
4	PMMA	6 ± 1	31 ± 2	63 ± 3
5	PEMA	5 ± 1	26 ± 2	69 ± 3
6	PEMA	5 ± 1	29 ± 2	66 ± 3

TABLE V
Pentad Fractions from Carbonyl Peak Analysis

Sample No.	Type	Pentad fractions, %					
		$mrrm$	$mrrr$	$rrrr$	$rmrm$ $mmrm$	$mmrr$ $rmrr$	$mmmm$ $mmmr$ $rmmr$
1	PMMA	5 ± 1	28 ± 3	33 ± 3	6 ± 1	24 ± 2	4 ± 2
2	PMMA	4 ± 1	28 ± 3	33 ± 3	7 ± 1	23 ± 2	5 ± 2
3	PMMA	5 ± 1	25 ± 3	35 ± 3	8 ± 1	23 ± 2	4 ± 2
4	PMMA	4 ± 1	23 ± 3	34 ± 3	8 ± 1	23 ± 2	6 ± 2
5	PEMA	2 ± 1	23 ± 3	41 ± 3	6 ± 1	23 ± 2	5 ± 2
6	PEMA	2 ± 1	19 ± 3	42 ± 3	7 ± 1	25 ± 2	5 ± 2

CONCLUSIONS

Sodium metabisulphite failed to initiate the polymerization of methyl and butyl acrylates but succeeded in polymerizing the methyl, ethyl, and hydroxypropyl methacrylates. All the obtained samples of the poly(hydroxypropyl methacrylate) polymers obtained by this method were insoluble in benzene, chloroform, and dimethyl sulphoxide.

A multinodal molecular weight distribution indicates the presence of different sites of reaction, namely, in the monomer layer, the water layer, at the interphase between the monomer and water, and on the surface of the substances present.

Use of soda lime glass of particle size ≤10 μm, increased the average molecular weights of the polymers obtained in its presence owing to the formation of fewer radicals.

ESR studies proved the presence of a radical polymerization mechanism. ^{13}C NMR studies showed that the polymers obtained were predominantly syndiotactic, and that the poly(ethyl methacrylate) had a slightly higher syndiotacticity than poly(methyl methacrylate).

References

1. A. R. Mukherjee, P. Ghosh, S. C. Chadha, and S. R. Palit, *Makromol. Chem.,* **80,** 208 (1967).

2. T. Yamaguchi, H. Tanaka, and A. B. Moustafa, *Chemistry and Industry,* J. Society of Chemical Industry, Publisher, London, 1974, p. 619.   Printed by Richard Madley Ltd., 54 Grafton Way, W.P 5LB England.

3. A. B. Moustafa, *Angew. Makromol. Chem.,* **39,** 1 (1974).

4. A. B. Moustafa and M. A. Diab, *Angew. Makromol. Chem.,* **45,** 41 (1975).

5. A. B. Moustafa and M. A. Diab, *J. Appl. Polym. Sci.,* **19,** 1585 (1975).

6. A. B. Moustafa, N. A. Ghanem, and M. A. Diab, *J. Polym. Sci., Polym. Chem. Ed.,* **13,** 1987 (1975).

7. Olfat Y. Mansour, and A. B. Moustafa, *J. Polym. Sci., Polym. Chem. Ed.* **13,** 2796 (1976).

8. A. B. Moustafa and A. A. Abd-El-Hakim, *J. Polym. Sci., Polym. Chem. Ed.,* **14,** 433 (1976).

9. T. Yamaguchi, T. Ono, Y. Saito, and S. Ohara, *Angew. Makromol. Chem.,* **53,** 65 (1976).

10. A. B. Moustafa and M. Abd-El-Maboud Sakr, *J. Polym. Sci., Polym. Chem. Ed.,* **14,** 2327 (1976).

11. A. B. Moustafa and M. Abd-El-Maboud Sakr, *Angew. Makromol. Chem.,* **55,** 11 (1976).

12. A. B. Moustafa and A. A. Abd-El-Hakim, *J. Appl. Polym. Sci.,* **20,** 2643 (1976).

13. A. B. Moustafa and A. A. Abd-El-Hakim, *J. Appl. Polym. Sci.* **21,** 905 (1977).

14. A. B. Moustafa, M. H. Nosseir, and N. E. Nashed, *Angew. Makromol. Chem.,* **52,** 71 (1976).

15. H. E. Pickett, Manfred J. R. Cantow, and Julian F. Johnson, *J. Appl. Polym. Sci.,* **10,** 917 (1966).

16. Y. Inoue, A. Nishioka, and R. Chujö, *Polym. J. Jpn.,* **4,** 535 (1971).