

Bulk Polymerization of Methyl Methacrylate in the Presence of Poly(Methyl Methacrylate). II. Effect of Oxygen

INTRODUCTION

In a previous paper¹ it was reported that the bulk polymerization of methyl methacrylate (MMA) at 90°C could be initiated by conventional (c-PMMA) as well as isotactic (i-PMMA) and syndiotactic poly(methyl methacrylate) (s-PMMA). The initiation by c-PMMA was already described by Melville and Watson² and discussed by Szwarc³ in terms of a possible specific arrangement of monomer molecules in the neighborhood of the polymer chains.

In recent discussions, Szwarc as well as Morton called our attention to a later study by Waltcher,⁴ who showed that the initiation was simply caused by decomposition of peroxides present in the chains of c-PMMA. Such peroxides could be formed during the radical polymerization of MMA in the presence of oxygen as first reported by Barnes et al.^{5,6}

Although the incorporation of peroxides into growing PMMA chains is quite acceptable for radical polymerization the explanation of Waltcher should not merely apply to the initiation of MMA by i-PMMA and s-PMMA prepared by ionic polymerizations.^{7,8} In order to check this point we repeated a number of experiments with different kinds of PMMA and paid special attention to the influence of oxygen.

EXPERIMENTAL

MMA was purified by distillation under reduced pressure over copper bronze. i-PMMA was purified by repeated precipitation from chloroform in petroleum ether (bp 40–60°C) and from acetone (after centrifugation to remove insoluble particles) in water. s-PMMA was first purified by precipitation from chloroform in methanol and washed with dilute HCl. Further purification was performed in the way described for i-PMMA.

In order to destroy possible peroxides in the polymer chains, i-PMMA was dissolved in toluene and heated at 90°C for 5 hr. After precipitation in petroleum ether the polymer was purified again. This heat treatment was introduced by Waltcher⁴ and appeared to be very effective for c-PMMA.

Data of the PMMA samples are listed in Table I. Viscosity-average molecular weights \bar{M}_v were determined in chloroform at 25°C by using the relationship $[\eta] = 4.8 \times 10^{-5} \bar{M}_v^{0.8}$ (dl/g) reported previously.⁹ The tacticity was measured in 10% solution in *o*-dichlorobenzene at 160°C by 60-MHz NMR spectroscopy.

Initially the polymerizations of MMA in the presence of 1 wt-% i-PMMA were performed in a 5-ml automatic dilatometer. It appeared difficult to obtain reproducible kinetic curves, partly due to differences in inhibition time (≈ 10 min at 90°C). Some final monomer conversions were estimated by isolation and weighing of the polymers.

TABLE I
Data of PMMA Samples Added to MMA

PMMA	$\bar{M}_v \times 10^{-5}$	Tacticity		
		I, %	H, %	S, %
i-PMMA (isotactic)	7.3	91	6	3
s-PMMA (syndiotactic)	3.7	4	8	88
c-PMMA (conventional)	4.6	4	35	61

Since oxygen dissolved in MMA might produce peroxides during an inhibition period,^{5,6} further experiments were carried out in sealed tubes. In these tubes the reaction mixture (about 8 ml) could be easily freed from oxygen by degassing on a 0.05 mm Hg vacuum line after freezing in liquid nitrogen. This procedure was repeated four times. After polymerization the tubes were opened and the polymers were isolated after precipitation in petroleum ether (bp 40–60°C), dried, and weighed.

As before,^{1,2,4} all polymerizations were carried out under diffused daylight.

RESULTS AND DISCUSSION

In the dilatometric experiments MMA conversions of about 85% were obtained after 24 hr at 90°C in the presence of 1 wt-% i-PMMA, and the initial rate of polymerization was about 5%/hr. As i-PMMA was thoroughly purified we could only imagine that oxygen or peroxides present in the monomer contributed to the initiation. Indeed, with our dilatometric filling technique it was not possible to prevent any contact of MMA with air.

Degassing of the reaction mixture on the vacuum line before polymerization in sealed tubes clearly demonstrated the great influence of dissolved oxygen. The initial rate of polymerization could be reduced fivefold by repeated degassing. So, at first sight dissolved oxygen turned out to be the major factor.

In order to trace the possible influence of PMMA as suggested by Waltcher,⁴ a series of experiments was carried out with different types of PMMA at higher concentration, viz., about 4 wt-%. All reaction mixtures were degassed four times on the vacuum line before sealing off the tubes. Some typical results are listed in Table II, which includes the dilatometric data mentioned above for comparison.

From our results it can be concluded that the rate of bulk polymerization of MMA at 90°C becomes very small (1.5–2%/hr) when MMA is freed from most of the dissolved oxygen. This small rate does not depend on the presence or absence of relatively small amounts (up to 4 wt-%) of preformed and purified i-, s-, or c-PMMA. When i-PMMA is preheated at 90°C in order to destroy possible peroxides the rate of polymerization does not change. Even our c-PMMA prepared by radical polymerization with bis(*p*-tert-butylcyclohexyl)dipercarbonate at room temperature seems free of peroxides, since it also yields the same small rate value. So, according to Waltcher⁴ and contrary to previous statements¹ we have to conclude that our purified polymers are not effective in initiating MMA. The persisting slow MMA conversion should be attributed to thermal polymerization or rather to radical polymerization initiated by traces of oxygen or peroxides in the MMA monomer^{5,6} which could not be removed on our vacuum line.

TABLE II
Influence of PMMA's on initial MMA conversion at 90°C

Expt.	PMMA type	PMMA concn, wt-%	MMA conversion, %/hr	Remarks
1	i-PMMA	1.0	5.0	Dilatometric (O ₂)
2	i-PMMA	3.8	1.8	
3	i-PMMA	3.9	1.9	Preheated i-PMMA
4	None	—	2.0	Same MMA as in expt. 3
5	s-PMMA	3.8	1.5	
6	s-PMMA	3.3	1.6	Extra purified s-PMMA
7	None	—	1.5	Same MMA as in expt. 6
8	c-PMMA	3.7	2.0	

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Received March 14, 1974
Revised May 8, 1974