Studies on the Radical Polymerization of Methyl Methacrylate in Bulk and in Benzene Using Totally Deuterated Monomer Technique

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(Received December 3, 1985)

ABSTRACT: Totally deuterated methyl methacrylate (MMA- d_8) was polymerized with AIBN in bulk at 60°C, and the resultant polymer was analyzed for the initiator fragment by ^1H NMR spectroscopy. Amount of the AIBN fragment at the beginning of the chain was found to be 1.15 per molecule, indicating 85% of the polymer molecules formed through disproportionation reaction. NMR analysis of the undeuterated PMMA prepared under the same conditions showed that the polymer contained 0.36 vinylidene double bond at the chain end. This is consistent with the results obtained from the P (MMA- d_8). P (MMA- d_8) prepared with BPO in benzene at 60°C had 1.20 initiator fragment per chain, 82% of which was phenyl group and 18% benzoyloxy one. Polymerizations in benzene with AIBN in the presence and absence of thiophenol were also examined.

KEY WORDS Methyl Methacrylate / Methyl Methacrylate Radical
Polymerization / Mechanism of Termination Reaction / Disproportionation /
Thiophenol / End Group Analysis / Deuterated Methyl Methacrylate /
Azobisisobutyronitrile / Benzoyl Peroxide / NMR /

Analysis of initiator fragments at the end of polymer chain is a straightforward method for understanding the mechanism of polymerization. It has been demonstrated utilizing ^{14}C -labeled α, α' -azobisisobutyronitrile (AIBN) that polystyrene radicals terminate exclusively by combination at the temperature up to 60°C while PMMA radicals undergo substantial disproportionation.^{1,2} However, the use of ^{14}C -labeled initiator only gives information on the number of initiator fragments and is not sensitive to how the fragment is incorporated into the polymer chain. Recently NMR studies were carried out to examine the end group of a polymer chain using a ^{13}C -,³⁻⁹ ^2H -,^{8,10} ^{19}F -,¹¹ or ^{15}N -labeled⁸ initiator. The NMR methods enable us to determine not only the number but also the structures of initiator fragments.

We have studied the mechanism of radi-

cal,¹²⁻¹⁴ cationic,¹⁵ and anionic¹⁶⁻¹⁹ polymerizations by the totally deuterated monomer technique where the totally deuterated monomer is polymerized with undeuterated initiator and the resulting polymer is studied by ^1H NMR spectroscopy. In the previous communication¹² totally deuterated MMA (MMA- d_8) was polymerized in toluene with undeuterated AIBN and benzoyl peroxide (BPO) and the relative importance of disproportionation and combination in termination reaction was estimated from the ^1H NMR spectra of the polymers. In this work MMA- d_8 was polymerized under several conditions with AIBN and BPO, and the resultant polymers were analyzed in detail by ^1H NMR spectroscopy. The amount of olefinic double bond at the end of the chain, which was formed through disproportionation reaction, was also analyzed by ^1H NMR spec-

troscopy. From the results the mechanism of initiation and termination is discussed in some detail.

EXPERIMENTAL

MMA- d_8 was prepared from acetone cyanohydrin- d_7 and methanol- d_4 ,²⁰ and purified by fractional distillation under nitrogen pressure. The distillate was dried over calcium dihydride and then vacuum-distilled. The degrees of deuteration for α -methyl, vinylidene methylene and methoxy methyl groups were found to be 99.4%, 99.5%, and 99.7%, respectively, by precision coaxial tubing method.²¹ MMA was obtained commercially and purified similarly to MMA- d_8 . Benzene was purified by the usual manner and distilled over sodium under nitrogen pressure. The distillate was dried with butyllithium and redistilled under high vacuum. Cobalt-tetraphenylporphine complex was prepared according to the literature.²²

Polymerization was carried out in a sealed glass ampoule under nitrogen pressure and the reaction mixture was poured into a large amount of methanol to precipitate the polymer formed. The precipitate was collected by filtration, washed several times with methanol and dried in vacuo at 60°C. Polymerization was also carried out in the presence of thiophenol to prepare the polymer without carbon-carbon double bond at the chain end.

The ^1H NMR spectra of the polymer were taken in nitrobenzene- d_5 on a JNM-FX100 (100 MHz) and a JNM-GX270 (270 MHz) Fourier transform NMR spectrometer (JEOL) at 110°C using hexamethyldisiloxane (HMDS) as the internal standard. The hydrogen content of the deuterated polymer sample was calculated from the ratio of the signal intensity of interest to the signal due to the remaining protons in nitrobenzene- d_5 used as a solvent for the measurement. The content of the remaining protons in nitrobenzene- d_5 was determined using precision coaxial tubing method.²¹

The amount of vinylidene protons at the chain end of undeuterated PMMA was evaluated from the intensity ratio of their signals at 5.4 and 6.14 ppm (*cf.* Figure 2) to the ^{13}C -satellite of methoxy proton resonance at 3.33 and 3.87 ppm in the spectrum measured in deuterated chloroform at 55°C.

The number average molecular weight of the polymer was measured in toluene at 60°C on a Hitachi 117 vapor pressure osmometer.

RESULTS AND DISCUSSION

MMA- d_8 was polymerized in bulk at 60°C with AIBN and the results are shown in Table I. Figure 1 shows the ^1H NMR spectrum of the polymer measured in nitrobenzene- d_5 at 110°C. Besides the signals due to the remaining protons in the monomeric units, two peaks of equal intensity were observed at 1.23 and 1.31 ppm. These two peaks showed the ^1H spin-lattice relaxation times, T_1 s of 1.0 s and disappeared when the polymer was prepared with BPO. These indicate that the signals are due to the methyl protons of the initiator fragment, 1-cyano-1-methylethyl group located at the beginning of the chain. The T_1 value eliminates the possibility that the peaks arise from contaminants of small molecules ($T_1 \approx 10$ s) or the protons of the groups within polymer chain ($T_1 \approx 0.1$ s). The splitting into two peaks is due to the adjacent asymmetric carbon in the polymer chain. The content of the initiator fragments was measured to be 0.0298 mmol/g-polymer, from which the number of fragments per polymer molecule was calculated to be 1.15. The precision of the measurements for five determinations was 2.7%.

It is well known that chain transfer reaction to initiator is of no importance in the polymerization of MMA with AIBN. The transfer constant to the MMA monomer is of the order of 10^{-5} ; that is, one transfer reaction to the monomer occurs for 10^5 propagation reactions. The degree of polymerization of the polymer is less than 4×10^2 ; therefore, transfer

Table I. Polymerization of MMA- d_8 by AIBN and BPO at 60°C

No.	Initiator		MMA- d_8	Solvent	Yield	M_n^a	Initiator fragment ^b
	mol l ⁻¹		mol l ⁻¹		%		mol mol ⁻¹
1	AIBN	0.37	9.32	None	23.4	38600	1.15
2	AIBN	0.01	1.00	Benzene	35.4	38850	1.13 ₅
3 ^c	AIBN	0.0046	0.92	Benzene	8.3	1400	0.97 ^d
4	BPO	0.0091	0.91	Benzene	30.0	47500	1.20
5 ^c	AIBN	0.37	9.36	None	24.4	44600	—

^a Determined by the vapor pressure osmometer.

^b Represents the number of initiator fragments per polymer molecule.

^c Polymerization was carried out in the presence of thiophenol (0.046 mol l⁻¹).

^d Represents the number of thiophenol fragments. The number of AIBN fragments was 0.02.

^e Undeuterated MMA was used.

Figure 1. ^1H NMR spectrum of poly(MMA- d_9) prepared in bulk by AIBN at 60°C (nitrobenzene- d_5 , 110°C , 100 MHz). The signals labeled X are due to remaining protons in the monomeric units.

to the monomer can also be neglected. Then, the number of initiator fragments, 1.15, means that 85% of polymer molecules are formed through disproportionation reaction and that half of them should contain double bond at the chain end.

Undeuterated MMA was polymerized in bulk at 60°C with AIBN (Table I, No. 5). The resultant polymer showed two small peaks in the olefinic proton region at 5.4 and 6.14 ppm in CDCl₃ at 55°C (Figure 2). The T_1 s for these peaks were about 0.5 s.

Figure 2. ^1H NMR spectrum of PMMA prepared with AIBN in bulk at 60°C (CDCl_3 , 55°C , 270 MHz).

* ^{13}C satellite band of CHCl_3 .

The vinylidene protons of MMA should show signals at 5.51 and 6.05 ppm if they exist. Then the peaks at 5.4 and 6.14 ppm must be assigned to the methylene protons of the vinylidene group which was formed through the route A of the disproportionation reaction (eq 1). Similarly to the case of MMA,²³ the lower- and higher-field peaks were assigned to the protons *cis* and *trans* to the methoxycarbonyl group, respectively, on the basis of the deshielding effect of the carbonyl group. Further splitting of the latter peak may be due to the tacticity of the dyad at the chain end. Intensity measurement of the peaks indicates that 36% of the polymer molecules contain the vinylidene double bond at the chain end. Terminal olefinic methine proton, possibly formed through route B, is expected to show signals at 6.5–7.0 ppm.* However, no signals of appreciable intensity were observed in this region. Then, the results mentioned above mean that

72% of the polymer molecules is formed through the disproportionation reaction. The difference between the results obtained from PMMA- d_8 and undeuterated PMMA may be partly due to the isotope effect in the termination reaction and partly due to the experimental error. It is also possible that a small amount of olefinic methine proton formed through route B existed in the polymer chain but could not be detected by NMR owing to the lower signal intensity. The study on these points is now underway and will be published elsewhere.

Enikolopyan *et al.* reported that the polymerization of MMA with AIBN in the presence of cobalt-porphyrin derivative complexes produced the oligomer having a vinylidene group at the chain end.²⁵ A higher molecular weight polymer of MMA was prepared according to Enikolopyan's procedure. MMA was polymerized with AIBN (0.1 mol% of

* Kimura *et al.* reported ^1H NMR data for a terminally unsaturated dimer, $\text{CCl}_3\text{-CH}_2\text{-C}(\text{CH}_3)(\text{COOCH}_3)\text{-CH}=\text{C}(\text{CH}_3)(\text{COOCH}_3)$; the chemical shift of the olefinic methine proton is $\delta=6.71$.²⁴

Figure 3. ^1H NMR spectra of (A) poly(MMA- d_8) and (B) PMMA prepared by AIBN in benzene at 60°C in the presence of thiophenol (5 mol% of monomer) (nitrobenzene- d_5 , 110°C , 100 MHz). X and Y represent signals due to remaining protons in the monomeric units and solvent, respectively.

MMA) in the presence of cobalt-tetraphenylporphine complex (2×10^{-3} mol% of MMA) at 60°C . The resultant polymer ($M_n = 11,600$) showed vinylidene proton signals just the same as those observed in Figure 2. This is strong evidence for the assignment mentioned above.

Figure 3A shows the ^1H NMR spectrum of the polymer of MMA- d_8 prepared with AIBN in benzene at 60°C in the presence of thiophenol. In the spectrum, there appear a multiplet due to the aromatic protons of a phenyl-

thio group at 6.8–7.3 ppm and the signal of the methine proton attached to the terminal MMA unit at 2.43 ppm. The signal due to the AIBN fragment at 1.23 and 1.31 ppm was much weaker than the former two signals. The intensity measurements indicate that almost all the polymer molecules contain one phenylthio group and one terminal methine proton in each molecule (Figure 3A), that is, the polymer molecules form entirely through the chain transfer reaction to thiophenol.

Undeuterated PMMA prepared under the same conditions gave no signals in the olefinic proton region in the spectrum (Figure 3B). This is additional clear evidence that the peaks at 5.4 and 6.14 ppm in Figure 2 should be assigned to the vinyl methylene protons at the chain end.

PMMA- d_8 prepared in benzene with AIBN at 60°C was found to have 1.13₅ initiator fragments per polymer molecule (Table I, No.

2). The chain transfer constant to the solvent is reported to be 0.4×10^{-5} in the polymerization of MMA in benzene at 60°C ,³² and the degree of polymerization of the PMMA- d_8 to be less than 4×10^2 . The effect of the transfer reaction to benzene can thus be ignored. Then, the number of initiator fragments obtained here, 1.13₅, is directly related to the relative importance of the disproportionation and combination reactions and indicates that 86.5% of

Table II. Fraction (*N*) of polymer molecules formed through disproportionation termination

No.	Initiator	Solvent	Temp	<i>N</i>	Lit.
			°C	%	
1	¹⁴ C-AIBN	Benzene	0	75	2
2	¹⁴ C-AIBN	None	25	84	1
3	¹⁴ C-AIBN	Benzene	25	80	1
4	Mn ₂ (CO) ₁₀ -PVTCA ^a	None	25	80	26, 27
5	¹⁴ C-AIBN	?	40	47	28
6 ^b	AIBN	None	60	85	This work
7 ^b	AIBN	Benzene	60	87	This work
8 ^b	BPO	Benzene	60	80	This work
9	¹⁴ C-AIBN	Benzene	60	92	2
10	¹⁴ C-AIBN	?	60	60	28
11	¹⁴ C-AIBN	Benzene	60	73	29
12	¹⁴ C-AIBN	None	60	73	30
13 ^c	¹⁴ C-AIBN	None	60	48	30
14	Mn ₂ (CO) ₁₀ -PVTCA ^a	None	60	84	26, 27
15	¹⁴ C-AIBN	?	80	72	28
16	Mn ₂ (CO) ₁₀ -PVTCA ^a	None	80	89	26, 27
17	ACVA ^d	?	90	~100	27, 31

^a Poly(vinyltrichloroacetate).^b CD₂=C(CD₃)COOCD₃ was used.^c CD₂=C(CD₃)COOCH₃ was used.^d γ,γ'-Azobis(γ-cyano-*n*-valeric acid). **Figure 4.** ¹H NMR spectrum of poly(MMA-*d*₈) prepared in benzene at 60°C with BPO (CDCl₃, 55°C, 100 MHz).

the polymer molecules form through the disproportionation reaction similarly to the polymerization in bulk.

Polymerization of MMA-*d*₈ was carried out in benzene at 60°C with BPO at the initial monomer concentration of 0.91 mol l⁻¹. The aromatic proton region spectrum of the resultant polymer in CDCl₃ at 55°C is shown in Figure 4. These resonances should be assigned to the initiator fragment at the beginning of the chain since the polymer prepared with AIBN under the same conditions showed no signals in this region. The number of initiator fragments was calculated to be 1.20, indicating again the predominance of disproportionation in the termination reaction (Table I). The value is slightly higher than that for the polymer prepared with AIBN. The difference may be attributable to the existence of transfer to BPO (transfer constant = 0.02)³³ while transfer to AIBN is reported to be negligible. Among the resonances of BPO fragments, the signals at 7.95 and 7.3–7.6 ppm were assigned to *o*-protons and *m*- and *p*-protons of the benzoyloxy group, respectively, and the residual peaks

to the phenyl group. The assignments were made by comparing the spectrum with those of model compounds such as methyl and ethyl benzoates. The relative number of benzoyloxy and phenyl groups at the beginning of the polymer chain was determined to be 18/82 from the intensity measurements. Bevington and his coworker reported, using BPOs labeled by ¹⁴C in different parts of the molecule, that the initiation was caused both by benzoyloxy and phenyl radicals in the polymerization of MMA in benzene at 60°C with BPO and the relative importance of the former to the latter becomes greater with increasing concentration of monomer.³⁴ From their experimental data, the relative numbers of benzoyloxy and phenyl groups in the polymers prepared at the monomer concentration of 0.91 mol l⁻¹ were estimated to be 21/79; these are in good agreement with our results obtained by the NMR method (*cf.* Table I, No. 4).

In Table II, the results on the relative importance of disproportionation and combination reactions reported in previous papers are summarized together with those obtained in this work. Most of the data indicate the predominance of disproportionation termination in polymerizations in bulk or in benzene in the temperature range from 0 to 90°C. However, it seems difficult to discuss these data in detail since the results obtained in the literatures were fairly scattered.

In conclusion, the predominance of disproportionation in the radical polymerization of MMA was demonstrated by analysis of initiator fragments using a totally deuterated monomer technique. This was also shown by analysis of unsaturated end groups in the polymer. Analysis of end groups should lead to a better understanding of the physical properties of polymers as well as the mechanism of polymerization. Our work is now being extended to polymerizations in various solvents and the results will be reported in the near future.

Acknowledgement. The authors are grate-

ful to Dr. R. Miura of the National Cardiovascular Center for measuring some of the NMR spectra and Mrs. F. Yano for her clerical assistance in preparing this manuscript.

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