End Groups of Poly(methyl methacrylate) as a Function of Molecular Weight Determined by Pyrolysis-Gas Chromatography

Hajime OHTANI, Minoru TANAKA, and Shin TSUGE*
Department of Synthetic Chemistry, Faculty of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagaya 464-01
(Received November 18, 1989)

End groups of poly(methyl methacrylate) (PMMA) radically polymerized with benzoyl peroxide (initiator) in toluene solution were investigated by pyrolysis gas chromatography as a function of molecular weight. The number-average molecular weights ($\bar{M}_n$) of fractionated PMMA samples were estimated from the relative peak intensities of characteristic pyrolysis products and were compared with those determined by size exclusion chromatography. The observed result suggested that the chain transfer reactions to the monomer might yield relatively smaller PMMA molecules. Furthermore, the relative peak intensities among aromatic products which reflect three kinds of aromatic chain ends were correlated to the $\bar{M}_n$ of the fractionated PMMAs. The result suggested that the chain transfer reaction to the solvent also tended to yield relatively smaller PMMA molecules whereas the polymerization initiated by the phenyl radical from the initiator yielded relatively larger PMMA molecules under given polymerization conditions.

The end groups of polymer chains sometimes have significant effects on the properties of the resulting polymeric mixture. Furthermore, the detailed chain end information of the given polymer system provides us with a significant clue for the associated polymerization mechanisms. On the other hand, polymers are generally considered as mixtures of molecules of varied molecular weight (MW). Thus, the investigation of the type and content of polymer chain ends as a function of MW has been of much interest in connection with properties of the polymers themselves and the polymerization mechanisms. However, the identification and determination of the end groups is no easy task because of their complexity and low concentration.

Recently, superconducting NMR techniques with greater sensitivity and resolution have been effectively utilized for the qualitative and quantitative determinations of the end groups in polymer chains.[1-10] On the other hand, it was demonstrated in our recent work[11,12] that high-resolution pyrolysis-gas chromatography (Py-GC) was successfully applied to the analysis of the end groups of poly(methyl methacrylate) (PMMA) prepared by radical polymerization. Observed pyrograms of PMMA were interpreted in terms of the kind and the amount of polymerization reagents incorpolated into the polymer chain ends. Moreover, the peak intensities of some characteristic products were correlated to some of the polymerization conditions.

In this work, a PMMA radically polymerized in toluene solution with benzoyl peroxide (BPO) as an initiator are investigated by Py-GC for its fractionated samples, and the type and contents of the chain ends are characterized as a function of MW. The results thus obtained are correlated to the associated polymerization mechanisms.

Experimental

Materials. The polymerization procedure is basically the same as that described previously.[11,12] Methyl methacrylate (MMA) monomer was obtained commercially and purified by a standard procedure. The monomer and toluene were distilled in a nitrogen atmosphere under reduced pressure. Polymerization was carried out in a 200-ml three-neck flask fitted with a nitrogen inlet on a water bath the temperature of which was regulated at 80 °C. Five ml of the monomer, 0.015 mg (0.3 w/v% to the monomer) of BPO and 50 ml of toluene introduced in the flask were subjected to the polymerization under a nitrogen atmosphere for 20 hours with stirring by a magnetic stirrer. The reaction mixture was poured into a large amount of hexane to precipitate the polymer formed. The polymer thus obtained was reprecipitated from its acetone solution into hexane. The presipitates were collected by filtration, washed several times with hexane, and dried in vacuo at 50 °C. This procedure gave the parent PMMA in 51.2% yield.

The fractionation of the parent PMMA was carried out by successive represipitations from its acetone solution by use of various composition of acetone/hexane mixtures as shown in Fig. 1. The recovery of the polymer is about 95% in each fractionation step and 84% as a whole. Number-average molecular weight ($\bar{M}_n$) and heterogeneity indices ($\bar{M}_w/\bar{M}_n$) of the five fractions obtained are estimated by using size exclusion chromatography (SEC) on the basis of polystyrene standards and shown in Table 1.

Py-GC Conditions. The high-resolution Py-GC system

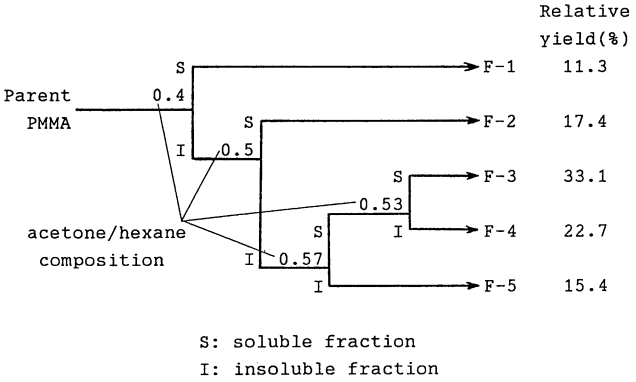

Fig. 1. Fractionation of the poly (methyl methacrylate) (PMMA) sample.

Table 1. Number-Average Molecular Weight (M_n) and Heterogeneity Indices of Fractionated PMMAs Estimated by SEC

Fraction	M_n ($\times 10^4$)[a)]	M_w/M_n
F-1	0.57	1.55
F-2	1.88	1.27
F-3	3.23	1.19
F-4	6.27	1.16
F-5	9.25	1.19

a) On the basis of polystyrene standards.

utilized in this work was basically the same as that described previously.[11,12] The Py-GC measurements were carried out on a gas chromatograph (Shimadzu GC-7A) equipped with a flame ionization detector (FID) and a high resolution fused-silica capillary column (Hewlett Packard, Ultra 1, 0.2 mm i.d.×50 m long) coated with immobilized dimethylsiloxane (0.33 μm thick). About 0.5 mg of the sample was pyrolyzed at 460 °C under a flow of nitrogen carrier gas using a vertical micro-furnace pyrolyzer (Yanagimoto, GP-1018) directly attached to the gas chromatograph. The 50 ml min^{-1} carrier gas flow at the pyrolyzer was reduced to 0.7 ml min^{-1} at the separation column by a spritter. The column temperature was programmed initially set at 0 °C by using a CO_2 cooling unit, then programmed to 250 °C at a rate of 4 °C min^{-1}. The identification of the characteristic peaks on the resulting pyrograms was mostly carried out by use of a gas chromatograph-mass spectrometer (GC-MS) system (Shimadzu QP-1000) to which the pyrolyzer was also attached.

Results and Discussion

Figure 2 shows the pyrogram of F-2 and most of the peaks identified by the GC-MS system are summarized in Table 2. Peak intensities relative to that of the monomer are listed in Table 3 for each fraction. In addition to the main peak (peak 4) of the MMA monomer formed through the depolymerization reaction, additional minor peaks are observed including MMA dimers and trimer. Among these, eight peaks (peaks 2, 6, 12, 19, 24, 30, 31, and 33) are identified as aromatic products which reflect the aromatic chain

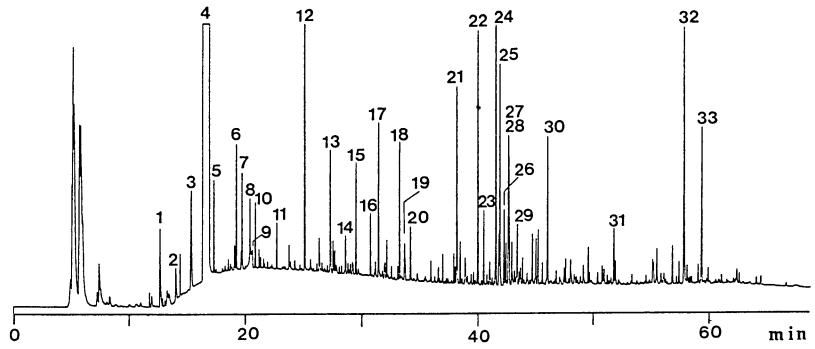

Fig. 2. Pyrogram of a fractionated PMMA (F-2).

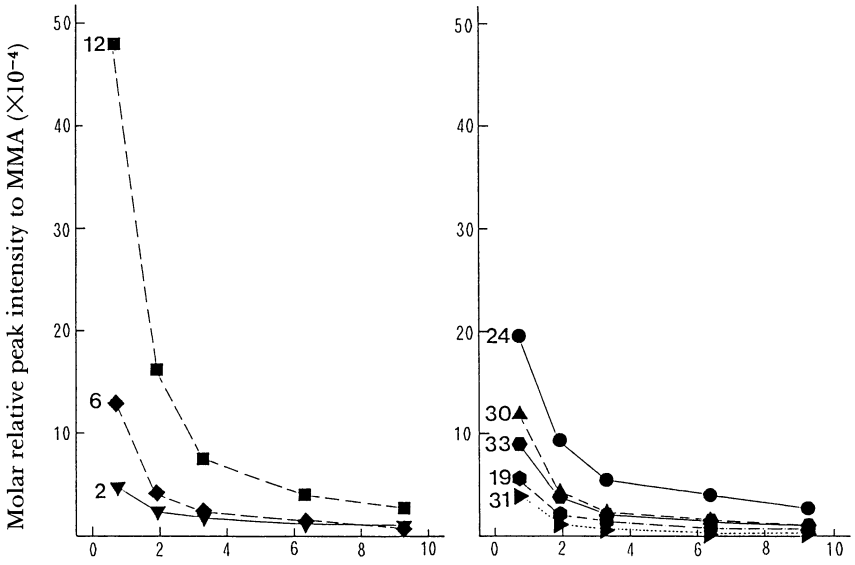

Fig. 3. Relationships between $\bar{M}_n$ of fractionated PMMAs and relative peak intensities of aromatic products to that of monomer. Peak numbers correspond to those in Fig. 2 and Table 2.

Table 2. Peak Assignment in the Pyrogram of PMMA Sample

Peak no.	MW	Structure	MMA[a] unit (m)	Phenyl group (p)	Carbon number (c)	C=C[b] bond (u)	Ester group (e)	Effective[c] carbon number (n)
1	88	$CH_3CH_2COOHCH_3$	1	0	4	0	1	2.75
2	78		0	1	6	0	0	6
3	102	$CH_3CH(CH_3)COOCH_3$	1	0	5	0	1	3.75
4	100	$CH_2=C(CH_3)COOCH_3$	1	0	5	1	1	3.65
5	116	$C_6H_{12}O_2$	1	0	6	0	1	4.75
6	92	 CH_3	0	1	7	0	0	7
7	116	$C_6H_{12}O_2$	1	0	6	0	1	4.75
8	114	$C_6H_{10}O_2$	1	0	6	1	1	4.65
9	86	$CH_2=C(CH_3)COOH$	1	0	4	1	0	2.9[d]
10	114	$C_6H_{10}O_2$	1	0	6	1	1	4.65
11	114	$C_6H_{10}O_2$	1	0	6	1	1	4.65
12	104	 $CH=CH_2$	0	1	8	1	0	7.9
13	142	$C_8H_{14}O_2$	2	0	8	1	1	6.65
14	140	$C_8H_{12}O_2$	2	0	8	2	1	6.55
15	156	$C_9H_{16}O_2$	2	0	9	1	1	7.65
16	140	$C_8H_{12}O_2$	2	0	8	2	1	6.55
17	140	$C_8H_{12}O_2$	2	0	8	2	1	6.55
18	158	$C_9O_{18}O_2$	2	0	9	0	1	7.75
19	136	 $COOCH_3$	0	1	8	0	1	6.75
20	158	$CH_3OCOCH=CHCH_2COOCH_3$	2	0	7	1	2	4.4
21	186	$C_9H_{14}O_4$	2	0	9	1	2	6.4
22	200	$C_{10}H_{16}O_4$	2	0	10	1	2	7.4
23	186	$C_9H_{14}O_4$	2	0	9	1	2	6.4
24	178	 $CH_2CH(CH_3)COOCH_3$	1	1	11	0	1	9.75
25	200	$C_{10}H_{16}O_4$	2	0	10	1	2	7.4
26	200	$C_{10}H_{16}O_4$	2	0	10	1	2	7.4
27	200	$C_{10}H_{16}O_4$	2	0	10	1	2	7.4
28	214	$C_{11}H_{18}O_4$	2	0	11	1	2	8.4
29	214	$C_{11}H_{18}O_4$	2	0	11	1	2	8.4
30	190	 $CH_2CH=C(CH_3)COOCH_3$	1	1	12	1	1	10.65
31	232	 $CH_2C(CH_3)(COOCH_3)CH=CHCH_3$	2	1	14	1	1	12.65
32	300	$CH_3C(CH_3)(COOCH_3)CH_2C(CH_3)(COOCH_3)CH=C(CH_3)COOCH_3$	3	0	15	1	3	11.25
33	276	 $CH_2C(CH_3)(COOCH_3)CH=C(CH_3)COOCH_3$	2	1	16	1	2	13.4

a) Number of MMA unit and the related structure in the fragment. b) Number of aliphatic unsturated carbon-carbon bond in the fragment. c) Effective carbon number for molar sensitivity correction of FID responce is calculated as follows:[7] Effective carbon number (n)=c−(0.1 u+1.25 e). d) Effective carbon number in carboxyl group is 0.

ends of the PMMA incorporating the residues of BPO and toluene.[11,12]

Figure 3 shows the relationships between the $\overline{M}_n$ of the fractions and the relative peak intensities of the aromatic products after making their molar sensitivity corrections for FID by using effective carbon number (n).[13] The peak intensities monotonously decrease with the rise in $\overline{M}_n$ because relative amounts of the chain ends decrease with the rise in $\overline{M}_n$. Provided that each PMMA molecule has only one aromatic end

Table 3. Relative Yield of the Fragments in the Pyrograms of Fractionated PMMAs

Peak no.	Relative yield[a]				
	F-1	F-2	F-3	F-4	F-5
1	0.17	0.09	0.06	0.04	0.04
2	0.08	0.04	0.03	0.02	0.02
3	0.25	0.15	0.10	0.08	0.07
4	100	100	100	100	100
5	0.01	0.06	0.04	0.03	0.03
6	0.25	0.08	0.04	0.02	0.02
7	0.10	0.07	0.05	0.04	0.03
8	0.10	0.04	0.03	0.02	0.02
9	0.08	0.07	0.06	0.04	0.06
10	0.08	0.04	0.03	0.02	0.02
11	0.06	0.03	0.03	0.02	0.01
12	1.04	0.35	0.16	0.09	0.06
13	0.19	0.10	0.07	0.04	0.04
14	0.04	0.03	0.03	0.01	0.01
15	0.14	0.08	0.06	0.04	0.04
16	0.07	0.05	0.04	0.02	0.02
17	0.17	0.12	0.11	0.06	0.06
18	0.24	0.10	0.06	0.05	0.04
19	0.11	0.05	0.03	0.01	0.01
20	0.07	0.04	0.03	0.02	0.02
21	0.29	0.16	0.10	0.08	0.06
22	0.29	0.19	0.14	0.11	0.10
23	0.10	0.06	0.04	0.04	0.03
24	0.53	0.25	0.15	0.10	0.07
25	0.18	0.17	0.12	0.13	0.10
26	0.08	0.07	0.05	0.05	0.04
27) 28)	0.39	0.22	0.15	0.12	0.09
29	0.09	0.05	0.03	0.03	0.03
30	0.35	0.13	0.07	0.04	0.02
31	0.13	0.05	0.02	0.01	0.01
32	0.44	0.24	0.16	0.14	0.11
33	0.33	0.14	0.08	0.05	0.03

a) Peak area count ralative to that of MMA monomer (%).

group, the ratio of (total number of MMA units)/(total number of aromatic groups) may correspond to the degree of polymerization of a given PMMA sample. Thus, $\overline{M}_n$ of a given PMMA sample can be estimated from the relative peak intensities after making molar sensitivity corrections for FID by using the following equation provided that the aromatic end groups and MMA backbone structures in the polymer chains are quantitatively recoverd on the pyrogram as either of the peaks 1—33;

$$\overline{M}_n = \frac{\sum_{i=1}^{33} (I_i \times m_i/n_i)}{\sum_{i=1}^{33} (I_i \times p_i/n_i)} \times (\text{MW of MMA})$$

where I_i is the intensity of peak i, and m_i, p_i, and n_i are the number of MMA unit and the number of aromatic group in the molecule associated to peak i, and its effective carbon number for FID, respectively. In this case, for example, the m_i number for peaks 13—18 which contain only one -$COOCH_3$ group was counted as 2 since they are originally formed from the MMA diad in the PMMA chain. The observed values for m_i, P_i, and n_i are also shown in Table 2. Thus estimated $\overline{M}_n$ values for the fractions by Py-GC are compared with those by SEC in Table 4. Although the estimated $\overline{M}_n$ values by both methods are almost comparable, those by Py-GC are always slightly larger than those by SEC. This result suggests that under the given polymerization conditions thermal initiation and/or the chain transfer to the monomer, which yield polymer chains without any aromatic chain ends, might take place to some extent over the recombination termination which yields polymer chains with both aromatic chain ends. Furthermore, the fact that the differences between the two $\overline{M}_n$ values (a/b in Table 4) become mostly larger in the smaller molecular weight fractions suggests that PMMA molecules formed by the recombination termination might more abundantly exist in the larger molecular

Table 4. Number-Average Molecular Weight (M_n) of Fractionated PMMAs Estimated by Py-GC and SEC

Fraction	M_n ($\times 10^4$)		a/b
	by Py-GC (a)	by SEC[a] (b)	
F-1	0.90	0.57	1.6
F-2	2.3	1.9	1.2
F-3	4.3	3.2	1.3
F-4	7.2	6.3	1.1
F-5	10.6	9.3	1.1

a) On the basis of polystyrene standards.

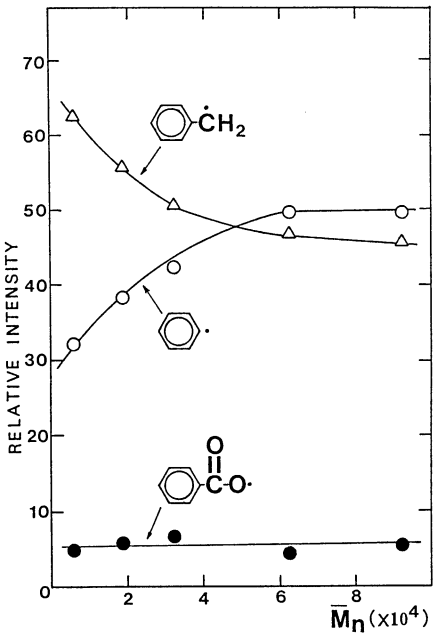

Fig. 4. Relationships between $\overline{M}_n$ of fractionated PMMAs and relative total peak intensities among aromatic products reflecting benzoyloxy-initiated (peak 19; ●), phenyl-initiated (peak 2+24+31+33; ○), and benzyl-initiated (peak 6+12+30; △) chain ends.

weight fractions.

Here, the observed aromatic products on the resulting pyrograms can be attributed to either of the following three kinds of aromatic chain ends; a) incorpolating a benzoyloxy radical from BPO (peak 19), b) a phenyl radical from BPO (peaks 2, 24, 31, and 33), and c) a benzyl radical from toluene (peaks 6, 12, and 30).[12] Figure 4 shows the relationships between the relative molar intensities of the three kinds of peaks and $\overline{M}_n$ of the fractions. Relative intensities of the solvent-incorpolating chain ends (Δ) decrease with the rise of $\overline{M}_n$ while those of the phenyl radical-initiated chain ends increase. This fact suggests the following reaction processes: At the first stage of the reaction the phenyl radical from the initiator predominantly initiates the polymerization of MMA to yield relatively larger PMMA molecules because of the initial higher concentration of the initiator and the monomer, whereas the contribution of the chain transfer to the solvent to yield smaller PMMA molecules is relatively enhanced at the later stage of the reaction because both the initiator and the monomer are consumed as a function of the reaction time.

Financial support from a Grant-in-Aid for Scientific Research No. 61470064 from the Ministry of Education, Science and Culture is gratefully acknowledged.

References

1) J. C. Bevington, J. R. Ebdon, and T. N. Huckerby, *Eur. Polym. J.*, **21**, 685 (1985).
2) D. E. Axelson and K. E. Russel, *Prog. Polym. Sci.*, **11**, 221 (1985).
3) K. Ute, T. Kitayama, and K. Hatada, *Polym. J.*, **18**, 249 (1986).
4) K. Hatada, T. Kitayama, and E. Masuda, *Polym. J.*, **18**, 395 (1986).
5) J. C. Bevington, S. W. Breuer, and T. N. Huckerby, *Angew. Makromol. Chem.*, **140**, 145 (1986).
6) T. Kashiwagi, A. Inaba, J. E. Brown, K. Hatada, T. Kitayama, and E. Masuda, *Macromolecules*, **19**, 2160 (1986).
7) P. Longo, A. Grassi, C. Pellecchia, and A. Zambelli, *Mcromolecules*, **20**, 1015 (1987).
8) J. L. Gerlock, D. F. Mielewski, D. R. Bauer, and K. R. Carduner, *Macromolecules*, **21**, 1604 (1988).
9) J. Devaux, D. Daoust, R. Legras, J. M. Dereppe, and E. Nield, *Polymer*, **30**, 161 (1989).
10) T. Kitayama, *Kobunshi*, **37**, 476 (1988).
11) H. Ohtani, S. Ishigro, M. Tanaka, and S. Tsuge, *Polym. J.*, **21**, 41 (1989).
12) H. Ohtani, M. Tanaka, and S. Tsuge, *J. Anal. Appl. Pyrolysis*, **15**, 167 (1989).
13) J. C. Sternberg, W. S. Gallaway, and D. T. L. Jones, "Gas Chromatography," ed by N. Brenner, J. E. Callen, and M. D. Weiss, Academic Press, New York (1962), p. 231.