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Characterization of Branched Alkyl End Groups of Poly(methyl methacrylate) by Pyrolysis−Gas Chromatography

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ABSTRACT: Branched alkyl end groups of poly(methyl methacrylate) (PMMA) polymerized radically with 2,2′-azobis(2,4,4-trimethylpentane) as an initiator were characterized by pyrolysis−gas chromatography (Py-GC). On the resulting pyrogram at 540 °C, characteristic products formed from the end group moiety due to the initiator, such as isobutane, isobutene, and so on, were clearly separated from those from the main chain. Then number-average molecular weight (M_n) of PMMA was determined by the ratio of the relative intensity of these peaks due to the end group and the main chain. After simple correction using a reference PMMA sample having different end groups, M_n values estimated by Py-GC agreed well with those obtained by size exclusion chromatography. Furthermore, determination of end groups well supported the assumption that disproportionation was dominant in termination in this polymerization system of MMA.

Introduction

Since end groups in polymers are generally attributed to an initiator and/or chain transfer and terminating agent incorporated into polymer chains, analysis of end groups is one of the most substantial approaches for assessing the mechanism of polymerization. Furthermore, the presence or absence of specific end groups often causes significant changes in the polymer properties, and thus precise characterization has eagerly been sought in recent multifunctionalization of polymeric materials. The characterization of end groups in a high molecular weight (MW) polymer sample, however, is not an easy task because of their very low relative concentration. Generally, nuclear magnetic resonance (NMR) has been most extensively used for characterization of end groups in polymers.[1−7] However, its sensitivity and resolution have not always been adequate for quantitative analysis of end groups in high-MW polymers.

Pyrolysis−gas chromatography (Py-GC) has been successfully utilized for end group analyses.[8−15] For example, the determination of end groups in anionically polymerized polystyrenes (PSs) was successfully carried out by Py-GC, where direct estimation of M_n of PSs ranging from a few thousands to ca. one million proved to be possible.[14] As for poly(methyl methacrylate) (PMMA), the end groups in macromolecules radically polymerized with azobis(isobutyronitrile) (AIBN) or benzoyl peroxide (BPO) as an initiator and several thiols as transfer agents were investigated and interpreted in terms of the polymerization mechanism.[8−11,15] In these cases, the associated end groups incorporated into PMMA, the nitrile groups from AIBN, and the thiol groups from the transfer agents were easily detected by use of a nitrogen−phosphorus detector and a sulfur-selective flame photometric detector, respectively.[8,11,15] Moreover, peaks of aromatic products characteristic of the end groups due to BPO were clearly discriminated from those of the main chain of PMMA on the basis of their mass spectra.[8−10]

PMMA is widely used for many optical materials because of its high transparency and low occurrence of birefringence. However, it is known that end groups due to peroxide initiators such as di-*tert*-butyl peroxide and dicumyl peroxide have strong absorption in the ultraviolet region, which often has influence on the visible region absorption.[16] Furthermore, when a peroxide initiator is used for the radical polymerization of methyl methacrylate (MMA), hydrogen abstractions often occur at the α-methyl and/or methyl ester groups, and the resulting polymer has optically undesirable branch structures.[17] On the other hand, an azo initiator has a relatively weak influence on the visible region. However, the typical azo initiator, AIBN, is difficult to distill to remove microparticulates, which cause light scattering in the resulting polymers.[16] On the other hand, a novel alkyl azo compound such as 2,2′-azobis(2,4,4-trimethylpentane) (ABTMP) can be used as an initiator usable in a vacuum-distilling higher temperature polymerization chamber to prepare PMMA. Therefore, the PMMAs thus obtained are expected to have excellent transparency.[16−18] However, branched alkyl end groups in the PMMAs due to the initiator are difficult to analyze by ^{1}H NMR even using solvents such as benzene-d_6 and nitrobenzene-d_5. In this study, the branched alkyl end groups in the PMMAs are characterized by Py-GC in terms of their number-average molecular weight (M_n).

Experimental Section

Samples. Two PMMA samples used in this work were radically polymerized in ampules in the presence of ABTMP as the initiator at 100 or 140 °C, respectively. Reagent grade

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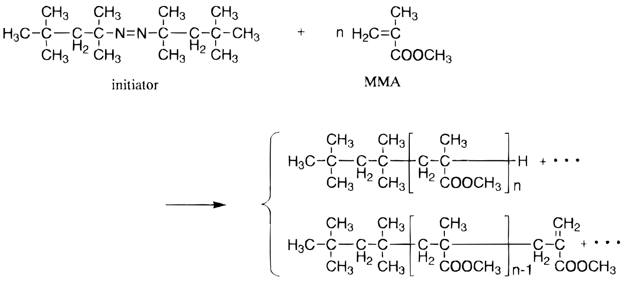
Table 1. Conditions for Polymerization Procedures and Average Molecular Weights of the Resulting Polymers

sample	feed composition initiator/MMA (mol/mol)	polymerization		drying		$M_n{}^a$ ($\times 10^5$)	$M_w{}^b$ ($\times 10^5$)	M_w/M_n
		temp (°C)	time (min)	temp (°C)	time (h)			
S-1	0.709/100	140	60	80	15	0.278	1.57	5.65
S-2	0.394/100	100	60	70	64	4.00	8.60	2.18

[a] M_n = number-average molecular weight. [b] M_w = weight-average molecular weight.

Scheme 1



ABTMP was obtained from Wako Pure Chemical Industries, Ltd., and used without further purification. Thus the PMMAs obtained were reprecipitated from their acetone solutions into hexane in order to remove the residual initiator and oligomers. Then, low- and high-MW PMMAs were dried in vacuo at 80 °C for 15 h and at 70 °C for 64 h, respectively. The detailed conditions for the polymerization and average MWs of the resulting polymers measured by size exclusion chromatography (SEC) are shown in Table 1.

When radical polymerization proceeds at higher temperatures in the presence of sufficient amounts of the initiator, it is well known that the propagation reaction is almost exclusively terminated by disproportionation rather than combination. Therefore, the chemical structures shown in Scheme 1 were expected to be valid for the resulting polymer molecules. Another PMMA sample ($M_n = 6.27 \times 10^4$) polymerized radically with BPO as an initiator was used as a reference sample with terminal groups different from those synthesized in the presence of ABTMP.[8-10]

Py-GC Measurement. The Py-GC system utilized in this work is basically the same as that described previously.[19] Py-GC measurements were carried out on a gas chromatograph (Hewlett-Packard 5890) equipped with a flame ionization detector (FID) and a fused-silica capillary column (Hewlett-Packard PONA, 50 m long × 0.20 mm i.d. coated with 0.50 μm cross-linked poly(dimethylsiloxane)). About 350 μg of the sample was pyrolyzed rapidly under the flow of a carrier gas (He) at 540 °C using a vertical microfurnace pyrolyzer (Yanaco GP-1018, improved type) directly attached to the injection port of the gas chromatograph. This pyrolyzer has a feedback circuit consisting of a thermocouple and PID (proportional, integral and derivative action) controller for precise temperature control. Furthermore, its furnace block in the pyrolyzer is located close to the injection port of the gas chromatograph and the joint connector between the pyrolyzer and the injection port is maintained near the maximum column temperature to prevent the condensation and/or desorption of the resulting pyrolysates. The optimum pyrolysis temperature of 540 °C was decided according to the best recovery of the products formed from end group moieties of the polymer. The pyrolysis products formed under the flow of He carrier gas at 60 mL/min were introduced into the column in the split mode with a split ratio of 60:1 and column head pressure of 200 kPa. The column temperature was held at 0 °C for 5 min by liquid carbon dioxide coolant to improve the resolution of the pyrolysis products with lower boiling points and then programmed to 280 °C at a rate of 4 °C/min. The identification of the characteristic peaks on the resulting pyrogram was mostly carried out by use of a gas chromatography/mass spectrometry (GC/MS) system (Shimadzu GCMS-QP1000) to which the pyrolyzer was also attached.

SEC Measurements. SEC measurements were carried out on a gel permeation chromatograph (TOSOH HLC-8020) equipped with a differential refractive index detector. A TOSOH HM column and two GMH$_{XL}$ columns connected in series were used in these measurements. A 0.2 mL sample solution (0.2 g/mL) was injected into the column held at 40 °C under a 1.0 mL/min flow of tetrahydrofuran. PS standards were used for the calibration of M_n.

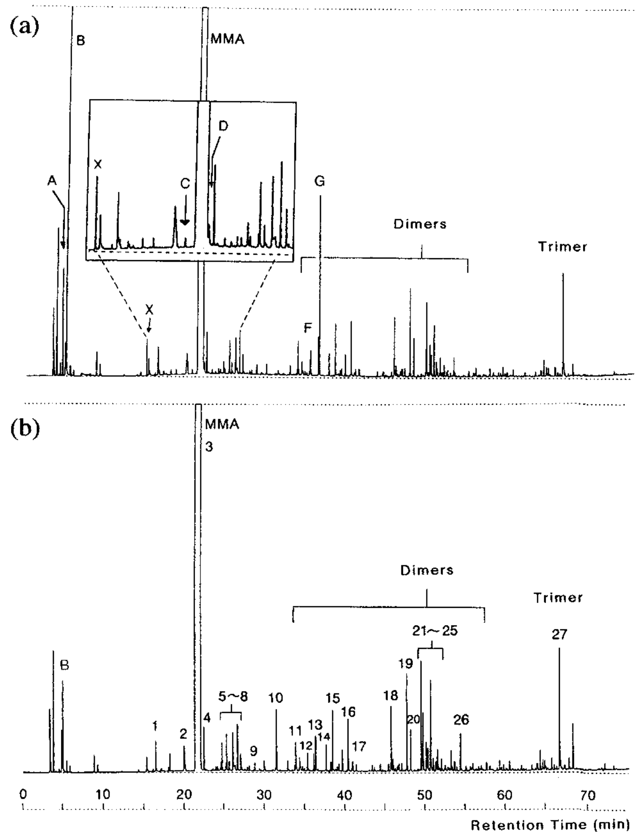


Figure 1. Comparison of pyrograms of PMMA polymerized with different initiators: (a) PMMA polymerized with ABTMP; (b) PMMA polymerized with BPO.[10]

Results and Discussion

Figure 1 shows pyrograms of (a) PMMA(S-1: $M_n = 2.78 \times 10^3$) initiated by ABTMP and (b) the reference PMMA sample initiated by BPO. Since PMMA has a tendency to depolymerize mostly into the original monomer at elevated temperatures, the main pyrolysis product is MMA monomer (ca. 95%). In addition, dimer peaks and a trimer peak are observed in the pyrograms. Furthermore, many minor components are also observed as well-separated peaks. Among these, the five peaks A, C, D, F, and G are observed only in pyrogram a. This result indicates that these components arise from the end moiety originating from the initiator, ABTMP. Additionally, peak B should be mostly attributed to one of the initiator-related products although that is also observed in pyrogram b even with weaker intensity. Actually, the relative intensity of peak B on the pyrogram for sample S-1 proved to be much larger than that for sample S-2 with smaller average MW.

Figure 2 shows a pyrogram of the intact initiator, ABTMP, measured under the same pyrolytic conditions.

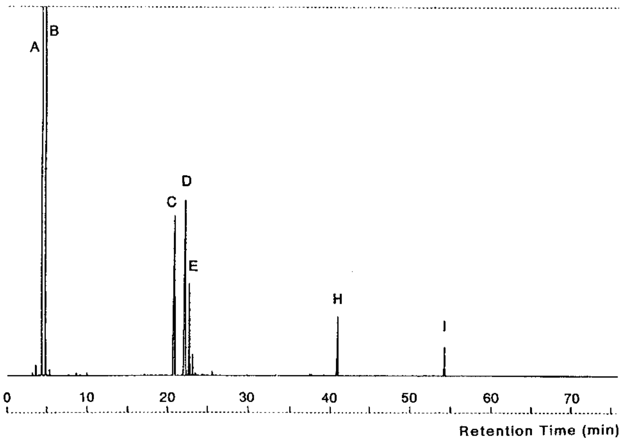
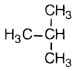
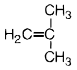
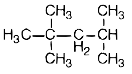
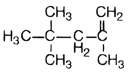
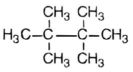
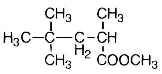
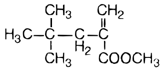
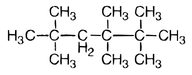
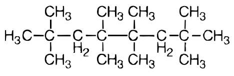


Figure 2. Pyrogram of the intact initiator, 2,2′-azobis(2,4,4-trimethylpentane).

Table 2. Assignment of Peaks Concerned with the Initiator Observed in the Pyrograms

peak	chemical structure	MMA units	end group units[a]	ECN[b]	source
A	 $H_3C{-}CH(CH_3)_2$	0	0.5	4.0	end moiety
B	 $H_2C{=}C(CH_3)_2$	0	0.5	3.9	end moiety & main chain
C	 $H_3C{-}C(CH_3)_2{-}CH_2{-}CH(CH_3)_2$	0	1.0	8.0	remaining initiator fragment
D	 $H_3C{-}C(CH_3)_2{-}CH_2{-}C(=CH_2){-}CH_3$	0	1.0	7.9	remaining initiator fragment
E[c]	 $H_3C{-}C(CH_3)_2{-}C(CH_3)_2{-}CH_3$	0	1.0	8.0	initiator
F	 $H_3C{-}C(CH_3)_2{-}CH_2{-}CH(CH_3){-}COOCH_3$	1	0.5	7.75	end moiety
G	 $H_3C{-}C(CH_3)_2{-}CH_2{-}C(=CH_2){-}COOCH_3$	1	0.5	7.65	end moiety
H[c]	 $H_3C{-}C(CH_3)_2{-}CH_2{-}C(CH_3)_2{-}C(CH_3)_2{-}CH_3$	0	1.5	12.0	initiator
I[c]	 $H_3C{-}C(CH_3)_2{-}CH_2{-}C(CH_3)_2{-}C(CH_3)_2{-}CH_2{-}C(CH_3)_2{-}CH_3$	0	2.0	16.0	initiator

[a] End group unit; C_8 = 1.0. [b] ECN; effective carbon number. [c] Observed only in the pyrogram of the intact initiator.

These peaks observed in Figure 1a and Figure 2 identified by Py-GC/MS are summarized in Table 2, while the assignment of the other peaks observed in Figure 1a,b is shown in Table 3. The peaks listed in Table 2 can be mostly attributed to the initiator-related fragments formed from the end group moiety of PMMA obtained with ABTMP.

However, the intensities of peaks C and D did not show any significant correlation with the M_n between samples S-1 and S-2, suggesting that these peaks were not significantly reflecting the end group moiety in the polymer chain obtained with ABTMP. On the other hand, a peak due to residual solvent (hexane), labeled X, was observed at 15 min in Figure 1a, suggesting the possible existence of remaining initiator agents and/or their fragments in the polymer system. However, because the other peaks originating from the initiator such as E, H, and I observed in Figure 2 were not observed in Figure 1a, peaks C and D can be regarded as indifferent to the remaining initiator agents in the polymer system. Thus, peaks C and D most probably originated from the remaining initiator fragments in the polymer system generated through the higher temperature polymerization of the PMMA even after re-precipitations followed by vacuum drying.

Table 3. Assignment of Common Peaks Concerned with the Main Chain of PMMA[10]

peak	MW	chemical structure	MMA units	ECN[a]
1	88	$CH_3CH_2COOCH_3$	1	2.75
2	102	$CH_3CH(CH_3)COOCH_3$	1	3.75
3	100	$CH_2{=}C(CH_3)COOCH_3$ (monomer)	1	3.65
4	116	$C_6H_{12}O_2$	1	4.75
5	92	$PhCH_3$[b]	0	7.00
6	116	$C_6H_{12}O_2$	1	4.75
7	114	$C_6H_{10}O_2$	1	4.65
8	114	$C_6H_{10}O_2$	1	4.65
9	114	$C_6H_{10}O_2$	1	4.65
10	104	$PhCH{=}CH_2$[b]	0	7.90
11	142	$C_8H_{14}O_2$	2	6.65
12	140	$C_8H_{12}O_2$	2	6.65
13	156	$C_9H_{16}O_2$	2	7.65
14	140	$C_8H_{12}O_2$	2	6.65
15	140	$C_8H_{12}O_2$	2	6.65
16	158	$C_9H_{18}O_2$	2	7.65
17	158	$CH_3OCOCH{=}CHCH_2COOCH_3$	2	4.40
18	186	$C_9H_{14}O_4$	2	6.40
19	200	$C_{10}H_{16}O_4$	2	7.40
20	186	$C_9H_{14}O_6$	2	6.40
21	200	$C_{10}H_{16}O_4$	2	7.40
22	200	$C_{10}H_{16}O_4$	2	7.40
23	200	$C_{10}H_{16}O_4$	2	7.40
24	214	$C_{11}H_{18}O_4$	2	8.40
25	214	$C_{11}H_{18}O_4$	2	8.40
26	190	$PhCH_2CH{=}C(CH_3)COOCH_3$[b]	1	10.65
27	300	$C_{15}H_{24}O_6$ (trimer)	3	11.25

[a] ECN = effective carbon number. [b] These peaks are only characteristics of PMMA initiated by BPO.

On the basis of the relative intensities of the characteristic peaks due to the end groups observed in the pyrogram, the M_ns of S-1 and S-2 were determined by use of the following equations, where the associated polymerization is assumed to yield polymer molecules having one initiator residue, the 2,2,4,4-tetramethylbutyl (C_8) group at the chain end,

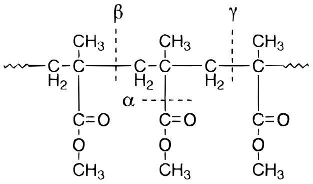
$$\mathrm{DP} = \frac{I_{\mathrm{MMA}}/3.65}{(I_A/4.0 + I_B/3.9 + I_F/7.75 + I_G/7.65)/2} \tag{1}$$

$$M_n = \mathrm{DP} \times 100 + 113 \tag{2}$$

where DP is the degree of polymerization, I_i is the intensity of peak i and divisors such as 3.65, 4.0, and so on are empirically effective carbon numbers, which compensate the molar sensitivity for the FID response, of the respective components.[20] Since only half fragments (C_4) of the end group (C_8) are reflected in the characteristic products (A, B, F, and G), the denominator in eq 1 is divided by 2. The values 100 and 113 in eq 2 are the molecular weights of the MMA unit and the end group residue (the 2,2,4,4-tetramethylbutyl group), respectively.

Thus calculated M_n values are shown in Table 3 together with the reference values measured by SEC. Generally, the M_n values obtained by Py-GC are some-

Scheme 2



what smaller than the reference values. The reason for this deviation could be attributed to the overestimation of the intensity of peak B. As mentioned earlier, peak B (isobutene) is also observed with even smaller intensity in the pyrogram of the reference sample initiated by BPO. This fact suggests that isobutene is also formed to some extent from the main chain of PMMA through side chain thermal cleavages at the α position followed by main chain scissions at β and γ (Scheme 2). Therefore, the contribution of this side reaction should be taken into consideration. Thus the corrected DP′ or M_n' values can be calculated by use of the following equations:

$$\frac{1}{\mathrm{DP}'} = \frac{1}{\mathrm{DP}} - k \qquad (3)$$

$$k = \frac{(I_{\mathrm{B}*}/3.9)/2}{I_{\mathrm{MMA}*}/3.65} \qquad (4)$$

where DP′ is the corrected degree of polymerization, k is the molar contribution of isobutene from the main chain of PMMA against the molar yield of MMA from the same chain obtained from Py-GC measurement of the reference PMMA sample, I_{i*} is the intensity of peak i observed in the pyrogram of the reference sample, and 3.65 and 3.9 are the same molar sensitivities in eq 1. The estimated value of k was 7.14×10^{-4} and its coefficient of variation (CV) value was 3.46% for three measurements. Table 4 summarizes the corrected values for the two samples. The corrected M_n values are in fairly good agreement with the reference values obtained by SEC. However, CV values for the corrected M_n became somewhat larger than those for the uncorrected version because one more additional experimental value with the reference PMMA sample was used for the correction.

By this method, determination of branched alkyl end groups without any heteroatoms and/or functional groups was successfully carried out. Additionally, the fairly good agreement between the observed M_n values by Py-GC and SEC shown in Table 4 strongly supports the validity of the assumption implicit in this method concerned with the termination mechanisms exclusively through disproportionation.

Table 4. Number-Average Molecular Weights Measured by Use of Py-GC and SEC

	M_n		
		Py-GC	
sample	SEC	DP × 100 + 113	DP′ × 100 + 113
S-1	2.78×10^4	2.17×10^4 (CV = 0.24%)[a]	2.55×10^4 (CV = 0.46%)
S-2	4.00×10^5	1.03×10^5 (CV = 3.65%)	3.71×10^5 (CV = 15.1%)

[a] CV (coefficient of variation) values were measured for three runs.

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