Quantification of End Groups in Anionically Polymerized Poly(methyl methacrylate)s by Pyrolysis−Gas Chromatography

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ABSTRACT: End groups in anionically polymerized standard poly(methyl methacrylate)s (PMMAs) in the range of number average molecular weight (M_n) = 2.0×10^4 to 1.3×10^6 with narrow molecular weight distribution were determined by pyrolysis−gas chromatography (Py-GC). The characteristic fragments reflecting the end groups on the pyrogram of the PMMAs were identified by comparison with those of a radically polymerized PMMA together with the mass spectra of the characteristic peaks on the resulting pyrograms taken by a gas chromatograph−mass spectrometer (GC-MS) system. Concentrations of the end groups determined from their relative peak intensities were interpreted in terms of M_n and then compared with their reference values from the manufactures and those estimated by ^{1}H-NMR. By this method, direct determination of the end groups was possible even for PMMA with $M_n \doteqdot 10^6$ without using any standard polymer samples.

Introduction

The characterization of polymer chain ends has been one of the most important subjects which give us valuable clues to clarify the polymerization mechanisms and to design new polymers with improved properties. The identification and determination of polymer chain ends are not easy tasks mainly because of their low concentrations in the polymer chains. However, the recent advent of various analytical techniques has made it possible to carry out the practical studies of the end groups of polymers. The radioactive isotope labeling method has been used over a long period to determine the initiator fragment incorporated at chain ends by measuring the specific activities of radioactive samples prepared with ^{14}C-labeled initiator.[1,2] In recent years, high-field NMR techniques have been successfully applied to study polymer chain ends.[1,3−5] A number of reports have been published on the NMR studies of the end groups of various polymers prepared with the initiators isotopically enriched with NMR-active nuclei such as ^{13}C, ^{2}H, ^{19}F, and ^{15}N.[6−10] In contrast, Hatada et al. polymerized totally deuterated methyl methacrylate (MMA) monomer with nondeuterated initiator to determine the content of the initiator fragments incorporated in the polymer chain by ^{1}H-NMR and discussed the mechanism of polymerization in detail.[11−14]

On the other hand, owing to recent developments in highly specific pyrolysis devices, highly efficient separation columns for gas chromatography (GC), and specific identification of the peaks in the pyrograms by GC−mass spectrometry (GC-MS), pyrolysis−GC (Py−GC) has made a great stride toward being a powerful tool for the structural characterization of polymeric materials.[15−19] Particularly, Py-GC is noted as an extremely sensitive technique as well as a simple and rapid one. So far, the fragments of initiators, chain transfer reagents, and solvents incorporated into the chain ends of the resulting polymer have been characterized by Py-GC for poly(methyl methacrylate)s (PMMAs) radically polymerized using various initiators such as benzoyl peroxide (BPO),[20−22] azobisisobutyronitrile,[23,24] and so on.[25]

The macromolecules synthesized through the radical polymerization generally have a variety of end groups, such as the initiator, chain transfer agent, and solvent residues, and the olefinic and saturated groups formed through disproportionation termination. Accordingly, it has been difficult to make detailed evaluation for the end group determination of the radically polymerized PMMAs by Py-GC. Recently, *n*-butyl end groups in anionically polymerized polystyrenes (PSt's) were studied by Py-GC.[26] The relative intensities of characteristic peaks of the end group moieties observed in the pyrograms were interpreted in terms of number average molecular weight (M_n). The M_n values thus estimated after an adequate correction for the contribution of the side reaction products were in good agreement with their reference values from the supplier of the PSt samples in the molecular weight range between ca. one thousand and one million.

In this work, Py-GC was applied to determine the end groups in a set of standard PMMAs having a wide range of M_n values which were supplied as the standard for the size exclusion chromatography (SEC). Since these samples possess not only narrow molecular weight distributions but also the molecular structure having an end group consisting of the initiator residue at one end and a saturated MMA unit at the other end, they are well suited to evaluate the reliability of Py-GC as a technique for end group analysis. Here the sensitivity and accuracy in the end group determination by Py-GC are compared with those by ^{1}H-NMR.

Experimental Section

Polymer Samples. Seven anionically polymerized PMMA samples (S-I to S-VII; Polymer Laboratories Ltd.) used in this work are the commercially available monodispersion standard ones for SEC with M_n ranging from 2.0×10^3 to 1.3×10^6. The reference M_n values

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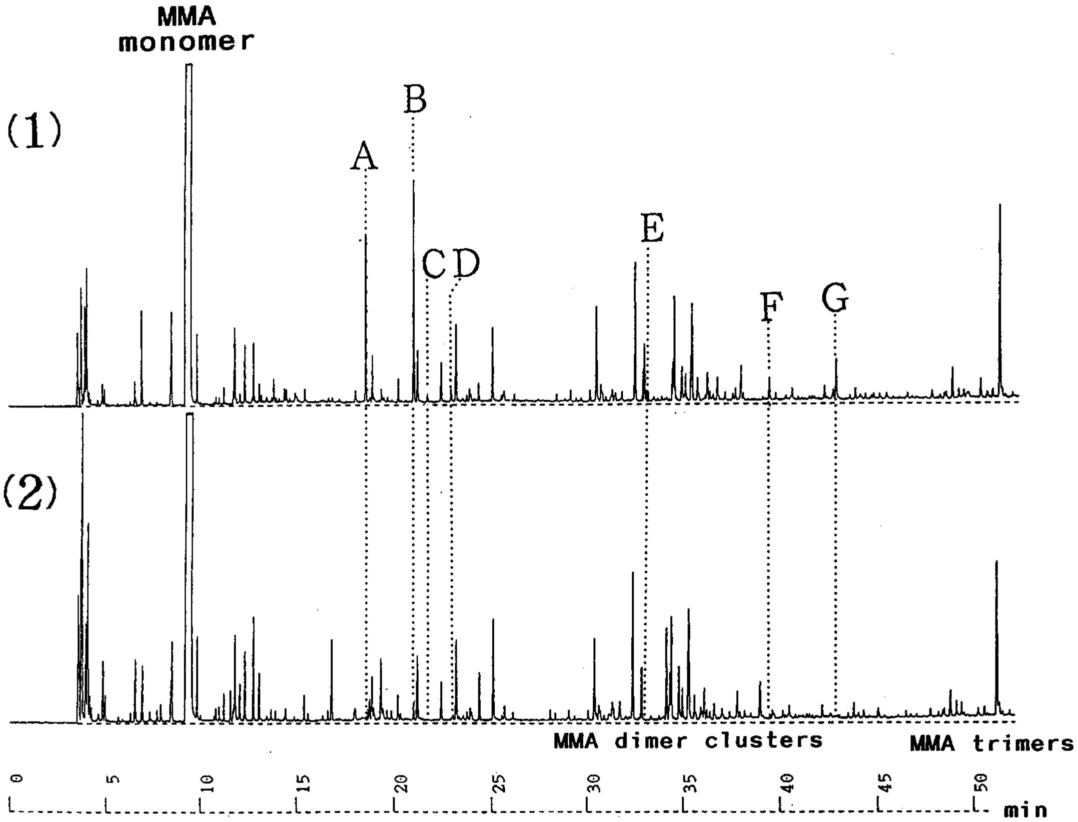


Figure 1. Pyrograms of PMMAs at 540 °C: (1) anionically polymerized PMMA (S-I; $M_n = 20\,200$); (2) radically polymerized PMMA (S_{ref}; $M_n = 62\,700$).

are determined by the manufacturer using SEC. In order to remove the residual solvents and oligomers in the PMMA samples, they were reprecipitated from their acetone solutions by use of methanol. Thus purified samples were dried in vacuo at 60 °C overnight.

A radically polymerized PMMA sample (S_{ref}: $M_n = 62\,700$)[22] prepared in toluene solution in the presence of BPO was also used as a reference sample after purification through reprecipitation.

Conditions for Py-GC. The Py-GC system utilized in this work is basically the same as that described previously.[27] A vertical microfurnace pyrolyzer (Yanaco GP-1018, improved type[25]) was directly attached to a gas chromatograph (Hitachi G-3000) with a flame ionization detector (FID). About 0.5 mg of the polymer sample was pyrolyzed under a flow of helium carrier gas. The pyrolysis temperature was set empirically at 540 °C to get optimum recovery of characteristic products reflecting both backbone and chain end moieties of the PMMA samples. A fused-silica capillary column (Hewlett-Packard PONA, 50 m long × 0.20 mm i.d. coated with 0.5 μm of polydimethylsiloxane immobilized through chemical cross-linking) was used. The 110 mL/min carrier gas flow at the pyrolyzer was split 140:1 to the separation column. The column temperature was programmed from 40 to 250 °C at a rate of 4 °C/min. Identification of the peaks on the pyrograms was carried out using a gas chromatograph–mass spectrometer (Shimadzu QP-1000) with an electron impact ionization source, to which the pyrolyzer was also directly attached (mass scan range, m/z 33–350; cycle time, 3 s; ionization energy, 70 eV).

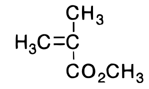
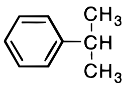
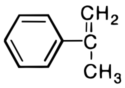
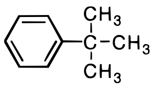
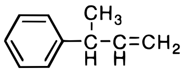
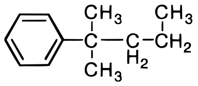
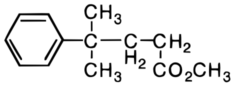
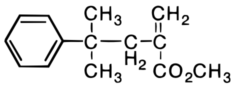
^{1}H-NMR Measurement. The ^{1}H-NMR spectra of the samples were measured on a Varian VXR500 spectrometer (500 MHz) to estimate the comparative data for the end groups. About 5 w/v % of the sample in acetone-d_6 was measured for 500 scans with a spectral width of 8000 Hz, a flip angle of 90°, and a pulse delay of 2 s.

Results and Discussion

The anionically polymerized standard PMMAs and the radically polymerized PMMA with BPO as an initiator have common backbone structures but have different end-group structures. Therefore, by comparing the pyrograms for the two types of PMMAs, the characteristic peaks reflecting the end groups in the standard PMMAs might be estimated. Typical comparative pyrograms for S-I ($M_n = 20\,200$) and S_{ref} ($M_n = 62\,700$) are shown in Figure 1. Since PMMA has a tendency to depolymerize, the main pyrolysis product on the pyrograms (about 95%) is the MMA monomer. In addition, various minor products including MMA dimers and trimers are also observed. However, the peaks of larger products than trimers were negligibly small even under high-temperature GC conditions with the oven temperature up to around 400 °C. This fact suggests that almost all the PMMA chains are reflected in the observed pyrograms as the peaks up to trimers. From detailed comparison of these pyrograms, the characteristic peaks (A–G) proved to be observed only in the pyrogram of S-I. Moreover, among the pyrograms for S-I to S-VII the relative intensities of peaks A–G monotonously decreased with the rise of M_n. These data suggest that the characteristic peaks of A–G are originated from the anionic initiator residue incorporated into the polymer chain.

The structures of these peaks reflecting the chain end were identified mostly by GC-MS. From the observed mass spectra, the relatively abundant peaks of A and B can be assigned as cumene and α-methylstyrene, respectively. These data strongly suggest that these

Table 1. Assignment of Peaks Concerned with the End Groups Observed in the Pyrograms along with That of MMA Monomer

peak	molecular weight	chemical structure	effective carbon number
MMA monomer	100	 $H_3C{=}C(CH_3)CO_2CH_3$	3.65
A	120		9.0
B	118		8.9
C	134		10.0
D	132		9.9
E	174		12.9
F	206		11.75
G	218		12.65

standard PMMA samples were prepared in the presence of a typical anionic initiator containing a cumyl group such as cumyl-K and that one end of these polymers would be terminated with a cumyl group. Therefore, the other mass spectra for the minor peaks of C−G were interpreted assuming that they were also formed from the moiety of the cumyl end group.

Thus estimated structures for A−G are summarized in Table 1 together with their molecular weights and relative molar sensitivities for the FID (effective carbon number; ECN).[28] Each peak area in the pyrogram divided by the ECN is to be proportional to the relative molar abundance. Provided that all of the polymer main chain depolymerizes to MMA and that the chain-end moiety is reflected as peaks A−G, M_n of a given PMMA sample can be estimated from the following equation:

$$M_n = [(I_{MMA}/3.65)/(I_A/9 + I_B/8.9 + I_C/10 + I_D/9.9 + I_E/12.9 + I_F/11.75 + I_G/12.65)] \times 100$$

where I_{MMA} and I_i are the peak intensities of MMA monomer and peaks i (i = A−G) on the pyrogram, the divisor of each peak intensity is the empirically calculated ECN shown in Table 1, and 100 is the molecular weight of MMA. In this calculation, only MMA monomer was taken into consideration for the product reflecting the main chain neglecting the minor dimer and trimer clusters, since the latter contribution, if any, introduced less than 1−2% difference in the resulting M_n values.

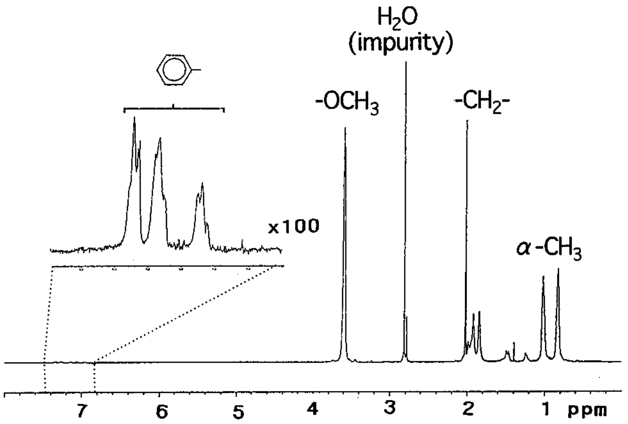


Figure 2. ^{1}H-NMR spectrum of PMMA. Sample: S-I (M_n = 20 200).

Table 2. Number Average Molecular Weight of Poly(methylmethacrylate)s Calculated from End-Group Analysis by Py-GC and ^{1}H-NMR

	number average molecular weight (M_n)		
sample	ref[a]	Py-GC	^{1}H-NMR
S-I	20 200	21 400	27 000
S-II	33 900	35 500	35 700
S-III	66 200	70 200	67 200
S-IV	91 400	103 000	98 700
S-V	296 000	317 000[b]	(213 000)
S-VI	797 000	731 000[c]	
S-VII	1 330 000	1 160 000	

[a] Reference M_n specified by the manufacturer. [b] CV = 1.4% for five measurements. [c] CV = 4.1% for five measurements.

Figure 2 shows a typical ^{1}H-NMR spectrum for a PMMA sample (S-I; M_n = 20 200). On the expanded partial spectrum (×100) around 7.1−7.4 ppm, three phenyl-proton peaks reflecting the cumyl chain ends are observed. Since the intensity ratio of these three peaks is about 2:2:1, they may correspond to the proton number of *o*-, *m*- and *p*-positions in the phenyl ring, respectively. On the other hand, the methoxy proton peak at about 3.6 ppm can be used as the key peak reflecting the backbone of the polymer chain. Using these peak intensities, M_n of a given PMMA sample can be estimated from the following equation:

$$M_n = \frac{I_{OMe}/3}{I_{Phe}/5} \times 100$$

where I_{OMe} and I_{Phe} are the intensity of the methoxy proton peak and the total intensity of three phenyl proton peaks, and 100 is the molecular weight of MMA.

Thus estimated M_n values by Py-GC and ^{1}H-NMR are compared with the reference values from the manufacturer in Table 2. Data by both Py-GC and ^{1}H-NMR are in fairly good agreement with the reference values for lower molecular weight samples (S-I to S-IV). However, considering the signal to noise (S/N) ratio for the observed ^{1}H-NMR spectra under the given spectral condition of 500 scans with a 2 s pulse delay, the estimation of M_n was limited to less than 3×10^5 or so even by the 500 MHz ^{1}H-NMR used in this work. In order to estimate the higher M_n values by NMR, much more numbers of scans should be needed to enhance the S/N ratio. Moreover, since the T_1 values for the end groups are generally larger than those for the main chains such as OCH_3, a much longer pulse delay time might be required to fulfill the sufficiently quantitative conditions for the measurement. On the other hand, Py-GC was able to estimate the M_n values up to ca. 1 × 10^6 with a reproducibility of about 4% or less for five repeated runs, although the M_n value observed by Py-GC for S-VII fairly deviated from the reference one mainly because of the difficulty in the accurate integration of the trace peaks reflecting the end-group moieties in such a high molecular weight sample.

Conclusions

Cumyl end groups in anionically polymerized PMMAs were precisely quantified by Py-GC even for the samples with $M_n = 10^6$, which were difficult to be analyzed even by NMR. For these PMMAs, moreover, it was not necessary to take into account any contribution of the side reaction products, which had affected to some extent the analysis of the *n*-butyl end groups in anionically polymerized PSt's.[26] Here M_n values for the PMMA samples can be directly estimated by the relative peak intensities between MMA formed from the polymer main chains through almost quantitative depolymerization and the characteristic products of the end groups on the observed pyrograms after making molar sensitivity corrections for those products. Consequently, this technique belongs to one of the absolute methods for determining M_n without using any standard polymer samples with known M_n, provided that all the characteristic products of the end groups are to be quantitatively assigned against those from the main chain for given linear polymeric systems.

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