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On-line GPC/NMR experiments using the isotactic poly(methyl methacrylate) with well-defined chemical structure

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SUMMARY

Gel permeation chromatography of isotactic PMMA has been performed on a chromatograph linked to a 500 MHz ^1H NMR spectrometer. ^1H NMR spectra of good resolution and high S/N ratio were collected over the entire chromatographic peak. The Mn of the polymer sample can be directly determined by intensity measurements of the proton signals due to the end-group and monomeric units, since the polymers used were prepared by the living polymerization initiated by $t\text{-}C_4H_9MgBr$. A good linear relation was obtained between the log(Mn) and elution time.

INTRODUCTION

Gel permeation chromatography (GPC) is one of the most popular methods for measuring the molecular weight of polymer and its distribution. Determination of molecular weight by GPC requires a calibration curve, and standard polystyrenes of narrow molecular weight distribution (MWD) are usually used for this purpose. Preparation of other standard polymers with different molecular weights and narrow MWD are generally difficult or laborious, and much attention has been given to empirical means of deriving calibrations for other polymers from that for polystyrene [1]. The only exception at present is detection of GPC chromatogram by light-scattering, in which the weight-average molecular weight (Mw) of a given polymer can be determined without a calibration curve [2]. Recent publications demonstrated the feasibility of an NMR spectrometer as a detector for HPLC [3,4]. The number-average molecular weight (Mn) of the polymer with well-defined structure can be simply determined by NMR provided that the intensity ratio of the signals due to monomeric units and the end-groups is measured with good accuracy. This paper will report the usefulness of a 500 MHz ^1H NMR spectrometer as an informative detector without a calibration curve for GPC.

EXPERIMENTAL

Isotactic PMMAs were prepared with $t\text{-}C_4H_9MgBr$ in toluene at -78°C [5]. These PMMAs have been found by ^1H NMR to contain one $t\text{-}C_4H_9\text{-}$ group at the α-end of the chain and their number average molecular weights (Mn's) can be determined by the intensity measurements of the ^1H NMR signals of $t\text{-}C_4H_9\text{-}$ and residual groups. The tacticities, Mn's and MWDs of the PMMA samples used in this work are summarized in Table 1.

The on-line GPC/NMR system consisted of a JASCO TRI ROTAR-V chromatograph and a JEOL JNM-GX500 spectrometer. A 5 mm quartz tubing (inner diameter = 2 mm) was used for the observation flow cell (Figure 1), and was mounted in the proton probe designed specially for the GPC/NMR system. The chromatograph equipped with a Shodex GPC column KF-802.5 (25 cm X 0.46 cm, maximum porosity = 2 X 10^4) was placed about 2 m from the superconducting magnet, and the connections between the chromatograph and the NMR cell were made with 3 m Teflon tubing (inner diameter = 0.3 mm). The volume within the coil region is about 0.06 mL. For RI detection, the connection to the NMR spectrometer was replaced with a Shodex SE-61 RI detector. Chloroform-d was used as an eluent and the flow rate was 0.2 mL/min. The ^{2}D NMR signal of the eluent was satisfactorily intense for internal lock and shimming of the magnetic field. The injected sample was 2 mg each. The ^{1}H NMR data, each consisted of 8192 data points covering 4500 Hz, were collected over the entire chromatographic peak and stored as 8 coadded scans every 24 s. The spin-lattice relaxation times (T_1's) of CH_3O- and t-C_4H_9- signals were found to be 1.02 s and 0.51 s, respectively, thus 45^o pulse and the repetition time of 3.0 s were employed for correct measurement of intensity of the signals. A line broadening factor of 0.55 Hz was applied.

Table 1 Isotactic PMMAs Used in This Work

Mn[a]	Mw/Mn[b]	Triad tacticity(%)[a]		
		mm	mr	rr
5,260	1.13	96.9	3.0	0.1
3,160	1.19	95.3	4.3	0.4

[a] Determined by ^{1}H NMR.
[b] Determined by GPC calibrated against standard polystyrenes.

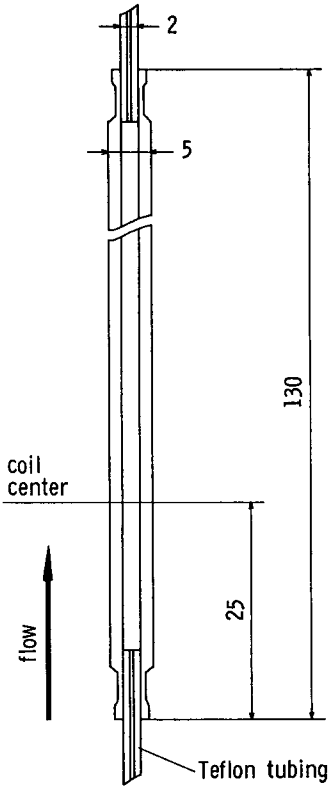

Figure 1 Schematic diagram of the 5 mm quartz tubing used for the NMR observation flow-cell. The figures indicate the length in mm.

RESULTS AND DISCUSSION

Figure 2 shows the ^{1}H NMR-detected GPC curves for the isotactic PMMAs with Mn's of 5260 and 3160. The curves (solid lines) were obtained by plotting the intensity of CH_3O- proton signal (3.6 ppm) against the elution time. Elution profiles of the sample at the chemical shift of any other signal can be derived from the data matrix. The GPC curves recorded with RI-detector are also shown in Figure 2. The difference between the elution times for the NMR-detected and the RI-detected elution curves resulted from the difference in the void volume of the connecting paths.

The ^{1}H NMR spectrum of the PMMA (Mn = 5260) stored as a single file during the elution time from 38.8 to 39.2 min. (cf. Figure 2) is shown in Figure 3. The signal-to-noise ratio (S/N) of the t-C_4H_9- proton signal is 48.5. The Mn of the PMMA detected in this file was calculated to be 6450,

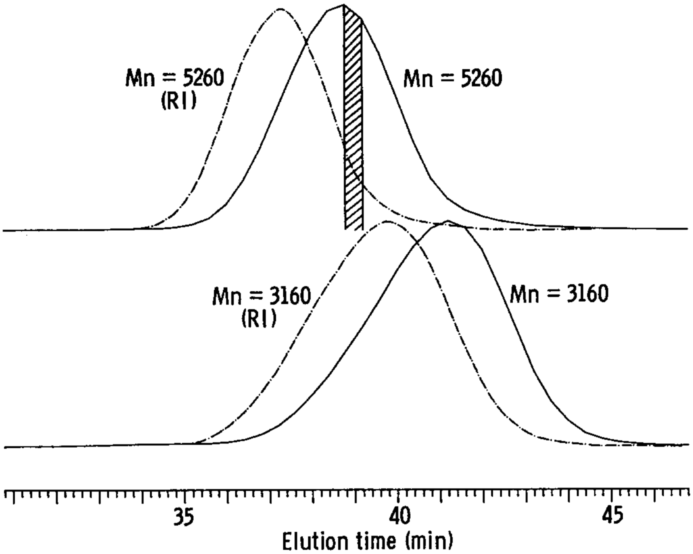

Figure 2 The ^{1}H NMR-detected GPC curves of the isotactic PMMAs with Mn's of 5260 and 3160. These curves were obtained by plotting the intensity of the CH_3O- proton signal (3.6 ppm). The RI-detected GPC curves are also shown.

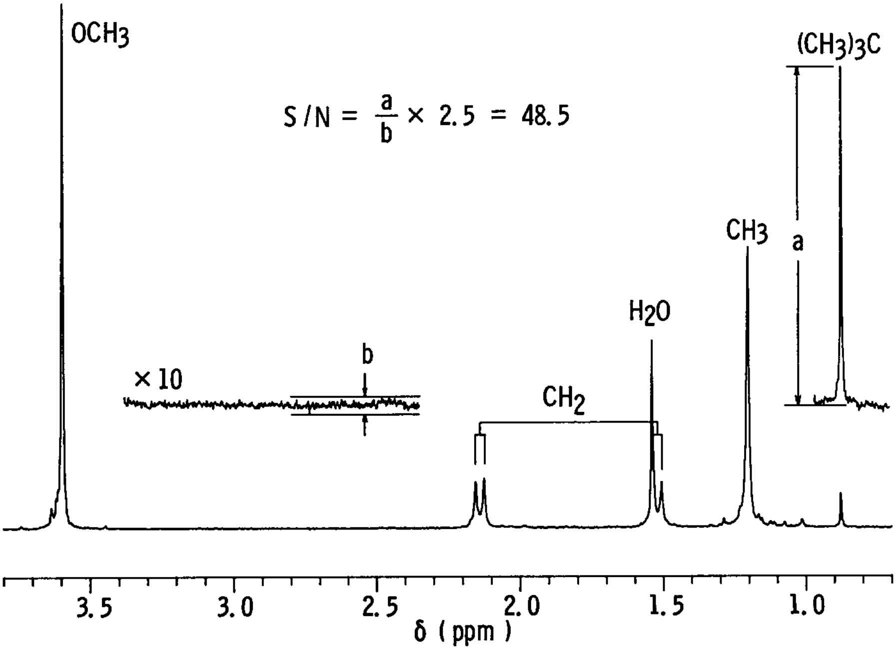

Figure 3 The ^{1}H NMR spectrum of the isotactic PMMA (Mn = 5260) stored as a single file at the elution time from 38.8 to 39.2 min. (45° pulse, 8 scans, 8192 data points covering 4500 Hz, line-broadening factor of 0.55 Hz.)

from the intensity ratio for the signal of CH_3O- to that of t-C_4H_9-. Similarly, spectra with good resolution and high S/N were obtained for all the files. Those files in which the S/N of the t-C_4H_9- proton signal was less than 9.0 were coadded with 2 or 3 contiguous files so that the ratio exceeded 9.0. The background signals due to the small amount of impurities in the eluent, other than the signal of H_2O, were completely eliminated by subtracting the base line absorbance, with some improvement of S/N of the spectrum. The molecular weight of the PMMA which has Mn of approximately 20000 would be determined in this manner if a GPC column having larger maximum porosity than that used in this work is applied.

The logarithm of Mn calculated from the ^1H NMR spectrum of each file is plotted against its elution time, and a good linear relation was obtained for both PMMA samples as shown in Figure 4 (solid lines). The slopes for the two sets of data were smaller than that for the calibration curve made by plotting the log(Mn) of the isotactic PMMAs (Mn = 12600, 5260 and 3160) against the peak-maximum elution time using RI-detection (a broken line indicated in Figure 4). This may indicate that diffusion of the elution band occurred to some extent in the connecting path and in the NMR flow cell, although the line shapes and the half-height widths of the NMR-detected GPC curves showed little difference from those of the RI-detected curves (cf. Figure 2). Further investigations are being made on the improvement in the arrangement of the chromatograph and spectrometer and in the design of the NMR flow cell.

However, the results mentioned here indicate the usefulness of on-line GPC/NMR for the preparation of GPC calibration curve when the polymer

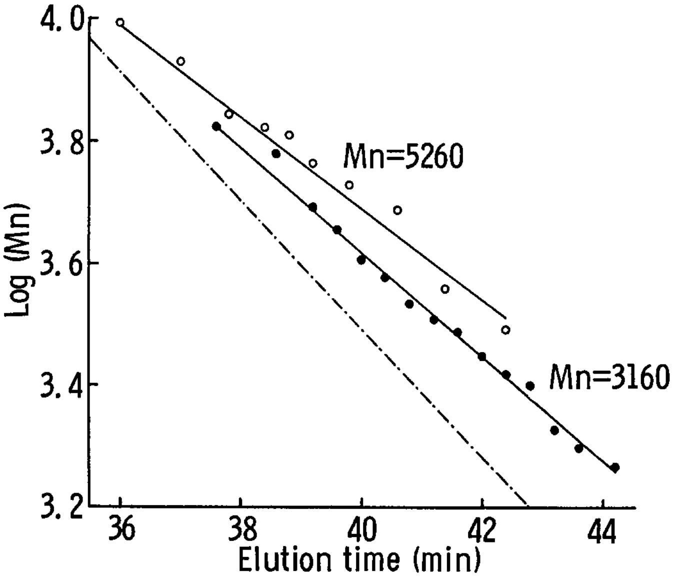

Figure 4 Plots of log(Mn) of isotactic PMMAs determined from the intensity ratio for the ^1H NMR signal of CH_3O- to t-C_4H_9- against elution time; Mn = 5260 (○), 3160 (●). The calibration curve made by plotting the log(Mn) of the isotactic PMMAs (Mn = 12600, 5260 and 3160) against the peak-maximum elution time using RI-detection is also shown.

samples of well defined structure are available. The major limitation in the on-line GPC/NMR is the sensitivity of NMR spectrometer. Our results clearly show a good applicability of the 500 MHz ^{1}H NMR spectrometer equipped with a 2 mm flow cell to on-line GPC/NMR as a sensitive and informative detector. Relatively short T_1 of polymer sample permits short pulse intervals and concurrently the increased data acquisition rate to improve the S/N of the spectra. Thus, the on-line GPC/NMR technique is highly promising in studying the molecular weight dependence of polymer properties such as tacticity and copolymer composition.

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