Determination of Molecular Weight of Poly(methyl methacrylate) by Deuterium NMR and Its Reliability

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(Received February 3, 1990)

ABSTRACT: The number average molecular weight M_n of the PMMA prepared by the living polymerization with $\text{CH}_3(\text{CD}_3)_2\text{CMgBr}$ was determined by the absolute method using deuterium NMR. The M_n value agreed well with that determined by proton NMR, based on the intensity ratio of the signal due to the methoxy group in monomeric units to the signal due to the $\text{CH}_3(\text{CD}_3)_2\text{C}-$ group at the left (initiating) end of chain. The results showed that M_n up to 10^5 can be determined reliably by deuterium NMR spectroscopy, when the experimental conditions are carefully arranged.

KEY WORDS Deuterium NMR / End-group Analysis / Molecular Weight
/ Poly(methyl methacrylate) / *t*-Butylmagnesium Bromide / Anionic
Polymerization / Living Polymerization /

Several papers have been published on the application of deuterium (^2H) NMR spectroscopy to the analysis of the end-groups in polymers.^{1–4} As already reported,^{1,2} end-group analysis by this technique offers some general advantages: (1) studies of the end-groups by NMR methods is more informative than those by radioactive techniques because they lead to understanding not only of the contents of the groups but also their structures, (2) the preparation of ^2H -labelled initiators such as 2,2'-azobisisobutyronitrile- d_{12} (AIBN- d_{12}) is easier and/or less expensive than that of initiators enriched with other isotope such as ^3H , ^{13}C , ^{14}C , or ^{15}N , and also than the preparation of totally deuterated monomers,^{5–7} (3) the natural abundance of deuterium is so little that the NMR signals for ^2H -enriched groups in a polymer are hardly affected by the "background" signals, due to the remainder of the polymer molecule.

Bevington and his coworkers^{1,2} observed the ^2H NMR signals due to the initiator fragments in the copolymers prepared by the polymeriza-

tion initiated with AIBN- d_{12} , although the authors were not concerned with intensity measurement of the signals. Hatada *et al.*³ polymerized styrene with AIBN- d_{12} and determined the content of the initiator fragments incorporated in the polymer chain by ^2H NMR; the polystyrene was found to contain 1.65 $(\text{CD}_3)_2\text{C}(\text{CN})-$ fragments per chain, which was consistent with the results of ^1H NMR analysis of the poly(styrene- d_8) prepared with undeuterated AIBN (1.59). The quantitative use of ^2H NMR spectroscopy in the determination of the degree of polymerization was also demonstrated for oligosaccharides.⁸

In the present work, the accuracy of end-group assay using ^2H NMR has been examined through the analysis of the poly(methyl methacrylate) (PMMA) carrying exactly one $\text{CH}_3(\text{CD}_3)_2\text{C}-$ group per chain. The PMMA was prepared by the living polymerization^{9,10} in toluene at -78°C initiated with *t*-butylmagnesium- d_6 bromide and terminated with methanol- d_4 :

Since the PMMA has exactly one $\text{CH}_3(\text{CD}_3)_2\text{C}-$ group per chain,^{9,10} we can evaluate the number average molecular weight M_n of the PMMA by ^2H NMR measurement from the equation $M_n = 6dc/sr$, where d is the isotopic purity (^2H) for the $\text{CH}_3(\text{CD}_3)_2\text{C}-$ group, c and s are the concentrations of the polymer sample (g-sample/g-solvent) and of ^2H of the nitrobenzene- d_5 added as an internal standard in the sample solution (gram deuterium/g-solvent), respectively, and r is the relative intensity of the $\text{CH}_3(\text{CD}_3)_2\text{C}-$ resonance to the standard.

The principal feature of the present technique is that the degree of polymerization DP of the identical sample can be determined also by means of ^1H NMR spectroscopy, from the intensity ratio of the ^1H signals due to the $\text{CH}_3(\text{CD}_3)_2\text{C}-$ and the $\text{CH}_3\text{O}-$ groups. M_n of the PMMA is then given by $(100.1 \times DP) + 65.1$, where the values 100.1 and 65.1 are the formula weight of the monomeric unit ($\text{C}_5\text{H}_8\text{O}_2$) and that of end-groups ($\text{C}_4\text{D}_6\text{H}_3 + \text{D}$), respectively. The DP value needs to be corrected for the isotopic purity of the $\text{CH}_3(\text{CD}_3)_2\text{C}-$ group. Reliability of the intensity measurement by ^1H NMR is well established.¹¹

EXPERIMENTAL

t-Butylmagnesium- d_6 bromide was prepared from *t*-butyl- d_6 bromide (21 mmol) and magnesium (31 mmol) in diethyl ether under dry nitrogen atmosphere. Concentrations of Mg^{2+} and $\text{CH}_3(\text{CD}_3)_2\text{CMg}-$ in the solution were determined as 0.712 M by chelatometric

titration, and 0.265 M by acid-base titration, respectively ($[\text{Mg}^{2+}]/[\text{CH}_3(\text{CD}_3)_2\text{CMg}-] = 2.69$). *t*-Butyl- d_6 bromide was synthesized in 84% yield from phosphorus tribromide and *t*-butanol- d_6 which was prepared from acetone- d_6 (Aldrich) and methylmagnesium bromide. Isotopic purity of the *t*-butyl- d_6 bromide was determined as 98.20% by mass spectroscopic analysis, thus the average composition of ^1H and ^2H nuclei in the *t*-butyl- d_6 group was 3.108 : 5.892.

Polymerization of MMA with *t*-butylmagnesium- d_6 bromide in toluene at -78°C was conducted in a procedure similar to that with *t*-butylmagnesium bromide.^{9,10} The polymerization was terminated by adding a small amount of methanol- d_4 to the polymerization mixture, and the mixture was poured into 300 ml of hexane. The precipitated polymer was recovered by filtration, and was freeze dried with benzene. The yield of the polymer was quantitative.

^1H NMR spectrum was measured on a JEOL JNM-GX500 spectrometer in nitrobenzene- d_5 solution at 110°C ; 16 scans were accumulated with a repetition time of 15 s, using a 90° observation pulse. ^2H NMR spectrum was recorded on a JEOL JNM-GSX400 spectrometer with a 10 mm multinuclear probe operated at 61.3 MHz and 110°C . Nitrobenzene containing a certain amount of nitrobenzene- d_5 (isotopic purity 99.55%) was employed as solvent. The concentration of ^2H in the solvent (s) was determined as $s = 5df/\text{MW}$ ($\text{C}_6\text{D}_5\text{NO}_2$), where d is the isotopic purity of the nitrobenzene- d_5 , f is the weight fraction of nitrobenzene- d_5 in the solvent and MW ($\text{C}_6\text{D}_5\text{NO}_2$) is the formula weight for $\text{C}_6\text{D}_5\text{NO}_2 = 128.15$. The magnetic field was internally-locked by the ^2H resonance due to nitrobenzene- d_5 and was shimmed by monitoring the resonance, then the field-lock was off just before the ^2H NMR measurement. The NMR data consisted of 8K data points covering 1227 Hz, and 64 scans were accumulated with a repetition time of 5.0 s using a 90°

(40.0 μs) pulse. A line-broadening factor of 0.15 Hz was applied. Chemical shift for the ^1H and ^2H NMR spectra referred to the signal due

Table I. ^1H and ^2H - T_1 values measured at 110°C for the PMMA prepared with $\text{CH}_3(\text{CD}_3)_2\text{CMgBr}$ in toluene^a

	T_1/s	
	^1H 500 MHz	^2H 61.3 MHz
$\text{CH}_3(\text{CD}_3)_2\text{C}-$	1.376	0.173
PMMA $\begin{cases} \text{CH}_3- \\ \text{CH}_3\text{O}- \end{cases}$	0.409	—
	1.104	—
$\text{C}_6\text{D}_5\text{NO}_2 \begin{cases} o- \\ m- \\ p- \end{cases}$	12.37 ^b	0.821
	12.61 ^b	0.815
	12.43 ^b	0.559

^a The sample PMMA-6K in Table III was used.

^b T_1 of the residual proton.

to *meta*- ^1H (residual) and *meta*- ^2H of nitrobenzene- d_5 as 7.352 ppm, respectively. Intensities of the ^1H and ^2H resonances were measured by digital integration. Spin-lattice relaxation time (T_1) was determined by the inversion-recovery method (Table I). The values confirm that the repetition time in the ^1H and ^2H NMR measurements exceeds five times T_1 of any relevant signal.

Mass spectra were recorded on a JEOL JMS-DX303HF spectrometer.

RESULTS AND DISCUSSION

Three PMMA samples PMMA-6K, PMMA-13K and PMMA-23K were prepared by the living polymerization initiated with *t*-butylmagnesium- d_6 bromide in toluene at -78°C . All these samples are highly isotactic ($mm >$

Figure 1. ^1H and ^2H NMR spectra of the PMMA (PMMA-23K) prepared with *t*-butylmagnesium- d_6 bromide in toluene at -78°C . (a) 500 MHz ^1H NMR spectrum measured in nitrobenzene- d_5 at 110°C ; (b) 61.3 MHz ^2H NMR spectrum measured in nitrobenzene/nitrobenzene- d_5 (95/5) at 110°C .

Table II. Concentrations of the PMMA prepared with $\text{CH}_3(\text{CD}_3)_2\text{CMgBr}$ (*c*) and of ^2H of $\text{C}_6\text{D}_5\text{NO}_2$ (*s*) in the sample solution and the relative intensity (*r*) of the ^2H NMR signals

Sample	c^a	s^b	<i>r</i>	$\sigma(r)^c$
	g/g	gram- $^2\text{H/g}$		
PMMA-6K	0.10327	0.002001	0.04613	0.00038
PMMA-13K	0.10066	0.001943	0.02331	0.00025
PMMA-23K	0.09684	0.001929	0.01238	0.00034

^a $c = \text{wt}(\text{PMMA}) / (\text{wt}(\text{C}_6\text{H}_5\text{NO}_2) + \text{wt}(\text{C}_6\text{D}_5\text{NO}_2))$ ^b $s = 5df/\text{MW}(\text{C}_6\text{D}_5\text{NO}_2)$; $d = 0.9955$ (isotopic purity of $\text{C}_6\text{D}_5\text{NO}_2$); $f = \text{wt}(\text{C}_6\text{D}_5\text{NO}_2) / (\text{wt}(\text{C}_6\text{H}_5\text{NO}_2) + \text{wt}(\text{C}_6\text{D}_5\text{NO}_2))$; $\text{MW}(\text{C}_6\text{D}_5\text{NO}_2) = 128.15$.^c Estimated standard deviations:

$$\sigma(r) = [\sum(r_i - r)^2 / (n - 1)]^{1/2}, \quad n = 5.$$

97%) and have a narrow molecular weight distribution ($M_w/M_n < 1.20$).

Figure 1a shows the 500 MHz ^1H NMR spectrum of PMMA-23K (see Table III) measured in nitrobenzene- d_5 at 110°C . The signal at 3.636 ppm is assigned to the CH_3O - group in the monomeric units and the signal at 0.823 ppm to the $\text{CH}_3(\text{CD}_3)_2\text{C}$ - group at the left (initiating) end of the chain. The intensity ratio of these two signals was determined as 220.5. This value was corrected for the isotopic purity of the $\text{CH}_3(\text{CD}_3)_2\text{C}$ - group to give the *DP* of this PMMA (228.4). Thus M_n of the polymer was calculated to be 22.93×10^3 on the basis of the formula weights of the monomeric unit and the terminal groups. M_n 's of PMMA-6K and PMMA-13K were determined by ^1H NMR in a similar manner (see Table III).

^2H NMR spectra of the PMMA samples were measured in nitrobenzene containing a certain amount of nitrobenzene- d_5 as an intensity standard. Table II gives the concentrations of the PMMA (*c*) and of ^2H of nitrobenzene- d_5 (*s*) in sample solutions. Figure 1b shows the 61.3 MHz ^2H NMR spectrum of PMMA-23K. The ^2H -nuclei in the $\text{CH}_3(\text{CD}_3)_2\text{C}$ - group resonates at 0.735 ppm; the chemical shift value is 0.088 ppm smaller than that of the ^1H -nuclei in the $\text{CH}_3(\text{CD}_3)_2\text{C}$ - group. The relative intensity (*r*) of the signal

Table III. The number average molecular weight M_n of the PMMA samples determined by VPO, ^1H NMR and ^2H NMR

Sample	$M_n/10^3$		
	VPO	^1H NMR	^2H NMR
PMMA-6K	6.17	6.80	6.47
PMMA-13K	12.49	13.21	12.84
PMMA-23K	22.28	22.93	23.89

due to the $\text{CH}_3(\text{CD}_3)_2\text{C}$ - group to the standard signal due to nitrobenzene- d_5 (7.3–8.0 ppm) was determined as 0.01929 (Table II). The ^2H NMR measurement was conducted five times for each sample, and the estimated standard deviation $\sigma(r)$ was within 3% of the mean value in all the cases. M_n 's of the PMMA samples were calculated as $M_n = 6dc/sr$.

Table III summarizes the results of the M_n measurements by VPO, ^1H NMR and ^2H NMR. The M_n values determined by ^1H and ^2H NMR are in good agreement with each other. The M_n values determined by VPO were about 5% lower than the values by ^1H and ^2H NMR. However, the formation of the PMMA without $\text{CH}_3(\text{CD}_3)_2\text{C}$ - group at the left end of chain seems to be unlikely. The reason is presently unknown. Considering the signal-to-noise ratio of the ^2H NMR spectrum of PMMA-23K (Figure 2b), little difficulty is

expected in the determination of M_n up to 10^5 by this method. The results mentioned here clearly indicate the good accuracy and good sensitivity of the end-group analysis of polymer by ^2H NMR spectroscopy, when the experimental conditions are carefully arranged.

Acknowledgments. The authors are grateful to Mrs. F. Yano for her VPO measurement. A part of this work was supported by a Grant-in-Aid for Scientific Research (No. 61430022) from the Ministry of Education, Science, and Culture of Japan.

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