NMR Measurement of Identical Polymer Samples by Round Robin Method I. Reliability of Chemical Shift and Signal Intensity Measurements

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ABSTRACT: The reliability of NMR data; chemical shift, signal intensity, and resolution, was examined on 26 NMR spectrometers by round robin method using radically prepared poly(methyl methacrylate) and solanesol as identical samples. In the case of poly(methyl methacrylate), the standard deviations (σ) of chemical shift measurements for proton and carbon signals were 0.0036—0.0071 and 0.054—0.307 ppm, respectively, with the FT instruments. The σ values for the proton signals measured with CW instruments were slightly larger; 0.0053—0.0169 ppm. The relative intensities of $3(\text{CH}_2 + \alpha\text{-CH}_3)/\text{OCH}_3$ were 4.94 ($\sigma=0.156$) by FT method and 4.95 ($\sigma=0.052$) by CW method, showing a good agreement with the theoretical value of 5. The values of triad tacticity obtained from the α -proton signals of the PMMA indicate a slight deviation from Bernoullian statistics. The relative peak intensities corrected by the NOE values in the ^{13}C NMR spectrum of PMMA agreed with the theoretical values within $\pm 10\%$ relative errors when determined with an appropriate pulse repetition time. In the case of solanesol a σ value for the measurement of proton chemical shift was 0.003 ppm with the FT method and 0.039 with the CW method, while the σ for ^{13}C chemical shift was less than 0.05 ppm.

KEY WORDS ^1H NMR / ^{13}C NMR / Poly(methyl methacrylate) /
Solanesol / α -Hydro- ω -hydroxy-*trans*-1,4-nonaisoprene / Round Robin
Method / Chemical Shift / Signal Intensity / Precision / Accuracy /

NMR spectroscopy has played an important role in many fields of polymer science, including the studies on structure, molecular motion and polymerization mechanism. Introduction of Fourier transform (FT) method and superconducting magnet in NMR technology has opened up new fields of investigation on polymer systems using NMR, besides making it a more powerful tool in routine analysis. However, few were reported on the reliability

of NMR data, including chemical shift, signal intensity, nuclear spin relaxation times and nuclear Overhauser effect (NOE) factor.¹⁻⁸ Especially, measurement of signal intensity is very important in polymer science. It can be easily understood after imaging how to determine microtacticities from NMR. It leads to the importance on the reliability of relaxation times and NOE factor, because they have to be determined from intensity. There have also

been doubts about the consistency between data obtained by different instruments in separate places.

In order to assess the reliability of NMR data, Research Group on NMR, the Society of Polymer Science, Japan (SPSJ), collected ^1H and ^{13}C NMR spectra of two identical samples, poly(methyl methacrylate) and solanesol, from a number of NMR spectrometers. Several non-members as well as SPSJ members*¹ were invited to participate in this cooperative project. This paper reports on the results of reliability and consistency of chemical shifts and signal intensities obtained from up to 26 NMR spectrometers.

The reports on the measurements of spin-lattice relaxation times and NOEs will be published in near future.⁹

EXPERIMENTAL

Poly(methyl methacrylate)

Materials. Methyl methacrylate (MMA) was purified by fractional distillation, dried over calcium dihydride and then distilled under high vacuum just before use.

Toluene, purified by usual method and dried over sodium, was mixed with a small amount of butyllithium to remove residual water and then distilled under high vacuum.

α,α' -Azobisisobutyronitrile (AIBN) was recrystallized from methanol.

Polymerization. Into a dried flask containing 5 mmol of AIBN, 0.5 liter of toluene and 1 mol of MMA were distilled under high vacuum. After filling the reaction vessel with dry nitrogen, it was immersed in a thermostat at 60°C for 24 h. Then, the reaction mixture was pour-

ed into 5 liters of methanol to precipitate the polymer formed. The polymer was collected by filtration, washed with methanol, and then dried at 50°C for 24 h. Yield was 79%.

Molecular Weight Determination. Gel permeation chromatography (GPC) of the PMMA was performed on a JASCO FLC-A10 chromatograph equipped with Shodex A-80M GPC column (50 cm $\times$ 2) using tetrahydrofuran as an eluent.

The number average molecular weight was also determined using a Hitachi 117 vapor pressure osmometer at 60°C in toluene.

$$\bar{M}_n(\text{GPC}) = 27400, \quad \bar{M}_n(\text{VPO}) = 28500,$$

$$\bar{M}_w(\text{GPC}) = 58000.$$

Solanesol

Solanesol was obtained commercially (Kuraray Co., Ltd.; purity >99%) and used without further purification.

Measurement

PMMA and solanesol samples were packed in glass vials and sent to collaborating test sites with a copy of instructions for NMR measurements, requesting the following measurement conditions;

solvent	CDCl_3
concentration	10 w/v%
internal standard	TMS
temperature	55°C for PMMA and 50°C for solanesol.

^1H NMR spectra were measured on CW and FT NMR spectrometers. ^{13}C NMR spectra were measured on FT NMR instruments. The memory used for acquisition was from 4 to 32 K for ^1H spectra and 8 to 32 K for ^{13}C

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Table I. Measurements of ^1H NMR spectra of PMMA by twenty-six spectrometers in 1982–1983

	Freq.	Instrument ^a	Temp	Int. ^b	Resolution ^c		Chemical shift ^d	
	MHz		°C		A	B	A	B
G	90	FX-90Q	55	4.89	0.099	0.1724	3.66 (0.06)	1.74 (0.05)
J	90	FX-90Q	50	—	0.082	0.1463	3.59 (−0.01)	1.64 (−0.05)
L	90	FX-90Q	55	4.74	0.094	0.1741	3.59 (−0.01)	—
O	90	FX-90Q	55	5.08	0.081	0.1394	3.60 (0.00)	1.65 (−0.04)
S	90	FX-90Q	55	4.99	0.086	0.1551	3.59 (−0.01)	1.73 (0.04)
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A	100	FX-100	55	5.03	0.070	0.0925	3.60 (0.00)	1.70 (0.01)
D	100	FX-100	55	5.14	0.067	0.0976	3.61 (0.01)	1.63 (−0.06)
E	100	PS-100 (FT)	55	3.81	0.119	0.2383	3.60 (0.00)	1.75 (0.06)
C	100	PS-100*	55	4.89	0.083	0.1283	3.59 (−0.01)	1.68 (−0.01)
F	100	PS-100*	55	4.60	0.070	0.1031	3.59 (−0.01)	1.67 (−0.02)
P	100	PS-100*	55	4.87	0.084	0.1263	3.62 (0.02)	1.72 (0.03)
R	100	PS-100*	55	5.00	0.096	0.2145	3.60 (0.00)	—
B	100	MH-100*	55	4.76	0.056	0.2081	3.62 (0.02)	1.78 (0.09)
J	100	MH-100*	55	5.01	0.088	0.1373	3.57 (−0.03)	—
Y	100	MH-100*	55	4.91	0.060	0.1082	3.59 (−0.01)	1.70 (0.01)
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H	200	FX-200	55	5.06	0.043	0.0255	3.59 (−0.01)	1.73 (0.04)
I	200	FX-200	55	4.95	0.047	0.0648	3.59 (−0.01)	1.66 (−0.03)
Q	200	FX-200	55	4.74	0.041	0.0535	3.60 (0.00)	1.71 (0.02)
M	200	XL-200	55	4.41	0.052	0.0369	3.66 (0.00)	—
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W	270	GX-270	50	4.96	0.040	0.0308	3.60 (0.00)	1.58 (−0.11)
Z	270	GX-270	55	5.15	0.038	0.0276	3.60 (0.00)	1.69 (0.00)
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X	360	AM-360	50	5.16	0.034	0.0175	3.59 (−0.01)	1.75 (0.06)
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K	400	FX-400	45	5.09	0.035	0.0131	3.60 (0.00)	1.76 (0.07)
U	400	GX-400	55	5.23	0.040	0.0078	3.60 (0.00)	1.60 (−0.09)
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N	500	GX-500	50	4.12	0.034	0.0170	3.60 (0.00)	1.56 (−0.13)
T	500	FX-500S	55	4.90	0.030	0.0100	3.59 (−0.01)	1.73 (0.04)

^a The asterisk denotes the continuous wave method.^b Relative intensity of $3(\text{CH}_2 + \alpha\text{-CH}_3)/\text{OCH}_3$.^c A, half-height width (ppm) of $\alpha\text{-CH}_3$ (*rr*) signal; B, $a/(b+c)$ see Figure 1.^d Chemical shifts (ppm) of OCH_3 (A) and H_2O (B) signals. The values in parentheses represent $(x_i - \bar{x})$.

spectra. The digital resolution of FT NMR spectrum was 0.0003–0.0025 ppm for ^1H spectra and 0.006–0.031 ppm for ^{13}C spectra. The pulse width was mostly 45° and the pulse repetition 4–20 s for ^1H spectra and 1–20 s for ^{13}C spectra. Peak area was measured by electronic integration or cutting out and weighing method. Accuracy and precision of intensity measurements by these two method were found to be in similar ex-

tent.⁸

Instruments

The number of instruments used was 26 as shown in the third column of Table I. They cover frequency range from 90 to 500 MHz. Data were collected from 1982 to 1983. A part of the results were compared with those obtained in 1969 using 6 continuous wave (CW) spectrometers.

RESULTS

¹H NMR Spectra of PMMA

¹H NMR spectra of the PMMA in CDCl₃ were measured on 26 spectrometers, whose resonance frequencies ranged from 90 to 500 MHz. Selected spectral data, including chemical shift, relative intensity and resolution, are listed in Table I.

Chemical Shift. Chemical shift data of methoxy (OCH₃) protons scatter only within ± 0.01 ppm, with a few exceptions (Table I). The standard deviation is 0.0038 ppm for 19 data obtained from FT instruments and 0.0169 ppm for 7 data obtained from CW ones (Table II). Standard deviations for α -methyl (α -CH₃) and methylene (CH₂) proton shifts are less than 0.01 ppm. The chemical shift of water which was incidentally introduced into sample solutions are also listed in Table I. The scattering of the values reflects the difference of water contents in the sample solutions which were found to be from 0.07 to 0.20%.

Resolution. In order to express the resolution of spectrum numerically, two kinds of values have been adopted; resolution index A, expressed by half-height width of the signal due to α -methyl protons in *rr* triad, and resolution index B, the ratio of the height at the lowest point between *rr* and *mr* triad methyl signals, *a*, and the sum of the heights of these two methyl signals, *b*+*c* (see Figure 1). Resolution index A represents sharpness of the peak, while resolution index B expresses the degree of peak separation. Both of resolution indices decreased with an increasing magnetic field strength. In particular, the index B decreased, by 1/10 from 90 MHz to 500 MHz (Table I).

Intensity. With only a few exceptions, relative intensity data, 3(CH₂+ α -CH₃)/OCH₃, agreed with the theoretical value of 5 within 5% deviation as shown in Table I. Among CW NMR spectrometers, a routine-type instrument, JNM-MH-100, appears to produce accurate results of quantitative determinations

Table II. ¹H NMR chemical shifts (ppm) and peak intensity of PMMA

Assignment	FT (<i>n</i> = 19)		CW (<i>n</i> = 7)	
	$\bar{x}$	σ^a	$\bar{x}$	σ^a
α -CH ₃ <i>rr</i>	0.869	0.0048	0.870	0.0056
<i>mr</i>	1.030	0.0036	1.033	0.0053
<i>mm</i>	1.214	0.0071	1.211	0.0077
CH ₂ <i>rrr</i>	1.823	0.0051	1.824	0.0085
<i>rrm</i>	1.897	0.0059	1.899	0.0081
OCH ₃	3.596	0.0038	3.600	0.0169
CHCl ₃	7.287	0.0143	7.298	0.0268
3(CH ₂ + α -CH ₃)/OCH ₃ ^b	4.938 ^c	0.1561 ^c	4.947	0.0523

^a $\rho = \sqrt{\sum (x_i - \bar{x})^2 / n}$.

^b Relative intensity.

^c *n* = 18.

Figure 1. NMR spectrum of α -CH₃ protons in PMMA measured in CDCl₃ at 55°C and 100 MHz.

comparable with those obtained from more elaborate ones.

Comparison with an Assessment in 1969. In 1969, a similar assessment was done by Hatada *et al.*² A CDCl₃ solution of PMMA synthesized by radical polymerization under similar

Table III. Measurements of ^1H NMR spectra of PMMA on six spectrometers in 1969

	Freq.	Instrument	Temp	Int. ^a	Resolution ^b		Chemical shift ^c	
	MHz		°C		A	B	A	B
A	60	A-60A	65	4.95	0.078	0.1587	3.59 (−0.02)	1.54 (−0.07)
B	60	C-60HL	65	4.99	0.115	0.2530	3.65 (0.04)	1.66 (0.06)
C	100	4H-100	59	5.03	0.068	0.1202	3.61 (0.00)	1.58 (−0.03)
D	100	4H-100	60	5.34	0.064	0.1028	3.58 (−0.03)	1.59 (−0.02)
E	100	4H-100	50	5.07	0.080	0.1446	3.63 (0.02)	1.68 (0.08)
F	100	HA-100	59	5.22	0.080	0.1771	3.59 (−0.02)	1.58 (−0.03)

^a Relative intensity of $3(\text{CH}_2 + \alpha\text{-CH}_3)/\text{OCH}_3$.^b A, half-height width (ppm) of $\alpha\text{-CH}_3$ (*rr*) signal; B, $a/(b+c)$ see Figure 1.^c Chemical shifts (ppm) of OCH_3 (A) and H_2O (B) signals. The values in parentheses represent $(x_i - \bar{x})$.

conditions to those for the PMMA sample used in the present assessment was subjected to the measurements on six CW instruments. Table III lists the old data to allow comparison with those collected at this time. Mean values and standard deviations, are summarized in Table IV. Comparison of the results obtained at 100 MHz in Tables III and IV with those in Tables I and II indicates that there is no substantial difference in the accuracy of relative intensity and resolution between these two sets of data. Mean values of chemical shift obtained in 1969 and at present are in agreement within 0.01 ppm for each peak. Standard deviations for chemical shift are slightly smaller in the present measurements than in 1969, while the deviation for relative intensity is smaller in the measurement in 1969. It is noteworthy that in both cases standard deviation for the chemical shifts of OCH_3 and CHCl_3 signals are larger than those for the shifts of other signals. A large standard deviation for H_2O signal obtained in 1969 may have reflected the difference in the temperature of measurement because the sample solution was the same for all the measurements.

^{13}C NMR Spectra of PMMA

The ^{13}C NMR spectra were measured on 24 instruments, whose resonance frequencies ranged from 15.0 to 125 MHz. The data are

Table IV. ^1H NMR chemical shifts (ppm) and peak intensity of PMMA measured by six spectrometers in 1969

Assignment	$\bar{x}$	σ^a
$\alpha\text{-CH}_3$ <i>rr</i>	0.880	0.0098
<i>mr</i>	1.041	0.0126
<i>mm</i>	1.226	0.0193
CH_2^b <i>rrr</i>	1.827	0.0100
<i>rrm</i>	1.905	0.0133
OCH_3	3.608	0.0223
CHCl_3^b	7.265	0.0190
H_2O	1.605	0.0489
$3(\text{CH}_2 + \alpha\text{-CH}_3)/\text{OCH}_3^c$	5.100	0.1368

^a $\rho = \sqrt{\sum (x_i - \bar{x})^2/n}$.^b Number of determinations: 5 for CH_2 , 4 for CHCl_3 .^c Relative intensity.

summarized in Tables V and VI.

Chemical Shift. All carbons except for methoxy one were sensitive to the tacticity of the polymer chain. The number of distinguishable peaks depends on magnetic field strength. In Table VI, mean values and standard deviations for chemical shift are listed with number of determinations, n . The deviations vary from 0.1 to 0.3 ppm, excluding those for methoxy and CDCl_3 carbons. Precisions of chemical shift for methoxy and CDCl_3 carbons were better than those for others, in contrast to the case of ^1H NMR. As compared with the case of solanesol, PMMA shows lower precision of

Table V. Measurements of ^{13}C NMR spectra of PMMA by twenty-three spectrometers in 1982–1983

	Freq.	Instrument	Temp	Int. ^a			Resolution ^b		Chemical shift ^c	
	MHz		°C	A	B	C	A	B		
B	15.0	FX-60	55	(2.30)	(3.00)	(2.90)	—	0.1448	17.17	(0.27)
R	15.0	FX-60Q	25	(4.02)	(3.49)	(4.29)	—	0.1078	16.57	(−0.33)
G	22.5	FX-90Q	25	0.91	1.95	1.03	—	0.1754	16.90	(0.00)
J	22.5	FX-90Q	50	(3.14)	(4.12)	(3.54)	—	0.0277	16.92	(0.02)
L	22.5	FX-90Q	55	1.05	2.11	1.10	0.115	0.0530	16.92	(0.02)
O	22.5	FX-90Q	55	0.85	1.98	0.99	0.158	0.1477	17.18	(0.28)
V	22.5	FX-90Q	55	0.84	2.01	1.07	0.100	0.0411	16.94	(0.04)
P	22.5	R90-H	23	0.81	1.86	0.99	0.084	0.0366	16.61	(−0.29)
A	25.0	FX-100	55	0.98	2.12	1.03	0.078	0.0308	17.01	(0.11)
C	25.0	FX-100	55	1.0	2.0	1.1	—	0.1172	16.81	(−0.09)
D	25.0	FX-100	55	1.22	2.11	1.11	0.131	0.0810	17.08	(0.18)
F	25.0	FX-100	55	0.83	1.91	0.95	—	0.0975	16.96	(0.06)
S	25.0	FX-100	55	0.76	1.98	1.03	—	0.0752	16.94	(0.04)
E	25.0	PS-100	55	(3.45)	(3.52)	(2.83)	—	0.1301	16.82	(−0.08)
H	50.1	FX-200	55	0.59	1.69	0.88	0.080	0.0126	16.91	(0.01)
I	50.1	FX-200	55	0.35	1.94	0.93	0.093	0.0393	17.10	(0.20)
Q	50.1	FX-200	55	0.67	1.74	0.94	0.110	0.0589	16.93	(0.03)
M	50.3	XL-200	55	1.15	2.22	1.60	—	0.0939	16.93	(0.03)
W	67.8	GX-270	50	0.40	1.38	0.65	0.081	0.0417	16.83	(−0.07)
Z	67.8	GX-270	55	0.55	1.52	0.75	0.074	0.0605	16.94	(0.04)
X	90	AM-360	50	0.43	1.33	0.70	0.100	0.0073	16.85	(−0.05)
K	100	FX-400	25	1.10	2.24	1.18	0.090	0.0494	16.46	(−0.44)
U	100	FX-400	55	0.33	1.54	0.67	0.059	0.0333	16.96	(0.06)
N	125	GX-500	50	(1.85)	(2.89)	(2.22)	0.061	0.0424	16.84	(−0.06)

^a Relative intensities of $\text{CO}/\alpha\text{-CH}_3$ (A), $(\text{OCH}_3 + \text{CH}_2)/\alpha\text{-CH}_3$ (B) and Quat.C/ $\alpha\text{-CH}_3$ (C). The values in parentheses were determined from peak heights.

^b A, half-height width (ppm) of CO (*rrrr*) signal; B, $a/(b+c)$ see Figure 2.

^c Chemical shifts (ppm) of $\alpha\text{-CH}_3$ (*rr*) signal. The values in parentheses represent $(x_i - \bar{x})$.

chemical shift (*cf.* Tables IV and XI).

Resolution. Resolution of ^{13}C NMR spectrum is expressed numerically by two indices as in the case of ^1H NMR; resolution index A, half-height width of carbonyl carbon signal in *rrrr* pentad, resolution index B, ratio of height at the lowest point between *rrrr* and *rrrm* pentad signals of carbonyl carbon and the sum of peak heights of them (see Figure 2). Both of resolution indices decreased with an increase of the magnetic field, although the improve-

ment in resolution was not as remarkable as in the case of ^1H NMR. Resolution indices in the case of ^{13}C NMR seem to scatter more widely, depending on individual instruments, than those in the case of ^1H NMR.

Intensity. Relative peak intensities for carbonyl, (methoxy + methylene) and quaternary carbons against α -methyl carbon are listed in Table V. Accuracy of these values were much poorer than those of ^1H NMR. Only four instruments were found to give data agreeable

Table VI. ^{13}C NMR chemical shifts (ppm) of PMMA measured by a number of spectrometers in 1982–1983

Assignment	$\bar{x}$	σ^a	n
$\alpha\text{-CH}_3$ <i>rr</i>	16.899	0.1661	24
<i>mr</i>	19.025	0.1120	24
<i>mm</i>	21.322	0.1579	17
Quat. <i>rr</i>	44.808	0.1257	24
<i>mr</i>	45.120	0.1211	24
<i>mm</i>	45.725	0.1047	20
OCH_3	51.667	0.0544	24
CH_2 <i>mrr</i>	52.755	0.1720	23
<i>mmr</i>	53.574	0.2140	20
<i>rrrrr</i>	54.249	0.3067	23
<i>rrrrm</i>	54.571	0.0984	22
<i>rrmrr</i>	54.636	0.0892	7
<i>rrmr</i>	54.710	0.0600	2
CDCl_3	77.070	0.0587	24
CO <i>rmmr</i>	176.053	0.1967	15
<i>mmmr</i>	176.250	0.0777	6
<i>mmrr</i> }	176.831	0.1227	23
<i>rmrr</i> }			
<i>rmrm</i>	177.018	0.1234	23
<i>rrrr</i>	177.646	0.1349	24
<i>rrrm</i>	177.918	0.1200	24
<i>mrrm</i>	178.205	0.1409	17
$\text{CO}/\alpha\text{-CH}_3$	1.183	0.2716	19
$(\text{OCH}_3 + \text{CH}_2)/\alpha\text{-CH}_3$	2.115	0.3927	19
Quat. C/ $\alpha\text{-CH}_3$	1.379	0.2179	19

$$^a \rho = \sqrt{\sum (x_i - \bar{x})^2 / n}.$$

Figure 2. NMR spectrum of CO carbon in PMMA measured in CDCl_3 at 55°C and 25.0 MHz.**Table VII.** Intensities of ^{13}C NMR signals of PMMA in CDCl_3 at 55°C

Freq. MHz	n^a	Signal intensity ^b					
		Observed			Corrected by NOE		
		A	B	C	A	B	C
22.5	3	0.86	1.93	1.00	1.11	2.15	1.07
25	3	0.86	2.00	1.00	1.04	2.07	1.08
50	3	0.54	1.45	0.92	0.87	1.80	1.14
67.5	1	0.55	1.52	0.75	1.01	1.94	0.96
90.6	1	0.43	1.33	0.70	0.62	1.61	0.72
100	1	0.33	1.54	0.67	0.66	2.05	0.84

^a Number of determinations.

^b A, B, and C denote the relative intensities of $\text{C}=\text{O}/\alpha\text{-CH}_3$, $(\text{OCH}_3 + \text{CH}_2)/\alpha\text{-CH}_3$ and Quat. C/ $\alpha\text{-CH}_3$.

Table VIII. Tacticity (%) of PMMA determined by ^1H NMR spectroscopy

	Instrument	I	H	S
O	FX-90Q	3.3	35.3	61.4
A	FX-100	2.8	34.0	63.2
D	FX-100	3.9	34.9	61.2
F	PS-100*	4.1	34.2	61.8
P	PS-100*	4.4	36.4	59.1
R	PS-100*	5.7	37.3	57.0
Y	MH-100*	3.3	34.2	62.5
H	FX-200	3.7	35.6	60.7
Q	FX-200	5.4	33.7	60.9
M	XL-200	5.0	35.0	60.0
W	GX-270	3.8	34.5	61.7
Z	GX-270	4.8	33.8	61.4
X	AM-360	4.3	33.6	62.2
K	FX-400	3.9	34.7	61.4
U	GX-400	3.4	34.9	61.7
N	GX-500	2.4	35.3	62.3
T	GX-500S	3.5	33.1	63.4
	$\bar{x}$	4.0	34.7	61.3
	σ	0.9	1.0	1.5

with theoretical values in all three relative intensities within $\pm 10\%$ deviation (A, C, G, L in Table V). The deviations were $\pm 20\%$ on

Table IX. Tacticity (%) of PMMA determined by ^{13}C NMR spectroscopy

Instrument		$\alpha\text{-CH}_3$			Quat. C		
		<i>I</i>	<i>H</i>	<i>S</i>	<i>I</i>	<i>H</i>	<i>S</i>
G	FX-90Q	2.7	38.1	59.3	4.6	34.0	61.3
O	FX-90Q	—	—	—	3.0	33.3	63.7
V	FX-90Q	4.4	33.0	62.6	6.3	31.2	62.5
P	R90-H	3.5	36.5	60.0	3.9	37.0	59.0
A	FX-100	2.7	36.8	60.5	3.1	33.4	65.3
C	FX-100	6.1	33.9	60.0	—	—	—
D	FX-100	2.0	32.7	65.3	5.2	29.8	65.0
F	FX-100	1.8	33.6	64.6	3.0	34.6	62.4
S	FX-100	3.2	35.4	61.3	3.3	35.4	61.4
H	FX-200	3.2	34.9	61.9	3.4	35.2	61.5
I	FX-200	2.5	36.6	60.8	4.2	35.4	60.4
Q	FX-200	2.2	34.9	62.9	2.4	31.3	66.4
W	GX-270	2.3	32.4	65.3	2.4	37.9	59.7
Z	GX-270	5.1	36.1	58.8	5.7	42.1	52.2
X	AM-360	1.8	34.2	63.9	1.9	35.9	62.2
K	FX-400	1.1	35.2	63.7	—	—	—
U	GX-400	3.7	34.7	61.5	4.3	38.7	57.0
N	GX-500	3.1	33.0	63.9	—	—	—
$\bar{x}$		3.0	34.8	62.2	3.8	35.0	61.3
σ		1.3	1.6	2.0	1.3	3.1	3.4

average for the data obtained from 22.5 or 25 MHz instruments. On the other hand, relative intensities obtained by 15 MHz and 50 MHz or higher frequency instruments generally show large negative deviations. One of the sources of errors in these quantitative measurements is the variation in NOE values. The NOE values for each carbon measured at 22.5 and 25 MHz were close to 2.99 and the differences between the types of carbon were not large enough to perturb the intensity measurements significantly. However, the NOE decreased with an increasing magnetic field strength strongly depending on the type of carbon.⁹ The relative peak intensities listed in Table V were corrected by the NOE values and the results are shown in Table VII. Agreement within $\pm 10\%$

Table X. Mean values of tacticity for PMMA measured at different field strength

Frequency/MHz	<i>n</i>	Tacticity/%			4IS
		<i>I</i>	<i>H</i>	<i>S</i>	<i>H</i> ²
100	6	4.0	35.2	60.8	0.79
200	3	4.7	34.8	60.5	0.94
270	2	4.3	34.2	61.5	0.90
360	1	4.3	33.6	62.2	0.95
400	2	3.7	34.8	61.5	0.75
400 ^a	(5)	3.5	33.6	62.9	0.78
500	2	3.0	34.2	62.8	0.64
500 ^a	(5)	3.2	34.0	62.8	0.70

^a Results from five runs on the same spectrometer.

relative errors were obtained in the measurements at the field strength of 22.5–67.5 MHz. The corrected values for 90.6 and 100 MHz

still showed the negative deviations. This may be due to saturation of the resonances since the pulse repetition of about 1 s were used in the measurements at 90.6 and 100 MHz in this work while the spin-lattice relaxation times increase by a factor of at most 2.5 when the magnetic field is changed from 25 to 100 MHz.⁹

Tacticity of PMMA Determined by ¹H and ¹³C NMR

Tacticity is one of the most valuable data obtainable from NMR spectra and stereochemical assignments of ¹H and ¹³C NMR spectra of PMMA are well established. Triad tacticities were determined from intensity ratios of split signals of α -CH₃ protons, and those of α -CH₃ and quaternary carbons (Tables VIII and IX). Mean values derived from these signals were in good agreement with each other, although the values from quaternary carbon signals show larger standard deviations than others. This may be the results of the smaller shifts between the peaks and of the narrower peak widths; the latter cause a smaller number of data point defining the line shape. In the assessment in 1969,²

mean values, $\bar{x}$, for each triad tacticities and their standard deviations, σ , were found to be as follows;

$$\begin{array}{lll} mm, & \bar{x} = 6.0\%, & \sigma = 1.0 \\ mr, & \bar{x} = 34.6\%, & \sigma = 1.4 \\ rr, & \bar{x} = 59.4\%, & \sigma = 2.3. \end{array}$$

The values agree with those obtained in the present assessment.

Configurational sequences of PMMA prepared by radical initiator was first reported to be described by Bernoullian statistics within experimental limits of resolution in the measurement at 60 MHz.¹⁰ Later, several re-investigations at higher magnetic field strength indicated that first-order Markovian statistics rather than Bernoullian statistics could apply to radically prepared PMMA.^{1,11,12} Mean values of tacticity measured by ¹H NMR at different frequencies were calculated from data in Table VIII and listed in Table X. The values of $4IS/H^2$, which is equal to unity when tacticity is completely described by Bernoullian statistics,¹³ are less than unity in all the measurements. The signal to noise ratio and the degree of peak separation were greatly enhanced at higher field strength. In order to make sure the deviation from unity, the

Table XI. ¹H NMR chemical shifts (ppm) and relative intensities of solanesol

Proton ^a	Chemical shift ^b				Relative intensity ^b			
	FT	(n=16)	CW	(n=4)	FT	(n=16)	CW	(n=4) Theory
<i>trans</i> CH ₃	1.598	(0.003)	1.581	(0.024)	23.92	(0.80)	23.93	(1.03) 24
$\alpha + \omega$ CH ₃	1.675	(0.002)	1.662	(0.029)	6.00	(0.50)	6.43	(0.59) 6
m CH ₂	2.004	(0.017)	1.094	(0.032)	32.55	(0.72)	32.03	(0.87) 32
ω CH ₂ OH	4.136	(0.004)	4.111	(0.046)	1.81	(0.22)	1.80	(0.21) 2
m =CH-	5.109	(0.016)	5.153	(0.051)	7.76	(0.55)	8.00	(0.08) 8
ω =CH-	5.415	(0.003)	5.447	(0.072)	0.98	(0.12)	0.93	(0.05) 1
CHCl ₃	7.246	(0.005)	7.231	(0.023)	—	—	—	—
Average		(0.003) ^c		(0.039) ^c		(0.44) ^c		(0.47) ^c

^a Notation: $\text{CH}_3-\overset{\text{CH}_3}{\underset{\alpha}{\text{C}}}=\text{CH}-\text{CH}_2-(\text{CH}_2-\overset{\text{CH}_3}{\underset{\text{m}}{\text{C}}}=\text{C}-\text{CH}_2)_7-\text{CH}_2-\overset{\text{CH}_3}{\underset{\omega}{\text{C}}}=\text{C}-\text{CH}_2-\text{OH}$

^b The values in parentheses represent standard deviation, $\sqrt{\sum (x_i - \bar{x})^2 / n}$.

^c The data on the signals due to CH₂ (2.0 ppm) and =CH (5.1 ppm) are omitted on the calculation.

Figure 3. ^1H NMR spectra of soranesol measured at 50°C in CDCl_3 at 500 (above) and 100 MHz (below).

measurements were made five times on the same spectrometers operated at 400 and 500 MHz, respectively. The results indicate the values of $4IS/H^2$ to be less than unity (Table X). Now it is very clear that the tacticity of radically prepared PMMA slightly deviates from Bernoullian.

^1H NMR Spectra of Solanesol

Solanesol is an all *trans*-1,4-nonaisoprene with hydroxy terminal (α -hydro- ω -hydroxy-*trans*-1,4-nonaisoprene). Owing to its low degree of polymerization, NMR signals of the terminal or its neighboring monomer units are distinguishable from those of in-chain units. Signal assignment was achieved by homo-decoupling in ^1H NMR, selective decoupling in ^{13}C NMR and comparison of the spectra with those of its isomers and homologues. The results of measurements are shown in Figure 3 and Table XI.

Chemical Shift. Standard deviations of chemical shifts obtained from FT NMR instruments were smaller than those from CW spectrometers. Average standard deviation of chemical shift, after omitting the values for the broad signals around 2.0 and 5.1 ppm, is 0.003 with the FT method and 0.039 with the CW

method. It is noteworthy that the mean standard deviation for the chemical shifts measured by FT method is the same order of magnitude as the digital resolution of the instruments. Relatively larger values of standard deviation for the peaks at 2.0 and 5.1 ppm may be ascribed to their broadness caused by complicated spin coupling and superimposed signals.

Intensity. Relative intensity of each signal is normalized so that the total intensity equals to 73, which is the total number of protons, excluding the hydroxy proton, in a solanesol molecule. There is not noticeable difference between the normalized intensities obtained by the FT and CW methods. Sum of the differences between the observed (I_{obs}) and the theoretical (I_{theo}) intensities, $\sum |I_{\text{theo}} - I_{\text{obs}}|$, varies widely from 1 to 8 depending on the instruments used. It is not clear whether the variation results from instrumental conditions, measurement conditions, sampling method or other causes.

^{13}C NMR Spectra of Solanesol

The ^{13}C NMR spectra were measured on 18 spectrometers (15–125 MHz). Table XII summarizes the results of measurements.

Table XII. ^{13}C NMR chemical shifts (ppm) of solanesol measured by a number of spectrometers

Assignment ^a	$\bar{x}$	σ^b	n	Assignment ^a	$\bar{x}$	σ^b	n
CH ₃ 5m	16.053	0.0243	18	=CH- 3 ω	123.624	0.0407	16
5 ω	16.288	0.0165	18	3 ω'	123.889	0.0261	16
5 α	17.667	0.0175	18	3 ω''	124.321	0.0332	10
CH ₂ 1 α	25.638	0.0282	18	3m	124.414	0.0320	16
4 α	26.462	0.0437	18	3 α	124.557	0.0309	15
4m	26.835	0.0418	18	=C- 2 α	131.137	0.0232	15
4 ω'	26.924	0.0304	5	2m	134.939	0.0290	16
1 ω	39.624	0.0242	16	2 ω''	135.021	0.0268	7
1m	39.798	0.0224	18	2 ω'	135.423	0.0358	16
CH ₂ OH	59.438	0.0321	18	2 ω	139.724	0.0339	16
CDCl ₃	77.030	0.0301	18

^b $\rho = \sqrt{\sum (x_i - \bar{x})^2 / n}$.

Figure 4. NMR spectra of olefinic carbons in solanesol measured at 50°C in CDCl₃ at 125 (above) and 50 MHz (below).

Standard deviation of each chemical shift is less than 0.05 ppm. ^{13}C Chemical shifts are more sensitive to the position of the monomeric unit along the molecular chain of solanesol than ^1H chemical shifts.

Isoprene units along the chain are named to be differentiated as shown in Table XII. While methyl carbons in α - and ω -units show different shifts from those in m-units, two kinds of methylene carbons in ω - and ω' -units as well as those in the α -unit show different shifts from those in m-units. In the case of unsaturated carbons, signals of methine and quaternary carbons in ω'' -unit as well as those in the ω' -unit appears separately from those of the corresponding carbons in m-units (Figure 4). Chemical shifts of these signals for ω'' -unit from those for m-units are less than 0.1 ppm, hence these peaks can be distinguished separately only by the instruments operated at no less than 50 MHz.

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