

SHORT COMMUNICATIONS

**Effect of NMR Signal from Initiator Fragment on Triad  
Tacticities of Poly(methyl methacrylate)s Formed  
by 2,2'-Azobisisobutyronitrile  
and Benzoyl Peroxide**

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It was reported that tacticity of the poly(methyl methacrylate) (PMMA) prepared with benzoyl peroxide (BPO) deviated slightly from Bernoullian statistics while that of PMMA formed by 2,2'-azobisisobutyronitrile (AIBN) was consistent with the Bernoullian.<sup>1,2</sup> However, it is unbelievable that the species of initiator affect the stereoregulation in the propagation reaction. In this work we found using the 500 MHz <sup>1</sup>H NMR spectra of the PMMA from AIBN that the two small methyl proton signals<sup>3,4</sup> of equal intensities attributed to the initiator fragment, (CH<sub>3</sub>)<sub>2</sub>C(CN)- at the α-end of the chain overlap indistinguishably with the isotactic and heterotactic α-methyl proton signals, respectively, in the <sup>1</sup>H NMR spectra measured at lower frequency, namely, 100 MHz.

PMMA's were prepared by AIBN and BPO in benzene at 60°C. The yields, molecular weights and their distributions are shown in Table I. <sup>1</sup>H NMR spectra of the polymers were measured in nitrobenzene-*d*<sub>5</sub> at 110°C on

JEOL FX-100 and GX-500 FT NMR spectrometers at 100 and 500 MHz, respectively. Chemical shifts were referred to hexamethyldisiloxane (HMDS) as an internal standard and converted to tetramethylsilane (TMS) scale (HMDS-TMS=0.109 ppm). A total of 32 transients were accumulated for each measurement. The pulse repetition time was 10 s.

Figure 1 shows 100 and 500 MHz <sup>1</sup>H NMR resonances of α-methyl protons of the PMMA prepared by AIBN. In the spectra measured at 500 MHz, the signals of AIBN fragments

**Table I.** Polymerization of MMA by AIBN and BPO in benzene at 60°C<sup>a</sup>

Initiator	Yield	$\bar{M}_n$		$\bar{M}_w/\bar{M}_n$
	%	VPO	GPC	
AIBN	14.7	31,300	30,300	1.5
BPO	10.4	45,500	43,400	1.7

<sup>a</sup> MMA, 20 mmol; Initiator, 0.2 mmol; benzene, 20 cm<sup>3</sup>; polymerization time, 2 h.

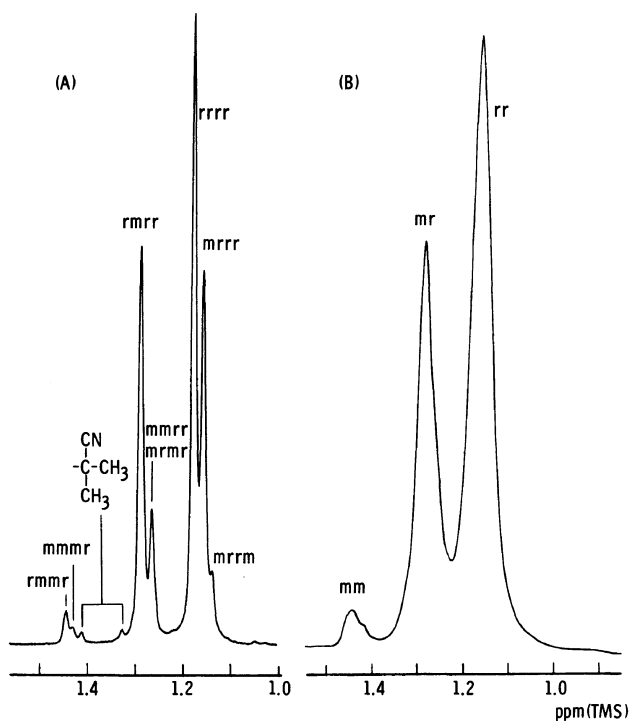


Figure 1. 500 MHz (A) and 100 MHz (B)  $^1\text{H}$  NMR spectra of  $\alpha$ -methyl protons of PMMA prepared with AIBN in benzene at  $60^\circ\text{C}$ .

could be observed separately from the isotactic and heterotactic triad signals of  $\alpha$ -methyl protons (Figure 1A). The assignment of the initiator fragment signals was confirmed by comparing the spectrum with that of poly(methyl methacrylate- $d_8$ ) prepared by AIBN and also with the spectrum of PMMA by AIBN- $d_{12}$ .<sup>5</sup> The triad tacticity of AIBN-polymerized PMMA was determined from the 500 MHz NMR spectrum by omitting the contribution of the initiator fragment signals. The corrected tacticity values thus obtained were slightly lowered in isotactic and heterotactic triads while increased in syndiotactic triad as compared with the data from the 100 MHz spectrum (Table II). The corrected tacticity is very close to the tacticity of PMMA prepared by BPO, which is independent of the NMR frequencies (Table II). When the degree of polymerization of PMMA exceeds 1000, the contribution of AIBN fragment signals can be

Table II. Fractions of triad tacticities for PMMA determined at 100 and 500 MHz with and without correction

Frequency MHz	Initiator	Tacticity/% <sup>a</sup>			$4IS/H^2$
		<i>I</i>	<i>H</i>	<i>S</i>	
100	AIBN	4.4	33.3	62.3	0.992
500	AIBN	3.7	35.0	61.2	0.745
500 <sup>b</sup>	AIBN	3.4	34.7	61.9	0.691
100	BPO	3.7	34.1	62.2	0.781
500	BPO	3.2	34.6	62.2	0.655

<sup>a</sup> Average values of five runs. Intensity measurement was done by cutting and weighing method.

<sup>b</sup> Corrected values for AIBN fragment signals.

neglected since the number of the initiator fragment in a polymer chain is about unity<sup>5</sup> and the relative fraction becomes negligibly small.

From the results mentioned above and summarized in Table II, it is concluded that the

tacticities of PMMAs prepared by AIBN and BPO are very similar to each other. The values of  $4IS/H^2$ , which is expected unity if stereoregulation in the propagation process obeys Bernoullian statistics,<sup>6</sup> are less than unity for both polymers. The deviation of tacticity of radically polymerized PMMA from Bernoullian statistics has been reported by several authors.<sup>7-9</sup> This deviation was unifiedly explained in this work with a term of NMR signal from initiator fragment.

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