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International Journal of Polymer Analysis and Characterization

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713646643>

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To cite this Article Nishiura, Takafumi , Kitayama, Tatsuki and Hatada, Koichi(2000) 'Carbon-13 NMR Spectra of Stereoregular Copolymers of Methyl and Butyl Methacrylates', *International Journal of Polymer Analysis and Characterization*, 5: 4, 401 – 413

To link to this Article: DOI: 10.1080/10236660008034635

URL: <http://dx.doi.org/10.1080/10236660008034635>

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Carbon-13 NMR Spectra of Stereoregular Copolymers of Methyl and Butyl Methacrylates

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(Received 17 March 1999; In final form 24 April 1999)

Highly isotactic and syndiotactic copolymers of methyl methacrylate (MMA) and butyl methacrylate (*n*-BuMA) with random monomer sequence distribution were prepared in toluene at -78°C with *t*-C₄H₉MgBr and *t*-C₄H₉Li/(C₂H₅)₃Al, respectively. ¹³C NMR spectra of carbonyl region of the copolymers were measured in chlorobenzene-*d*₅ at 115°C and 125 MHz and analyzed in regard to both monomer sequence and configurational sequence distributions. ¹³C NMR spectra of radically prepared poly(MMA-*ran*-*n*-BuMA)s were also analyzed based on the assignments established by the analysis of the spectra of the stereoregular copolymers.

Keywords: Stereoregular polymer; Polymethacrylate; ¹³C NMR; Monomer sequence distribution; Configurational sequence distribution

INTRODUCTION

Recent advances in NMR technology have afforded us with detailed information on polymer structure: fractions of longer configurational sequences in vinyl homopolymers, monomer sequence in copolymers, and structural defects in polymer chains, such as head-to-head or tail-to-tail linkages and end groups. Even with these advanced NMR methods, analysis of copolymer structure is still perplexing when the

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chemical shifts of the signals are sensitive to both configurational sequences and monomer sequences. However, it is much easier to analyze signals of the copolymer with high stereoregularity because the signals must be simple in the absence of splitting due to the stereochemical sequences. We have reported that the polymerization of methyl methacrylate (MMA) with $t\text{-C}_4\text{H}_9\text{MgBr}$ in toluene at low temperature gives highly isotactic PMMA with narrow molecular weight distribution (MWD)^[1,2] and that combinations of $t\text{-C}_4\text{H}_9\text{Li}$ and trialkylaluminums (R_3Al) polymerize MMA in toluene at low temperature to form highly syndiotactic PMMA with narrow MWD.^[3,4]

In this work, highly isotactic and syndiotactic copolymers of MMA and butyl methacrylate ($n\text{-BuMA}$) with random monomer sequence distribution were prepared in toluene at low temperature with $t\text{-C}_4\text{H}_9\text{MgBr}$ and $t\text{-C}_4\text{H}_9\text{Li}(\text{C}_2\text{H}_5)_3\text{Al}$, respectively, and the carbonyl carbon signals of their 125 MHz ^{13}C NMR spectra were analyzed in terms of configurational pentad sequences and monomer triad sequences. Because of the high stereoregularity, the spectra were much simpler than that of the copolymer prepared with a radical initiator and the splittings due to the tacticity and comonomer sequences could be distinguished easily. Based on the assignments for the stereoregular copolymers, the signal assignment for the carbonyl carbon spectrum of the radically prepared poly(MMA-*ran-n*-BuMA),^[5,6] which was first reported by Brar and Kapur^[5] and later pointed out to be in error,^[6] was reinvestigated.

EXPERIMENTAL

Monomers were purified by fractional distillation, dried over calcium dihydride and vacuum-distilled just before use. $t\text{-C}_4\text{H}_9\text{MgBr}$ was prepared from $t\text{-C}_4\text{H}_9\text{Br}$ and magnesium turnings in diethyl ether. $t\text{-C}_4\text{H}_9\text{Li}$ and $(\text{C}_2\text{H}_5)_3\text{Al}$ were obtained commercially and used as heptane solutions. Stereospecific copolymerizations were carried out in glass ampoules under dry nitrogen according to the procedures reported previously.^[4,7,8] The reactions were terminated with methanol at the polymerization temperature. After the solvent and unreacted monomers were removed under vacuum, the residue was dissolved in benzene. Insoluble materials were removed from the benzene solution

by centrifugation and the polymeric material was recovered by freeze-drying the supernatant liquid. Radical copolymerizations were carried out in toluene with azobisisobutyronitrile (AIBN) at 60°C under nitrogen pressure and the copolymers obtained were isolated similarly to the stereospecific polymerizations.

^{13}C NMR spectra were measured on a JNM GX500 (JEOL) spectrometer at 115°C and 125 MHz using chlorobenzene- d_5 as a solvent. Molecular weights were determined on a JASCO FLC-A10 SEC chromatograph equipped with Shodex SEC columns A80M and KF803 connected in series using tetrahydrofuran as an eluent. SEC chromatograms were calibrated against standard polystyrene samples.

Simulated NMR spectra were obtained by using Apple Macintosh LC630 personal computer with MATHEMATICA ver 2.2.

RESULTS AND DISCUSSION

Preparation and Characterization of Stereoregular Copolymers of MMA and *n*-BuMA with Random Monomer Sequence Distribution, Poly(MMA-*ran*-*n*-BuMA)s

Isotactic poly(MMA-*ran*-*n*-BuMA)s were prepared with *t*-C₄H₉MgBr in toluene at -78°C for 72 h. The copolymers obtained were almost completely isotactic but the MWDs were bimodal. Syndiotactic copolymers were prepared with *t*-C₄H₉Li-(C₂H₅)₃Al in toluene at -78°C for 72 h. The copolymers were about 90% syndiotactic in triads and of narrow molecular weight distribution. Radical copolymerizations of MMA and *n*-BuMA were carried out in toluene at 60°C with AIBN. The molecular weights, their distributions, copolymer compositions and tacticities for some of the copolymers are shown in Table I.

^{13}C NMR Spectra of Copolymer

Figure 1 shows the carbonyl regions of the ^{13}C NMR spectra of highly syndiotactic 1:1 copolymer of MMA and *n*-BuMA [(a); No. 2 in Table I] and highly isotactic 1:1 copolymer of MMA and *n*-BuMA [(b); No. 1 in Table I]. The spectral pattern of the strong triplets centered at 177.5 and 177.2 ppm for the syndiotactic copolymer (Figure 1(a)) depends on the copolymer composition; the relative intensity of

TABLE I Copolymerization of MMA and *n*-BuMA

No.	Initiator	$[MMA]_0$		Yield (%)	$[MMA]^a$		\bar{M}_n		Tacticity (%)		
		$[MMA]_0$	$[n-BuMA]_0$		$[MMA]$	$[n-BuMA]$	\bar{M}_w	\bar{M}_n	<i>mm</i>	<i>mr</i>	<i>rr</i>
1	<i>t</i> -C ₄ H ₉ MgBr ^c	0.98		100	0.96 (49.0)		10 200	4.46	97	2	1
2	<i>t</i> -C ₄ H ₉ Lj/(C ₂ H ₅) ₂ Al ^d	1.00		100	1.00 (50.0)		15 700	1.09	3	11	86
3	AIBN ^e	2.83		38.3	2.79 (73.6)		54 000	1.63	—	—	—
4	AIBN ^e	1.44		38.5	1.44 (59.0)		59 950	1.58	—	—	—
5	AIBN ^e	0.73		37.0	0.73 (42.1)		61 790	1.61	—	—	—

^aUnit mole ratio in copolymer determined by ¹H NMR. The figures in parentheses represent the MMA contents in mol%. ^bDetermined by SEC. ^cMonomer/toluene = 20 mmol/10 ml, monomer/initiator = 100 mol/mol, temperature -60°C, time 72 h. ^dMonomer/toluene = 10 mmol/10 ml, monomer/initiator = 100 mol/mol, temperature -78°C, time 72 h. ^eMonomer/toluene = 1/1 v/v, monomer/initiator = 100 mol/mol, temperature 60°C, time 24 h.

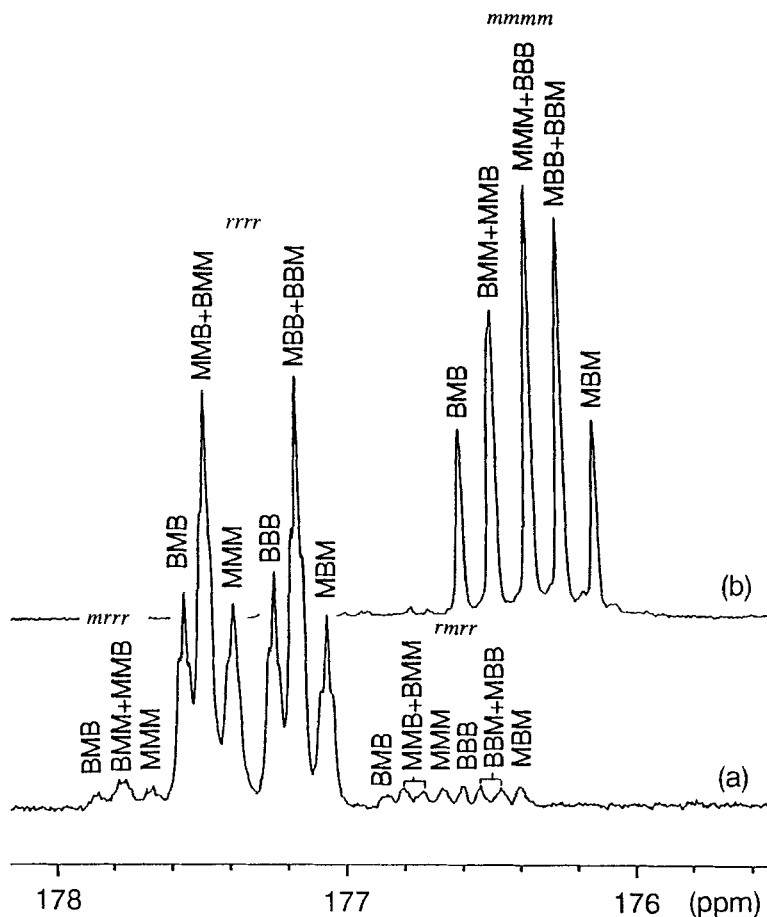


FIGURE 1 Carbonyl carbon NMR signals of syndiotactic poly(MMA-*ran*-*n*-BuMA) prepared by *t*-C₄H₉Li/(C₂H₅)₃Al (a) and isotactic poly(MMA-*ran*-*n*-BuMA) prepared by *t*-C₄H₉MgBr (b). Symbols M and B in the figure represent MMA and *n*-BuMA units in the copolymer, respectively.

the peak at 177.5 to that at 177.2 ppm increased with an increase in the contents of MMA units, and the intensity ratio agreed well with the ratio of MMA and *n*-BuMA units in the copolymer. From the results these triplets were assigned to the carbonyl carbons of the central monomer units of MMA(= M)- and *n*-BuMA(= B)-centered triads in *rrrr* configurational sequences with increasing magnetic field as shown in the figure. The assignments of the peaks in terms of monomer

sequence triads were made by comparing the spectral patterns of the copolymers with different copolymer compositions. Relative intensities of the three peaks in each triplet in Figure 1 are almost 1 : 2 : 1. The ratio of MMA and *n*-BuMA units in the copolymer is 1 : 1 as shown in Table I. Thus the comonomer sequence distribution is almost random in the copolymer.

The multiplets centered at 177.8 and 176.6 ppm are due to the carbonyl carbons in *mrrr* and *rmrr* configurational sequences, respectively. The tactic sequence assignments are based on those for PMMA and other polymethacrylates. Fine splittings in these multiplets are due to the monomer sequence distribution. Since these configurational sequences are unsymmetrical, four peaks are possible for M- or B-centered triad as indicated in Figure 1(a); M-centered triad with *mrrr* configuration consists of *mBrMrBr*, *mMrMrBr*, *mBrMrMr* and *mMrMrMr*, M-centered triad with *rmrr* configuration *rBmMrBr*, *rMmMrBr*, *rBmMrMr* and *rMmMrMr*, and B-centered triad with *rmrr* configuration *rBmBrBr*, *rBmBrMr*, *rMmBrBr* and *rMmBrMr* with increasing order of magnetic field. Signals due to B-centered sequences with *mrrr* configuration should be overlapped with those of M-centered sequences with *rrrr* configuration. The peaks for *mMrMrBr* and *mBrMrMr* are not separated well. The assignments for *rMmMrBr* and *rBmMrMr* and those for *rBmBrMr* and *rMmBrBr* are interchangeable, as indicated in Figure 1(a).

Very similarly the five peaks around 176.4 ppm in the spectrum of isotactic copolymer (Table I, No. 1) were assigned to the overlap of the two triplets centered at 176.5 and 176.3 ppm due to the M- and B-centered triads in *mmmm* configurational sequence as depicted in Figure 1(b). The intensity measurement of the five peaks indicated that the copolymer is also random.

The peak assignments for copolymer sequences indicated in Figure 1 were made using the copolymers with different compositions; for example, the peak intensities for M-centered triads increased with an increase in MMA content in the copolymer and among the triad peaks MMM peak increased in association with the decrease of BMB peak in their intensities.

The results mentioned above clearly indicate that the peak separations due to the configurational triad sequences range from 0.5 to 1.0 ppm while the separation due to the triad monomer sequences

from 0.05 to 0.1 ppm, that is, the former is ten times larger than the latter. A recent publication by Brar and Kapur^[5] described the assignments for the carbonyl carbon signals of poly(MMA-*co-n*-BuMA) prepared with benzoyl peroxide, in which the peak separations due to configurational sequences were ignored. However, our results in this work clearly indicate that the assignments made by Brar and Kapur are incorrect. Incorrectness of the assignment by Brar and Kapur was pointed out also by Moad and Willing^[6] using radically prepared copolymers of MMA and *n*-BuMA, either of which was enriched with ¹³C at the carbonyl carbon, but they did not show detailed assignment.

Figure 2 shows carbonyl carbon NMR signals of three poly(MMA-*ran-n*-BuMA)s with different compositions prepared with AIBN in toluene at 60°C. Tacticity of PMMA prepared under the same conditions ($mm=0.04$, $mr=0.32$, $rr=0.64$) is very similar to that of poly(*n*-BuMA) ($mm=0.03$, $mr=0.32$, $rr=0.65$). It is reasonable to assume that the co-tacticities of the copolymers are very similar to those of both homopolymers. The fractions of M-centered triads (MMM, MMB and BMB) should increase with increasing MMA content in the copolymer and the fraction of B-centered triads (BBB, BBM and MBM) should increase with increasing content of *n*-BuMA units. This is reflected in the spectra in Figure 2, which can be easily realized when Figure 2 is compared with Figure 1.

In reference to the peak assignments for monomer sequence triad of the isotactic and syndiotactic copolymers, the peak assignments for radically prepared copolymers (MMA content 59 mol%, No. 4 in Table I) were made in the following way as shown in Figure 3. The peak assignments for *rr*-centered pentad sequences in the range from 177 to 178 ppm were made based on the spectrum of syndiotactic poly-(MMA-*ran-n*-BuMA) (see Figure 1(a)) and on the fact that configurational pentad signals are usually observed in the order of *rrrr*, *mrrr* and *mrrm* with decreasing magnetic field in the spectra of homopolymers of MMA and *n*-BuMA. The assignments for *mm*-centered pentad sequences could also be made in a similar manner based on the spectrum of the isotactic copolymer (see Figure 1(b)) and the fact that *mmmm*, *mmmr* and *rmmm* signals appear in the order of increasing magnetic field in the spectra of the homopolymers.

The peak assignment for the *mr*-centered sequences were made in the following manner. Chemical shifts of the signals due to MMM and

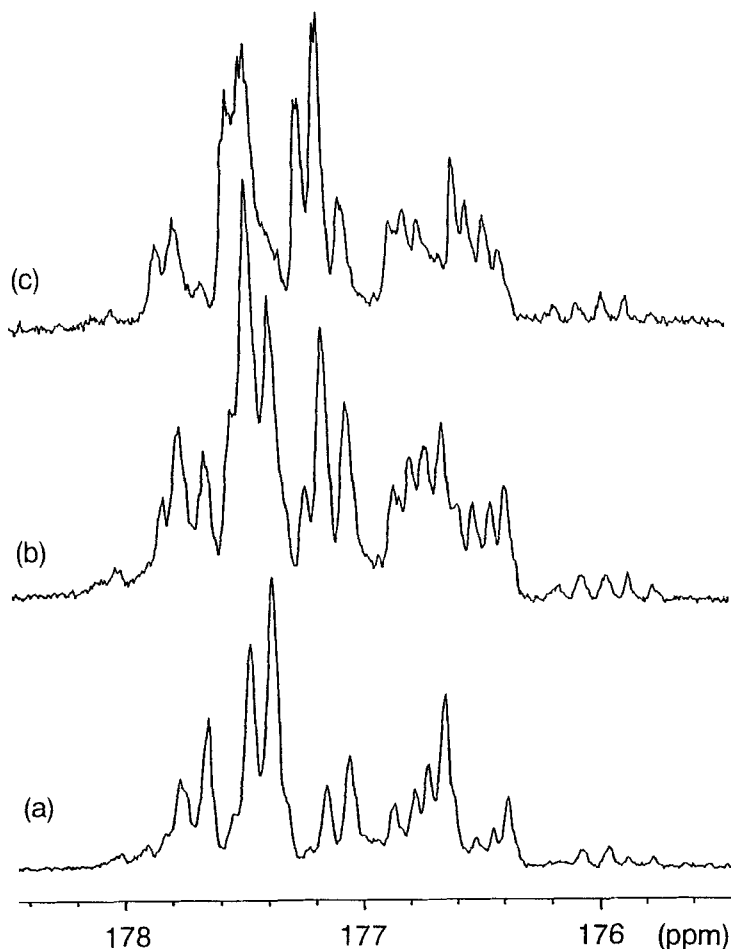


FIGURE 2 Carbonyl carbon NMR signals of poly(MMA-*ran-n*-BuMA) prepared with AIBN in toluene at 60°C. MMA content; (a) 73.6 mol%, (b) 59.0 mol%, (c) 42.1 mol%.

BBB homosequences in the four configurational sequences of *rmrr*, *rmmr*, *mmrr* and *mrrm* were determined based on the peak assignments for the corresponding homopolymers. Signals for *rmrr* pentad are already assigned in the spectrum of the syndiotactic copolymer (Figure 1(a)). The assignments and the chemical shift determinations for other three configurational pentads were made by assuming the

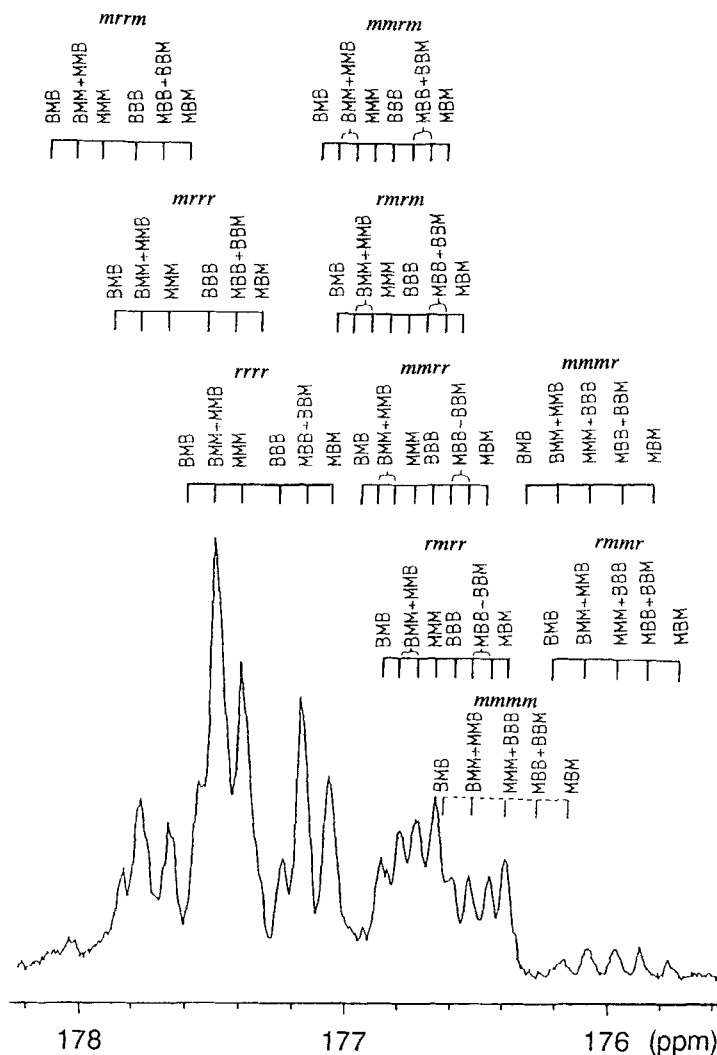


FIGURE 3 Assignments of carbonyl carbon NMR signals of poly(MMA-ran-n-BuMA) [copolymer (b) in Figure 2] at triad level in monomer sequence and at pentad level in configurational sequence.

same spectral patterns and almost the same chemical shift differences between the peaks as those for the *mrrr* pentad signals.

The fractions for all the triad monomer sequences shown in Figure 3 were calculated assuming terminal model for the copolymerization

and Bernoullian statistics for stereoregulation in radical copolymerization. As to the monomer reactivity ratios for the copolymerization, the values from Ref. [9] ($r_M = 1.20$, $r_B = 1.27$) were used. Though the yields of the copolymers are nearly 40%, the copolymer compositions are close to those calculated from these r_1 and r_2 values. Thus the estimation of the fractions of comonomer sequences based on r_1 and r_2 values should be reasonable. From these values, conditional probabilities P_{MB} and P_{BM} (probabilities of addition of *n*-BuMA to a growing chain with an MMA-end and that of MMA to the *n*-BuMA-end, respectively) were calculated to be 0.367 and 0.531 by the following two equations:

$$P_{MB} = \frac{1}{(1 + r_M[M]/[B])},$$

$$P_{BM} = \frac{1}{(1 + r_B[B]/[M])}.$$

By using the resulting values of P_{MB} and P_{BM} , and the observed copolymer compositions of MMA (P_M) and *n*-BuMA ($P_B = 1 - P_M$), fractions of comonomer sequence triads are determined by the following equations:

$$P_{MMM} = P_M(1 - P_{MB})^2,$$

$$P_{MMB} = P_MP_{MB}(1 - P_{MB}),$$

$$P_{BMM} = P_BP_{BM}(1 - P_{MB}),$$

$$P_{BMB} = P_BP_{BM}P_{MB},$$

$$P_{BBB} = P_B(1 - P_{BM})^2,$$

$$P_{BBM} = P_BP_{BM}(1 - P_{BM}),$$

$$P_{MBB} = P_MP_{MB}(1 - P_{BM}),$$

$$P_{MBM} = P_MP_{MB}P_{BM}.$$

As mentioned above, the triad tacticities of radically prepared homopolymers of MMA and *n*-BuMA are very close to each other. So a single value of the probability of meso addition $P_m = 0.197$ was determined from the averaged value of tacticities of the two homopolymers and used to calculate configurational pentad fractions based on Bernoullian statistics; for example $[rrrr] = (1 - P_m)^4 = 0.4158$. Then, the fractions of the monomer sequence triads in certain tactic pentads shown in Figure 3 can be calculated as shown in Table II. For example,

TABLE II Calculated fractions of triad comonomer sequences and of tactic pentad sequences of each triad comonomer sequence in poly(MMA-*ran-r*-BuMA) (No. 4 in Table I)^a

Configurational pentad sequence ^b	Comonomer triad sequence ^b							
	MMM (0.236 ₄)	MMB (0.137 ₁)	BMM (0.137 ₈)	BMB (0.079 ₉)	BBB (0.090 ₂)	BBM (0.102 ₁)	MBB (0.101 ₆)	MBM (0.115 ₀)
<i>mmmm</i>	(0.001 ₆)	0.000 ₂	0.000 ₂	0.000 ₁	0.000 ₁	0.000 ₂	0.000 ₂	0.000 ₂
<i>mmmr</i>	(0.012 ₃)	0.001 ₇	0.001 ₇	0.001 ₀	0.001 ₁	0.001 ₃	0.001 ₂	0.001 ₄
<i>mmrr</i>	(0.025 ₀)	0.003 ₄	0.003 ₄	0.002 ₀	0.002 ₃	0.002 ₆	0.002 ₅	0.002 ₉
<i>mmrmm</i>	(0.012 ₃)	0.001 ₇	0.001 ₇	0.001 ₀	0.001 ₁	0.001 ₃	0.001 ₂	0.001 ₄
<i>mmrrr</i>	(0.050 ₀)	0.006 ₉	0.006 ₉	0.004 ₀	0.004 ₅	0.005 ₁	0.005 ₁	0.005 ₈
<i>mmrrm</i>	(0.050 ₀)	0.011 ₈	0.006 ₉	0.004 ₀	0.004 ₅	0.005 ₁	0.005 ₁	0.005 ₈
<i>mmrrr</i>	(0.204 ₀)	0.048 ₂	0.028 ₁	0.016 ₅	0.018 ₄	0.020 ₈	0.020 ₇	0.023 ₈
<i>mmrrm</i>	(0.025 ₀)	0.003 ₄	0.003 ₄	0.002 ₀	0.002 ₃	0.002 ₆	0.002 ₅	0.002 ₉
<i>mmrrr</i>	(0.204 ₀)	0.048 ₂	0.028 ₁	0.016 ₅	0.018 ₄	0.020 ₈	0.020 ₇	0.023 ₈
<i>rrrr</i>	(0.415 ₈)	0.057 ₀	0.057 ₃	0.033 ₂	0.037 ₅	0.042 ₅	0.042 ₂	0.047 ₈

^aFollowing parameters used for the calculation: $P_{M_1} = 0.59$, $P_{M_2B} = 0.367$, $P_{BM} = 0.531$, $P_{M_1} = 0.197$, $[M]_0/[B]_0 = 1.44$.

^bThe figures in parentheses represent total probabilities of each sequence.

the fraction of MMM triad in *rrrr* pentad was calculated to be $P_{\text{MMM}} \times [rrrr] = 0.236_4 \times 0.415_8 = 0.098_3$.

Fractions of all the sequences are shown in Table II. From the data in Table II, NMR spectrum of the radically prepared copolymer (No. 4 in Table I, Figure 3) was simulated by using the following Lorentz function:

$$f(x) = \sum \left[\frac{I_i W^2}{W^2 + 4(\delta_i - x)^2} \right],$$

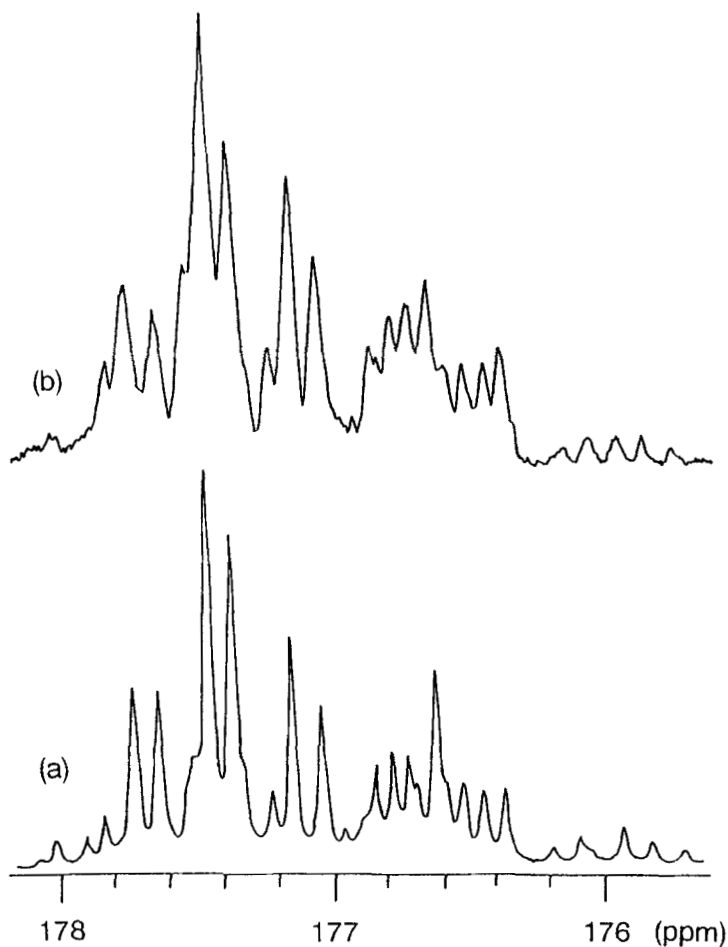


FIGURE 4 Calculated (a) and observed (b) spectra of poly(MMA-*ran-n*-BuMA) containing MMA units of 59.0%.

where I_i and δ_i are peak intensity and chemical shift of each peak, respectively, and W half-height widths of the peaks which are assumed to be the same for all the peaks.

The calculated spectrum with line width W of 3.5 Hz is very close to the observed spectrum as shown in Figure 4, indicating the validity of the peak assignment in the present work. The spectral patterns of isotactic, syndiotactic and radically prepared copolymers of MMA and ethyl methacrylate^[7,8,10] are very similar to those of the corresponding poly(MMA-*ran-n*-BuMA). This indicates that the peak assignment for poly(MMA-*ran-n*-BuMA) can be widely applicable to other methacrylate copolymers. Studies are now being continued.

Acknowledgments

The authors are indebted to Mr. Masanori Yamamoto for his collaboration in preparing the stereoregular copolymers.

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