

4 Copolymer

4.1 NMR Analysis of Composition and Sequence in Copolymers

Structural analysis of copolymers is very important from both scientific and industrial points of views. High-resolution NMR analysis is particularly effective in the study of vinyl copolymers and reveals the structural and sequence details that cannot be detected by any other means. Copolymer composition can be determined very easily by NMR, particularly by ^1H NMR, and the method is usually more accurate than other traditional analytical methods, such as elemental analysis.

The 500 MHz ^1H NMR spectra of copolymers of MMA and AN [poly(MMA-*co*-AN)s] with three different comonomer compositions (samples 1, 2 and 3) are

Table 4.1. Compositional analysis of poly(MMA-*co*-AN) by 500 MHz ^1H NMR with a single spectrometer [1, Terawaki Y, Kitayama T, Hatada K unpublished results]. The figures in parentheses represent the standard deviation σ (%)

Run	MMA unit contents of the copolymer (%)		
	Sample 1	Sample 2	Sample 3
1	36.9	50.3	66.4
2	36.9	50.5	66.6
3	37.0	50.3	67.0
4	36.9	50.4	66.7
5	36.7	50.6	65.4
Average	36.9 (0.27)	50.4 (0.23)	66.4 (0.82)
Average ^a	37.5 (3.72)	52.0 (9.45)	67.1 (6.66)
^{13}C NMR ^b	36.1 (4.39)	49.9 (3.90)	65.2 (3.07)
^{13}C NMR ^c	35.6 (2.10)	49.6 (1.11)	64.2 (1.36)

^a The results obtained by a round-robin method from 45 different spectrometers whose frequencies range from 90 to 500 MHz [1].

^b The results obtained by a round robin method from 23 different spectrometers whose frequencies range from 22.5 to 125 MHz [1].

^c The results obtained at 125 MHz by gated decoupling without NOE with a single spectrometer (Terawaki Y, Kitayama T, Hatada K unpublished results).

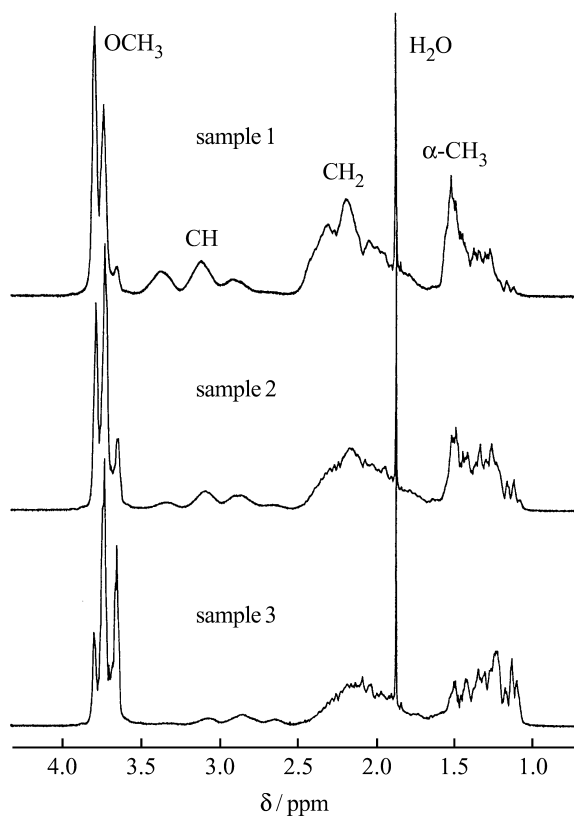


Fig. 4.1. 500 MHz ^1H NMR spectra of poly(MMA-co-AN)s in nitrobenzene- d_5 at 110 $^\circ\text{C}$ [1]

shown in Fig. 4.1. The copolymer compositions can be determined from the relative intensities of the signals due to the OCH_3 protons of MMA units and the CH proton of AN units. The results of analyses with a single spectrometer are shown in Table 4.1 (Terawaki Y, Kitayama T, Hatada K unpublished results). The standard deviations, σ , of the determinations are about 1% or less.

The series of experiments were also carried out with a round robin method by the Research Group on NMR, SPSJ [1]. The averaged results of the composition determinations with 45 different spectrometers operated at different frequencies (90–500 MHz) are also shown in Table 4.1 and agreed well with those obtained using a single 500 MHz spectrometer. The values of σ for the composition determinations by the round-robin method were about 4–9%. The deviation for sample 1 was smaller than the deviations for samples 2 and 3, which have smaller AN contents than sample 1. Larger σ values for samples 2 and 3 may be due to the fact that the methine proton signals are broad multiplets [1]. The copolymer compositions could also be determined from the 125 MHz NMR signal intensities of CO (MMA) and CN (AN) carbons with complete decoupling and agreed well with those obtained from ^1H NMR spectra (Table 4.1) [1, Terawaki Y, Kitayama T, Hatada K

Table 4.2. Comonomer sequences in copolymers poly(A-co-B) made of nonprochiral monomers [2]

Diad	AA	AB or BA	BB
Triad	AAA BAA (or AAB) BAB		BBB ABB (or BBA) ABA
Tetrad	AAAA BAAA (or AAAB) BAAB	AABA (or ABAA) BABA (or ABAB) AABB (or BBAA) BABB (or BBAB)	BBBB ABBB (or BBBA) ABBA

unpublished results]. The agreement may be ascribed to the similar NOE values for CO (1.13) and CN (1.06) carbons. ^{13}C NMR analysis with gated decoupling by a single spectrometer gave highly precise copolymer compositions that are consistent with the results from ^1H NMR (Table 4.1).

The properties of a copolymer depend not only on its composition but also on comonomer sequence and stereochemical sequence. Although compositional analysis can be achieved by several methods other than NMR, quantitative analysis on sequence distribution can be made only by NMR spectroscopy. If a copolymer is produced only from nonprochiral monomers, such as comonomers of the type $\text{CH}_2=\text{CX}_2$, there exists a set of sequences shown in Table 4.2; there are no stereo-

Table 4.3. Configurational sequences in copolymers poly(A-co-B) made of prochiral monomers

diad	<i>m</i>	AA 	AB (or BA) 	BB
	<i>r</i>			
triad ^a	<i>mm</i>	AAA 	BAA (or AAB) 	BAB
	<i>mr</i>			
	<i>rr</i>			

^a Ten others with BBB, ABB (or BBA) and ABA triads.

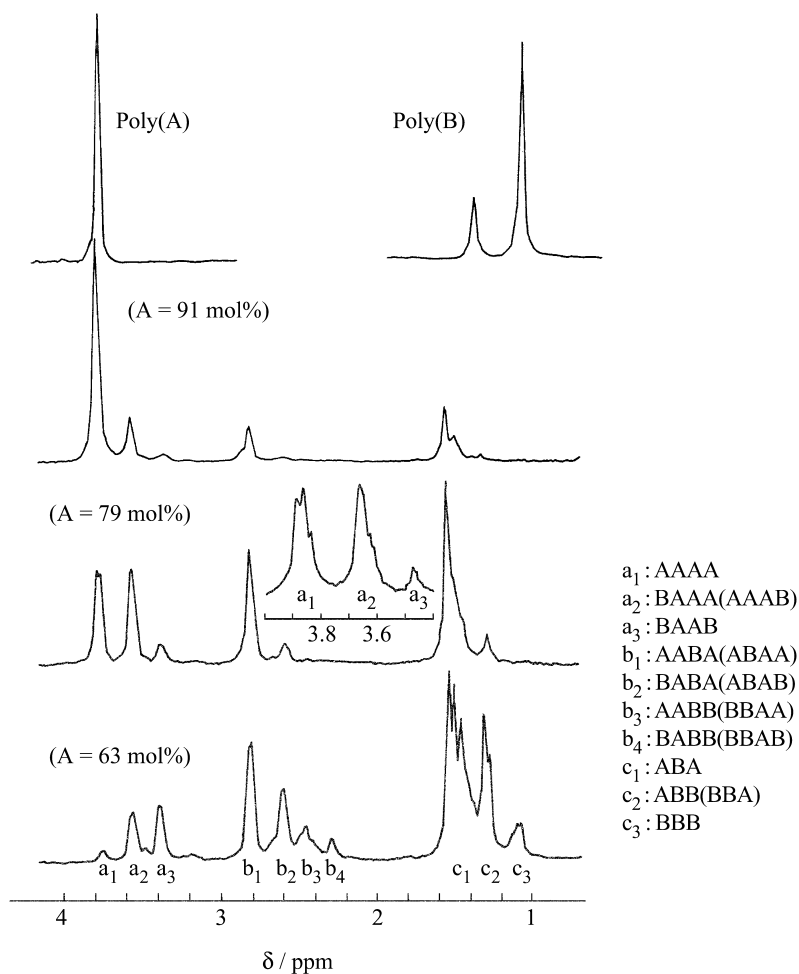


Fig. 4.2. 60 MHz ^1H NMR spectra measured in S_2Cl_2 at 130°C of homopolymers of vinylidene chloride (A) and isobutylene (B), and copolymers of A and B [3]

chemical sequences [2]. If a copolymer is prepared from prochiral monomers, such as comonomers of the type $\text{CH}_2=\text{CHX}$ or $\text{CH}_2=\text{CXY}$, configurational sequences are to be considered (Sect. 3.1) and there exist sets of sequences for diads and triads as shown in Table 4.3 [2]. The number of the sequences in n -ads increases largely with n .

A typical example of a copolymer that shows peak splittings only due to the comonomer sequences shown in Table 4.2 is the copolymer of vinylidene chloride (A) and isobutylene (B). The ^1H NMR spectra of poly(A), poly(B), and poly-(A-co-B)s with different compositions are shown in Fig. 4.2 [3]. Although the spectra were taken at 60 MHz many years ago, they clearly show the peak splittings due to the triad and tetrad comonomer sequences. It is natural that the spectra

show no splittings due to the configurational sequences and spin-spin coupling. As a result, the peak assignments are easily and reasonably made by the inspection of the spectra of copolymers with different compositions. Three peaks in the range 3.2–3.9 ppm (a_1 , a_2 , a_3) can be assigned to the methylene protons ($-\text{CCl}_2-\text{CH}_2-\text{CCl}_2-$) in the AA-centered tetrads and four peaks at 2.2–3.0 ppm (b_1 , b_2 , b_3 , b_4) methylene protons [$-\text{CCl}_2-\text{CH}_2-\text{C}(\text{CH}_3)_2-$ or $-\text{C}(\text{CH}_3)_2-\text{CH}_2-\text{CCl}_2-$] in the AB- or BA-centered tetrads. The peaks at 1.0–1.6 ppm (c_1 , c_2 , c_3) are overlaps of the methyl proton peaks in B-centered triads and the methylene proton peaks in the BB-centered tetrads. Although the peak separation is not enough to distinguish the triad and tetrad peaks, the whole pattern appears to show the triad distribution. All the assignments are indicated in Fig. 4.2. The fine splittings observed at peaks a_1 – a_3 and c_1 – c_3 may be attributed to the hexad and pentad sequences, respectively.

Even with advanced NMR methods, structural analysis of copolymers is a very difficult task when the chemical shifts of the signals are sensitive to both configurational and monomeric sequences. It should be easier to analyze signals of the copolymer with high stereoregularity since the signals have to be simple enough in the absence of splitting due to the configurational sequences. The carbonyl carbon NMR signals of isotactic, syndiotactic, and atactic copolymers of MMA and *n*-butyl methacrylate (*n*-BuMA) [poly(MMA-*co*-*n*-BuMA)] measured in chlorobenzene- d_5 at 115 °C and 125 MHz are shown in Fig. 4.3 [4]. The isotactic copolymer was prepared with *t*-C₄H₉MgBr in toluene and was almost completely isotactic. So the five peaks around 176.4 ppm should be ascribed to MMA (M) and *n*-BuMA (B) centered monomer sequences of triads in *mmmm* configurational sequences; these are the overlap of the two triplets centered at 176.6 and 176.3 ppm due to the M- and B-centered triads as shown in Fig. 4.3a. The assignments were made by comparing the spectral patterns of the copolymers of different copolymer compositions. The intensity measurement of the five peaks indicated that the relative intensities of the three peaks in each triplet are almost 1:2:1, i.e., the copolymer is random in its monomer sequence.

The tacticity of the syndiotactic polymer that was prepared with *t*-C₄H₉Li/(C₂H₅)₃Al in toluene is rather low (86% in the *rr* triad) compared with that of the isotactic polymer (97% in the *mm* triad) and shows the signals due to *mrrr* and *rmrr* configurational sequences as well as those due to the *rrrr* sequences in the spectrum (Fig. 4.3b). The two strong triplets centered at 177.5 and 177.2 ppm were assigned to M- and B-centered triads in *rrrr* configurational sequences, respectively, as shown in the figure. The peak assignments were made similarly to that for the isotactic polymer. The intensity measurement of the six peaks indicated that the monomer sequence distribution in the copolymer is also random [4]. The multiplets centered at 177.8 and 176.7 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 pentad sequences are unsymmetrical, four peaks are possible for M- and B-centered triads, respectively, as indicated in Fig. 4.3b. For example,

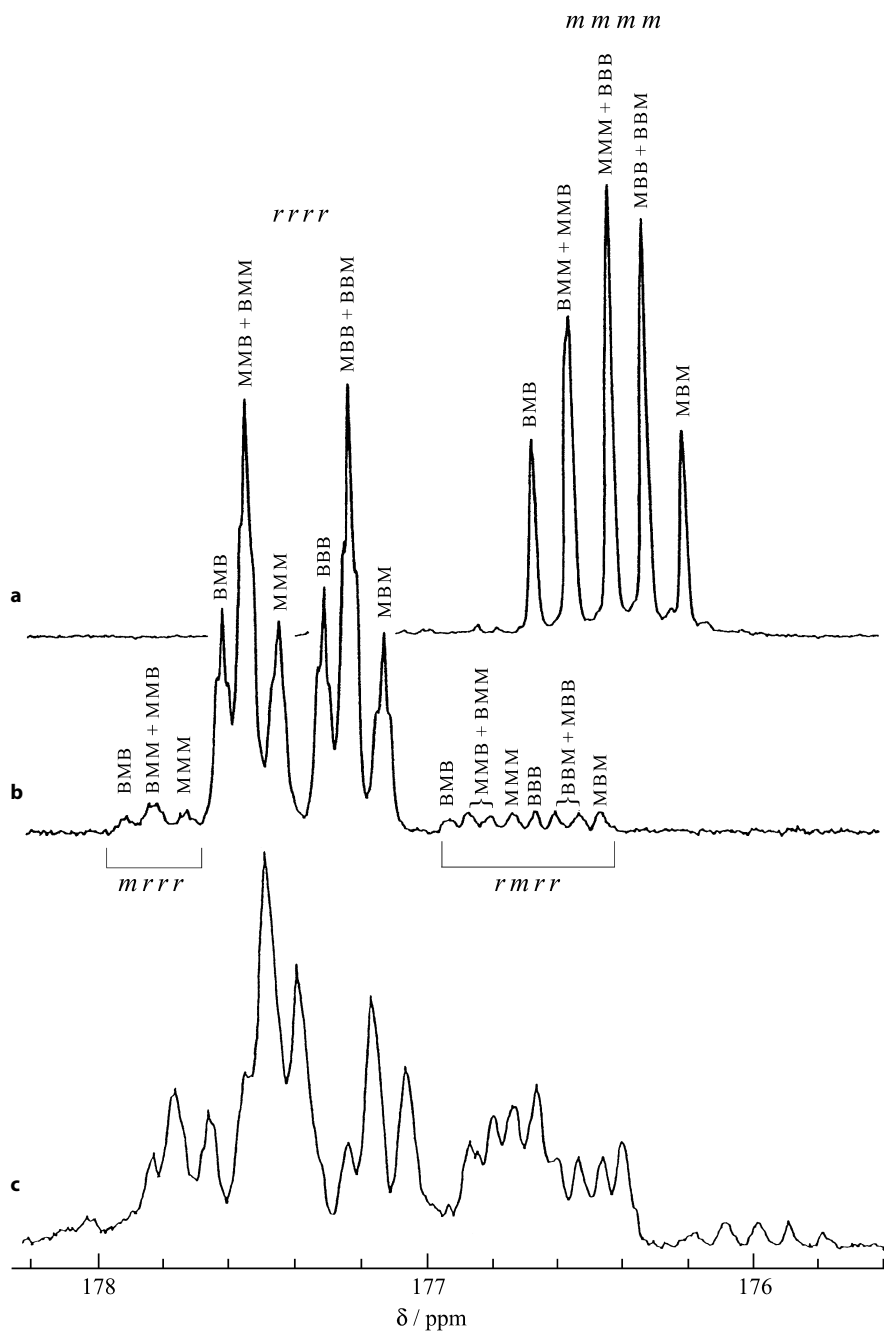


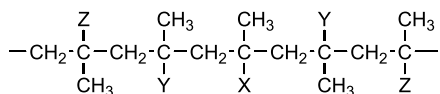
Fig. 4.3. Carbonyl carbon NMR signals of **a** isotactic (M:B=49:51), **b** syndiotactic (M:B=50:50), and **c** atactic (M:B=59:41) copolymers of MMA and *n*-BuMA prepared with $t\text{-C}_4\text{H}_9\text{MgBr}$, $t\text{-C}_4\text{H}_9\text{Li}$, $(\text{C}_2\text{H}_5)_3\text{Al}$, and AIBN, respectively, measured in chlorobenzene- d_5 at 115 °C [4]. *M* and *B* represent MMA and *n*-BuMA units in the copolymer, respectively

the M-centered triad with the *rmrr* configuration consists of *rBmMrBr*, *rMmMrBr*, *rBmMrMr*, and *rMmMrMr* with increasing order of magnetic field.¹ The signals due to *rMmMrBr* and *rBmMrMr* sequences show different chemical shifts from each other, although the assignments for these two peaks cannot be made explicitly [4].

The signals of atactic poly(MMA-*co-n*-BuMA) (59 mol% MMA units) prepared with AIBN in toluene are shown in Fig. 4.3c. The spectrum is a complex multiplet owing to the coexistence of most of the monomeric and configurational sequences in detectable amounts. The peak assignments for the copolymer were made on the basis of the previously mentioned assignments for the isotactic and syndiotactic copolymers referring to the assignments for the stereoregular homopolymers of methacrylates and are shown in Fig. 4.4. The peak assignments were confirmed by the calculation of the fractions for all the triad monomer sequences assuming a terminal model for the copolymerization and Bernoullian statistics for stereoregulation in the radical copolymerization [4].²

NMR is also useful for the structural analysis of block copolymers which are often prepared by living polymerization methods. Polymerization of methacrylates by *t*-C₄H₉MgBr is a living one and can produce block copolymers of methacrylates. The 500 MHz ¹H NMR spectra of PMMA-*block*-PEMA (B) and PEMA-*block*-PMMA (C) are shown in Fig. 4.5 together with the spectra of a mixture of PMMA and PEMA (D) and poly(MMA-*co*-EMA) (A) all of which were prepared using *t*-C₄H₉MgBr. The PMMA-*block*-PEMA was prepared by polymerizing EMA with PMMA anion and the PEMA-*block*-PMMA was prepared by polymerizing MMA with PEMA anion [5]. In the spectra of the block copolymers the methylene protons showed two sets of AB quartet signals due to the PMMA block and the PEMA block (Fig. 4.5b,c), clearly indicating that both blocks are highly isotactic. The corresponding signals of the methylene protons in the random copolymer (Fig. 4.5a) showed much more complicated splittings (1.75 ppm) or broadening

¹ For example, *rBmMrBr* represents the following sequence, where X is -COOCH₃, Y is -COOC₄H₉, and Z is X or Y.



² Under the assumption of the terminal model, the monomer sequence distribution can be estimated from monomer reactivity ratios, r_M and r_B , by introducing probability parameters, $P_{MB}=1/(1+r_M[M]/[B])$ and $P_{BM}=1/(1+r_B[B]/[M])$, where M and B denote MMA and *n*-BuMA. For example, the probability or fraction of MMM triad, P_{MMM} , can be calculated as $P_{MMM}=P_M(1-P_{BM})^2$ (P_M is the MMA content in the copolymer). As to the tacticity, the probability of meso addition, P_m , in the radical copolymerization was determined from average triad tacticity to be 0.197, in this particular case. By assuming Bernoullian statistics for stereoregulation, the fraction of MMM triad in the *rrrr* pentad, for example, can be calculated as $P_{MMM}(1-P_m)^4$.

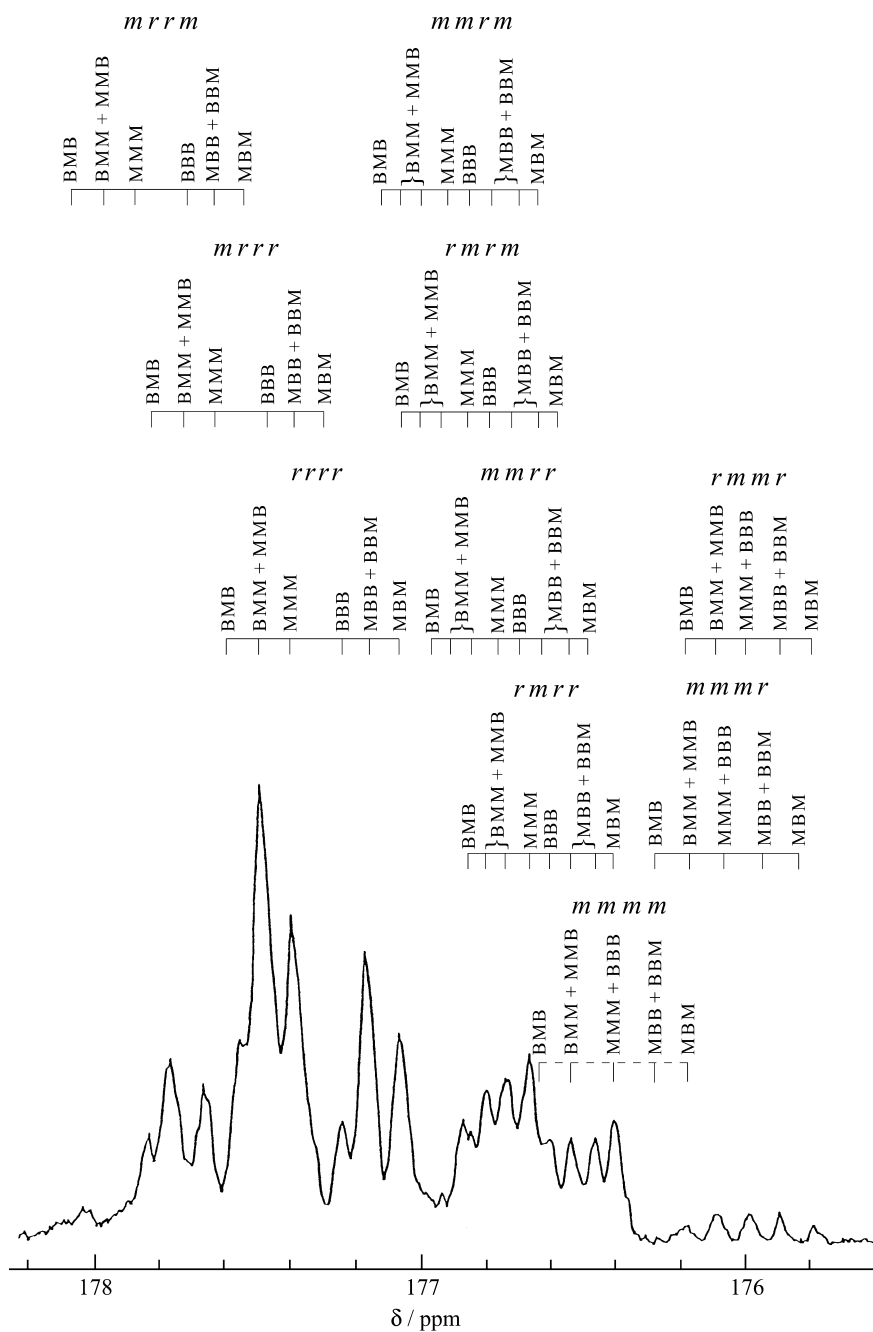


Fig. 4.4. Assignments of carbonyl carbon NMR signals of poly(MMA-co-*n*-BuMA) (M:B=59:41) (copolymer c in Fig. 4.3) at the triad level in the monomer sequence and at the pentad level in the configurational sequence [4]. *M* and *B* in the figure represent MMA and *n*-BuMA units in the copolymer, respectively

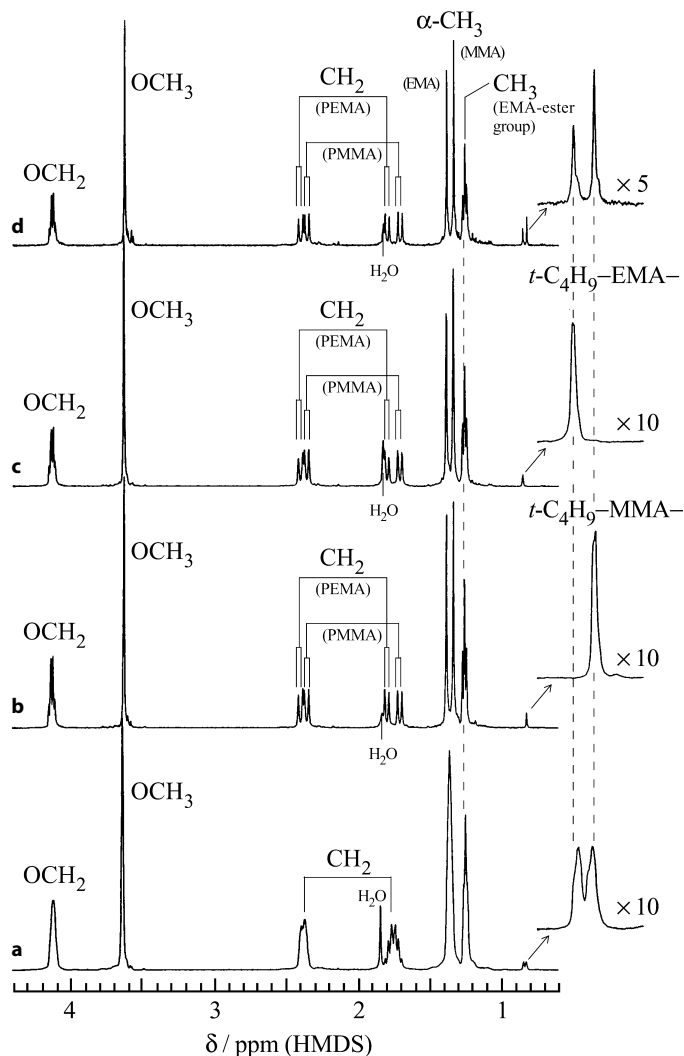


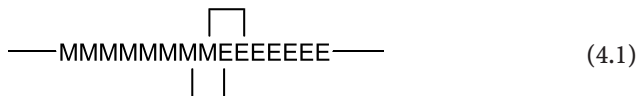
Fig. 4.5. **a–d** 500 MHz ^1H NMR spectra of highly isotactic copolymers of MMA and EMA prepared with $t\text{-C}_4\text{H}_9\text{MgBr}$ in toluene at -60°C , measured in nitrobenzene- d_5 at 110°C . **a** Poly(MMA-*co*-EMA); **b** PMMA-*block*-poly(EMA); **c** poly(EMA)-*block*-PMMA; **d** PMMA+poly(EMA) [5]. 45° pulse, pulse repetition time 20 s, 3,000 scans

(2.4 ppm) owing to the presence of different types of monomer sequences. Similar spectral differences between the block and random copolymers are also observed in the other signals. Thus, these ^1H NMR signals are good and clear indications for distinguishing the block and random copolymers of MMA and EMA.

NMR spectra of the block copolymers are expected to be almost the superpositions of the spectra of the corresponding homopolymers. However, the signals due to initiator fragments (0.8–0.9 ppm) provide information for distinguishing

the block copolymers from the mixture. The PMMA-*block*-PEMA (Fig. 4.5b) and PEMA-*block*-PMMA (Fig. 4.5c) showed single t -C₄H₉ signals at 0.823 and 0.852 ppm, respectively, which are assigned to the initiator fragments attached to the PMMA and PEMA sequences, respectively. On the other hand, the mixture of PMMA and PEMA, both of which were prepared with the same initiator t -C₄H₉MgBr, shows signals of two types of initiator fragments as indicated in Fig. 4.5d. The t -C₄H₉ signals in the two block copolymers provide the information whether the block copolymer was prepared from the PMMA anion or the PEMA anion [5].

In the carbonyl carbon region of the 125 MHz ¹³C NMR spectrum measured in CDCl₃ at 55 °C the diblock copolymer PMMA-*block*-PEMA shows two strong signals at 176.51 and 176.37 ppm, with weak signals of equal intensity at 176.60 and 176.28 ppm. The two strong signals were assigned to the MMM and EEE triads in the isotactic pentad configuration, *mmmm*, respectively, by referring to the spectra of isotactic PMMA and isotactic PEMA. The two weak signals of equal intensity were assigned to MME and MEE triads in the *mmmm* configuration by comparing the spectrum with that of the corresponding random copolymer, which should exist at the switching point of MMA and EMA sequences:



NMR Spectroscopy of Polymers

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2004, XII, 228 p., Hardcover

ISBN: 978-3-540-40220-6