^{13}C n.m.r. sequence analysis of ethylene–α-methylstyrene copolymers

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Ethylene–α-methylstyrene (EMS) copolymers were prepared by anionic polymerization using butyllithium and *N,N,N′,N′*-tetramethylethylenediamine (TMEDA) as an initiator. The ^{13}C n.m.r. spectra of EMS copolymers are observed and assigned mainly using two kinds of n.m.r. techniques: ^{13}C distortionless enhancement by polarization transfer (d.e.p.t.) and the two-dimensional incredible natural abundance double quantum transfer experiment (2D-INADEQUATE). The monomer composition, the sequence distribution in the triad level and the number-average sequence length are determined on the basis of the ^{13}C n.m.r. results.

(Keywords: ^{13}C n.m.r.; ethylene–α-methylstyrene; 2D-INADEQUATE)

INTRODUCTION

Ethylene–α-methylstyrene (EMS) copolymers were first prepared using alkyllithium as initiator by Anderson and Mullineaux[1]. These copolymers were regarded as alternating copolymers and had a high glass transition temperature ($T_g > 50°C$). More recently, EMS copolymers have been prepared using butyllithium and *N,N,N′,N′*-tetramethylethylenediamine (TMEDA) as an initiator under low ethylene pressure ($\leqslant 50\,kg\,cm^{-2}$)[2]. These copolymers are rubber-like at room temperature ($T_g < 40°C$) and are expected to be useful as elastomers, adhesives and modifiers for commercial polymers.

Since the mechanical properties of such EMS copolymers are essentially affected by the monomer compositions and sequence distributions in the chain, it is very important to study the microstructures of the copolymers in detail. ^{13}C n.m.r. spectroscopy is one of the most powerful techniques for this purpose.

In the n.m.r. approach, the spectral assignment of the polymers must be carried out. The recently developed two-dimensional incredible natural abundance double quantum transfer (2D-INADEQUATE) ^{13}C n.m.r. technique[3,4] has been successfully used to assign the ^{13}C n.m.r. spectra of synthetic polymers such as ethylene–propylene copolymers[5,6], stereoirregular polypropylene[7] and regioirregular polypropylene[8].

In this paper, we tried to assign the ^{13}C n.m.r. spectra of EMS copolymers using mainly the 2D-INADEQUATE n.m.r. technique. Then, the monomer composition, the sequence distribution in the triad level and the number-average sequence length were determined.

EXPERIMENTAL

Materials

The anionic copolymerization of α-methylstyrene (Ms) and ethylene (E) was carried out using the following procedure. TMEDA and butyllithium were dissolved in dried cyclohexane (400 ml) at 10–80°C in a 1 l autoclave and then Ms was added. Ethylene was charged under a constant pressure of 4–50 $kg\,cm^{-2}$ during the polymerization for 2–150 h. The polymerization was terminated by adding 10 ml of methanol and then the solution was poured into 2 l of methanol. The precipitated EMS copolymer was separated from the solution by filtration and dried in vacuum. The conditions of the anionic polymerization of the four EMS copolymers are listed in *Table 1*.

The weight-average molecular weights (M_w) of the EMS copolymers were in the range 14 000–23 000 and their polydispersities (M_w/M_n) were in the range 1.9–2.7. These values were determined by g.p.c. (Waters Associates, model 50C) at 135°C with a GMH-HT6 column (Tosoh Co., 7.5 mm i.d. × 60 cm). The eluent was 1,2,4-trichlorobenzene, and standard polystyrenes ($M_w/M_n = 1.0$–1.9) were used for molecular weight calibration. No detectable amounts of unsaturated bonds in the chain were observed in the ^1H n.m.r. spectra of these copolymers. Poly(α-methylstyrene) was purchased from Aldrich Chemical Co. Ltd.

^{13}C n.m.r. measurements

^{13}C n.m.r. spectra were measured at 130°C using a JEOL-EX400 n.m.r. spectrometer operated at 100.1 MHz.

The polymer samples were dissolved in mixtures of 1,2,4-trichlorobenzene and benzene-d_6 (9:1 v/v). The polymer concentration used was 70 $mg\,ml^{-1}$ except for 2D-INADEQUATE n.m.r. measurement where the concentration was 200 $mg\,ml^{-1}$.

Tetramethylsilane was used as an internal chemical shift reference. The ^1H gated decoupled ^{13}C n.m.r. spectrum was measured under the following conditions: repetition time 30 s, pulse angle 45° and 2000 scans.

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Table 1 Conditions of the anionic polymerization of ethylene and α-methylstyrene

Sample	TMEDA ($mmol\,l^{-1}$)	BuLi[a] ($mmol\,l^{-1}$)	Ms ($g\,l^{-1}$)	Ethylene pressure ($kg\,cm^{-2}$)	Temperature (°C)	Time (h)
A	2.6	1.7	27	40	50	4
B	12.5	8.4	27	40	10	2
C	2.6	1.7	13	12	40	6
D	62.7	42.0	137	20	10	2

[a] BuLi, butyllithium

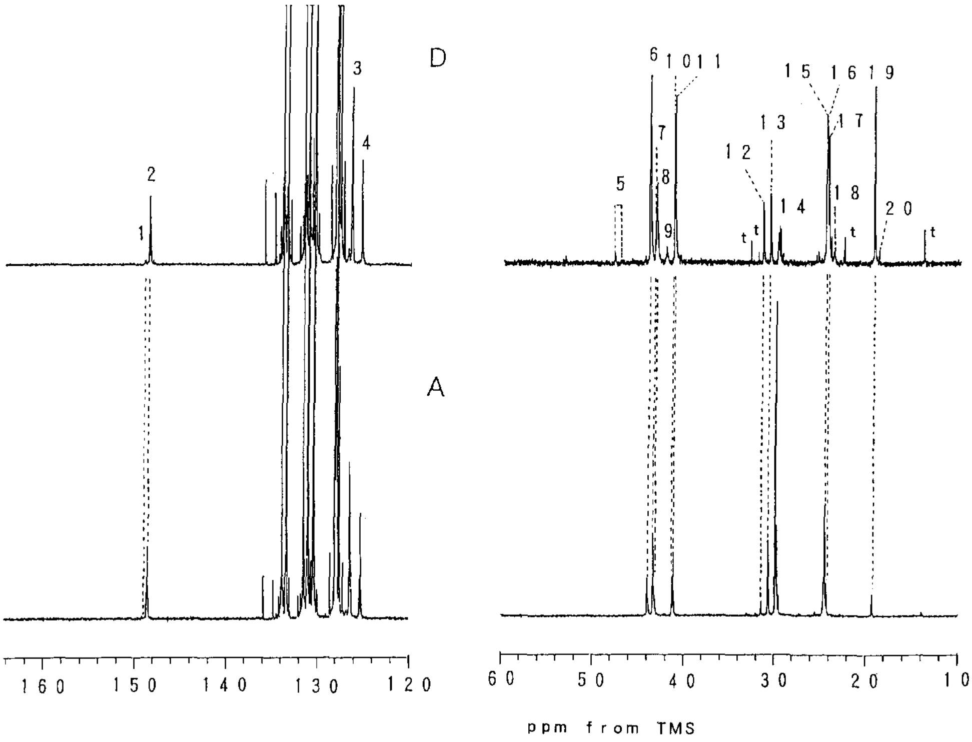

Figure 1 ^1H gated decoupled ^{13}C n.m.r. spectra of EMS copolymers, samples A and D. Pulse repetition time: 30 s, pulse angle: 45° and 2000 scans. The signals labelled 't' are due to the terminal butyl group derived from the initiator

The 2D-INADEQUATE spectrum was measured using the following pulse sequence: $90°\text{-}1/4J\text{-}180°\text{-}1/4J\text{-}90°\text{-}t_1/2\text{-}135°\text{-}t_2/2$ (acquisition). The delay time $1/4J$ was set to be 7.14 ms corresponding to the ^{13}C–^{13}C coupling constant (35 Hz). Free induction decays accumulated 800 times at each mixing time (t_1) were stored. The data matrix of the time domain was $2048(t_2) \times 128(t_1)$ and that of the frequency domain was expanded to $4096(t_2) \times 256(t_1)$ by zero filling. The repetition time of each pulse sequence was 2.0 s. The row and column frequencies were 14200 and 7100 Hz, respectively. ^{13}C distortionless enhancement by polarization transfer (d.e.p.t.) was also performed for peak assignment.

The nomenclature suggested by Carman and Wilkes[9] for ethylene–propylene copolymers is used for the EMS copolymers. Methylene carbons (S) in the polymer main chain are designated by two Greek letters showing their positions relative to the nearest quaternary carbons of the Ms unit on both sides. Methylene carbons distant by four or more bonds from the nearest quaternary carbon of the Ms unit are designated by 'δ^+'. The aromatic ring in the Ms unit is designated by 'ϕ'.

RESULTS AND DISCUSSION

Assignments of the ^{13}C n.m.r. spectra of EMS copolymers

Figure 1 shows ^1H gated decoupled ^{13}C n.m.r. spectra of EMS copolymers (samples A and D). The peaks at 127–136 ppm are assigned to the solvents (1,2,4-trichlorobenzene and benzene-d_6). The peaks designated by 't' at 13.90, 22.57, 32.00 and 32.82 ppm are assigned to the terminal butyl group arising from the initiator.

It is necessary to assign the peaks to the types of carbon in the sample. For this purpose, d.e.p.t. observation was performed and *Figure 2* shows the spectrum obtained. In the spectrum of $\theta = 135°$, the peaks of methyl and methine carbons should appear upward, methylene carbons downward and the quaternary carbons should disappear. In the case of $\theta = 45°$, the peak of the quaternary carbons should disappear and the peaks of the other three types of carbon should appear upward. For example, peak 15 is assigned to the CH_2 carbon. There are no CH peaks in the chemical shift range 19–45 ppm, because only the CH carbons of the aromatic ring exist in the EMS copolymer. Therefore, peak 16 is exclusively assigned to the CH_3 carbon of the Ms unit. The assignments of the peaks to the carbon species are summarized in *Table 2*.

In order to assign the peaks to the specified carbons in the comonomer sequences, the 2D-INADEQUATE spectrum was observed. *Figure 3* shows the expanded INADEQUATE spectrum (19–45 ppm) of sample A. The carbon peaks from three kinds of comonomer sequences, MsEMs, MsEEMs and MsEE(E)$_n$ ($n \geq 1$), were easily assigned as shown by the solid lines in the figure as follows.

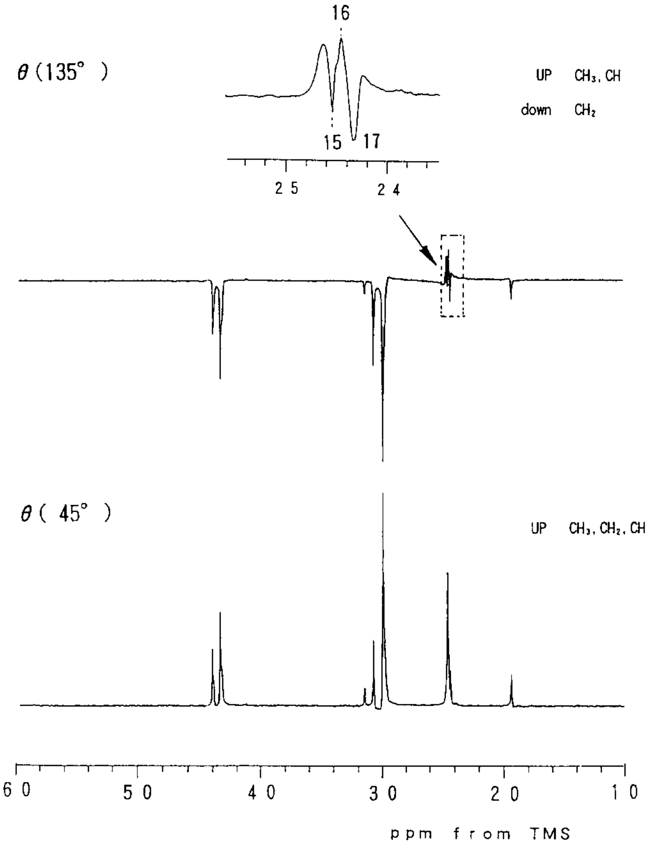

Figure 2 D.e.p.t. ^{13}C n.m.r. spectra of sample A. 'θ' represents the degree of the proton irradiation pulse

The quaternary carbon peak, 10, at 41.30 ppm of the Ms unit is connected to the S $\alpha\gamma$ peak, 6, at 43.98 ppm. The S $\alpha\gamma$ peak, 6, is also connected to the S $\beta\beta$ peak, 19, at 19.33 ppm, which is connected to only the S $\alpha\gamma$ peak, 6. These connectivities indicate the presence of the MsEMs sequence in the chain.

Next, the quaternary carbon peak, 11, at 41.20 ppm of the Ms unit is connected to the S $\alpha\delta^+$ peak, 8, at 43.25 ppm, which is also connected to the S $\beta\delta^+$ peak, 17, at 24.28 ppm. Then, the latter peak, 17, is connected to the S $\gamma\gamma$ peak, 12, at 31.44 ppm, which is connected to only the S $\beta\delta^+$ peak, 17. These connectivities indicate the presence of the MsEEMs sequence.

The presence of the MsEE(E)$_n$ ($n \geq 1$) sequence is proved as follows. The quaternary carbon peak, 11, at 41.20 ppm is also connected to the S $\alpha\delta^+$ peak, 7, at 43.38 ppm except for peak 8. Then, peak 7 is connected to the S $\beta\delta^+$ peak, 15, at 24.51 ppm and to the S $\gamma\delta^+$ peak, 13, at 30.61–30.72 ppm and to the S $\delta^+\delta^+$ peak, 14, at 29.56–29.91 ppm. These spectral connectivities are present in the MsEE(E)$_n$ ($n \geq 1$) sequence of sample A. Thus, all peaks of sample A in the high field region, 10–50 ppm, were assigned to the specified carbons in the comonomer sequences in the triad level.

Figure 4 shows the expanded ^1H gated decoupled ^{13}C n.m.r. spectrum of sample D. The assignment of sample D was also performed with the 2D-INADEQUATE method.

Table 2 ^{13}C n.m.r. assignment of the EMS copolymer (sample D)

Peak no.	Chemical shift (ppm from TMS)	Carbon type[a]	Sequence[b]
1	149.16	Quaternary C(ϕ)	M_2, M_2E
2	148.58	Quaternary C(ϕ)	E_1, E_2, E_n
3	126.30–126.46	CH(ϕ)	E_1, E_2, E_n, M_2, M_2E
4	125.27	CH(ϕ)	E_1, E_2, E_n, M_2, M_2E
5 ①	47.84	S $\alpha\alpha$	M_2
②	46.96	S $\alpha\alpha$	M_2
6	43.98	S $\alpha\gamma$	E_1
7	43.38	S $\alpha\delta^+$	E_n
8	43.25	S $\alpha\delta^+$	E_2
9	42.15	Quaternary C(Ms)	M_2
10	41.30	Quaternary C(Ms)	E_1
11	41.20	Quaternary C(Ms)	E_2, E_n
12	31.44	S $\gamma\gamma$	E_2
13	30.61–30.72	S $\gamma\delta^+$	E_n
14	29.56–29.91	S $\delta^+\delta^+$	E_n
15	24.51	S $\beta\delta^+$	E_n
16	24.46	CH_3	E_1, E_2, E_n
17	24.28	S $\beta\delta^+$	E_2
18	23.75	CH_3	M_2, M_2E
19	19.33	S $\beta\beta$	E_1
20	18.85	S $\beta\beta$	M_2E

[a] Determined by the d.e.p.t. ^{13}C n.m.r. technique

[b] E_1, E_2, E_n, M_2 and M_2E represent the MsEMs, MsEEMs, MsEE(E)$_n$ ($n \geq 1$), EMsMsE and EMsMsEMs sequences, respectively

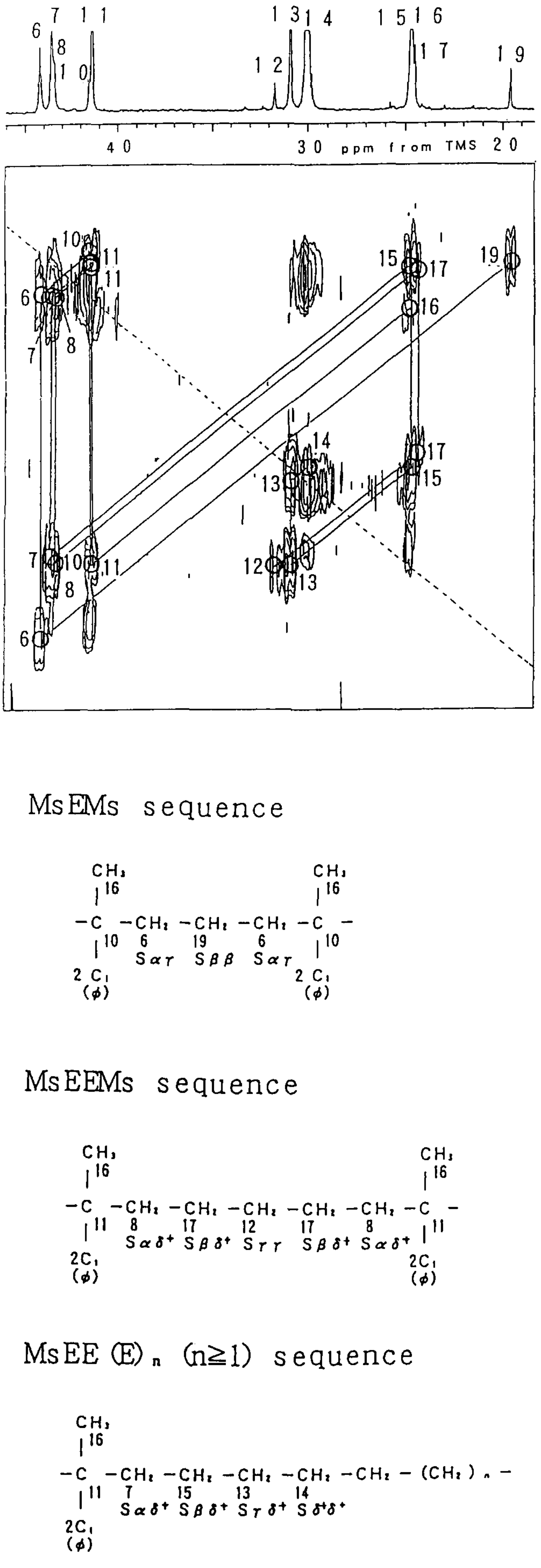

Figure 3 Expanded 2D-INADEQUATE n.m.r. spectrum of sample A. The assignment is shown in the structural formulae for the MsEMs, MsEEMs and MsEE(E)$_n$ ($n \geq 1$) sequences

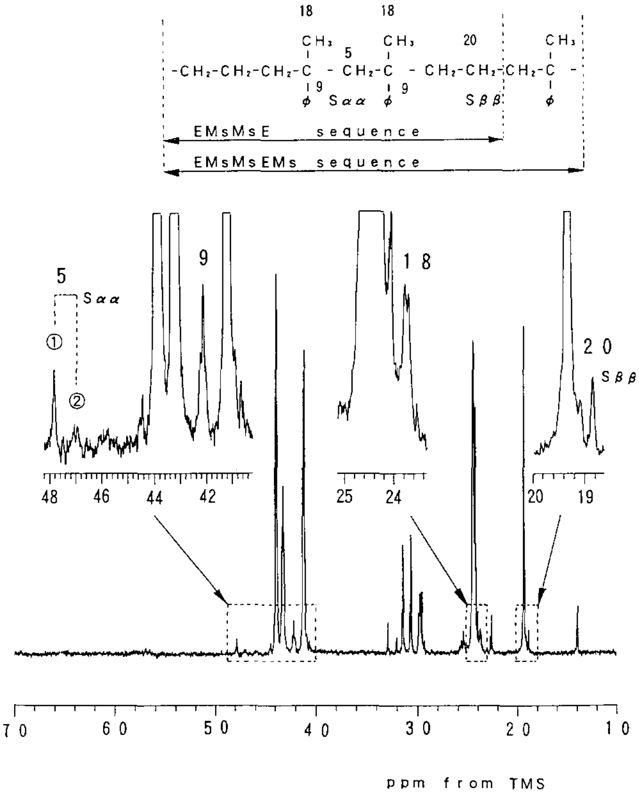

Figure 4 ^1H gated decoupled ^{13}C n.m.r. spectrum of sample D. The assignments for peaks 5, 9, 18 and 20 are shown in the structural formulae for the EMsMsE and EMsMsEMs sequences

New peaks 5-① (CH_2 carbon), 5-② (CH_2 carbon), 9 (quaternary carbon), 18 (CH_3 carbon) and 20 (CH_2 carbon), which could not be observed clearly in the spectrum of sample A, were found. Thus, the number of peaks increases and some peaks show further splittings. The ^{13}C–^{13}C connectivities of these carbons could not be observed clearly in the 2D-INADEQUATE spectrum because of their small peak intensities. The fraction of Ms unit is considerably larger in sample D than that in sample A (*Table 1*). Thus, successive Ms units, –MsMs–, are expected to be found in sample D. If successive Ms units are included in the EMsMsE sequence, the relative peak intensities should be 2:2:1 for two CH_3 carbons, two quaternary carbons and one S α α carbon, respectively. The relative peak intensities of peak 18 (CH_3 carbon), peak 9 (quaternary carbon) and the sum of peaks 5-① and 5-② (CH_2 carbons) are 2:2:1, respectively. Thus, these new peaks observed in the spectrum of sample D are assigned to the EMsMsE sequence. In addition, peaks 5-① and 5-② might be assigned to the tactic splitting due to diad configuration of successive Ms units. The CH_2 carbon peak, 20, is observed whenever the EMsMsE sequence exists in the EMS copolymers and, therefore, can be assigned to the S β β carbon in the MsMsEMsE or MsMsEMsMs sequences.

The assignment of the ^{13}C n.m.r. spectrum of poly(α-methylstyrene) has been established[10,11]. The chemical shift of the S α α carbon of this polymer is 60–63 ppm, while that of the S α α carbon in the EMsMsE sequence of sample D is 47–48 ppm. This indicates that there are no long sequences of Ms unit such as Ms(Ms)$_n$Ms ($n \geq 1$) in the EMS copolymers examined in this work. The assignment of the peaks of the EMS copolymer, sample D, is summarized in *Table 2*. The

Table 3 Sequence distribution in the triad level, monomer composition and the number-average sequence length of the EMS copolymers determined from the ^{13}C n.m.r. spectra

	Triad sequence distribution (mol%)						Monomer composition (mol%)		Monomer number-average sequence length	
Sample	EEE	MsEE	EMsE	MsEMs	MsMsE	MsMsMs	E	Ms	nE	nMs
A	45.2	25.8	21.4	7.6	–[a]	–	78.6	21.4	3.8	1.0
B	36.1	30.6	25.7	7.0	0.6	–	73.7	26.3	3.3	1.2
C	49.3	22.7	20.7	7.3	–	–	79.3	20.7	4.3	1.1
D	8.5	25.5	39.9	24.1	2.4	–	58.1	41.9	1.6	1.1

[a] Not detected

sequence analysis of these copolymers was made from the area of the peaks assigned here.

Triad sequence distributions

It is possible to determine the triad distributions by the following equations. This is essentially the same approach as that reported for the ethylene–1-hexene copolymer by Randall and Esieh[12] and the ethylene–propylene copolymer by Kakugo *et al.*[13].

$$\mathrm{EEE}=(I_{14}/2+I_{13}/4)/K \tag{1}$$

$$\begin{aligned}\mathrm{EEMs}&=(I_{15}+I_{17})/K\\&=[(I_{15}+I_{16}+I_{17})-(I_{10}+I_{11})]/K\end{aligned} \tag{2}$$

$$\mathrm{EMsE}=(I_{10}+I_{11})/K \tag{3}$$

$$\mathrm{MsMsE}=I_9/K \tag{4}$$

$$\mathrm{MsEMs}=(I_{19}+I_{20})/K \tag{5}$$

where K is given by the equation:

$$\begin{aligned}K=&(I_{14}/2+I_{13}/4)+(I_{15}+I_{17})+(I_{10}+I_{11})\\&+I_9+(I_{19}+I_{20})\end{aligned} \tag{6}$$

where I_n is the peak intensity and the subscript denotes the peak number shown in *Table 2*. The triad sequence distribution using equations (1)–(6) is summarized in *Table 3* for samples A–D.

Monomer composition

The monomer composition can be calculated from the triad distributions by the following equations[12,13]:

$$\begin{aligned}\mathrm{Ms}&=(\mathrm{MsMsE}+\mathrm{EMsE})/T\\&=(I_9+I_{10}+I_{11})/T\end{aligned} \tag{7}$$

$$\begin{aligned}\mathrm{E}&=(\mathrm{EEE}+\mathrm{EEMs}+\mathrm{MsEMs})/T\\&=[(I_{14}/2+I_{13}/4)+(I_{15}+I_{16}+I_{17})\\&\quad-(I_{10}+I_{11})+(I_{19}+I_{20})]/T\end{aligned} \tag{8}$$

where T is given by the equation:

$$\begin{aligned}T=&\,\mathrm{MsMsE}+\mathrm{EMsE}+\mathrm{EEE}+\mathrm{EEMs}+\mathrm{MsEMs}\\=&\,I_9+I_{13}/4+I_{14}/2+I_{15}+I_{16}+I_{17}+I_{19}+I_{20}\end{aligned} \tag{9}$$

The monomer composition is listed in *Table 3* for samples A–D. Since samples A and C are soluble in $CDCl_3$, the monomer composition was also determined from the ^{1}H n.m.r. spectra in this solvent. The contents of E and Ms units were 79.3 and 20.7% for sample A, and 79.5 and 20.5% for sample C. These values are in agreement with those determined from the ^{13}C n.m.r. spectra (78.6 and 21.4% for sample A; 79.3% and 20.7% for sample C) within experimental error. This supports the validity of the present ^{13}C n.m.r. assignment.

Monomer average sequence length

The run number (Nr) defined by Harwood and Ritchey[14] is given from the triad distributions by the equation:

$$\mathrm{Nr}=\mathrm{MsEMs}+\mathrm{MsEE}/2 \tag{10}$$

The number-average sequence lengths of α-methylstyrene (nMs) and ethylene (nE) are given by the following equations:

$$\mathrm{nMs}=\mathrm{Ms}/\mathrm{Nr} \tag{11}$$

$$\mathrm{nE}=\mathrm{E}/\mathrm{Nr} \tag{12}$$

The results of the monomer composition, the sequence distribution in the triad level and the number-average sequence length for four kinds of EMS copolymers are summarized in *Table 3*.

The ethylene content increases in the order of samples C, A, B and D. This corresponds to an increase in ethylene triad in the samples. The average sequence length of the Ms unit is close to unity, indicating that the Ms unit tends to be isolated in these samples. The T_g values of samples A and D are -10 and 37°C, respectively. Therefore, it should be noted that the T_g value of the EMS copolymer increases with increase in alternating character of the comonomer sequence as well as the monomer composition.

REFERENCES

1 Anderson, W. S. and Mullineaux, R. D. *Am. Chem. Soc. Polym. Prepr.* 1966, **7**, 126

2 Kijima, M. *Jpn Pat. 2-236111* 1990

3 Bax, A., Freeman, R. and Kempsell, S. P. *J. Am. Chem. Soc.* 1980, **102**, 4849

4 Bax, A., Freeman, R., Frenkiel, T. A. and Leuitt, M. H. *J. Magn. Reson.* 1981, **43**, 478

5 Hikichi, K., Hiraoki, T., Ikura, M., Higuchi, H., Eguchi, K. and Ohuchi, M. *Polym. J.* 1987, **19**, 1317

6 Hayashi, T., Inoue, Y., Chujo, R. and Asakura, T. *Polymer* 1989, **20**, 895

7 Ando, T., Yamanobe, T. and Asakura, T. *Prog. NMR Spectrosc.* 1990, **22**, 349

8 Asakura, T., Nakayama, N., Demura, M. and Asano, A. *Macromolecules* 1992, **25**, 4876

9 Carman, C. J. and Wilkes, C. E. E. *Rubber Chem. Technol.* 1971, **44**, 781

10 Inoue, Y., Nishioka, A. and Chujo, R. *Makromol. Chem.* 1972, **156**, 207

11 Elgert, K. F., Wicke, R., Stutzel, B. and Ritter, W. *Polymer* 1974, **16**, 467

12 Randall, J. C. and Esieh, E. T. *Am. Chem. Soc. Symp. Ser.* 1984, **247**, 131

13 Kakugo, M., Naito, Y., Mizunuma, K. and Miyatake, T. *Macromolecules* 1982, **15**, 1150

14 Harwood, H. J. and Ritchey, W. M. *J. Polym. Sci., Polym. Lett. Edn* 1964, **2**, 601