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^{13}C NMR Signal Assignment of Styrene/Butadiene Copolymer

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ABSTRACT: ^{13}C NMR signals of styrene/butadiene copolymer (SBR) were analyzed using low molecular weight model compounds corresponding to styrene/1,4-butadiene and styrene/1,2-butadiene structures together with partially deuterated copolymer. Aliphatic carbon signals were assigned in terms of diad or triad sequences of the styrene unit and three isomeric butadiene units: cis-1,4; trans-1,4; and 1,2. Signal splittings due to the tacticity and cotacticity of 1,2-butadiene and styrene units were also assigned. Head-to-tail arrangements were confirmed for 1,2-butadiene and styrene units in SBR prepared with free-radical initiators.

Introduction

Styrene/butadiene copolymer (SBR) has a complicated sequence structure that comprises units of styrene and cis-1,4, trans-1,4, and 1,2 units of butadiene. Thus, in order to analyze the structure of SBR, it is necessary to determine the sequence distribution of these four units and the configurational sequence of 1,2-butadiene and styrene units.

^{13}C NMR spectroscopy has been applied to the determination of the microstructure of SBR.[1-4] Aided by ^{13}C NMR studies of polybutadiene and polystyrene, Katritzky et al. assigned signals of aliphatic carbons in terms of diad sequences.[1] However, it was found that in polybutadiene some aliphatic carbons in the sequences containing more than two 1,2 units showed split signals reflecting diad or higher stereochemical configurations.[5,6] Recently it was suggested that assignment of most of the signals due to 1,2 units should take into account the triad sequence of the isomeric units.[6] Therefore, the signals of SBR should also be assigned by considering signal splittings due to the stereosequences of 1,2-butadiene and styrene units and by considering triad or higher sequences of the four units. Katritzky et al.[2] also determined the diad population of the four units in SBR including 1,4-butadiene units, i.e., trans–trans, trans–cis, cis–trans, and cis–cis diads, using aliphatic carbon signals. However, it seems impossible to determine the diad populations of 1,4-butadiene units because the methylene signal in the trans–trans sequence appears at the same chemical shift as that in the trans–cis sequence. In addition, the cis–cis and cis–trans sequences cannot be distinguished by aliphatic carbon signals even in polybutadiene.[6,7]

Segre et al.[3,4] assigned the ^{13}C NMR of SBR in terms of triad sequences of the four units by using the shift factors determined for each monomeric unit. However, their method predicts no signal splittings due to the tacticity and cotacticity of 1,2-butadiene and styrene units; consequently, they assigned these signal splittings by assuming the presence of tail-to-tail linkages of 1,2-butadiene and styrene units.

In a previous paper, we assigned the ^{13}C NMR spectrum of polybutadiene on the basis of signal assignments for butadiene oligomers and determined the diad sequence distribution in various polybutadienes.[6] In this paper, ^{13}C NMR spectra of SBR samples are assigned by using model compounds corresponding to styrene sequences, butadiene sequences, and styrene/butadiene sequences of various isomeric units as well as with reference to the spectrum of partially deuterated SBR.

Experimental Section

Styrene/Butadiene Model Compounds. Styrene was polymerized with butyllithium initiator (styrene:butyllithium = 1:1), using an alkenyl chloride as chain terminator. The oligomer containing one styrene unit was separated from the reaction mixture by GPC. The diastereomers of 6-phenyl-8-vinyltridecane were separated by HPLC using styrene/divinylbenzene gel as a stationary phase and 2,2,4-trimethylpentane as an eluent.

Cis–Trans Isomerization. Isomerizations of *cis*-7-phenyldodec-3-ene and *trans*-6-phenyltridec-8-ene were carried out in benzene (about 2 wt %) by irradiating with a high-pressure mercury lamp for 180 min in the presence of diphenyl disulfide (2.0 wt %) under nitrogen at 18 °C.[8]

Synthesis of Terminating Reagents. 1-Chloro-*cis*-3-hexene (I). In a 200-mL, two-necked, round-bottomed flask fitted with a mechanical stirrer were placed 25 mL (0.21 mol) of *cis*-3-hexen-1-ol (Tokyo Kasei) and 68.7 mL of pyridine. *p*-Toluenesulfonyl chloride (44.5 g, 0.23 mol) was added at 0 °C. The mixture was then stirred for 1 h at a temperature below 10 °C, poured into a beaker containing 127 mL of hydrochloric acid (specific gravity 1.19), and stirred at 0 °C for 3 h. The resulting tosylate was extracted with pentane, and the pentane solution was washed successively with dilute hydrochloric acid and water and dried over magnesium sulfate. After removal of pentane, 52.4 g (98%) of *cis*-3-hexen-1-ol tosylate was obtained. A mixture of 32.46 g (0.13 mol) of the tosylate, 52.8 g (1.24 mol) of lithium chloride, and 200 mL of dimethylformamide was gently refluxed for 3 h with stirring in a 500-mL, round-bottomed flask fitted with reflux condenser. The reaction mixture was cooled to room temperature and extracted with methylene chloride. The extract was washed with water, dried over sodium bicarbonate, and distilled under reduced pressure to give 8.83 g (57%) of 1-chloro-*cis*-3-hexene (purity 98%, bp 44 °C/90 mmHg).

1-Chloro-2-heptene (II) and 3-Chloro-1-heptene (III). Acrolein (33.4 mL, 0.50 mol) in 75 mL of diethyl ether was added to butylmagnesium bromide prepared from 53.9 mL (0.50 mol) of butyl bromide and 12.56 g (0.52 mol) of magnesium turnings. The reaction mixture was poured into 200 mL of saturated ammonium chloride solution, and the ethereal layer was collected. After the ether was evaporated, the product was distilled under reduced pressure to yield 33.35 g of 1-hepten-3-ol (bp 74 °C/26 mmHg). Into a solution of 33.35 g (0.29 mol) of 1-hepten-3-ol in 24.9 mL (0.31 mol) of pyridine was dropped 23.9 mL (0.32 mol) of thionyl chloride at 0 °C, and the mixture was stirred at 0 °C for 4. The product was extracted with diethyl ether, and the extract was washed with water and dried over magnesium sulfate. After removal of the ether, the product was distilled under reduced pressure to give 10.1 g of 3-chloro-1-heptene (bp 88 °C/125 mmHg) and 13.1 g of 1-chloro-2-heptene (bp 96 °C/125 mmHg).

3-(Chloromethyl)-1-heptene (IV). A mixture of 52.7 g (0.40 mol) of 1-chloro-2-heptene and 3-chloro-1-heptene was reacted with 9.99 g (0.41 mol) of magnesium in diethyl ether. The Grignard solution was treated with formaldehyde generated by the pyrolysis of 18 g of paraformaldehyde. The reaction product was hydrolyzed with saturated ammonium chloride solution followed by extraction with ether. The organic layer was evaporated and distilled under reduced pressure to give 16.9 g of 3-(hydroxymethyl)-1-heptene (bp 57 °C/4 mmHg). The resulting alcohol was chlorinated with thionyl chloride as above to give 22.8 g of 3-(chloromethyl)-1-heptene (bp 50 °C/20 mmHg).

Polymer Samples. Styrene-α-d_1 and styrene-β,β-d_2 were prepared by the method of Wall and Brown.[9] The isotopic purity was >99%. Poly(styrene-α-d_1-*co*-butadiene) and poly(styrene-β,β-d_2-*co*-butadiene) were prepared in hexane solution at 60 °C with a total monomer concentration of 8.0 mol/L, using 0.2 mol/L of azobis(isobutyronitrile) (AIBN) as initiator. Styrene/butadiene copolymer was prepared in a similar way using benzoyl peroxide (BPO) or AIBN (0.05 mol/L) as initiator. The copolymers were isolated by pouring the reaction mixtures into a large excess of methanol and purified by precipitation from benzene solution with methanol.

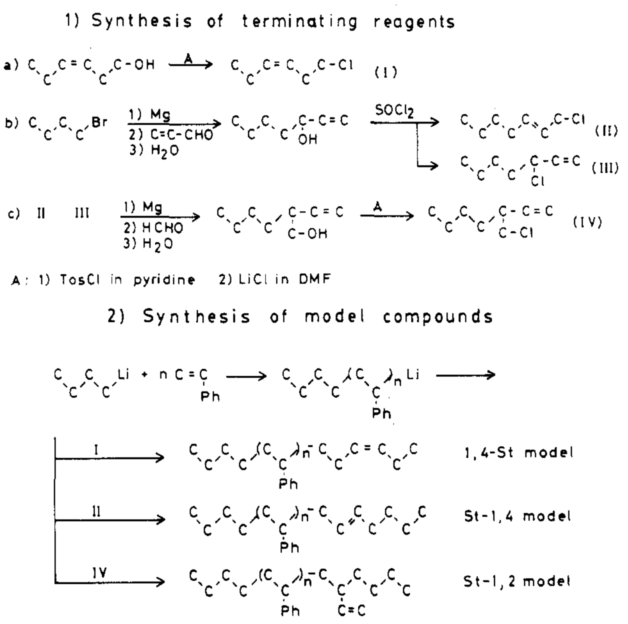


Figure 1. Synthesis of model compounds.

NMR Measurements. The ^{13}C NMR spectra were recorded at ambient temperature (ca. 30 °C) with a JEOL FX-200 at 50.1 MHz. Concentrations of the polymer samples were approximately 20% (w/v) in deuteriochloroform; 10-mm sample tubes were used for polymer samples and 5-mm tubes for model compounds. Chemical shifts were read from deuteriochloroform and were converted to a tetramethylsilane scale ($CDCl_3$: 77.00 ppm). The spectral conditions were as follows: spectral width, 8 kHz (160 ppm); number of data points (FID), 16K; pulse repetition rate, 4 s; number of scans, 2000–4000.

Results and Discussion

Styrene/Butadiene Model Compounds. The ^{13}C NMR spectrum of SBR has been analyzed based on the ^{13}C NMR studies of polybutadiene and polystyrene.[1,2] By this method, no precise information was obtained on the signals of carbon atoms between the butadiene and styrene units. Segre et al. estimated the effect (shift factor) of a double bond in a butadiene unit and of a phenyl group in a styrene unit from data on low molecular weight model compounds containing only one isomeric unit.[3,4] By the combination of shift factors, they calculated chemical shifts for carbon atoms in triad sequences of the four units. However, these model compounds are too simple to provide information on signal splittings that reflect the stereosequence of vinyl and phenyl groups.

Model compounds containing more than two monomeric units are indispensable for predicting the precise chemical shifts of the carbon atoms in various types of linkages in SBR. We have already prepared a series of low molecular weight model compounds corresponding to only butadiene sequences and styrene sequences.[6,10,11] In addition, model compounds containing both styrene and butadiene units were synthesized from styryllithium by coupling with an alkenyl chloride corresponding to a 1,4- or a 1,2-butadiene unit (Figure 1), followed by GPC separation of the compound containing one styrene unit. Each carbon signal was assigned by selective decoupling measurement or by comparison of the chemical shifts of butadiene oligomers[6] and

Table I
Structure and Shift Factor of Model Compounds (1)

symbol	structure		chem shift, ppm	shift factor, ppm
C	$C_4H_9CH_2CH{=}CH\overset{\alpha}{C}H_2\overset{\beta}{C}H_2\overset{\gamma}{C}H_2C_3H_7$	α	27.27	−2.44
		β	29.87	0.17
		γ	29.24	−0.12
T	$C_4H_9CH_2CH{=}CH\overset{\alpha}{C}H_2\overset{\beta}{C}H_2\overset{\gamma}{C}H_2C_3H_7$	α	32.71	3.00
		β	29.75	0.05
		γ	28.95	−0.41
V	$C_4H_9CH_2\overset{\alpha}{C}(CH{=}CH_2)\overset{\beta}{C}H_2\overset{\gamma}{C}H_2C_3H_7$	α	44.26	14.55
		β	35.16	5.46
		γ	26.96	−2.40
S	$C_4H_9CH_2\overset{\alpha}{C}(C_6H_5)\overset{\beta}{C}H_2\overset{\gamma}{C}H_2C_3H_7$	α	45.99	16.24
		β	36.84	7.09
		γ	27.57	2.18

styrene oligomers with pentyl terminal groups on both sides.[11]

As a model of a 1,4–styrene linkage, 7-phenyldodec-3-ene was prepared by coupling styryllithium with *cis*-1-chloro-3-hexene. The trans isomer (TS) was obtained by isomerization of cis isomer. The content of trans isomer at equilibrium was >90%, compared with 80% in isomerized polybutadiene.[12]

As a model of a styrene–1,4 sequence, 6-phenyltridec-8-ene was prepared by coupling styryllithium with 1-chloro-2-heptene. The product was almost pure trans isomer (ST), and the cis isomer (SC) was obtained by isomerization. The equilibrium mixture contained about 20% of the cis isomer.

The model compound corresponding to a styrene–1,2 sequence was prepared in a similar way from styryllithium and 3-chloromethyl-1-heptene followed by GPC fractionation of 6-phenyl-8-vinyltridecane. This fraction was separated into two diastereomers by HPLC using polystyrene gel as a stationary phase and 2,2,4-trimethylpentane as an eluent. Because both fractions showed almost identical ^1H NMR spectra, the component eluting earlier was assigned as the threo isomer (SVr), and the other as the erythro isomer (SVm), by analogy with the elution order of 1,2-butadiene and styrene oligomers.[6,10]

Table I lists the chemical shifts and shift factors of carbon atoms α, β, and γ to the double bond or phenyl group of model compounds consisting of only one butadiene or styrene unit.[6,11] The shift factors of the double bond and phenyl group were calculated from the chemical shift differences between the model compound and the corresponding *n*-alkane. Shift factors derived from model compounds corresponding to diad sequences are listed in Table II.

Each of the VV, SV, VS, and SS models has a pair of diastereomers. The difference in shift factors between the diastereomers is greatest for the β carbon, ranging from 1.3 to 2.0 ppm compared with <0.5 ppm for the other carbons. The shift factor of the β carbon in the isomer having side groups on the same side (meso or erythro) is smaller than the opposite isomer by ~1.5 ppm for the vinyl group and ~2.0 ppm for the phenyl group. The shift factors are practically independent of the type of adjacent group, i.e., vinyl or phenyl. These effects of stereosequences of phenyl and vinyl units were not considered in the signal assignments by Katritzky and by Segre.[1-4]

The chemical shifts of carbon atoms in SBR can be calculated by adding the shift factors to the chemical shift of a carbon in the long methylene linkage, 29.71 ppm (Table III).

^{13}C NMR Spectra of SBR and Partially Deuterated SBR. Figure 2 shows the ^{13}C NMR spectra of SBR containing 30 mol % styrene units. Signals of methine and methylene carbons overlapped each other in the region 38–44 ppm. The methine signals were separately measured by the distortionless enhancement by polarization transfer (DEPT) technique[13] with θ of 90° (Figure 1b). Methylene signals were obtained by subtracting methine signals from completely decoupled spectra so that signals around 45.5 ppm almost completely disappeared (Figure 1c); signals in this region are chiefly attributed to the methine carbon of a styrene unit as judged from the spectrum of poly(butadiene-*co*-styrene-α-d_1) (Figure 4a). Similar broad methylene carbon signals were observed for polybutadiene containing a large quantity of 1,2 units at 39.5–41.7 ppm and for polystyrene at 41.5–46.5 ppm.[6,10]

Figure 3a shows the ^{13}C NMR spectrum of poly(butadiene-*co*-styrene-β,β-d_2) containing 43 mol % styrene-β,-

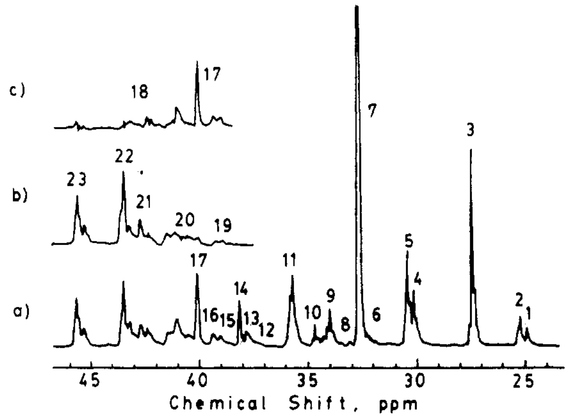


Figure 2. ^{13}C NMR spectra of SBR prepared with benzoyl peroxide (styrene content, 28 mol %). (a) Complete decoupling spectrum. (b) CH subspectrum. (c) CH_2 subspectrum.

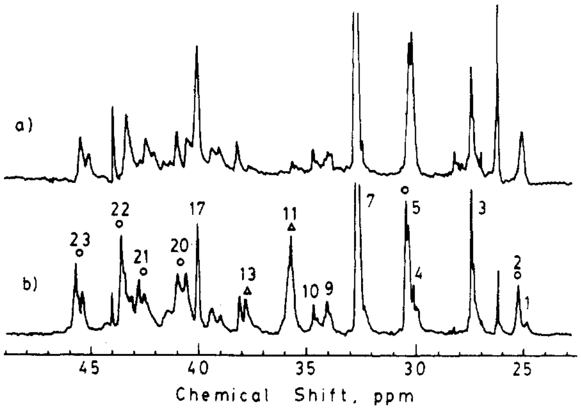
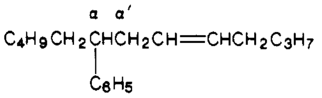
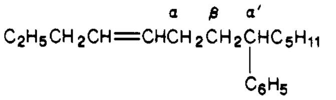
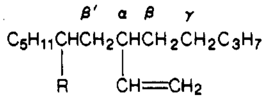
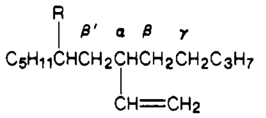
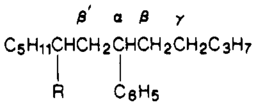
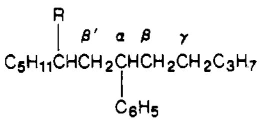
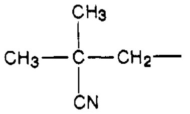


Figure 3. ^{13}C NMR spectra of poly(butadiene-*co*-styrene-β,β-d_2) (a) and SBR (b) prepared with AIBN (styrene content, 43 mol %). (△) Signal disappeared by deuteration. (○) Signal shifted to upfield by deuteration.

Table II
Structure and Shift Factor of Model Compounds (2)

symbol	structure		shift factor, ppm	
St-1,4(SC, ST)	 $C_4H_9CH_2\underset{C_6H_5}{\overset{\alpha}{C}}H\overset{\alpha'}{C}H_2CH{=}CHCH_2C_3H_7$		cis	trans
		α	16.57	16.64
		α′	4.97	10.49
1,4-ST(CS, TS)	 $C_2H_5CH_2CH{=}CH\overset{\alpha}{C}H_2\overset{\beta}{C}H_2\underset{C_6H_5}{\overset{\alpha'}{C}}HC_5H_{11}$		cis	trans
		α	−4.54	0.83
		β	7.24	7.18
		α′	15.82	15.73
VVm, SVm	 $C_5H_{11}\underset{R}{C}H\overset{\beta'}{C}H_2\underset{CH{=}CH_2}{\overset{\alpha}{C}}H\overset{\beta}{C}H_2\overset{\gamma}{C}H_2C_3H_7$		R: $CH{=}CH_2$	R: C_6H_5
		α	11.37	11.75
		β	4.61	4.85
		β′	10.77	12.77
VVr, SVr	 $C_5H_{11}\overset{R}{C}H\overset{\beta'}{C}H_2\underset{CH{=}CH_2}{\overset{\alpha}{C}}H\overset{\beta}{C}H_2\overset{\gamma}{C}H_2C_3H_7$		R: $CH{=}CH_2$	R: C_6H_5
		α	11.85	11.96
		β	6.12	6.23
		β′	10.77	12.35
VSm, SSm	 $C_5H_{11}\underset{R}{C}H\overset{\beta'}{C}H_2\underset{C_6H_5}{\overset{\alpha}{C}}H\overset{\beta}{C}H_2\overset{\gamma}{C}H_2C_3H_7$		R: $CH{=}CH_2$	R: C_6H_5
		α	13.16	13.55
		β	6.28	6.82
		β′	12.77	14.71
VSr, SSr	 $C_5H_{11}\overset{R}{C}H\overset{\beta'}{C}H_2\underset{C_6H_5}{\overset{\alpha}{C}}H\overset{\beta}{C}H_2\overset{\gamma}{C}H_2C_3H_7$		R: $CH{=}CH_2$	R: C_6H_5
		α	13.59	13.55
		β	8.24	8.22
		β′	12.34	13.63

β-d_2 units, prepared with AIBN. This copolymer showed two sharp signals at 43.9 and 26.1 ppm, which were not observed in copolymers prepared with BPO initiator. These signals are assigned to the methylene and methyl carbons in the terminal group.


$CH_3-\underset{CN}{\overset{CH_3}{C}}-CH_2-$

CH_3: 26.1 ppm
CH_2: 43.9 ppm

The spectrum of partially deuterated copolymer was measured by the DEPT technique with θ of 45°, where only protonated carbons were observed. Therefore, the deuterated carbon signals can be distinguished by comparing the spectra of partially deuterated (Figure 3a) and ordinary SBR (Figure 3b). Signals 11 and 13 of Figure 3b, around 35.7 and 37.8 ppm, are virtually absent in Figure 3a, indicating these signals are from the β carbon of a styrene unit. Signal 18, which is a broad signal from 39 to 46 ppm, decreased greatly, indicating this signal is also from the β carbon of a styrene unit.

In addition, other signals were shifted upfield by deuteration, reflecting the isotope effect of deuterium on the adjacent carbons. Therefore, the shifted signals are assigned to the carbon atoms adjacent to the deuterated carbon. Signals 2 and 5 shifted upfield by 0.4 ppm and overlapped with signals 1 and 3, respectively (Figure 3a). The methine signals 20, 21, 22, and 23 also shifted upfield.

Parts a and b of Figures 4 show the ^{13}C NMR spectra of poly(butadiene-*co*-styrene-α-d_1) and SBR, respectively. Similar signal disappearance and upfield shifts are observed in the spectrum of this partially deuterated polymer. Signals 21, 22, and 23 disappeared or decreased in intensity (Figure 4a), indicating that they represent the methine carbon of a styrene unit. Signals 10, 11, 13, 16, and 17 shifted upfield by 0.1 ppm, indicating that they represent carbon atoms adjacent to the methine carbon of a styrene unit. Of these five signals, 11 and 13 are assigned to the methylene carbon of a styrene unit as described above, and the others are assigned to carbon atoms in a 1,4-butadiene unit linked to styrene. The isotope effect in the copolymer containing styrene-α-d_1 is only one-fourth of that of the copolymer containing styrene-β,β-d_2, reflecting the smaller number of deuterium atoms in the former.

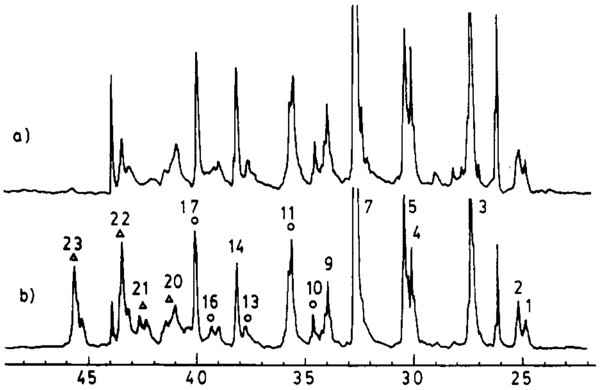


Figure 4. ^{13}C NMR spectra of poly(butadiene-*co*-styrene-α-d_1) (a) and SBR (b) prepared with AIBN (styrene content, 25 mol %). (△) Signal disappeared by deuteration. (○) Signal shifted to upfield by deuteration.

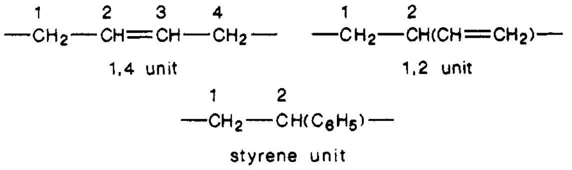
The ^{13}C NMR signals of SBR are assigned by comparison of the observed chemical shifts with the calculated values, by direct information from the spectra of partially deuterated polymers, and by reference to the signal assignments of polybutadiene.[6] The results are listed in Table III.

Table III
Signal Assignment of SBR

signal	obsd	calcd	sequence[a]	C[b]
1	24.9	24.87	C–v	4
2	25.2	25.17	C–s	4
		27.32–27.44	C–1, 4	4
		27.32–27.44	1,4–C	1
4	30.1	30.31	T–v	4
5	30.4	30.54	T–s	4
6	31.9–32.3	31.88–32.12	b–v(m)–C	1
7	32.7	32.76–32.88	T–1,4	4
		32.76–32.88	1,4–T	1
		32.73	1,4–v–C	1
8	33.1–33.9	33.39–33.50	b–v(r)–C	1
		33.55–34.09	b–s(m)–C	1
9	33.9–34.3	35.21–35.33	1,4–V–1,4	1
10	34.4–34.8	34.37–34.73	1,4–V–b(m)	1
		34.68	1,4–s–C	1
11	35.4–36.0	36.89–36.95	1,4–S–1,4	1
		36.04–36.07	1,4–S–b(m)	1
		35.88–36.11	1,4–V–b(r)	1
		35.42–35.51	b–s(r)–C	1
12	37.2–37.5	37.32–37.56	b–v(m)–T	1
13	37.8	37.98–38.12	1,4–S–b(r)	1
14	38.1	38.17	1,4–v–T	1
15	38.9–39.1	38.83–38.94	b–v(r)–T	1
16	39.2–39.5	38.96–39.53	b–s(m)–T	1
17	40.1	40.20	1,4–s–T	1
18	39–46	40.93–40.95	b–s(r)–T	1
		39–42	b–V	1
		41–47	b–S	1
19	38.5–39.5	38.68–39.59	b–V–b	2
20	40.1–41.6	41.12–41.45	b–S–b	2
		40.67–41.55	1,4–V–b	2
		41.13–41.84	b–V–1,4	2
21	42.4–42.95	42.46–43.18	1,4–S–b	2
22	42.95–43.6	42.92–43.47	b–S–1,4	2
		43.90–44.31	1,4–V–1,4	2
23	45.3–45.8	45.63–46.04	1,4–S–1,4	2

[a] Signals are assigned to the carbons in the unit designated by the capital letter. C, cis-1,4; T, trans-1,4; V, 1,2; S, styrene unit; 1,4, cis-1,4 or trans-1,4 unit; b, 1,2 or styrene unit. [b] Carbon attoms are denoted as in text.

In this assignment, C-4 of *cis*-1,4-butadiene units is split into the three signals 1, 2, and 3, depending on whether the following unit is 1,2-butadiene, styrene, or 1,4-butadiene. Similarly, C-4 of the *trans*-1,4-butadiene unit is split into the three signals 4, 5, and 7. On the other hand, C-1 of the *cis*-1,4-butadiene unit is split according to the nature of the preceding unit. When the preceding unit is 1,4-butadiene, C-1 of the cis unit resonates as signal 3, whereas when the preceding unit is 1,2-butadiene or styrene, C-1 of the *cis*-1,4 unit is split into signals 6, 7, 8, 10, and 11, depending on the nature of the more remote unit and on the tacticity or cotacticity of 1,2 and/or styrene units. Similarly, C-1 of the *trans*-1,4 unit is split into signals 7, 12, 14, 15, 16, 17, and 18. Thus, C-1 of the 1,4 unit has a complicated splitting, reflecting the diad and triad sequences of the four units. The carbon atoms are denoted as follows:

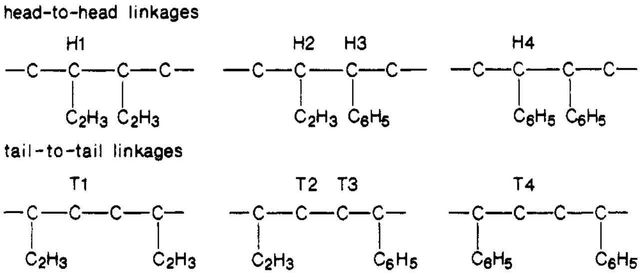


$$-\overset{1}{C}H_2-\overset{2}{C}H=\overset{3}{C}H-\overset{4}{C}H_2- \qquad -\overset{1}{C}H_2-\overset{2}{C}H(CH=CH_2)-$$

$$-\overset{1}{C}H_2-\overset{2}{C}H(C_6H_5)-$$

When C-1 of a 1,2 or styrene unit is preceded by a 1,2 or styrene unit, it resonates in the wide chemical shift range 39–46 ppm, reflecting the sequence length and the tacticity or cotacticity of 1,2 and styrene units. We did not make a detailed assignment of signals in this region. Carbon-1 of a 1,2 unit in a 1,4–1,2 sequence is split into three signals that depend on the type and stereosequence of the following unit: 1,4 unit (signal 9); 1,2 or styrene unit in meso or erythro configuration (signal 10); 1,2 or styrene unit in racemo or threo configuration (signal 11). Carbon-1 of a styrene unit in a 1,4–styrene sequence also shows similar splittings depending on the type and stereosequence of the following unit.

In this signal assignment, only head-to-tail linkages of styrene and 1,2 units are considered. If the head-to-head and tail-to-tail linkages of 1,2 and styrene units are present, new signals would be expected to appear around 50, 60, 33, and 34 ppm.



The calculated chemical shifts (ppm) are as follows: H1, 49.72; H2, 51.35; H3, 61.46; H4, 63.08; T1, 32.76; T2, 32.98; T3, 34.44; T4, 34.66. In the spectrum of SBR, no signal was observed in the chemical shift range 48–70 ppm, indicating the absence of head-to-head linkages. Around 33 ppm, a large signal denoted as 7 appears, so it is difficult to judge whether or not T1 and T2 carbons are present. However, considering the fact that the amount of tail-to-tail linkage of 1,2 units is negligible in polybutadiene prepared with a free-radical initiator,[6] we consider that tail-to-tail linkage of 1,2 units is also negligible in SBR prepared with a free-radical initiator. Signal 10 (~34.5 ppm) is assigned to the methylene carbons of a butadiene unit. If a T3 or T4 carbon is present in SBR, signal 10 would be expected to decrease in intensity in the spectrum of poly(butadiene-*co*-styrene-β,β-d_2), because T3 and T4 are the β carbons of a styrene unit. However, signal 10 in the partially deuterated copolymer exhibited no appreciable decrease in intensity compared to ordinary SBR (Figure 3), which suggests that the tail-to-tail linkage of styrene units is also negligible or absent. Therefore, we conclude that 1,2 and styrene units are principally arranged in head-to-tail linkages.

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Registry No. C, 6508-77-6; T, 6434-76-0; St-1,4 (SC), 117942-53-7; St-1,4 (ST), 117942-54-8; 1,4-St (CS), 117942-55-9; 1,4-St (TS), 117942-56-0; VVm, 109801-08-3; SVm, 117942-57-1; VVr, 117942-58-2; SVr, 117942-59-3; SSm, 99265-07-3; SSr, 99265-06-2; *cis*-3-hexen-1-ol, 928-96-1; *p*-toluenesulfonyl chloride, 98-59-9; *cis*-3-hexen-1-ol tosylate, 34019-85-7; 1-chloro-*cis*-3-hexene, 21676-01-7; acrolein, 107-02-8; butyl bromide, 109-65-9; 1-hepten-3-ol, 4938-52-7; 3-chloro-1-heptene, 55682-98-9; 1-chloro-2-heptene, 41792-05-6; formaldehyde, 50-00-0; 3-(hydroxymethyl)-1-heptene, 53045-66-2; 3-(chloromethyl)-1-heptene, 50774-70-4; (styrene)(butadiene) (copolymer), 9003-55-8.

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Photocross-Linking in a Magnetic Field: Behavior of a Poly(styrene-*co*-butadiene) Containing Ketones or Covalently Bound Keto Groups

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ABSTRACT: A poly(styrene-*co*-butadiene) (SBR) was photocross-linked in the presence of various ketones at 20 °C. The degree of cross-linking was determined by sol/gel analysis. The cross-linking efficiency increased in the order deoxybenzoin, benzophenone, dibenzyl ketone, *p*-methylbenzophenone. For comparison, the SBR was modified with phenylacetyl chloride, whereby phenylacetylphenyl groups were formed, and then photocross-linked in the absence of additives; the cross-linking efficiency was relatively low. Experiments were carried out without magnetic field and with external homogeneous magnetic fields between 42 and 975 mT. Even low-flux densities (42 mT) brought about a definite effect. The magnetic field effect reached its highest value at about 240 mT in all experiments. The smallest influence of the magnetic field was observed for the SBR with phenylacetylphenyl groups. The results are discussed using radical pair theory.

Introduction

Photoreactions in a polymer matrix are of interest to modern science and technology for photoprocesses (e.g., "microlithography"), optical memory systems, or solar energy conversion.[1] They are also important for the theory of energy transfer, migration in polymers, and segment mobility.[2-4] The present paper is concerned with photocross-linking in an external magnetic field.

Interest in the investigation of chemical reactions in magnetic fields has grown in recent years. The difference in the results (e.g., product yields or cross-linking densities) received without and with the influence of a magnetic field can be denoted "magnetic field effect". In the following, we only consider reactions with radical intermediates. The magnetic field effect can here be interpreted by the radical pair theory, which is also the theoretical background of CIDNP spectroscopy.[5]

Most investigations describing magnetic field effects have been concerned with low molecular chemistry, for example, photochemical reactions in micellar solutions, in particular the photolysis of ketones.[6,7] Some work in polymer chemistry has also been published. First, the cross-linking of 1,4-polybutadiene by photolysis of peroxides in the presence of phenanthrene was investigated in the magnetic field.[8] Second, the influence of a magnetic field on photocross-linking of bromo- and chloromethylated polystyrene in the presence of thioxanthone was described.[9] Third, a magnetic field effect was found in the photocross-linking of a poly(styrene-*co*-butadiene) (SBR) in the presence of ketones such as deoxybenzoin.[10] The keto groups were covalently linked to the polymer chain in additional experiments.[11] The photocross-linking yield increased in a magnetic field (in contrast to cross-linking of 1,4-polybutadiene with bis(2,4-dichlorobenzoyl) peroxide[8,12,13]). For example, 15–20% more cross-linking (measured by sol/gel analysis) was found with dispersed ketones and 3–10% more cross-linking for the copolymer with keto groups at a flux density B of 1.0 T.

The magnetic field effect, plotted as a function of the flux density (B), at the beginning increases with B and seems normally to attain a constant value at relatively low magnetic fields.[9,12] But the absolute value can also pass a maximum at a certain value of B. Experimental examples are provided by the (Z)–(E) photoisomerization of stilbene[14] and the photolysis of *p*-chlorodibenzyl ketone or 1,2-diphenyl-2-methylpropanone.[15]

In the present investigation, the flux density dependence of the magnetic field effect on the photocross-linking of copolymer/ketone systems is described for the first time. On the one hand, an SBR was cross-linked in the presence of deoxybenzoin ($C_6H_5CH_2COC_6H_5$), benzophenone ($C_6H_5COC_6H_5$), dibenzyl ketone ($C_6H_5CH_2COCH_2C_6H_5$), or *p*-methylbenzophenone ($CH_3C_6H_4COC_6H_5$). On the other hand, the SBR was modified by Friedel–Crafts reaction of the phenyl groups of the copolymer with phenylacetyl chloride and then photocross-linked; this polymer contained phenylacetylphenyl groups ($C_6H_5CH_2COC_6H_4$–) which correspond to deoxybenzoin.

Experimental Section

Materials. The SBR was supplied by Goodyear (SBR-E-3024, 10 wt % styrene). It was purified from a solution in methylene chloride by precipitation with methanol. The ketones used were commerical products (p.a.) of Fluka without further purification.

For photocross-linking, a solution of 2 wt % copolymer in methylene chloride was prepared. The ketone was added and dissolved. Then the solvent was evaporated and the remaining mixture vacuum-dried and kept in the dark at 5 °C.

The copolymer with covalently bound phenylacetylphenyl groups was received by reaction of the SBR with phenylacetyl chloride as described previously.[11]

Photocross-Linking. Polymer foils (thickness 25 μm) were received by pressing 2 mg of the copolymer/ketone mixture or the copolymer with phenylacetylphenyl groups between two glass plates. The foils were fixed to a thermostated (20 °C) aluminum block positioned between the poles of the electromagnet (Bruker BE 10/B-Z 11ha) and irradiated with a 150-W high-pressure mercury lamp (Hanau TQ 150) at a distance of 80 cm.[10] All

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