In Ogura's work with styrene–methacrylic acid based ionomers[9] the peak absorbance at 1560 cm^{-1} is shown to be constant from ambient to 200 °C. This phenomenon is not a result of sample loss, as this trend is reversed during the cooling cycle. However, due to anhydride formation, the integrated area is slightly less after the experiment than before. At present there remains no explanation for this behavior.

Conclusions

The absorbances at 1700 and 1750 cm^{-1}, assigned to the dimer and monomer carbonyl stretch, respectively, can be used in an infrared analysis to determine the temperature dependence of hydrogen bonding in ethylene–methacrylic acid copolymers. The presence of carbonyls due to oxidation products introduced during polymerization does not significantly affect the determination of peak absorbances or integrated absorbances in this region. Unambiguous results cannot be obtained by using only the 935-cm^{-1} band to determine thermodynamic parameters. The heat of dissociation for the two polymers investigated was calculated to be 12 kcal/mol of dimer, which is in good agreement with previous values determined for both polymers and low molecular weight carboxylic acids. The dimerization is essentially complete at room temperature.

The behavior of carboxyl groups in the partially neutralized salt is similar to that of the parent acid copolymer. At room temperature nearly all the free acid groups are paired as hydrogen-bonded dimers. An equilibrium between monomer and dimer is established at elevated temperatures with a heat of dissociation of 20 kcal/mol in the case of S6.1NA(45). The carbonyl asymmetric stretch located near 1565 cm^{-1} in the sodium salt consists of at least two overlapping peaks at room temperature. The shoulder at 1580 cm^{-1} decreases relative to the main peak (1560 cm^{-1}) as temperature is increased. Contrary to results by other workers on similar ionomers, a decrease in peak and integrated absorbance for the total 1565-cm^{-1} peak is observed with increasing temperature. This behavior is reversible with decreasing temperature.

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High-Resolution NMR Spectra of Hydrogenated Poly(phenylbutadienes). Styrene–Ethylene Alternating Copolymer and Poly(4-phenyl-1-butene)

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ABSTRACT: Alternating styrene–ethylene copolymers are prepared by hydrogenating 1,4-poly(1-phenylbutadiene) and 1,4-poly(2-phenylbutadiene). The stereostructure of the alternating copolymer was not revealed by the ^1H NMR spectrum. The ^{13}C NMR spectra, on the other hand, showed fine structure attributed to dyad or triad stereosequence distributions. These spectra indicated that the alternating copolymers obtained from 1,4-poly(1-phenylbutadiene) polymerized in THF and 1,4-poly(2-phenylbutadiene) are atactic and suggested that the sample prepared from 1,4-poly(1-phenylbutadiene) polymerized in benzene is slightly preponderant in syndiotactic sequences. The hydrogenation of 3,4-poly(1-phenylbutadiene) gives the polymer corresponding to poly(4-phenyl-1-butene). The ^{13}C NMR spectrum of the hydrogenated polymer shows that it is not stereoregular, as compared with the spectrum of isotactic poly(4-phenyl-1-butene).

There have been several papers dealing with preparation and characterization of alternating copolymers[1-3] or head-to-head polymers[4,5] by hydrogenation of 1,4-polydienes. It is of interest to prepare polymers which are

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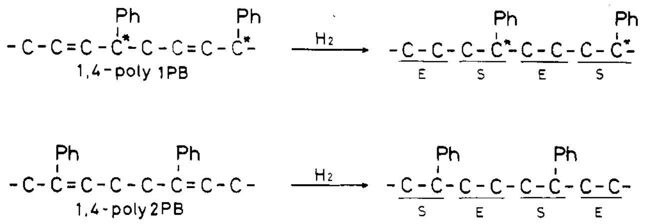
Scheme I



difficult to obtain by a simple polymerization process.

Recently, the stereostructures of an alternating ethylene–propylene (E–P) copolymer prepared by hydrogenating 1,4-polypentadiene and 1,4-polyisoprene were compared by Elgert et al.[1,2] and Audisio et al.[3] In their ^{13}C NMR spectra several carbon resonances were affected by dyad or triad stereosequences.

We have previously studied the microstructures of poly(1-phenylbutadiene) (poly1PB)[6] and poly(2-phenylbutadiene) (poly2PB).[7] In these studies high 1,4-polymers (1,4-poly1PB and 1,4-poly2PB) and pure 3,4-poly1PB were obtained. In this paper we have prepared alternating styrene–ethylene (S–E) copolymers by hydrogenating 1,4-poly1PB and 1,4-poly2PB and have studied the high-resolution ^{13}C and ^{1}H NMR spectra of these polymers. In addition, poly(4-phenyl-1-butene) (poly4P1BT) has been obtained by hydrogenating 3,4-poly1PB and characterized by ^{13}C NMR spectra.

Experimental Section

Monomers. *trans*-1-Phenyl-1,3-butadiene (1PB) and 2-phenyl-1,3-butadiene (2PB) were prepared by the methods described in previous papers.[6,7] 4-Phenyl-1-butene (4P1BT) was obtained from Tokyo Kasei Co., Ltd., and purified by distillation over $LiAlH_4$.

Polymers. 1,4-Poly1PB-T (trans-1,4, 79%; cis-1,4, 11%; 3,4, 10%) was prepared with *t*-BuLi in THF at -78 °C.

1,4-Poly1PB-B (trans-1,4, 66%; cis-1,4, 26%; 3,4, 8%) was prepared with *t*-BuLi in benzene at 20 °C.

3,4-Poly1PB (3,4, 100%) was prepared with $AlEt_3$–$TiCl_3$ (Al/Ti = 1.2) in toluene at 30 °C (toluene, 10 mL; $AlEt_3$, 1.08 mmol; 1PB, 15 mmol).

1,4-Poly2PB (cis-1,4, 98%; 1,2, 2%) was prepared with sodium–naphthalene in THF at 57 °C.

Isotactic poly4P1BT was prepared with $AlEt_3$–$TiCl_3$ (Al/Ti = 1.2) in toluene at 30 °C (toluene, 20 mL; $AlEt_3$, 0.34 mmol; 4P1BT, 35 mmol).

Hydrogenation Procedure. Hydrogenation was carried out with *p*-toluenesulfonylhydrazide (TSH) in refluxing *p*-xylene;[8] the molar ratio of TSH to the monomeric unit of the polymers was 2.5:1. This procedure must be carried out twice for the complete hydrogenation of 1,4-poly2PB.

^{1}H and ^{13}C NMR Spectra. The ^{1}H NMR spectrum was recorded with a Varian HR 220 (220 MHz), using a 10% (w/v) $CDCl_3$ solution. ^{13}C NMR spectra were measured with a JEOL JNM FX100 (25.0 MHz) and a JEOL JNM FX200 (50.2 MHz), using 5–10% (w/v) $CDCl_3$ solutions. Conditions for the ^{13}C measurements were as follows: spectral width, 4 kHz (for 25.0 MHz) and 8 kHz (for 50.2 MHz); data points, 8192 and 16 384; pulse width, 7 μs (42°) and 7 μs (30°); pulse repetition, 2.0 s; number of transients, 1000–40 000.

Results and Discussion

Hydrogenation of both 1,4-poly1PB and 1,4-poly2PB can give S–E alternating copolymers, as shown in Scheme I. In the case of 1,4-poly1PB, the configurations of the methine carbons will be retained after hydrogenation. Therefore, the tacticity of the hydrogenated polymer is not changed from that of the 1,4-poly1PB. On the other hand, only asymmetric hydrogenation can give stereospecific polymer in the case of 1,4-poly2PB. Such a hydrogenation, however, cannot be carried out in good yield since asymmetric hydrogenation catalysts are known to be inactive to trisubstituted double bonds. Nonasymmetric hydrogenation inevitably leads to atactic alternating copolymers.

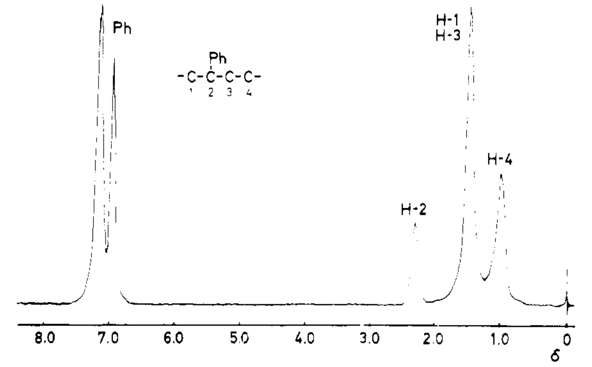


Figure 1. 220-MHz ^{1}H NMR spectrum of an S–E alternating copolymer prepared from 1,4-poly2PB.

Table I
Chemical Shifts[a] of S–E Alternating Copolymer and Poly4P1B

	C-1	C-3	C-2	C-4	phenyl	arom C-1′
S–E alternating copolymer	36.6		45.4		125.6	146.0
	36.7			25.2		
			45.5		127.5	146.1
	36.9			25.4		
	37.0		45.6		128.0	146.2
poly4P1B (isotactic)	33.2	36.9	32.4	40.0	125.6 128.3	142.7

[a] Ppm from Me_4Si.

Microstructures of Poly(phenylbutadienes). It is essential to obtain pure 1,4-polymers for the preparation of an S–E alternating copolymer. As described in the previous paper, we could not obtain a pure 1,4-poly1PB. Even under optimum conditions, 79–66% trans-1,4 units are contaminated with 11–26% cis-1,4 units and 10–8% 3,4 units. In the ^{13}C NMR spectra of the polymers, some of the resonances had fine structure due to the microstructure distribution of monomeric units. Stereostructure of the methine carbon cannot be observed in the ^{13}C NMR spectra and ^{1}H NMR spectra. Thus, we did not know the tacticity of the 1,4-poly1PB. Information concerning the tacticity, however, should be obtainable after hydrogenating the polymer and simplifying its structure.

On the other hand, almost pure 1,4-poly2PB was obtained. We can prepare a pure S–E alternating copolymer from this polymer.

220-MHz ^{1}H NMR Spectrum of S–E Alternating Copolymer. Figure 1 shows the ^{1}H NMR spectrum of an S–E alternating copolymer prepared by hydrogenating 1,4-poly2PB. The absence of olefin proton resonances indicates that hydrogenation was complete. As mentioned above, this alternating copolymer should be atactic because the hydrogenation was not asymmetric. As all the resonances in the spectrum appeared broad, the differences in chemical shift caused by tacticity of the polymer could not be observed. The ^{1}H NMR spectrum of hydrogenated 1,4-poly1PB is essentially the same as that shown in Figure 1.

25.0-MHz ^{13}C NMR Spectra of S–E Alternating Copolymer. Figure 2A shows the ^{13}C NMR spectrum of an S–E alternating copolymer prepared by hydrogenating 1,4-poly2PB. In contrast to the ^{1}H NMR spectrum, the backbone and aromatic C-1′ carbon resonances are split, owing to the tacticity of the polymer. The chemical shifts of the resonances are listed in Table I. The lowest field

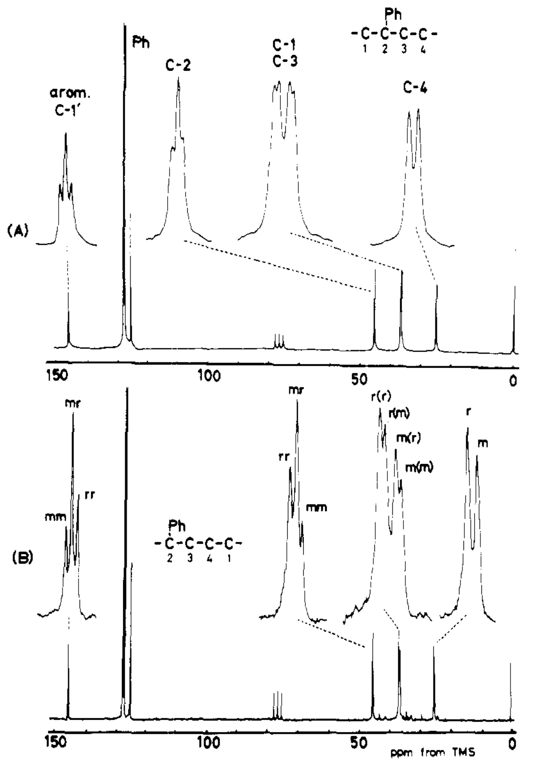
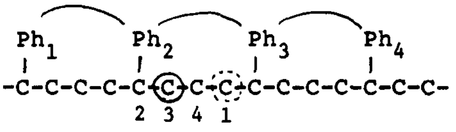


Figure 2. 25.0-MHz ^{13}C NMR spectra of S–E alternating copolymers prepared from (A) 1,4-poly2PB and (B) 1,4-poly1PB-B. In the upper traces the abscissas are expanded 16 times.

Scheme II



peak in the aliphatic region is assigned to the C-2 carbon because of a doublet resonance in the off-resonance spectrum. The structure of the polymer is symmetrical after hydrogenation. Therefore, the C-1 and C-3 carbons are equivalent and have the same chemical shift if the stereostructure is not taken into account. Considering the additivity law of chemical shifts in ^{13}C NMR spectra, the highest field resonance is assigned to the C-4 carbon and the multiplet peaks are assigned to C-1 and C-3 carbons. The aromatic C-1′ and C-2 carbon resonances are both split into three peaks (approximate intensity ratio 1:2:1), indicating a long-range stereochemical effect of triad sequences. The C-4 carbon resonance is split into two peaks (approximate intensity ratio 1:1) by dyad sequences. These intensity ratios indicate that the alternating copolymer is completely atactic, as predicted above. The C-1 and C-3 carbon resonances appear as four peaks. This splitting can be interpreted as follows. Let us consider the C-3 carbon in Scheme II. The resonance of this carbon is separated into two peaks, owing to the relative configuration between Ph_2 and Ph_3, that is, meso (m) or racemic (r). These two peaks are further split into two peaks with strong overlapping due to the relative configuration between Ph_2 and Ph_1. The C-1 carbon is also split in a similar manner, owing to the relative configuration between Ph_2 and Ph_3 and, further, between Ph_3 and Ph_4. The intensity ratio of the four peaks is 1:1:1:1, also showing that this alternating copolymer is atactic.

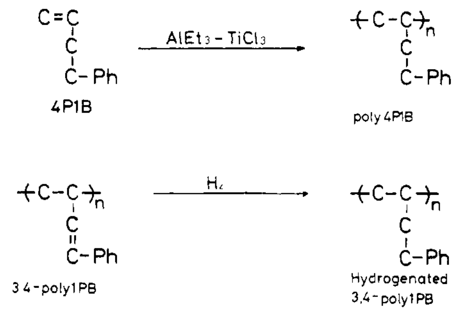
The E–P alternating copolymer previously reported has a methyl substituent in place of a phenyl group. In this case,[1-3] the C-2 and C-4 (following our notation) carbon resonances appear as singlet peaks, respectively, giving no information concerning tacticity. The stereostructure was shown only by two carbon resonances; namely, the methyl carbon resonance was split into three peaks by triad sequences, and the C-1 and C-3 carbon resonances appear as four peaks in the same manner as observed in this study.

We now discuss S–E alternating copolymers prepared from 1,4-poly1PB. Before hydrogenation the tacticity of the polymer could not be revealed even if the ^{13}C NMR spectra were employed as described before. However, in the spectrum of the hydrogenated 1,4-poly1PB, all the resonances had fine structure. By the hydrogenation of the polymer, slight chemical shift differences in the flanking cis-1,4 and trans-1,4 units disappeared, and the chemical shift differences caused by the tacticity can be observed clearly. The ^{13}C NMR spectrum of the alternating copolymer prepared from 1,4-poly1PB-T (polymerized in THF) is essentially the same as Figure 2A, indicating that it is also an atactic sample. Assuming that the tacticity of the polymer is not changed by hydrogenation, it is concluded that the 1,4-poly1PB-T is atactic. The tacticity is not controlled by the anionic polymerization because the propagating chain ends are considered to be a solvent-separated ion pair in THF. When a stereospecific 1,4-poly1PB can be obtained, assignments of the split ^{13}C resonance of the alternating copolymer is possible after hydrogenation. However, such a stereospecific polymerization could not be carried out by anionic initiators or Ziegler-type catalysts. Further, an asymmetric initiator (*n*-BuLi–spartein complex) did not give optically active polymer. Thus, the assignments of the split peaks still cannot be carried out.

Figure 2B shows the ^{13}C NMR spectrum of the alternating copolymer prepared from 1,4-poly1PB-B (polymerized in benzene). In the spectrum some deviations from the intensity ratios expected for the completely atactic polymer can be observed. The tacticity will be slightly controlled by the interaction between the anion chain end and the countercation in considering the association of the polymer living chain ends. If the phenyl substituent has the same effect as the methyl group of the E–P alternating copolymer on the chemical shift of the C-1 and C-3 carbon resonances, the split peaks are tentatively assigned as shown in Figure 2B. In the assignment of the C-1 and C-3 carbon resonances, m(r), for example, means that the resonance is split by an m dyad and then further split by an adjacent r dyad (in Scheme II, for the C-3 carbon, the Ph_2–Ph_3 dyad is m and the Ph_1–Ph_2 dyad is r). Following this assignment, the assignment of the aromatic C-1′ carbon resonance of the alternating copolymer is consistent with that of an aromatic C-1 carbon resonance of polystyrene.[9] In the spectrum of the polystyrene, the lower field resonance of the aromatic C-1 carbon is attributed to isotactic sequences and the higher field signal to syndiotactic sequences.[9] These results support the conclusion that the S–E alternating copolymer prepared from 1,4-poly1PB-B is slightly predominant in syndiotactic sequences. However, the same shielding influence of the phenyl substituent on m and r dyads as caused by the methyl substituent in the E–P alternating copolymer is questionable. Therefore, the assignment of the m and r dyads mentioned above is not certain and may be interchanged.

Preparation of Poly(4-phenyl-1-butene). Pure 3,4-poly1PB was obtained by Ziegler-type catalysts in the course of the synthesis of the 1,4-polymer. The hydrogenation of the 3,4-poly1PB gives the polymer corresponding to poly4P1BT, as shown in Scheme III. On the

Scheme III



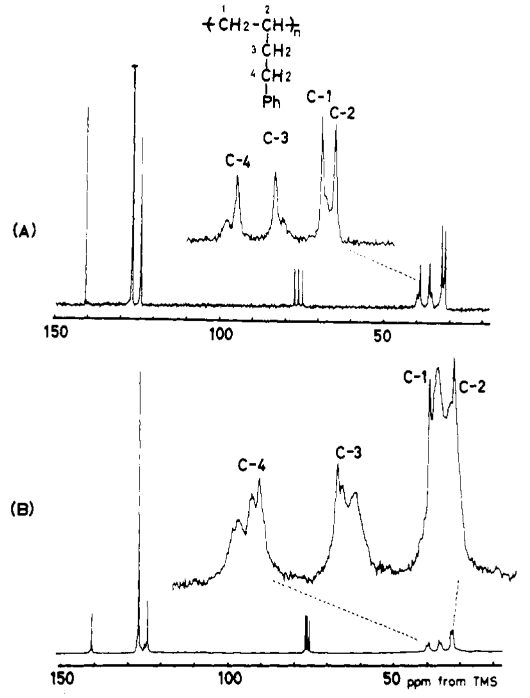


Figure 3. ^{13}C NMR spectra of (A) isotactic poly4P1BT (25.0 MHz) and (B) hydrogenated 3,4-poly1PB (50.2 MHz). In the upper traces the abscissas are expanded (A) 4 and (B) 8 times.

other hand, 4P1BT is considered to be polymerized to an isotactic-rich polymer by a Ziegler-type catalyst. It is interesting to compare the stereostructures of these two polymers.

Figure 3A shows the ^{13}C NMR spectrum of the predominantly isotactic poly4P1BT prepared by $AlEt_3$–$TiCl_3$,[10] and Figure 3B shows the spectrum (50.2 MHz) of the hydrogenated 3,4-poly1PB. The 50.2-MHz spectrum shows better resolution than the 25-MHz spectrum. The assignment of C-2 carbon was carried out by off-resonance decoupling, and the other aliphatic resonances are assigned using the additive parameters reported by Conti et al.[11] In Figure 3B, the aliphatic carbon resonances appear as complex multiplets. The lower field peak of the C-3 resonance and the higher field peak of the C-4 resonance (as compared with Figure 3A) are attributed to isotactic sequences. The other split peaks, however, could not be interpreted in terms of simple triad sequences. This must arise from higher order sequence distribution or unidentified structural features of the polymer. However, from the spectrum it is safe to say that the poly4P1BT prepared from 3,4-1PB is not stereoregular. Assuming that the tacticity of the 3,4-poly1PB is not changed by hydrogenation, the 3,4-poly1PB is regarded as also atactic. In the ^{13}C NMR spectrum of the 3,4-poly1PB several resonances had fine structures attributed to stereostructure. However, since we did not know the tacticity of the polymer, we could not determine them. Thus, the $AlEt_3$–$TiCl_3$ catalyst system polymerizes the diolefin to the atactic 3,4-polymer, whereas it polymerizes the α olefin to the isotactic polymer.

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