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MICROSTRUCTURES OF A HYDROGENATED STYRENE-BUTADIENE COPOLYMER BY ^{13}C NMR

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ABSTRACT

The microstructure and sequence distribution of a styrene-ethylene-butene-1 copolymer obtained by quantitative hydrogenation of emulsion styrene-butadiene rubber (SBR) was determined using ^{13}C NMR. The results show that the polymer has 82% $(CH_2)_{>6}$ units arising due to BBB', SBB and BBB triads (B = hydrogenated 1,4 butadiene, B' = butene-1and S = styrene). The presence of long crystallizable methylene sequences results in a melting endotherm at 45°C for the hydrogenated SBR.

INTRODUCTION

Hydrogenation is a useful chemical method of polymer modification which can lead to polymers with unusual and novel monomer sequences which are otherwise inaccessible or difficult to prepare by conventional polymerization methods. For example, a strictly alternate copolymer of ethylene and propylene can be prepared by hydrogenation of synthetic 1,4 polyisoprene [1] and natural rubber [2]. Hydrogenated chloroprene elastomers (HCR) [3], hydrogenated poly(acrylonitrile-co-butadiene) [4] (HNBR), hydrogenated natural rubber [2] (HNR) and hydro-

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genated synthetic poly(isoprene) [5] (HIR) have been characterized by NMR. However, the microstructure of a hydrogenated poly(styrene-*co*-butadiene) (HSBR) has not been examined by ^{13}C NMR, which is a very useful tool for determination of microstructure and sequences in copolymers since the chemical shift is sensitive to differences in comonomer and stereochemical sequences [6, 7]. Recently, we have reported the quantitative hydrogenation of emulsion SBR using Ru based catalysts [8]. This prompted us to examine the microstructure of HSBR by ^{13}C NMR spectroscopy. Additionally, the sequence structure of HSBR, namely, styrene-ethylene-butene-1 copolymer should reflect the sequence of styrene and butadiene in emulsion SBR, on which only limited information is available.

There have been only a few prior reports on the characterization of the structure of copolymers of styrene and ethylene. Sujuki *et al.* [9] hydrogenated 1,4 poly(2-phenylbutadiene) and characterized the resulting polymer by ^{13}C NMR. The presence of three distinct peaks ($S_{\alpha\gamma}$, $S_{\beta\beta}$ and $T_{\delta\delta}$) indicated that the resulting polymer is an alternating copolymer of ethylene and styrene.

$$\text{-CH(Ph)-}C_{\alpha\gamma}H_2\text{-}C_{\beta\beta}H_2\text{-}C_{\alpha\gamma}H_2\text{-CH(Ph)-}CH_2\text{-}$$

Soga *et al.* [10] copolymerized ethylene and styrene using $TiCl_3$ and $Cp_2Ti(CH_3)_2$ and characterized by ^{13}C NMR. 1 mol% styrene was incorporated into the copoly-mer. Lu *et al.* [11] carried out copolymerization of styrene and ethylene using supported $TiCl_4/NdCl_3$ catalyst which was characterized by ^{13}C NMR. and DSC. They distinguished various types of carbon and also determined the sequence distribution in the copolymer containing 47 mol% styrene (Table 1). Kakugo *et al.* [12] copolymerized ethylene and styrene using $(TBP)Ti(OPr^i)_2$-MAO [15] (TBP = thiobis (4-methyl-6-t-butylphenol) and characterized different types of carbon by ^{13}C NMR. Recently, Endo and Otsu [13] studied isomerization of 2-butene followed by the copolymerization with styrene using $TiCl_3$-TEAL. Ethylene and styrene have also been copolymerized using $TiCl_3$-MAO [14] and isopropylidene(cyclopentadienyl)(9-fluorenyl)zirconium dichloride-MAO [15] and have been characterized using ^{13}C NMR. There are reports of characterization of hydrogenated polybutadiene and ethylene-lbutene copolymers by ^{13}C NMR [16]. Since emulsion SBR has appreciable amounts of 1,2 and 1,4 content, the hydrogenated SBR is actually a terpolymer of styrene, ethylene and 1-butene. Details regarding sequence length and microstructural characterization are not available for this kind of polymer.

EXPERIMENTAL

Materials

SBR was hydrogenated using $RuCl_2(PPh_3)_3$ according to the procedures described previously [8].

Analysis

^1H NMR of SBR and HSBR were recorded on a 90 MHz Brucker spectrometer and ^{13}C NMR. spectra obtained on an MSL 300 model Brucker instrument at 75.5 MHz at room temperature. The spectra were recorded in $CDCl_3$ under quantitative conditions (45° pulse, pulse delay of 10 seconds). 2500 scans were accummulated to obtain a satisfactory S:N ratio. DSC analysis was performed on a Mettler-20 thermal analyzer.

RESULTS AND DISCUSSION

^1H NMR of SBR (Figure 1) shows that it has 15 mol% 1,2 butadiene content. As the degree of hydrogenation increases the peaks due to protons at δ = 4.8 to 5.3 slowly disappear indicating the quantitative hydrogenation of SBR (Figure 2). ^1H noise decoupled ^{13}C NMR spectrum and the DEPT (distortionless enhancement by polarization transfer) spectrum of SBR and HSBR are shown in Figures 3-6. Figure 3 indicates that SBR contains 12% styrene (13% calculated by ^1H NMR) and 88% butadiene. Also, about 12% butadiene (15% calculated by ^1H NMR) has undergone 1,2 type addition. Methyl, methylene, methine and quarternary carbons in SBR and HSBR have been distinguished by DEPT spectrum (Figure 6). Figure 4 shows that there are four types of carbon in aromatic regions (designated by A, B, C and D in Figure 4) and 11 types of carbons in the aliphatic regions. There are a number of reports on the methods of analysis of monomer sequences and sequence lengths of copolymers of ethylene and propylene and other α-olefins [5]. Randall studied the effect of aromatic substitution on the aliphatic hydrocarbon polymers [17]. Using the method of Grant-Paul [18] and Randall [5, 7, 16, 17] the chemical shifts of different triad sequences have been calculated and are given in Table 1. For the sake of simplicity 1,4, 1,2 and styrene content are designated as B, B' and S, respectively. Chemical shift assignments due to different triads of styrene-ethylene copolymers prepared by various methods are given in Table 1.

Table 1: Chemical Shifts (δ) of different triad sequences of HSBR in ^{13}C NMR and comparison with the literature report of Styrene and Ethylene copolymers

Carbon Type	Present Work			Coploymer of Styrene and Ethylene*		Copolymer of Styrene and Ethylene#	Alternate Copolymers of Styrene and Ethylene@
	Peak no. (in Fig 5)	δ (ppm)	Sequences	δ (ppm)	Sequences	δ (ppm)	δ (ppm)
$T_{\delta\delta}$	1	45.98	BSB, SBS	46.25	ESE	46.00	45.40
$T_{\delta\delta}$	3	38.80	BB'B	-	-	-	-
$T_{\beta\delta}$	2	43.32	SB'B, BSB', SBB'	43.66	SSE	43.80	-
$T_{\beta\beta}$	-	-	-	41.33	SSS	41.60	-
$S_{\alpha\alpha}$	3	38.80	SB'B, BSB', SBB'	43.66	SSS	-	-
$S_{\alpha\delta}$	4	36.89	BSB, SBS, SBB	37.18	$(SEE)_{n>1}$	-	-
$S_{\alpha\delta}$	5	33.17	BB'B, BBB'	-	-	-	-
$S_{\alpha\gamma}$	-	-	-	36.24	SES	37.00	36.60
$S_{\gamma\gamma}$	5	33.17	SBS, SBB'	32.05	SEES	-	-

Carbon Type	Present Work			Coploymer of Styrene and Ethylene*		Copolymer of Styrene and Ethylene#	Alternate Copolymers of Styrene and Ethylene@
	Peak no. (in Fig 5)	δ (ppm)	Sequences	δ (ppm)	Sequences	δ (ppm)	δ (ppm)
$S_{\gamma\delta}$	6	30.08	SBB, SBB', BBB'	30.08	$(SEEE)_{n>1}$	-	-
$S_{\delta\delta}$	7	29.63	SBB, BBB', BBB	29.95	$(EE)_{n>1}$	-	-
$S_{\beta\delta}$	8	27.54	SBS, SBB'	27.84	$(SEE)_{n>1}$	-	-
$S_{\beta\delta+}$	9	26.68	SBB, BB'B	-	-	-	-
$2B_2$	10	25.83	$-CH_2-$ of ethyl group	-		-	-
$S_{\beta\beta}$		-	-	-		25.70	25.20
$1B_2$	11	10.78	$-CH_3$ of ethyl branching	-	-	-	-

*Ethylene and styrene were copolymerized with supported $TiCl_4/NdCl_3$ (Ref. 11)

Ethylene and styrene were copolymerized with $(TBP)Ti(OPri)_2$ & MAO system; TBP = thiobis(4-methyl-6-t-butylphenol) (Ref. 12)

@ Prepared by the hydrogenation of 1,4 poly(2-phenylbutadiene) (Ref. 9)

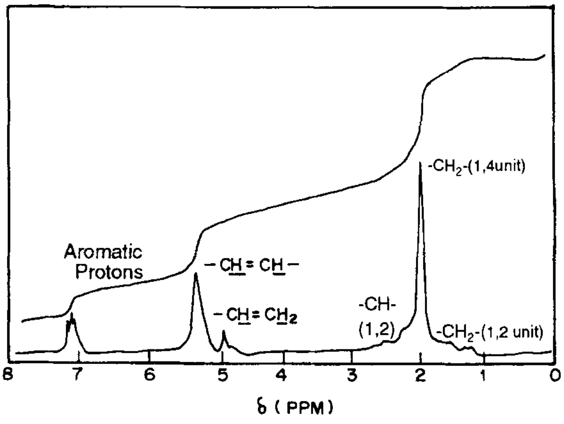

Figure 1. ^1H NMR of SBR

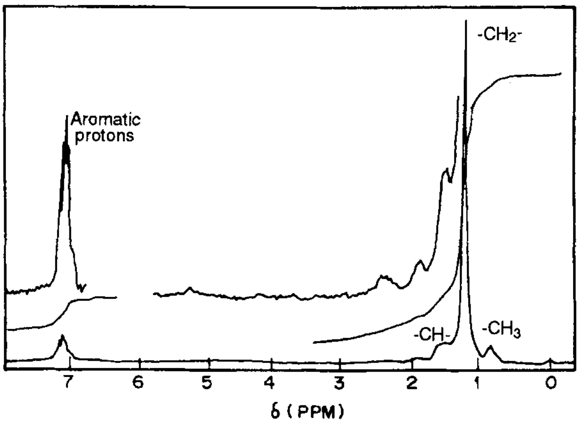

Figure 2. ^1H NMR of HSBR

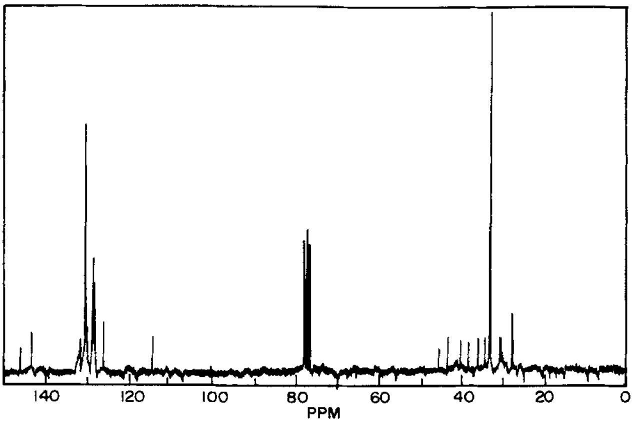

Figure 3. ^{13}C NMR of SBR

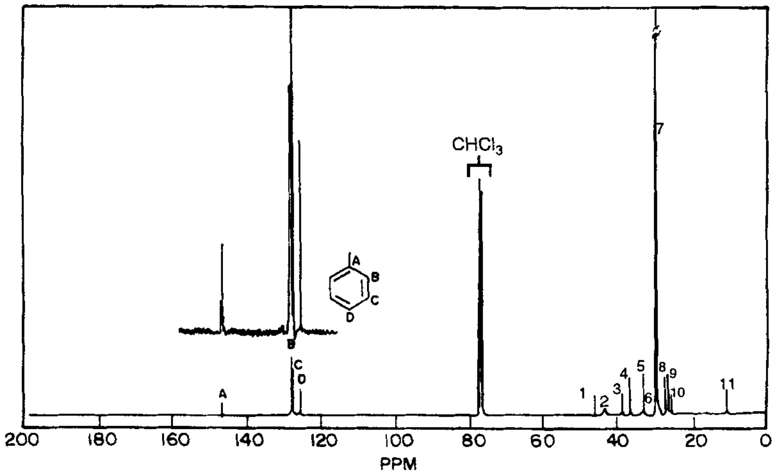

Figure 4. ^{13}C NMR of HSBR

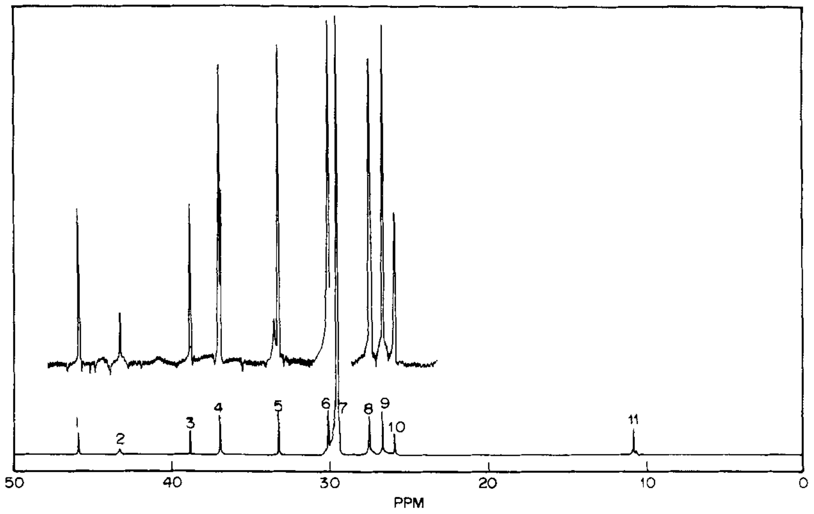

Figure 5. Amplified region of δ = 0 - 50 ppm of ^{13}C NMR of HSBR

Absence of methylene peaks in the region of 42-45 ppm is indicative of absence of SS sequences [17]. This is expected since the mole percent of styrene unit is very low (only 13%). Peaks 1 and 2 in Figure 5 are due to $T_{\delta\delta}$ and $T_{\beta\delta}$, respectively, which are according to the literature report. Peak 3 is due to $T_{\delta\delta}$ of BB'B and $S_{\alpha\alpha}$ of SB'B and BSB' sequences [7]. Absence of peaks at 35.1 (due to $T_{\beta\beta}$ of B'B'B') and at 41.0 (due to $S_{\alpha\alpha}$ of B'B'B') indicates that there is no B'B'B'

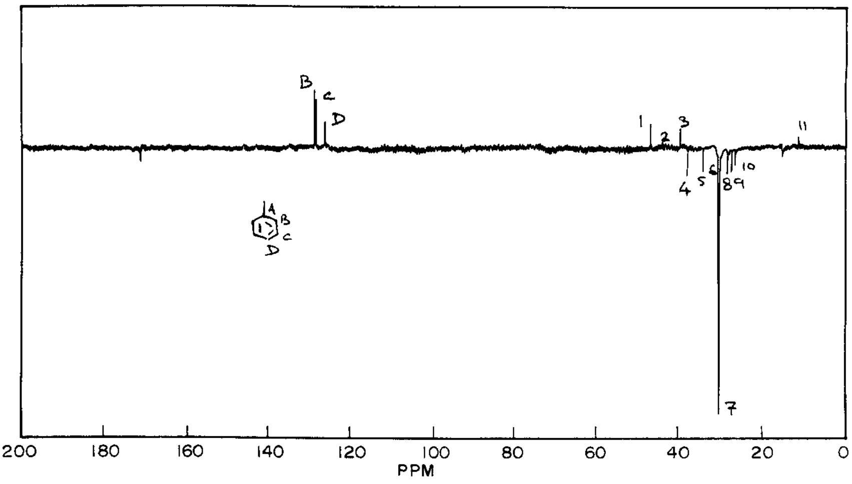

Figure 6. DEPT spectrum of HSBR

Table 2: Chemical Shifts of various -CH_2- sequences of HSBR

Types of Carbon	Chemical Shifts (δ) (ppm)	Methylene Sequences	Integral Area	Sequence Length (%)
$S_{\alpha\alpha}$	38.80	$(CH_2)_1$	1.034	4.8
$S_{\alpha\beta}$	Absent	$2(CH_2)_2$	-	-
$S_{\beta\beta}$	Absent	$(CH_2)_3$	-	-
$S_{\beta\gamma}$	Absent	$2(CH_2)_4$	-	-
$S_{\gamma\gamma}$	33.17	$(CH_2)_5$	1.529	7.2
$S_{\gamma\delta}$	30.08	$2(CH_2)_6$	2.290	5.6
$S_{\delta\delta}$	29.63	$(CH_2)_{>6}$	17.720	82.4

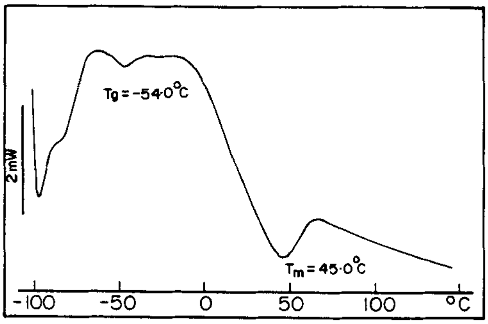

Figure 7. DSC thermogram of HSBR

sequence in HSBR. It is according to our expectation as the mole percent of 1,2 butadiene content in SBR is very low.

The length of $-CH_2-$ can be calculated by using Randall's method [19] (Table 2). The absence of $S_{\alpha\beta}$ types of carbons indicates that there is no $(-CH_2-)_2$ which can arise only in case of inverted addition of two styrene units or one styrene and one butadiene unit (1,2 addition) [17]. Absence of peaks $S_{\beta\beta}$ and $S_{\beta\gamma}$, indicates the absence of $(-CH_2-)_3$ and $(-CH_2-)_4$ sequence in HSBR. However, sequences such as CH_2, $(CH_2)_5$, $(CH_2)_6$ and $(CH_2)_{>6}$ are present. The quantification of these sequence lengths indicates that HSBR has about 82% $(CH_2)_{>6}$ unit. The abundance of $(CH_2)_{>6}$ sequences induce crystallinity in these segments. This has been confirmed by DSC measurement, which shows an endotherm at 450°C (Figure 7). Thus, HSBR has appreciable crystallinity (ΔH = 15.2 J/g). HSBR shows a high intensity $S_{\delta\delta}$ peak [$(CH_2)_{>6}$] which arises due to the presence of SBB, BBB' and BBB.

CONCLUSION

Chemical shifts of various carbons in HSBR have been assigned and the possible sequences identified . HSBR has a considerable amount of crystallinity due to the presence of $(CH_2)_{>6}$ units of about 82%.

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