

STYRENE SEQUENCE DISTRIBUTION OF STYRENE-BUTADIENE COPOLYMERS

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Abstract-The aromatic proton peak shape in 400MHz ^1H -NMR spectra for commercially available styrene-butadiene copolymers is classified into the five categories corresponding to the styrene sequence distribution obtained by ozonolysis-GPC. The relationship between the sequence length and peak splitting was also investigated.

Key words styrene-butadiene copolymer, ^1H -NMR, ozonolysis, styrene sequence distribution

The styrene sequence distribution of styrene-butadiene copolymers (SB-copolymer) is one of the important factors to understand the relationship between the polymer structure and properties. ^1H -NMR and ^{13}C -NMR spectroscopy are widely used for sequence analyses of copolymers, however, ^{13}C -NMR has not been applied for determination of styrene sequence of SB-copolymers because of its complication. The determination of block styrene using ^1H -NMR based on the upfield shift of ortho-protons in phenyl group was developed by Mochel et.al.[1][2]. Despite the simplicity of the method, there remains some ambiguity in the relationship between the sequence distribution and peak shape, especially, in the high-field NMR spectra. On the other hand, ozonolysis-GPC method provides quantitative information about the sequence distribution of styrene and 1,2-unit[3], however, this is very complicated and time consuming. In this work, through the analysis of various SB-copolymers and polystyrene oligomers by 400MHz ^1H -NMR and ozonolysis-GPC, we discuss the relationship between the peak splitting of aromatic protons and styrene sequence length.

EXPERIMENTAL

Fractionation of polystyrene oligomer

The polystyrene oligomer (TOSOH A-500) was fractionated into each component by preparative GPC with G2000HG column (TOSOH). The purity of each fraction was determined by analytical GPC and mass spectrometry.

 ^1H -NMR measurement of polystyrene oligomers and SB-copolymers

^1H -NMR spectra were obtained with a JEOL GX400 NMR spectrometer in CDCl_3 solution at room temperature. Chloroform (CHCl_3) in the solvent was used as an internal standard for the chemical shift, which gave a peak at 7.26ppm.

Ozonolysis-GPC of SB-copolymers

Ozone from a ozone generator was introduced through a glass filter into a polymer solution at -50 to -55 C until the excess of ozone was detected by a color change of potassium iodide aqueous solution attached to the outlet of the reaction vessel. Ozonide was decomposed to alcohols with lithium aluminum hydride in tetrahydrofuran. GPC measurements were made with S8020 GPC(TOSOH) using G2000HXL analytical column(TOSOH).

RESULTS AND DISCUSSION

Through the observation of 400MHz ^1H -NMR spectra of commercially available SB-copolymers which include emulsion-SBR, solution-SBR, and SB or SBS block copolymers, we find that the aromatic proton peak shape is classified into

the five categories as shown in Fig. 1. The GPC curves of ozonolysis products for each type of SB-copolymers are shown in Fig. 2. It is obvious that $^1\text{H-NMR}$ spectrum of each category reflects a characteristic styrene sequence distribution. Five categories classified by $^1\text{H-NMR}$ and ozonolysis-GPC are as follows;

1. completely block copolymers
2. block SB-copolymers including a small amount of short styrene sequence
3. random SB-copolymers including a small amount of long block styrene sequence
4. SB-copolymers including short block styrene sequence
5. completely random SB-copolymers

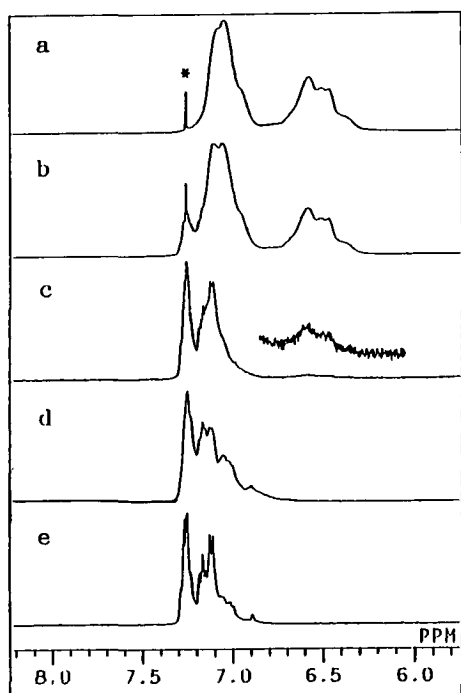


Fig. 1 Aromatic proton spectra of styrene-butadiene copolymers

* CHCl_3 in the solvent

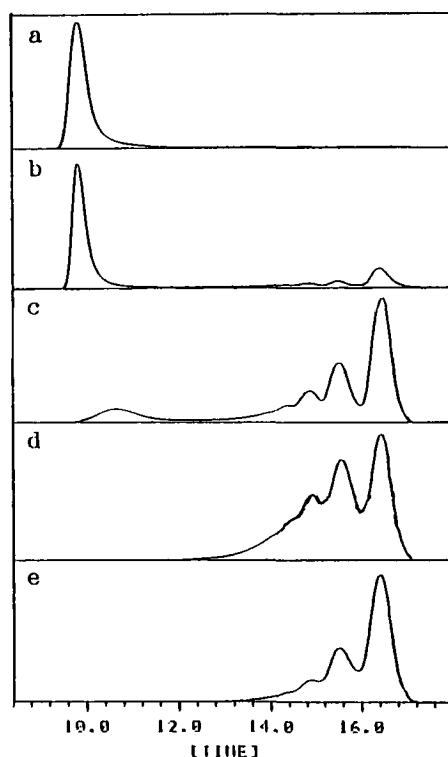


Fig. 2 Ozonolysis-GPC curves of styrene-butadiene copolymers

The aromatic proton signal of copolymers in Category 1, 2, and 3, were divided into two peaks at 6.85ppm as shown in Fig. 1a, 1b, and 1c. The peaks at a higher field were assigned to the ortho-protons in a long block styrene. Copolymers in Category 1 had only a long block styrene sequence as shown in Fig. 2a, thus the intensities of the two peaks were in a ratio of 3 to 2. The copolymers in Category 2 were block copolymers, but also included short sequences less than 6 units (Fig. 2b), which exhibited small peak from 7.2 to 7.3ppm in $^1\text{H-NMR}$ spectrum (Fig. 1b). For Category 3, their styrene sequences were mainly less than 6 units, but also included a long block sequence which molecular weight was more than several thousand (Fig. 2c). In the case of Category 2 and 3, the content of the block styrene was determined from the intensities of the two peaks divided at 6.85ppm.

As shown in Fig. 2d, copolymers in Category 4 did not show a long block sequence like Category 1, 2, or 3, but included a certain amount of short block sequence longer than 6 units, which was believed to effect on the physical properties. The aromatic proton peak in this category shifted to the higher field than 6.85ppm, but it was difficult to distinguish ortho-proton peak (Fig. 1d).

SB-copolymers in Category 5 had only short styrene sequences in the range of 1 to 6 units as shown in Fig. 2e. Their aromatic proton signal was observed from 6.85 to 7.4ppm, and the upfield peak of ortho-proton was not detected (Fig. 2e).

The boundary between Category 4 and 5 is not clear, and difficult to define the "block" styrene. To clarify the relationship between the styrene sequence length and the peak splitting in the short block, ^1H -NMR spectra of the fractionated polystyrene oligomers were investigated. Fig.3 shows the aromatic proton signals for n-hexylbenzene and the fractionated styrene oligomers. n-Hexylbenzene and the dimer showed a complicated peaks from 7.1 to 7.4ppm. The signals for the trimer, tetramer, and pentamer were clearly divided into two peaks with an intensity ratio of 3 to 2, but their peak valley were not similar to a long block styrene. On the other hand, signals of the oligomers which have more than 6 units were broad and could not be divided clearly.

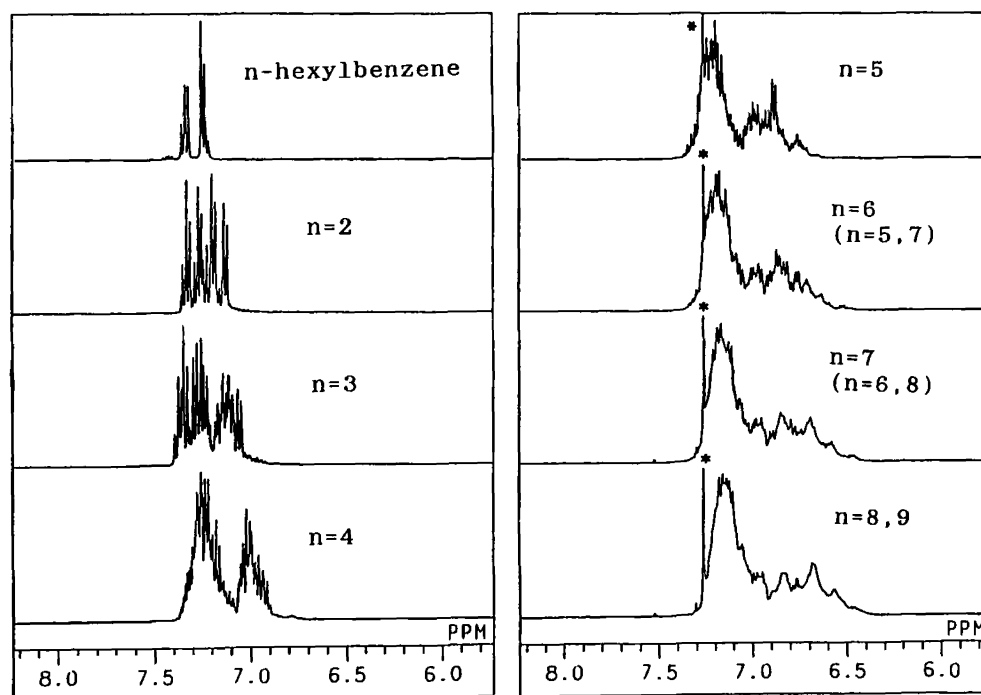


Fig. 3 Aromatic proton spectra of styrene oligomers
* CHCl_3 in the solvent

Fig. 4 shows the relationship between the peak parameters and styrene length. It is clear that all parameters shift gradually to a higher field with an increase of the sequence length. Thus it is very difficult to obtain quantitative information on the sequence distribution of SB-copolymers in Category 4 and 5. However, the longest sequence in these polymers could be estimated from the peak end on the higher field side. To determine the longest styrene sequence length of these polymers, a study by the mass spectrometry of ozonolysis products is in progress.

From these observation, one can conclude that 400MHz ^1H -NMR spectrum provides the useful information on the styrene sequence in the styrene-butadiene copolymers.

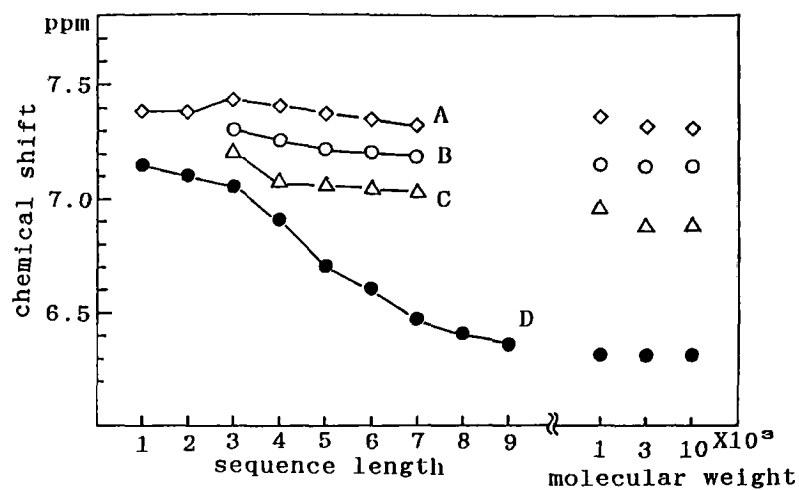


Fig. 4 Relationship between peak parameters and styrene sequence length

- A: peak start on the lower field side
- B: peak top at a lower field
- C: peak valley or point at which area was divided with a ratio of 3 to 2
- D: peak end on the higher field side

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