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End-Group Effect of Styrene Oligomers on the ^{13}C NMR Chemical Shift

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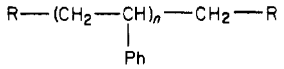
ABSTRACT: Styrene oligomers from dimer to pentamer and having propyl (Ib) and pentyl end groups (Ic) were prepared and separated into each diastereomer. The ^{13}C NMR chemical shifts of methylene and phenyl C(1) carbons of these oligomers were compared to those of oligomers with methyl end groups (Ia) as reported by Jasse et al. Oligomers of Ib and Ic have almost identical chemical shifts for these carbons, while Ia shows slightly different chemical shifts. The resonating order of the carbons in diastereomers of Ib and Ic is almost the same as that of the configurational sequences in polystyrene. It is proved that Ib and Ic oligomers are good models for the analysis of the ^{13}C NMR spectrum of polystyrene.

Introduction

Many oligomers possessing known chemical and stereochemical structures have been prepared for the elucidation of the structure of vinyl polymers. Usually oligomers having methyl end groups have been prepared through a long synthetic route. In the case of polystyrene, oligomers with methyl end groups (Ia) have been prepared up to tetramer and separated into diastereomers. These oligomers are synthesized by Grignard reactions or other condensation reactions.[1-4]



$$R{-}(CH_2{-}\underset{\displaystyle Ph}{\underset{|}{CH}})_n{-}CH_2{-}R$$

Ia, R = H
b, R = CH_2CH_3
c, R = $CH_2CH_2CH_2CH_3$

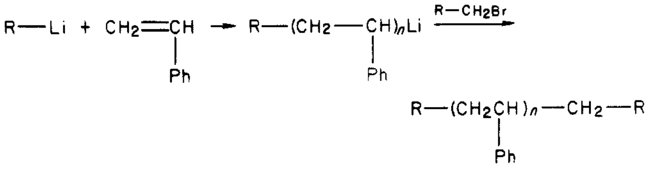
However, it is difficult to prepare longer oligomers using these reactions because it is difficult to obtain the starting materials.

The ^{1}H or ^{13}C NMR spectra of the oligomers with methyl end groups were measured in order to analyze the spectra of polystyrene.[1-4] However, these oligomers have failed to provide useful information for the analysis of NMR spectra of polystyrene, because the ^{1}H and ^{13}C spectra from these types of oligomers differed somewhat from those of the polymer.

Styrene oligomers with any desired average degree of polymerization can be obtained through oligomerization of styrene after initiating with alkyllithium. We have prepared symmetric oligomers having propyl end groups (Ib) by the oligomerization of styrene after initiating with ethyllithium and terminating with 1-bromopropane. The oligomer mixture was separated into pure *n*-mers up to 12-mers, and 2–5-mers were fractionated into diastereomers.[5] In our previous paper we have demonstrated that the styrene oligomers with propyl end groups exhibited the same splitting pattern for the methine proton as polystyrene[6] and have found that the resonating order of methylene and phenyl C(1) carbon of polystyrene was almost equal to those of the corresponding carbons in the pentamer of Ib.[7,8] In this report ^{13}C NMR signals of the styrene oligomers having propyl and pentyl end groups (Ib and Ic) were analyzed and their chemical shifts were compared with those of Ia. The effect of end groups of the styrene oligomers on the ^{13}C NMR chemical shift is discussed.

Experimental Section

Oligomers of Ib and Ic. Styrene oligomers with propyl and pentyl end groups were prepared by anionic oligomerization of styrene after initiating with alkyllithium and terminating with 1-bromoalkane:



$$R{-}Li + CH_2{=}\underset{\displaystyle Ph}{\underset{|}{CH}} \rightarrow R{-}(CH_2{-}\underset{\displaystyle Ph}{\underset{|}{CH}})_nLi \xrightarrow{R{-}CH_2Br} R{-}(CH_2\underset{\displaystyle Ph}{\underset{|}{CH}})_n{-}CH_2{-}R$$

Ib, R = CH_2CH_3
c, R = $CH_2CH_2CH_2CH_3$

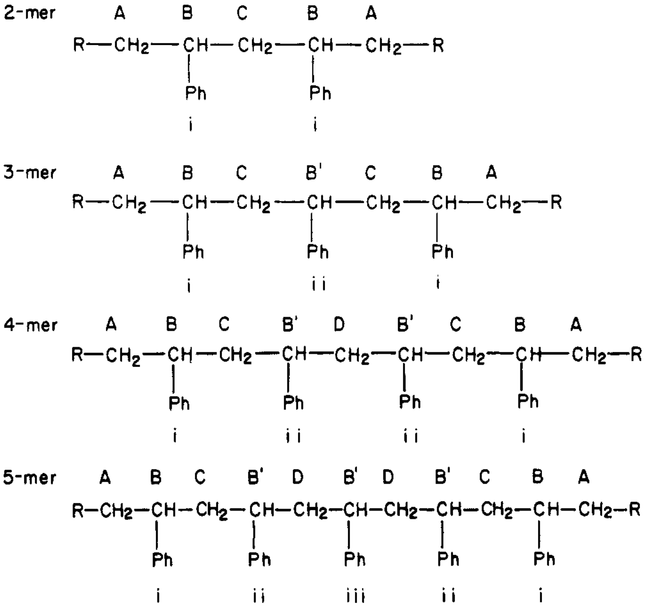
The mixture of the oligomers having different degrees of polymerization was separated into pure *n*-mers by gel permeation chromatography. The dimer to the pentamer of Ib and the dimer to the tetramer of Ic were separated into diastereomers by liquid chromatography using styrene–divinylbenzene copolymer gel as a stationary phase and diisopropyl ether as an eluent.[5]

^{13}C NMR Measurements. ^{13}C NMR spectra were recorded on a JEOL FX-200 spectrometer (50.1 MHz) in a deuteriochloroform solution at room temperature (ca. 35 °C) with a pulse repetition time of 3 s and with a 45° pulse angle. Chemical shifts were read from tetramethylsilane added as an internal standard.

Results and Discussion

Signal Assignments of Ib and Ic. The diastereomers of the dimer and the trimer were identified by ^{1}H NMR spectroscopy.[6] The diastereomers of the tetramer and the pentamer of Ib were identified by using the results of the dimer and the trimer.[8]

Aliphatic carbon signals were assigned to the external methylene, internal plus central methylenes, and methine carbons by selectively decoupling the protons around 1.4 ppm (A), 1.8 ppm (C and D), and 2.0–2.5 ppm (B and B′), respectively. The carbon atoms and the phenyl groups are noted as follows:



$$\text{2-mer}\quad \mathrm{R{-}\overset{A}{CH_2}{-}\underset{\underset{i}{Ph}}{\overset{B}{CH}}{-}\overset{C}{CH_2}{-}\underset{\underset{i}{Ph}}{\overset{B}{CH}}{-}\overset{A}{CH_2}{-}R}$$

$$\text{3-mer}\quad \mathrm{R{-}\overset{A}{CH_2}{-}\underset{\underset{i}{Ph}}{\overset{B}{CH}}{-}\overset{C}{CH_2}{-}\underset{\underset{ii}{Ph}}{\overset{B'}{CH}}{-}\overset{C}{CH_2}{-}\underset{\underset{i}{Ph}}{\overset{B}{CH}}{-}\overset{A}{CH_2}{-}R}$$

$$\text{4-mer}\quad \mathrm{R{-}\overset{A}{CH_2}{-}\underset{\underset{i}{Ph}}{\overset{B}{CH}}{-}\overset{C}{CH_2}{-}\underset{\underset{ii}{Ph}}{\overset{B'}{CH}}{-}\overset{D}{CH_2}{-}\underset{\underset{ii}{Ph}}{\overset{B'}{CH}}{-}\overset{C}{CH_2}{-}\underset{\underset{i}{Ph}}{\overset{B}{CH}}{-}\overset{A}{CH_2}{-}R}$$

$$\text{5-mer}\quad \mathrm{R{-}\overset{A}{CH_2}{-}\underset{\underset{i}{Ph}}{\overset{B}{CH}}{-}\overset{C}{CH_2}{-}\underset{\underset{ii}{Ph}}{\overset{B'}{CH}}{-}\overset{D}{CH_2}{-}\underset{\underset{iii}{Ph}}{\overset{B'}{CH}}{-}\overset{D}{CH_2}{-}\underset{\underset{ii}{Ph}}{\overset{B'}{CH}}{-}\overset{C}{CH_2}{-}\underset{\underset{i}{Ph}}{\overset{B}{CH}}{-}\overset{A}{CH_2}{-}R}$$

where A is external methylene, B and B′ are end methine and internal methine, C is internal methylene, D is central methylene, and i, ii, and iii are end-, inner-, and central-phenyl groups. In this report meso (m) and racemic (r) are used when the two consecutive phenyl groups are attached respectively on the same and opposite side of the main chain.

The external methylene carbons of Ib and Ic resonated around 40 and 38 ppm, respectively, for the r end and 38 and 36 ppm, respectively, for the m end. The end- and internal-methine carbons resonated around 43 and 41 ppm, respectively, for both Ib and Ic. The internal- and the central-methylene carbons were sensitive to the configurational sequences and resonated over the wide range of 47–40 ppm. The assignments of the internal- and the central-methylene signals were carried out by considering the signal intensity for the symmetric tetramers such as rrr, rmr, mrm, and mmm isomers and by comparing the chemical shifts of the corresponding signals of the dimer, trimer, and other isomers. Figure 1 shows the chemical shifts of the internal- and the central-methylene carbons of Ib oligomers. Good correlations were observed among the corresponding carbons of the dimer to pentamer, which demonstrates the validity of the identification of the diastereomers as well as the validity of the signal assignments.

In the case of Ia oligomers phenyl C(1) carbon of the end group resonated in the range of 146.7–148.0 ppm, while that of the inner group in the range of 145–146 ppm. Therefore, the phenyl C(1) carbon signals of Ia oligomers can be assigned by the chemical shift range. On the other hand, in the case of Ib and Ic the phenyl C(1) signals of the end, the inner, and the central groups appeared in the same chemical shift range of 145.0–146.5 ppm. The phenyl C(1) carbon signals of the symmetric isomers of the trimer and the pentamer were assigned by considering the signal intensities and the other phenyl C(1) carbon signals were assigned by comparing the chemical shifts of the corresponding carbons of the other isomers. For example, the C(1) carbons of the end units of both *m*mm and *m*mr isomers are expected to reesonate at similar chemical shifts in the neighborhood of the phenyl C(1) carbon signal of the end unit in the *m*m trimer. These carbons were assigned as shown in Figure 2a. Similarly, a chemical shift resemblance is expected for the corresponding phenyl C(1) carbons of two isomers of tetramer having the same triad sequence and for those of two isomers of the pentamer having the same tetrad sequence. The correlation of the phenyl C(1) chemical shifts among the corresponding isomers are shown in Figure 2.

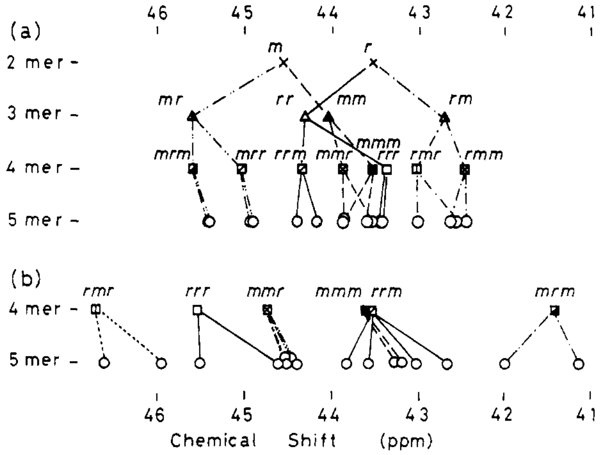


Figure 1. Chemical shift of the internal (a) and central methylene carbons (b) of Ib oligomers.

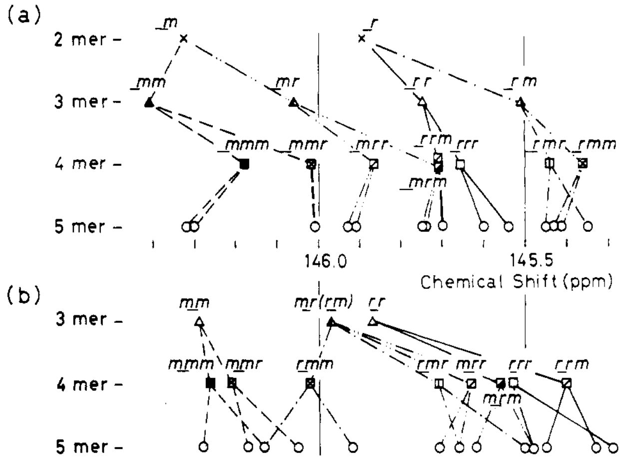


Figure 2. Chemical shift of phenyl C(1) carbon in the end (a) and inner units (b) of Ib oligomers.

End-Group Effect on the ^{13}C NMR Chemical Shift. ^{13}C NMR chemical shifts of the internal methylene carbon and the phenyl C(1) carbons of the end and inner units are shown in Figure 3 for the trimers of Ia–c. The internal methylene and C(1) carbons of the end unit of the Ia trimer are shifted downfield by 1.5–2.0 ppm compared to the Ib and Ic trimers; this may be attributed to the smaller number of γ- and δ-carbons for the Ia trimer. It is noteworthy that the carbons in the Ib trimer have almost the

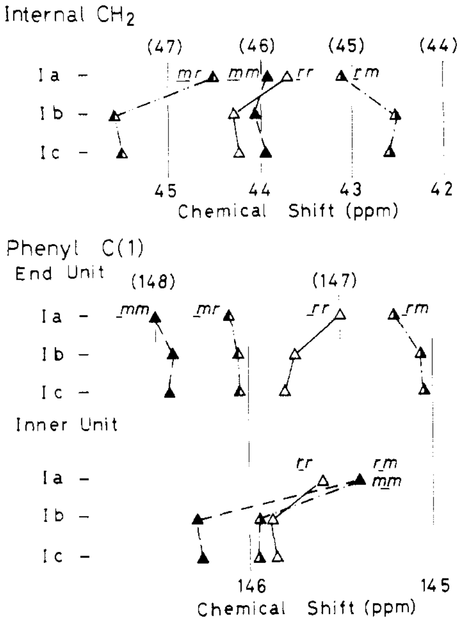


Figure 3. End-group effect on the chemical shift of internal methylene and phenyl C(1) carbons of styrene trimer.

same chemical shift as those in the Ic trimer. Therefore, it can be estimated that carbons in the Ib oligomer have almost the same chemical shift as the carbons in the oligomer having end groups longer than propyl.

The internal methylene carbons resonated in the order *mr* < *rr* < *mm* < *rm* for the Ib and the Ic trimers, and *mr* < *mm* < *rr* < *rm* for the Ia trimer. A slight difference of the resonating order is also observed for the central methylene carbons of the tetramers: from downfield to upfield in the order r*m*r < r*r*r < m*m*r < r*r*m, m*m*m < m*r*m for the Ib tetramer and r*m*r < m*m*r < r*r*r < m*m*m < r*r*m < m*r*m for the Ia tetramer. The latter is obtained by calculating the effects of γ-carbon and phenyl ring current by Tonelli.[9] In the case of polystyrene, methylene carbon resonated in the order rmr < rrr < mmr < rrm, mmm < mrm.[7,8,10] This resonating order is equal to those of the central methylene carbon of the Ib and Ic tetramer, indicating that these oligomers are more appropriate than the Ia oligomer to analyze the methylene carbon signal of polystyrene.

The phenyl C(1) carbon of the end unit resonated in the order *mm* < *mr* < *rr* < *rm* for all three types of trimers. However, the resonance order of the phenyl C(1) carbon in the inner unit of the Ia trimer is completely different from those of the Ib and Ic trimers: from downfield to upfield *mm* < *rm* < *rr* for the Ib and Ic trimers and *rr* < *rm*, *mm* for the Ia trimer. A similar difference is observed for the C(1) carbon of the inner unit of the tetramers (Figure 4). In the case of the Ib and Ic tetramers the inner C(1) carbon resonated in the order *mm*m < *mm*r < *rm*m < *rm*r < *mr*r < *mr*m < *rr*r < *rr*m. Thus, for the Ib and Ic oligomers the C(1) carbon of the inner group of trimer and tetramer resonated in the order x*mm*y < x*mr*y < x*rr*y (x, y = m or r). This resonating order also held for the C(1) carbon of the inner and the central groups of the Ib pentamer. On the other hand, the C(1) carbon of the inner groups of the Ia tetramer resonated in the order *rr*m, *mr*r < *rm*m (or *mm*r) < *rm*r < *mm*m < *mm*r (or *rm*m), *rr*r < *mr*m. Thus, it can be concluded that the Ia oligomer has no regularity in the resonating order of the inner phenyl C(1) carbon on the level of the triad sequence. Furthermore, it is unusual that the inner C(1) carbon of the mmm isomer of the Ia tetramer resonated in the middle of those of the other isomers because the C(1) signal of isotactic polystyrene resonated in the most downfield position.[11] By considering this unusual resonating order and also because of the smaller chemical shift range of the inner phenyl C(1) carbon in Ia tetramer, Jasse et al.[4] analyzed the C(1) signals of polystyrene using the C(1) signal of the end group of the Ia tetramer instead of using that of the inner group.

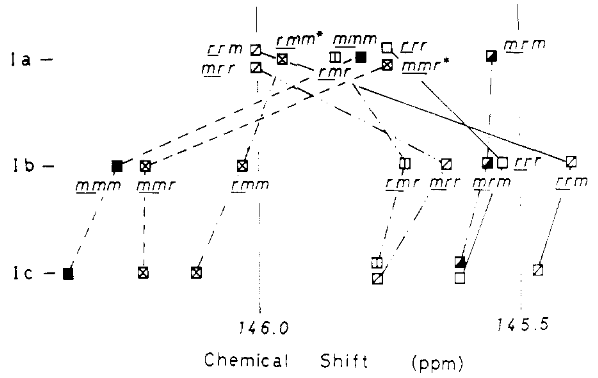


Figure 4. End-group effect on the chemical shift of inner phenyl C(1) carbon of the tetramer. (*) Signal assignment can be interchanged.

It is reported that the phenyl C(1) carbon of polystyrene splits, reflecting the pentad configuration,[7,8] and that some signals are sensitive to the heptad sequences.[12] Therefore, the pentamer is required as the shortest model to analyze the phenyl C(1) signal of polystyrene. The central phenyl C(1) carbon of the Ib pentamer resonated in the order mmmm < mmmr < mmrm, mmrr < rmmr, mrmr, rrmr < rrrm < rrrr < mrrm. In the case of polystyrene, phenyl C(1) carbon resonated in the order mmmm, mmmr < rmmr < mmrm, mmrr < rmrm, rrmr < rr.[7,8,12] The resonating order of the Ib pentamer is equal to that of polystyrene except the signal due to the rmmr. Thus, the Ib pentamer is proved to be a good model to assign the phenyl C(1) signal of polystyrene. On the other hand, it is questionable that the Ia pentamer provides reliable information to analyze this signal because of the peculiar resonating order of the inner phenyl C(1) carbon of the Ia trimer and tetramer. This peculiar resonating order of the Ia oligomer may arise from the small end groups, which cause the oligomer to assume different conformations from those of the other oligomers and polystyrene. It is concluded that the Ib and Ic oligomers are appropriate models to analyze the methylene and phenyl C(1) signals of polystyrene.

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