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Microstructure of Polyisoprene in Polystyrene-b-Polyisoprene Copolymer

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요 약 : 상온에서 2차 부틸 리튬을 개시제로 사용하여 벤젠 용매 하에서 음이온 중합법으로 합성된 폴리스티렌/폴리이소프렌 이블록공중합체중 폴리이소프렌 블록의 미세구조를 수소핵자기 공명 분광법을 이용하여 조사하였다. 그 결과 폴리이소프렌 블록의 미세구조는 폴리스티렌 블록의 존재에 의하여 영향을 받지 않으며 같은 조건에서 중합된 폴리이소프렌 단일중합체의 미세구조와 실험오차내에서 동일하다는 것을 확인하였다.

Abstract : Microstructure of polyisoprene block in polystyrene-b-polyisoprene copolymers, prepared at room temperature by anionic polymerization in benzene using sec-butyl lithium as an initiator, was examined by proton magnetic resonance spectroscopy. It is confirmed that the microstructure of the diene block is not altered by the presence of polystyrene block and is identical within experimental uncertainty with that of homopolyisoprene prepared under the same condition.

INTRODUCTION

For anionically polymerized dienes, it is well established that their microstructure is greatly influenced by polymerization conditions such as the type and concentration of initiator, the nature of solvents etc.[1~3] Polar solvents, especially tetrahydrofuran, can alter the polyisoprene (PI) structure from high cis-1,4 obtained in hydrocarbon media to mainly 3,4.[4] Aliphatic solvents, e.g., hexane and cyclohexane, lead to a slightly higher cis-1,4 content than aromatic solvents without a significant effect on side-vinyl content while the absence of any solvents is known to yield the highest attainable cis-1,4 content.[4,5] In bulk or in aliphatic hydrocarbon solvents, a decrease in initiator concentration leads to a noticeable increase in cis-1,4 content without any significant change in side vinyl content while the effect is absent in aromatic hydrocarbon solvents.[5,6]

It is also known that the microstructure of isoprene units in the anionically prepared random copolymer of styrene and isoprene was greatly affected by the styrene contents. The 1,4 content decreases with the amount of styrene added.[7] To the best of our knowledge, however, there has not been a systematic study on the microstructure of diene in block copolymers but it has been generally assumed that the microstructure of dienes in block copolymers is the same as that of homo dienes prepared under the same polymerization condition.

A typical preparation method of diblock copolymers by anionic polymerization is the sequential polymerization of corresponding monomers. For the case of polystyrene-b-polyisoprene (PS-b-PI) copolymers, styrene monomer is commonly introduced first because the trans-initiation of isoprene by styryl anion is much faster than the reverse sequence.[2] In this case, the atmosphere of the growing chain end of isoprenyl anion contains a polystyrene (PS) block and thus one may expect the possibility that the microstructure of polyisoprene block would be affected by the presence of the polystyrene block. In this note, we report an experimental confirmation that the polyisoprene microstructure in PS-b-PI copolymers is independent on the styrene content and identical with that of homo polyisoprene prepared under the same experimental condition.

EXPERIMENTAL

Our polymerization scheme is practically the same as that of Morton and Fetters using glass break seals under high vacuum.[5] Benzene and sec-butyl lithium were used as the solvent and the initiator, respectively. Most of the diblock copolymers were prepared by sequential addition of styrene and isoprene monomers. In order for a critical comparison, we have prepared two block copolymers by the reverse addition order, i.e., isoprene first and then styrene. In this case, a small volume of THF was added after the polymerization of

polyisoprene block to facilitate the trans-initiation of styrene. At room temperature, typically 5 and 24 hours were allowed for the complete polymerization of styrene and isoprene. After the polymerization of the first block, a small portion of polymerization solution was sealed off as a precursor for composition and molecular weight analysis. Concentrations of the monomers and initiator in polymerization mixture were in the range of 1.4-5.3% (w/v) and 6.5×10^{-6}-6.0×10^{-3} M depending on the molecular weight of block copolymers. Total 17 independently prepared PS-b-PI copolymers were used in this study.

^{1}H nuclear magnetic resonance (NMR) spectra of block copolymers were obtained from ~1% block copolymer solution in $CDCl_3$ by a 300 MHz FT spectrometer (Bruker). Microstructure of the polyisoprene part was analyzed based on the peak assignment by Tanaka et al.[8] Also the composition of block copolymers were calculated from the peak areas characteristic of polystyrene and polyisoprene.

Molecular weights of precursors were obtained by gel permeation chromatography (GPC) with tetrahydrofuran as the eluent and those of whole block copolymers were calculated based on the composition determined by NMR. The molecular weights of some block copolymers were also determined by light scattering for comparison. Polydispersity index, M_w/M_n was obtained from GPC chromatograms in THF using a calibration curve determined with polystyrene standards.

RESULTS AND DISCUSSION

In Fig. 1, a typical NMR spectrum of PS-b-PI is displayed. The composition of a block copolymer was obtained from the integrated peak areas at near 6.5 and 7.1 ppm from aromatic protons of PS part and at 4.7 (3.4 addition) and 5.1 ppm (1,4 addition) from vinyl protons of PI part. Molecular weight of a block copolymer was obtained as described in the experimental section. These results are tabulated in Table 1. Sample codes represent
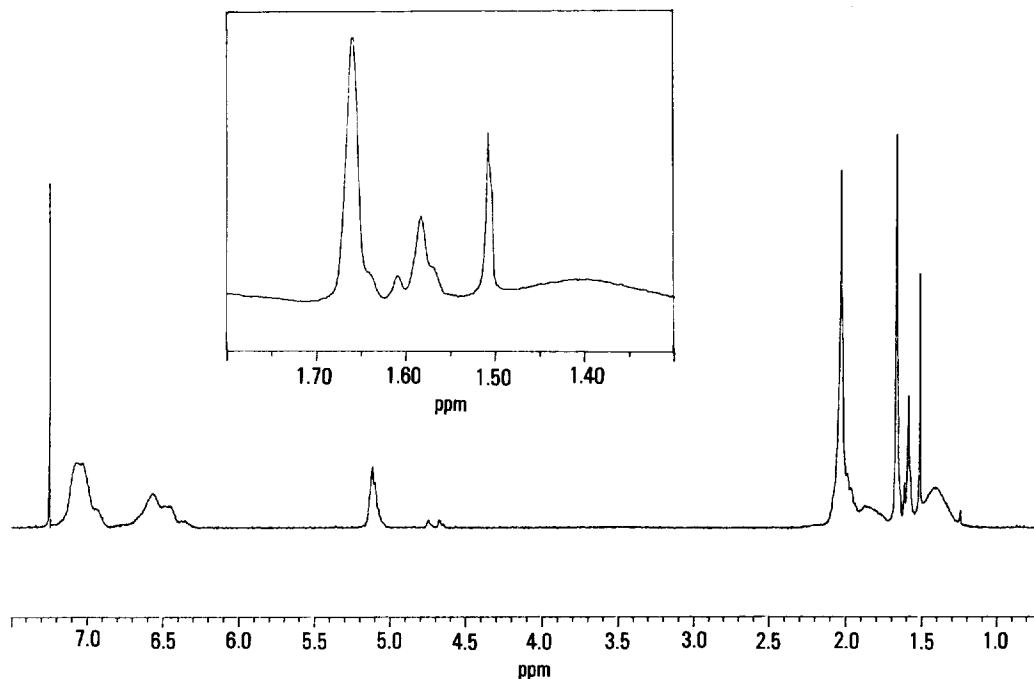
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Fig. 1. A typical proton magnetic resonance spectrum of a PS-b-PI block copolymer (SI 114). In the inset, a zoomed portion of the spectrum near 1.6 ppm showing the methyl protons of isoprene units is shown. See the text for details.

the order of monomer addition, i.e., SI means styrene first and vice versa. The following numbers indicate the sequence of preparations which spans longer than a year. The "Mixture" in the table is not a block copolymer but a mixture of two homopolymers as shown in the table. The composition of the mixture by NMR analysis, 62.3% is consistent with the weight fraction of homo polystyrene used to make the mixture, 63%. Also some results from light scattering analysis are shown in the parenthesis and they are again in good agreement with the molecular weights determined by GPC and NMR. Therefore, our characterization scheme for composition and molecular weight is found to be satisfactory. For IS block copolymers, the composition should be likewise reliable, but their molecular weights are subject to the error arised from the GPC analysis based on the calibration with PS standards. Since this paper concerns with microstructure only, however, these values are presented

just for a rough estimation.

In the inset of Fig. 1, the portion of the spectrum is zoomed from which the ratio of cis-1,4 and trans-1,4 contents can be determined. In this region, the characteristic peaks of PI methyl proton resonance (1.67 ppm : cis-1,4 ; 1.61 ppm : 3,4 ; 1.59 ppm : trans-1,4) were overlapped by the broad peaks from aliphatic hydrogens in PS block. (The sharp peak at 1.51 ppm is from the residual water.) The content of each microstructure was determined by manual deconvolution assuming symmetric peak shape. The microstructure determined by this deconvolution procedure was not much different from the integrated peak area obtained without consideration of the peak overlap. The results are also summarized in Table 1. From Table 1, one can note that 3,4 contents fluctuate a little but remain practically the same as that of homo PI amounting 7-8%. On the other hand, cis-1,4 content varies from 70% for homo PI to 61.7%

Table 1. Characteristics of PS-b-PI Copolymers

Sample code	$M_w(\times 10^{-3})$		M_w/M_n[a]		wt%[b] of PS	Microstructure(%)[b]		
	PS[a]	PS-b-PI[c]	PS	PS-b-PI		cis-1,4	trans-1,4	3,4
SI 105	11.5	14.2	1.08	1.09	81.2	61.7	30.1	8.2
SI 112	103.0	127.8 (124)[d]	1.03	1.07	80.6	61.9	30.8	7.3
SI 108	22.0	27.8	1.02	1.02	79.2	62.8	28.7	8.5
SI 20	67.0	87.7	1.04	1.09	76.4	63.9	28.0	8.1
SI 110	167.0	223.6 (228)[d]	1.03	1.08	74.7	63.6	26.7	9.7
SI 103	106.0	166.0	1.13	1.19	64.1	65.1	27.3	7.6
SI 111	297.8	496.3	1.03	1.14	60.6	66.8	25.9	7.3
SI 114	76.1	127.2 (140)[d]	1.04	1.07	59.6	66.8	26.7	6.5
SI 109	12.6	22.4	1.04	1.02	56.2	66.6	26.4	7.0
SI 101	68.3	123.0	1.09	1.16	55.5	66.2	25.7	8.1
SI 107	4.0	7.2	1.11	1.03	55.3	66.9	26.0	7.1
SI 22	38.0	74.2	1.04	1.03	51.2	67.3	25.6	7.1
SI 106	6.5	16.9	1.07	1.07	38.5	67.7	24.9	7.4
SI 113	46.6	133.9 (123)[d]	1.04	1.04	34.8	68.9	24.4	6.7
SI 21	17.0	77.3	1.04	1.05	22.0	69.1	23.7	7.2
IS 116[e]	116.4	165.8	1.05	1.04	30.0	68.2	25.8	6.0
IS 117[e]	39.7	106.0	1.03	1.09	74.0	63.8	28.9	7.3
Mixture	PS(63 wt%)+PI				62.3	67.2	26.3	6.5

[a] determined by GPC

[b] apparent microstructure determined by NMR

[c] determined by GPC and NMR

[d] determined by light scattering

[e] prepared by the polymerization of PI block first

and so does trans-1,4 content accordingly. Homo PI's prepared under the similar condition as that of block copolymers always yield a well reproducible microstructure, having 70% cis-1,4, 23% trans-1,4, and 7% 3,4 units, which is consistent with the values found in the literatures.[5,9] The apparent variation found in PS-b-PI copolymers is displayed in Fig. 2 where the contents of three microstructures are plotted against the styrene composition in diblock copolymers. The figure appears to show a good correlation between the microstructure of isoprene units and the block composition. Nonetheless, it turned out to be a well disguised artifact.

In order to confirm the observed trend, we carried out two additional experiments. First, we examined block copolymers prepared by the polymerization of PI block first, i.e., IS 116 and IS 117. If the observed trend is related with the PS block content, the isoprene units in these copolymers should show the same microstructure as that of homo PI since there is no PS block while the PI block is polymerized. Secondly, we examined a mixture of a homo PS and a homo PI, which is again supposed to yield the microstructure of homo PI. From these experiments, we found a rather surprising result that the apparent microstru-
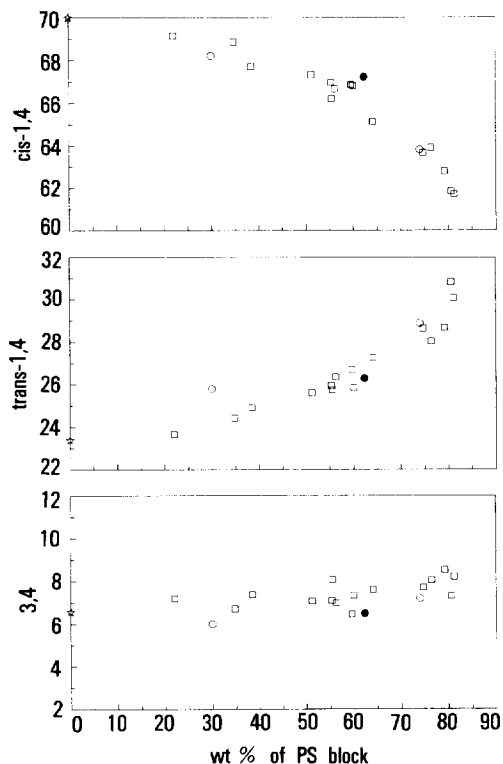
Fig. 2. Apparent microstructures of PS-b-PI diblock copolymers determined by NMR as a function of the block composition. A filled circle represents a mixture of homo polystyrene and polyisoprene and open circles represent IS 116 and 117 which were prepared by reverse monomer addition order. The microstructure of homo polyisoprene is shown by ☆.

ctures of these specimens follow the identical trend to those of SI block copolymers. These results are plotted as a filled circle (Mixture) and open circles (IS 116 and 117) in Fig. 2. It is clear that the apparent microstructures of three different kinds of specimens are indistinguishable. This result unambiguously confirms that the observed trend from Fig. 2 is nothing but an artifact and we reach the conclusion that the microstructure of the diene block is identical with that of homo-PI within experimental uncertainty.

It is difficult to elucidate the cause of the artifact arised from NMR analysis. Uncertainty involved in this NMR analysis seemed to be sufficiently small ; the integrated peak area of the well separated peaks such as aromatic hydrogens from PS block yielded the stoichiometric ratio of corresponding hydrogens better than 2% and the reproducibility was also within 2% when we examined the independently prepared solutions of the same block copolymer. Also, as discussed previously, the NMR measurement yields the accurate composition of the mixture of PS and PI. Therefore, it is more likely that the error was introduced during the deconvolution process although the evidence is yet to be established. Nontheless, it is clear that the microstructure of polyisoprene blocks, prepared by anionic polymerization in benzene by sec-butyl lithium as an initiator, is indistinguishable from that of homo polyisoprene prepared under the same condition. We close this report by calling attention for such a pitfall in practicing the microstructure analysis by NMR measurement.

REFERENCES AND NOTES

1. S. Bywater, *Adv. Polym. Sci.*, **4**, 66 (1965).
2. M. Morton, "Anionic Polymerization Principles and Practice", Academic Press, New York, 1983.
3. H. L. Hsieh, R. C. Farrar, and K. Udipi, *ACS Symp. Ser.*, **166**, 389 (1981).
4. D. J. Worsfold and S. Bywater, *Can. J. Chem.*, **42**, 2884 (1964).
5. M. Morton and L. J. Fetters, *Rubber Chem. Technol.*, **48**, 359 (1975).
6. E. R. Santee, Jr., L. O. Malotky, and M. Morton, *Rubber Chem. Technol.*, **46**, 1156 (1973).
7. A. V. Tobolsky and C. E. Rogers, *J. Polym. Sci.*, **40**, 73 (1959).
8. Y. Tanaka, Y. Takeuchi, M. Kobayashi, and H. Tadokoro, *J. Polym. Sci. Part A-2*, **9**, 48 (1971).
9. F. Schue, D. J. Worsfold, and S. Bywater, *Macromolecules*, **3**, 509 (1970).