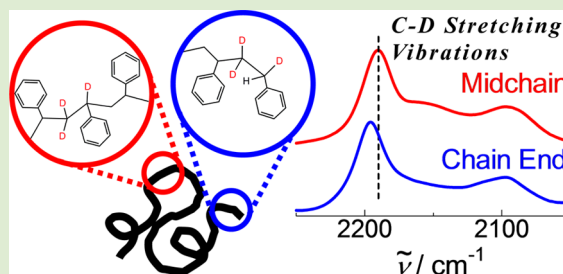


Rapid Stretching Vibration at the Polymer Chain End

Yohei Miwa,^{*,†} Taro Udagawa,[†] Osamu Urakawa,[‡] Shogo Nobukawa,[§] and Shoichi Kutsumizu[†][†]Department of Chemistry and Biomolecular Science, Faculty of Engineering, Gifu University, Yanagido, Gifu 501-1193, Japan[‡]Department of Macromolecular Science, Graduate School of Science, Osaka University, 1-1 Machikaneyama, Toyonaka, Osaka 560-0043, Japan[§]School of Materials Science, Japan Advanced Institute of Science and Technology, 1-1 Asahidai, Nomi, Ishikawa 923-1292, Japan

Supporting Information

ABSTRACT: Stretching vibrations of aliphatic C–D bonds at the chain end and midchain site of partially deuterated polystyrene (PS) were determined by Fourier transform infrared (FT-IR) spectroscopy. It was first found that the stretching vibration at the chain end is more rapid compared to that at the midchain site in the glassy bulk state. The difference in the frequencies of the stretching vibrations at the chain end and midchain site changed little even when the PS was dissolved in toluene. Moreover, the DFT vibrational frequency calculations showed that the C–D bonds at the end site intrinsically have higher vibrational frequency because of lower intramolecular interactions at the chain end. From these results, it was concluded that the main origin for the local rapid stretching vibration at the chain end is not intermolecular effects but reduced intramolecular interactions induced by the discontinuity of the repeating unit at the chain end.



Chain ends are a common and unique local structure of polymers and they often play important roles in the physical properties, e.g., the glass transition,^{1–4} fragility,^{2,4–6} surface,⁷ and interface⁸ properties, etc., of polymeric materials. Therefore, understanding the properties of chain ends is a fundamental and important subject in polymer science. The discontinuity of the repeating unit affects both inter- and intramolecular properties at chain ends: The segmental density, entanglements, steric hindrances, etc. at the chain end are expected to be reduced compared to the midchain site. Therefore, it is generally recognized that chain ends locally have higher molecular mobility compared to the midchain site.

For example, by means of specular neutron reflectivity, Welp et al. showed that the diffusion of the end segment of polystyrene (PS) is higher compared to the center segment because of reduced entanglements around chain ends.⁹ As for the segmental motion, Lund et al. and Miwa et al. studied the segmental mobility of chain ends of PS above the glass transition temperature (T_g) using dielectric spectroscopy^{10–12} and electron spin resonance^{13,14} techniques, respectively. They showed that the rate of segmental motion at the chain end is approximately double compared to the midchain segments at $T_g + 50$ K. In this case, reduced segmental density around chain ends was considered as the main origin of the higher segmental mobility. However, the difference in the segmental mobilities at the chain end and midchain segment decreased approaching the T_g .^{10–12} Moreover, the local T_g around chain ends was comparable to the bulk T_g .¹⁴ These results indicate that the mobilities of chain ends and midchain segments are averaged out in the vicinity of the T_g due to the enhanced cooperativities between neighboring segments.

The above studies clearly show that respective motional modes are affected by different features of chain ends depending on the magnitude and mechanism of the motion; the motions with relatively large magnitude, such as the diffusion and segmental motion, at the chain end are mainly affected by the intermolecular properties around the chain ends. On the other hand, properties of local motions with small magnitude, such as vibrations of chemical bonds, at chain ends are totally unknown.

The present study is the first work on the direct determination of the stretching vibration at chain ends of polymers. In the present study, we employed position-selective deuteration for the recognition of local vibrational motions, and as shown in Figure 1, partially deuterated PSs at the chain end and midchain, denoted as D3-E-PS and D3-M-PS, respectively, were synthesized. As shown in Table 1, we first detected the more rapid stretching vibration of the aliphatic C–D bond at the chain end than that at the midchain site. Is this caused by intermolecular properties, e.g., reduced segmental density, around chain ends or intramolecular ones at the chain end? The subject of this work is to reveal the main origin of the rapid stretching vibration at the chain end.

It is well-known that the aliphatic C–D stretching vibrations are observed in the range 2000–2300 cm^{-1} . As shown in Figure 2(B), nondeuterated PS does not show any strong IR absorptions in this range; therefore, small IR absorptions of

Received: December 7, 2013

Accepted: January 8, 2014

Published: January 10, 2014

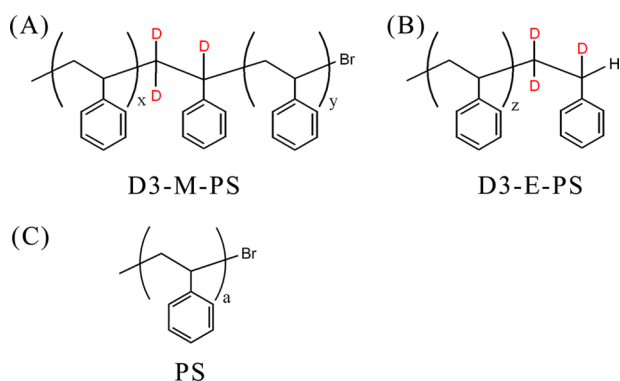


Figure 1. Chemical structures of partially deuterated PSs at midchain (A) and chain end (B) and nondeuterated PS (C).

Table 1. Experimental Frequencies for C–D Stretching Vibrations for Each Sample

sample	$\nu_{as,CD_2}/\text{cm}^{-1}$	$\nu_{s,CD_2}/\text{cm}^{-1}$	ν_{CD}/cm^{-1}
D3-M-PS	2191.2	2094.3	2152
D3-E-PS	2196.5	2099.0	2163
difference ^a	5.3	4.7	11
D3-M-PS/toluene ^b	2191.7	2094.5	2155
D3-E-PS/toluene ^b	2197.1	2099.4	2168
difference ^a	5.4	4.9	13

^aThe difference between D3-M-PS and D3-E-PS for each band. ^bThe concentration is 10 wt %.

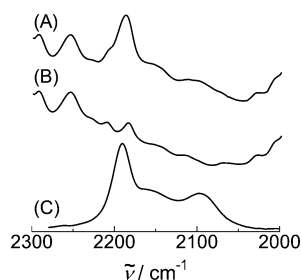


Figure 2. Original FT-IR spectra for D3-M-PS (A) and nondeuterated PS (B) in the bulk state and the differential spectrum (C).

the deuterated sites in the specimens are detectable. In the present work, the differential spectrum between the partially deuterated PS and nondeuterated PS was obtained as shown in Figure 2(C). In Figure 3, differential FT-IR spectra for the D3-M-PS and D3-E-PS in the bulk state and those in the toluene solution with the concentration of 10 wt % measured at 298 K are shown. The partially deuterated PS shows three bands, asymmetric and symmetric stretching vibrations of CD_2 (ν_{as,CD_2} and ν_{s,CD_2}) and stretching vibration of CD (ν_{CD}) at ca. 2191, 2094, and 2152 cm^{-1} , respectively. An example of the band deconvolution with the Voigt function is shown in Figure 3(A). The frequencies of ν_{as,CD_2} , ν_{s,CD_2} , and ν_{CD} obtained by the band deconvolution and the differences in those for the D3-M-PS and D3-E-PS in the bulk and toluene solution are listed in Table 1. The D3-E-PS shows distinctly higher frequencies compared to the D3-M-PS in the bulk state. This indicates that the stretching vibrations at the chain end are more rapid compared to those at the midchain site in the glassy bulk state.

Sung et al. showed that the rate of the photoisomerization of azobenzene attached at the chain end of PS is higher than that attached at the midchain site at room temperature in the bulk

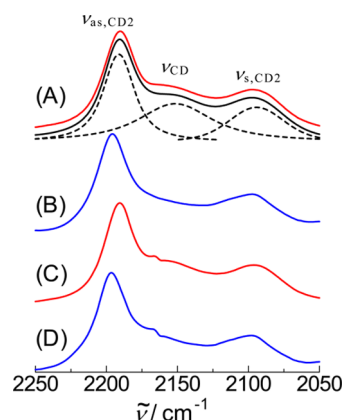


Figure 3. Differential FT-IR spectra for D3-M-PS (A) and D3-E-PS (B) in the bulk state and D3-M-PS (C) and D3-E-PS (D) in the toluene solution with the concentration of 10 wt %, respectively. An example of the band deconvolution of the experimental spectrum is shown in (A). Broken lines are each component, and the black solid line is the sum of broken lines.

state.¹⁵ However, the difference in the rate of the photoisomerization at the chain end and midchain site became negligible when the PS was dissolved in toluene. From this result, they considered that the effect of the label position along the chain on the photoisomerization is small; therefore, they concluded that the more rapid photoisomerization at the chain end in the glassy bulk state is due to the lower segmental density around the chain end. Namely, the photoisomerization at the chain end was mainly affected by the “intermolecular” property around the chain end in the glassy bulk state. On the other hand, as shown in Table 1, the differences in the stretching vibrational frequencies for the D3-E-PS and D3-M-PS are essentially the same in the bulk state and toluene solution. This result is clearly suggesting that the effect of intermolecular interactions on the stretching vibration is small and the main origin of the rapid C–D stretching vibrations at the chain ends is “intramolecular” properties at the chain end.

To verify if the stretching vibrations of the C–D bond at the chain end of the PS are intrinsically rapid without intermolecular interactions, the DFT harmonic vibrational frequency calculations were performed. In this case, a single trimer of styrene partially deuterated at the end or center site in a vacuum atmosphere was used for the calculation (Figure 4),

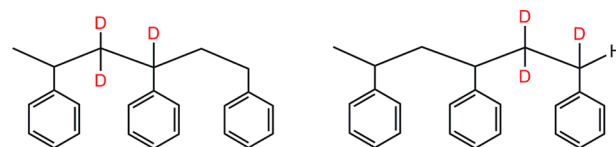


Figure 4. Model molecules used for DFT harmonic vibrational frequency calculations.

and thus, the effect of intermolecular interactions was eliminated. The optimization of the molecular structure and determination of the vibrational frequencies were performed by means of M06 DFT/6-31G* and B3LYP DFT/6-31G* methods in the GAUSSIAN09 program package.¹⁶ As shown in Figure S1 (Supporting Information), syndiotactic, heterotactic, and isotactic triads in the PS are determined to 29, 69, and 2%, respectively. Therefore, the calculations were separately carried out for each tacticity. The optimized

structures of each stereoisomer are shown in Figures S2 and S3 (Supporting Information). The M06 DFT/6-31G* and B3LYP DFT/6-31G* give essentially the same conclusion; therefore, only the vibrational frequencies obtained by the M06 DFT/6-31G* are listed in Table 2. The result of the B3LYP DFT/6-

Table 2. Frequencies of C–D Stretching Vibrations for the Isolated Styrene Trimer Computed at the M06 DFT/6-31G*

tacticity	deuterated site	$\nu_{as,CD_2}/\text{cm}^{-1}$	$\nu_{s,CD_2}/\text{cm}^{-1}$	ν_{CD}/cm^{-1}
isotactic	center	2270.4	2197.4	2200.0
	end	2273.2	2200.1	2237.2
heterotactic	center	2265.5	2192.7	2209.3
	end	2270.4	2195.9	2252.0
syndiotactic	center	2262.5	2188.4	2230.8
	end	2269.7	2195.0	2251.0

31G* is shown in the Supporting Information. The calculated vibrational frequencies are typically higher than the experimental ones because the real vibrations are anharmonic, whereas harmonic vibration is assumed in the calculation. As is well-known, the frequencies of the methylene symmetric and asymmetric stretching vibrations are sensitive to the conformation of chain molecules.¹⁷ In fact, the calculated frequencies are dependent on the tacticity. Here, the conformation of the optimized structure differed for each stereoisomer. This indicates that the vibrational frequency of the aliphatic C–D bond is affected by the intramolecular interactions. Importantly, the stretching vibrations at the end are more rapid compared to those at the center site in either stereoisomer. Moreover, the rapid stretching vibrations are shown for only the end monomer unit in the syndiotactic 9mer of styrene (Table S2, Supporting Information). These results clearly show that the aliphatic C–D bonds at the chain end intrinsically have higher vibrational frequencies compared to those at the midchain site due to lower intramolecular interactions at the chain end.

In conclusion, we have first detected the more rapid stretching vibration at the polymer chain end compared to that at the midchain site in the glassy bulk state using the partially deuterated PS. The differences in the stretching vibrational frequencies at the chain end and midchain site changed little even when the PS was dissolved in the toluene solution where the intermolecular interactions are largely different from the glassy bulk state. Moreover, the DFT vibrational frequency calculations showed that the aliphatic C–D bonds at the end site of the isolated styrene trimer intrinsically have more rapid stretching vibrations because of lower intramolecular interactions at the terminal. These data provide compelling evidence that the main origin of the local rapid stretching vibration at the chain end is not the intermolecular effect but the intramolecular property of the chain end. Reduced intramolecular attractive interactions at the chain end induced by the discontinuity of the repeating unit are reasonably considered as the specific reason.

EXPERIMENTAL SECTION

Preparation of Partially Deuterated PS. The D3-M-PS was prepared via a random copolymerization of styrene and deuterated styrene with atom transfer radical polymerization (ATRP).¹⁸ The concentration of deuterated styrene was 2 mol %. The number average molecular weight (M_n) and the molecular weight distribution (M_w/M_n) are 11.0 kDa and 1.16, respectively. The D3-E-PS was prepared via an addition of a deuterated styrene to a PS chain end using ATRP.

The nondeuterated PS with the M_n and M_w/M_n of 11.4 kDa and 1.25, respectively, was first polymerized by ATRP. After the purification of the PS, a deuterated styrene was further added to the chain end of the PS. The addition of less than one deuterated styrene to each PS chain end was controlled by feeding of deuterated styrene. After the reaction, the PS was further reacted with tributyltin hydride to remove the bromo at the chain end.¹⁹ The M_n and M_w/M_n were changed little by the addition of the deuterated styrene. The tacticity of the PS was determined by ¹³C NMR.²⁰

FT-IR Measurements. FT-IR measurements were performed on the transmittance mode at 2 cm^{-1} optical resolution in a nitrogen atmosphere at 298 K. The samples placed between two KBr plates were annealed at 393 K for one hour and cooled to room temperature at the rate of 1 K min^{-1} in a nitrogen atmosphere. For the FT-IR measurement on the PS/toluene solution, the solution was injected between KBr plates with a 2 mm spacer.

Calculations. All calculations were performed by means of the GAUSSIAN09 program package. Geometrical parameters were minimized without any constraint on the M06 DFT/6-31G* and B3LYP DFT/6-31G* methods; the optimized molecular structure and vibrational frequencies were determined.

ASSOCIATED CONTENT

Supporting Information

Experimental details and result of the B3LYP DFT/6-31G* calculation. This material is available free of charge via the Internet at <http://pubs.acs.org>.

AUTHOR INFORMATION

Corresponding Author

*E-mail: y_miwa@gifu-u.ac.jp.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This study was supported by Japan Society for the Promotion of Science (JSPS), Grant-in-Aid for Young Scientists (B), 25810072, 2013

REFERENCES

- (1) Fox, T. G.; Flory, P. J. *J. Appl. Phys.* **1950**, *21*, 581–591.
- (2) Santangelo, P. G.; Roland, C. M. *Macromolecules* **1998**, *31*, 4581–4585.
- (3) Rizos, A. K.; Ngai, K. L. *Macromolecules* **1998**, *31*, 6217–6225.
- (4) Robertson, C. G.; Roland, C. M. *J. Polym. Sci., Part B: Polym. Phys.* **2004**, *42*, 2604–2611.
- (5) Kunal, K.; Robertson, C. G.; Pawlus, S.; Hahn, S. F.; Sokolov, A. P. *Macromolecules* **2008**, *41*, 7232–7238.
- (6) Bormuth, A.; Henritzi, P.; Vogel, M. *Macromolecules* **2010**, *43*, 8985–8992.
- (7) Kajiyama, T.; Tanaka, K.; Takahara, A. *Macromolecules* **1997**, *30*, 280–285.
- (8) Tanaka, K.; Tateishi, Y.; Okada, Y.; Nagamura, T.; Doi, M.; Morita, H. *J. Phys. Chem. B* **2009**, *113*, 4571–4577.
- (9) Welp, K. A.; Wool, R. P.; Agrawal, G.; Satija, S. K.; Pispas, S.; Mays, J. *Macromolecules* **1999**, *32*, 5217–5138.
- (10) Lund, R.; Plaza-García, S.; Alegría, A.; Colmenero, J.; Janoski, J.; Chowdhury, S. R.; Quirk, R. P. *Macromolecules* **2009**, *42*, 8875–8881.
- (11) Lund, R.; Plaza-García, S.; Alegría, A.; Colmenero, J.; Janoski, J.; Chowdhury, S. R.; Quirk, R. P. *J. Non-Cryst. Solids* **2010**, *356*, 676–679.
- (12) Plaza-García, S.; Alegría, A.; Lund, R.; Alegría, A.; Colmenero, J.; Janoski, J.; Quirk, R. P. *Macromolecules* **2011**, *44*, 7810–7819.
- (13) Miwa, Y.; Shimada, S.; Urakawa, O.; Nobukawa, S. *Macromolecules* **2010**, *43*, 7192–7199.
- (14) Miwa, Y.; Urakawa, O.; Doi, A.; Yamamoto, K.; Nobukawa, S. *J. Phys. Chem. B* **2012**, *116*, 1282–1288.

(15) Sung, C. S. P.; Gold, I. R.; Turro, N. J. *Macromolecules* **1984**, *17*, 1447–1451.

(16) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, H.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. A.; Staroverov, V. N.; Keith, T.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. *Gaussian 09*, Revision B.01; Gaussian, Inc.: Wallingford, CT, 2010.

(17) Badia, A.; Cuccia, L.; Demers, L.; Morin, F.; Lennox, R. B. *J. Am. Chem. Soc.* **1997**, *119*, 2682–2692.

(18) Matyjaszewski, K.; Patten, T. E.; Xia, J. *J. Am. Chem. Soc.* **1997**, *119*, 674–680.

(19) Coessens, V.; Matyjaszewski, K. *Macromol. Rapid Commun.* **1999**, *20*, 66–70.

(20) Smith, L. M.; Coote, M. L. *J. Polym. Sci., Part A: Polym. Chem.* **2013**, *51*, 3351–3358.