High-Pressure Infrared Spectroscopy of Molecular Conformations of Diblock Oligomers α-Decyl-ω-hydroxyoligo(oxyethylene)s in the Solid State

Koichi Fukuhara,* Maki Shoden, and Hiroatsu Matsuura
Department of Chemistry, Graduate School of Science, Hiroshima University, Kagamiyama,
Higashi-Hiroshima 739-8526

(Received September 6, 2000; CL-000834)

Molecular conformations of diblock oligomers $H(CH_2)_{10}$-$(OCH_2CH_2)_mOH$ (m = 2, 4, and 6) in the solid state were studied at high pressures (1–2 GPa) by IR spectroscopy. The oxyethylene chain in the oligomers with m = 2 and 4 assumes the all-*trans* planar conformation, while that in the oligomer with m = 6 assumes the helical conformation. The stabilized planar structure of the oxyethylene chain at high pressures is explained by increased intermolecular cohesive forces in the alkyl block reinforced by external pressures.

The oxyethylene chain assumes a helical form with a repeated *trans–gauche–trans* conformation for the O–CH_2–CH_2–O segment in the solid state.[1] Another form of the oxyethylene chain in the solid state is an all-*trans* planar form, which was found for some of the alkyl–oxyethylene diblock oligomers $H(CH_2)_n$-$(OCH_2CH_2)_mOH$ (abbreviated as C_nE_m) and the alkyl–oxyethylene–alkyl triblock oligomers $H(CH_2)_n(OCH_2CH_2)_mO(CH_2)_{n'}H$-($C_nE_mC_{n'}$) in the solid state at liquid nitrogen temperature.[2–11] It is interesting to note that the conformation of the oxyethylene chain in the C_nE_m oligomers changes from the planar form to the helical form with an increase in the number of oxyethylene units (m). For example, the conformation of the oxyethylene block of the $C_{10}E_m$ oligomers with $m \leq 3$ is all-*trans* planar, while the conformation of the oxyethylene block of the oligomers with $m \geq 4$ is helical.[4–6] Such chain-length dependent conformational behavior is associated with the different rates of crystallization of the constituent blocks of the C_nE_m oligomers on cooling of the liquid substances.[11]

Pressure is another important factor, besides temperature, that controls crystallization of substances.[12] Pressure-induced crystallization has actually been applied to polymers,[13–16] polymer blends,[17–20] amorphous solids,[21] and proteins.[22] It is expected that pressure affects the rates of crystallization of the constituent blocks of the C_nE_m oligomers, giving rise to chain-length dependent conformational polymorphism which may be different from that which occurs in the cooling process. In this letter, we report the conformational behavior of the diblock oligomers $C_{10}E_2$, $C_{10}E_4$, and $C_{10}E_6$ in the solid state at high pressures.

$C_{10}E_2$ was synthesized in our laboratry,[4,5] while $C_{10}E_4$ and $C_{10}E_6$ were supplied by Nikko Chemicals Co. All materials were purified by vacuum distillation. The IR spectra of the $C_{10}E_m$ oligomers solidified by pressure were measured at ambient temperature at 1–2 GPa by using a high-pressure diamond anvil cell (DAC). Sample paste of liquid $C_{10}E_m$ mixed with calcium fluoride powder (a pressure-transmitting medium) was placed inside a 0.3-mm diameter pressure chamber bored in a 0.3-mm thick Inconel gasket mounted on the DAC. The reproducibility of the observed spectra was confirmed by the measurements on different samples of the same compound. Pressure was monitored by using luminescence of a ruby chip located in the pressure chamber.[23] The IR spectra of $C_{10}E_m$ (m = 2, 4, and 6) solidified by cooling were also measured at liquid nitrogen temperature at ambient pressure for comparison with the high-pressure spectra. The spectra were recorded on a JASCO FT/IR-620 Fourier transform spectrometer with a spectral resolution of 4 cm^{-1}.

Figure 1 shows the IR spectra of $C_{10}E_2$, $C_{10}E_4$, and $C_{10}E_6$ solidified by pressure and cooling. When pressure was applied to the liquid samples of $C_{10}E_m$, the drastic spectral changes were observed at about 0.5 GPa, with which the solidification of the samples was confirmed. Pressure-solidified $C_{10}E_4$ gave an IR spectrum different from the spectrum obtained by cooling of the liquid. $C_{10}E_2$ and $C_{10}E_6$ solidified by pressure gave spectra essentially the same as those solidified by cooling. The molecular conformations of the pressure-solidified $C_{10}E_m$

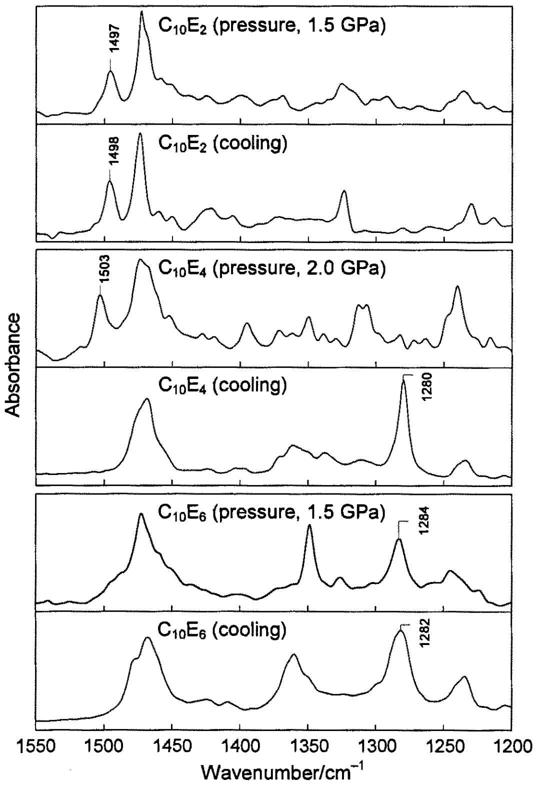

Figure 1. IR spectra of $C_{10}E_m$ (m = 2, 4, and 6) solidified by pressure and cooling. The pressure-solidified substances were measured at the pressures indicated in the figure and all the cooling-solidified substances were measured at liquid nitrogen temperature.

Copyright © 2000 The Chemical Society of Japan

oligomers were examined by comparing their spectra with the spectra of the cooling-solidified oligomers, for which the molecular conformations have been established in our Raman spectroscopic studies.[4–6]

Comparison of the IR spectra in Figure 1 shows that the spectra are classified into two types according to the characteristic spectral features. In the spectra of $C_{10}E_2$ (solidified by pressure and cooling) and $C_{10}E_4$ (pressure), a conspicuous band was observed around 1500 cm^{-1}. In the spectra of $C_{10}E_4$ (cooling) and $C_{10}E_6$ (pressure and cooling), on the other hand, a strong, prominent band was observed at about 1280 cm^{-1}. These spectral observations indicate that the two spectral types correspond to two types of molecular forms. The less important differences of the IR spectra between the pressure-solidified and the cooling-solidified substances of $C_{10}E_2$ or $C_{10}E_6$ are explained by different intermolecular forces acting in the relevant solids.

The molecular form of cooling-solidified $C_{10}E_2$ at liquid nitrogen temperature has been shown to be a highly extended γ form,[4–6] i.e., the all-*trans* conformation except for the terminal OCH_2–CH_2OH part in the *gauche* conformation. The molecular form of cooling-solidified $C_{10}E_4$ and $C_{10}E_6$ has been shown to be the β form,[4–6] in which the alkyl chain assumes the all-*trans* conformation except for the CH_2CH_2–CH_2O part and the entire oxyethylene chain assumes a helical conformation. These previous conformational analyses were performed on the basis of Raman spectroscopic observations with the aid of the established conformational key bands.[24]

In the light of the previous results, the molecular form of pressure-solidified $C_{10}E_2$ and $C_{10}E_4$ is determined to be the γ form. The characteristic bands at 1497 cm^{-1} for $C_{10}E_2$ and 1503 cm^{-1} for $C_{10}E_4$ are assigned to the CH_2 scissoring mode of the *trans* CH_2OCH_2–CH_2OCH_2 segment.[5] The molecular form of pressure-solidified $C_{10}E_6$, on the other hand, is determined to be the β form. The strong band at 1284 cm^{-1} for this oligomer is assigned to the CH_2 twisting mode and is a conformational key band of the helical oxyethylene chain.[11,24] The results of the molecular forms of the pressure-solidified and cooling-solidified $C_{10}E_m$ oligomers are summarized in Table 1. It is important to note that for $C_{10}E_4$ the pressure solidification gave the highly extended γ form, while the cooling solidification gave the β form with the helical oxyethylene chain.

Table 1. Molecular forms of $C_{10}E_m$ (m = 2, 4, and 6) in the solid state

Method of solidification	$C_{10}E_2$	$C_{10}E_4$	$C_{10}E_6$
Pressure	γ	γ	β
Cooling	γ	β	β

Our previous studies on the cooling-solidified C_nE_m oligomers have shown that the number of oxyethylene units in the all-*trans* planar conformation is at most three.[4–6] The chain-length dependent conformational behavior of the C_nE_m and $C_nE_mC_{n'}$ oligomers solidified by cooling has been interpreted in terms of the conformational competition between the alkyl chain and the oxyethylene chain, namely the competition between the intermolecular packing or cohesive energy of the alkyl block and the intramolecular conformational energy of the oxyethylene chain.[11]

In the case of pressure solidification, the length of the all-*trans* planar oxyethylene chain in the C_nE_m oligomers is extended to four monomeric units, as revealed in the present work. The literature[25] indicates that the change in density of the alkyl chain in going from the liquid phase to the solid phase is larger than that of the oxyethylene chain. Accordingly, pressure should yield stronger cohesive forces in the alkyl block of the C_nE_m oligomers than in the oxyethylene block. This consideration leads to the conclusion that the planar zigzag structure of the oxyethylene chain with four monomeric units attained at high pressures is associated with the preferential crystallization of the alkyl block and is stabilized by increased intermolecular cohesive forces in the alkyl block reinforced by external pressures.

This work was partially supported by a Grant-in-Aid for Scientific Research No. 10640492 from the Ministry of Education, Science, Sports, and Culture, Japan.

References and Notes

1 H. Tadokoro, "Structure of Crystalline Polymers," Wiley, New York (1979).
2 H. Matsuura and K. Fukuhara, *Chem. Lett.*, **1984**, 933.
3 H. Matsuura and K. Fukuhara, *J. Phys. Chem.*, **90**, 3057 (1986).
4 K. Fukuhara and H. Matsuura, *Chem. Lett.*, **1987**, 1549.
5 H. Matsuura and K. Fukuhara, *J. Phys. Chem.*, **91**, 6139 (1987).
6 H. Matsuura, K. Fukuhara, S. Masatoki, and M. Sakakibara, *J. Am. Chem. Soc.*, **113**, 1193 (1991).
7 S. Masatoki, K. Fukuhara, and H. Matsuura, *J. Chem. Soc., Faraday Trans.*, **89**, 4079 (1993).
8 K. Fukuhara, T. Sagawa, S. Kihara, and H. Matsuura, *J. Mol. Struct.*, **379**, 197 (1996).
9 K. Fukuhara, F. Sakogawa, and H. Matsuura, *J. Mol. Struct.*, **405**, 123 (1997).
10 K. Fukuhara, S. Masatoki, T. Yonemitsu, and H. Matsuura, *J. Mol. Struct.*, **444**, 69 (1998).
11 K. Fukuhara, K. Hashiwata, K. Takayama, and H. Matsuura, *J. Mol. Struct.*, **523**, 269 (2000).
12 P. W. Bridgman, *Proc. Am. Acad. Arts Sci.*, **51**, 55 (1915).
13 A. Keller, G. Goldbeck-Wood, and M. Hikosaka, *Faraday Discuss.*, **95**, 109 (1993).
14 W. Li and M. Radosz, *Macromolecules*, **26**, 1417 (1993).
15 J. A. Parker, D. C. Bassett, R. H. Olley, and P. Jaaskelainen, *Polymer*, **35**, 4140 (1994).
16 S. Brückner, P. J. Phillips, K. Mezghani, and S. V. Meille, *Macromol. Rapid Commun.*, **18**, 1 (1997).
17 K. D. Petrenko, V. P. Privalko, and Yu. S. Lipatov, *Polymer*, **31**, 1283 (1990).
18 C. Nakafuku, H. Nakagawa, M. Yasuniwa, and S. Tsubakihara, *Polymer*, **32**, 696 (1991).
19 C. Nakafuku and N. Toyonaga, *Polymer*, **33**, 2370 (1992).
20 C. Nakafuku, *Polymer*, **34**, 4166 (1993).
21 F. Ye and K. Lu, *Phys. Rev. B*, **60**, 7018 (1999).
22 K. Visuri, E. Kaipainen, J. Kivimäki, H. Niemi, M. Leisola, and S. Palosaari, *Bio/technology*, **8**, 547 (1990).
23 J. R. Ferraro, "Vibrational Spectroscopy at High External Pressures," Academic Press, London (1984), p. 51.
24 H. Matsuura and K. Fukuhara, *J. Polym. Sci., Part B*, **24**, 1383 (1986).
25 "CRC Handbook of Chemistry and Physics," 81st ed., ed. by D. R. Lide, CRC Press, Boca Raton (2000).