CHEMISTRY LETTERS, pp. 169-172, 1978. Published by the Chemical Society of Japan

MOLECULAR CONFORMATIONS OF TRI- THROUGH PENTAMETHYLENE GLYCOL DIMETHYL ETHERS AS MODEL COMPOUNDS OF POLYETHERS

Hiroatsu MATSUURA and Hiromu MURATA
Department of Chemistry, Faculty of Science, Hiroshima University,
Higashisenda-machi, Hiroshima 730

Raman and infrared spectra were measured for $CH_3O(CH_2)_nOCH_3$ (n=3–5) as model compounds of polyethers $[-O(CH_2)_n-]_p$. The spectral observations, combined with the normal coordinate treatment, indicated that the conformational stabilities of the model compounds are closely related to the chain conformations of the polymers.

Crystal structures of a series of polyethers $[-O(CH_2)_n-]_p$ have been studied by the X-ray diffraction method by Tadokoro et al.[1] For analyzing the chain conformations and the conformational stabilities of these polymers, detailed studies on the model compounds $CH_3O(CH_2)_nOCH_3$ by the vibrational spectroscopic method are important, since the conformations of various simple aliphatic ethers have been thoroughly investigated by this method and knowledge on the conformational stabilities has been accumulated.[2,3] The previous study[3] on the vibrational spectra and the rotational isomerism of $CH_3O(CH_2)_2OCH_3$ indicated that the stabilities of various conformers of this compound are in fact closely related to the chain conformation of poly(oxyethylene) $[-O(CH_2)_2-]_p$. In this letter, we report on the results of spectral analyses of $CH_3O(CH_2)_nOCH_3$ (n=3–5) as model compounds of polyethers $[-O(CH_2)_n-]_p$ and discuss the conformational stability in relation to the chain conformations of the polymers.

In the present study, the Raman and infrared spectra of the model compounds were measured in the liquid state at room and lower temperatures, the glassy state (only for n=3), and the crystalline state. The normal coordinates were treated for various conformers of these compounds by utilizing the force constants determined previously for aliphatic ethers.[4]

Figure 1 shows the Raman spectra of the model compounds in the various states in the region 1000–700 cm^{-1} together with the calculated frequencies for the typical conformers. In this frequency region, the bands due to the CH_2-O stretching vibrations and the CH_2 rocking vibrations are observed, the former vibrations giving much stronger Raman intensities than the latter vibrations. The results of the normal coordinate treatment indicate that the CH_2-O stretching frequencies are sensitive to the skeletal conformation of the molecule, particularly the conformation about the $CH_2CH_2-CH_2O$ axis. Accordingly, the CH_2-O stretching bands are good key bands for analyzing the Raman spectra and are of use in identifying the conformers existing in each state. As seen in Fig. 1, many bands are observed in the liquid state but only a few persist in the crystalline state. For the trimethylene compound (n=3), the strongest band of the liquid state at 875 cm^{-1} remains to be the strongest in the crystalline state, suggesting that one of the dominant conformers in the liquid state is also a conformer existing in the crystalline state. On the other hand, in cases of the tetramethylene compound (n=4) and the pentamethylene compound (n=5), the strongest liquid-state bands at 840 and 868 cm^{-1}, respectively, disappear in the crystalline state and the bands at 950 and 943 cm^{-1}, not prominent in the liquid-state spectra, persist in the crystalline state with stronger intensities. All of the bands mentioned above are evidently due to the skeletal stretching modes associated primarily with the CH_2–O stretching vibrations and the very strong intensities indicate that they are totally symmetrical modes.

With reference to the results of the normal coordinate calculations (Fig. 1) in conjunction with the above spectral observations, it is clearly shown that the conformer of the trimethylene compound existing in the crystalline state is the trans-gauche-gauche-trans form (TGGT form) for a series of the CH_3O–CH_2–CH_2–CH_2–OCH_3 bonds, that of the tetramethylene compound is the TTTTT form, and that of the pentamethylene compound is the TTTTTT form. The planar molecular structure of the tetra- and pentamethylene compounds is further evidenced by the observation of the very intense Raman bands at 301 and 254 cm^{-1}, respectively, which are assigned to the accordion-like modes of the extended forms. The trimethylene compound, on the other hand, exhibits no such band in the skeletal deformation region.

Two groups of strong Raman bands are observed in the liquid state at 960–930 and 840–820 cm^{-1} for the tetramethylene compound and at 970–940 and 880–850 cm^{-1} for the pentamethylene compound. According to the results of the normal coordinate calculations, most of the bands belonging to the higher-frequency group and all of the bands belonging to the lower-

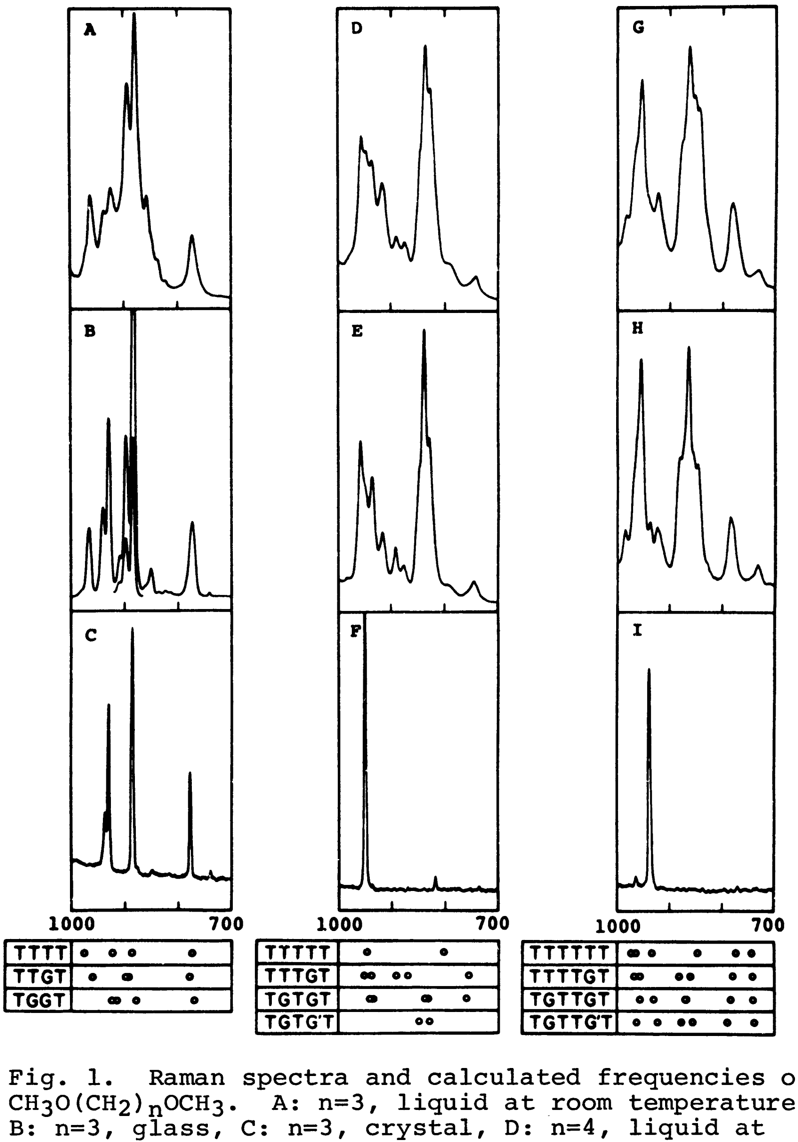

Fig. 1. Raman spectra and calculated frequencies of $CH_3O(CH_2)_nOCH_3$. A: n=3, liquid at room temperature, B: n=3, glass, C: n=3, crystal, D: n=4, liquid at room temperature, E: n=4, liquid at -50°C, F: n=4, crystal, G: n=5, liquid at room temperature, H: n=5, liquid at -40°C, I: n=5, crystal.

frequency group are associated primarily with the CH_2—O stretching vibrations of the CH_2CH_2—CH_2O part in the gauche conformation (see Fig. 1). The corresponding bands of the trimethylene compound are observed at 928 and 884 cm^{-1} in the crystalline state. The CH_2—O stretching bands for the CH_2CH_2—CH_2O part in the trans conformation appear in the region 970—930 cm^{-1}. Of the two CH_2—O stretching vibrations in a molecule with the trans CH_2CH_2—CH_2O groups, the symmetrical mode is strong in the Raman spectra but the antisymmetrical mode is very weak or inactive in the Raman effect. Thus, for molecules of the type $CH_3O(CH_2)_nOCH_3$ a strong Raman band in the region 900—800 cm^{-1} is a key band of the gauche conformation of the CH_2CH_2—CH_2O part. In fact, the molecule of $CH_3O(CH_2)_2OCH_3$ which takes the TGT form in the crystalline state gives a very strong Raman band at 857 cm^{-1}.$^{3)}$

The temperature dependence of the Raman intensities was measured in the liquid state in order to examine relative conformational stabilities among possible rotational isomers. The bands of the trimethylene compound at 875 and 923 cm^{-1}, both persisting in the crystalline state, become prominently stronger as compared with other bands as temperature is lowered. The intensities of some other bands such as those at 337 and 470 cm^{-1}, which remain on crystallization, are also much stronger at lower temperatures. Accordingly, the TGGT form is the most stable in the liquid state. For the tetramethylene compound, the Raman intensity of the 840 cm^{-1} band is most largely enhanced in the liquid state at lower temperatures. This band, together with other intensity-enhanced bands such as those at 461 and 580 cm^{-1}, is assigned to the TGTGT form and/or the TGTG'T form with reference to the results of the normal coordinate calculations. The bands of the pentamethylene compound in the liquid state at 868 and 958 cm^{-1} in the CH_2—O stretching region and those at 401 and 561 cm^{-1} in the skeletal deformation region are stronger, as compared with other bands, at lower temperatures. These bands are readily assigned to the TGTTGT and TGTTG'T forms on the basis of the normal coordinate analyses, although many conformers are expected for this compound. It is important to note that the most stable isomer in the liquid state takes the gauche conformation about the CH_2CH_2—CH_2O axis for any of the three model compounds in common. The stable isomer of $CH_3O(CH_2)_2OCH_3$ in the liquid state has been found to be the TGT form with the gauche OCH_2—CH_2O group.$^{3)}$ Thus, the high stability of the gauche conformation about the CH_2CH_2—CH_2O and OCH_2—CH_2O axes in a series of compounds $CH_3O(CH_2)_nOCH_3$ is now established. This result is also consistent with the previous finding that the gauche conformation about the same axis in $CH_3O\cdot(CH_2)_2CH_3$, $CH_3O(CH_2)_3CH_3$, and $CH_3CH_2O(CH_2)_2CH_3$ is as stable as the trans conformation.$^{2)}$

The stable conformations of the polyethers and the corresponding model compounds are given in Table 1. The conformers of the model compounds existing in the crystalline state correspond completely to the chain conformations of the polymers in the most stable crystal modification. This fact suggests that the stability of the polymer-chain conformation in crystal is determined almost within a chain length of the monomer unit. Thus, the molecules corresponding to the chemical structure of the monomer unit of the polymers are shown to be good model compounds for studying more extensively the nature of the polymer structure. The most stable conformer of the model compounds in the liquid state is not always the same as the isomer existing in the crystalline state. This implies that the conformational stability in the crystalline state is associated, to fairly large extent, with the intermolecular forces in addition to the intramolecular forces. The stable conformations in the liquid state, where the intramolecular forces may well overwhelm the intermolecular forces, are likely to be determined by the combined stabilities of local structures in the molecule. On the other hand, the molecular structure in crystal is specified more significantly by the longer-range forces of the intermolecular as well as the intramolecular interactions. In the case of the polyethers discussed in the present study, the gauche conformation of the $CH_2CH_2-CH_2O$ part is expected to be further stabilized in appropriate solvents where the interactions between the polymer molecules and between the polymer molecule and the solvent molecule are small. More detailed studies on the model compounds, which are now in progress, will make it possible to discuss more closely conformational stabilities of the polyethers.

Table 1. Molecular conformations of polyethers and model compounds

Polymer[a]	Model compound	
	Crystalline state	Liquid state[b]
$-CH_2(-O-CH_2-CH_2-)_pO-$ T G T (more stable) T T T	$CH_3-O-CH_2-CH_2-O-CH_3$[c] T G T	TGT and others
$-CH_2(-O-CH_2-CH_2-CH_2-)_pO-$ T G G T (most stable) T T $\bar{G}$ T T T T T	$CH_3-O-CH_2-CH_2-CH_2-O-CH_3$ T G G T	TGGT and others
$-CH_2(-O-CH_2-CH_2-CH_2-CH_2-)_pO-$ T T T T T	$CH_3-O-CH_2-CH_2-CH_2-CH_2-O-CH_3$ T T T T T	TGTGT, TGTG'T and others
	$CH_3-O-CH_2-CH_2-CH_2-CH_2-CH_2-O-CH_3$ T T T T T T	TGTTGT, TGTTG'T and others

a) Ref. 1. b) The conformers specifically indicated are more stable than others.
c) Ref. 3.

References

1) K. Imada, T. Miyakawa, Y. Chatani, H. Tadokoro, and S. Murahashi, Makromol. Chem., 83, 113 (1965); H. Tadokoro, Y. Takahashi, Y. Chatani, and H. Kakida, Makromol. Chem., 109, 96 (1967); Y. Takahashi, I. Sumita, and H. Tadokoro, J. Polym. Sci. Polym. Phys., 11, 2113 (1973); Y. Takahashi and H. Tadokoro, Macromolecules, 6, 672 (1973).

2) T. Shimanouchi, Y. Ogawa, M. Ohta, H. Matsuura, and I. Harada, Bull. Chem. Soc. Jpn., 49, 2999 (1976).

3) Y. Ogawa, M. Ohta, M. Sakakibara, H. Matsuura, I. Harada, and T. Shimanouchi, Bull. Chem. Soc. Jpn., 50, 650 (1977).

4) T. Shimanouchi, H. Matsuura, Y. Ogawa, and I. Harada, J. Phys. Chem. Ref. Data, in press.

(Received December 9, 1977)