CHEMISTRY LETTERS, pp. 991-994, 1986.

RAMAN SPECTRA OF LIQUID COMPLEXES OF POLYETHYLENE GLYCOLS WITH ALKALI METAL SALTS

Kazuo KASATANI and Hiroyasu SATO*
Chemistry Department of Resources, Faculty of Engineering,
Mi'e University, Tsu 514

Raman spectra of liquid complexes of polyethylene glycols (PEG) with alkali metal salts are characterized by an intense polarized band near 860 cm^{-1}. This band can be used as a useful monitor of complex formation. It indicates a nearly symmetric ordering of the PEG chain around the metal cation.

The formation of complexes between polyethers and metal salts has been recognized for over 20 years. Metal complexes of cyclic oligomers, crown ethers, and acyclic oligomers, polyethylene glycols (PEG), are useful as phase-transfer catalysts, while polymer, polyethylene oxide (PEO) complexes with alkali metal salts have been attracting current interest as polymer materials with ionic conductivity.

In order to study structures and characteristics of these complexes, X-ray diffraction, NMR and IR techniques have been applied. However, the studies with Raman spectra seem to be very limited. Sato and Kusumoto,1) and Fouassier and Lassegues2) have obtained Raman spectra for a number of crown ether-alkali metal salt complexes. They observed an intense polarized band near 870-860 cm^{-1}, and assigned it to a totally symmetric A_{1g} mode involving an oxygen ring breathing motion. Recently, Takeuchi et al.,3) by normal coordinate calculations, assigned this band to an in-phase (A_{1g}) mode of C-O stretching vibrations coupled with the CH_2 rocking vibrations. Papke et al.4) observed similar bands in the Raman spectra of complexes of PEO with alkali metal salts.

Complexes of PEG and its derivatives with metal salts have been investigated by ^1H NMR and IR techniques, and the influence of PEG chain length and that of the metal cation on the complexation equilibria were clarified.5) The crystal structures of the complexes of PEG or its derivatives with heavy metal salts, such as $HgCl_2$,6) $CdCl_2$,7) and $Sr(SCN)_2$8) were determined by X-ray diffraction.

In the present study, Raman spectra of liquid complexes of PEG with alkali metal salts were measured. Such a study will clarify the mechanism of complexation in liquid phase in terms of the ring conformation, and provide useful information on the role of these complexes in the phase-transfer catalysis.

Chemically pure grade PEG9) #200 ($\bar{n}$ = 4.1), #300 ($\bar{n}$ = 6.4), #400 ($\bar{n}$ = 8.7), and #600 ($\bar{n}$ = 13.2) (Nakarai), E.P. grade $NaClO_4$ (Nakarai), G.R. grade $KClO_4$ (Nakarai), and 99% $RbClO_4$ (Kishida) were used as received. Salts were dissolved directly in liquid PEG without any solvent. Raman spectra were recorded using a

JASCO CT-80D double monochromator and a Hamamatsu Photonix R-649/C-1050 photomultiplier-photon counting unit. The excitation line at 488.0 nm was obtained from a Spectra-Physics model 164 Ar^+ laser. The Raman shift was calibrated with indene. IR spectra were obtained by a JASCO IR-810 spectrometer.

Figure 1 shows the Raman spectra of PEG #400 with and without $NaClO_4$. The molar ratio of the salt to PEG was 1 : 1 in this case. The Raman spectrum of salt-PEG mixture is characterized by the appearance of an intense and sharp band near 860 cm^{-1}. This band can be used as a useful monitor of complex formation. In the following it is shown that the detailed investigation of complex formation can be made rather easily by using this band.

Figure 2 shows the Na^+ concentration dependence on the intensity of the 860 cm^{-1} Raman band of the complex. The numbers on the abscissa indicate the mole fraction of Na^+. The relative intensity of the complex band (≈860 cm^{-1}) obtained with ClO_4^- (ν_4 624 cm^{-1}) as an internal standard is plotted as ordinate. The relative intensity of the complex band increases with increasing molecular weight of PEG. PEG #200 has a low capability of complex formation. Yanagida et al.[5a)] concluded that, in methanol, a significant complexation with sodium ion was observed for PEG's longer than hexaethylene glycol, based on a ^1H NMR study. Our finding is in good accordance with that of them. In the case of the PEG #400, complex formation is depressed for the mole fraction more than 0.5. In both cases of PEG #400 and #600, in the lower

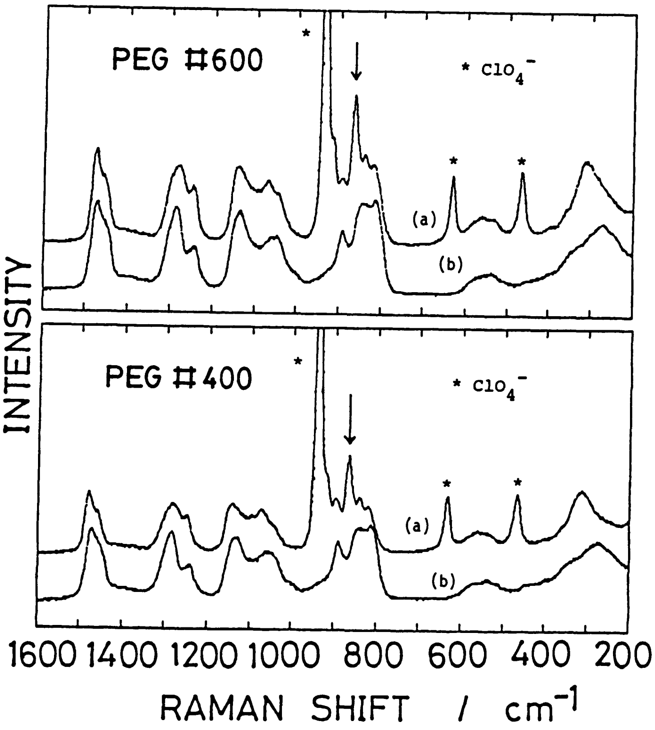

Fig. 1. Raman spectra of PEG #400 and #600. (a) PEG with $NaClO_4$ (molar ratio 1 : 1). (b) Neat PEG. Arrows indicate the band near 860 cm^{-1} characteristic of the complex.

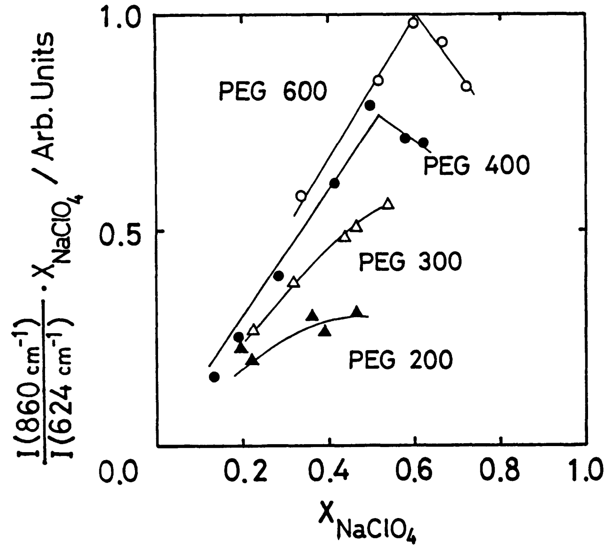

Fig. 2. The Na^+ concentration dependence of the intensity of the Raman band of the complex.

region of the mole fraction the intensity of the complex band is proportional to the Na$^+$ mole fraction, which means most of the Na$^+$ ions form complex. PEG #400 probably forms 1 : 1 complex only, while PEG #600 seems to form 1 : 2 complex at higher Na$^+$ concentrations.

The characteristic band of the complex near 860 cm^{-1} shifted slightly to higher wave number with molecular weight of PEG, namely, 855 cm^{-1}, 857 cm^{-1}, 860 cm^{-1}, and 862 cm^{-1} for PEG #200, #300, #400, and #600, respectively.

The Raman spectra of the complexes of PEG's with KClO$_4$ and RbClO$_4$ were similar to those with NaClO$_4$. The variation of metal cation hardly affected the Raman shift of the characteristic bands near 860 cm^{-1}, though in the case of the complexes of crown ethers the characteristic bands were shifted to lower wave number with larger alkali cation.[3]

Figure 3 shows that the complex band near 860 cm^{-1} is highly polarized. This band indicates a nearly symmetric ordering of oxygens of PEG chain around the metal cation. The similar band has been observed in the Raman spectra of alkali salt complexes of crown ethers[1-3] and polymer, PEO.[4] The complex of 18-crown-6 with potassium ion has D_{3d} symmetry, and has a (TGT TGT)$_3$ conformation,[10] where T, G, and $\bar{G}$ denote trans, gauche, and minus gauche, respectively. For example, TGT implies that internal rotations about the bond sequence O-CH$_2$-CH$_2$-O are trans, gauche, and trans, respectively. Papke et al.[4] proposed a (TGT T$\bar{G}$T)$_n$ conformation model for PEO-NaX complexes based on vibrational data. Okamura and Chatani[11] determined the conformation of PEO-NaI complex in the crystalline state to be (TGT TGT T$\bar{G}$T)$_n$ by means of X-ray diffraction. Based on these facts, we concluded that PEG-alkali metal salts complexes in liquid phase must have a TGT unit of conformation around the metal ion, while molten PEG has trans CH$_2$-CH$_2$ groups in part.[12]

Yanagida et al.[5b] compared IR spectra of crystalline PEG or glymes and those of their crystalline complexes, and observed the greatest changes on complex formation in the region 1200-1000 cm^{-1}. IR spectra of the latter were very similar to those of the crown ether complexes. From these facts they concluded that the structures of the crystalline complexes of PEG would be very similar to those of crown ethers.

We observed the band due to OH stretching vibration of the PEG #400-Na$^+$ complex at 3490 cm^{-1} in the IR spectrum. This frequency is higher than that for the neat PEG #400 (3350 cm^{-1}), indicating weaker hydrogen bonding in the complex. Both terminal hydroxyl groups in a PEG molecule must be coordinated to Na$^+$ ion because no

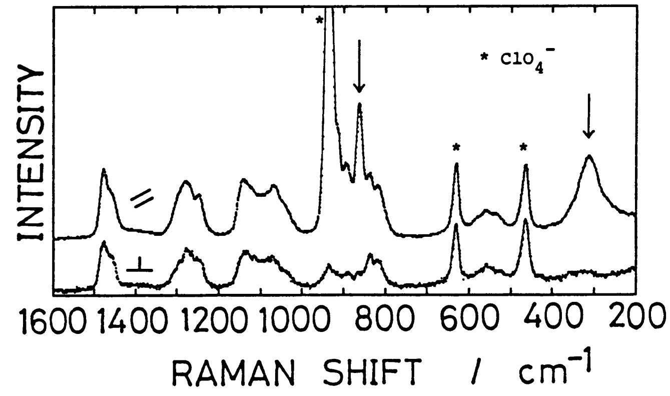

Fig. 3. Polarized Raman spectra of PEG #400 - NaClO$_4$ mixture (Mole fraction of NaClO$_4$ is 0.62). Arrows indicate the polarized bands.

splitting or broadening of the OH stretching band for the complex was observed. Other significant changes of IR spectra on complex formation were not observed except the small increase of the intensity of the bands due to antisymmetric CH stretching mode at 2920 cm^{-1} and antisymmetric CH_2 bending mode at 1480 cm^{-1}. The characteristic band near 860 cm^{-1} was not observed in the IR spectra, which means that the PEG complex with alkali cation has a highly symmetric conformation for which this band is IR inactive.

Whether the conformation of the complexes of PEG's with alkali metal salts is similar to that of crown ethers or to that of PEO, in other words, pseudocyclic or helical, cannot be determined by vibrational spectra only. X-Ray analysis for the complexes of heptaethylene glycol with $Sr(SCN)_2$ showed that the structure of this complex is very similar to those of the crown ethers.7) In the central part of the complex, a TGT-T$\bar{G}$T-TGT comformation is observed. A molecular mechanics calculation suggests that the (TGT T$\bar{G}$T) conformation is favorable for complexes of a PEG derivative, pentaglyme, with alkali ions.13) These facts suggest that crown ether-like conformation is more favorable for PEG-alkali ion complexes than the other one .

The authors thank Mr. T. Ito for his help in experiment.

References

1) H. Sato and Y. Kusumoto, Chem. Lett., 1978, 635.
2) M. Fouassier and J.-C. Lassegues, J. Chim. Phys. Phys.-Chim. Biol., 75, 865 (1978).
3) H. Takeuchi, T. Arai, and I. Harada, J. Mol. Struct., in press.
4) B.L. Papke, M.A. Ratner and D.F. Shriver, J. Phys. Chem. Solids, 42, 493 (1981).
5) a) S. Yanagida, K. Takahashi, and M. Okahara, Bull. Chem. Soc. Jpn., 51, 1294 (1978); b) S. Yanagida, K. Takahashi, and M. Okahara, ibid., 51, 3111 (1978).
6) R. Iwamoto, Bull. Chem. Soc. Jpn., 46, 1114 (1973); R. Iwamoto, ibid., 46, 1118 (1973); R. Iwamoto, ibid., 46, 1123 (1973).
7) R. Iwamoto and H. Wakana, J. Am. Chem. Soc., 98, 3764 (1976).
8) H. Ohmoto, Y. Kai, N. Yasuoka, N. Kasai, S. Yanagida, and M. Okahara, Bull. Chem. Soc. Jpn., 52, 1209 (1979).
9) The figures indicate the nominal average molecular weight. The figures ($\bar{n}$) in parentheses are the average numbers of oxyethylene units, calculated from the average molecular weight.
10) J.D. Dunitz, M. Dobler, P. Seiler, and R.P. Phizackerley, Acta Crystallogr., Sect. B, 30, 2733 (1974).
11) S. Okamura and Y. Chatani, Polymer Preprints, Japan, 34, 2089 (1985).
12) H. Matsuura and T. Miyazawa, J. Polym. Sci. A-2, 7, 1735 (1969); J.L. Koenig and A.C. Angood, J. Poly. Sci., A-2 8, 1787 (1970); J. Maxfield and I.W. Shepherd, Polymer, 16, 505 (1975); H. Matsuura and K. Fukuhara, J. Mol. Struct., 126, 251 (1985).
13) G. Wipff, P. Weiner, and P. Kollman, J. Am. Chem. Soc., 104, 3249 (1981).

(Received April 2, 1986)