

## **Structural and electrical studies on poly(ethylene oxide) complexed with inorganic salts**

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### SUMMARY

Poly(ethylene oxide) (PEO) complexes were synthesized in methanol solution with five different alkali and earth alkali metal perchlorates. The intermolecular association was studied in solution with NMR and the structures of the formed solid complexes were analysed by IR-spectroscopy and X-ray-diffractometry. The conductivities of pure PEO and of the complexes were measured in vacuum and at room temperature. The variation in the properties of the samples is due to the association of PEO with charged ions.

### INTRODUCTION

Our work has focused on studying the interactions between different polymer chains in solutions, and the structure of the formed complex. A model polymer used in this field is poly(ethylene oxide). This polymer also forms an interpolymer complex with various inorganic salts. These complexes have physical properties which differ from those of the pure polymer. Several workers have studied the conductivities of alkali metal salt-PEO complexes (1-5). Complexed polymers of this sort have conductivities as high as  $10^{-4} \text{ Scm}^{-1}$ . The PEO complexes are solid electrolytes (1,6). In the present paper, attention has been focused primarily on PEO and its interactions with  $\text{LiClO}_4$ ,  $\text{NaClO}_4$ ,  $\text{KClO}_4$ ,  $\text{Mg}(\text{ClO}_4)_2$  and  $\text{Ba}(\text{ClO}_4)_2$ .

### EXPERIMENTAL

Commercial samples of poly(ethylene oxide) and various inorganic salts were used in the study. The molecular weights of the polymer were 4000, 10000, 15000 and 60000. The salts studied were alkali metal and earth alkali metal perchlorates;  $\text{NaClO}_4$ ,  $\text{LiClO}_4$ ,  $\text{KClO}_4$ ,  $\text{Mg}(\text{ClO}_4)_2$  and  $\text{Ba}(\text{ClO}_4)_2$ . The salts and the polymer were dried under a vacuum at  $70^\circ\text{C}$ . The methanol used as solvent was dried over molecular sieves. The complexes were prepared by dissolving the polymer in methanol to give 2% and 5% solutions, and different amounts of the metal salts (PEO unit / Me = 0.2, 0.4, 0.6 and 1.0) were added to this solution.

$^1\text{H}$ - and  $^{13}\text{C}$ -spectra were obtained on a JEOL FX-200 FT NMR spectrometer. The measurements were made in methanol solutions containing deuterated methanol as locking agent. The chemical shifts were compared to the carbon resonance of methanol and to the proton resonance of its methyl group. Experimental data for spectral acquisition were as follows. The proton spectrum was extended from 383 Hz to 1383 Hz, and the carbon spectrum from 1161 Hz to 5161 Hz with 16 K data points and  $45^\circ$  pulses. The pulse delay was 5 s for  $^1\text{H}$  and 2 s for  $^{13}\text{C}$ .

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The X-ray diffraction measurements were made with a DRON-UM1 diffractometer using wide-angle X-ray scattering.  $2\theta$  was recorded from  $10^\circ$  to  $30^\circ$ .

The infra-red spectra were measured on a Perkin Elmer 457 Spectrophotometer using the KBr-pellet technique.

The conductivity measurements were carried out in a vacuum at room temperature using the 2-probe method. The samples were pressed pellets with a weight of about 200 mg.

## RESULTS AND DISCUSSION

The polymer salt complexes were all prepared in the same way, the aim being to detect differences which could be attributed to the cation of the perchlorate used. It is known that the association of PEO with alkali metal ions leads to a change in the polymer conformation (7-8). The complexation phenomenon was studied in methanol solution since the cation is not so hydrated as in an aqueous solution, and association not prevented. This can be seen from the  $^1\text{H}$  and  $^{13}\text{C}$  measurements. When the solutions were concentrated, a new phase separated out which differed from the polymer. The behaviour of the phase is dependent on the salt used.

Table 1 shows the chemical shifts of PEO protons and carbons. The concentrations of samples were 2% and 5%. The greatest effect can be observed with  $\text{NaClO}_4$ . The salt moves the shift of PEO carbon to the upper magnetic field. This is the result of PEO association with positively charged ions; the interaction that occurs between oxygen and ions will reduce the electron density around the methylene carbons. At the same time, the chemical shift of PEO protons moves toward a lower magnetic field. The molecular weight does not affect the chemical shifts. Figure 1 shows the effect of varying concentration of salt at constant polymer concentration. The change is more pronounced at low salt concentrations, and levels off at higher concentrations. This is in agreement with the results of Ibemesi and Kinsinger (9). The NMR measurements show that the association between oxygen and ions in solution is not local because there are no new chemical shifts at either low or high ion concentrations. However, the effect of the ions is equal to all oxygen atoms in the polymer chains.

Table 1. Variation in the chemical shifts for  $^1\text{H}$ - and  $^{13}\text{C}$ - spectral lines of PEO 4000 in the presence of different salts with molar ratio  $[\text{salt}] / [-\text{OCH}_2\text{CH}_2-] = r = 1$ .

PEO 4000 / salt	Chemical shift in ppm			
	H		C	
	2%	5%	2%	5%
-	3.64	3.64	70.71	70.93
$\text{LiClO}_4$	3.64	3.65	70.51	70.56
$\text{NaClO}_4$	3.70	3.70	69.73	69.92
$\text{KClO}_4$	3.66	-	70.20	-
$\text{Mg}(\text{ClO}_4)_2$	3.64	3.65	70.31	70.30
$\text{Ba}(\text{ClO}_4)_2$	-	-	-	-

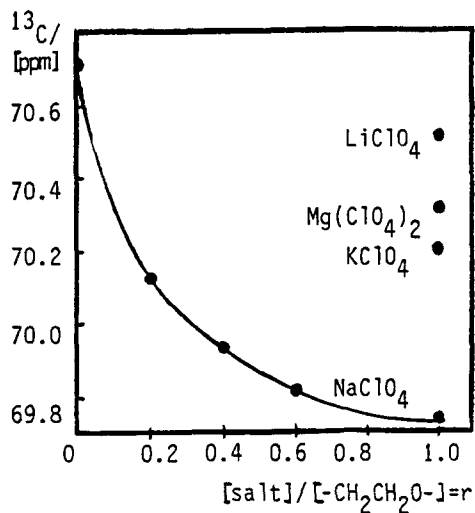


Figure 1. Chemical shifts of carbons in methanol solutions (2%).

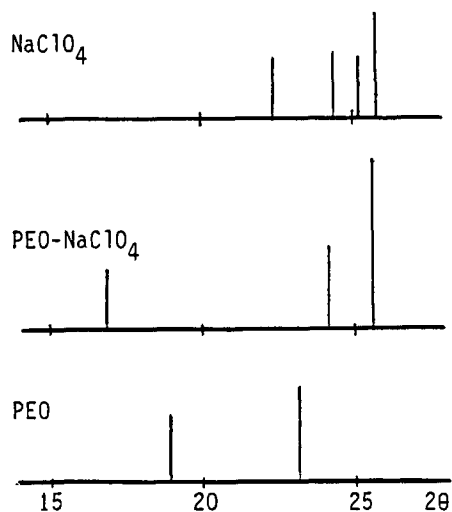


Figure 2. Histograms of X-ray diffraction patterns for the PEO-NaClO<sub>4</sub> measurements.

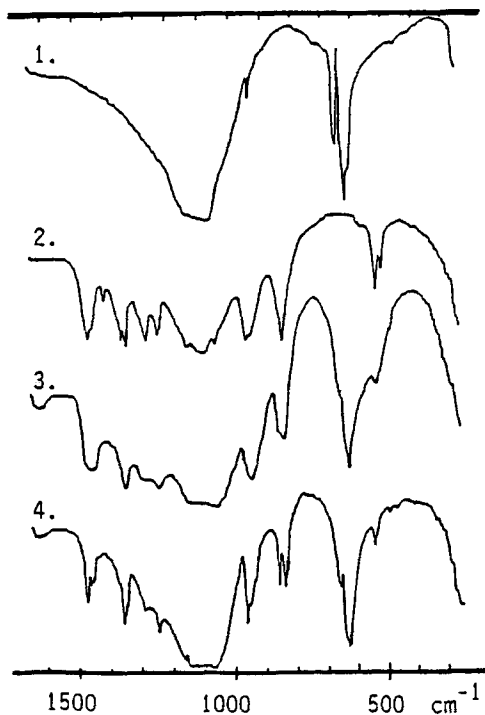


Figure 3. The IR-spectra of

- 1) pure NaClO<sub>4</sub>
- 2) pure PEO 4000
- 3) mechanical mixture of 1 and 2
- 4) association complex of 1 and 2

from 1650 cm<sup>-1</sup> to 250 cm<sup>-1</sup>.

The histograms of the x-ray diffraction patterns at  $2\theta = 15^\circ - 27^\circ$  measured for PEO,  $\text{NaClO}_4$  and complex are shown in Figure 2. Comparison of the spectra shows that the spectrum of the complex is completely different compared with that of the polymer and of the pure salt. This suggests that the helix structure of the polymer has been broken up, and it has been replaced by a new structure which is completely different from the structure of pure salt (4,10).

Figure 3 shows the IR-spectrum of a pure polymer, a pure salt, their mechanical mixture and association complex over the region  $1650-250 \text{ cm}^{-1}$ . The absorption bands of the complex have substantial differences compared with those for PEO and salt separately. It should be noted that CO bending at  $530-510 \text{ cm}^{-1}$  characteristic of the pure PEO shifts to  $540 \text{ cm}^{-1}$  in the spectrum of the complex, and the band at  $845 \text{ cm}^{-1}$  is divided into three bands:  $830, 840$  and  $860 \text{ cm}^{-1}$ . These changes indicate that the normal movement of polymer chains is prevented. The same trend is observed in the case of the other complexes too. This means that the association takes place on the molecular level.

Table 2. The electrical conductivities of pure PEO with different molecular weights and of its inorganic complexes. ( Molar ratio =  $[\text{salt}] / [-\text{OCH}_2\text{CH}_2-] = r = 1$  ).

Polymer	Salt	Conductivity ( $\text{Scm}^{-1}$ )
PEO 4000	-	$1.4 \cdot 10^{-18}$
	$\text{LiClO}_4$	$1.8 \cdot 10^{-5}$
	$\text{NaClO}_4$	$7.2 \cdot 10^{-6}$
	$\text{KClO}_4$	$5.3 \cdot 10^{-6}$
	$\text{Mg}(\text{ClO}_4)_2$	$7.3 \cdot 10^{-7}$
	$\text{Ba}(\text{ClO}_4)_2$	$7.1 \cdot 10^{-7}$
PEO 10000	-	$2.5 \cdot 10^{-18}$
	$\text{LiClO}_4$	$2.0 \cdot 10^{-5}$
	$\text{NaClO}_4$	$7.1 \cdot 10^{-6}$
PEO 15000	-	$2.6 \cdot 10^{-18}$
	$\text{LiClO}_4$	$2.1 \cdot 10^{-5}$
	$\text{NaClO}_4$	$7.0 \cdot 10^{-6}$
PEO 600000	-	$1.5 \cdot 10^{-18}$
	$\text{LiClO}_4$	$1.7 \cdot 10^{-5}$
	$\text{NaClO}_4$	$6.9 \cdot 10^{-6}$
PEO 4000	$\text{NaClO}_4, r = 0.2$	$3.2 \cdot 10^{-8}$
	"- $r = 0.4$	$9.8 \cdot 10^{-8}$
	"- $r = 0.6$	$7.5 \cdot 10^{-7}$

According to Table 2, it is evident that a) there are no significant differences in the conductivities of PEO-complexes with different molecular weights and b) PEO-LiClO<sub>4</sub> complexes have the highest electrical conductivities. This is caused by the small ion radius of lithium.

#### REFERENCES

1. C. K. Chiang, *Polymer* 22, 1454 (1981).
2. C. C. Lee and P. V. Wright, *Polymer* 23, 681 (1982).
3. J. M. Parker, P. V. Wright and C. C. Lee, *Polymer* 22, 1307 (1981).
4. P. R. Payne and P. V. Wright, *Polymer* 23, 690 (1982).
5. D. J. Bannister, G. R. Davies, J. M. Ward and J. E. McIntyre *Polymer* 25, 1291 (1984).
6. R. Dupon, D. H. Whitmore and D. F. Shriver, *J. Electrochem. Soc.* 128, 715 (1981).
7. E. A. Bekturov, S. E. Kudaibergenov, Z. Kh. Bakauova, V. Zh. Ushanov and G. S. Kanapyanova, *Polymer Communications* 26, 81 (1985).
8. E. A. Bekturov, S. E. Kudaibergenov, V. Zh. Ushanov, S. S. Saltybaeva, *Makromol. Chem., Rapid Commun.* 6, 515 (1985).
9. J. A. Ibemesi and J. B. Kinsinger, *J. Polym. Sci. Polym. Chem. Ed.* 18, 1123 (1980).
10. C. D. Robitaille and D. Fauteux, *J. Electrochem. Soc.* 133, 315 (1986).

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