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EFFECT OF SOLVENTS ON THE NETWORK ORDER IN POLY(POLYETHYLENE GLYCOL) PHOSPHATES

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ABSTRACT

A set of network polymers (PPEGPs) obtained by polycondensation of polyoxyethylene glycols and phosphorous oxychloride, have been characterized in respect of their paracrystalline behavior both in dry and solvent-swollen states. A definite structure property correlation has been established between the polyoxyethylene (POE) link length at one hand, and their XRD patterns and degree of swelling at the other.

INTRODUCTION

Crosslinked polymeric network with polyoxyethylene (POE) link units have been reported earlier[1,2]. These polymers containing POE link units exhibit high absorbing power of moisture and ability to swell in aqueous suspensions.

The polymers were designed to simulate structures of crown ethers of varying cavity sizes for cation binding. They were subjected to XRD analyses to ascertain if any regular network conforming to crown ether structures had been generated. The polymers, in general, have spongy feel and rubbery consistency. As would be expected, they were found to be basically amorphous.

The XRD patterns, however, reveal some interesting trends. While the features of the XRD patterns, in general, remain virtually unaltered, definite shifts in the angles corresponding to the paracrystalline humps of individual polymers were observed when they were equilibrium swollen in water.

In the present communication, we report this characteristic XRD behavior of PPEGPs and analyze them in the light of possible solvation sites in the polymer and its consequent effects on the network structures.

EXPERIMENTAL

Synthesis of Polymers : The polymers were synthesized following standard procedure reported earlier[1].

Equilibrium Swelling : The equilibrium swelling of the polymers were measured as the apparent swollen volume of the polymers relative to their original volume in dry states.

XRD Measurement : X-Ray diffraction patterns of the five polymers in dry and equilibrium solvent swollen states were recorded on a Philips X-ray Diffractometer (type PW1710) using Ni-filtered CuK_α radiation in the angular (2θ) range 5^o to 70^o at an operating voltage of 35KV and current of 30 mA.

Calculation of Degree of Paracrystallinity : The areas under crystalline and amorphous reflections were determined in arbitrary units. Degree of crystallinity (x_c) and the amorphous content (x_a) were calculated as per the method of Matthews et al[3] and using the relations

$$x_c = \frac{I_c}{I_c + I_a}, \quad x_a = \frac{I_a}{I_c + I_a}$$

Here I_c and I_a are the areas under certain selected paracrystalline reflections and amorphous scattering respectively after due correction for background scattering.

RESULTS

X-Ray diffractograms of the network under dry and equilibrium water-swollen conditions are shown in Fig.1.

General Features of the Diffractograms : It is seen from the figures that none of the polymers exhibited any sharp reflections, characteristic of well grown defectless crystalline domains. Rather, a broad hump of significant intensity superimposed over a continuum of background scattering could be observed in the diffractogram of each polymers in their water-swollen state. Further, there is clear impression that the humps are, in fact, formed by overlapping of two or more broad reflections. A rough resolution of such a broad hump from PDGP into two broad peaks is shown in Fig.1. In dry states, however, the hump is represented almost exclusively by a single broad reflection.

The very nature of the resolved peaks from PDGP indicates that they better represent structure between paracrystalline and amorphous. The reflections at lower 2θ values being comparatively sharper has been taken to represent paracrystalline domains, while the others at higher 2θ have been taken to represent the amorphous domains in the network.

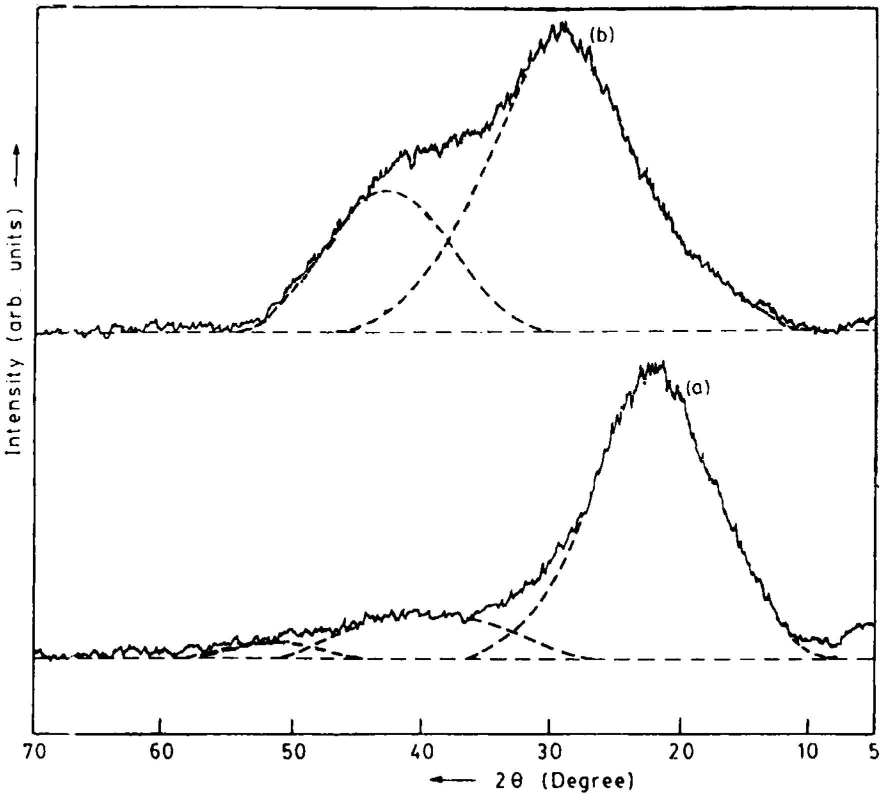

Figure 1 XRD pattern of PDGP with deconvoluted amorphous scattering and paracrystalline reflections; (a) dry and (b) water-swollen states.

Percent crystallinity, as referred to here, therefore, relates to paracrystallinity and has been calculated by using the same basic equation given earlier.

General Trends : It is observed from the diffractograms that the intensity of the first reflection in dry state is smaller with smaller POE link length in the PPEGPs (not shown here). The broadness of the first reflection also varies, broadness increasing with decreasing link length.

Table-1 summarizes the variation in 2θ values with link length of the PPEGPs. A clear trend of 2θ values and the percent paracrystallinity both in dry and in equilibrium water-swollen state can be observed as the unit POE link length is varied. In the dry state 2θ values corresponding to paracrystalline peak decreases with the increase in unit link length to an ultimate constant value of around 21.8^{o}. The percent paracrystallinity, however, increases steadily from 80% for PEGP to an almost a limiting value of 89% for PPEGP-300.

In the water-swollen state the variation of 2θ values with POE link length is virtually absent. A constant 2θ value of about 29^{o} can be observed for all the polymers in their equilibrium water-swollen state. However, in general, there is increment in percent crystallinity with increases in POE link length. The data clearly show that there is an appreciable order in the network structure in each polymer which is, however, susceptible to changes with POE link length and swelling by water.

DISCUSSION

Yeates and Booth[4] have reported strong reflections at $\theta = 9.6^{o} - 9.7^{o}$ for poly(oxyethylene), and $\theta = 11.6^{o} - 11.7^{o}$ for oligo(oxyethylene). The limiting 2θ value for PPEGPs in this investigation was measured to be 21.8^{o} in PPEGP-300 for the first broad reflections. Incidentally this 2θ value is very close to the mean of strong reflections for poly- and oligo(oxyethylene) i.e., $9.7^{o} + 11.7^{o} = 21.4^{o}$.

TABLE 1

Variation of peak 2θ values and percent paracrystallinity in PPEGPSs in dry and water-swollen states

	Dry		Water-swollen state	
Polymer[a]	2θ (degrees)	Paracrystallinity, %	2θ (degrees)	Paracrystallinity, %
PEGP	24.3	80	29.4	79
PETP	23.0	81	29.4	78
PDGP	21.8	89	29.1	79
PTGP	22.0	89	29.2	80
PPEGP-300	21.8	89	29.0	86

a) PEGP = Poly(ethyleneglycol)phosphate;
PDGP = Polydigolphosphate;
PTGP = Polytrigolphosphate;
PETP = Co-polyphosphate of 1:1 molar mixture of ethyleneglycol and trigol; and
PPEGP-300 = Polyphosphate of polyethyleneglycol, M.W. 300

It appears, therefore, that in the dry state the network structure largely retains the order of arrangement as in poly- and oligo(oxyethylene). This order is, however, subject to variation depending upon the degree of inherent strains in a crosslinked network and, obviously, with the length of the oxyethylene link unit in PPEGPs. A shorter link length would naturally correspond to less order and the observed higher 2θ value of the first peak reflection may be taken to correspond to an altogether new short-range arrangement.

In the water-swollen states the first paracrystalline peak maxima shift by about 5-7° (Table 1). These shifts may be due to either or both of the two possibilities. First, in the equilibrium swollen condition, water is imbibed maximum into the matrix. As a result, all the link units in the network will be stretched around the phosphate groups. This would restrict the alignment of the segments and lead to a new less ordered structure (diminished paracrystallinity) with higher 2θ values of the first reflection. The data in Table 1 also show that the 2θ values for all the PPEGPs in their equilibrium water-swollen states are constant at approximately 29^{o}. This implies that the imbibed water stretches the link units to structures having almost the same order of oxyethylene segmental arrangements in the water-swollen network. The second possibility is the contamination of the reflections from PPEGPs with that of the imbided water itself. Like all other liquids, water exhibits characteristic radial distribution pattern in its X-ray diffraction. The most intense reflection from water at room temperature has been reported at around $2\theta \sim 31^{o}$ by Norten, Danford, and Levy[5]. This value is close to the peak 2θ of 29.4^{o} observed for the equilibrium swollen PPEGPs. It appears that the diffraction pattern of water-swollen polymers is grossly representative of the imbibed liquid water itself.

Although it is difficult to asses the relative importance of the above two possibilities, some facts are, however, worth noting. It is seen from the data in Table-2 that shifts in peak 2θ values of the first reflection from PDGP increase parallely with degree of its swelling irrespective of the nature of the solvent (water, methanol, acetonitrile and dioxane). This parallelism perhaps discounts the possibility of contamination of the first reflections with those of the imbibed solvent. Rather, it is the swelled network, no

TABLE 2

2θ values for paracrystalline reflections from PDGP after equilibrium swelling in various solvents

	Dry	Equilibrium swollen in			
		water	methanol	acetonitrile	dioxane
2θ (degree)	21.8^{a}	29.1	23.7 $(24.4)^{b}$	21.4	21.2 $(24.4)^{b}$
Swelling (%)	–	500	250	40	40

(a) The apparently dry polymer does retain certain amount of moisture which is responsible for observed higher 2θ values compared to that in case of acetonitrile or dioxane.

(b) Data in parentheses are the experimental most intense peak-2θ values for reflections from the short-range orders in the respective liquids.

matter how and by which solvent the swelling has been effected, which determines the shifts in peak-2θ values of the first reflection. Also to be noted from the data is the fact that the peak-2θ values for the equilibrium swollen PDGP in different solvents is independent of its most intense peak-2θ. Thus methanol having almost the same peak-2θ values of around 24.4° as that of liquid dioxane, offers higher value of first peak reflection from PDGP (23.7°) than from dioxane (21.2°). Further it has been observed that the amount of water retained by the PPEGPs systematically shifts the peak-2θ values of the first reflections from the polymers to proportionately higher values.

Swelling Behavior : Swelling behavior of the polymers varied widely depending upon the polyoxyethylene (POE)

TABLE 3

Swelling behavior of PPEGPs in different solvents

Polymers	Degree of swelling[a], (%), in			
	water	methanol	acetonitrile	dioxane
PEGP	750	-	15	-
PETP	700	-	33	-
PDGP	500	250	40	40
PTGP	450	-	66	-
PPEGP-300	350	-	-	-

a) Percent (V/V), at room temperature (27°C)

unit link length and solvent used. The observed order of swelling of the polymers in water at room temperature is PEGP > PETP > PDGP > PTGP > PPEGP-300 (Table-3). PEGP showed the maximum equilibrium swelling of about 750% in water at 300K. It appears that phosphate group is responsible for the observed swelling in water and the degree of swelling is directly related to phosphate content in the polymers. With other solvents like acetonitrile, dioxane and tetrahydrofuran, the degree of swelling is insignificantly small. With methanol, however, swelling of about 250% has been recorded in PDGP. The results indicate that protic solvents like water and methanol are more efficient in solvating the phosphate group, presumably through hydrogen bonding.

CONCLUSION

1. The study shows that the polyoxyethylene link units maintain a definite order of arrangement of

oxyethylene segments leading to distinct paracrystallinity in the PPEGPs network polymers. The order increases with increasing link lengths. A limiting maximum order is attained possibly beyond about 8 units of oxyethylene segments that closely approximates the crystalline order in polyoxyethylene.

2. In their equilibrium water-swollen states, the PPEGPs, in general, show some reduced order of arrangements of the oxyethylene segments compared to that in their dry state. The relative shifts in 2θ values for paracrystalline reflections of the PPEGPs on being equilibrium swollen in various solvents increase with the degree of swelling, possibly due to increased disorder in the network induced by higher degree of swelling.

3. The degree of swelling of the polymers has been more in protic solvents than in approtic ones.

4. In the case of water, the degree of swelling is more with PPEGPs containing higher proportion of phosphate group, which implies that the swelling is primarily contributed to by the solvation of phosphate groups presumably through strong hydrogen bonding.

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