

# Interaction of poly(ethylene oxide) with solvents: 1. Preparation and swelling of a crosslinked poly(ethylene oxide) hydrogel

N. B. Graham\*, N. E. Nwachuku and D. J. Walsh

*Department of Pure and Applied Chemistry, University of Strathclyde, Glasgow G1 1XL, UK*

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Crosslinked polymer gels containing over 90 wt% poly(ethylene oxide) have been made and their swelling in a large number of solvents studied. The results confirm previous observations that the interaction of poly(ethylene oxide) with water is quite different from the interaction with most other solvents. Formamide also appears to be anomalous. The crosslinked polymer, swollen with water, shows dramatic syneresis between 0° and 100°C but at 100°C still retains approximately three molecules of water for each ether oxygen.

**Keywords** Hydrogel; poly(ethylene oxide); networks; syneresis; poly(urethane); formamide

## INTRODUCTION

Poly(ethylene oxide) is a well known and industrially important polymer much used in the many commercially-available high and low molecular weight grades in the pharmaceutical and textile industries, as excipients in drug formulation, or as fibre-forming aids. It is also used in many other industries in the form of surface-active agents when combined with hydrocarbon moieties and in the manufacture of esters, polymers, polishes, lubricants, mold release agents and in water treatment<sup>1</sup>. A detailed understanding of the interaction of water with this polymer backbone is thus obviously of importance and it might be thought that now, more than fifty years after its significant use in industry, this interaction would be very well understood. This is not so, however. The compatibility of poly(ethylene oxide) with water is generally described in terms of rather vague hydrogen bonding and/or in terms of the Flory-Huggins interaction parameter, both of which are inadequate in the context of poly(ethylene oxide) in water which we have found forms at least two specific hydrates<sup>2</sup>. One of these appears to be a distinct species which survives considerable aqueous dilution. A complete understanding of the compatibility or behaviour of poly(ethylene oxide) solutions in water, or other solvents mixed with water, must take the formation of such specific hydrates into account. Crosslinked poly(ethylene oxide) hydrogels were synthesized in these laboratories for their technological use in an isothermal separation process for the concentration of dispersions and also for the formulation of controlled release dosage forms of drugs. Both applications require a knowledge of the nature of the interaction of the hydrogel with a wide variety of solvents and led to the studies to be reported in this series of papers. This first deals with the preparation of a particular crosslinked poly(ethylene oxide) which,

being water-insoluble but water-swelling is a convenient system with which to study the degree of interaction of the polymer with a variety of solvents. The preparation of precisely reproducible crosslinked polymers is difficult and in this study identical batches of raw materials were used and samples were prepared by an identical procedure, so that the results of various swelling tests would be comparable.

The swelling of a crosslinked polymer is often described by the expression below developed by Flory<sup>3</sup>.

$$l_n(1 - v_{2m}) + v_{2m} + \chi_1 v_{2m}^2 = -(V_1/\bar{v}M_c) \left( 1 - \frac{2M_c}{M} \right) \left( v_{2m}^{1.3} - \frac{v_{2m}^2}{2} \right)$$

where  $v_{2m}$  = the polymer concentration at equilibrium swelling;  $\chi_1$  = the interaction parameter;  $\bar{v}$  = the specific volume of the polymer;  $V_1$  = the molar volume of the solvent;  $M_c$  = the molecular weight between crosslinks and where  $1 - \frac{2M_c}{M}$  is the correction factor for chain ends.

Walsh<sup>4</sup> has however commented that networks containing either hydrogen bonding or crystallinity cannot be expected to fit the above equation. As the networks of poly(ethylene oxide) described in this paper contain significant crystallinity and exhibit hydrogen bonding interaction with solvents capable of such bonding, it would not be reasonable to expect the equation above to be very useful in predicting the solvent swelling of these networks. Instead the much more empirical, but more broadly applicable, solubility parameter has been used<sup>5</sup>.

Table 1 Method and drying procedures for 4 different PEG samples

	Specimen	% Water content
1	Molten fraction as supplied	2.12
2	Sample dried as above	0.004
3	Sample as supplied with 1% extra water deliberately added, and then dried as described above	0.004
4	Sample dried as above, but allowed to solidify, exposed to the atmosphere	0.027

Table 2 Composition of crosslinked polymer gel

	PEG 6000	TMP	MDI
Molar composition	1.0	0.5	1.886
% Weight composition	91.768	1.026	7.205
Actual weights (in gm) used	286.18	3.20	22.49

## EXPERIMENTAL

### Materials

(i) *2-ethyl-2-hydroxymethyl propane-1,3-diol (TMP)*. This was dried at 353 K under a vacuum of ca. 270 Nm<sup>-2</sup> for 4 h while simultaneously bubbling in a stream of dry nitrogen. It was then stored molten in an oven at 339 K until use.

(ii) *PEG 6000*. (PEG is an abbreviation for poly(ethylene glycol)). This material was obtained as a gift from ICI Ltd. It was vacuum dried at 373–393 K for six hours as for TMP. It was stored molten in a sealed flask in an oven at 339 K until use. This drying process however only removed the residual water, but not impurities, as the polymer still showed slight acidity (m.p. 338 K).

The PEG 6000 was characterized by gel permeation chromatography when the following values for molecular weights  $\bar{M}_w$  and  $\bar{M}_n$  were obtained relative to polystyrene standards.

$$\bar{M}_n = 4.196 \times 10^3 \quad : \quad \bar{M}_w = 8.838 \times 10^3$$

$$\bar{M}_w/\bar{M}_n = 2.11$$

The water content of the PEG 6000 was determined by the Karl Fischer method<sup>6,7</sup>. Four different specimens were examined to check both the method and the drying procedure (see Table 1).

Thus the drying method used is efficient enough to reduce the water content to a trace value of 0.004%. The dried sample was appreciably hygroscopic and was stored in a sealed container.

The hydroxyl number and acid number of the dried PEG 6000 were determined by standard methods<sup>8,9</sup>. The 'number' used to calculate the equivalent quantity of MDI for stoichiometric reaction was the sum of the hydroxyl number and the acid number. Thus for the polymer described in this paper the dried PEG 6000 was found to have a hydroxyl number of 18.87 and an acid number of 2.35 giving a combined value of 21.22.

### 4,4'-diphenylmethane diisocyanate (MDI)

This was obtained as a gift from ICI Ltd. and was distilled at 453–463 K at a reduced pressure of ca. 270 Nm<sup>-2</sup> to yield a colourless liquid which solidified on standing at room temperature. It was stored in the deep freeze in a sealed glass container until time for use (m.p. 311 K).

### Preparation of the crosslinked polymer gel

The composition chosen and used was as shown in Table 2.

The TMP was added to the PEG in a round bottomed flask, and both were allowed to stand at 343 K. To the molten pure MDI in a beaker, was added two drops of benzoyl chloride to retard the eventual gelation reaction, so that adequate mixing was achievable before filling the mould. With the benzoyl chloride retarder, the pot life is prolonged from less than a minute to three minutes.

The molten MDI and benzoyl chloride was then poured into the homogeneous mixture of polyols. The entire mixture was rapidly stirred for about 15 seconds, degassed under vacuum for two minutes, and then quickly poured into a rectangular mould with a lid, preheated to 343 K the metal parts having been coated with a commercial spray containing fluorinated polymer. The mould was closed and left in the oven at 373 K for at least 15 h to complete the reaction. When the mould cooled, the opaque white block of polymer was removed and stored, away from moisture until time for use.

### Swelling experiments

Thin slices of the polymer, approximate weights 10 mg, were each allowed to stand in over fifty different solvents at 298 K or other selected temperature. The solvents were of solubility parameters ranging from 6.6 cal<sup>1/2</sup> ml<sup>-3/2</sup> to 22 cal<sup>1/2</sup> ml<sup>-3/2</sup> selected from the three classes of differently hydrogen bonding index from the weakly bonding straight chain hydrocarbons, through the moderately bonding esters and ketones, to the strongly bonding acids and alcohols<sup>5</sup>.

The samples were removed at intervals of 48 h, immediately blotted dry and placed in a tared weighing vial sealed with a glass stopper and weighed. When no further increase in weight between weighings was observed, the maximum equilibrium swelling was calculated for each solvent. The samples took approximately one week to reach equilibrium.

Plots of these equilibrium swelling values are shown in Figures 1 to 4, illustrating the behaviour in four different groupings of the solvents. In spite of the efforts to obtain precisely reproducible blocks of polymer by control of the factors above it will be noticed by reference to the water swelling figures in Figures 5 and 6 that significant discrepancies were found between different batches of polymer. This paper concerns itself with trends rather than absolute values of swelling and the results in each figure are from samples cut from a single block from a single batch and are thus comparable.

## RESULTS AND DISCUSSION

The plot of solvent swelling against solubility parameter for solvents with a low hydrogen bonding capacity is shown in Figure 1. It can be clearly seen from this plot that

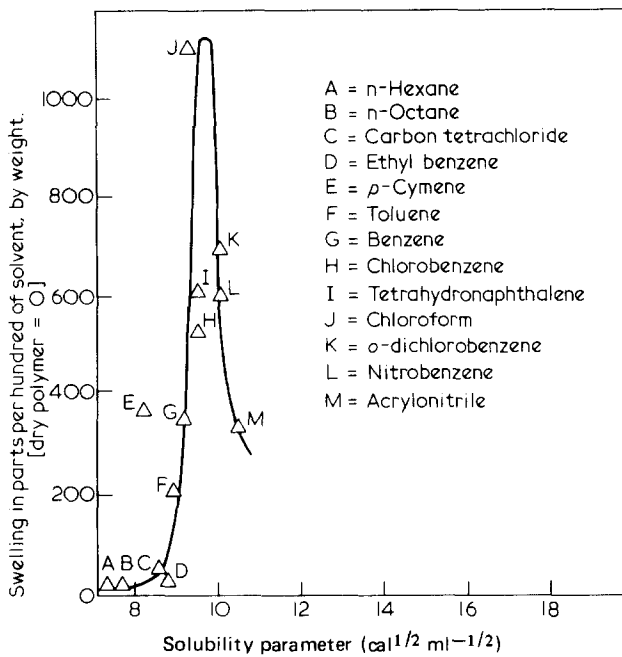


Figure 1 Swelling of PEO gels in chlorinated, nitrated and unsubstituted hydrocarbons at 298 K

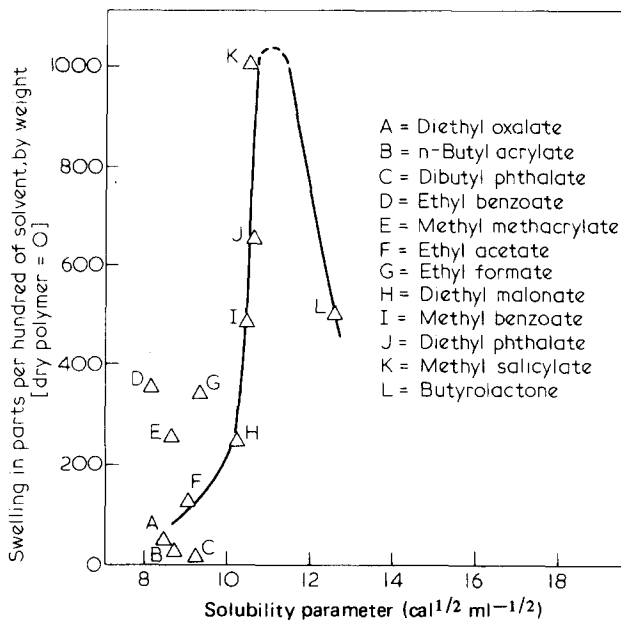


Figure 2 Swelling of PEO gels in esters at 298 K

a quite sharp maximum of swelling is obtained at approximately 9.8 close to the solubility parameter of chloroform (9.3). Similar peaks can be obtained for esters (Figure 2) and aldehydes (Figure 3) though if these two groups are plotted together the presence of peaks is not as obvious. The solubility parameter at the peak varies from *ca.* 9.8 for chlorinated, nitrated and unsubstituted hydrocarbons, aldehydes and ketones to 11.0 for esters. With the strongly hydrogen bonding solvents in Figure 4 a sharp maximum of swelling is obtained close to benzyl alcohol (11.9) at a solubility parameter of *ca.* 12.2 from which one might conclude that hydrogen bonding plays a significant role in the compatibility of poly(ethylene oxide) with solvents. The plot of strongly hydrogen bonding solvents (Figure 4) contains three apparently

anomalous points for methanol, formamide and water which require further investigation and explanation. To throw more light on this anomaly the equilibrium swelling of the polymer was studied in a variety of solvents at different temperatures. A summary of these results for a few hydrogen-bonding solvents is provided in Figure 5. It can be clearly seen that the swelling solvents fit into two groups. Those for which the degree of swelling increases with temperature and the anomalous solvents, water and formamide whose swelling decreases significantly with rise in temperature.

Three other points are noteworthy in Figure 5. The first of these is that among the group of solvents which increase in their ability to swell the crosslinked poly(ethylene oxide) there is in each case a sudden increase in the rate of change of swelling with temperature at about 27°C. Secondly, methanol, formamide and acetic acid also show

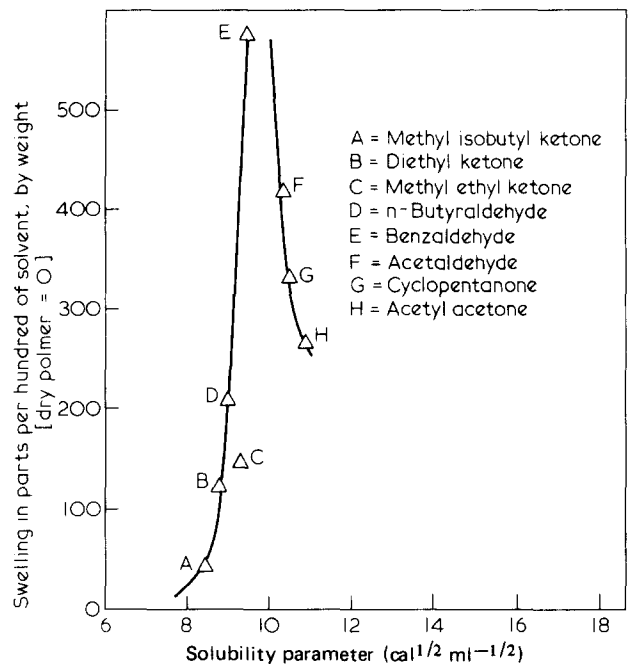


Figure 3 Swelling of gel in aldehydes and ketones at 298 K

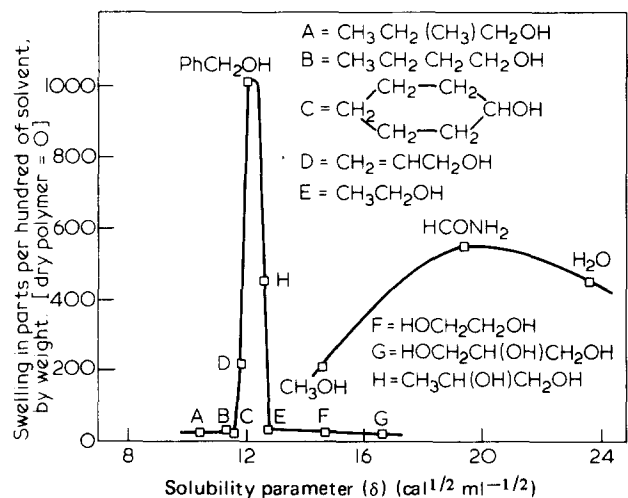


Figure 4 Swelling of gel in various alcohols, formamide and water at 298 K

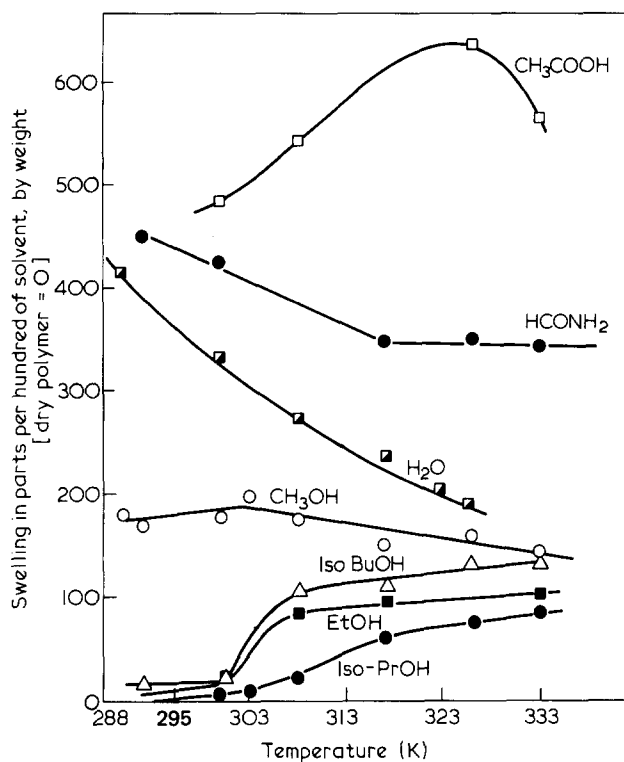


Figure 5 Equilibrium swelling vs. temperature

breaks in slope of their degree of swelling-temperature plots at temperatures of between 293–328 K. Though the point is not present in Figure 5 methanol has a degree of swelling of only 30 pph at 273 K.

Finally, water alone of all the solvents so far evaluated does not show such a break and has by far the steepest, even spectacular, decrease in the degree of swelling as the temperature is increased. The more normal behaviour of gels with swelling solvents is an increase in the degree of swelling with temperature. Thus the esters *n*-propyl-, amyl-, and *sec*-butyl acetates, isobutylformate, diethylmalonate, diethylmalonate and di-amylphthalate along with the ketones methylpropylketone, acetylactone and benzaldehyde were all shown to have a much higher degree of swelling at 330 K than at 298 K. These to date have not been investigated in detail.

The equilibrium swelling of water was studied again over a wider temperature range and the results are presented in Figure 6. This plot shows, in addition to the large shrinkage and syneresis of the polymer between 273 K and 373 K a reasonable straight line plot over much of this range showing that the degree of swelling is directly proportional to negative reciprocal temperature. The results contain a surprise in that the gel at 373 K still contains 112.6 pph of water. It is generally assumed that very high molecular weight poly(ethylene oxide) is insoluble in water at 373 K and it might have been expected that the degree of polymer swelling at this temperature would be close to zero. These results clearly demonstrate that poly(ethylene oxide) at 373 K is still able to associate with a significant quantity of water. In this particular case it is almost exactly three molecules of water per  $-\text{O}-\text{CH}_2\text{CH}_2-$  unit. This serves to demonstrate the great strength of binding of the water to the poly(ethylene oxide). Indeed, using the poly(ethylene oxide) units attached to surfactant molecules Heusch<sup>11,12</sup> has demonstrated that at the cloud point they precipitate

in combination with one mole of water per ether group and that a number of specific hydrates exist in these low molecular weight species.

We believe that the swelling behaviour in the different solvents can be qualitatively explained as follows. The crosslinked polymer contains a significant proportion of crystallinity. Thus for any appreciable degree of swelling to occur the latent heat of fusion for these crystallites must be supplied. In the case of solvents such as isobutanol the solubility parameter is considerably different to that of the polymer so that the  $\Delta H$  of mixing will be positive and cannot provide the energy to melt the crystallites. The swelling does not occur until above the crystalline melting temperature when the positive entropy of mixing provides the driving force. The swelling increases normally with temperature above the crystalline melting temperature. Solvents such as benzyl alcohol and chloroform closely match the solubility parameter of the poly(ethylene oxide) crystallites and presumably possess a high enough energy from the interaction provided by hydrogen bonding to provide a negative value for the enthalpy of mixing and cause melting of the crystallites below 298 K along with the expected high degree of swelling anticipated for a solvent with  $\Delta H_{\text{mix}}$  zero or negative and  $\Delta S_{\text{mix}}$  positive.

Water is assumed to have a strongly negative enthalpy of mixing with poly(ethylene oxide) sufficient to cause melting of the crystallites at 298 K. The entropy change is however known to be negative<sup>13</sup> and hence the term  $-T\Delta H_{\text{mix}}$  in the equation  $\Delta G_{\text{mix}} = \Delta H_{\text{mix}} - T\Delta S_{\text{mix}}$  has a positive value which increases with temperature and reduces the free energy of mixing as the temperature rises. The result is a decrease in the degree of swelling.

We thus believe that there is an overall disordering process occurring in the swelling of the crosslinked polymer by most solvents but an ordering process for water and probably for formamide. This ordering process in water is most probably the tight binding of water into specific hydrates.

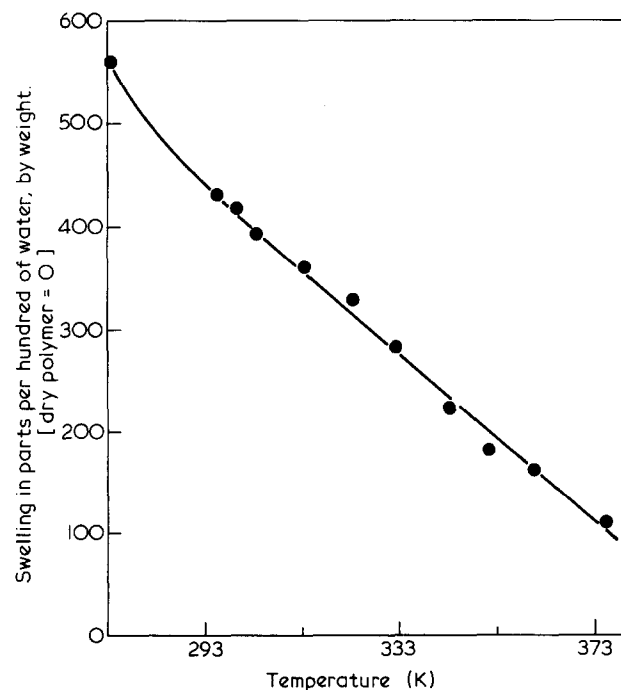


Figure 6 Equilibrium swelling of gel in water

## CONCLUSIONS

It has been demonstrated that the swelling of the cross-linked polymers is a powerful, yet quite simple, tool for the investigation of poly(ethylene oxide)/solvent interactions. Water is not a particularly good swelling solvent for the poly(ethylene oxide) gels and in common with formamide shows an anomalous swelling/temperature relationship. Water in particular appears to promote significant ordering on admixture with the polymer to which it binds in greater than molar equivalent quantities to at least 373 K. This raises the question of the nature of this ordering and very strong complexation and indicates that when homopolymer poly(ethylene oxide) separates out from water at *ca.* 373 K the poly(ethylene oxide) chain does not separate as an anhydrous polymer but rather in the form of a still highly hydrated complex.

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