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Polypyrrole in poly(ethylene oxide) gels with copper(II) chloride: a hybrid conducting polymer

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The electrical properties of poly(ethylene oxide) gels incorporated with $CuCl_2$ and polypyrrole were investigated with respect to temperature, concentration of $CuCl_2$ and the degree of crosslinking. Highly conducting gels were obtained even at low concentrations of $CuCl_2$ and polypyrrole. The activation energy for conduction and effect of crosslinking and swelling in methanol on the electrical properties strongly indicate the hybrid nature of these materials. The conduction process was predominantly of the electronic semimetallic type with some contribution from ionic mobility.

(Keywords: polypyrrole; poly(ethylene oxide); copper(II) chloride)

INTRODUCTION

Poly(ethylene oxide) (PEO) forms a number of complexes with inorganic salts. These have been extensively investigated in the past for their electrical properties and are mainly used as solid polymer electrolytes[1-7]. Previous reports on such complexes show that they have only moderate conductivity at room temperature, which increases to sufficiently high levels (usable for battery applications) only at high temperatures near or above the melting point (>70°C) of the polymer matrix. Further, the high degree of crystallinity obtained in some of these complexes restricts the ionic mobility and hence there have been attempts in the past to introduce groups or salts that prevent crystallization of the material[7-10]. In some of the studies, the ionic polymers have been crosslinked or copolymerized with other groups that also prevent crystallization[11,12]. However, their conductivity is not enhanced very much because of the counteracting effects of restricted chain mobility, increase of glass transition temperature, etc.[13,14]. Recently, ionically conducting polymeric gels have been studied not only for solid electrolyte applications but also for their potential use in transducers, actuators and electrokinetically driven systems[15-17]. The electrical conductivity of these gels plays an important role in their electromechanical response. As we recently reported[18-20], it is possible to grow conducting polymers such as polypyrrole (PPy) on or within PEO complexes and high conductivity values can be obtained. It was therefore thought that it might be possible to obtain a hybrid material consisting of an ionically conducting PEO gel as one component, the other component being conducting PPy deposited therein. Results of our investigations on the electrical properties of such a combination of polymer networks are reported in the present paper.

EXPERIMENTAL

The PEO gels were prepared by using polyethylene glycol (PEG, molecular weight 4050, Breox Pharmaceutical grade, British Petroleum, UK) and dicyclohexyl methane 4,4'-diisocyanate (Desmodur W, Bayer Chemicals, Germany) with 1,2,6-hexane triol (Aldrich Chemical Company, Gillingham, UK) as the crosslinking agent. PEG was dried in a stream of nitrogen under reduced pressure for 6 h prior to use. The prepolymer was obtained after mixing all the above components together with ferric chloride as catalyst in the desired quantities as listed in *Table 1*. The prepolymer was poured into preheated polypropylene moulds and cured at 95°C for 4 h. The crosslinking reaction was essentially according

Table 1 Composition of PEO gels

Sample code	PEG 4000 (g)	Desmodur W (ml)	1,2,6-Hexane triol (g)	$FeCl_3$ (mg)
PEG-1HT	40	6.1	1.32	9.56
PEG-2HT	40	9.7	2.64	10.60
PEG-3HT	40	13.3	3.97	11.64
PEG-4HT	40	17.0	5.29	12.68

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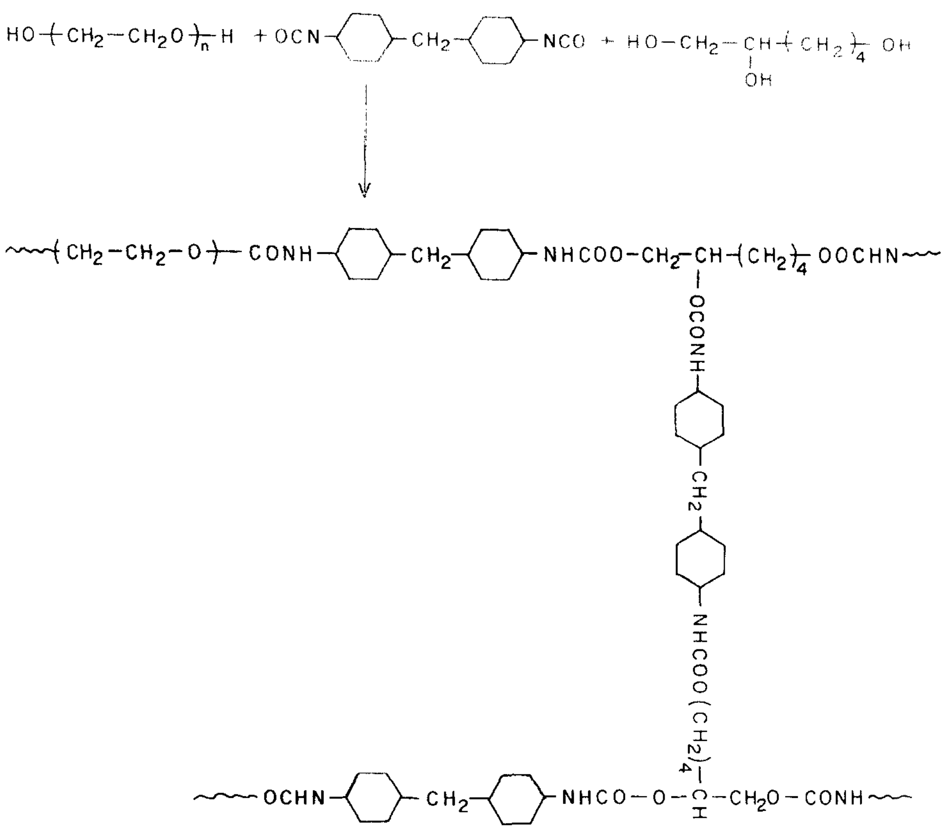

Scheme 1

to *Scheme 1*. The gelled blocks were removed and cut to the required dimensions (2 cm × 1 cm × 0.1 cm) for further studies. The complete details of preparation and characterization of these hydrogels are given elsewhere[21–24].

The deposition procedure of PPy in these gels was essentially the same as that reported earlier for PEO complexes[18–20]. The gels were first swollen in methanol containing various amounts of copper(II) chloride ($CuCl_2$, Loba Chemie, India), ranging from 0 to 50% by weight for a period of 24 h. For complexing PEO, $CuCl_2$ was chosen since it can initiate PPy formation by vapour deposition *in situ* while other salts such as NaI and $Li(CF_3)SO_3$ do not yield any PPy. These were then removed and excess solvent was blotted off by filter paper. The equilibrium uptake of the solvent and the salt was estimated from the difference in weights before and after swelling, as well as the dry weight. The gels containing $CuCl_2$ were then exposed to pyrrole (Aldrich Chemical Company, USA) vapours saturated in a desiccator at 25°C for 20 h. The structure and electrical conductivity of these samples were studied in the same manner as reported earlier[18,19,26]. The changes in the electrical conductivity due to swelling and/or deformation of the gels with PPy were monitored by forming a two-terminal cell using thin platinum foil wrapped on them at 0.5 cm apart, attaching leads and dipping the same in pure solvent.

RESULTS AND DISCUSSION

The PEO gels with various degrees of crosslinking were first investigated for structure, swelling and $CuCl_2$ uptake. The wide-angle X-ray diffraction scans (WAXS) for the dry gels are shown in *Figure 1* together with that for pure PEO polymer (curve A). An interesting observation is that there is a fair degree of crystallinity present in these gels, which is seen to decrease with increase of crosslinking (see inset in *Figure 1*). Even at the highest level of crosslinking units (4 moles hexane triol/mole PEG, sample PEG-4HT) there is some molecular order present in the gel, as can be surmised from the weak but distinct WAXS peak occurring at $2\theta = 24°$. Since the WAXS for the gels has a close similarity to that for pure PEO, this crystalline order arises from the PEO moieties. However, there are slight differences in the *d*-spacings for the WAXS patterns of uncrosslinked PEO and its gels, which also show much broader diffraction peaks than that of pure PEO. These differences can arise due to the small domain size and constrained crystalline growth in the presence of additional comonomer (Desmodur W) which gives amide linkages in the crosslinked network, as compared to the large spherulitic domains observed for homopolymer PEO.

Since the preconditioning step to PPy deposition consisted of soaking the gels in a methanolic solution of $CuCl_2$, it was thought to be appropriate to study their swelling behaviour, by measuring solvent and/or salt uptake after equilibrium (24 h). *Figure 2* shows the solvent uptake expressed as the ratio of $(S_w - S_d)/S_d$ where S_w and S_d are the wet and dry weights of the gel after equilibrium swelling at different $CuCl_2$ concentrations. It is evident that these gels take up large amounts of solvent and salt and, most interestingly, this occurs even at a high concentration of the ionic species in the solution. The degree of swelling of ionic gels is usually expected to decrease with addition of salts to the external swelling medium, mainly due to the counterion effects, charge

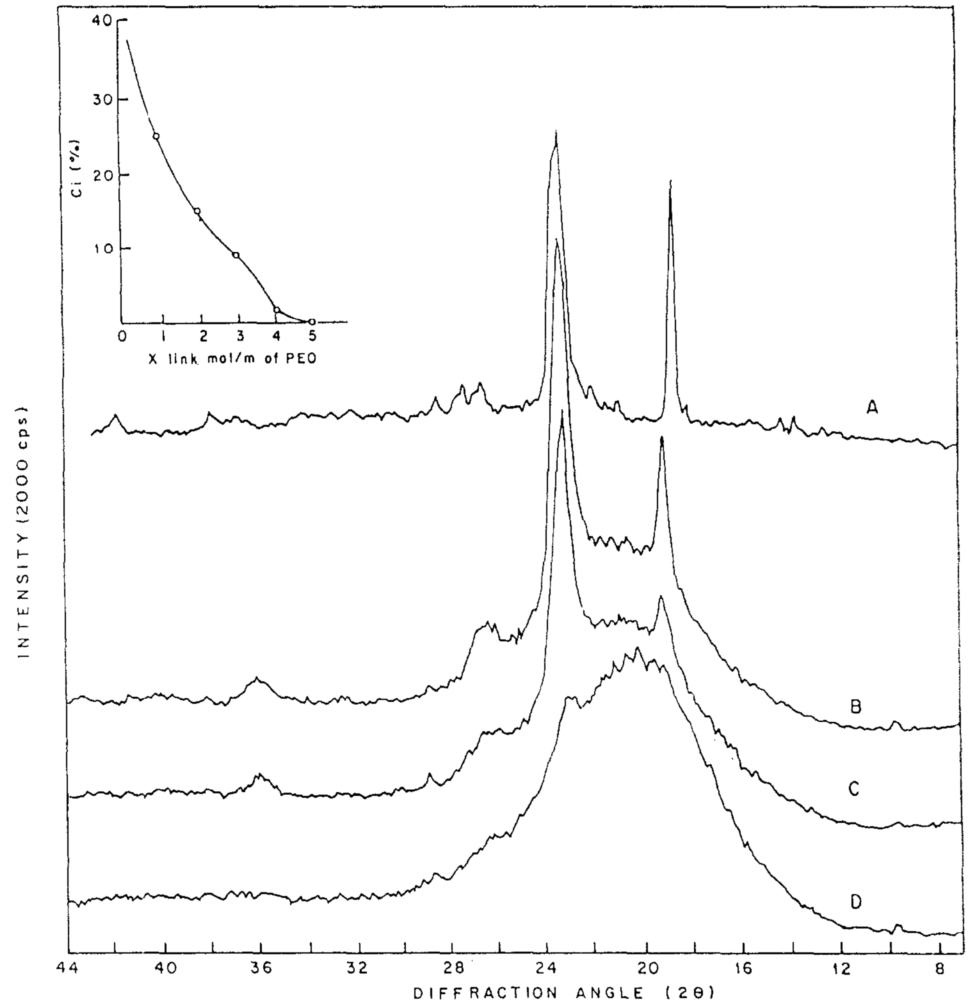

Figure 1 Wide-angle X-ray diffraction scans for PEO gels having different degrees of crosslinking. Curve A: uncrosslinked PEO; curves B–D: crosslinker concentrations of 1, 2 and 4 moles hexane triol/mole PEG, respectively

neutrality condition etc.[27,28]. In fact, in many cases this leads to collapse of the swollen gels[29]. On the other hand, we observe in the present case an increase in the degree of swelling with the increase of salt concentration which may in the first instance appear quite unusual. However, it is known that PEO homopolymer becomes increasingly soluble in methanol (as well as other solvents) by the addition of small amounts of alkali metal salts due to complexation and change in polymer solvent interaction parameter[30]. Such effects can lead to higher solvent uptake or degree of swelling in the gels and subsequent incorporation of $CuCl_2$ in the same. These results are also relevant to the electrical response to the gels in the swollen state, which is discussed later in the paper.

The electrical resistivity (ρ) of the PEO gels containing only $CuCl_2$ was quite high at room temperature and ranged from 10^9 to $7.5\times10^7\,\Omega$cm depending on the concentration of the added salt. In contrast, with the inclusion of PPy in these gels, the electrical resistivity dropped very sharply, as shown in *Figure 3*, and attained a low limiting value which was dependent on the initial concentration of $CuCl_2$ as well as on the degree of crosslinking. The high resistivity values are typical of those observed for a number of PEO homopolymer complexes with alkali metal salts, which are ionically conducting materials[1–7]. The low resistivity after incorporation of PPy suggests that the electrical transport may be mainly governed by electronic, rather than ionic, conduction. In order to delineate the two processes, further studies were carried out on temperature dependence of conductivity and the effect of crosslinking. *Figure 4* shows the set of curves for temperature variation of resistivity for the dry gels PEG–1HT (1 mole hexane triol/mole PEG) containing various concentrations of $CuCl_2$ and PPy deposition. Similar curves for $\log\rho$–$1/T$ variation were also observed for other gels (not shown here). It is seen that, whereas the gels containing only $CuCl_2$ show a sharp variation in resistivity with temperature, gels containing PPy show little variation of ρ with T, especially at high $CuCl_2$ concentration. The former is reminiscent of ionically conducting PEO complexes while the latter is expected for a semimetallic conducting polymer[31].

On the other hand, if one considers the variation of electrical properties of these gels containing the same $CuCl_2$ concentration but different degrees of crosslinking, as shown in *Figures 5* and *6*, it becomes evident that there is a notable effect of crosslinking on the resistivity (*Figure 5*), its temperature variation (*Figure 6*) and the

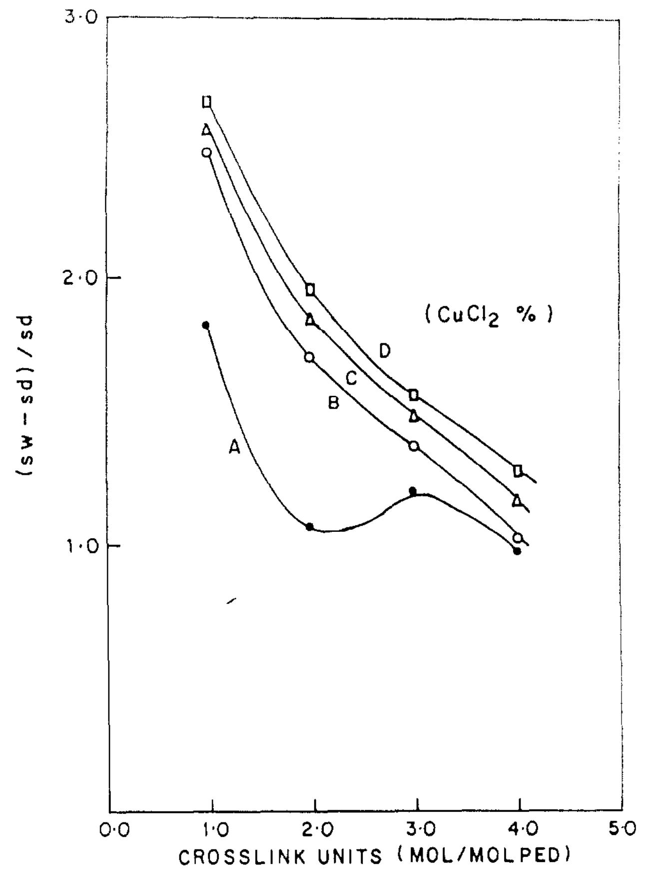

Figure 2 Swelling behaviour of PEO gels in methanol containing different concentrations of $CuCl_2$. Curves A to D correspond to $CuCl_2$ contents of 10, 15, 20 and 30 wt%, respectively

activation energy for charge transport (see curves E_1 and E_2, *Figure 5*). If the electrical conduction was purely electronic through the PPy moieties, one would expect only a small activation energy, which would not be affected by stiffening of the PEO chains or the gel network. In the cases where electrical conductivity is associated with ionic transport through the polymer, the chain mobility, glass transition temperature and complex formation play an important role in governing the properties. Thus we have a hybrid material which shows predominantly electronic semimetallic conduction with some contribution from ionic mobility to the total conductivity value.

The ionically conducting gels are potentially useful materials for electrochemical transducers, actuators, artificial muscles, etc.[15–17]. In these applications, their electrical properties in the swollen state are of prime importance. Hence the resistivity of the PEO gels containing PPy was monitored continuously after placing them in pure methanol, which would lead to swelling. Some very interesting observations were made during these studies. *Figure 7* shows the resistivity as a function of time for two samples containing 5% and 15% $CuCl_2$ with PPy. The resistivity is seen first to decrease slightly then to increase rapidly by almost one order of magnitude up to a certain time (100 s) and then to decrease again to attain a low limiting value. This behaviour is seen in both samples but is more pronounced for samples having a higher concentration of $CuCl_2$. This unusual response may be explained as follows. The resistivity of PPy is known to increase after exposure to organic vapours

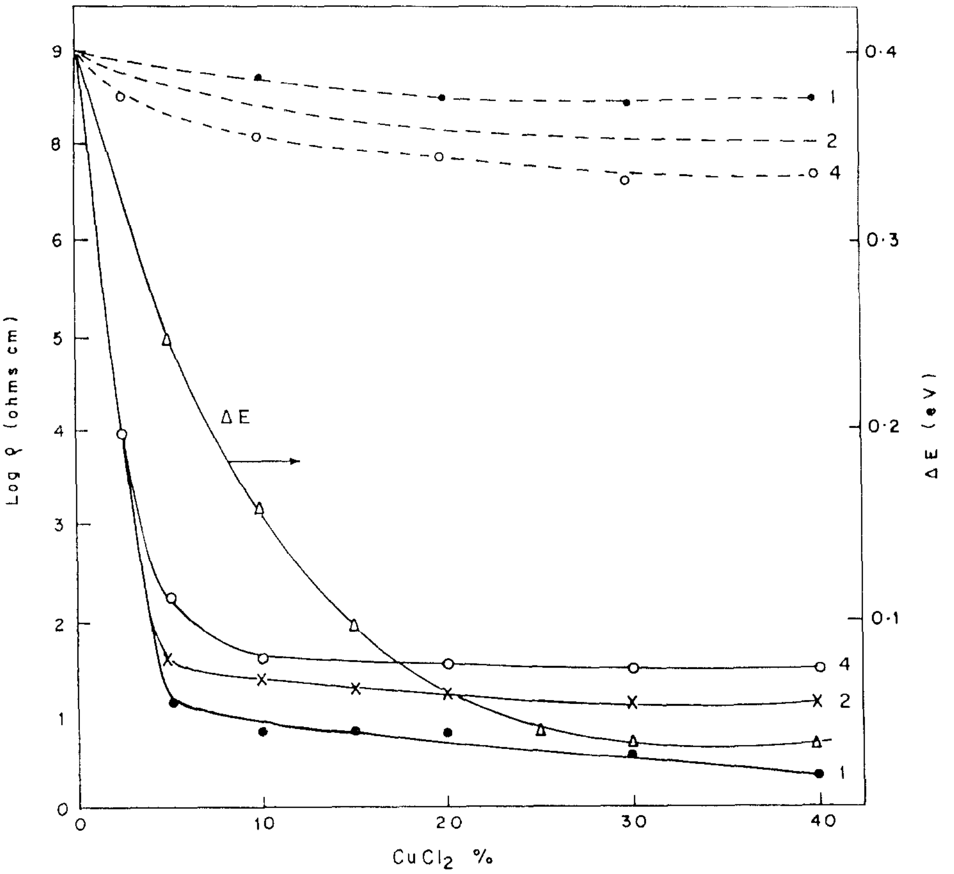

Figure 3 Electrical resistivity of PEO gels as a function of $CuCl_2$ concentration. (---) Samples without PPy; (—) samples with PPy. The numbers next to the curves indicate hexane triol concentration. The variation of activation energy for PEG–1HT gel is also indicated

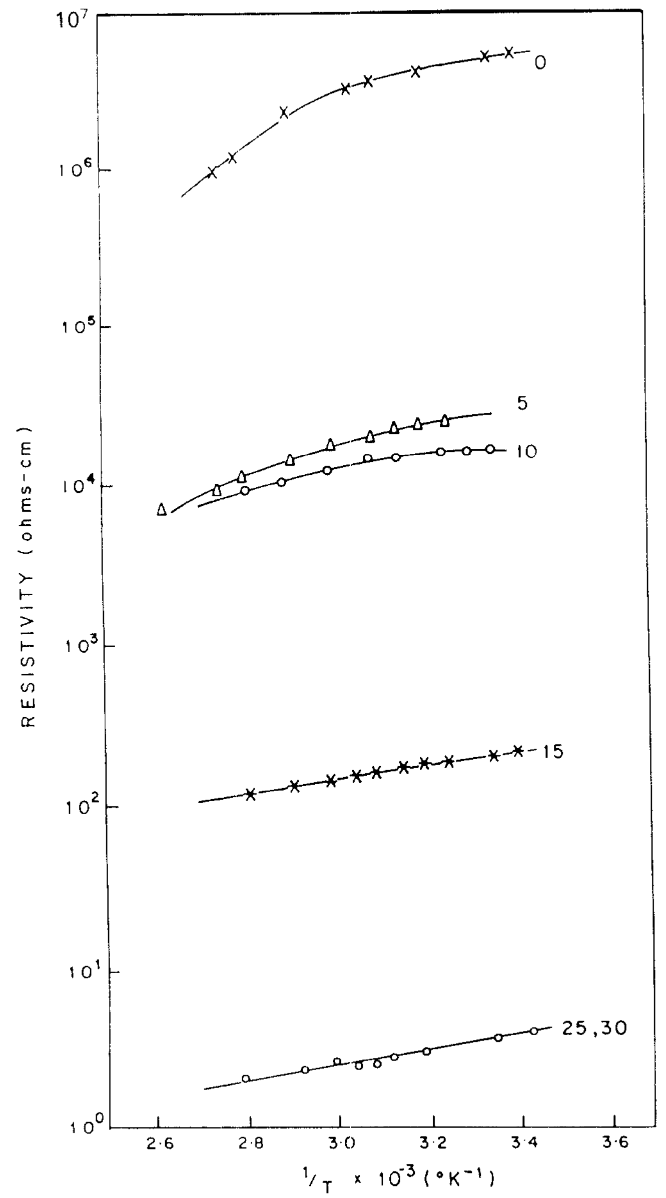

Figure 4 Temperature dependence of resistivity for PEG–1HT gel with different concentrations of $CuCl_2$ after PPy incorporation. The numbers next to the curves indicate wt% $CuCl_2$

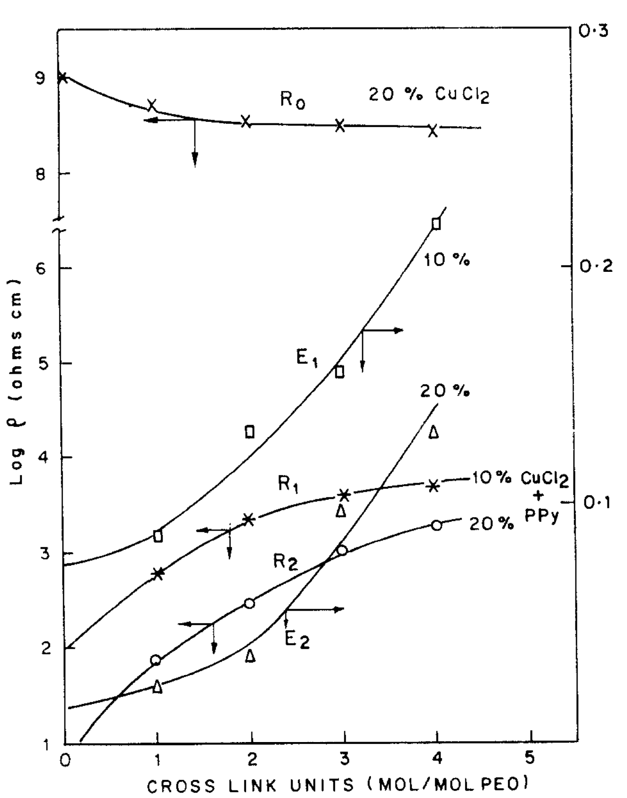

Figure 5 Effect of crosslinking on the electrical properties of PEO gels containing 10 and 20 wt% $CuCl_2$ with PPy. Curves R_1, R_2, resistivity; E_1, E_2, activation energy; R_0, resistivity of PEO gel (20 wt% $CuCl_2$) without PPy (shown for comparison)

solvents such as methanol[32–34]. On the other hand, increase of solvation/dissociation of the ionic species in the swollen gel causes higher conductivity[35,36]. Since we have a combination of these in our hybrid PEO gels with PPy, one obtains both the effects of increasing and decreasing electrical resistivity with exposure to methanol. In the unswollen state it is the conductivity through PPy that dominates the behaviour, while in the swollen state, the ionic conduction through the gel is the major factor governing the electrical property. Interestingly, these two occur at different time domains during the swelling experiments. Further studies are being carried out on these various aspects and will be reported in the near future.

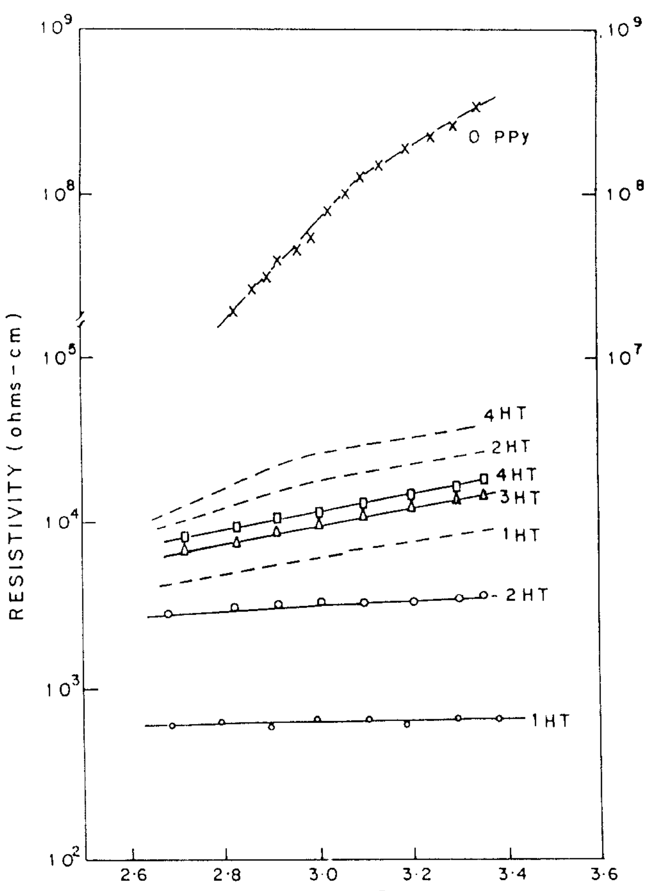

Figure 6 Effect of crosslinking on the temperature dependence of electrical resistivity of PEO gel containing 10 wt% $CuCl_2$ (– – –) and 20 wt% $CuCl_2$ (—) with PPy

CONCLUSIONS

PEO gels having different levels of crosslinking and complexed with $CuCl_2$ possess high electrical resistivity. However, these can be made highly conducting at room

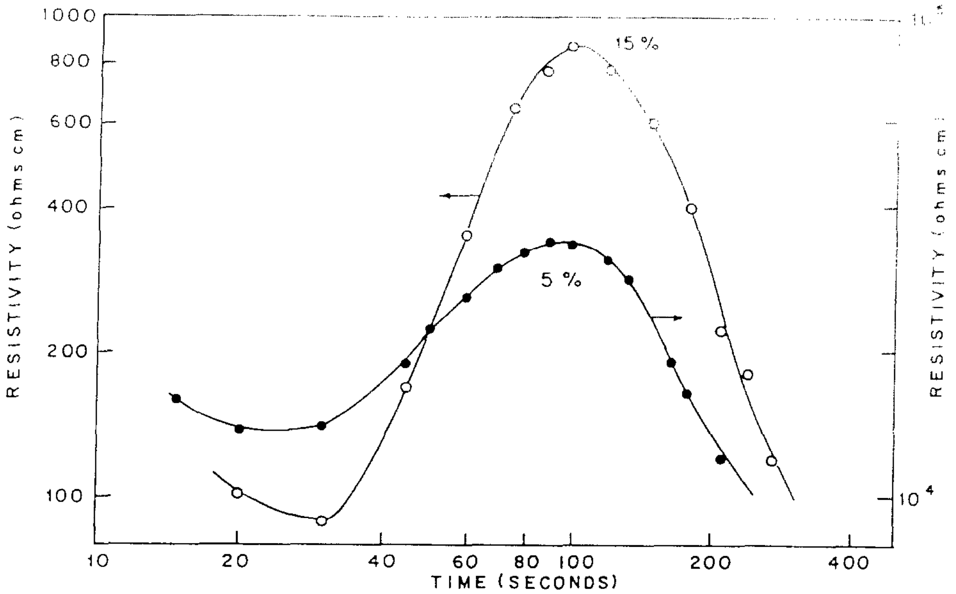

Figure 7 Effect of swelling on the electrical resistivity of PEO gels with PPy containing (●) 5 wt% $CuCl_2$ (right-hand scale) and (○) 15 wt% $CuCl_2$ (left-hand scale)

temperature by incorporating polypyrrole even at small concentrations (< 10% by weight). The temperature dependence of conductivity, together with the effects of dopant concentration and crosslinking, suggest that the electrical transport in these materials is of a mixed type: predominantly semimetallic through the PPy network, along with some contribution from the ionic mobility in the PEO matrix. The change in resistivity monitored during the swelling process in methanol exhibited a very unusual trend: it increased initially but attained a low value after 150 s. This could also be explained on the basis of hybrid conductivity of the samples.

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