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INTELLIGENT NETWORKS BASED ON POLY(OXYETHYLENE)

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Abstract : Films of PEO and PEO blends were efficiently crosslinked by exposure to ultraviolet radiation with high-pressure mercury lamp. Photochemical crosslinking proceeded in the presence of photoinitiator such as benzophenone or pentaerythritol triacrylate. PEO networks obtained by UV irradiation in the presence of potassium salts (thiocyanate, perchlorate and triflate) as templates showed enhanced cation binding ability for Li^+ and Na^+ cations. Cationic networks were prepared from crosslinked PEO modified with ethyl methacrylate dimethyl dodecyl ammonium bromide. Stimuli-sensitive hydrogels (pH and temperature) were prepared from combinations of PEO and poly-N-isopropyl acryl amide, polyvinyl methyl ether, polyvinyl acetate and poly-2-vinyl pyridine subjected to UV irradiation.

INTRODUCTION

Poly(oxyethylene) (PEO) derivatives have become the subject of intensive scientific research in the last 3 decades. The reasons for the growing interest in this field are the unique set of properties of PEO derivatives, their universal application and the ready availability of the initial polymer. The most important properties of PEO are: solubility in water and many organic solvents, formation of PEO-salt complexes, lack of toxicity and FDA approval for internal consumption, rapid clearance from the body, lack of immunogenicity, high mobility in water and large exclusion volume in water. Crosslinked polymers based on PEO form an important class of novel materials with a number of possible applications, such as wound dressings (Ref. 1) controlled drug release systems

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(Refs. 2,3) phase transfer catalysts (Ref. 4) semipermeable membranes (Ref. 5) solid electrolytes for batteries (Ref. 6) and many other.

In our previous publications we reported on the synthesis and characteristics of PEO-based networks (Refs. 3,7). The synthetic methods previously outlined by us involved crosslinking, carried out in aqueous solutions of PEO with ionizing radiation such as γ-irradiation (^{60}Co source) (Ref. 8) or with a high energy (1-10 MeV) electron beam from a Van de Graaf generator (Ref. 5). Both methods are expensive and inconvenient as the sources are not generally available and the preparation of water swollen gels leads to a loss of energy and renders the scaling up for production difficult.

We have recently developed a method for photochemical crosslinking of PEO films by exposure to ultraviolet irradiation with a high-pressure mercury lamp in the presence of hydrogen abstracting photoinitiators (Ref. 9). The gel fraction yield exceeds 90% and the number-average molecular weight between crosslinks, M_c varies from 3000 to 10^5. The degree of crosslinking can be controlled by changing the irradiation temperature. The ease, the relative safety, and the low cost of UV induced crosslinking provide significant advantages of various application possibilities over the usual radiation methods.

The goal of our investigation is to use the UV irradiation technique for the preparation of a new family of films of crosslinked polymers based on PEO combinations with:

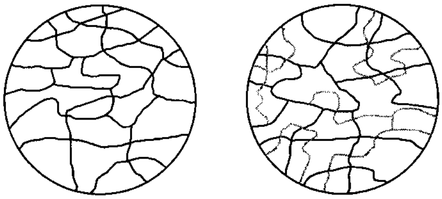
- water soluble pH sensitive and temperature-responsive polymers
- amphiphilic blockcopolymers, hydrophobic polymers and polymer-supported strong ligands
- unsaturated quaternary ammonium salts
- inorganic salts

The individual systems studied are presented in Table 1. The polymer combinations are held together by permanent entanglements. Due to their interlocking configuration, the state of phase separation obtained at the end of their synthesis remains frozen so that their properties are not influenced by ageing. They are well suited for combination of highly incompatible polymer pairs.

In accordance with our expectations PEO based networks will retain the sensitivity of the incorporated polymers, as well as the activity of the bound functional groups. Because of the hydration and mobility of the PEO chain segments, ligands and ions tethered to the network display an activity similar to that of a freely soluble molecule. A “memory” effect is liable to occur during crosslinking of PEO films loaded with inorganic salts. On the other hand, when coupled to another molecule or macromolecule, many of the PEO properties are transferred to the conjugate. In this way environmentally- responsive or "smart" versions of PEO hydrogels could be prepared as well.

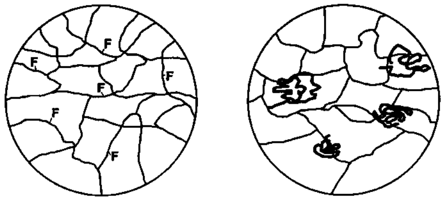
The following hypothetical scheme shows the different types of PEO based hydrogels :

HYPOTHETICAL SKETCH OF DIFFERENT TYPES OF PEO BASED HYDROGELS



Conventional PEO hydrogel

PEO - Polymer 2 composed hydrogel



PEO hydrogel with supported function F
F : quaternary ammonium salt or strong ligand (TMEDA)

PEO hydrogel with hydrophobic domains

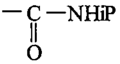
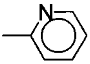
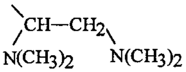
Scheme 1

EXPERIMENTAL

Preparation of PEO Blends by Casting from Solution

PEO (Polyox N-12K, $M_v = 1.10^6$) was added under intensive stirring to a CH_2Cl_2 or CH_3CN solution (3%) containing the additive (another polymer, monomer or salt) and the photoinitiator (benzophenone (BPh) or pentaerythritol triacrylate (PETA)). The homogeneous viscous solution was cast into a glass or teflon Petri dish kept in the dark, and the solvent allowed to evaporate in air. The samples (thickness 100 μm - 200 μm) were subjected to drying for several hours under vacuum prior to irradiation.

Tab. 1. Additives used in sensitive PEO-based hydrogels

Type	Name	Sensitive group	Expected properties
Polymer	PVAc	$-OCOCH_3$	Hydrophilic/hydrophobic balance Mechanical strength Chemical modification
	PVME	 $-\overset{\vert}{C}HOCH_3$	Temperature sensitive
	PNIPAAm	 $-\underset{\underset{O}{\Vert}}{C}-NHiP$	Temperature sensitive
	P2VPy		pH sensitive
	PEO/AGE-copolymer modified with TMEDA		Complex forming properties pH sensitive Strong ligand properties
Monomer	$EM(CH_3)_2C_{12}H_{25}NBr$	$-\overset{+}{N}(CH_3)_2C_{12}H_{25},Br^-$	pH sensitive Sensor for humidity PT catalyst
Salt	KSCN $KClO_4$ KCF_3SO_3	pseudo-crown ether entities	Memory in cation binding properties

UV Irradiation of PEO- Blends

The irradiation was carried out with a *TQ 150 ORIGINAL HANAU* high-pressure 150 W mercury lamp provided with a quartz tube and a cooling jacket. It was put in a glass vessel equipped with another thermostated jacket. The PEO blends were fixed on the inner side of the glass wall. To avoid quenching by oxygen, the irradiation was carried out under a constant flow of nitrogen.

Gel Fraction Determination

The irradiated blends were weighed and extracted with a proper solvent. The gel fraction (GF) equals (weight of extracted sample divided by initial weight)×100%.

Swelling Measurements

The equilibrium degree of swelling ES (weight of swollen sample/weight of dry sample) was determined as follows: dry discs of 10 mm diameter from the crosslinked sample were equilibrated in distilled water and chloroform for at least 48 hrs, removed from the solvent, blotted with filter paper and weighed. Then they were dried to constant weight under vacuum and weighed again.

DSC Measurements

The DSC curves were obtained with a Perkin-Elmer DSC -2 thermal analysis system at a standard heating and cooling rate of $10^0C\ min^{-1}$. Samples of ca. 12 mg were run in an argon atmosphere over a temperature range of -60^0C to $+150^0C$. Indium ($T_m = 156.6^0C$) was used for temperature calibration. The crystallinity indices of the networks were calculated as a ratio of the molar enthalpy of melting of the PEO phase and that of a 100% crystalline polymer (8.276 kJ/mol) (Ref. 10).

NMR Analysis

Proton NMR spectra of network gels were taken in $CDCl_3$ on a Bruker- 250 Mhz apparatus.

Electroconductivity Measurements

The measurements were performed in a dry nitrogen atmosphere in a cell using a precision automatic digital RCL impedance meter at fixed frequency of 1khz. Lithium electrodes were used.

RESULTS AND DISCUSSION

Amphiphilic PEO based networks. UV crosslinking of blends of PEO with poly(vinyl acetate)

Because of the high water content of PEO hydrogel, its mechanical strength is weak, and may limit its practical applications. Another important gel property is the degree of swelling and the hydrophilic(HPL)/hydrophobic(HPB) balance of the network. Both characteristics can be altered by modifying the PEO networks with other hydrophobic or hydrophilic components. Poly(vinyl acetate) (PVAc) was chosen. Incorporated in the network matrice this polymer can be fully or partially hydrolized thus producing gels with quite different amphiphilic properties. On the other hand it is well known (Ref. 11) that PEO-PVAc blends are miscible in the melt over the entire composition range.

Tab.2. UV crosslinking of blends of PEO with poly(vinyl acetate).

UV irradiation under a flow of argon at [BPh]/[-EO-+-VAc-] = 5 x 10^{-3}; Irradiation time = 40 min. PEO, M_v = 1 x 10^{6}; PVAc, M_n = 68600 (Union Carbide, AYAT)

[PEO] : [PVAc] blend	[PEO] : [PVAc] network	Irradiation temperature °C	GF, %	ES, H_2O	ES, $CHCl_3$	T_m, °C	X_c DSC	X_c* DSC
In the presence of benzophenone								
1:0	1:0	25	91.7	4.4	5.1	60.5	0.64	0.64
		70	97.7	5.5	9.0	63.1	0.62	0.62
10:1	10:1	25	95.3	5.8	10.5	61.5	048	0.48
	8:1	70	96.8	7.3	15.1	58.3	0.57	0.60
5:1	5:1	25	86.8	6.5	12.6	60.5	0.41	0.57
	6:1	70	89.6	7.4	18.2	57.5	0.39	0.52
3:1	3:1	25	94.3	5.2	14.9	56.0	0.30	0.49
	3:1	70	91.7	6.1	16.3	57.9	0.33	0.54
2:1	3:1	25	72.4	7.0	19.8	62.1	0.33	0.54
	2:1	70	81.3	6.6	22.2	56.0	0.27	0.54
In the absence of benzophenone**								
10:1	15:1	25	56.5	9.6	17.0	61.1	0.49	0.55
	26:1	70	66.5	6.9	13.8	60.3	0.48	0.52
5:1	10:1	25	80.4	6.0	13.9	59.4	0.43	0.52
	12:1	70	86.5	4.7	11.2	59.5	0.41	0.48
3:1	4:1	25	41.2	-	-	61.1	0.26	0.39
	3:1	70	62.1	-	-	58.6	0.31	0.51
2:1	7:1	25	40.7	-	-	62.3	0.32	0.41
	3:1	70	59.9	-	-	60.1	0.21	0.35

* The values are normalized against the weight fraction of PEO

** Blends annealed at 150°C for 15 min and quenched

PVAc belongs to the so-called crosslinkable by UV irradiation type of polymers. Although PVAc also undergoes chain scissions under the influence of UV light, the free radicals produced are usually quite active so that they either recombine immediately (cage effect) or terminate by hydrogen abstraction, thereby forming a new free radical that can recombine with another polymeric radical. Therefore, we assume that some crosslinked graft PEO-PVAc copolymer is formed during UV irradiation.

The composition dependence of the efficiency of UV induced crosslinking of the blends is shown in Table 2. PVAc is almost completely incorporated in the network in the presence of photoinitiator. The gel fraction yield tends to fall when raising the content of PVAc in the blend. The increased content of PVAc causes a small change of ES in water and a rise of ES in chloroform. The experiments carried out at a higher temperature (70^{0}C) showed better results with respect to GF yield. At 70 ^{0}C PEO is above its melting temperature and PVAc is above its glass temperature, which creates preconditions for better mixing of the components and consequently - for better crosslinking.

Another important result is the effective crosslinking of PEO-PVAc blend in the absence of photoinitiator. UV crosslinking of PEO-PVAc blends without benzophenone results in lower gel fraction yields. In this case the influence of annealing and high temperature irradiation on GF is substantial. Annealing prior to irradiation usually causes more than 20% increase of GF.

It is well known that the presence of PVAc in the blend leads to a drastic reduction of the overall rate of crystallization of PEO. The crystalline regions are smaller and less perfect than those formed in the absence of the non-crystallizable component (Ref. 12). The same effect is observed for the PEO-PVAc networks by the calorimetric measurements. As seen from Table 2 the degree of crystallinity of PEO is 10 to 15% lower than for an analogously obtained network of pure PEO. It seems that polymeric films of good dimensional and chemical stability for application as solid electrolytes can be prepared by UV crosslinking of blends of PEO with non-crystallyzing polymers like PVAc.

Thermoresponsive PEO based networks. UV and γ-irradiation crosslinking of blends of PEO with poly(vinylmethyl ether) and poly(N-isopropylacrylamide)

Poly(N-isopropylacrylamide) (PNIPAAm) and poly(vinylmethyl ether) (PVME) are the most popular members of a class of polymers that display inverse solubility in aqueous solution upon heating. Their macromolecular transition from a hydrophilic to a hydrophobic structure occurs rather abruptly close to their lower critical solution temperature (LCST). The most important swelling-deswelling kinetics of a gel can be regulated by diffusion in the polymer network (Ref. 13). One of the routes to accelerate changes in gel swelling is the modification of the gel molecular architecture. The properties of crosslinked PNIPAAm and PVME can be manipulated by crosslinking their blends with PEO. In this way it is possible to control the degree of swelling, the HPL/HPB balance of the network, and the rate of the gel swelling changes by the presence of an essentially inert ingredient,while the swelling transition temperature remains unperturbed.

PEO/PNIPAAm networks

The conventional PNIPAAm gel demonstrated slow deswelling due to diffusion- controlled mechanism accompanying the skin layer formation. Okano et al. were the first to synthesize IPN networks from PNIPAAm/PEO-PDMS-PEO triblock copolymer (Ref. 14). It was suggested that the degree of swelling of IPNs can be controlled without changing the swelling transition temperature. Macromolecules tend to avoid PEO in an aqueous medium. This "avoidance phenomenon" might be due to the unfavourable adsorption to PEO (PEO segments,resp.) which will result in a loss of polymer chain mobility and a decrease in entropy. Usually each network in the swollen PEO-based IPNs exists independently, with a different morphology from the dried bulk state. The loss of entropy counteracts the loss of ethylene oxide-unit bounded water when macromolecular interaction occurs. In the case of hydrophilic PEO graft chains the association with PNIPAAm network segments will form water paths within the skin layer of the shrinking PNIPAAm gel (Ref. 15). Therefore a faster deswelling was observed. Some preliminary results of crosslinking of PEO-PNIPAAm resp.PEO-NIPAAm blends are shown in Table3. It is noteworthy to consider the possibility to obtain PEO/PNIPAAm network by using the initial monomer NIPAAm, instead of its polymer. This route considerably simplifies the reaction procedure. As it is seen in Table 3 there is no substantial difference in the properties of the networks obtained by the two procedures.

Tab. 3. Crosslinking of aqueous solutions of PEO and PNIPAAm or NIPAAm by γ-irradiation (5 Mrad).

[PEO]: [NIPAAm] in solution	[PEO]: [PNIPAAm] in solution	[PEO]: [PNIPAAm] network	GF %	ES^{25} H_2O	ES^{40} H_2O
2.3 : 1		3.5 : 1	84	13.5	6.3
	2.3 : 1	3:1	70	13.0	4.0
1 : 1		1.2 : 1	83	12.0	4.0
	1 : 1	1.2 : 1	74	18.0	6.0

PEO/PVME Networks

The LCST of PVME is approximately 38^{0}C. PVME molecules in aqueous solution are successfully crosslinked by irradiation with an electron beam or gamma rays (Ref. 16). Their hydrogels exhibit very fast volume changes between 20^{0}C and 40^{0}C. The mixed PEO/PVME network was synthesized by UV crosslinking of blends of PEO with PVME.

Table 4. UV crosslinking of PEO with poly(vinyl methyl ether).

UV irradiation under argon. Irradiation time 40 min. PEO, $M_v=1\times10^6$

[PEO]: [PVME] network	$T_{irr.}$ °C	GF %	ES^{25} H_2O	ES^{40} H_2O	T_m °C	X_c DSC	X_c* DSC
In the presence of PETA (5%)							
3.2:1	25	63	5.3	4.0	64.4	0.50	0.71
4.3:1	25	51	8.4	6.3	63.8	0.39	0.51
2.4:1	70	68	7.5	5.3	61.7	0.38	0.58
3:1	70	85	5.6	4.4	61.6	0.44	0.63
In the presence of BPh [BPh]/[-EO-+-VME-]=5x10^{-3}							
0.9:1	70	60	8.2	4.0	59.7	0.32	0.79
5.2:1	70	67	11.6	6.1	60.0	0.36	0.45

X_c* - The values are normalized against the weight fraction of PEO

Gel hydrophobicity in PEO/PVME and PEO/PNIPAAm thermosensitive hydrogels can be controlled by the ratio between the polymer composites in the network. This may be successfully used when loading the network with biologically active substances. For example, small differences in the HPL/HPB balance may largely affect the local partitioning of different important substrates such as enzymes.

The transition of the swelling power between the HPL and the HPB state should be reversible. This was confirmed by repetitive measurements of the swelling ability by changing the temperature alternately between 25^{0}C and 40^{0}C (Table 4).

pH sensitive PEO based networks. UV crosslinking of blends of PEO with poly(2-vinyl pyridine)

The combination of PEO and poly(2-vinyl pyridine) (P2VP) will produce a hydrogel, that may display the intelligent properties of the mixed networks. It has been known that a crosslinked polymer gel bearing weakly acidic / or weakly basic pendant groups will imbibe solvent to an extent depending on pH and the ionic strength of the solution bathing the gel (Ref. 17). It can be expected that PEO/P2VP hydrogels containing pyridine pendant groups will swell in an acidic medium and shrink in a basic one.

Tab. 5. UV induced crosslinking of PEO-P2VP blends.

Blends of PEO(80wt%) and P2VP(20wt%); [BPh]/[PEO] = 5×10^{-3}; Irradiation time = 40 min; UV irradiation under a constant flow of nitrogen; The thickness of the films: 100 - 150 μm.

No	[PEO]/P2VP] network (^{1}H-NMR)	$T_{irr.}$ °C	GF, %	Equilibrium Swelling in H_2O pH=3	pH=7	pH=9
1	56 : 1	25	69.6	11.2	10.4	6.6
2	17 : 1	70	83.8	6.6	5.0	4.4
3*	12 : 1	70	88.8	11.6	10.7	11.1
	in the presence of $LiClO_4$ ([-EO-]/[Li^+] = 10 : 1)					
4	39 : 1	25	68.8	18.7	17.2	16.4
5	12 : 1	70	80.4	12.6	9.1	8.5

* The network was quaternized with CH_3I. Degree of quaternization ~ 20%.

As seen from Table 5 crosslinking is enhanced when the irradiation temperature exceeds the melting point of PEO crystallites, and GF rises some 10-20% as in the case of PEO/PVAc blends. In accordance with previously published data (Ref. 18) PEO/P2VP blends at weight ratios of 4 to 1, respectively, containing different $LiClO_4$ concentrations, are solid elastomeric materials with ionic conductivities as high as $6.0\ x10^{-6}$ S cm^{-1}. The last two examples from Table 5 reveal that a successful crosslinking of these blends is possible by UV-irradiation. Our preliminary measurements show that their ionic conductivity at 50°C is 1.0×10^{-5} S cm^{-1}, more than one order of magnitude higher than that of the initial blends. This research should be futher persued, as it provides a simple method for direct production of solid polymeric electrolytes.

Unfortunately, the pH-sensitivity of the swelling properties of PEO/P2VP networks is rather low. ES falls less than 35% by shifting from acidic to alkaline aqueous medium. Example 3 from Table 5 refers to a network quaternized with CH_3I with a degree of quaternization about 20%. ES rises two times in comparison with the original network. A significant swelling dependence on pH could probably be obtained by increasing the hydrophobicity of this cationic gel, e.g. by using longer chain alkyl halides as quaternizing agents.

Template effect in the UV-crosslinking of PEO in the presence of potassium salts

The tendency of PEO to form complexes with a wide variety of metal salts is known to be caused by the association of the ether oxygens of the polymer chain with the cation. The specific cooperative interaction between the cations and the ethylene oxide ligands leads to the formation of preorganized structures. The metal ion can be used as a reaction-directing matrice, thus influencing the mode of chemical reactions performed with PEO. Shirai and Tanaka (Ref. 19) revealed that polyesters of p-phenylene diacrylate and oligoethylene glycols photocrosslinked in the presence of potassium acetate as a template possess an enhanced cation binding. It is important to establish whether the geometry of the metal ion-PEO ligand complexes can be fixed by photocrosslinking pure high molecular weight PEO-metal salt composites. Although the UV-irradiation yields networks with random crosslinks, some fixing of the solvated entities resp. some specific recognition of the PEO networks can be expected after salt washing. This in turn would lead to changes in the cation binding properties of the obtained networks.

The occurrence of PEO-alkali metal salt complexes in the solid state generally involves the preformation of ion-polymer complexes in solution. Acetonitrile was used as a good solvent for both the PEO and all the salts studied. In such a solvent with a relatively low donor number (Ref. 20), the PEO segments are able to wrap the cation in an oxygen ethereal coil. When films of PEO/MtX mixtures were irradiated, they became insoluble. The irradiated PEO samples were weighed and then extracted with acetone by Soxhlet extraction for 48 hrs to remove unreacted PEO, the sensitizer and the alkali salts. The removal of these contaminants was checked by ^{13}C NMR spectroscopy and plasma emission spectroscopy.

Cation-binding properties of PEO networks

The binding of picrate salts to the photochemically crosslinked PEO was studied in THF by using the ratio $\mathbf{K}^* = \mathbf{R}_{\mathbf{MtX(PiMt)}}/\mathbf{R}_0$, where $\mathbf{R}_{\mathbf{MtX}} = [PiMt]_b/[PiMt]_s$ denotes the binding ability of PEO-N obtained by UV crosslinking in the presence of alkali metal salt and $\mathbf{R}_0 = [PiMt]_b/[PiMt]_s$ for the PEO-N obtained without salt additive. $\mathbf{K}^*$ stands for the enhanced binding ability of PEO-N influenced by the salt additive. Since $\mathbf{K}^*$ is not the equilibrium constant (the Klotz expression was not used), the binding experiments were carried out in a very narrow range of PiMt concentrations ($1.2.10^{-5}$ - $1.6.10^{-5}$ M) and with equal amounts of PEO-N (10 mg). The $\mathbf{K}^*$ values are presented in Table 6.

Tab. 6. Effect of potassium salts presented as additives during crosslinking reaction on the alkali picrate binding ability of PEO networks in THF

Type of PEO-N **Photoinitiator** **Crosslinking temperature** **Salt added**	$\frac{[EO]}{[MtX]}$	$K^*_{Mt^+}$			
		PiLi	**PiNa**	**PiK**	**PiCs**
1. PEO, BPh, 40°C					
KSCN	5	16.3	10.1	2.9	3.0
KSCN	20	11.4	7.5	1.4	1.5
$KClO_4$	5	7.1	3.2	1.5	1.6
2. PEO, PETA, 25°C					
KSCN	4	4.0	4.7	1.3	-
KCF_3SO_3	4	20.0	10.2	1.6	-
3. PEO, PETA, 70°C					
KSCN	4	9.1	4.3	1.3	
KCF_3SO_3	4	-	2.5	1.2	

In almost all cases the fraction of alkali picrate bound to PEO networks crosslinked in the presence of alkali thiocyanide, perchlorate and triflate, exceeded that found for PEO photocrosslinked in the absence of template salt. For all potassium salts examined, the cation binding ability order was $Li^+ < Na^+ < Cs^+ < K^+$, the same as found for PEO-N obtained in the absence of alkali metal salts (Ref. 21).

It is obvious that the template effect is manifested by an enhanced binding of especially LiPi and NaPi to PEO networks, obtained in the presence of potassium thiocyanate, perchlorate and triflate. This finding suggests that K^* acts as a template during the photocrosslinking process. We assume that the effect of the potassium salts is a result of the higher tendency of larger cations to form crosslinked coordination bonds between neighboring chain segments. The unit cell of the KSCN complex has oxygen binding sites coming from two PEO chains (Ref. 22). If more than one chain is involved the cation could constitute a crosslink. The cage structure leads to a great number of hypothetical topologies involving cyclic, bicyclic or catenane structures. Obviously during the photocrosslinking process some of them are preserved by permanent entanglements. In this way the cation-binding capacity of PEO-N can be improved by a simple procedure that might be an advantage over the use of crown ethers and polycrown ethers for some future applications.

PEO-networks modified with tetraalkyl ammonium salt

Cationic PEO networks bearing hydrophobic long alkyl substituents are likely to display some peculiar properties, especially in an aqueous solution. The immobilization of a quaternary ammonium salt (QAS) with a long alkyl group introduces the hydration shell of the ions into the hydrogel, which helps to maintain the water content balance. Due to hydrophobic interactions, micelle-like domains form which exhibit a strong influence on the structural parameters of the network.

PEO/QAS networks have been first obtained as a product of γ–irradiation of degassed dilute aqueous solutions (Ref. 23). We synthesized PEO hydrogels carrying a lipophilic QAS via UV irradiation of a film composed of PEO/ethylmethacrylate dimethyldodecylammonium bromide ($EM(CH_3)_2C_{12}H_{25}NBr$)/BPh prepared from methylene chloride solutions. The molar ratio between PEO and $EM(CH_3)_2C_{12}H_{25}NBr$ was varied in the range of 15 to 5. The presence of covalently immobilized QAS on the PEO chains was detected by the IR and NMR spectra of the extracted crosslinked films. $EM(CH_3)_2C_{12}NBr$ takes part in the network formation by double bond opening.

Compared to the pure PEO network, the gel fraction yield of the mixed networks is slightly lower. Composition dependence of the efficiency of UV- induced crosslinking of the PEO-$EM(CH_3)_2C_{12}H_{25}NBr$ blends is shown in Table 7.

Tab.7. Characteristics of PEO-EM$(CH_3)_2C_{12}H_{25}$ABr networks.

[PEO]:[QAS] blend	[PEO]:[QAS] network	T_{irr} °C	GF, %	ES, H_2O	ES, $CHCl_3$	T_m °C	Degree of crystallinity (DSC) network
1 : 0	1 : 0	25	91.7	4.4	5.1	60.5	0.64
1 : 0	1 : 0	70	97.1	5.5	9.0	63.1	0.62
15 : 1	20 : 1	25	89.2	4.1	6.6	65.2	0.67
15 : 1	20 : 1	70	92.2	4.6	8.1	51.0	0.52
10 : 1	16 : 1	25	84.3	4.2	7.2	64.0	0.70
10 : 1	15 : 1	70	85.9	4.9	8.2	50.4	0.47
5 : 1	7 : 1	25	84.6	3.5	10.2	64.1	0.62
5 : 1	7 : 1	70	85.9	3.6	12.1	46.3	0.44

An increase in EM$(CH_3)_2C_{12}H_{25}$NBr concentration leads to stronger hydrophobic interactions between the dodecyl chains (presence of hydrophobic domains) as manifested by a lower degree of swelling in water, and a higher one in chloroform.

At 70^{0}C PEO-EM$(CH_3)_2C_{12}H_{25}$NBr blends changed their appearance due to the fusion process while keeping their form and size. Irradiation temperature of 70^{0}C favours crosslinking since partial crystal melting leads to a larger amorphous phase where the crosslinking takes place. Greater mobility of the polymer segments provides an increased number of mutual contacts as well. DSC data were used to analyze the crystallization behaviour of the PEO- EM$(CH_3)_2C_{12}H_{25}$NBr networks. There is a considerable difference between the first and second heating run for all measured samples (Figure 1). In the first heating scan besides the typical PEO melting endotherm, another endotherm appears in a broad temperature interval from 20^{0}C to 140^{0}C. On reheating after non-isothermal crystallization with a rate of 10^{0}C/min. this endotherm disappears. However, after keeping the sample at room temperature it restores its form. The endotherm is associated with the absorption of an equilibrium amount of water at a given temperature, pressure and humidity. This property of PEO- $EM(CH_3)_2C_{12}H_{25}NBr$ crosslinked films can be successfully used as a sensor for humidity. The possible response is a change in conductivity at 30°C from $2x10^{-8}$ S/cm in the absence of water to $6x10^{-8}$ S/cm when water becomes bound.

Crosslinking at temperatures above the melting points of the polymer and the salt, substantially changes the network structure (Table 7).

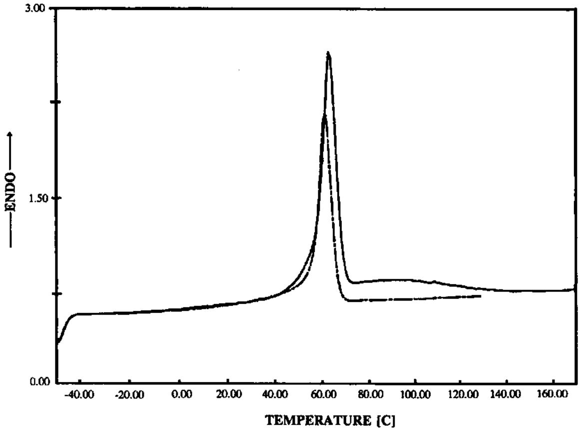


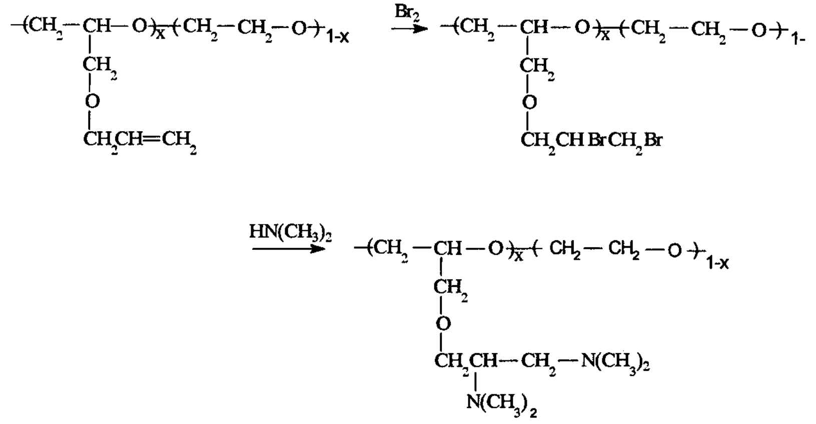
Fig.1 **DSC thermograms of a PEO-$EM(CH_3)_2C_{12}H_{24}ABr$ network with initial [PEO] : [QAS] ratio 10:1**

(————) first heating ; (---------) second heating

Synthesis of PEO networks having pendant TMEDA ligands via chemical modification of copolymer of allylglycidyl ether with EO

It is well known that N,N,N',N'- tetramethylethylenediamine (TMEDA) dramatically accelerates organolithium reaction rates, improves product yields, and alters product distributions (Ref.24). TMEDA seems to display a highly substrate-dependent affinity for lithium. The TMEDA-Li$^+$ interaction is very strong due to the bidentate nature of TMEDA ligands (Ref. 25). The synthesis of PEO based networks with pendantTMEDA ligands gives rise to possible application of these materials as phase transfer catalysts and in lithium batteries. The strategy used to introduce dialkylamine or quaternary ammonium groups in the functional PEOs was to modify the copolymer bearing allyl groups in two steps followed by UV crosslinking . The first step is bromination of the unsaturated side chains, yielding the dibromo derivative, followed by its substitution with dialkylamine or quaternization with trialkylamine.

The reaction procedure is shown on the next scheme:



Scheme 2. Modification of the copolymer of allylglycidylether with EO

The ^1H NMR spectrum in $CDCl_3$ of the initial copolymer reveals signals at 5.2 ppm (=CH_2) and 5.8 ppm (=CH). In the spectrum of the brominated product these peaks were not detected which is in favour of a complete bromination. After treatment of brominated copolymer with an excess of Me_2NH, the ^1H NMR and the thin layer chromatographic analysis indicate a complete conversion of the starting material to copolymer with pendant Me_2N- groups (peak at 2.5 ppm, singlet). The TMEDA modified copolymer was successfully UV crosslinked. In comparison with pure PEO network the modified network possesses enhanced cation binding ability towards LiPi salts.

CONCLUSION

Despite the large amount of work in the area of PEO derivatives, novel PEO based materials continue to be prepared. Our studies in this field clearly show that films of PEO blends can be efficiently crosslinked by UV irradiation in the presence of hydrogen-abstracting photoinitiator. In principle, PEO based hydrogels and films with any desired property can be obtained by varying the amount and type of additives (usually monomers or polymers). The nontoxic character of most components in the PEO-based networks stimulate us to examine further their properties as environmentally acceptable gel materials. Now we should begin searching for practical applications of these new materials. The most promising areas are drug delivery systems, polymer electrolytes, membrane technology, sensors and polymer supported phase transfer catalysis.

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