

U.V. irradiation-induced crosslinking of solid poly(ethylene oxide) modified with tetraalkyl ammonium salt

M. Doytcheva^a, R. Stamenova^{a,*}, V. Zvetkov^b and Ch.B. Tsvetanov^a

^a*Institute of Polymers, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria*

^b*Central Laboratory of Physical Chemical Mechanics, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria*

(Revised 23 December 1997)

Crosslinked poly(ethylene oxide) (PEO) modified with a quaternary tetraalkyl ammonium salt, ethyl methacrylate dimethyldodecylammonium bromide, was prepared by exposure of the solid blend to ultraviolet radiation from a high-pressure 150 W mercury lamp. The photochemical crosslinking of the blends proceeded in the presence of benzophenone as a hydrogen-abstracting agent. Gel fraction yield exceeded 85%, equilibrium swelling in water varied from 3.0 to 5.0, and the equilibrium swelling in chloroform from 6.5 to 12.5. The networks obtained have been characterized by elemental analysis, i.r., ¹H n.m.r., and d.s.c. measurements and their microstructure, water absorption and equilibrium swelling have been discussed. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: crosslinked poly(ethylene oxide); quaternary ammonium salts immobilization; photocrosslinking)

INTRODUCTION

The combination of poly(ethylene oxide) (PEO) and a quaternary ammonium salt (QAS) will produce a hydrogel with a variety of properties. PEO is a biocompatible, nonionic, water-soluble polymer of considerable industrial significance. Crosslinked polymers based on PEO form an important class of new materials with a number of applications, such as: wound dressings¹; controlled release drugs systems^{2,3}; phase transfer catalysts⁴; semipermeable membranes⁵; solid electrolytes for batteries⁶; and many others. An essential drawback of the hydrogels is the significant decrease of mechanical strength observed in the water-swollen state. An attempt to improve the wet strength is the introduction of a hydrophobic component; however, this reduces the hydrophilicity and usually results in an unacceptable drop in the equilibrium water content. Immobilization of a quaternary ammonium salt with a long alkyl group introduces the hydration shell of the ions into the hydrogel, which helps to maintain the water content balance. Cationic PEO networks bearing hydrophobic long alkyl substituents are likely to display some peculiar properties, especially in an aqueous solution.

PEO-QAS networks have been first obtained as a product of γ - irradiation of degassed dilute aqueous solutions⁷. Recently, it has been shown that PEO could be successfully crosslinked by irradiation with ultraviolet (u.v.) light with benzophenone as an initiator^{8,9}. Ease, relative safety and low cost are the significant advantages of u.v.-induced crosslinking in solid state over γ irradiation of aqueous solutions. The purpose of this study was to obtain PEO hydrogels carrying a lipophilic quaternary ammonium salt, based on ethyl methacrylate dimethyldodecylammonium bromide (EMDMDAB), and to examine the structural parameters and properties of the networks.

EXPERIMENTAL

Materials and solvents

Benzophenone (BPh) puriss. (Koch Light Laboratories Ltd.) was used without further purification. Methylene chloride and chloroform of analytical grade (Fluka) were used as received. Technical-grade methylene chloride (ICI) was used for extraction only. Commercial poly(ethylene oxide) of molecular weight 1 000 000 (Polyox[®]N-12 K, produced by Union Carbide Corp.) was used without further purification. EMDMDAB was prepared as previously reported¹⁰. Anal. Calcd. for EMDMDAB: C, 59.11%; H, 9.85%; N, 3.45%. Found: C, 57.70%; H, 9.85%; N, 3.48%.

Sample preparation

Preparation of PEO samples by casting from solution. PEO (3 g) was added under intensive stirring to a CH₂Cl₂ (100 ml) solution containing the quaternary ammonium salt and the photoinitiator. Methylene chloride was the solvent of choice because of its volatility and solubility properties. The homogeneous viscous solution was cast onto a glass Petri dish kept in the dark and the solvent was allowed to evaporate in air. The samples were subjected to additional drying for 1 h under vacuum at room temperature prior to irradiation. The thickness of the samples was measured with a micrometer and varied between 170 and 200 μ m.

U.V. irradiation of PEO samples. 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 quartz jacket. It was put in a glass vessel equipped with another thermostated jacket. The PEO-EMDMDAB samples were fixed on the inner side of the glass wall. To avoid oxygen quenching, the irradiation was carried out under a constant flow of argon. The highest intensity of the u.v. lamp was found to be emitted in a 4–5 cm zone

* To whom correspondence should be addressed

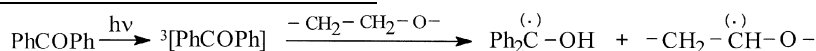
around the light source. Larger samples revealed a lower degree of crosslinking out of this zone. Therefore, 30×80 mm rectangular samples for irradiation were cut out of the originally prepared circular ones. The duration of irradiation was 40 min, the initial 10 min being necessary for reaching the standard emission of the u.v. lamp.

Sample characterization

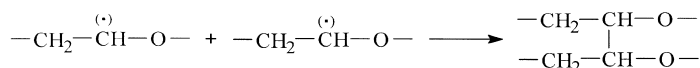
Gel fraction determination. The irradiated PEO-EMDMDAB samples were weighed and then extracted with methylene chloride in a Soxhlet apparatus for 24 h. After extraction they were dried to constant weight under vacuum and weighed. Gel fraction (GF) = (weight of extracted sample/initial weight) \times 100%.

Swelling measurements. The equilibrium degree of swelling, ES (weight of swollen sample/weight of dry sample) was determined at room temperature. Dry disks of 10 mm diameter from the crosslinked sample were equilibrated in distilled water and chloroform for at least 72 h, then removed from the solvent, blotted with filter paper and weighed. Then they were dried to constant weight under vacuum and weighed again.

Methods. The d.s.c. curves were obtained with a Perkin-Elmer DSC-2C thermal analysis system at standard heating and cooling rate of $10^\circ\text{C min}^{-1}$. Samples of $ca. 10 \pm 0.2$ mg dry gel were run in an argon atmosphere over a temperature range from -60 to 180°C (for first heating) and from -60 to 140°C (for second heating). The first melting followed by non-isothermal crystallization, and the second melting have been monitored. The first heating was used to determine the enthalpy of desorption, ΔH_d (or the negative enthalpy of absorption, ΔH_a) as a difference between the total enthalpy,



ΔH_t , measured in the interval $-20 \div 140^\circ\text{C}$ and the enthalpy of melting, $\Delta H_m'$, measured in the interval $-20 \div 70^\circ\text{C}$. All enthalpy quantities are given in kJ kg^{-1} of initial mass of the



sample, m_o . The mass loss, Δm , has been measured after the end of each experiment. The annealing at 180°C for 10 min and the non-isothermal crystallization at a cooling rate of $10^\circ\text{C min}^{-1}$ eliminates the thermal history of the samples. The enthalpy of melting, ΔH_m , in kJ kg^{-1} of dry sample, i.e. $m_o - \Delta m$, and the peak maximum temperature, T_m , of the

second heating have been used as representative characteristics of the melting process. D.s.c. data from the melting experiments are summarized in Table 1. ΔH_m of the second heating was used for calculation of ΔH (Table 4) taking PEO content determined from the elemental analysis.

Samples of $ca. 20 \pm 0.5$ mg aqueous swollen gel (dry weight of $ca. 5.2 \pm 0.1$ mg) were measured with a Perkin-Elmer DSC-7 apparatus. They were hermetically sealed in aluminum pans, cooled to -60°C and then heated up to 10°C at a rate of $2.5^\circ\text{C min}^{-1}$. The cooling rate of $2.5^\circ\text{C min}^{-1}$ was observed to be the maximal rate at which the enthalpy of melting of the pure water (6.01 kJ mol^{-1})¹¹ did not depend on the cooling rate. Indium and zinc were used for temperature calibration for both instruments.

The degree of crystallinity was estimated as a mole ratio between experimentally determined enthalpy of melting, ΔH , and the enthalpy of melting of a 100% crystalline polymer ($\Delta H^\circ = 8.276 \text{ J mol}^{-1}$)¹².

I.r. spectra were recorded on a UR-20 spectrometer (Carl Zeiss, Jena). The ^1H n.m.r. spectra were recorded on a Bruker-250 WM spectrometer. Elemental analysis (C,H,N) of the dry gels was performed on a instrument Carlo Erba.

RESULTS AND DISCUSSION

Crosslinking experiments were carried out in the presence of benzophenone as a photoinitiator. Benzophenone was selected because of its high hydrogen abstraction efficiency. The concentration of BPh was $5 \times 10^{-3} \text{ mol mol}^{-1}$ (2 wt%). The photochemical processes it undergoes are presently well understood¹³. On photon absorption, BPh undergoes several photophysical processes, affording an n,π^* triplet state which proceeds to the reduction of BPh and PEO radical formation:

Photochemical crosslinking mainly occurs by recombination of two macroradicals producing carbon-carbon bonds between the main chains:

The ammonium salt incorporation in the PEO chains is most likely to take place via the methacrylate double bond cleavage.

Benzophenone and the photoproducts arising from it, as well as the soluble (sol) fraction after irradiation, were removed by subjecting the samples to extraction for 24 h.

Table 1 Thermodynamic parameters obtained from d.s.c. thermograms of PEO-EMDMDAB networks

Initial mole ratio [PEO]/[QAS]	Irradiation temperature ($^\circ\text{C}$)	First melting				Second melting	
		ΔH_t (kJ kg^{-1})	ΔH_m^1 (kJ kg^{-1})	$-\Delta H_a$ (kJ kg^{-1})	Δm (wt%)	ΔH_m (kJ kg^{-1})	T_m ($^\circ\text{C}$)
100:0	25	147.9	147.9	—	—	124.0	62.4 ± 0.2
15:1	25	132.0 ± 7.0	90.0 ± 0.3	40 ± 5.0	3.5 ± 0.5	84.8 ± 0.9	64.8 ± 0.3
10:1	25	145.5 ± 5.0	86.0 ± 3.5	60 ± 5.0	4.5 ± 0.5	80.5 ± 2.3	64.0 ± 0.1
5:1	25	130.0 ± 0.5	45.5 ± 5.0	85 ± 5.0	5.5 ± 0.5	49.8 ± 0.7	64.0 ± 0.1
100:0	70	142.9	142.9	—	—	124.0	60.6 ± 0.2
15:1	70	117.0 ± 7.0	59.0 ± 3.7	40 ± 5.0	7.0 ± 0.5	75.5 ± 0.9	49.6 ± 1.6
10:1	70	119.0 ± 4.5	54.5 ± 0.7	65 ± 5.0	7.0 ± 0.5	63.4 ± 0.1	49.1 ± 1.3
5:1	70	132.5 ± 4.0	29.5 ± 4.5	105 ± 5.0	7.0 ± 0.5	40.5 ± 2.5	47.8 ± 1.5

with CH_2Cl_2 . Extending the extraction time over 24 h did not provide greater amounts of sol fraction.

In order to investigate whether the crosslink density varies throughout the thickness of the samples, two identical films were crosslinked as follows: the first was irradiated twice with the same side exposed to the u.v. light source; the second was irradiated twice as well—on both sides of the film. The data shown in *Table 2* indicate that both methods of irradiation produce a similar crosslinking efficiency. Double-side irradiation gives slightly higher values for gel fraction and degree of crosslinking. The disk prepared by single-side irradiation rolled up rapidly when soaked in water, whereas the disk irradiated on both sides retained its form in water and remained flat during swelling. This observation reveals that PEO films are not completely homogeneous in crosslink density through their thickness.

The ratio between EMDMDAB and PEO was varied in the range of 1:15 to 1:5 mol EMDMDAB per mol PEO, which corresponds to 38–68 wt% EMDMDAB. Two independently prepared samples for each ratio and irradiation temperature were analysed. The presence of covalently immobilized EMDMDAB on the PEO chains is detected by the i.r. spectra of the extracted crosslinked films. After u.v. irradiation followed by extraction, characteristic bands of the EMDMDAB appear: 1730 cm^{-1} (acrylate carbonyl group); 1467 cm^{-1} (methylene groups of dodecyl chain); $960\text{--}1000\text{ cm}^{-1}$ (C–N). The characteristic band of the acrylate carbonyl group shifts from 1720 cm^{-1} (prior to irradiation) to 1730 cm^{-1} after irradiation. This confirms the saturation of QAS double bond during u.v. irradiation. The

characteristic band of the double bond, 1630 cm^{-1} , disappears after irradiation; furthermore, there is no signal for vinyl protons at $\delta = 4.8\text{--}5.1$ ppm in the ^1H n.m.r. spectrum. It is obvious that EMDMDAB takes part in the network formation by the double bond opening. An EMDMDAB immobilization on the PEO during the u.v.-induced crosslinking by hydrogen abstraction from the $-\text{CH}_2-$ groups of the dodecyl chain also cannot be excluded.

The composition of the PEO–EMDMDAB networks is determined by ^1H n.m.r. and elemental analysis (*Table 3*). The discrepancy between the two methods is due to the fact that swollen gels were used for ^1H n.m.r. which reduces the accuracy of the composition determination. The reliable data from the elemental analysis were only used for result discussion and calculations. They show that EMDMDAB is not fully included in the networks.

The composition dependence of the efficiency of u.v.-induced crosslinking of the PEO–EMDMDAB blends is shown in *Table 3* and *Figure 1*. The gel fraction yield (GF) falls with the increase of EMDMDAB content in the blends. Compared to the GF of the PEO network, the one of the mixed networks is slightly lower. A maximum value of the gel fraction is observed at the lowest content of EMDMDAB (38 wt%). As is seen from *Table 3* and *Figure 1*, the equilibrium swelling in water falls from 4.4 to 3.5–3.6 when passing from pure PEO network to PEO–QAS network with the highest salt content, while ES in chloroform increases from 5.1 to 9.4–10.2 in the same order. This considerable change of the equilibrium swelling which decreases in water and rises in the lipophilic solvent CHCl_3 is most probably

Table 2 Crosslinking of PEO–EMDMDAB film samples exposed to u.v. irradiation from one side or from both sides

Irradiation conditions	T_{irr} (°C)	GF (%)	ES, H_2O	ES, CHCl_3
I and II irradiation (one side exposed to u.v.)	25	85.0	5.6	9.0
	25	86.4	4.9	7.6
	70	90.8	5.2	11.7
I irradiation (one side) and II irradiation (opposite side exposed to u.v.)	25	88.0	4.0	6.5
	25	89.2	4.1	6.6
	70	91.4	4.7	6.5
	70	92.2	4.6	9.1

U.v. irradiation under a flow of argon at $[\text{BP}]/[-\text{EO}-] = 5 \times 10^{-3}$. Initial ratio: $[-\text{EO}-]/[\text{EMDMDAB}] = 15:1$. Irradiation time, 40 min; thickness, $180\ \mu\text{m}$

Table 3 Characteristics of PEO–EMDMDAB networks

Type I networks ($T_{\text{irr}} = 25^\circ\text{C}$)					Type II networks ($T_{\text{irr}} = 70^\circ\text{C}$)				
No.	[PEO]/[QAS]	GF (%)	ES, H_2O	ES, CHCl_3	No.	[PEO]/[QAS]	GF (%)	ES, H_2O	ES, CHCl_3
	^1H n.m.r. ^a (elem. anal.) ^b					^1H n.m.r. ^a (elem. anal.) ^b			
PEO network									
1		91.7	4.4	5.1	2		97.1	5.5	9.0
Initial [PEO]/[QAS] = 15:1 (38 wt%)									
3	30:1 20:1	88.0	4.0	6.5	5	15:1 22:1	91.4	4.7	6.5
4	18:1 20:1	89.2	4.1	6.6	6	9:1 20:1	92.2	4.6	9.1
Initial [PEO]/[QAS] = 10:1 (48 wt%)									
7	15:1 18:1	80.6	4.3	6.7	9	9:1 15:1	85.7	4.9	9.5
8	13:1 16:1	84.3	4.2	7.2	10	10:1 15:1	85.9	4.9	8.2
Initial [PEO]/[QAS] = 5:1 (64 wt%)									
11	6:1 8:1	81.4	3.6	9.4	13	5:1 8:1	82.8	3.6	12.6
12	7:1 7:1	84.6	3.5	10.2	14	5:1 7:1	85.9	3.3	12.1

^aMole ratio determined by ^1H n.m.r. of swollen gel in CDCl_3

^bMole ratio determined by elemental analysis

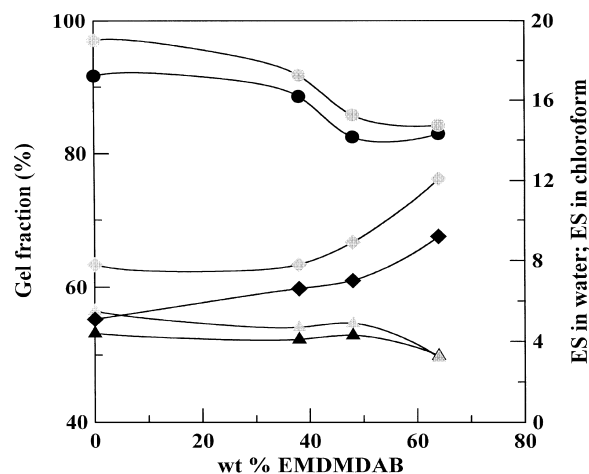


Figure 1 Dependence of the gel fraction yield and equilibrium swelling on the composition of the network. GF: ●, $T_{\text{irr}} = 25^{\circ}\text{C}$; ○, $T_{\text{irr}} = 70^{\circ}\text{C}$; ES in water: ▲, $T_{\text{irr}} = 25^{\circ}\text{C}$; △, $T_{\text{irr}} = 70^{\circ}\text{C}$; ES in CHCl_3 : ◆, $T_{\text{irr}} = 25^{\circ}\text{C}$; ◇, $T_{\text{irr}} = 70^{\circ}\text{C}$

due to the increasing concentration of the hydrophobic dodecyl chains in the mixed networks.

The temperature dependence of u.v.-induced crosslinking was examined at irradiation temperatures of 25 and 70°C . At 70°C , PEO–EMDMDAB blends changed their appearance due to the fusion process, while keeping their form and size. A slight increase of GF and ES occurred with the rise of temperature. An irradiation temperature of 70°C favoured better crosslinking, since crystal melting leads to a larger amorphous phase where the crosslinking is taking place. The greater mobility of the polymer segments provides an increased number of mutual contacts as well.

D.s.c. data (Tables 1, and 4) are used for analysing the melting and crystallization behaviour of the PEO–EMDMDAB networks. There is a considerable difference between the first and the second heating run for all measured networks illustrated in Figure 2a for sample 9 from Tables 3 and 4. At the first heating, besides the typical PEO melting

endotherm, another one appears in a broad temperature interval from -20 to 140°C . At the second heating, this endotherm disappears after non-isothermal crystallization with a rate of $10^{\circ}\text{C min}^{-1}$. However, after keeping the sample for 24 h at room temperature it restores its form. After the second heating the sample mass, measured immediately after the experiment, is 3–7% (Δm in Table 1) less than the original. This endotherm is associated with the absorption of an equilibrium amount of water at a given temperature, pressure and humidity.

The melting behaviour of two types of PEO–EMDMDAB networks is presented in Table 4: type I networks were obtained by u.v. irradiation of the blend in a solid state at 25°C ; type II networks were obtained by irradiation at 70°C when fusion of the polymer crystal phase and the salt takes place. Some pertinent d.s.c. traces are illustrated as an example in Figure 2b. Taking into account the relatively low accuracy of ΔH determination, it is obvious from Table 4 that the heat of melting of type I networks does not depend on the QAS content. T_m as well as $T_{\text{onset}} = 57.4 \pm 0.4^{\circ}\text{C}$ of these networks are nearly constant, whereas the heat of melting of type II networks, i.e. their degree of crystallinity, is lower and decreases by increasing the salt content. For most of these type II networks a great depression of T_m , exceeding more than 10°C , is observed.

The constant melting characteristics for the pure PEO network and for type I networks of an increasing QAS content imply that the thermodynamic and kinetic factors governing the crystallization process are the same in both types of networks. These networks crystallize irrespective of the crosslinked amorphous phase. An experimental evidence for this assumption is the fact that all crystallization exotherms of type I networks normalized against the PEO content can be almost superimposed in a single Avrami-type crystallization curve. The photocrosslinking in solid state occurs predominantly in the amorphous phase, and eventually on the surface of the defect crystallites. Therefore a likely morphological pattern for type I networks seems to contain a non-crosslinked or loosely crosslinked

Table 4 Thermal properties and crystallinity of PEO–EMDMDAB networks

	Type I networks ($T_{\text{irr}} = 25^{\circ}\text{C}$)				Type II networks ($T_{\text{irr}} = 70^{\circ}\text{C}$)			
	No.	ΔH^a (kJ kg $^{-1}$)	T_m ($^{\circ}\text{C}$)	Degree of crystallinity	No.	ΔH^a (kJ kg $^{-1}$)	T_m ($^{\circ}\text{C}$)	Degree of crystallinity
PEO								
Prior to irradiation		138	67.4	0.73				
After irradiation and extraction	I	124	62.4	0.66	2	124	60.6	0.66
Initial [PEO]/[QAS] = 15:1 (38 wt.%)								
Prior to irradiation		128	63.1	0.68				
		132	65.0	0.70				
After irradiation and extraction	3	123	64.5	0.65	5	98	47.3	0.52
	4	125	65.2	0.67	6	99	51.0	0.52
Initial [PEO]/[QAS] = 10:1 (48 wt.%)								
Prior to irradiation		129	61.4	0.68				
		131	64.0	0.69				
After irradiation and extraction	7	119	63.9	0.63	9	96	48.8	0.51
	8	131	64.0	0.70	10	88	50.4	0.47
Initial [PEO]/[QAS] = 5:1 (64 wt.%)								
After irradiation and extraction	11	105.7	64.0	0.56	13	82	49.4	0.43
	12	117.1	64.1	0.62	14	83	46.3	0.44

^a ΔH in kJ kg $^{-1}$ PEO in the sample. Maximal error < 9%

fraction forming crystallites of similar to that of the linear PEO thickness, which are surrounded by a densely cross-linked amorphous fraction like a shell.

Since the degree of crystallinity of type II networks

decreases with the increase of the QAS content, and T_m is much lower than T_m of the pure PEO network, a different more homogeneous microstructure for this type of network is expected. This microstructure should be characterized by

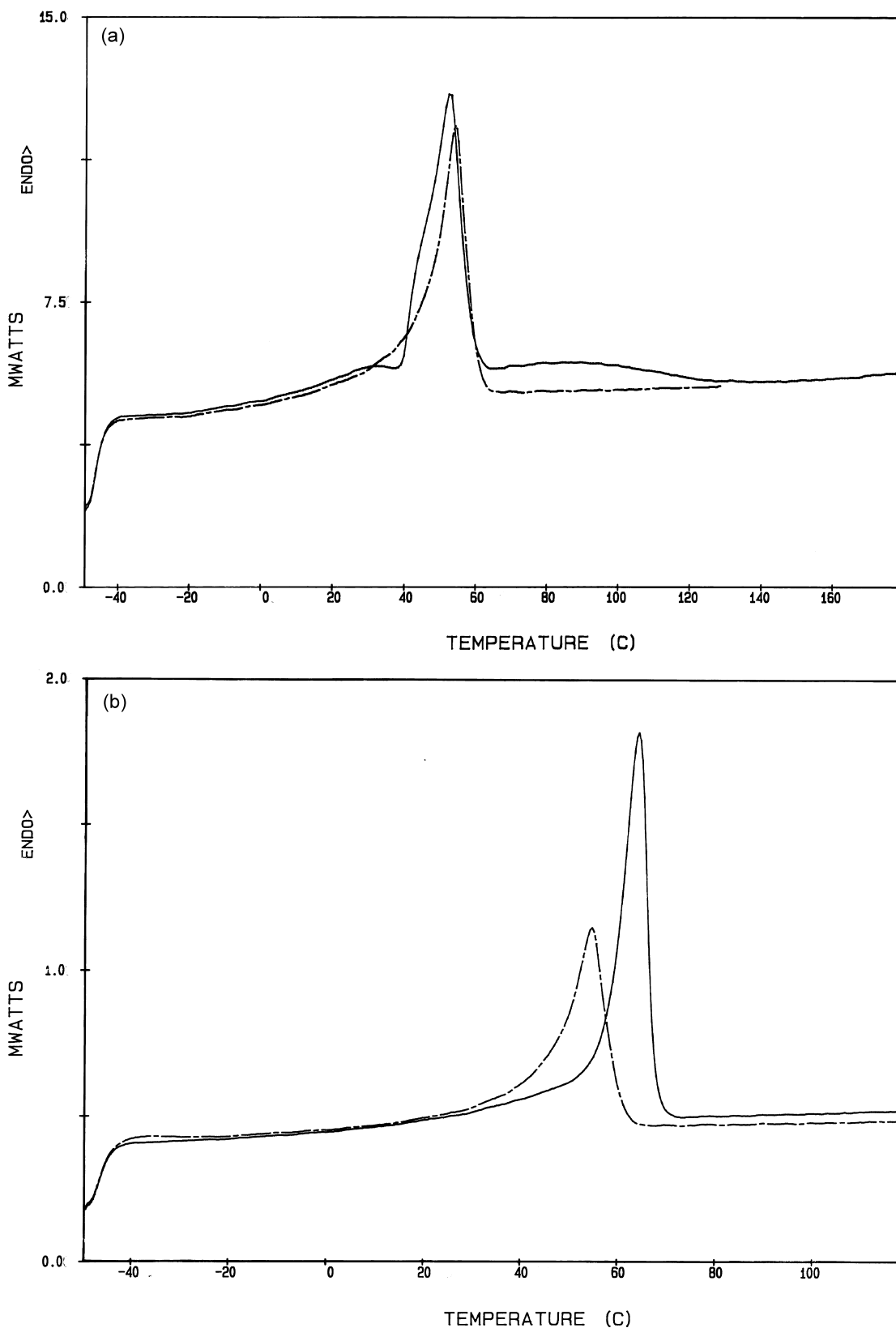


Figure 2 D.s.c. thermograms of PEO-EMDMDAB network with initial ratio 10:1 (48 wt.% EMDMDAB): (a) first (—) and second (•••) heating of sample 9; (c) crystallization of samples 7 (—) and 9 (•••); (d) endotherm of water melting (in mW mg^{-1} of water) of fully swollen samples. (—) Type I networks ($T_{\text{irr}} = 25^\circ\text{C}$), sample 7; (•••••): type II networks ($T_{\text{irr}} = 70^\circ\text{C}$), sample 9; (b) second heating of type I networks ($T_{\text{irr}} = 25^\circ\text{C}$), sample 7 (—) and type II networks ($T_{\text{irr}} = 70^\circ\text{C}$), sample 9 (•••)

a larger but not so densely crosslinked amorphous phase and by smaller in size and quantity crystallites. This conclusion is confirmed by the non-isothermal crystallization at $10^{\circ}\text{C min}^{-1}$ which seems to be a non-Avrami type (Figure 2c).

An evaluation of the water absorption in the PEO–EMDMDAB networks is possible on the basis of the

thermodynamic interpretation of this process:

$$\Delta H_t - \Delta H_m' = \Delta H_d = -\Delta H_a \quad (1)$$

where ΔH_t is the total enthalpy (-20 – 140°C); $\Delta H_m'$ the enthalpy of melting of PEO (-20 – 70°C); ΔH_d the enthalpy of water desorption; ΔH_a the enthalpy of water absorption. The ΔH_a and Δm values for the two types of network are

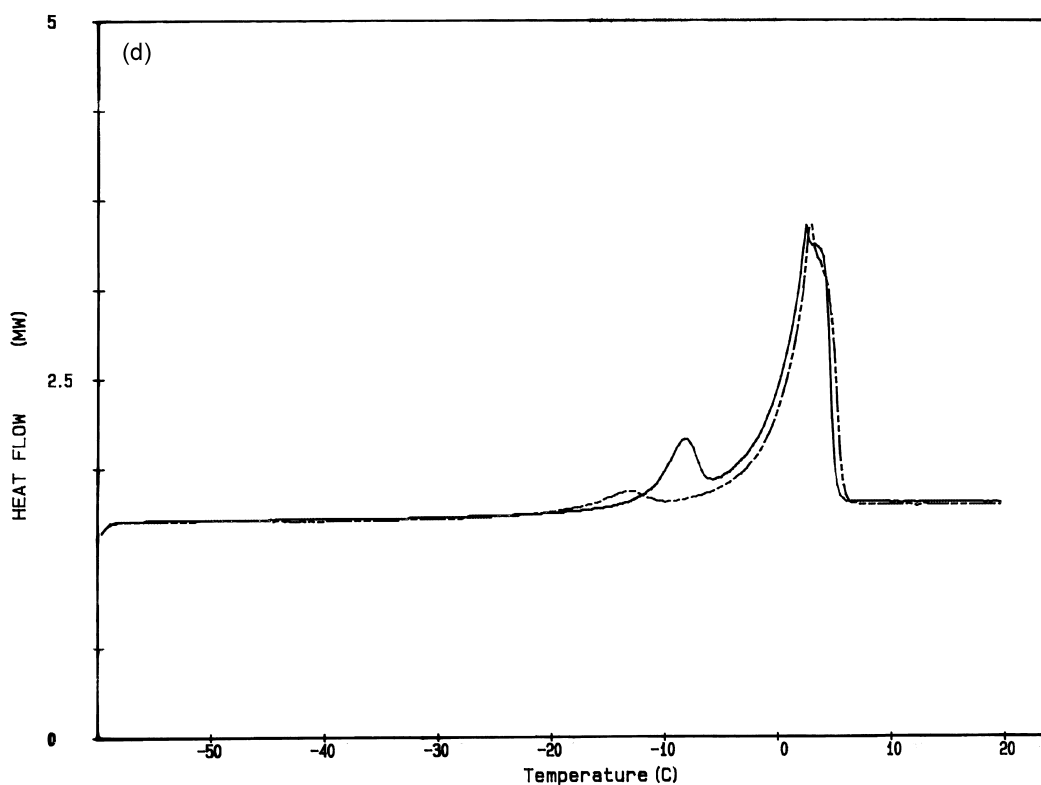
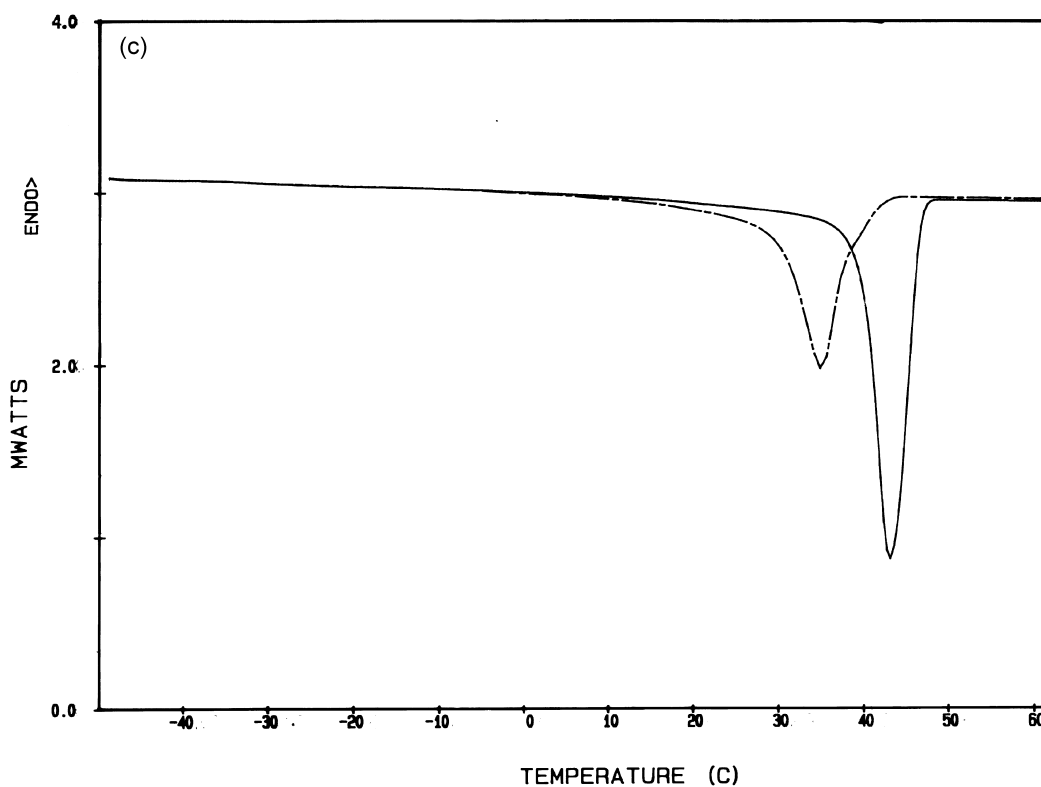


Figure 2 Continued

presented in *Table 1*. Despite the low accuracy of Δm determination, it is observed that type II networks absorb practically an equal amount of moisture, about 7 wt%, whereas ΔH_a and Δm of type I networks increase proportionally to the salt content. ΔH_a grows in absolute value by increasing the content of the quaternary salt in the network. The more rapid increase of ΔH_a of type II networks when raising their QAS content, corresponds to a measurable decrease of the amount of crystalline phase, i.e. during water absorption the imperfect crystallites have melted even at ambient temperature. These results imply that the water absorption capacity is closely associated with the microstructure of the two types of network. Networks obtained at higher temperatures (type II) with a larger amorphous phase and lower average crosslink density are more sensitive to plasticization by moisture.

D.s.c. analysis of fully swollen PEO-EMDMDAB hydrogels allows us to estimate the enthalpy of mixing of the networks with water at high water concentrations (*Figure 2d*). According to the procedure of Graham *et al.*¹⁴ the enthalpy of mixing of PEO-QAS gels with water can be determined by measuring the loss of the enthalpy of fusion of water in the temperature interval -40 to $+5^\circ\text{C}$:

$$-\Delta H_{\text{mix}} = \Delta H_f^\circ - \Delta H_f \quad (2)$$

where ΔH_f° is the enthalpy of fusion of pure water; ΔH_f is the measured enthalpy of fusion in kJ kg^{-1} of water in the hydrogel normalized against the weight of the swollen sample (kJ kg^{-1} swollen gel). The following values of the enthalpy of mixing have been determined: ΔH_{mix} of sample 7 (see *Table 3*, type I networks) is 39 kJ kg^{-1} ; ΔH_{mix} of sample 9 (see *Table 3*, type II networks) is -55 kJ kg^{-1} . ΔH_{mix} of pure PEO hydrogel (sample 1, *Table 3*) at ambient conditions is -18.5 kJ kg^{-1} , which corresponds quite well with the values obtained by Graham *et al.*¹⁴.

The increase of the negative ΔH_{mix} with rising the QAS content in the networks is due either to the larger amorphous phase or to the melting of imperfect PEO crystallites. The higher negative values of ΔH_{mix} for type II networks suggest a greater amorphous phase and more imperfect crystallites in comparison with type I networks. The swelling process is energetically favourable ($-\Delta H_{\text{mix}}$ increases) but entropically restricted (equilibrium swelling in water decreases). The decrease of ES values in water is probably caused by the higher percent of hydrophobic component. ES in the thermodynamically good solvent CHCl_3 changes in the opposite direction when increasing the QAS content, and

the effect on type II networks is stronger again. The values of ΔH_{mix} and the equilibrium swelling of the two types of networks are consistent. The melting behaviour as well as the thermodynamic interpretation of the swelling processes indicate that the two types of network possess different structures.

CONCLUSION

Cationic PEO networks were easily obtained by u.v. irradiation of blends of the linear polymer and the vinyl double bond containing quaternary ammonium salt. The microstructure, water absorption and equilibrium swelling of these modified PEO networks are strongly affected by the amphiphilic quaternary ammonium salt and the crosslinking conditions.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge the financial support by Union Carbide Corporation, and the National Foundation for Scientific Research, Sofia, project X-401.

REFERENCES

- Lang, S. L. and Webster, D. F., UK Pat. Appl. 2,093, 702 and 2,093, 703, 1982.
- Graham, N. B. and McNeill, M. E., *Biomaterials*, 1984, **5**, 27.
- Lambov, N., Stanchev, D., Peikov, P., Belcheva, N., Stamenova, R. and Tsvetanov, C., *Pharmazie*, 1995, **50**(H.2), 126.
- Tsanov, T., Stamenova, R. and Tsvetanov, C., *Polymer*, 1993, **34**, 617; *Polym. J.*, 1993, **25**, 853.
- K. A. Dennison, Ph.D. Thesis, Massachusetts Institute of Technology, 1988.
- Hooper, A. and North, J. M., *Solid State Ionics*, 1983, **9&10**, 1161.
- Tsanov, T., Vassilev, K., Stamenova, R. and Tsvetanov, Ch., *J. Polym. Sci., Part A: Polym. Chem.*, 1995, **33**, 2623.
- Sloop, S., Lerner, M., Stephens, T., Tipton, A., Paull, D. and Stenger-Smith, J., *J. Appl. Polym. Sci.*, 1994, **53**, 1563.
- Doytcheva, M., Dotcheva, D., Stamenova, R., Orahovats, A., Tsvetanov, C. and Leder, J., *J. Appl. Polym. Sci.*, 1997, **64**, 2299.
- Hamid, S. M. and Sherrington, D. C., *Polymer*, 1987, **28**, 332.
- Lide, D. R., Ed-in-Chief, *Handbook of Chemistry and Physics*, 76th edn, CRC Press, Boca Raton, New York, London, Tokyo, 1995.
- Wunderlich, B., *Macromolecular Physics*, Vol. 3, Academic Press, New York, 1984.
- Turro, N. J., *Modern Molecular Photochemistry*, The Benjamin/Cumming Co., Inc., Menlo Park, CA, 1978.
- Graham, N. B., Zulfiqar, M., Nwachuku, N. E. and Rashid, A., *Polymer*, 1990, **31**, 909.