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Amphiphilic poly(ethylene oxide)/poly(dimethylsiloxane)polymers: 1. Synthesis and characterization of cross-linked hydrogels

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Abstract

Three types of poly(ethylene oxide) (PEO) networks cross-linked by silicone-based compounds have been formed. One type of network prepared from allyl-substituted poly(ethylene glycol) (PEG), is stable whereas the other two are degradable. The degree of swelling of the resulting hydrogels depends strongly on the PEO/silicone ratio and on temperature. From the weight fraction of soluble material in the networks, the extent of cross-linking reaction has been estimated. The molecular weight between cross-links has been calculated independently from the weight fraction of soluble material in the networks and from swelling data.

Keywords: Hydrogels; Silicone; Cross-link; Poly(ethylene oxide); Poly(ethylene glycol)

1. Introduction

Hydrogels may be conveniently described as hydrophilic polymers that are swollen by, but do not dissolve in water. This is usually achieved by a low degree of cross-linking, as in the case of conventional elastomers, which means that hydrogels are effectively water-swollen polymer networks. Although many naturally occurring polymers may be used to produce this type of materials, the structural versatility available in synthetic hydrogels has given them distinctive properties, which in turn have enhanced their practical utility. Due to characteristic properties such as swellability in water, hydrophilicity, biocompatibility, and lack of toxicity, hydrogels have been utilized in a wide range of biological, medical, and pharmaceutical applications [1–4]. Also, hydrogels have become the material of choice as drug carriers in controlled release applications [5,6].

Synthetic and semisynthetic hydrogels based on physical [7,8], chemical [9], or photochemical cross-linking [10] have been developed which offer improvements in the barrier and degradation properties of gels. Considerable amount of work has been carried out on hydrogels based on hydroxyethyl methacrylate (HEMA) [11–14]. Measurements of the physical properties and water binding behavior of various copolymer hydrogels prepared by hydroxyalkyl acrylates and methacrylates with nonhydrophilic monomers have been reported [15]. Copolymers and terpolymers containing *N*-vinyl-2-pyrrolidone find wide range of applications in the field of hydrogels [16,17]. Less attention has been paid to poly(-ethylene glycol) (PEG)-based hydrogels. The routes leading to the formation of end-linked poly(ethylene oxide) (PEO) gels discussed in the literature usually

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involve a reaction between PEO terminal hydroxyl groups and different aromatic or aliphatic pluriisocyanates ([18–20] and references therein). Cima [21] has prepared nondegradable cross-linked PEG star hydrogels with high ligand capacity as matrices for coupling the desired cell-binding ligands. Lactide-based poly(-ethylene glycol) polymer networks (GL-PEG) prepared by UV photopolymerization using two nontoxic macromers, triacrylated lactic acid oligomer emanating from a glycerol center (GL) and monoacrylated PEG, have also been reported [22]. These materials have been developed for use as polymer scaffolds in tissue engineering, which have cell-adhesion resistant, ligand-immobilizable, and biodegradable characteristics. Another potential route to gel formation is through enzymatic cross-linking of synthetic macromolecular precursors. For example, a formation of hydrogel network by cross-linking functionalized PEG and a lysine-containing polypeptide through the action of a natural tissue enzyme, transglutaminase, has been demonstrated recently [23].

There is considerable interest in the preparation of new hydrogels based on polymers with selective water solubility. PEO/poly(dimethylsiloxane) copolymers are interesting possible candidates for such networks. PEG and PEO are hydrophilic polyethers which have received much attention for use in biomaterials due to its low interfacial energy with water, relative structural stability, lack of binding sites for reactive proteins, high chain mobility, and steric stabilization effects [24]. PEO materials are of interest also as result of its low degree of protein adsorption and cell-adhesion [25–28]. Recently, PEO was modified with either a quaternary tetraalkyl ammonium salt [29] or acrylate [30] to construct polymer networks. The reactions leading to the formation of end-linked PEO gels discussed in the literature usually involve the handling of sensitive, highly hygroscopic cross-linkers. Several side reactions are known to impede the desired main reaction and unwarranted by-products tend to contaminate the resulting gel. In the present work, we introduce a new method for producing cross-linked PEO networks. Poly(dimethylsiloxane) (PDMS) compounds are known for their biocompatibility, high oxygen permeability, low surface tension and surface activity [3,4]. Variable solubility may be obtained by utilizing the strong temperature dependence of PEO solution and by the introduction of a silane cross-linker. The hydrophobic nature of the silane compounds combined with the hydrophilic nature of the PEG result in an amphiphilic network with tunable properties dependent upon the siloxane/PEO ratio. Three types of networks will be addressed.

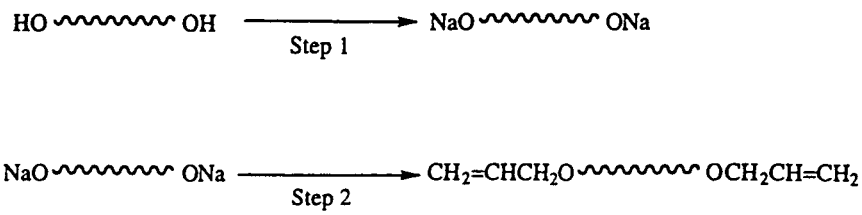
2. Experimental

2.1. Materials

Poly(ethylene glycol)s PEG-400 (Merck), PEG-600 (Sigma) and PEG-8000 (Sigma) were dried at 105°C under vacuum for a few hours before use. The cross-linkers tetrakis(dimethylsiloxy)silane $(HSiMe_2O)_4Si$ (United Chemical Technologies, 99% functional material by GC/MS) and tetraethoxysilane $(EtO)_4Si$ (United Chemical Technologies) were used as received. Either stannous-2-ethyl hexanoate (Sigma, 95%) or platinum complex (*cis*-dichlorobis(diethylsulfate)platinum(II)) (Strem, 2% in toluene) were used as the catalyst. Allyl bromide (Aldrich, 99%) was distilled before use. Sodium hydride (Aldrich, 60% dispersion in mineral oil) and anhydrous THF (Aldrich, 99%) were used without further purification. Analytical grade toluene was used as a solvent for the cross-linking reaction.

2.2. Synthesis of allyl-substituted poly(ethylene glycol)

PEO diallyl ethers were prepared from the parent PEG according to a Williamson synthesis [31]: reaction of allyl bromide over the sodium alcoholate in THF solution at room temperature (Scheme 1). In a typical synthetic experiment, a few grams of NaH (60% in mineral oil) were added under nitrogen to 100–150 ml solution of PEG in dry THF (cf. Table 1). The reaction mixture was stirred for approximately 1 h at room temperature. A solution of allyl bromide in dry THF was then added dropwise (ca. 50 ml) to the reaction mixture. The resulting mixture was further stirred at room temperature for a few hours. After separation in a centrifuge (4000 rpm), the solvent was evaporated under reduced pressure to give the product (in the case of PEG-8000, after centrifugal separation, the solution phase was removed and chloroform was added to dissolve most of the solid. Centrifugal



Scheme 1. Synthesis of allyl-substituted PEG-substitution of hydroxyl end groups by allyl groups.

separation was run once again, then the solvent was evaporated under reduced pressure to give the product).

The exact specific conditions for the synthesis of the different allyl-substituted PEGs are listed in Table 1.

2.3. Formation of the networks

Type I. In a typical experiment, platinum-based catalyst (9 μl) was added to a mixture of allyl-substituted PEG-8080 (2.8336 g), cross-linker tetrakis(dimethylsiloxy)silane $(HSiMe_2O)_4Si$ (0.0633 g) and toluene (1.2508 g). The concentration of polymer in the reaction mixture was 70%. The stoichiometric ratio of reactants defined as the ratio of initial molar concentration of silane groups to that of vinyl groups:

$$r = [SiH]_0/[Vi]_0, \quad (1)$$

is equal to one in this case (r=1). The reaction mixture was stirred at 80°C under argon for 7 h. The dry network was obtained by vacuum removal of the toluene solvent. Four different networks based on allyl-substituted PEG were obtained. These are specified in Table 2.

Type II. Platinum-based catalyst (9 μl) was added to a mixture of PEG-8000 (2.4612 g), cross-linker tetrakis(dimethylsiloxy)silane $(HSiMe_2O)_4Si$ (0.0579 g) and toluene (1.0409 g). The reaction mixture was stirred at 80°C under argon for 32 h. The dry network was obtained after vacuum removal of the toluene solvent.

Table 1
Conditions for the synthesis of allyl-substituted poly(ethylene glycol)s

PEVi	PEG (g)/ THF (ml)	NaH (g)	T_1 (h)	Allyl bromide (g)/THF (ml)	T_2 (h)	Yield (%)	Form of final product
480	20.51/100	5.08	0.5	14.8/50	40	90	Light yellow liquid
680	16.78/150	3.00	0.5	9.00/50	48	98	Light yellow liquid
8080	14.06/150	0.48	1.5	1.45/50	48	98	White powder

* T_1: reaction time for the first step; T_2: reaction time for the second step.

Table 2
Summary of networks formed from poly(ethylene oxide)

Networks	Pre-polymer	Cross-linker	Type of network	Reaction time*	Other
A	PEVi-480	$(HMe_2SiO)_4Si$	Type I	2 h (40 min)	Stable no-degradation
B	PEVi-680	$(HMe_2SiO)_4Si$	Type I	3 h (80 min)	Stable no-degradation
C	PEVi-8080	$(HMe_2SiO)_4Si$	Type I	7 h (30 min)	Stable no-degradation
D	PEVi-8080	$(HMe_2SiO)_4Si$	Type I	24 h (30 min)	Stable no-degradation
E	PEG-8080	$(HMe_2SiO)_4Si$	Type II	33 h (24 h)	Unstable degradation upon swelling
F	PEG-400	$(EtO)_4Si$	Type III	48 h	Unstable degradation upon swelling

*Total time system allowed to react (actual time for completion may be smaller). The number in () is the time after which the reaction mixture cannot be stirred.

Type III. PEG-400 (2.6690 g) was mixed with the catalyst stannous 2-ethyl hexanoate (0.1542 g), and with exactly the stoichiometric amount (0.7068 g) of the cross-linking agent tetraethoxysilane $(EtO)_4Si$. The reaction mixture was allowed to react under vacuum at room temperature for a total of two days.

The specific details of the conditions used to prepare the different types of networks are given in Table 2.

2.4. Swelling of the networks

The equilibrium solvent content of the swollen network was measured by weight difference as follows. After swelling 0.3 to 0.7 g of the dry cross-linked network in distilled water (or benzene), any water (benzene) on the surface of the hydrogel sample was removed by careful blotting with absorbent paper before the sample was transferred to a pre-weighed sample dish. The sample was weighed, then dried under vacuum at room temperature. The equilibrium solvent content was calculated from the weight differences of the swollen and dry gel.

2.5. The weight fraction of soluble material in the networks

The weight fraction of soluble material in the networks was obtained from the weight difference of the dry network before and after swelling.

3. Results and discussion

3.1. Synthesis of allyl-substituted poly(ethylene glycol)

Allyl-substituted PEG bis-macromonomers may be prepared from the parent PEO glycols according to a Williamson synthesis [31]. As shown in Scheme 1, the first step is to prepare sodium alcoholate from the PEG pre-polymer. There are several ways to convert the hydroxyl group to sodium alcoholate. One of them is to react PEG with sodium in the presence of naphthalene in THF solution. Another method is to react PEG with sodium hydride in THF solution under nitrogen at room temperature. In our work, the latter method was used. For PEG- 400 and 600, this reaction was very fast and no remaining hydroxyl group are detectable by FTIR when the reaction is carried out for 30 min (Table 1). However, in the case of PEG-8000, it took 90 min for the reaction to reach completion. Since the reaction rate depends on the concentration of hydroxyl groups, it takes longer for the reaction involving the higher molecular weight PEG to be completed.

In the second step, a solution of allyl bromide in dry THF was added dropwise to the reaction mixture which resulted from the first step. The reaction was completed only after stirring the reaction mixture at room temperature for about two days. Three allyl-substituted PEGs, PEVi-480, PEVi-680 and PEVi-8080 were obtained with 90–98% of yields (Table 1).

A typical IR spectrum is shown in Fig. 1. As one can see, two peaks at 1648.39 and 3078.23 cm^{-1} assigned to the allyl group are observed in the product

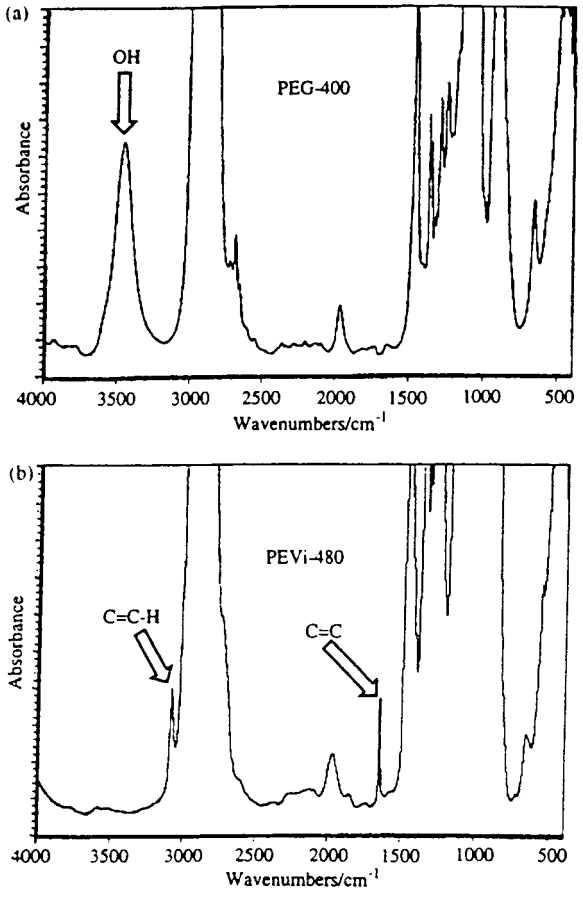


Fig. 1. IR spectra of (a) PEG-400 and (b) allyl-substituted PEG-480.

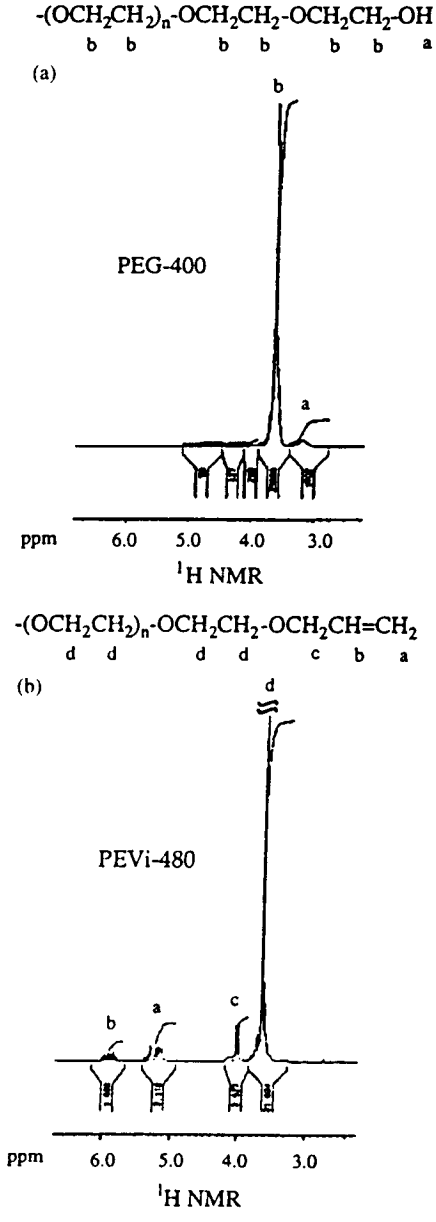


Fig. 2. ^{1}H NMR of PEG-400 and allyl-substituted PEG-480.

(PEVi-480). Whereas, the peak related to the hydroxyl group in the PEG has completely disappeared. PEVi-680 gave a similar IR spectrum. These results demonstrate that the conversion of hydroxyl groups to allyl groups is quantitative. Due to the low concentration of terminal groups in the case of PEG-8000, it was impossible to detect neither the OH nor the allyl groups by FTIR. The substitution in the case of this polymer has been verified by means of NMR as discussed below.

Fig. 2 shows an example of ^{1}H NMR of original PEG-400 and the allyl-substituted PEG (PEVi-480) bis-macromonomer. It is clearly seen from ^{1}H NMR spectra that the hydroxyl group to allyl group substitution was completed quantitatively. This is shown by the complete disappearance of the hydroxyl group peak in PEG-400, peak *a* in the upper Fig. 2, and by the newly formed peak of allyl group in the macromonomer (PEVi-480), which can be seen in the lower portion of Fig. 2 and in Table 3: *a* 5.13–5.32 ppm; *b* 5.81–6.00 ppm. This indicates that each terminal hydroxyl group in the PEG was substituted by an allyl group. The ^{1}H NMR results are summarized in Table 3.

The chemical structure of the PEG and PEVi was also characterized by ^{13}C NMR. Fig. 3 shows representative ^{13}C NMR spectra of PEG and PEVi. The macromonomer PEVi-480 structure was confirmed by the presence of allyl groups at 116.41 and 134.34 ppm and by the disappearance of terminal hydroxyl carbons, which is assigned by the peak *a* in the upper portion of Fig. 3. The ^{13}C NMR results are summarized in Table 4.

As discussed above, due to the low concentration of allyl group in PEVi-8080, no peak related to the double bond (allyl group) was detected in its IR

Table 3
^{1}H NMR of allyl-substituted poly(ethylene glycol) (in ppm)

	$-(OCH_{2_d}CH_{2_d})_n-OCH_{2_d}CH_{2_d}-OCH_{2_c}CH_b=CH_{2_a}$			
	a	*b*	*c*	*d*
PEVi-480	5.13–5.32	5.81–6.00	4.00–4.04	3.56–3.76
PEVi-680	5.15–5.32	5.82–6.01	4.01–4.04	3.57–3.66
PEVi-8080	5.14–5.33	5.82–6.03	4.00–4.04	3.52–3.71

Table 4
^{13}C NMR of allyl-substituted poly(ethylene glycol) (in ppm)

	$-(OCH_{2_f}CH_{2_f})_n-OCH_{2_e}CH_{2_d}-OCH_{2_c}CH_b=CH_{2_a}$					
	a	*b*	*c*	*d*	*e*	*f*
PEVi-480	116.41	134.34	71.66	67.37	68.95	70.10
PEVi-680	116.96	134.69	72.12	68.57	69.33	70.49
PEVi-8080	117.03	134.72	72.16		69.37	70.51

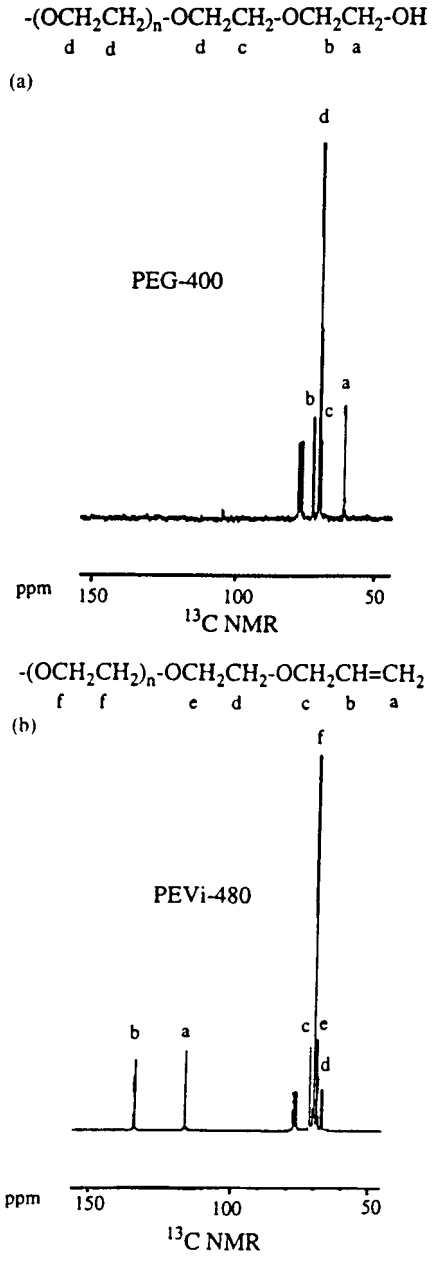


Fig. 3. ^{13}C NMR of PEG-400 and allyl-substituted PEG-480.

spectrum. However, the NMR results (Tables 3 and 4) demonstrate that the conversion of hydroxyl group in the PEG to allyl group in the bis-macromonomer is complete. As shown in Table 3, ^{1}H NMR measurements show two groups of peaks at 5.14–5.33 and 5.82–6.03 ppm, which are assigned to the double bonds in allyl-substituted PEG (PEVi-8080). This is also confirmed by the ^{13}C NMR spectrum, in which two peaks at 117 and 135 ppm assigned to the double bonds in the PEVi-8080 are observed.

3.2. Formation of the networks

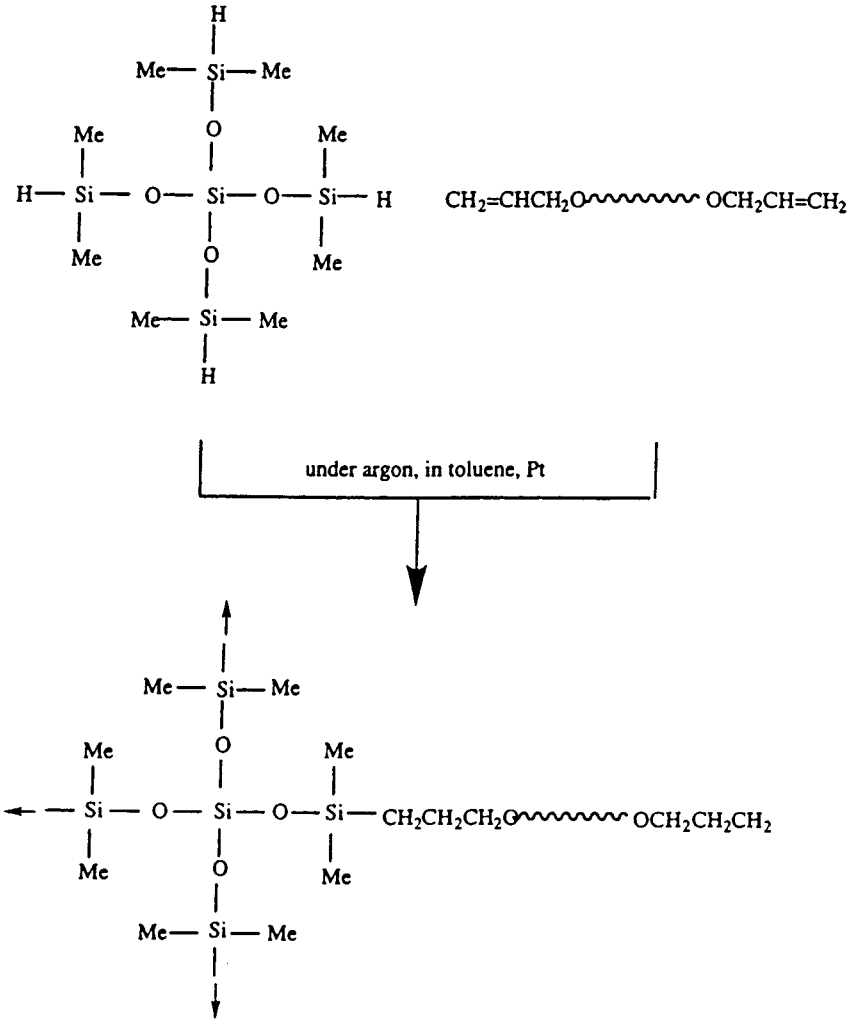
Polymer networks are generally prepared from chain molecules by cross-linking certain chain units corresponding to different chains. A network could be formed by cross-linking via chemical bonds, ionic interactions, hydrogen bonds, hydrophobic interactions, or physical bonds [32]. A network formed in a random way has a highly complex structure in that there is generally a relatively broad distribution of network chain lengths, a significant fraction of imperfections such as dangling chain ends, and presumably some entanglements between neighboring chains which act to some extent as physical cross-links [33–36]. It would be desirable to be able to introduce cross-links in a less random manner so that network structure and the average distance between cross-linking (mesh size) is more uniform. This type of network has advantage in applications related to membrane performance and diffusion barriers. Of the new synthetic techniques being developed for this purpose, those showing the greatest promise involve the joining of polymer chains exclusively at their ends. In this work, three possible ways to construct PEG-based networks have been investigated.

Type I. As shown in Scheme 2, the networks are constructed by mixing the allyl-substituted PEG and cross-linker tetrakis(dimethylsiloxy)-silane ($HSiMe_2O)_4Si$ in toluene under argon atmosphere. The stoichiometric ratio of reactants was one ($r=1$) and the network was formed at 80°C by the hydrosilation reaction.

This reaction is commonly used to form PDMS networks [37,38]. The evolution of structure in this system is well characterized, and the chemistry of its cure has been studied extensively [39–42]. The extent of side reaction of cross-linker hydride silane groups was found to be negligible.

Four networks of this type, namely network A, B, C and D were prepared (Table 2).

Type II. If the allyl-substituted PEG used in the type I reaction is replaced by PEG, another type of network could be formed (Scheme 3). It should be stressed that,

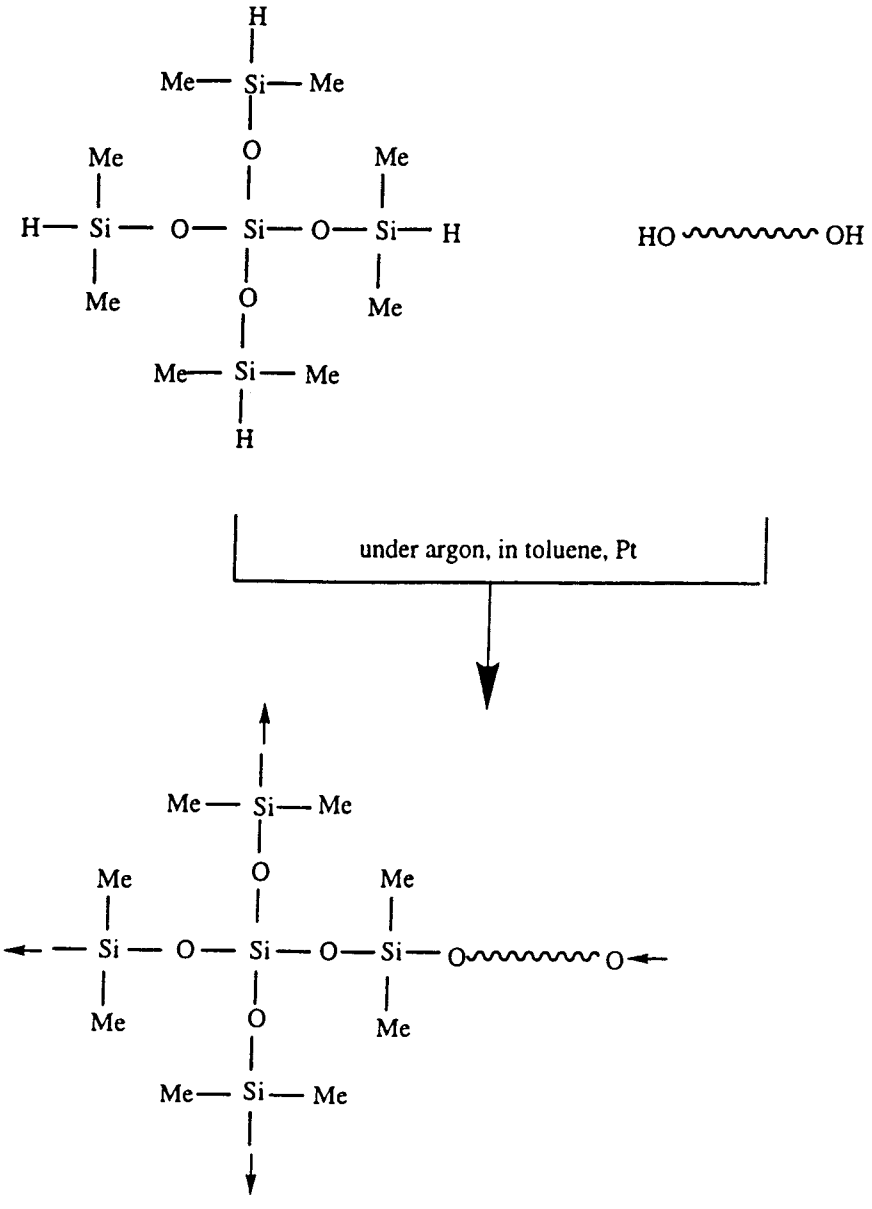


Scheme 2. Formation of type I networks.

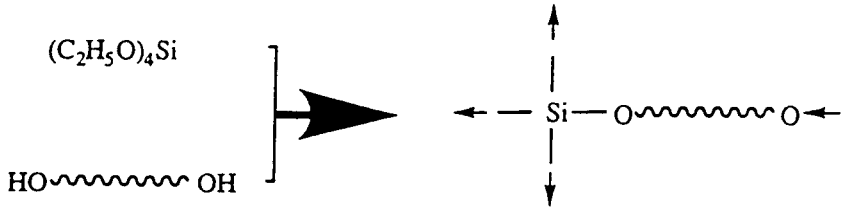
this time the PEO chains are linked to the cross-linker by a Si–O–C bond, instead of the Si–C bond in the type I. The latter bond is stronger and less likely to undergo hydrolysis to which the former is quite sensitive. One network of this type (Table 2, network E) has been prepared.

Type III. Scheme 4 shows the formation of another network. In this case, PEG is allowed to react with the cross-linker tetraethoxysilane $(EtO)_4Si$ under vacuum at room temperature. This reaction is also commonly used to form PDMS networks from silanol terminated polymers [43]. The networks were tested for unreacted C_2H_5O groups using the Zeisel alkoxy group analysis [47]. The fact that no C_2H_5O groups were detected, and based on the known sensitivity of the method, the desired end-linking reaction achieved at least 90% completion. One network of this type (Table 2, network F) has been prepared.

It is noteworthy that gels formed by type I reaction are stable and show no sign of degradation even after repeated swelling by different solvents. However, gels formed by type II or type III reactions are not stable and show quick degradation when they are swollen in water. This difference between type I and type II (or



Scheme 3. Formation of type II network.



Scheme 4. Formation of type III network.

III) is result of the bond type, by which the PEG chains are linked to the cross-linker (Si–O–C vs. Si–C). Networks type II and III may be useful for water swellable degradable devices. The following sections in this work will only focus on type I networks, i.e., networks A–D.

3.3. The equilibrium swelling by water of the hydrogels

The amount of water absorbed by a hydrogel network is quantitatively represented by the equilibrium water content (EWC), or by w_1, the equilibrium water fraction which is the weight fraction of water in the swollen hydrogel

$$w_1 = \frac{\text{weight of water in the gel}}{\text{total weight of hydrated gel}}. \quad (2)$$

The EWC is the most important single property of a hydrogel, influencing as it does the permeability, mechanical, surface and other properties of the gel.

The EWC was measured at room temperature for the hydrogels formed by the cross-linked allyl-substituted PEG (type I networks). The final value given is an average of the results from three determinations. As shown in Table 5, for networks A, B and C, the EWC for the hydrogels increases from 0.41 to 0.62 and 0.96, respectively.

The effect of temperature on the equilibrium water content in hydrogels is also investigated. The EWC was measured at three different temperatures and the results are summarized in Table 6. The EWCs in these PEG-based hydrogels decrease with the increasing of temperature. This is as expected due to the LCST type phase diagram of PEG in water. It also demonstrates that the swelling temperature shows a remarkable effect on EWC in hydrogels. By increasing the temperature, a well swollen hydrogel could be deswollen gradually. This high degree of temperature dependence may be used for sensitive control of swelling.

Table 5
The EWCs of hydrogels at 25°C

	Networks		
	A	B	C
1	0.41	0.63	0.96
2	0.42	0.61	0.96
3	0.40	0.61	0.96
Average	0.41	0.62	0.96

Table 6
The effect of temperature on the EWCs

	Networks		
	A	B	C
25°C			
1	0.41	0.63	0.96
2	0.43	0.61	0.96
3	0.40	0.61	0.96
Average	0.41	0.62	0.96
45°C			
1	0.35	0.50	0.95
2	0.33	0.53	0.95
3	0.34	0.52	0.95
Average	0.34	0.51	0.95
65°C			
1	0.27	0.43	0.94
2	0.26	0.46	0.94
3	0.26	0.44	0.94
Average	0.26	0.44	0.94

Three species of network B were repeatedly swollen in water, benzene and water. The EWC in the hydrogel before and after swelling in benzene were compared and the results are listed in Table 7. It was found that there was no difference between the EWC before swelling in benzene and that after swelling in benzene. This demonstrates that the networks are stable and there is no degradation even after repeated swelling by different solvents.

3.4. Weight fraction solubles (w_s) in the networks

The amount of soluble material in a network at any given extent of reaction is of practical interest. It could be used, for instance, to estimate the degree of the

Table 7
Swelling of network B

	Weight fraction			
	1	2	3	Average
Water	0.63	0.64	0.63	0.63
Benzene	0.85	0.86	0.86	0.86
Water	0.63	0.64	0.65	0.64

reaction, by which the network is formed [44]. Also, the weight fraction of soluble material in the networks can be used to calculate the molecular weight between cross-links in a network [45]. The weight fraction of soluble material in the networks is defined by the following equation:

$$w_s = 1 - \frac{\text{weight of dry polymer network after swelling}}{\text{weight of dry polymer network before swelling}}. \quad (3)$$

Up to the gel point all molecules are finite, thus the weight fraction of solubles, w_s, is unity. Beyond the gel point molecules are rapidly incorporated into the network and w_s decreases quickly. The weight fraction of soluble material in the network was measured for networks A, B and C, and the results are summarized in Table 8. As we can see, going from networks A to B and C, w_s increases from 0.0625 to 0.1464 and 0.3817. These results indicate that network A formed from PEVi-480 is more complete than the one formed from PEVi-680 (network B) which inturn is more complete than network C formed from PEVi-8080.

3.5. Estimation of the conversion (p) for the cross-linking reaction

According to the theory of Miller and Macosko [44], the following three equations are used to calculate w_s at a given degree of the reaction, p (where p is defined as fraction of end groups on the polymer chain that have reacted, and the stoichiometric ratio between polymer reactive groups and cross-linker reactive groups is taken as r=1):

$$P(F_A^{out}) = (1/p^2 - 3/4)^{1/2} - 1/2, \quad (4)$$

$$P(F_A^{out}) = pP(F_B^{out}) + (1 - p), \quad (5)$$

$$w_s = w_{A4}P(F_A^{out})^4 + w_{B2}P(F_B^{out})^2, \quad (6)$$

Table 8
Weight fraction of soluble material in the network (w_s)

	Networks		
	A	B	C
1	0.0645	0.1501	0.3800
2	0.0607	0.1449	0.3899
3	0.0624	0.1442	0.3753
Average	0.0625	0.1464	0.3817

in which, w_{B2} and w_{A4} are the weight fractions of polymer and cross-linker, respectively. The probabilities $P(F_A^{out})$ and $P(F_B^{out})$ have the same meaning as in the original paper [44].

The weight fraction of soluble material in the networks (w_s) at different p are calculated by assuming that the weight between cross-likable sites is 480, 680 and 8080, respectively. The relationship between w_s and p is shown in Fig. 4. From the measured w_s (cf. Table 8), the conversion of reactants (p) is estimated as 79%, 73% and 66% for networks A, B and C, respectively.

Two reasons could in principle lead to imperfection of the networks in our system: the first is the conversion of hydroxyl groups of the PEG to allyl groups in the pre-polymers, the second is the cross-linking reaction. As discussed above, NMR and IR spectra have confirmed that each terminal hydroxyl group in the PEG was completely derivatized by the allyl group. Thus, one has to conclude that the imperfection of the networks results from the cross-linking reaction itself. During the course of the cross-linking reaction a problem is encountered. After approximately 30–60 min gel has been formed and it is impossible to continue stirring the reaction mixture. It is possible that due to high viscosity and low mobility the reactants have difficulty in diffusing towards each other. To check this point we formed network D which is similar in all respects to network C except it was allowed to react three times longer than network C. Only a minor change in p (68% vs. 66% for C) is observed.

3.6. The calculation of molecular weight between cross-links (M_c) from the swelling data

Another important network parameter is the average molecular weight between cross-links (M_c) which is useful in understanding properties of networks [35]. It is directly related to the degree of conversion of network forming reaction described above.

According to the theory of Flory [33], the following relationship are used in order to calculate M_c:

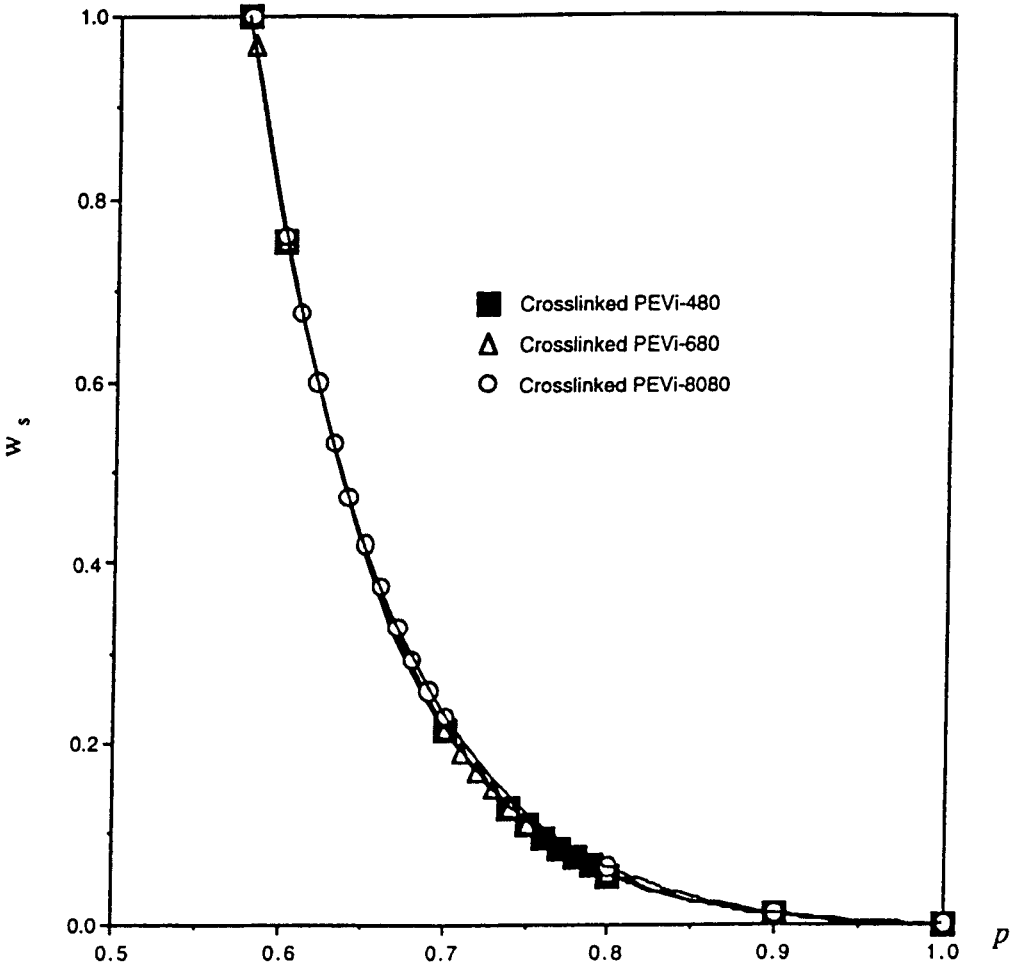


Fig. 4. The relationship between fraction of solubles (w_s) and conversion of end functional group on the PEO (p) for stoichiometric ratio value r=1.

$$\ln(1-\phi_2)+\phi_2+\chi\phi_2^2+v_e v_1(\phi_2^{1/3}-2\phi_2 f^{-1})=0, \quad (7)$$

where v_1 is the molar volume of water (18.05 cm^3 mol^{-1} at 25°C), f the functionality of cross-links (we assume f=4 in our case), v_e the effective cross-linking density, ϕ_2 the volume fraction of polymer in the swollen hydrogel and χ is the polymer–solvent interaction parameter.

From v_e the effective molecular mass between cross-links (M_c) can be calculated via the equation:

$$M_c = \rho/v_e, \quad (8)$$

in which ρ is the polymer density.

Obviously, the molecular weight between cross-links (M_c) could also be calculated by the recursion method [45] from the measured weight fraction of soluble material in the networks (w_s). The molecular weight between cross-links in the networks are calculated by Eqs. (7) and (8) and listed in Table 9.

As shown in Table 9, the calculated M_c for network C is much higher than the molecular weight of prepolymer chain. This is obviously as result of the imperfection of the networks. If each chain is successfully reacted with two cross-linking groups, the result is an "ideal" or "model" network and the network chains would have the same average length and distribution of lengths as the sample of noncross-linked

Table 9
The calculated M_c values

	Networks		
	A	B	C
Density of polymer (g/cm^3)	1.0473	1.0649	1.2118
ϕ_2	0.5751	0.3641	0.0347
χ[a]	0.7751	0.5641	0.2347
M_c	421	739	20239 (20735)[b]

[a]The χ values are calculated according to the equation $\chi=0.2+\phi_2$ (this equation is obtained by fitting the experimental χ data from the CRC Handbook of Polymer–Liquid Interaction Parameters and Solubility Parameters (Ed Allan, F.M. Barton, CRC Press, Florida, 1990)).

[b]The number in () is calculated from the measured weight fraction of soluble material in the networks (w_s).

chains from which it was prepared. In other words, M_c will decrease continuously from infinity at the gel point to the weighed sum of the pre-chain and two arms of the cross-linker upon $p=1$. Table 9 shows that network A and B have M_c close to expected. For network C we also computed M_c from the Macosko–Miller relations based on the value of p. The two methods give identical values for M_c.

It should be noted that in addition to the assumptions inherent to the Flory model [46] we have also neglected the contribution of the cross-linker to χ.

4. Conclusions

In this work, three types of cross-linked networks based on poly(ethylene oxide) have been synthesized. Type I, gels for which the networks are prepared by cross-linking of allyl-substituted PEG with tetrakis(-dimethylsiloxy)-silane $(HSiMe_2O)_4Si$ cross-linker. These gels are stable and show no sign of degradation even after repeated swelling by different solvents. Networks of type II and type III, which are prepared by cross-linking of the PEG with either $(HSiMe_2O)_4$ or with $(EtO)_4Si$, are not stable and gradually degrade when they are swollen in water.

Selective water swellability of the networks could be obtained by controlling the PEG content in the networks and by controlling the temperature. By increasing the temperature, a well swollen hydrogel could be deswollen gradually.

The weight fraction of soluble material in the networks (w_s) measured and the molecular weight between cross-links M_c calculated show that the synthetic networks are not perfect. The imperfection of the networks results from the cross-linking reaction itself, but the exact source of the problem is not clear. Current work is underway to improve the conversion of the cross-linking reaction.

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