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New Neutral and Ionic Poly(ethylene oxide) Networks by Radical Polymerization

Konstantin S. Kazanskii

N. N. Semenov Institute of Chemical Physics, Russian Academy of Sciences,
ul. Kosygina 4, 117977 Moscow, Russia

SUMMARY: New opportunities resulting from a turn to radical polymerization in the synthesis of poly(ethylene oxide) (PEO) networks are discussed and exemplified. Several series of such networks have been prepared by radical homo- and copolymerization in aqueous media of "macromonomers", i.e. partly methacrylated poly(ethylene glycol) (PEG) of varied molecular weight (MW $\cong$ 2000 - 12000) and functionality ($f_n \cong 1.25 - 1.8$). This family of gels as a whole has the volume swelling degree Q in the range of 10 to 200 ml/ml. The hydrogels are characterized by means of Q, elastic modulus, swelling pressure, and with the use of some probes.

The swelling behaviour of neutral hydrogels of this kind is briefly resumed. The multifunctional junctions formed in the propagation reaction of methacrylate end groups determine their main peculiarity. Anomalous elastic behaviour of the swollen networks prepared at high concentration of polymer has been observed and attributed to the network chains stretching of the same nature as in polymer stars or brushes. The junctions' functionality ($F \approx 20 - 300$) is evaluated from these data as well as from MW of the soluble models of network junctions.

The PEO networks with charged units in junctions have been obtained by copolymerization of macromonomers with some ionic (meth)acrylic monomers. These gels display all the polyelectrolyte features, e.g. enhanced Q values in water (up to 50 - 70) and, contrary to neutral PEO gels, the strong dependence on salt content. However, the osmotic contribution of mobile ions into swelling is shown to be low due to localization of charges in the junctions.

The hydrogels that combine PEO and polymethacrylic acid chains capable of interpolymer complexation have been prepared and studied. They show much higher swelling in pure water (Q up to 200), strong deswelling by NaCl, and very sharp drop in swelling (ca. two order in Q) at pH $\approx$ 4.5 - 5.5 due to complexation.

Introduction

As a starting material for hydrogels, PEO has been attracting considerable interest for a long time. The existing technique of PEO networks preparing consists practically of the γ-radiation crosslinking of high MW polymer in aqueous solutions and the reaction of PEGs with pluriisocyanates. Only the second of these two approaches can be considered really as a design of the network [1], although both methods have a lot of disadvantages. At the same time, the majority of hydrogels is known to be prepared by the radical polymerization, which is becoming more and more universal and controlled.

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Some years ago we started our efforts towards the synthesis of PEO networks via polymerizable derivatives of PEG. Originally this work was aimed at the immobilization of liquid-crystalline dispersion of DNA by incorporating into an inert gel matrix just on the gelation step [2]. More recently, some general questions arose: To what extent the structure of these networks can be controlled? What is this structure? How to introduce charged groups into the network by this method to vary its swelling behaviour? This paper sums up some results of our recent attempts to solve at least a part of these problems.

Non-ionic hydrogels by radical polymerization

The initial idea of the whole approach consists in the synthesis of methacrylate derivatives of relatively long chain PEGs followed by their radical polymerization in aqueous media. The methacrylation methods are well developed, and we use one of them for preparing the series of derivatives [2, 3], called here "macromonomers" only for convenience sake. We are not striving to reach the complete PEG functionalization: quite simple evaluations show that average functionality $f_n \approx 1.5$ is sufficient to obtain network with a minor content (less than 7%) of the initial PEG. Some data for a small part of macromonomers used in our works are shown in Table 1.

Table 1. Partly methacrylated poly(ethylene glycol)s ("macromonomers") used in PEO hydrogels synthesis.

MM [a]	2000	4000		6000	12000	
Code	A	B	C	D	E	F
f_n [b]	1.71	1.45	1.70	1.52	1.25	1.56
P_2 [c]	0.73	0.53	0.72	0.58	0.39	0.61

[a] Nominal MW of a parent PEG.

[b] Number-average methacrylate functionality of macromonomer (from UV spectra [2]).

[c] Fraction of PEO dimethacrylate in the functionalized PEG evaluated on the assumption of equal reactivity of OH-groups in the functionalization reaction: $P_2 = p^2$, where the conversion of OH-groups $p = f_n /2$.

These macromonomers are readily polymerized in aqueous solutions with routine initiators in a broad range of polymer concentration. The network structure and thermodynamic state of hydrogels formed have been studied by several methods [3].

It should be noted that the polymer networks formed in this particular case should differ in their structure from those prepared, for example, by end linking via polyaddition reaction. The gelation proceeds here through the polymerization of terminal groups that combine to form macromolecular junctions. The chain length, that is functionality of a single junction (F), can be very high. Being obviously hydrophobic, these chains must exist in aqueous media in various forms and play a considerable part in the swelling of the whole network.

Thus, it was of interest to clear up the real state of the network chains and junctions and potentialities of this approach in preparing PEO gels of a controlled structure.

Crosslinking density of hydrogels is known to be easily obtained from the elastic modulus G according to the theory of rubber elasticity. For a gel at the state of preparation it gives a number of elastically active chains as a measure of the crosslinking density n_c^0. On the other hand, just for the preparation state the same value can be estimated from the composition of the polymerizing system, if we assume that only dimethacrylate chains become elastically active being included in the network. So, in this particular case: $n_c^0 = (C_p^0 / M_n) \cdot P_2$, where C_p^0 is the concentration of polymer of a given M_n in a reaction mixture. The correlation of experimental modulus G_0 with the calculated n_c^0 is consistent with the theory [4]. Thus, omitting some details, we can admit as a rough approximation that the crosslinking density of this kind of networks is close to that taken from the simplest model. In other words, we are able to control this value by varying the MW, functionality, and concentration of macromonomer. There is an exception at high polymer concentrations which is examined further.

The thermodynamic state of a swollen network can be estimated by the analysis of the modulus and swelling pressure π dependencies on Q at the equilibrium state. Both these approaches reveal a marked decrease in the solvent power of water upon going from the solution to swollen PEO gel.

As to the modulus, it is usually considered as a function of swelling in form of equation $G_e \sim Q_e^{-\mu}$ with the exponent μ determined by the thermodynamic state of the system and equal to 2.25, 3.0, and infinity for a good, theta, and poor solvents, respectively. The experimental data follows this law with μ close to 4.0, which is evidently consistent with the situation of a poor solvent. This is most probable due to the influence of hydrophobic polymethacrylate chains on the whole network state.

Swelling pressure allows direct evaluating an interaction parameter χ for the network under study. The $\pi(Q)$ diagrams of hydrogels were obtained by both deswelling technique and direct method [3, 5]. Their treatment within the framework of the Flory approach for neutral networks resulted in the χ equal to 0.462. This value is much higher as compared with 0.425 for linear PEO and provides one more evidence for the significant deterioration of thermodynamic situation at the gelation stage.

The hydrophobic nature and contribution of methacrylate chains is supported qualitatively by our data on the behaviour of a luminescent probe, 8-anilinonaphtalene-1-sulphonic acid (ANS), in a solutions and gels of PEO. This probe is known to be very sensitive to the fate of hydrophobic fragments. In particular, it has been shown that luminescence intensity increases sharply just during gelation in the presence of this probe as well as in the course of the ANS absorption by a swollen gel sample [6]. This work is still in progress.

The mentioned hydrophobic impact of macromolecular junctions on hydrogel swelling is obviously negative. Nevertheless, the radical polymerization of methacrylated PEGs represents a quite convenient synthetic approach that extends the PEO gels preparative technique as a whole. Maximal values of swelling degree close to 30 - 40 ml/ml are reached and can be still increased when needed.

Non-classical elastic behaviour of PEO hydrogels and structure of network junctions

However, what really is the state of a network chain if its end group is bound to a multifunctional knot? Does it change its conformation and size in comparison to those in solution? These questions are quite natural if we remember the situation in polymer stars and brushes. So, we can *a priory* expect that chains can be somewhat extended due to topological constraints in the vicinity of a knot.

We have obtained recently experimental data consistent with this point of view. Fig. 1 shows the series of typical diagrams of elastic modulus G vs. swelling degree Q, the latter being changed by successive swelling or deswelling steps. These curves can be subdivided into two kinds in relation to the classical $G \sim Q^{-1/3}$ correlation characteristic of the Gaussian elasticity. As is seen, in case of long-chain of precursors (MW 6000 and 12000) the elastic behaviour of gels is quite close to this law: slopes are equal to – 0.34 and – 0.31 (± 0.030) for curves 6 and 7, respectively. Thus, long chains are unperturbed by their binding into the network.

As for all the other diagrams, they are more or less non-classical, especially at high initial concentrations of macromonomer in a polymerizing system. It means that network chains are stretched already at the preparation state and exhibit non-Gaussian behaviour at subsequent swelling.

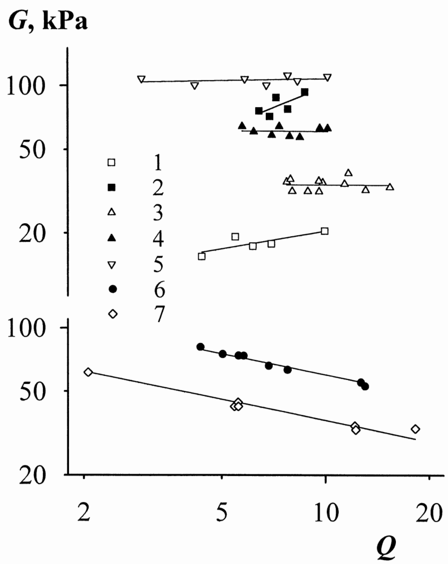

Figure 1. The shear modulus as a function of the volume swelling degree for hydrogels obtained from PEO methacrylates of different MW (see codes in Table 1) at various concentrations: 1 – macromonomer A, C_p^0 = 0.119 g/ml; 2 – A, 0.163; 3 – C, 0.124; 4 – C, 0.160; 5 – B, 0.200; 6 – D, 0.202; 7 – E, 0.214. Straight lines are given only to show the trends of the series of experimental.

It is more or less evident that the longer is the chain, the less multifunctional terminal knots affect it. But the idea of chain stretching can be formalized, which results finally in the values of average number of chains F bound in a junction [7]. These values turn out to increase in parallel with the concentration of polymerizing groups and to be of the order of 100-300 conforming to some published data on other types of poly(macromonomer)s, e.g. polystyrene. Quite recently the analysis of this problem lead us to an attempt at the preparing and study of the soluble models of a network junction. To prepare them, strictly monofunctional PEO macromonomers (MW 2000 and 5000) have been synthesized, thoroughly characterized by means of several methods, and then polymerized to series of branched PEO [8]. Some selected data on precursors and their polymers are shown in Table 2.

As is seen, the polymerization of macromonomers leads to soluble products with the F values of the same order as their analogues in networks. On the average, the lengths of polymethacrylate chains of soluble star- or comb-shape models seem to be somewhat lower than those in a network, which can be reasonable due to the possible difference in termination of growing radicals in both cases. At the moment it is not clear what is the form and dimensions of these branched PEO in water, although definite distinction in the data on F obtained with RI and LS detectors (Table 2) is an indirect evidence of their compact, probably, star-shape form.

Table 2. Monofunctional methacrylate macromonomers and their polymerization products [8]

Macromonomers [a)]				Poly(macromonomer)s [b)]			
MM	[η], dl/g	M_η	f_n	$M_w \times 10^{-3}$, (RI)	F_{RI} [c)]	$M_w \times 10^{-3}$, (LS)	F_{LS} [c)]
2000	0,077	2040	0,89	148	74	255	128
				100	50	185	93
5000	0,150	5030	0,95	191	38	564	113
				292	58	357	71

[a)] Nominal molecular weight of parent MPEG, viscometry data, and functionality are given for macromonomers.

[b)] Polymerization with $K_2S_2O_8$ - $Na_2S_2O_3$ (1.4 mmol/l, 30°C, first line) and 4,4'-azobis(4-cyanovaleric acid (0.6 mmol/l, 60°C, second line) as initiators; polymer concentration is ca. 0.20 g/ml.

[c)] Chain length or number of branches obtained from LC curves with refractive index (RI) and light scattering (LS) detectors, respectively.

It is worthy to note finally that the order of F value by itself is too high and needs to be reduced. The current art of controlled radical polymerization provides us some new opportunities, such as atom transfer or catalytic chain transfer polymerization allowing preparing relatively low-molecular polymers. Our first experiments revealed the potentialities of both these approaches in the variation of junction functionality and, consequently, the structure and swelling of these PEO hydrogels.

Charged PEO hydrogels by radical copolymerization

The use of radical polymerization, absolutely non-typical of PEO chemistry, opens up some more new opportunities in hydrogels synthesis. One of them consists in introducing the charged groups into networks in order to make their swelling more variable. The ionic groups are known to enhance swelling of gels and make them sensitive to various electrochemical stimuli. A quite natural way to partly ionic hydrogels in this particular case is the copolymerization of macromonomers with "small" ionic monomers.

For our first attempt we chose potassium salts of 2-acrylamido-2-methyl-1-propanesulfonic (APSA-K) and methacrylic acids (MAA-K); some details of the synthesis are given in Ref. [9]. Both comonomers are water-soluble and relatively strong electrolytes, so that they can be fully dissociated as monomer units of the network chains. The copolymerization reaction was carried out to the complete consumption of methacrylic groups under control by UV spectra, so that the compositions of initial mixture of monomers and resulting copolymer were identical.

It should be emphasized that the network junctions only can be charged by this way while PEO chains as usual are completely neutral. So, the ionization extent of a network can be estimated in two ways. By analogy with statistically charged systems we can relate the number of ionic groups in a gel to the whole monomer units that results in the average charge density of a network β_n. Being normalized to the sum of the polymerizing groups, the same number is a measure of the ionization degree of a junction β_j. Obviously that $\beta_n << \beta_j$.

The swelling behaviour of gels obtained is shown in Fig. 2a.

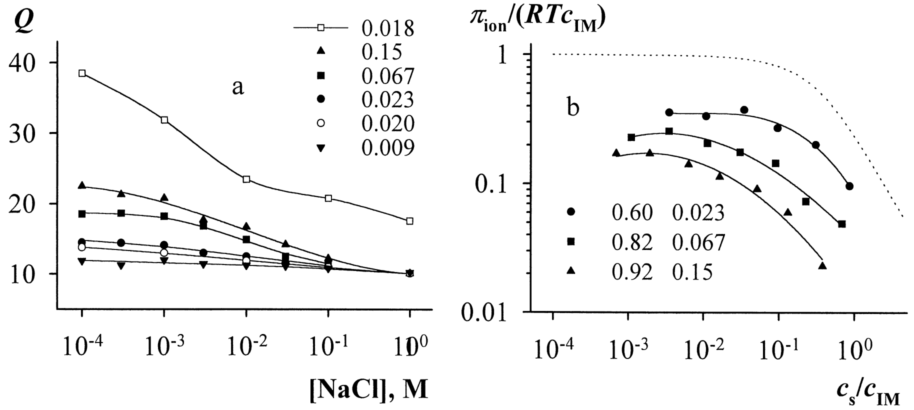

Figure 2. The swelling behaviour of charged PEO networks: a – the swelling degree vs. salt concentration for hydrogels obtained from macromonomers E (upper curve) and B (lower curves) with APSA-K (open points) and MAA-K (full points); numbers show the β_n values of gels; b - to the illustration the osmotic efficiency of ionic groups in the swelling of hydrogels prepared from macromonomer B and MAA-K; values of β_j (first number) and β_n (second number) are shown; for symbols see the text.

As is evident from the plots, the gels swell in water more significantly due to the charge effect, this effect being more pronounced in case of longer network chains, which looks quite natural. The second, what should be noted, the sodium chloride introduced into solution depresses seriously the gel swelling, which is not characteristic of neutral PEO gels [10]. All these ionic effects are shown to be practically independent of the charged group nature (APSA or MAA) and determined only by their content in the network.

Thus, the copolymerization of PEO macromonomers with some ionic (meth)acrylic monomers gives rise to hydrogels with a typical polyelectrolyte behaviour. The influence of the charged groups is rather universal and probably determined by the Donnan effect, i.e. by the difference of mobile ion concentrations inside and outside a gel. It is of interest to evaluate what is the efficiency of charges localized in the network junctions exclusively. To do that, it is necessary to analyze the swelling pressure of a gel and split it into polymer, ionic, and elastic contributions. One way to do this is to study the shear modulus as a function of swelling at varied salt concentration, and as a result the ionic contribution into swelling pressure π_{ion} can be obtained (Ref. [9]).

In form, normalyzed to the ionic pressure of counterions (C_{IM} is concentration of ionic monomer in gel) calculated in an ideal-gas approximation, the values of π_{ion} are shown in Fig. 2b as a function of salt concentration. The upper curve here refers to an ideal Donnan equilibrium. Comparison shows that the osmotic efficiency of mobile ions is rather low and diminishes with a charge density. The most probable reason is just the localization of charged units within the network that results in the counterion condensation. As is easy to see, the highest effect of charges (osmotic coefficient ca. 0.45) relates to the sample with $\beta_j \approx 0.6$, while the ionization degree of the network (β_n) is very low and scarcely exceeds 2%.

Despite the low effect of ionic groups, the insertion of them in macromolecular junction makes the network swelling affected by the ionic content of an outer medium. Another series of ionic PEO gels with charges distributed within the network chains were prepared in our recent work [11]. The salt effects in the swelling of those gels were not analyzed in details, however their swelling degree Q in water was as much as ca. 100 ml/ml.

The influence of ionic component of the network becomes much more pronounced in case of its complexation with PEO chain. This case is exemplified here with fragments of our recent work on the gels composed of PEO and poly(methacrylic acid) (PMAA) chains. These gels were prepared by copolymerization of MAA with the same PEO macromonomers at pH close to 7.0 to avoid complexation; the molar ratio of PEO to PMAA units (R) was varied.

The swelling behaviour of stoichiometric gels of this kind is shown in Fig. 3. As is seen from Fig. 3a, a sharp pH effect takes place with a collapse near pH 5.0, which is characteristic of strong complexation between the two polymer components of the networks. Neither the position on pH scale nor the amplitude of this drop in swelling depends on the lengths of PEO (from 90 to 270) and PMAA (from 60 to 180) chains. Together with data of N.Peppas on the similar gels with much shorter PEO chains ([12] and references thereof), this independence of chain length maybe is the most typical feature of the crosslinked complexes contrary to their analogues in solutions. This fact is worthy of more detailed consideration.

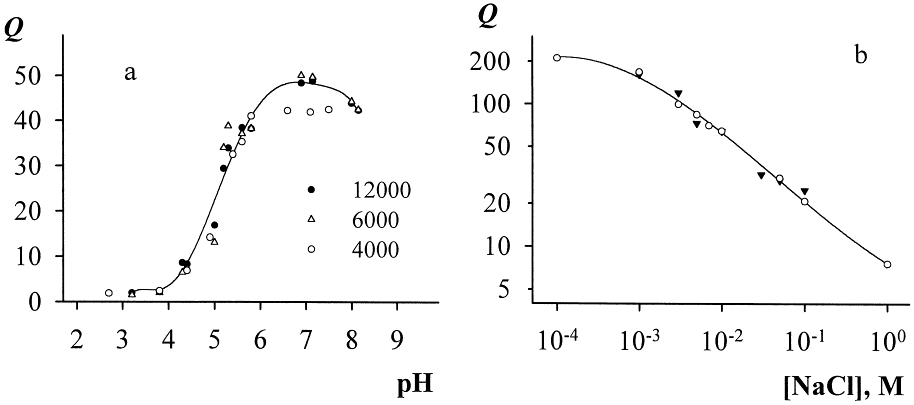

Figure 3. The swelling behaviour of networks consisting of PEO and PMAA chains: a – pH dependence of swelling degree Q for gels obtained from PEO precursors of different MW (B, D, and F in Table 1; I = 0.1 mol/l); b – influence of NaCl concentration on the swelling of gels (macromonomer F, pH 7.0).

In the absence of complexation, that is at pH higher 7.0, these hydrogels behave as typical polyelectrolite gels with very high Q values in pure water and their strong dependence on NaCl concentration (Fig. 3b). The degree of swelling in water as well as the amplitude of the collapse is naturally decreasing in transition to non-stoichiometric composite gels with R > 1.0. Crosslinking density and charge contribution are probably the most important factors affecting behaviour of non-stoichiometric networks.

Conclusion

From the results obtained it may be concluded that radical polymerization of long chain, partly methacrylated PEGs is a convenient and simple way to PEO gels of varied network structure and swelling. The gelation in aqueous media under mild conditions is perhaps the most attractive features of this approach. In case of neutral gels, the network chains length as well as the number of them bound in a junction are fully controlled by MW, f_n, and C_p^0 of macromonomer. Introducing of the charged groups makes the swelling of these gels affected by the salts nature and concentration in outer media. In the case of interpolymer complex formation with PEO, pH complements the number of the factors affecting the gel swelling.

This family of PEO gels, both neutral and ionic, can be used for immobilization of some objects different in their nature and size both directly at the gelation step or by absorption any object in a preformed and swollen gel sample.

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