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Swelling, Elasticity and Structure of Hydrogels Prepared via bis-Macromonomers of Poly(ethylene oxide)

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Summary: The effect of swelling on the shear modulus was studied for hydrogels prepared by radical polymerization of methacrylate-terminated poly(ethylene oxide) (PEO) bis-macromonomers of different molecular weight. Gels made of long chains (M = 12000 or 6000) display classical softening upon swelling, whereas gels made of shorter chains (M = 4000 or 2000) remain rigid or even stiffen. The abnormal behaviour is explained by a specific character of network junctions presented by polymethacrylate chains in which each unit is linked with a PEO network chain. It is assumed that the interactions among densely grafted PEO chains result in their stretching on polymerization and non-affine deformation on swelling, which stiffen the gel. This is verified by the data on copolymer (macromonomers – 2-hydroxyethyl methacrylate) gels that have lesser densities of PEO chains attached to the junctions and show weaker stiffening on swelling. The osmotic pressure of gels was estimated from the swelling pressure and shear modulus. Similar to the mixing pressure of equivalent PEO solutions, it varies as the 9/4 power of polymer concentration. At the same time, it is lower than the mixing pressure. This indicates that the junctions make only quantitative changes in the osmotic properties of macromonomer chains.

Keywords: hydrogels; junction structure; macromonomers; osmotic pressure; shear modulus

Introduction

During the past few years, polymer hydrogels prepared by radical polymerization of PEO bis-macromonomers have attracted considerable interest as biocompatible media.[1-4] In this connection, certain efforts have been devoted to study the swelling and elastic properties of such gels.[5-8] It was found that gels prepared at high concentrations of a bis-macromonomer of low molecular weight (M = 4000) exhibit unusual elastic behaviour.[6] In spite of rather high length and flexibility of network chains, they stiffen upon swelling at rather low swelling degrees. To explain this effect, it was assumed that the bis-macromonomer chains are stretched

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when their terminal (methacrylate) groups are linked together to form network junctions of high functionality.[6] The osmotic properties of polymer gels have been studied for a long time. However, gels prepared from bis-macromonomers were not systematically examined and the effect of high functionality of junctions was not considered.

Our aim here is to better understand the origin of unusual elastic properties of bis-macromonomer-based gels. A second aim is to investigate their osmotic properties.

Experimental

PEO bis-macromonomers with methacrylate terminal groups were synthesized from poly(ethylene glycol) (PEG) samples (Loba Chemie, Merck, $M = 2000$, 4000, 6000 and 12000) by the reaction of hydroxyl terminal groups with methacryloyl chloride as described elsewhere.[1] As seen by UV spectra, the average number of methacrylate groups per one PEO chain was about 1.5. 2-hydroxyethyl methacrylate (HEMA) (Merck) was distilled under argon (67 ^{0}C, 400 Pa).

PEO hydrogels were prepared by radical polymerization of bis-macromonomers in aqueous solution. PEO-HEMA hydrogels were obtained by co-polymerization of the bis-macromonomer of $M = 4000$ and HEMA. Conditions of polymerization were described previously.[6,8] The fraction of soluble polymer was found to be around 11 % for gels prepared with the initial macromonomer concentration in the range 0.16 g/g $\leq c_0 \leq$ 0.21 g/g and 20 % at $c_0 = 0.12$ g/g. A large part of this polymer is unfunctionalized PEG existing in the macromonomers (to the extent of about 6 %).

The swelling pressure was measured by the osmotic deswelling technique.[9] The gel samples were equilibrated with aqueous solutions of high-molecular-weight PEG (Merck, $M = 40000$) of known osmotic pressure.[10] In this way, the swelling pressure was determined as a function of swelling degree. In parallel, the shear modulus was measured. The swelling pressure for the gel made of the longest chains ($M = 12000$) was also measured by the direct mechanical method.[11] The results show (see Figure 3) that the penetration of PEG chains inside the gel introduces a negligible error into the deswelling measurements.

In some experiments, the swelling degree was varied by adding small portions of water to as-prepared gels or by allowing some water to evaporate slowly from these gels and swollen gels.

The shear modulus was determined by penetration technique as described elsewhere.[7,12] A spherical indenter of radius $R = 1.9$ mm was used. Its penetration depth h measured as a function of applied force f was plotted against $f^{2/3}$ to give a reasonably straight line. The modulus was calculated from the slope b of this line as $G = 3/(16b^{3/2}R^{1/2})$. Standard deviation in modulus measured for several specimens of a gel was typically about 6%.

Results and Discussion

Elastic Modulus of Gels. We focus our attention on the variation of the shear modulus G with the swelling degree Q ($Q = 1/\phi$, where ϕ is the volume fraction of polymer). As Q varies in a small range and the lengths and flexibility of network chains are high, one can expect the chains to obey Gaussian statistics and the gel modulus to decrease with increasing swelling degree.

Figure 1 shows representative modulus data for poly(bis-macromonomer) hydrogels. The gels exhibit different behaviour depending on the length of the precursor chains. In case of long precursor chains ($M = 12000$ or 6000), the modulus does decrease with increasing swelling degree. Its variation is consistent with the classical prediction $G \sim Q^{-1/3}$ (dashed lines in Figure 1) based on assumptions of Gaussian statistics and affine expansion of network chains.[13] For gels made of shorter chains ($M = 4000$ or 2000), the modulus remains constant or even increases with increasing Q. Its variation is approximated by the power law $G \sim Q^{m}$ with exponent $m \geq 0$ (solid lines in Figure 1). Table 1 shows the value of m for all gels analysed. As seen by the exponent values, deviations from the "normal" modulus decrease are more pronounced for gels prepared with higher concentrations and lower molecular weights of bis-macromonomer.

The "abnormal" variation of modulus seems related with a polymer nature of junctions in poly(bis-macromonomer) networks. As shown in Figure 2, these junctions (i.e., methacrylate chains) resemble backbones of comb molecules with densely grafted side chains. This resemblance implies that the topological interactions between PEO network chains are essential. These interactions are similar to those existing in comb molecules and other types of polymer brushes.[14,15] They are obviously significant when the junction chain size R_j is equal to or higher than the network chain size R_n (see Figure 2); otherwise, the configuration of network chains is almost unperturbed by the junctions. This agrees with the effects of bis-macromonomer molecular weight M and concentrations c_0 on the elastic behaviour. Indeed, the length of methacrylate chains (and hence R_j) should increase with the concentration of polymerizable groups c_0/M, i.e., when c_0 increases and M decreases. At the same time, R_n obviously decreases with decreasing M. Therefore, the condition for significant topological interactions ($R_j \geq R_n$) should be met at low M and high c_0, i.e., just in the range of "abnormal" behaviour.

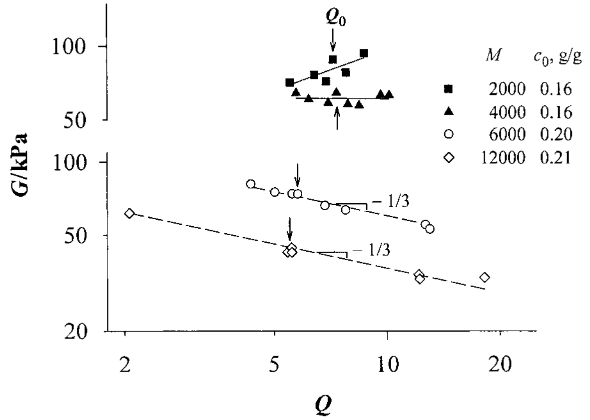

Fig. 1. Double logarithmic plot of shear modulus against swelling degree for PEO gels prepared from bis-macromonomers of different molecular weight. The dash lines drawn through the data show the classical slope of −1/3. The solid lines present more general power law fits to the data. Arrows indicate the swelling degree in the preparation state.

Table 1. Parameters of approximations $G \sim Q^m$ and $\pi_{osm} = B\phi^n$ for PEO gels and solutions.

M	c_0 g/g	c_e[a)] g/g	m	n	B MPa
2000	0.12	0.103	0.39 ± 0.04		
2000	0.16	0.134	0.55 ± 0.22	2.44 ± 0.43	11.6 ± 0.7
4000	0.12	0.077	−0.01 ± 0.10	2.24 ± 0.09	14.4 ± 0.2
4000	0.16	0.115	0.00 ± 0.10	2.27 ± 0.05	13.5 ± 0.1
4000	0.20	0.117	0.58 ± 0.15		
6000	0.20	0.090	−0.34 ± 0.03	2.34 ± 0.05	16.7 ± 0.2
12000	0.15	0.046	−0.37 ± 0.08		
12000	0.20	0.066	−0.32 ± 0.03	1.94 ± 0.16	19.0 ± 0.4
Solution				2.25	27.5 (B_s)

[a)] Polymer concentration of gels swollen to equilibrium in water.

On the other hand, the topological interactions arise when PEO network chains strongly overlap near junctions. This is the case for homopolymer networks. However, in copolymer networks, the distance between PEO branches along the junction is higher (Figure 2). Therefore, the topological interactions here should be weaker and the elastic behaviour of copolymer networks should be closer to the classical one. This is consistent with the data on PEO-HEMA hydrogels. For these gels, the shear modulus also varies as Q^{m}. The values of exponent m are equal to 0.58 ± 0.15, 0.32 ± 0.08, and 0.08 ± 0.06 respectively at the HEMA fractions of 0, 0.61, and 0.74. Comparison of these values shows that the modulus variation $G(Q)$ does approach the "normal" modulus decrease when the fraction of HEMA in the junction chains increases.

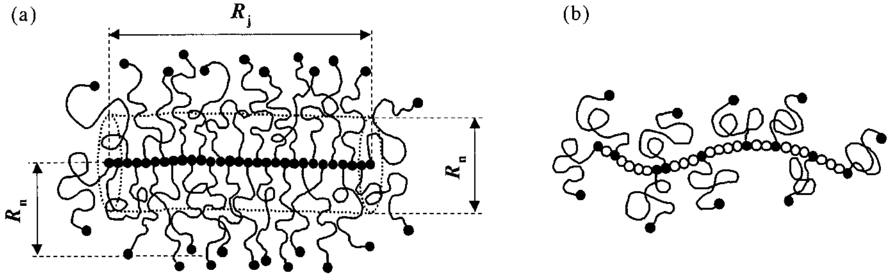

Fig. 2. Architecture of junctions in network obtained via bis-macromonomers: (a) homopolymer networks, (b) copolymer networks. Solid lines: PEO network chains. Circles: units of methacrylate junction chains. Open circles: units of a "small" co-monomer.

The topological interactions between PEO chains presumably make two contributions to the deviations of the elastic behaviour from the "normal" one. First, they result in the stretching of PEO chains. These chains are stretched like the side chains in comb polymers; they become stretched during the polymerization when macromonomer terminal groups form the junction chains. This stretching can cause deviations from Gaussian elasticity and, hence, an increase of shear modulus with increasing swelling degree.[6] Second, the topological interactions are assumed to lead to non-affine deformation of PEO network chains on swelling, which also contribute to the deviations from the "normal" behaviour. It may be argued that the network chain size R_n increases with Q more strongly (as $Q^{1/2}$) than the whole gel size (changing as $Q^{1/3}$). (This result is evident from the idea that the network is a dense packing of cylindrical "brushes" one of which is depicted in Figure 2.) This leads us to the conclusion that the shear modulus is independent of swelling degree. Thus, the stretching of network chains on polymerization and their non-affine deformation on swelling seem to be main reasons for the observed anomaly in the elastic behaviour.

A competing explanation for this anomaly could be based on the theory of Grosberg that states the number of entanglements between network chains to be an increasing function of swelling degree.[16] (Note that theories of non-phantom networks[16-18] suggest contradictory predictions in this regard.) However, the gels under study hardly have entanglements since the macromonomer solutions used in their synthesis were unentangled. Indeed, the molecular weight between entanglements is $M_e = 2200$ for linear PEO in bulk[19] and estimated as $M_e \approx 2200\phi_0^{-1.25} \approx 20000$ for the solution with $c_0 = 0.2$ g/g. The latter value of M_e is much higher than the macromonomer molecular weights. This difference is particularly high for gels with the "abnormal" behaviour (when $M \leq 4000$). Thus, it seems that entanglements make no contribution to the gel modulus.

Osmotic pressure of gels. The osmotic pressure in polymer gels can be characterized by measuring the swelling pressure exerted by the network immersed in a solvent. Figure 3 shows the swelling pressure measured for several PEO gels. As expected, the swelling pressure strongly depends on the swelling degree. The lower the macromonomer molecular weight M and the higher c_0, the stronger is the observed dependence.

The swelling pressure π can be expressed as a sum of the osmotic pressure π_{osm} leading to the gel swelling and the elastic pressure π_{el} that restricts swelling.[13] The value of π_{el} can be approximated by the shear modulus G especially when G varies with the swelling degree by the classical law.[20,21] This allows evaluation of the osmotic pressure of gels. Results of such evaluations are shown in Figure 4. Here, they are compared with the osmotic pressure of semi-dilute PEO solutions.[10] It is seen that the osmotic pressure of gels is lower than that of the solutions. A similar discrepancy was observed earlier for several other gel-solvent systems.[21,22] The dependence of the osmotic pressure of gels on the polymer concentration may be approximated by a power law. The results of this approximation – the interaction coefficient B and exponent n – are shown in Table 1. The exponents for all gels are close to the exponent 9/4 characteristic of a good-solvent solution.[23] This implies that the osmotic pressure in the poly(bis-macromonomer) gels is dominated by the excluded volume interaction that is similar to the interaction in the PEO solution. The interaction coefficient B is lower than B_s, the similar coefficient for the solution. At the same time, when the macromonomer molecular weight increases, these coefficients approach each other.

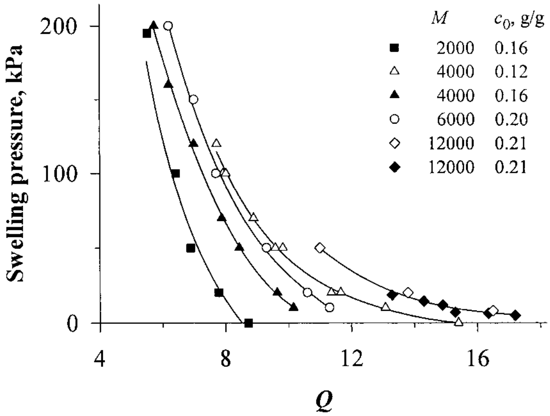

Fig. 3. Swelling pressure as a function of swelling degree for poly(bis-macromonomer) gels prepared with different M and c_0. Filled diamonds: data of mechanical measurements; other symbols: data on osmotic deswelling.

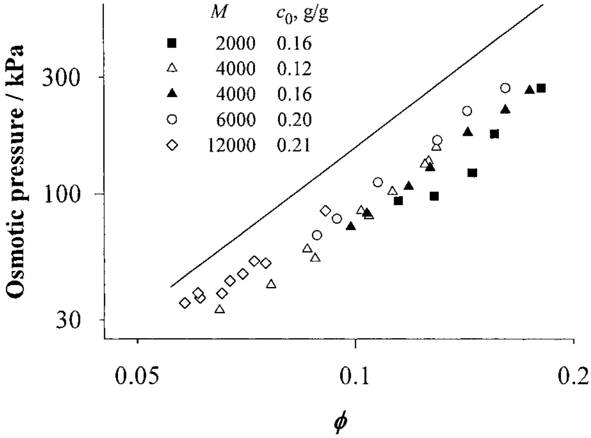

Fig. 4. Osmotic contribution to the swelling pressure of PEO gels prepared with different M and c_0. The straight line with the slope of 9/4 shows the osmotic pressure of semi-dilute PEO solutions.

The lower value of *B* can be explained by assuming that the PEO segments located near the junction chains make a negligible contribution to the osmotic properties of network. Although these segments create an osmotic pressure, this pressure is "expended" in preventing the hydrophobic junction chains from collapse and in stretching PEO chains near the junctions. The fraction of such osmotically hidden segments obviously increases with decreasing molecular weight of bis-macromonomer. This agrees with the experimental data.

Conclusions

Elastic properties of hydrogels based on PEO bis-macromonomers depend on the length and initial concentration of these chains. Abnormal variation of shear modulus with the swelling degree is observed at low molecular weights and high initial concentrations of macromonomers. This behaviour is explained by the polymer nature of the network junctions that results in stretching of PEO chains during the gel preparation and their non-affine deformation upon swelling. However, a rigorous theoretical description is yet to be developed. Osmotic pressure in poly(bis-macromonomer) gels is dominated by the excluded volume interaction characteristic of the equivalent PEO solutions. This interaction is however modified quantitatively. It is likely that PEO segments located in a junction area do not contribute to the "macroscopic" osmotic pressure.

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