# Swelling and elasticity of hydrogels based on poly(ethylene oxide) macroinimer

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**Abstract: A novel method for the preparation of hydrogels based on poly(ethylene oxide) (PEO) is presented. A PEO macroinimer possessing both polymerizable and radical generation sites was used to obtain hydrogels having dangling PEO chains. It was shown that PEO macroinimer acts during photopolymerization, both as a monomer and a crosslinker and thus, leads to the formation of hydrogels of various swelling capacities and moduli of elasticity.**
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**Keywords:** poly(ethylene oxide); macroinimer; hydrogel; swelling; elasticity

## INTRODUCTION

Hydrophilic gels called hydrogels are crosslinked materials absorbing large quantities of water without dissolving. These materials have received considerable attention for use as specific sorbents and as support carriers in biomedical engineering. Extensive work has been reported in the literature for the swelling behaviour of hydrogels based on acrylamide (AAm) monomers. Attention has turned in recent years to the swelling and collapse phenomena of AAm-based hydrogels that are observed when a hydrogel network is brought into contact with a solvent.[1] Although much has been reported on the swelling behaviour of such gels, only a few studies reported the properties of hydrogels based on poly(ethylene oxide)s (PEOs).[2–6] Poly(ethylene glycol)s or the equivalent high molecular weight PEOs are commercially available in various molecular weights and widely used in many pharmaceutical applications. Hydrogels derived from PEOs are useful in biomedical and pharmaceutical applications because of their biocompatibility and high water contents.

Here, we report a novel method for the preparation of hydrogels based on PEOs and their swelling and elasticity properties. A PEO macroinimer (macromer-based initiator) possessing both polymerizable and radical generation sites was used to obtain hydrogels with high swelling capacities (Scheme 1). It has previously been shown that such macroinimers could be prepared by taking advantage of the living polymerization of ethylene oxide.[6] Thus, anionic polymerization

of ethylene oxide with the corresponding amino functional initiator, and termination of the living ends with methacryloyl chloride yield the corresponding macroinimer.

Hydrogels were prepared by UV photopolymerization of the macroinimer at various initial concentrations in dichloromethane as a solvent, using benzophenone as a photoinitiator. As will be seen below, the PEO macroinimer acts during photopolymerization both as a monomer and a crosslinker and so leads to the formation of hydrogels of various swelling capacities and moduli of elasticity.

## EXPERIMENTAL
### Materials

Benzophenone was recrystallized from ethanol. Dichloromethane (99.8%, Baker) was extracted first with sulfuric acid, then with 5% NaOH solutions. After washing with water, the dichloromethane was dried over anhydrous $CaCl_2$ and $CaH_2$ and finally distilled with a fractionation column. PEO macroinimer with perfect functionality of one for both amino and methacrylate groups and number-average molecular weight of $1180 \, g \, mol^{-1}$, as determined with NMR spectroscopy, was prepared as described previously.[6]

### Synthesis of hydrogels
Photopolymerization of PEO macroinimer was carried out in dichloromethane, as the polymerization solvent, at room temperature in the presence of benzophenone
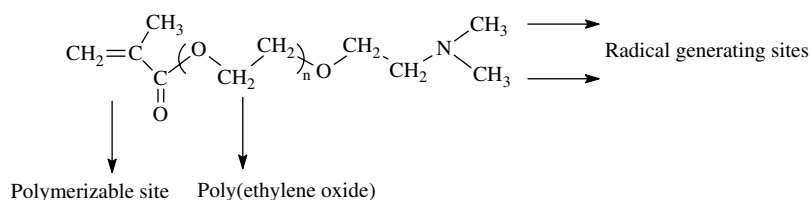
**Scheme 1.** Structure of the macroinimer used.

as the initiator. The amount of benzophenone was fixed throughout our studies at $2.4 \times 10^{-2}\,\mathrm{mol}\,\mathrm{l}^{-1}$, while the initial macroinimer concentration was varied over a wide range. To illustrate our synthetic procedure, we give details for the preparation of the hydrogel with 45 wt% PEO macroinimer in the feed composition.

PEO macroinimer (0.55 g) was dissolved in 0.50 ml of dichloromethane at room temperature. After nitrogen bubbling for 10 min, 2.1 mg of benzophenone was added to the solution and the solution was poured into a glass tube of 4 mm internal diameter. Thereafter, 10 min of nitrogen bubbling was required through the solution to obtain reproducible results. The glass tube was then sealed and the polymerization was initiated by irradiation using a merry-go-round type photoreactor equipped with 16 Philips 8W/O6 lamps emitting light nominally at 350 nm, and a cooling system. The polymerization was conducted for 21 h at room temperature.

**Gel fraction and swelling ratio**
Water was chosen as the extraction solvent for the crude hydrogels and employed at room temperature. After polymerization, the reaction was stopped by cooling the mixture in an ice−water bath. The crude hydrogels, 4 mm in diameter, were freed from the glass tubes and were cut into samples of about 5 mm length. Each sample was then placed in an excess of water, and the solvent was replaced every other day over a period of at least 2 weeks until no further extractable polymer could be detected. The hydrogels after extraction were carefully deswollen in a series of water−methanol mixtures with increasing methanol contents. This solvent exchange process facilitated final drying of the hydrogel samples.[7] They were then washed several times with methanol and dried at 80 °C under vacuum to constant weight. The weight fraction of gel, $W_g$, was calculated as

$$W_{\mathrm{g}} = \frac{\text{weight extracted, dry gel}}{\text{weight PEO macroinimer}} \qquad (1)$$

In order to obtain the equilibrium degree of swelling of the hydrogels, they were immersed in water for at least 2 weeks during which water was replaced every other day. The swelling equilibrium was tested by weighing the samples. To achieve accuracy, three measurements were carried out on samples of different lengths taken from the same gel. The weight swelling ratio of the hydrogels after equilibrium swelling $q_w$, and after preparation $q_F$ were calculated as

$$q_{\mathrm{w}} = \frac{\text{weight equilibrium swollen gel}}{\text{weight extracted, dry gel}} \qquad (2a)$$

$$q_{\mathrm{F}} = \frac{\text{weight gel after preparation}}{\text{weight extracted, dry gel}} \qquad (2b)$$

The interpretation of swelling measurements was made on the basis of volume fraction of crosslinked polymer at equilibrium swelling, and after the gel preparation, designated by $v_2$ and $v_2^0$, respectively, where the volume fraction is defined as the volume of polymer divided by total volume. These variables are related to weight fractions by the relationships.

$$v_2 = \left[1 + \frac{(q_{\mathrm{w}} - 1)\rho}{d_1}\right]^{-1} \qquad (3)$$

$$v_2^0 = \left[1 + \frac{(q_F - 1)\rho}{d}\right]^{-1} \qquad (4)$$

where $\rho$, $d$ and $d_1$ are the densities of polymer $(1.0\,\mathrm{g}\,\mathrm{ml}^{-1})$, the reaction solution $(1.336\,\mathrm{g}\,\mathrm{ml}^{-1})$, and the swelling agent water $(1.0\,\mathrm{g}\,\mathrm{ml}^{-1})$, respectively.

**Mechanical measurements**
Uniaxial compression measurements were performed on gels just after preparation. All the mechanical measurements were conducted in a room thermostated at $24 \pm 0.5$ °C. Stress−strain isotherms were measured by using an apparatus previously described.[8] Briefly, a cylindrical gel sample of about 5 mm in length was placed on a digital balance (Sartorius BP221S, readability and reproducibility: 0.1 mg). A load was transmitted vertically to the gel through a rod fitted with a poly(tetrafluoroethylene) (PTFE) end-plate. The compressional force acting on the gel was calculated from the reading of the balance. The resulting deformation was measured after 20 s of relaxation by using a digital comparator (IDC type Digimatic Indicator 543-262, Mitutoyo Co), which was sensitive to displacements of $10^{-3}$ mm. The measurements were conducted up to about 15% compression. Reversibility of the isotherms was tested by recording the force and the resulting deformation during both force-increasing and force-decreasing processes. The two processes yielded almost identical stress−strain relationships. From the repeated measurements, the standard deviations in the modulus value were less than 3%. The sample

weight loss during the measurements, due to water evaporation, was negligible. The elastic modulus $G$ was determined from the slope of linear dependence:

$$f = G(\lambda^{-2} - \lambda) \tag{5}$$

where $f$ is the force acting per unit cross-sectional area of the undeformed gel specimen, and $\lambda$, is the deformation ratio (deformed length/initial length). Typical stress–strain data correlated according to eqn (5) are shown in Fig 1 for hydrogels prepared at varying initial macroinimer concentrations.

For a homogeneous network of Gaussian chains, the elastic modulus of gels after preparation $G$ is related to the network crosslink density by[9,10]

$$G = A \frac{\rho}{\overline{M}_c} RT v_2^0 \tag{6}$$

where $\overline{M}_c$ is the molecular weight of the network chains, $R$ is the gas constant and $T$ is the temperature. The front factor $A$ equals 1 for an affine network and $1 - 2/\phi$ for a phantom network, where $\phi$ is the functionality of the crosslinks.

## RESULTS AND DISCUSSION

PEO macroinimer was photopolymerized at various initial concentrations in dichloromethane. The reaction time was set at 21 h. Figure 2 shows the weight fraction of gel $W_g$ plotted as a function of the initial macroinimer concentration $c$. No gel formation was observed if $c$ was less than 38 wt%. If $c$ exceeds 38 wt%, the gel fraction $W_g$ rapidly increases and attains a limiting value of $0.80 \pm 0.05$. This means that about 80% of the macroinimer used in the feed were incorporated
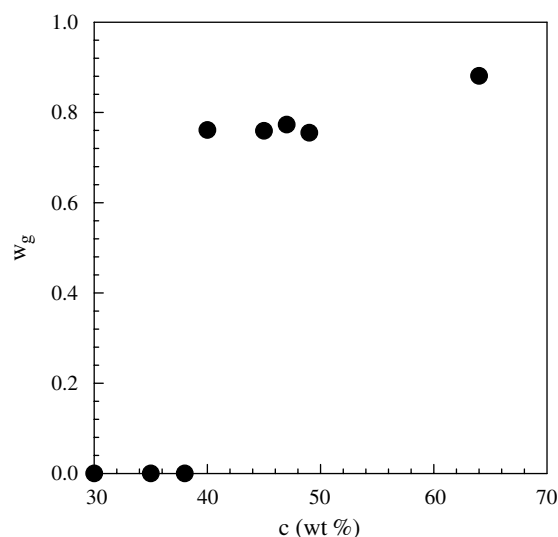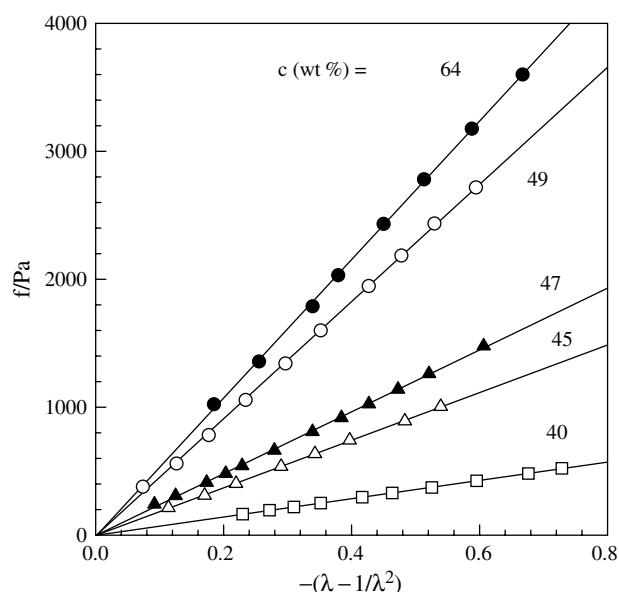


**Figure 2.** Weight fraction of gel $W_g$ shown as a function of the initial macroinimer concentration $c$ used in the hydrogel preparation.

into the network structure, while 20% remained unreacted and/or formed soluble species in the reaction system, even at macroinimer concentrations as high as 64% (Fig 2).

Formation of an infinite network indicates that the functionality of the PEO macroinimer during photopolymerization is greater than two, which needs some comments. As shown in Scheme 1, PEO macroinimer has a vinyl group at one end, and a dimethylamino group at the other end, which may generate radicals in the presence of benzophenone under UV radiation, according to Scheme 2. Hydrogen abstraction from one of the methyl groups adjacent to amino group by a photoexcited benzophenone molecule leads to the formation of macroinimer and ketyl radicals, where the latter radical is known to undergo coupling and thus is ineffective in initiating the polymerization reactions. Part of the initially difunctional macroinimer becomes trifunctional as a result of the hydrogen abstraction reaction, which seems to be responsible for the formation of an infinite network in the reaction system.

During photopolymerization, primary radicals may form on the monomeric macroinimer and on the growing or dead polymer molecules, as illustrated in Scheme 3. These reactions constitute the initiation step of photopolymerization. The primary radicals thus formed may react intramolecularly or intermolecularly. The intramolecular reactions may occur along the monomer or along the growing chain and do not change the molecular weight of the molecules. In contrast, intermolecular reactions between radical species and pendant vinyl groups lead to the formation of branched and, finally, network structures in the system. In Scheme 3, we also speculated that hyperbranched molecules are formed, which may appear as intermediate steps during the gel formation process.



**Figure 1.** Typical stress–strain data for the hydrogels just after their preparation. The initial macroinimer concentration $c$ used in the hydrogel preparation is indicated in the Figure.
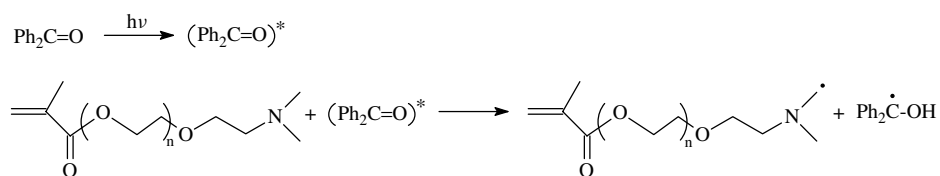
**Scheme 2.** Photoinduced generation of radicals.
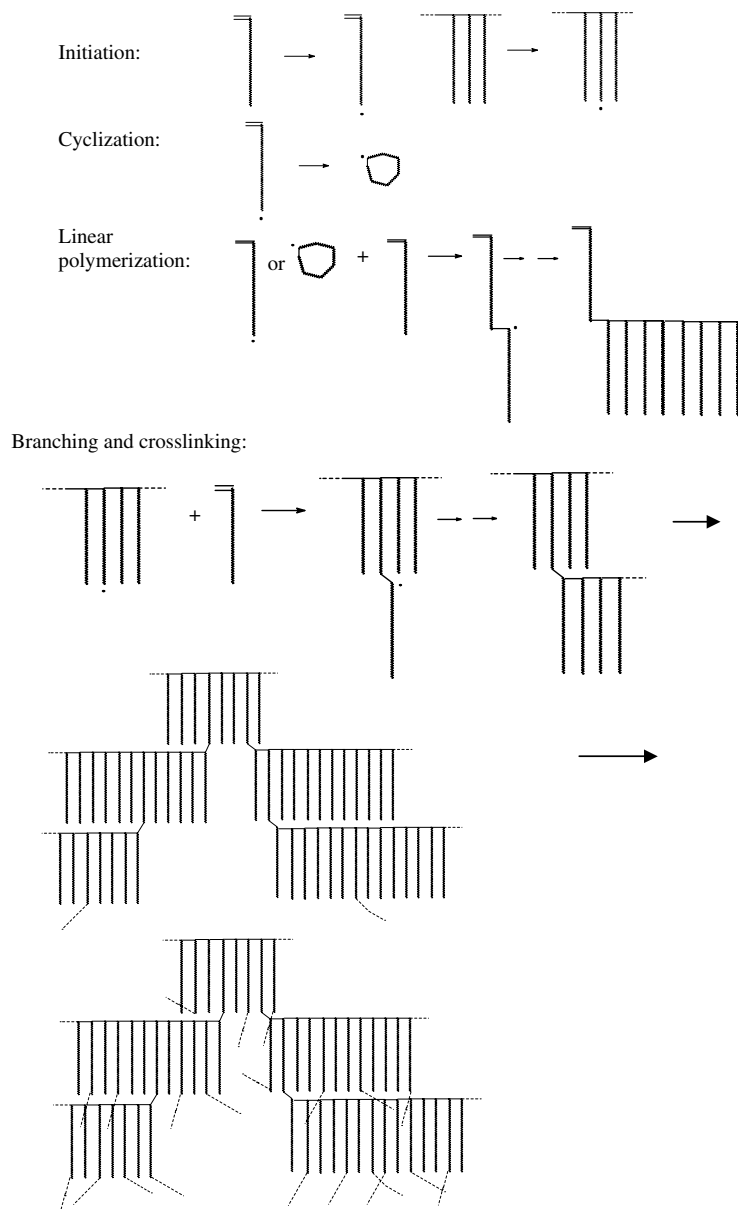


**Scheme 3.** Reaction steps in UV polymerization of the macroinimer.

The data in Fig 2 indicate that 20% of the macroinimer form cyclic, linear, and branched molecules while 80% attach to the infinite network after photopolymerization.

In Fig 3, the equilibrium weight swelling ratio $q_w$ of the hydrogels in water and the modulus of elasticity $G$ of hydrogels just after their preparation are shown as a function of the initial macroinimer concentration $c$. Hydrogels formed at $c$ close to the critical concentration 38% have an elastic modulus of 800 Pa; they are able to absorb about 120 times

their own mass of water. The value of $q_w$ rapidly decreases while $G$ increases as $c$ is increased, indicating increasing extent of crosslinking reactions on rising the initial macroinimer concentration. This is the result of decreasing extent of cyclization reactions as the monomer concentration increases in gel formation processes.[11]

Assuming phantom network behaviour, the molecular weight of the network chains $\overline{M}_c$ was calculated using eqn (6). For calculations, the crosslink points are assumed to be trifunctional ($\phi = 3$). Results of
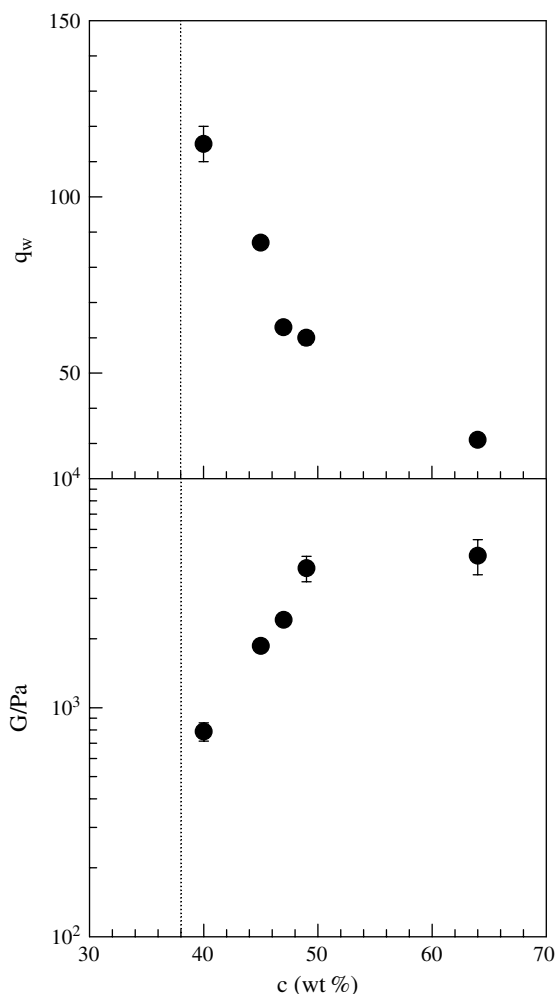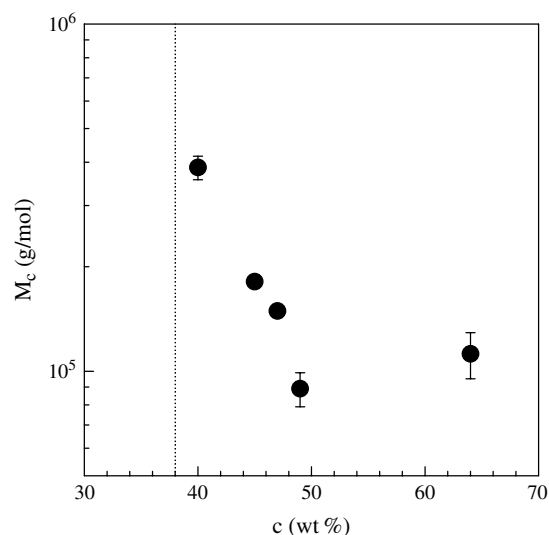
**Figure 3.** Equilibrium weight swelling ratio of the hydrogels in water $q_w$ and modulus of elasticity of the hydrogels just after their preparation $G$, shown as a function of the initial macroinimer concentration $c$. The dotted line represents the critical macroinimer concentration for gel formation.



**Figure 4.** Molecular weight of the network chains $\overline{M}_c$ in the hydrogels shown as a function of the initial macroinimer concentration $c$. The dotted line represents the critical macroinimer concentration for gel formation.
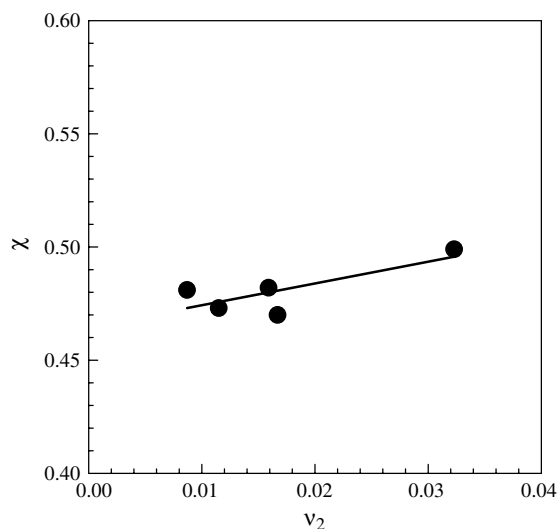


**Figure 5.** The $\chi$ parameter for the system PEO-network–water shown as a function of the equilibrium swelling volume fraction $v_2$.

calculations are shown in Fig 4 plotted against the macroinimer concentration $c$. It is seen that $\overline{M}_c$ values are in the range of $90 \times 10^3 - 400 \times 10^3 \, \mathrm{g\,mol^{-1}}$. This indicates that the number of macroinimer units between two effective crosslinks vary between 90 and 400; thus, the hydrogels consist of loosely crosslinked network chains. Indeed, we observed that the gels equilibrium swollen in water were too weak to withstand the elasticity measurements. Some physical split in the gel sample was also observed during the swelling process of the hydrogel samples in water.

The polymer–solvent interaction parameter $\chi$ between the networks and water was calculated from their equilibrium swelling volume fraction $v_2$ together with their crosslink densities $\overline{M}_c$ from the Flory–Rehner expression for a phantom network:[9]

$$\chi = -\frac{\left(1 - \dfrac{2}{\phi}\right)\dfrac{\rho}{\overline{M}_c} V_1 (v_2^0)^{2/3}(v_2)^{1/3} + \ln(1 - v_2) + v_2}{v_2{}^2}$$

(7)

where $V_1$ is the molar volume of water ($18 \, \mathrm{ml\,mol^{-1}}$). Results of calculations for five different initial

concentrations $v_2^0$ are shown in Fig 5 plotted against the polymer volume fraction $v_2$. The value of $\chi$ slightly increases with increasing polymer concentration for $v_2$ ranging between 0.01 and 0.03. An average value of $\chi = 0.48 \pm 0.01$ was obtained, which is exactly equal to the $\chi$ parameter of the poly(acrylamide)–water system.[12,13] Thus, as with the AAm-based hydrogels, water is a good solvent for hydrogels derived from PEO macroinimer.

## CONCLUSION

We described in this note the synthesis of a novel type of hydrogel based on PEO with a high swelling capacity in water and a low modulus of elasticity. Ethylene oxide units exist as dangling chains in the hydrogels. Such soft gels having dangling chains are

known to collapse or expand easily upon external stimulus because one side of the chains is free. Work is in progress to increase the mechanical strength of the hydrogel by copolymerization of the macroinimer with hydrophilic monomers.

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