Structural Characteristics and Swelling Behavior of Poly(ethylene glycol) Diacrylate Hydrogels†

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ABSTRACT: Poly(ethylene glycol)s (PEGs) in the molecular weight range 200−3400 were derivatized at both ends with acryloyl chloride. These poly(ethylene glycol) diacrylates (PEGDAs) on homopolymerization yield cross-linked networks whose M_c values should correspond to the molecular weight of the PEGDA macromer. M_c values calculated according to the Flory−Rehner equation compare very well with the theoretical values for low concentrations of low molecular weight monomers. Those at high concentrations and higher molecular weights are always lower than the expected values. Attempts to resolve the equilibrium swelling and elastic components indicate that the phantom model gives a better fit.

Introduction

Poly(ethylene glycol)s (PEGs) have a curious combination of properties. They possess one of the simplest molecular structures, yet exhibit the most complicated solubility pattern. Thus they are extremely soluble in water, and also in a variety of organic solvents such as acetonitrile, chlorinated hydrocarbons, and benzene, but not in aliphatic hydrocarbons or ethylene glycol or glycerol. This preferential behavior is assumed to be entropy driven and dependent on chain configuration.[1,2]

Our interest in PEG arose precisely because of this anomalous solubility pattern. Investigating the performance of hydrogels, we often felt the advantages of working with an amphigel: a gel that can swell appreciably in both aqueous and organic media, even if not to the same extent. Several of the gel-mediated reactions we envisaged demanded this dual character. Indeed we did try [poly(methyl methacrylate)/poly(acrylic acid)] systems, but change of solvent from aqueous to organic or vice versa brought in drastic complications since each polymer selectively underwent a coil−globule transition.[3] In comparison we were convinced that PEGs are better candidates, since the network will respond uniformly to a given ambience. We anticipated no synthetic problems in forming the network because the terminal hydroxyl groups are susceptible to a variety of chemical reactions rendering easy derivatization.[4−9]

Another attractive feature of PEGs is that they come in a wide range of molecular weights. This immediately opened up an excellent possibility to tackle one of the long-standing problems of networks, namely, the uncertainty of M_c, the average molecular weight between cross-links in a polymer network. M_c is the most important structural parameter of a network. All macroscopic and microscopic properties of the network are determined by this parameter. In the conventional monovinyl monomer−divinyl monomer (MVM−DVM) type cross-linking reaction, the cross-links are introduced at random. Though statistical and dynamic models have been proposed to assess the course of reaction and thus to make reasonable assumptions regarding M_c values, there is a large discrepancy between the theoretically predicted values and those obtained from their swelling or elastic property measurements.[10] The presence of other network imperfections such as loops and dangling chains complicates matters further. Indeed attempts have been made to synthesize networks with precise M_c values mainly with poly(dimethoxy sulfoxide) networks[11] but with limited success.

PEGs can be easily converted into diacrylates (PEGDA).[4−7] Polymerization of the PEGDA, should, theoretically yield a structure as shown in Figure 1. The uncertainty of M_c encountered in the conventional MVM−DVM polymerization is conspicuously absent here because the M_c value will be essentially the molecular weight of the PEG monomer used. It is reasonable to assume that the two acrylate groups, since they are placed far apart, will behave as independent moieties.[12] We decided to carry out solution cross-linking of the PEGDAs. It is thus explicit that the flexibility of the network segment will depend on two factors: the size of the intervening $-(CH_2CH_2O)_n-$ sequence and the concentration of the PEGDA. At this stage we do not make any assumptions regarding network imperfections such as loops or dangling chains.

The polymerizations of PEGDAs have been reported but most of these have been purely kinetic studies.[8,9,12−14] PEGDAs have been polymerized in both bulk and solution.[14−17] Many schools have observed an increase in the reaction rate with increase in the number of ethylene glycol units in the macromer.[12,18] A systematic approach to analyze the network character on the basis of the molecular weight of the PEG building block never seems to have been attempted. In this paper we first report the synthesis and characterization of PEGDA networks; next, we estimate the M_c values based on the Flory−Rehner equation and compare it with expected values. Finally, we test the suitability of the phantom and affine models to the equilibrium swollen PEGDA gels.[1,20,22,25]

Experimental Section

PEGs (MW ranging from 200 to 3400) were from Sigma and Aldrich. Acrylic acid was from Fluka. Benzoyl chloride, triethylamine, sodium hydroxide, dichloromethane (DCM), benzene, tetrahydrofuran (THF), ammonium persulfate (APS), and hydroquinone were laboratory reagents. Tetramethylethylenediamine (TEMED) was from Aldrich. Double-distilled water was used throughout.

For the preparation of acryloyl chloride, we adopted the method of Stempel.[21] In brief, a mixture of acrylic acid and

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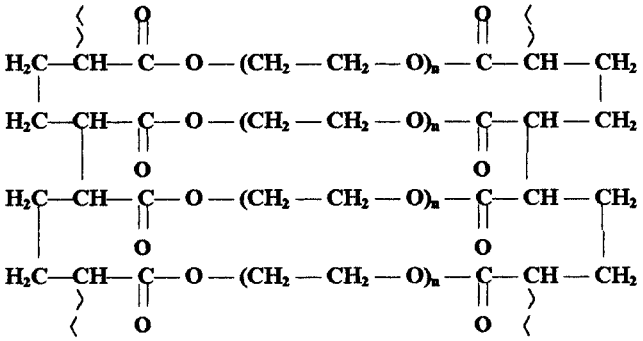

Figure 1. Idealized representation of PEGDA network. Dangling ends and loops are not shown.

benzoyl cholride (1:2 mole ratio) was distilled through a fractionating column; the distillate was collected in a receiver flask having ~0.5 g of hydroquinone. This distillate was again distilled through the same fractionating column and the product, acryloyl chloride, was collected between 72 and 74 °C.

Preparation of PEGDA. PEG was dissolved in DCM and calculated amounts of acryloyl chloride and triethylamine were added to the flask dropwise, maintaining the temperature below 10 °C. The reaction was then allowed to proceed at room temperature for 6 h. The precipitated triethylamine hydrochloride salt was filtered off. The filtrate was washed with 10% NaOH and then with distilled water until it became neutral. Residual water was removed by drying over anhydrous $MgSO_4$. It was then filtered and the solvent was removed in a rotavapor to get the product, the diacryloyl derivative of PEG (PEGDA). Lower homologues of PEGDA (MW 200−600) were light brown viscous liquids, PEGDA(1000) was a semisolid, whereas higher homologues (MW 1500−3400) were white, waxy solids. PEGDAs were characterized by IR spectra.

Preparation of Hydrogels and Swelling Studies. Aqueous solutions of PEGDAs of varying concentrations (10−40% w/w in water) were polymerized with ammonium persulfate (1% w/v) as the initiator. The solutions were heated in a water bath (70 °C) until gelation took place (about 15−30 min). There is a concentration threshold for gelling. Higher homologues of PEGDA required higher weight percentages for gelling. The gels were dried at room temperature for several days to constant weight.

The swelling studies were performed at room temperature (27 °C) by immersing the weighed dry blocks in water. The swollen gels were lifted, patted dry, and weighed at regular intervals until equilibrium was attained.

The percentage equilibrium swelling and amount of gel fraction were calculated from the swollen and dry weights of the gel.[20]

$$\text{percentage equilibrium swelling} = (W_e - W_d)/W_d \times 100 \quad (1)$$

$$\text{percentage gel fraction} = W_d/W_i \times 100 \quad (2)$$

where W_i is the initial weight of the gel before swelling, W_e is the weight of the gel at equilibrium swelling, and W_d is the weight of the dried gel after equilibrium swelling.

The percentage porosity (% *P*) of the networks, after drying the water-swollen gels can be calculated by the relation[22]

$$\text{percentage porosity (\% P)} = V_d/(1 + V_d) \times 100 \quad (3)$$

where V_d is the volume ratio of water imbibed to the gel phase in the equilibrium swollen state.

Results and Discussion

Sufficiently concentrated hot aqueous or organic solutions of PEGDAs gel upon the addition of an initiator APS. The gelation is irreversible and is inhibited by hydroquinone. In the IR spectra of the gel material, the double-bond signals at 1635, 1620, 1408, and 811 cm^{-1} are conspicuously absent, suggesting that unreacted double bonds are absent.

Table 1. Percentage of Gel Fraction in Aqueous Medium

	PEGDA concn (% w/w)		
sample	20	30	40
PEGDA(200)	53.48	54.24	59.54
PEGDA(300)	56.02	53.66	60.13
PEGDA(400)	66.90	64.92	70.44
PEGDA(600)	76.04	79.76	79.85
PEGDA(1000)	66.52	70.27	72.82
PEGDA(1500)		67.01	69.89
PEGDA(2000)		55.50	55.84
PEGDA(3400)		59.73	64.16

Depending on the molecular weight of the macromer, there is a threshold concentration[21] below which the gel does not form. For lower monomers, the value is ~10% and for the higher PEGs ~30%. At lower concentrations the number of monomers may be too low to form a continuous network.

The efficiency of polymerization in aqueous medium (Table 1) is rather low, as indicated by the gel fraction. It never climbs above 75−80%, staying mostly in the range of 50−60%.

The higher homologues polymerized faster than the lower ones, as reported earlier by several workers. The longer the size of the intervening sequence between the two terminal acrylate groups, the greater will be their mobility. The presence of a solvent could also improve this situation.

The general swelling behavior of these hydrogels in aqueous and organic media is shown in Figure 2. From the equilibrium swelling values we calculated the percent porosity of the gels (Figure 3). As expected, porosities rise with the PEGDA molecular weight and fall with concentration.

Calculation of M_c Values. Theoretical treatments often resort to a number of assumptions to convert a real situation into an idealized model. If there are no independent means of assessing the real situation, then the model remains hypothetical. The estimation of M_c values is a typical case. Usually swelling or elasticity equations developed for perfect tetrafunctional networks are used to evaluate M_c. But how do we cross-check these values?

Figure 1 shows an idealized representation of the network formation in PEGDA polymerization. Despite all possible side reactions and network imperfections, the M_c values should largely correspond to the molecular weight of the intervening PEG sequence.

The average network dimensions (M_c) of the cross-linked matrix can be calculated using the Flory−Rehner relation[19,20]

$$q^{5/3} = M_c(\rho V_s)(0.5 - \chi_{12})C_x^{-2/3} \quad (4)$$

where $q = 1/\Phi_2$ and Φ_2 is the volume fraction of the polymer in the gel swollen to equilibrium, V_s is the volume of the solvent imbibed at equilibrium swelling, χ_{12} is the polymer−solvent interaction parameter, ρ is the density of the solvent, M_c is the average molecular weight between the cross-links, and C_x is the concentration of the polymer as in the cross-linked state. The polymer-solvent interaction parameter for PEG−water system has been reported[24] to be 0.45.

The dimensions listed in Table 2 show an astonishing correspondence for low concentrations of low molecular weight PEGs. With both increasing concentration and

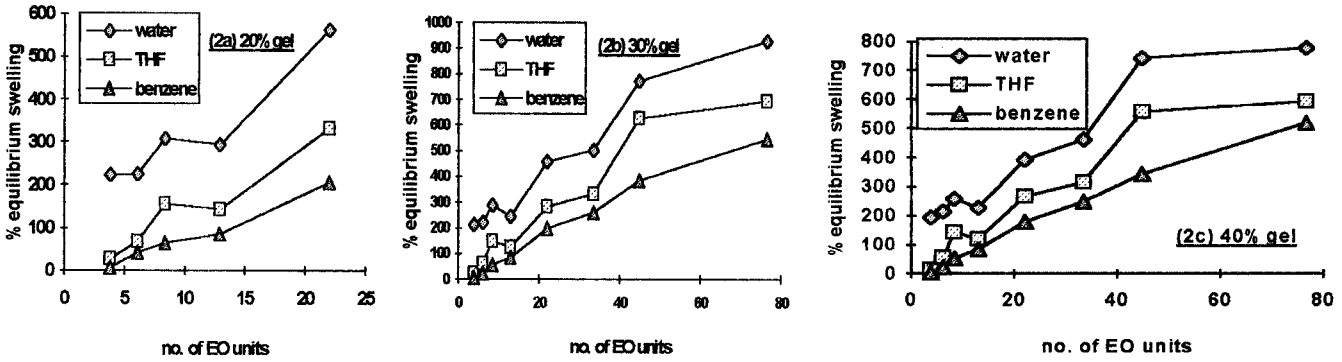

Figure 2. Equilibrium swelling (%) as a function of number of EO units.

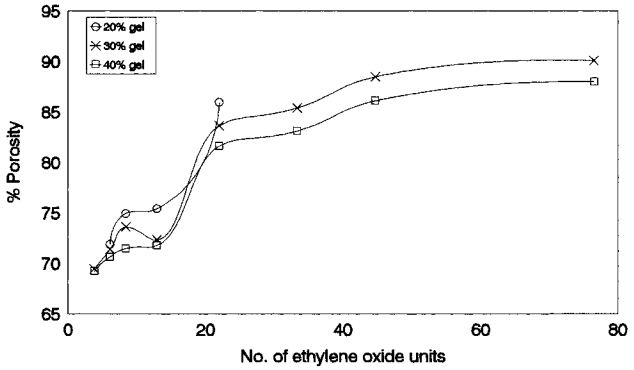

Figure 3. Porosity (%) as a function of number of EO units.

Table 2. Average Network Dimensions (M_c)

		PEGDA concn (% w/w)		
sample	theor MW	20	30	40
PEGDA(200)	308	326	268	249
PEGDA(300)	408	344	273	248
PEGDA(400)	508	524	473	436
PEGDA(600)	708	588	498	482
PEGDA(1000)	1108	1396	1116	951
PEGDA(1500)	1608		1314	1066
PEGDA(2000)	2108		1637	1207
PEGDA(3400)	3508		2202	1678

molecular weight the values diverge. The obvious explanation could be that, at low concentration for the smaller PEGs, interchain interactions are fewer producing fewer entanglements. But as either the concentration or the molecular weight increases, the probability of entanglement increases and consequently M_c values decrease.

However, [PEGDA−water] provides an isolated example. The M_c values calculated according to eq 4 in reality reflect the extent of chain stretching and hence are solvent dependent. In a good solvent, the chain stretches most. It appears that, at low concentration, the lower molecular weight PEG chains attain maximum possible dimension in water.

Swelling Models for PEGDA Hydrogels. The swelling equilibrium of a hydrogel is in many ways similar to an osmotic equilibrium, because in both phenomena, the movement of solvent molecules is dependent on their chemical potential difference between the two phases. At equilibrium, this difference is zero, i.e.

$$\mu_{\text{solvent}}(\text{gel}) = \mu_{\text{solvent}}(\text{bath}) \tag{5}$$

The driving force for the movement of solvent molecules into a gel material can also be characterized as swelling pressure $\Delta\Pi_{\text{swelling}}$, a composite force with at least three accepted components.

$$\Delta\Pi_{\text{swelling}} = \Delta\Pi_{\text{mixing}} + \Delta\Pi_{\text{elastic}} + \Delta\Pi_{\text{ionic}} \tag{6}$$

$\Delta\Pi_{\text{mixing}}$ is the extensive solvation of the polymer network; $\Delta\Pi_{\text{elastic}}$ is the stretching of the segments under the influence of solvation. $\Delta\Pi_{\text{ionic}}$ has a more complex character, which takes into account interactions between fixed and mobile ions in the gel and between mobile ions in the solvent bath. Because PEGDA networks are nonionic, we can steer clear of the complexities of $\Delta\Pi_{\text{ionic}}$. $\Delta\Pi_{\text{mixing}}$ is conventionally described by the Flory−Huggins theory[1]

$$\Delta\Pi_{\text{mixing}} = -(RT/V_1)\,[\ln(1-\Phi_2) + \Phi_2 + \chi_{12}\Phi_2^2] \tag{7}$$

where R is the gas constant, T is temperature, Φ_2 is the volume fraction of polymer in the swollen hydrogel, V_1 is the molar volume of the solvent, and χ_{12} is the polymer−solvent interaction parameter.

Expressions for $\Delta\Pi_{\text{elastic}}$ have been derived for two models: the affine network[1] and phantom network.[25] The essential difference between these two models is in their assumptions on cross-link fluctuations. The affine model presupposes that the cross-links are so totally interrelated that in effect there are no fluctuations. On the other hand, the phantom model assumes independent oscillations of cross-links. However, the real situation could be somewhere intermediate. The cross-links might neither be rigidly held in a topological space nor be totally independent in their dynamics. Fluctuations to the extent permitted by the segmental flexibility will be occurring. For the isotropic swelling of perfect tetrafunctional networks, the following expressions have been derived

phantom

$$\Delta\Pi_{\text{elastic}} = -NC_cRT[(\Phi_2/\Phi_{2c})^{1/3}] \tag{8}$$

affine

$$\Delta\Pi_{\text{elastic}} = -2C_cRT[(\Phi_2/\Phi_{2c})^{1/3} - {}^1/_2(\Phi_2/\Phi_{2c})] \tag{9}$$

where R, T, and Φ_2 have the same significance as in the previous equation, and C_c is the cross-links in the reference state, N is an empirical parameter, and Φ_{2c} is the volume fraction of the polymer reference state. In the original theory, $N = 1$. The number of cross-links (C_c) and the volume fraction (Φ_{2c}) in the reference state per unit volume are calculated on the basis of the effective monomer concentration for the observed gel

Table 3. Comparison of $\Delta\Pi_{mixing}$ with $\Delta\Pi_{elastic}$ of Phantom and Affine Models (cal °C mL^{-1})

sample	PEGDA concn (% w/w)	phantom $1/N$ ($\Delta\Pi_{elastic}$)	$\Delta\Pi_{mixing}$	affine $\Delta\Pi_{elastic}$
PEGDA(200)	20	−173.68	211.80	407.28
	30	−306.30	225.54	1176.26
	40	−540.96	242.52	3515.99
PEGDA(300)	20	−188.22	189.78	1160.54
	30	−255.54	222.90	1350.33
	40	−228.91	247.44	141.19
PEGDA(400)	20	−104.22	157.56	75.06
	30	−138.24	165.36	35.34
	40	−181.20	181.86	26.34
PEGDA(600)	20	−78.42	154.44	24.54
	30	−119.88	175.98	21.96
	40	−158.58	179.88	23.96
PEGDA(1000)	20	−40.26	84.36	−18.18
	30	−58.32	99.42	−21.42
	40	−76.98	112.20	−37.68
PEGDA(1500)	30	−38.94	88.08	−12.24
	40	−49.20	102.78	−30.00
PEGDA(2000)	30	−22.74	68.64	−12.66
	40	−28.98	83.58	−20.28
PEGDA(3400)	30	−13.68	58.62	−10.32
	40	−19.26	71.52	−15.36

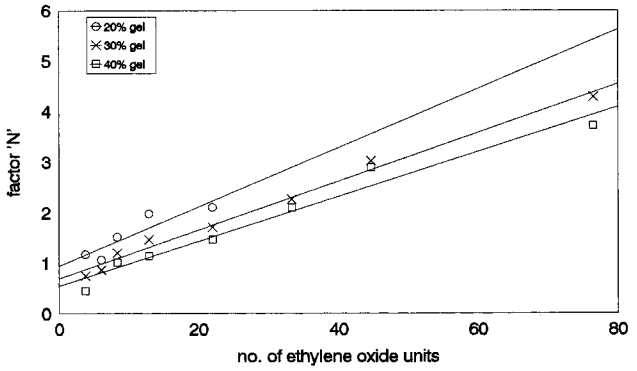

Figure 4. Variation of factor N as a function of number of EO units.

fraction. At equilibrium, for the PEGDA hydrogels,

$$\Delta\Pi_{mixing} = -\Delta\Pi_{elastic} \tag{10}$$

We calculated the elastic contribution according to both the phantom and affine models and compared these values with the mixing contribution calculated from eq 8. The values are listed in Table 3.

The affine model yields negative values for higher homologues. In eq 9 for $\Delta\Pi_{elastic}$, the last term on the right-hand side stands for the modification of the chemical potential due to the elastic reaction of the network structure, accounting for the entropy distribution of the effective cross-links over the space.[1] If this term becomes larger, then the overall value for $\Delta\Pi_{elastic}$ will turn out to be negative. The results suggest that networks with higher homologues have higher entropy. This is reasonable because larger chains will indeed have more elastic entropy compared to shorter chains. The phantom model is more accommodative because of the flexible parameter N, which varies with the molecular weight of the PEGDA macromer and with the gel concentration. Figure 4 shows the trend in the value of N. It begins near unity and increases with PEGDA molecular weight and decreases with gel concentration. At higher PEGDA concentrations, N may reach a minimum limiting value. These results are slightly at variance with those of Baker et al.,[26] who observed that the value of N, computed from compressive stress−strain moduli for poly[acrylamide-*co*-[(methacrylamido)-propyl]trimethylammonium chloride] hydrogels increased with the total monomer concentration. Though we do not have an adequate explanation for this, both results lead to the conclusion that N is a structural parameter. This is logical, since the flexibility of the segment will certainly depend upon the length of the segment.

Conclusions

This study on the determination of structural features of PEGDA networks from swelling behavior brings into focus two important points. First, the Flory−Rehner equation generates realistic M_c values giving due allowance to chain entanglements. It appears difficult to synthesize networks with precise M_c values even using well-defined macromers as precursors, because of the probability of physical entanglements. Second, the phantom model appears more adaptive than the affine models for the elastic contributions to network swelling.

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