Enhancement and control of cross-linking of dimethylaminoethyl methacrylate irradiated at low dose rate in the presence of ethylene glycol dimethacrylate

C. Uzun, M. Hassnisaber, M. Şen *, O. Güven
Polymer Chemistry Division, Department of Chemistry, Hacettepe University, 06532 Beytepe, Ankara, Turkey

Abstract

In the present work ternary systems composed of dimethylaminoethyl methacrylate/water/ethylene glycol dimethacrylate (DMAEMA/water/EGDMA) were prepared at varying compositions and irradiated with gamma rays up to 4 kGy. The hydrogels thus prepared were characterized with respect to their swelling properties, network structures and mechanical properties by compression tests. Molecular weight between cross-links (M_c) and effective cross-linking density (m_e) of DMAEMA/EGDMA hydrogels were calculated from swelling and shear modulus data obtained from compression tests. The results have shown that simple compression analyses and equations derived from Phantom network theory can be used for the determination of effective cross-link density of hydrogels without needing some polymer-solvent based parameters as in the case of swelling based determinations. By using theoretically and experimentally calculated cross-link densities, the cross-linking enhancement efficiency of EGDMA was calculated. It has been found that added EGDMA can facilitate the cross-linking reactions effectively during irradiation and improves the cross-linking efficiency approximately eightfold when used only 0.05% concentration in the initial monomer mixture.

Keywords: Hydrogel; Poly(dimethylaminoethyl methacrylate); Cross-link density; Radiation cross-linking

1. Introduction

Highly cross-linked polymers are generally chemically prepared from their monomers or polymers in the presence of cross-linking agents. It is also very well known that ionizing radiation induced simultaneous polymerization and cross-linking has some advantages over chemical cross-linking and it is widely used in recent years for the synthesis of various hydrogels for biomedical applications.

One of the basic parameters that describes the structure of a hydrogel network is the molecular weight between cross-links or cross-link density for highly swollen network. Several theories have been proposed to calculate the average molecular weight between cross-links. In the highly swollen state, the constrained junction theory indicates that a real network exhibits properties closer to those of the phantom network model. The following derived equation using the phantom network model is valid for natural or non-ionic structures [1,2].

* Corresponding author. Tel./fax: +90-312-2977989.
E-mail address: msen@hacettepe.edu.tr (M. Şen).

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Here $\bar{M}_c$ is the average molecular weight of network chains, $v_{2m}$ is the polymer volume fraction of cross-linked polymer in equilibrium with swollen gel, $V_1$ is the molar volume of the swelling agent, $\chi$ is the polymer-solvent interaction parameter, $\phi$ is the functionality, $\bar{v}$ is the specific volume of the polymer and $v_{2r}$ is the polymer volume fraction in the relaxed state, i.e. after cross-linking but before swelling.

In recent years rubberlike elasticity and uniaxial deformation experiments have been used for the characterization of various types of polymeric systems by many researchers. For uniaxial deformation, the statistical theories of rubber elasticity yield Eq. (2) for gaussian chains.

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

where $f$ is the force acting per unit cross-sectional area of the undeformed gel specimen, $G$ is the elastic modulus of the sample and $\lambda$ is the deformation ratio (deformed length/initial length). For a homogeneous network of gaussian chains, the elastic modulus of gel swollen to equilibrium, $G$, is related to the network cross-link density by Eq. (3) [3].

$$G = A \frac{\rho RT \bar{v}_{2r}^{2/3}}{\bar{M}_c^{1/3}},$$

where $\rho$ is the polymer density. The prefactor $A$ equals 1 for an affine network and $(1 - 2/\phi)$ for a phantom network.

The effective cross-link density, $v_e$, of a cross-linked structure can be obtained from the results of compressive measurements using Eqs. (2)–(4):

$$\bar{M}_c = \frac{\rho}{v_e}. \quad (4)$$

In our recent studies, we observed that pure dimethylaminoethyl methacrylate (DMAEMA) monomer and its aqueous solutions show very low tendency to cross-linking when irradiated with gamma rays at low dose rates. However, when this monomer is irradiated in the presence of a chemical cross-linker, ethyleneglycol dimethacrylate (EGDMA), in very low concentrations, the percentage gelation increases abruptly and gelation reaches 100% even at very low irradiation doses [4]. In the present work ternary systems composed of DMAEMA/water/EGDMA were prepared at varying compositions and irradiated with gamma rays up to 4 kGy. The hydrogels thus prepared were characterized with respect to their swelling properties, network structures and mechanical properties by compression tests. By using theoretically and experimentally calculated cross-link densities, the cross-linking enhancement efficiency of EGDMA was calculated.

2. Experimental

The two monomers used in this study, namely, DMAEMA and EGDMA were obtained from Aldrich. For the preparation of mechanically stable hydrogels, 65% DMAEMA and 35% water containing mixture was prepared, and 0.01%, 0.05%, 0.5%, 1.0% and 2.0% by volume EGDMA were added to these solutions. Monomer solutions thus prepared were placed in PVC tubes of 4 mm diameter and irradiated to 4.0 kGy in air at ambient temperature in a Gammacell 220 type $\gamma$ irradiator at a fixed dose rate of 0.18 kGy/h. For the investigation of the effect of EGDMA on the gelation of DMAEMA, DMAEMA/water mixture was irradiated in the absence of EGDMA under the same conditions. Hydrogels obtained in long cylindrical shapes were cut into pieces of 3–4 mm and stored for later evaluations. Volume percentages of EGDMA in the hydrogels denoted as P(DMAEMA)-1, P(DMAEMA)-2, P(DMAEMA)-3, P(DMAEMA)-4 and P(DMAEMA)-5 are 0.05, 0.1, 0.5, 1.0 and 2.0, respectively.

Washed and dried hydrogels (3–4 mm thickness) were left to swell in a solution of desired pH ($\approx 7.0$) and temperature ($\approx 25$ °C). Swollen gels removed from water at regular intervals were dried superficially with filter paper, weighed and placed in the same bath. The measurements were continued until a constant weight was reached for each sample. Elastic properties and elastic modulus of hydrogels were determined by using a Zwick Z010...
model Universal Testing Instrument and uniaxial compression module.

3. Results and discussion

3.1. Preparation of PDMAEMA and P(DMAEMA/EGDMA) hydrogels

When pure DMAEMA monomer is irradiated with gamma rays, polymerization and cross-linking reactions take place simultaneously. The total dose required for 5% gelation of DMAEMA hydrogels has been found to be 30 kGy when DMAEMA was irradiated at 0.18 kGy/h dose rate. However, when this monomer is irradiated in the presence of water (35% water) the percentage gelation increases and gelation reaches 50% at 4.0 kGy dose. On the other hand, when aqueous solution of this monomer is irradiated in the presence of chemical cross-linker EGDMA in very low concentrations (0.01%), the percentage gelation increases abruptly and gelation reaches 100%, even at 4.0 kGy irradiation dose [4].

3.2. Swelling behavior of P(DMAEMA/EGDMA) hydrogels

For the characterization of the network structure and determination of effective cross-link density of prepared hydrogels, the swelling properties at pH 7 were first investigated. Swelling experiments were continued until a constant value of swelling was reached for each sample. This weight was used to calculate the volume fraction of polymer $v_{2m}$ and the equilibrium degree of swelling (EDS), $Q$, see Eq. (5):

$$ Q = 1/v_{2m} = (1 + \rho/\rho_w(w^{-1} - 1)), \quad (5) $$

where $\rho$ and $\rho_w$ are the densities of swollen gel and water; $w$ is the weight fraction of polymer in swollen gel. The EDS is defined as $Q = 1/v_{2m}$. Some information about the structural properties of hydrogels necessary for the determination of $M_c$ and $v_c$ are collected in Table 1. The other relevant experimental parameters to be used with Eq. (1) are as follows: molar volume of the solvent $V = 18.0 \text{ cm}^3/\text{mol}$ and the number of branches originating from a cross-link site, $\phi = 3.0$. The $\chi$ parameters of hydrogels were calculated by using Eq. (6) [5]:

$$ \chi = 1/2 + v_{2m}/3. \quad (6) $$

By using these relevant experimental parameters $M_c(M_{c(s)})$ and $v_c(v_{c(s)})$ are calculated and collected in Table 1. To account for calculations of these parameters from swelling experiments, the subscript “s” was used in abbreviations. The effect of EGDMA concentration on the cross-link density of DMAEMA hydrogels is clearly seen from these results.

3.3. Mechanical properties of P(DMAEMA/EGDMA) hydrogels

For the investigation of the effect of EGDMA on the mechanical properties of hydrogels and for the determination of $M_c(M_{c(m)})$ and $v_c(v_{c(m)})$, uniaxial compression was applied using the Universal Testing Instrument. Due to calculation of these parameters from mechanical experiments the subscript “m” was used in abbreviations. Typical stress–strain curves of hydrogels are given in Fig. 1. As can be seen from the figure, the magnitude of strain percentage at maximum deformation decreased with increasing EGDMA content and stress percentage increased. Shear modulus values of hydrogels were calculated by using elastic

<table>
<thead>
<tr>
<th>Gel Name</th>
<th>Swelling (%)</th>
<th>$v_{2m}$</th>
<th>$v_{2r}$</th>
<th>$\tau$</th>
<th>$\chi$</th>
<th>$M_{c(s)}$</th>
<th>$v_{c(s)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>P(DMAEMA)-1</td>
<td>3380</td>
<td>0.2089</td>
<td>0.7902</td>
<td>0.9157</td>
<td>0.571</td>
<td>10,000</td>
<td>1.09 x 10^{-4}</td>
</tr>
<tr>
<td>P(DMAEMA)-2</td>
<td>3320</td>
<td>0.2149</td>
<td>0.7504</td>
<td>0.9041</td>
<td>0.572</td>
<td>7690</td>
<td>1.44 x 10^{-4}</td>
</tr>
<tr>
<td>P(DMAEMA)-3</td>
<td>2550</td>
<td>0.2539</td>
<td>0.7561</td>
<td>0.9030</td>
<td>0.585</td>
<td>4000</td>
<td>2.76 x 10^{-4}</td>
</tr>
<tr>
<td>P(DMAEMA)-4</td>
<td>2550</td>
<td>0.2721</td>
<td>0.7776</td>
<td>0.9021</td>
<td>0.591</td>
<td>3350</td>
<td>3.31 x 10^{-4}</td>
</tr>
<tr>
<td>P(DMAEMA)-5</td>
<td>1296</td>
<td>0.4101</td>
<td>0.5593</td>
<td>0.9012</td>
<td>0.637</td>
<td>475</td>
<td>2.33 x 10^{-3}</td>
</tr>
</tbody>
</table>
deformation theory and Eq. (2) [3]. When the equation is applied to the initial stages of deformation, plots of $f$ versus $\lambda^{-2}$ yield straight lines, Fig. 2, where $\lambda$ is deformation ratio and equal to $L/L_0$, $L_0$ and $L$ are the lengths of the undeformed and deformed hydrogels during compression, respectively. The $G$ value was calculated from the slope of lines and listed in Table 2. By using $G$ values and other relevant experimental parameters, $M_c$ and $v_e$ were calculated and collected in Table 2. As can be seen from Table 2 the magnitudes of $M_c$ and $v_e$ calculated from mechanical properties are close to the calculated values obtained by using swelling experiments. Slight differences can be attributed to the uncertainty on the value of the $\chi$ parameter used in the theoretical equations.

3.4. Cross-linking efficiency of gamma rays on the preparation of $P$(DMAEMA)/EGDMA) hydrogels

For the determination of cross-linking efficiency of gamma rays on the preparation of $P$(DMAEMA/EGDMA) hydrogels, the theoretical $M_c$ and $v_t$ values were first calculated. The theoretical cross-link density $v_t$ is given as follows, in terms of mole content of EGDMA($n_{GDMA}$) and DMAEMA($n_{DMAEMA}$) and the average molecular weight of the repeating unit, $M_r$, assuming complete consumption of EGDMA and DMAEMA.

$$v_t = \frac{\rho}{M_c} = \frac{1}{2} \frac{n_{DMAEMA}}{n_{GDMA}} M_r.$$  

As shown in Table 2, the theoretical cross-link density of DMAEMA hydrogel increased from $6.20 \times 10^{-6}$ to $2.46 \times 10^{-4}$ with increasing amount of EGDMA, ranging from 0.05% to 2.0%. The large differences observed between the experimentally calculated and theoretical cross-link densities is assumed to be due to non-consideration of cross-linking efficiency of gamma rays in the

<table>
<thead>
<tr>
<th>Gel Name</th>
<th>$G$ (kPa)</th>
<th>$M_c$</th>
<th>$v_e$</th>
<th>$M_t$</th>
<th>$v_t$</th>
</tr>
</thead>
<tbody>
<tr>
<td>P(DMAEMA)-1</td>
<td>65.9</td>
<td>22,400</td>
<td>4.87</td>
<td>176,000</td>
<td>6.20</td>
</tr>
<tr>
<td>P(DMAEMA)-2</td>
<td>148.1</td>
<td>8970</td>
<td>1.23</td>
<td>88,000</td>
<td>1.26</td>
</tr>
<tr>
<td>P(DMAEMA)-3</td>
<td>441.5</td>
<td>3200</td>
<td>3.46</td>
<td>17,690</td>
<td>6.26</td>
</tr>
<tr>
<td>P(DMAEMA)-4</td>
<td>624.6</td>
<td>2370</td>
<td>4.67</td>
<td>8900</td>
<td>1.24</td>
</tr>
<tr>
<td>P(DMAEMA)-5</td>
<td>693.8</td>
<td>1950</td>
<td>5.69</td>
<td>4500</td>
<td>2.46</td>
</tr>
</tbody>
</table>
theoretical calculation. The experimentally found cross-link density of P(DMAEMA)-1 hydrogel is 8 times higher than its theoretically calculated counterpart. This value decreased to 5.5 and 2.3 when 0.5% and 2.0% EGDMA was used in the gel preparation, respectively. It has been proposed that \( v_e \) varies with \( v_t \) according to \( v_e = a + \beta v_t \), where \( a \) is the value of effective cross-linking in the absence of any chemical cross-linker, and it may arise from physical cross-linking or cross-linking induced when gamma or e-beam irradiation is used in the synthesis [6]. The parameter \( \beta \) is a measure of cross-linking efficiency when \( a = 0 \), and its magnitude is usually <1. From the plot of \( v_e \) versus \( v_t \) (Fig. 3) it has been observed that, there is no linear relation between these two parameters unlike the expected. The exponential increase may be due to changing of cross-link efficiency of EGDMA and gamma rays at higher EGDMA concentrations. For the lower EGDMA content or initial region of the \( v_e \) versus \( v_t \) curve, the \( \alpha \) and \( \beta \) values were calculated as \( 3.8 \times 10^{-5} \) and 4.9 respectively. Similarly, an unusual \( \beta \) value was also observed by Davis and Huglin [6]. The inverse of the \( \alpha \) value, which is equivalent to 26,300 relates to, \( \bar{M}_e \), for DMAEMA cross-linked by gamma rays to 4 kGy dose in the in the absence of EGDMA. The lower \( \bar{M}_e \) values obtained in this study indicate that EGDMA is facilitating the cross-linking reaction effectively during irradiation, and that it improves the cross-linking efficiency of gamma rays depending on its concentration.

4. Conclusion

It has been found that small amount of EGDMA can facilitate the cross-linking of DMAEMA effectively during low dose rate gamma irradiation and improves the cross-linking efficiency approximately eightfold when used only about 0.05% concentration in the initial monomer mixture. Furthermore, the experimental results clearly showed that simple compression analyses and equations derived from Phantom network theory can be used for the determination of effective cross-link density of hydrogels without needing some polymer-solvent based parameters.

Acknowledgement

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