Poisson’s Ratio of Polyacrylamide (PAAm) Gels

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ABSTRACT

Poisson’s ratio ($\mu_0$) of polyacrylamide (PAAm) gels was estimated. The value of $\mu_0$ for PAAm gels was found to be 0.457, which is close to that for poly(vinyl alcohol) (PVA) gels swollen in the mixture of dimethylsulfoxide (DMSO) and water, but is higher than the value for PVA hydrogels.

1 INTRODUCTION

As is well known, Poisson’s ratio ($\mu_0$) is one of the important elastic parameters.1 So far, the mechanical properties of polymer gels have been widely investigated, but the studies on $\mu_0$ of the polymer gels are quite limited. We have reported the values of $\mu_0$ for poly(vinyl alcohol) (PVA) gels swollen in various solvents.2 The network was formed by physical crosslinks in PVA gels employed in the previous study. The value of $\mu_0$ for PVA gels swollen in a mixture of dimethylsulfoxide (DMSO) and water (DMSO:water = 8:2) has been estimated to be 0.47,2 which is close to the incompressible limit ($\mu_0 = 1/2$). On the other hand, the PVA hydrogels, which are swollen in water and presumably contain larger crosslink domains3 than those in PVA gels in the mixed solvent, have shown a low value of $\mu_0$ (≈ 0.43) compared with that of PVA gels swollen in the mixed solvent.2 Since both the mixture and water are good solvents,3 the flexibility of a free chain is considered to be almost the same. This suggests that the difference of $\mu_0$ for the gels is governed by a degree of restriction of the network chains by crosslink points. The mobility of the network chains might be closely related to the size of the
crosslink domains, because the PVA chains anchored at the large crosslink domains must be less mobile. It is very interesting to examine \( \mu_0 \) for chemically crosslinked gels where the crosslink domains are very small, and to compare the value to those for physically crosslinked gels. This will give us the detailed information on the effects of the size of the crosslink region on \( \mu_0 \) through the flexibility of the network chains. In this study, we have estimated \( \mu_0 \) of polyacrylamide (PAAm) gels swollen in water, and compared the value of \( \mu_0 \) to those for PVA gels swollen in the mixed solvent as well as water.

2 EXPERIMENTAL

PAAm gels were prepared by radical copolymerization of acrylamide (AAm) and methylenebisacrylamide (MBA). Ammoniumpersulfate was used as an initiator. The molar concentration of AAm was 5 mol/l and that of MBA 0.01 mol/l. The total monomer concentration in kg/m\(^3\) (\(c_0\)) was 270, which corresponded to about 27 wt\%. The solution was poured in the rectangular metal mold and was kept at 33\(^\circ\)C for gelation. The gels were then removed from the mold and immersed in water until equilibrium swelling was achieved. It took about ten days for equilibration. The equilibrium concentration (\(c_\infty\)) for the gels was around 8 kg/m\(^3\).

The gel samples used for mechanical tests were rectangular in shape and the cross-sectional area was about 9 mm \(\times\) 9 mm. An Orientec tensile tester (RTM-250) with a water bath was used for mechanical testing. The temperature was kept at 25\(^\circ\)C during the experiment. The stretched direction was designated as the \(x\)-direction, and \(y\) and \(z\) directions were those perpendicular to the stretched direction. Table 1 represents the

<table>
<thead>
<tr>
<th>Sample</th>
<th>(L_{\infty}(\text{mm}))</th>
<th>(v(\text{mm/min}))</th>
<th>(E_0(\text{kPa}))</th>
<th>(\mu_0)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PAAm27P1</td>
<td>32.4</td>
<td>0.5</td>
<td>34.5</td>
<td>0.464</td>
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<tr>
<td>PAAm27P2</td>
<td>36.6</td>
<td>3.0</td>
<td>34.0</td>
<td>0.467</td>
</tr>
<tr>
<td>PAAm27P3</td>
<td>35.0</td>
<td>3.0</td>
<td>37.0</td>
<td>0.442</td>
</tr>
<tr>
<td>PAAm27P4</td>
<td>34.0</td>
<td>3.0</td>
<td>36.0</td>
<td>0.442</td>
</tr>
<tr>
<td>PAAm27P5</td>
<td>41.8</td>
<td>3.0</td>
<td>35.5</td>
<td>0.472</td>
</tr>
<tr>
<td>PAAm27P6</td>
<td>46.7</td>
<td>3.0</td>
<td>36.0</td>
<td>0.454</td>
</tr>
<tr>
<td>PAAm27P7</td>
<td>29.0</td>
<td>30.0</td>
<td>48.0</td>
<td>0.461</td>
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<tr>
<td>PAAm27P8</td>
<td>33.5</td>
<td>300</td>
<td>44.0</td>
<td>0.456</td>
</tr>
</tbody>
</table>
Poisson’s ratio of polyacrylamide (PAAm) gels

Sample code, initial sample length (the initial cross-head distance, \(L_{x0}\)), the cross-head speed (\(v\)), the initial Young’s modulus (\(E_0\)) and \(\mu_0\). The stretch ratios parallel and perpendicular to the stretched directions (\(\lambda_x\) and \(\lambda_y\), respectively) were calculated by \(\lambda_i = l_i/l_{i0}\) \((i = x, y)\), where \(l_{i0}\) is the dimension in the \(i\)-direction at rest. The quantity \(l_x\) as well as \(l_{x0}\) corresponded to the distance between two marked points at the center of the gel and was measured by using a magnified picture on the video screen. \(l_y\) (and also \(l_{y0}\)) was the width in the central region of the gel specimen near the marked points. Poisson’s ratio (\(\mu_0\)) was calculated by \(\mu_0 = -\ln \lambda_y/\ln \lambda_x\), and the initial strain rate (\(\dot{\varepsilon}_0\)) by \(\dot{\varepsilon}_0 = v/L_{x0}\).

3 RESULTS AND DISCUSSION

Figure 1 shows typical plots of \(-\ln \lambda_y\) against \(\ln \lambda_x\), as an example, for PAAm27P3. The data points can be well described by a straight line. The line was determined by the least square method. The intercept in the figure originates from the experimental errors in determining \(\lambda_x\) and \(\lambda_y\). We estimated \(\mu_0\) from the slope of the line. For PAAm27P3, we have \(\mu_0 = 0.442\). The other samples also showed almost the same linearity as PAAm27P3, although we do not show them here. Figure 2 shows the dependence of \(\mu_0\) on \(\dot{\varepsilon}_0\). As can be seen from this figure, \(\mu_0\) is independent of \(\dot{\varepsilon}_0\). For PVA gels swollen in the mixed solvent composed of DMSO and water, \(\mu_0\) was independent of \(\dot{\varepsilon}_0\). Table 1 summarizes the values of \(\mu_0\) for all specimens examined in this study. The average value of \(\mu_0\) with standard deviation (SD) is 0.457 ± 0.011. Although SD is a little large, the

\[
\begin{array}{c}
\text{PAAm27P3} \\
\text{Cs}=270\text{kgm}^{-3} \\
v=3\text{mmmin}^{-1} \\
\mu_0=0.442
\end{array}
\]

Fig. 1. Plots of \(-\ln \lambda_y\) against \(\ln \lambda_x\), for PAAm27P3. Here, \(\lambda_y\) and \(\lambda_x\) respectively stand for the stretch ratios parallel and perpendicular to the stretched direction.
average is closer to that for PVA gels swollen in the mixture of DMSO and water than that for PVA hydrogels. Since water is considered to be a good solvent for PAAm, a PAAm chain is as flexible as a PVA chain in the mixed solvent or water when the chain ends are free. The PAAm chains in the gel are anchored at both ends by crosslinks, if we ignore the dangling chains. For such chains, the mobility of the network chain is mainly governed by the size of the crosslink region; the large crosslink domains restrict much the mobility of the polymer chains in the gel. Then, the fact that $\mu_0$ for PAAm gels is closer to that for the PVA gels swollen in the mixed solvent than $\mu_0$ of the PVA hydrogel originates from the small crosslink domains for PAAm gels and PVA gels in the mixed solvent compared with the crosslink domains for PVA hydrogels.

The size of the crosslink region for PAAm gels will be smaller than that for the PVA gels in the mixed solvent, because the former is chemically crosslinked and the latter is formed by physical crosslinks. This suggests that $\mu_0$ of the PAAm gel is larger than that of the PVA gels in the mixed solvent contrary to the experimental results. The difference in $\mu_0$ between PAAm gels and PVA gels in the mixed solvent is of order of magnitude 0.01, which is well within the experimental errors. Polymer gels with highly mobile network chains may have the limiting value of $\mu_0$ around 0.47. The limiting value of $\mu_0$ is smaller compared with the value of the incompressible limit (1/2). Although the domain size for PAAm gels and PVA gels in the mixture is different, the size is too small to affect the mobility of the network chains, which governs the value of $\mu_0$, for both gels.
REFERENCES