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Peculiar extensibility of swollen statistical hydrogels with structural nanoheterogeneities

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ABSTRACT

An inherent structural nanoheterogeneity in statistical hydrogels leads to a peculiarity in macroscopic tensile properties. Some types of statistical hydrogels with considerable degrees of non-uniform distribution of cross-link, which are formed via free radical copolymerization of mono- and bi-functional monomers, are unusually extensible: The elongation at break before and after equilibrium swelling remains almost unchanged, although the gels undergo a significant increase in volume by swelling, i.e., a finite degree of pre-stretching of network strands. This peculiar extensibility emerges exclusively in uniaxial stretching whereas it is not observed in biaxial stretching including equi-biaxial and planar extension. The concentration ranges of the mono- and bi-functional monomers which result in the gels with the peculiar extensibility are revealed. The two-dimensional SAXS patterns of the uniaxially stretched swollen gels with marked extensibility show the presence of a spatially long-range structure of ca. 50 nm which results from the significantly non-affine deformation of the networks composed of densely and loosely cross-linked regions.

1. Introduction

Hydrogels have great potential in various applications, especially as biomaterials in tissue engineering applications such as artificial cartilage, nerves and muscles. Improvement of mechanical properties of hydrogels has received much attention because these medical applications need hydrogels to endure considerable mechanical strain and stress in practical use. Much effort has been made to toughen the hydrogels, including double network gels [1], nano-composite gels [2], tetra-arm polyethylene glycol gels [3], hydrophobic bilayer gels [4], hybrid gels consisting of hydrophilic and crystalline polymer networks [5], etc. Topological network structure is a fundamental and governing factor for the mechanical properties of gels. It has long been known that the formation process of classical statistical polymer networks is accompanied by significantly non-uniform spatial distribution of cross-links, unless a special care is taken in cross-linking reaction [6,7]. The small angle X-ray or neutron scattering measurements revealed the presence of the spatially long-range structures in the gels which are absent in the un-cross-linked polymer solutions with the same concentrations [6,7]. The presence of the structural nanoheterogeneity has been observed for various types of gels, but it still remains unclear how such structural nanoheterogeneity is reflected in the macroscopic mechanical properties of gels. It has been reported for Tetra-PEG gels and slide-ring gels that the uniform network structures significantly contribute to the enhancement of mechanical properties: Tetra-PEG gels are composed of network strands with uniform length [3], and slide-ring (polyrotaxane) gels have a function to homogenize the network structure under imposed deformation via movable cross-links along the network strands [8]. In contrast, it has also been known that the introduction of the bimodality or trimodality to the length of network strands considerably enhances the mechanical performance of elastomers [9,10]. These results suggest that the effect of structural uniformity on the mechanical properties is not simple, and the spatial scale of heterogeneity is also crucial [11].

Gels and elastomers undergo “swelling”, i.e., isotropic expansion of polymer networks, when immersed in solvents. The degree of swelling of neutral networks is primarily governed by the solubility of the constituent polymers in solvents as well as the amounts of cross-link [12,13]. The qualitative effects of swelling on the mechanical properties of gels seem simple: The extensibility as well as the modulus becomes lower, as the swelling degree increases. The

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reduction in modulus mainly results from a decrease in cross-link density, and the reduction in extensibility originates from the pre-stretch of network strands caused by swelling. It is also known that the inherent structural nanoheterogeneity in gels and elastomers becomes more obvious by swelling, because the soft regimes with low cross-link densities expand more largely than the rigid regimes with high cross-link densities [6,7]. How does the emerged nanoheterogeneity upon swelling influence the mechanical properties of swollen gels? The nanoheterogeneity of the swollen gels has been extensively investigated, but the correlation between the structural heterogeneity and mechanical properties is left unsettled.

Free radical copolymerization of mono-functional monomers and di-functional cross-linkers is known as a classical scheme for gelation, and this scheme results in polymer networks with considerably non-uniform spatial distribution of cross-links [6,7]. The structural nanoheterogeneity depends on the concentrations of the monomers and cross-linkers. The present paper demonstrates the emergence of the peculiarity in extensibility of swollen gels that originates from markedly non-affine deformation of network strands due to the structural nanoheterogeneity: The extensibility remains almost unchanged before and after swelling, despite the finite degree of swelling, for the gels prepared in the certain concentration regimes of monomer and cross-linker. We also show that the unusually extensible swollen gels in the uniaxially stretched state exhibit the characteristic patterns of small angle X-ray scattering which are expected for the polymer networks with considerably non-uniform distribution of cross-links. Further, we present that the peculiarity in extensibility is observed exclusively in uniaxial stretching, and not observed in general loading including several types of biaxial stretching. This specific dependence of extensibility on the stretching mode indicates that the structural nanoheterogeneity significantly affects the local strain and/or stress fields. We reveal the concentration regimes of monomer and cross-linker for the emergence of the unusual extensibility in the swollen gels, and also discuss what type of structural inhomogeneity leads to non-affine deformation resulting in high extensibility. The results in present study provide an intriguing example of the remarkable effects of the structural nanoheteregeneity on macroscopic mechanical properties, and they also give significant information about the molecular design of the polymer gels with excellent mechanical properties.

2. Experiment

2.1. Hydrogel preparation

Acrylamide (AAm) and N,N'-methylenebisacrylamide (BIS) were employed as monomer and cross-linker, respectively. The polyacrylamide (PAAm) gels were prepared by radical copolymerization of AAm and BIS using ammonium persulfate and N,N,N′,N′-tetramethylenediamine as the initiator and accelerator, respectively. The reactant mixtures with various concentrations of AAm and BIS (which were designated as C_M and C_X, respectively) were dissolved in water, and the aqueous solutions were poured into a Teflon® mold. The gelation was performed at 20 °C for 24 h. The resultant gel sheet specimens were used for the measurements as "as-prepared" gels. The as-prepared gels were immersed in water till the equilibrium was attained. The surrounding water was renewed several times during the swelling procedures in order to exclude the materials which were not incorporated into permanent networks. It was confirmed that no further change in the weight of the fully swollen gels occurred by renewing the water, in order to remove thoroughly the unreacted materials from the gels. The fully swollen gels were also employed for the measurements as "swollen gels". The gels of $C_M \approx 5$ wt% were so soft that they could undergo considerable bending by the self-weights, which impeded the biaxial tensile measurements in the as-prepared states. The gels in the range of $C_M \geq 10$ wt%, which showed no finite self-bending, were employed for the measurements.

The degrees of equilibrium swelling (Q_S) were evaluated from the weights of the specimens in the fully swollen and dry states. The corresponding values of the as-prepared gels are given by $Q_0 = (C_M + C_X)^{-1}$. The characteristics of each specimen are summarized in Table 1. In the sample codes PAG-X-Y, X and Y indicate C_M and C_X, respectively.

2.2. Tensile measurements

Uniaxial tensile measurements were conducted at 25 °C with AC-500C (T.S.E. Co., Ltd., Japan) using the rectangular specimens with the dimensions of 30 × 4 × 2 mm. The cross-head speed was 0.1 mm/s which was sufficiently slow to exclude the time effect on stress. The specimens were elongated till the rupture occurred. Biaxial tensile measurements were made at 25 °C with a custom-made biaxial tester using the square sheet specimens with the dimensions of 65 × 65 × 2 mm. The details of the biaxial tester were described elsewhere [14]. Two types of biaxial stretching were employed: Equibiaxial extension where the specimens are equally stretched in the two directions, and planar extension where the specimens are stretched while the dimension in one direction is kept unchanged. The cross-head speed was 0.1 mm/s.

The data of the extensibility were obtained from the specimens which broke at the middle positions, while the data of the specimens broken at the edges near the clamps were excluded from the analysis. The extensibility data used in the analysis were the average values of at least three corresponding data.

2.3. Small angle X-ray scattering measurements

The two-dimensional SAXS (2d-SAXS) data were measured using the BL-10C beamline in the Photon Factory of KEK [15], Tsukuba with an X-ray energy of 12.4 keV (the wavelength of X-ray was 0.1488 nm). PILATUS 2M (DECTRIS Ltd., Baden, Switzerland) was used as a 2-dimensional detector that was set at a position of 162.0 cm apart from the sample position. The sheet samples of the swollen gel with a thickness of 2.0 mm were set at the hand-made stretching fixture by grapping both ends of the sheet with a couple of jaws. The hand-made stretching fixture enabled us to conduct the in-situ 2d-SAXS measurements under stretching of the sheet

Table 1
Sample characteristics.

Sample	C_M (wt%)	C_X (wt%)	Q_0	Q_S	G_0 (kPa)	G_S (kPa)
PAG-10-0.06	10.0	0.0549	9.95	20.7	3.94	2.56
PAG-10-0.1		0.109	9.89	15.0	7.33	6.81
PAG-20-0.01	20.0	0.0137	5.00	17.8	14.7	5.74
PAG-20-0.02		0.0206	4.99	16.1	15.3	6.82
PAG-20-0.03		0.0274	4.99	15.7	17.2	8.01
PAG-20-0.06		0.0549	4.99	14.0	21.7	10.8
PAG-20-0.1		0.109	4.97	12.1	26.6	14.6
PAG-20-0.2		0.219	4.95	9.89	33.9	24.4
PAG-20-0.3		0.299	4.93	9.70	37.0	29.2
PAG-30-0.1	30.0	0.109	3.32	9.17	42.3	26.2
PAG-30-0.2		0.219	3.31	10.0	57.2	33.9
PAG-30-0.3		0.299	3.30	8.44	80.8	37.3
PAG-40-0.06	40.0	0.0549	2.50	9.30	69.6	29.6
PAG-40-0.1		0.109	2.49	8.86	73.6	33.8
PAG-40-0.2		0.219	2.49	8.85	88.1	45.1
PAG-40-0.3		0.299	2.48	7.35	110	54.1