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Complete List of Authors:	<p>Mayumi, Koichi; The University of Tokyo, The Institute for Solid State Physics  Aomura, Kosuke; The University of Tokyo, The Institute for Solid State Physics  Yasuda, Yusuke; The University of Tokyo, Department of Advanced Materials Science, Graduate School of Frontier Sciences  Yamada, Takeshi; Neutron Science and Technology Center, Comprehensive Research Organization for Science and Society  Sakai, Takamasa; The University of Tokyo, Department of Bioengineering, Graduate School of Engineering</p>

**Quasi-elastic Neutron Scattering Study on Dynamics of Polymer Gels  
with Controlled Inhomogeneity under Uniaxial Deformation**

Kosuke Aomura<sup>1,2</sup>, Yusuke Yasuda<sup>1</sup>, Takeshi Yamada<sup>3</sup>, Takamasa Sakai<sup>4</sup>,

Koichi Mayumi<sup>1,2\*</sup>

<sup>1</sup> Material Innovation Research Center (MIRC) and Department of Advanced Materials Science, Graduate School of Frontier Sciences, The University of Tokyo, 5-1-5 Kashiwanoha, Kashiwa, Chiba 277-8561, Japan.

<sup>2</sup> The Institute for Solid State Physics, The University of Tokyo, 5-1-5 Kashiwanoha, Kashiwa-shi, Chiba, 277-8581 Japan.

<sup>3</sup> Neutron Science and Technology Center, Comprehensive Research Organization for Science and Society (CROSS), IQBRC Bldg., 162-1 Shirakata, Tokai, Naka, Ibaraki 319-1106, Japan

<sup>4</sup> Department of Bioengineering, Graduate School of Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo, Japan.

\* Correspondence: [kmayumi@g.ecc.u-tokyo.ac.jp](mailto:kmayumi@g.ecc.u-tokyo.ac.jp) (K.Mayumi)

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**Abstract**

We study the segmental and monomer dynamics of polymer gels with controlled inhomogeneity under uniaxial deformation by means of quasi-elastic neutron scattering (QENS). In order to clarify the effect of the homogeneity of network structure on the polymer dynamics in gels, we compare two types of polymer gels with controlled homogeneity: a homogeneous Tetra-PEG gel (Homo-gel) prepared from uniform Tetra-arm pre-polymers and heterogeneous Tetra-PEG gel (Hetero-gel) with a small amount of shorter Tetra-PEG pre-polymer. The different inhomogeneity in Homo-gel and Hetero-gel has little effect on the average relaxation time of the chain dynamics in the undeformed state. The difference in the local dynamics in the gels is emphasized under uniaxial deformation: while Homo-gel shows a relaxation mode, Hetero-gel exhibits a bimodal distribution of relaxation times with a slow dynamic mode ascribed to highly stretched short strands, which causes a more brittle macroscopic fracture compared with that in the case of Homo-gel.

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## 1. Introduction

Hydrogels, cross-linked polymer networks containing water, are expected to be applied for biomaterials such as artificial cartilage, vessels, and prosthetic joints due to their high water content and biocompatibility [1]. For the applications as the biomaterials, the mechanical toughness of polymer gels is not enough and needs to be improved. The reason for the brittleness of polymer gels is the heterogeneous strain distribution caused by their inhomogeneous network structure [2, 3]. When a polymer gel is stretched, local stress concentrates on at short strands between cross-links. The stress-concentrated strands are highly stretched and become potential fracture onsets, which dominates the macroscopic fracture properties of polymer gels. The stress concentration under deformation can be visualized by the introduction of mechanically-responsive chemical groups, mechanophores into polymer networks [4-6]. The mechanophores emit light in response to applied force, and serve as molecular sensors to detect the stress concentration in deformed polymeric materials. However, the complexity of the synthesis procedures for the mechanophores and their miscibility with polymer matrices limit their broad application to polymeric materials.

Here, we focus on the molecular dynamics of polymer chains to detect the strain distribution in polymer networks without adding any probes. Polymer chains exhibit

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hierarchical dynamics on various time and spatial scales: cooperative diffusion of polymer networks, Rouse/Zimm mode corresponding to dynamics of connected segments, and the monomer diffusion mode [7-21]. The segment and monomer dynamics in cross-linked polymer gels in the un-deformed state have been studied by quasi-elastic neutron scattering (QENS) techniques [9-21]. However, to the best of our knowledge, the segment/monomer dynamics in deformed polymer gels have not been observed yet.

In this study, the segment/monomer dynamics of polymer gels under uniaxial deformation is investigated by means of QENS. In order to clarify the effect of heterogeneity in polymer network structure, we prepared two types of polymer gels with controlled heterogeneities: a homogeneous Tetra-PEG gel prepared by end-cross-linking of Tetra-arm prepolymers (Homo-gel) [22], and heterogeneous Tetra-PEG gel (Hetero-gel) containing a small amount of Tetra-PEG prepolymers with shorter arms [23]. Hetero-gel shows a more brittle fracture behavior than Homo-gel, which suggests a stress-concentration occurs in Hetero-gel under deformation. From QENS results, we demonstrate how the homogeneity of the network structure affects the segment/monomer dynamics of polymer gels in the un-deformed and stretched states. Hetero-gel exhibits an elastic component in its dynamic scattering factor, which corresponds to the slow dynamics of highly stretched strands and is a molecular origin of the brittleness of

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polymer gel.

## 2. Experimental Section

### 2.1 Sample Preparation

We prepared the Tetra-PEG gels by end-crosslinking of N-hydroxysuccinimide (NHS)-terminated Tetra-PEG and amino-terminated Tetra-PEG. The homogeneous Tetra-PEG gel, Homo-gel (Figure 1 (a)) was fabricated by using NHS-terminated and amino-terminated Tetra-PEGs with the same total molecular weight, 20 k (SUNBRIGHT PTE-200HS and PTE-200PA, NOF Corporation (Tokyo, Japan)). The heterogeneous Tetra-PEG gel, Hetero-gel (Figure 1 (b)) was prepared from PTE-200HS, PTE-200PA, and amino-terminated Tetra-PEG with a smaller total molecular weight, 5k (SUNBRIGHT PTE-50PA, NOF Corporation (Tokyo, Japan)) [23]. The strand length in Hetero-gel is not uniform, but bimodal.

For Homo-gel, the two Tetra-PEGs, PTE-200PA and PTE-200HS, were dissolved separately in 0.1 M phosphate buffer (pH = 7.0) with the polymer concentration of 10 wt%. The phosphate buffer was prepared by mixing disodium phosphate, phosphoric anhydride, and sodium hydrogen anhydride in D<sub>2</sub>O. The two solutions of PTE-200PA and PTE-200HS were mixed and injected into a mold, and were left to stand

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for a day to proceed with the gelation reaction. Finally, we obtained a sheet of the Hetero-gel with 1 mm thickness. Hetero-gel was prepared from PTE-200HS and PTE-200PA/PTE-50PA solutions. The concentration of PTE-200HS was 10 wt%, while the concentrations of PTE-200PA and PTE-50PA were 8.5 wt% and 2.5 wt% in the PTE-200PA/PTE-50PA solution, respectively. The gelation process of Hetero-gel was the same as that of Homo-gel. The final concentration of PTE-50PA in Hetero-gel was 1.25 wt%.

Also, as a reference, we prepared Tetra-PEG solutions with the same compositions as the Tetra-PEG gels (Homo-gel and Hetero-gel). For a comparison with Homo-gel and Hetero-gel, we prepared 10 wt % PTE-200HS solution and PTE-200PA/PTE-50PA solution, respectively. The solvent of both the solutions was 0.1 M deuterated phosphate buffer. In the PTE-200PA/PTE-50PA solution, the concentrations of PTE-200PA and PTE-50PA were 8.75 wt% and 1.25 wt%, respectively.

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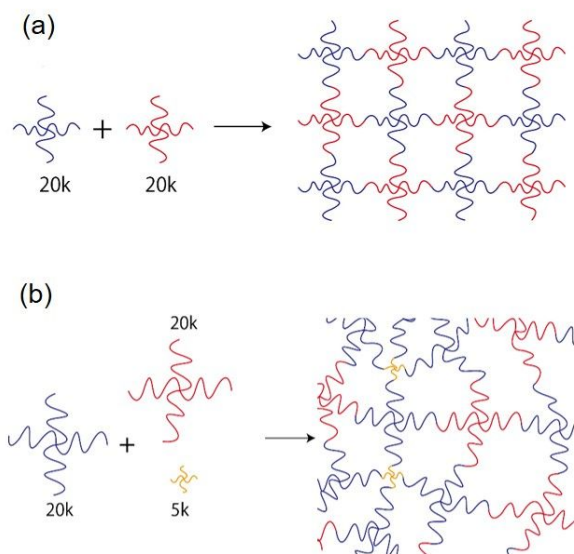


Figure 1. Schematic illustrations of (a) Homo-gel and (b) Hetero-gel.

## 2.2 Uniaxial tensile test

Uniaxial tensile tests on Homo-gel and Hetero-gel were performed on a mechanical testing apparatus (EZ-S-500N, SHIMADZU, Kyoto, Japan). For the tensile tests, we used stripe-shaped gel specimens with 1 mm thickness and 3 mm width. The initial gap between cramps was 20 mm. The cross-head speed was set as 50 mm/min.

## 2.3 Quasi-elastic neutron scattering

For the QENS measurements of un-deformed Homo-gel and Hetero-gel, we prepared gel sheets (40 mm  $\times$  42 mm  $\times$  1 mm) and covered them with aluminum foils. The gel sheets were put into aluminum cylinder cells having 14 mm inner diameter with 0.25 mm of thickness. For the QENS experiments on the stretched Tetra-PEG gels

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(Homo-gel and Hetero-gel), the gel sheets were cut into smaller specimens (10 mm×20 mm×1 mm for extension ratio  $\lambda = 2$  and 10 mm×13 mm×1 mm for  $\lambda = 3$ ). Each specimen was stretched with hands to the length of 40 mm, and the strain was maintained by fixing the edges of the specimen on an aluminum foil via an epoxy adhesive. For each extension ratio, 4 specimens were attached on the aluminum foil. The stretched gel specimens were set in a 2-mm gap of concentric double cylinder aluminum cells having 14 mm inner diameter of the outer cylinder and 10 mm outer diameter of the inner cylinder. In order to avoid the scattering from the adhesives, the top and bottom parts of the cells were covered with cadmium sheets. The Tetra-PEG solutions were set into a 1-mm gap of concentric double cylinder aluminum cells having 14 mm inner diameter of the outer cylinder and 12 mm outer diameter of the inner cylinder. All the aluminum cells were sealed by indium wire.

The QENS measurements were conducted using a time-of-flight near-backscattering spectrometer DNA BL02, at Materials and Life Science Experimental Facility (MLF) at the Japan Proton Accelerator Research Complex (J-PARC) in Ibaraki, Japan [24, 25]. The energy resolution was 2.8 and 3.6  $\mu\text{eV}$  for gels and solutions, respectively, and the energy transfer ranged from -0.02 to 0.1 meV. The incident neutron beam and scattering vector were perpendicular to the stretching direction of the gels as

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shown in Figure 2. The covered angle of the Si(111) analyzed was from  $-14$  to  $21^\circ$  and from  $-30$  to  $138^\circ$  in vertical and horizontal directions, respectively. The amplitude of the scattering vector,  $Q$ , was in the range of  $0.125$  to  $1.825 \text{ \AA}^{-1}$ . Each measurement was carried out at  $300 \text{ K}$  for  $6$  hours with  $500 \text{ kW}$  proton beam power. The data were circular averaged in the data reduction. To extract the dynamics of the solute, the scattering from the solvent was removed by subtraction based on the volume fraction.

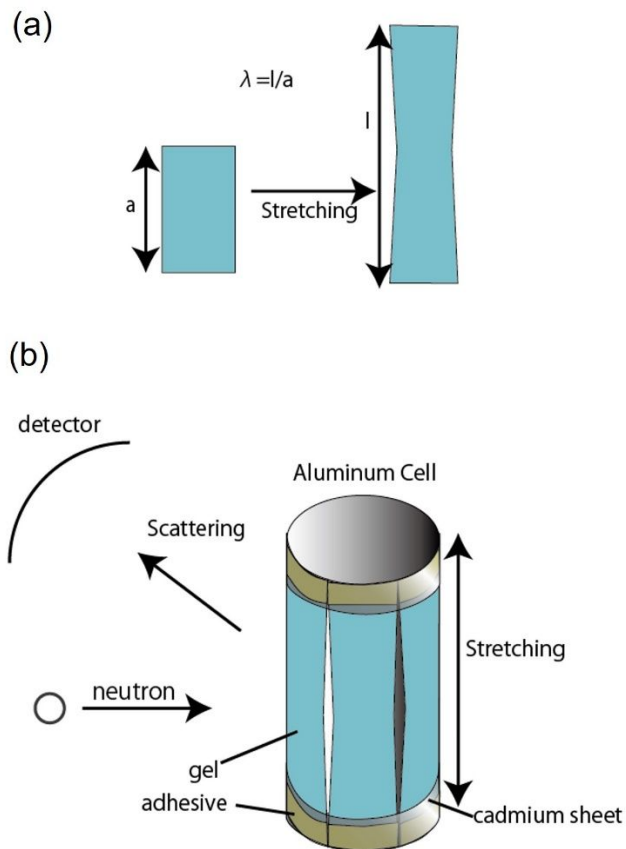


Figure 2. (a)Schematic illustration of stretching gels. (b)Schematic illustration of experimental set-up for QENS measurements of stretched gels.

### 3. Results and Discussion

#### 3.1 Tensile Tests

Figure 3 shows the stress-extension ratio ( $\sigma - \lambda$ ) curves of Homo-gel and Hetero-gel. The Young's moduli of Homo-gel and Hetero-gel are 49 kPa and 50 kPa, respectively, which suggests that the average network densities in these two gels are almost the same [23]. However, Hetero-gel fractures at the extension ratio  $\lambda = 4.5$ , while Homo-gel can be stretched up to  $\lambda = 7$ . Since Hetero-gel contained short Tetra-PEG, the network structure was heterogeneous compared with Homo-gel. This heterogeneity of the network structure causes stress concentration on the short strands under stretching and the lower strain at break for Hetero-gel. This result is consistent with the previous work on bimodal Tetra-PEG gels [23].

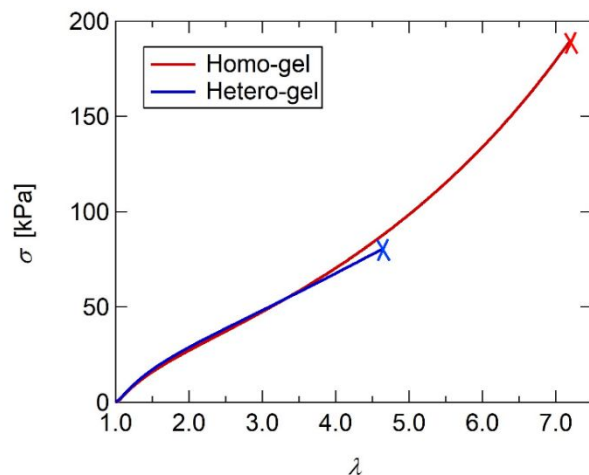


Figure 3. Stress-extension ratio curves of Homo-gel and Hetero-gel.

### 3.2 Effect of Gelation on Polymer Dynamics

The effect of gelation on polymer chain dynamics was studied by comparing QENS results of the Tetra-PEG solutions and gels. Figure 4 (a) shows dynamic structure factors  $S(Q, \omega)$  of the Tetra-PEG precursor solutions and gels at  $Q = 0.35 \text{ \AA}^{-1}$ . Both Homo- and Hetero-gels show no elastic component attributed to slow dynamics compared to energy resolution. The dynamic structure factors were fitted using KWW function:

$$S(Q, \omega) = \left\{ \text{FT} \left[ A \exp \left( - \left( \frac{t}{\tau} \right)^\beta \right) \right] \right\} \otimes R(Q, \omega) \quad (1)$$

where  $\tau$  is relaxation time,  $\beta$  is the stretching exponent corresponding to the distribution of  $\tau$ ,  $A$  is the amplitude of the relaxation mode, FT is the Fourier transform,  $R(Q, \omega)$  is the resolution function. The data of vanadium was utilized for the resolution function. As shown in the dashed lines in Figure 4 (a), the measured  $S(Q, \omega)$ 's were fitted well with Eq. (1). From the obtained  $\tau$  and  $\beta$ , the average relaxation time  $\langle \tau \rangle$  can be calculated as follows:

$$\langle \tau \rangle = \frac{\tau}{\beta} \Gamma \left( \frac{1}{\beta} \right) \quad (2)$$

where  $\Gamma$  is the gamma function. Figure 4 (b) shows the  $Q$  dependence of  $\langle \tau \rangle$  for the Tetra-PEG solutions and gels. For all the samples, in the lower  $Q$  regime ( $Q < 0.5 \text{ \AA}^{-1}$ ),  $\langle \tau \rangle$  is proportional to  $Q^{-3}$  corresponding to Zimm dynamics, while  $\langle \tau \rangle$  decays as  $Q^{-2}$

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reflecting the monomer diffusion mode for  $Q > 0.5 \text{ \AA}^{-1}$ . Homo-gel and Hetero-gel show almost the same  $\langle \tau \rangle$ , suggesting that the degree of the inhomogeneity in the network structure does not influence the segment/monomer dynamics of the polymer networks in the un-deformed state. This is consistent with the homogeneous network structure of the Tetra-PEG gels confirmed by previous small-angle neutron scattering (SANS) and neutron spin echo (NSE) studies [19, 26, 27]. Figure 4 (c) shows the  $Q$  dependence of  $\beta$  for the Tetra-PEG gels and solutions. In the case of the Tetra-PEG solutions,  $\beta$  for  $Q > 0.5 \text{ \AA}^{-1}$  is about 0.9 close to 1 corresponding to the monomer diffusion with a single relaxation mode, while  $\beta$  in the low- $Q$  regime ( $Q < 0.5 \text{ \AA}^{-1}$ ) is around 0.8 and the deviation from 1 is ascribed to the non-Brownian Zimm dynamics. Compared with the Tetra-PEG solutions, the cross-linked gels show lower  $\beta$ . At lower  $Q$  below  $0.5 \text{ \AA}^{-1}$  where Zimm dynamics was observed,  $\beta$  of Homo- and Hetero-gels is close to  $2/3$ , which is consistent with previous NSE results of Tetra-PEG gels [19] and theoretical prediction of Zimm model [21].

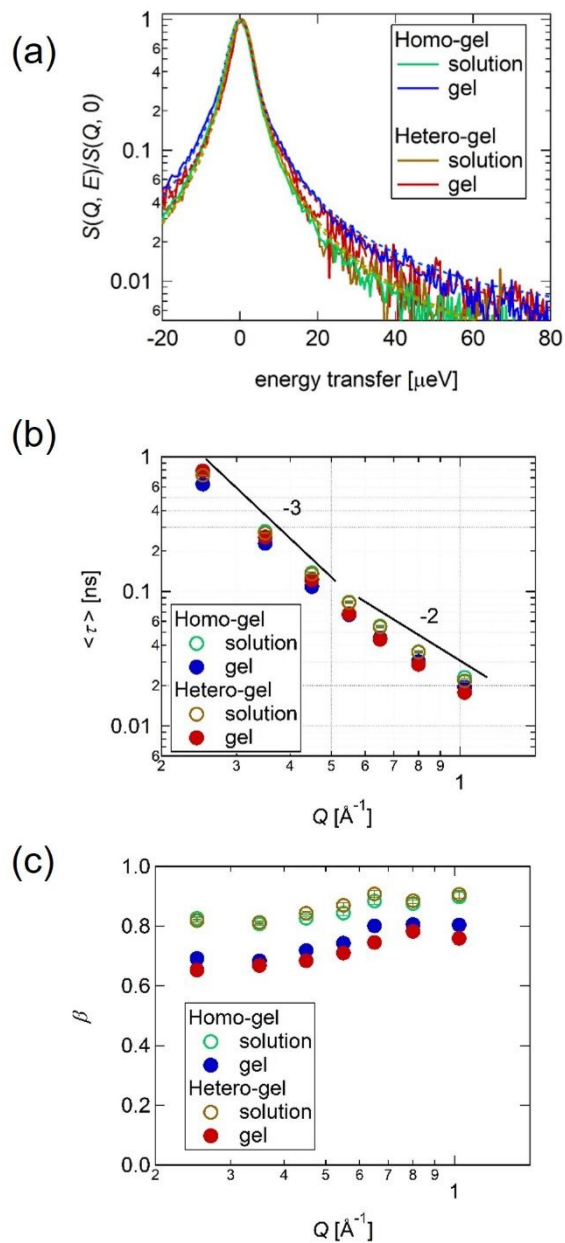


Figure 4. (a) Dynamics structure factors  $S(Q, \omega)$  at  $Q=0.35 \text{ \AA}^{-1}$ , (b)  $Q$  dependence of average relaxation time  $\langle \tau \rangle$ , (c)  $Q$  dependence of stretching exponent  $\beta$  for the Tetra-PEG gels and solutions.

### 3.3 Effect of Stretching on Polymer Dynamics in Gels

Next, Figures 5 (a) show  $S(Q, \omega)$  for Homo-gel under uniaxial deformation ( $\lambda = 1, 2, 3$ ) at  $Q=0.8 \text{ \AA}^{-1}$ . The dynamic structure factors were fitted with Eq. (1) and the fitting results are shown as the solid lines. As shown in Figure 5 (b), the average relaxation times  $\langle \tau \rangle$  of Homo-gel decrease with increasing stretching, and the segment/monomer dynamics in the gel are accelerated by stretching. Interestingly,  $\beta$  for the homogeneous gel is not changed with stretching (Figure 5 (c)), suggesting that the local deformation in the gel is kept homogeneous (Figure 5 (d)).

Figures 6 (a) shows  $S(Q, \omega)$  Hetero-gel under uniaxial deformation ( $\lambda = 1, 2, 3$ ) at  $Q=0.8 \text{ \AA}^{-1}$ . A sharp elastic peak corresponding to slow chain dynamics with a broad base was observed under deformation ( $\lambda= 2, 3$ ), while only a broad peak was seen for the un-deformed state ( $\lambda=1$ ). This means that the slow chain dynamics appears only for the deformed Hetero-gel. Therefore, in these cases,  $S(Q, \omega)$ 's were fitted by the following equation with the sum of the KWW function for the relaxation component and delta function for the elastic component:

$$S(Q, \omega) = \left\{ \text{FT} \left[ A_1 \delta(\omega) + A_2 \exp \left( - \frac{t}{\tau} \right)^\beta \right] \right\} \otimes R(Q, \omega) \quad (3)$$

The elastic component can be ascribed to a slow chain dynamics of highly stretched short strands. When Hetero-gel is stretched, the short strands oriented to the stretching direction

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are strongly stretched and the chain dynamics of the highly deformed chains is suppressed. Figures 6 (b) and (c) show the  $Q$  dependence of the average relaxation time  $\langle\tau\rangle$  and stretching exponent  $\beta$  for the quasi-elastic component fitted with the KWW function, respectively. The relaxation component corresponds to the dynamics of the rest of polymer strands except for the highly stretched chains. As shown in Figure 6 (b), although the average relaxation time becomes shorter with stretching, the extension ratio dependence of the average relaxation time for Hetero-gel is weaker than that for Homo-gel (Figure 5 (b)). The weak dependence of the relaxation time suggests that the stress/strain concentration on some short strands in Hetero-gel relaxes the local deformation of the other polymer strands mainly composed of long chains (Figure 6(d)). As shown in Figure 6(c),  $\beta$  of the QENS component is almost independent of  $\lambda$ , which means that the relatively relaxed strands are deformed uniformly with stretching. The average fraction of the elastic component,  $A_1/(A_1+A_2)$  is 1.4 % for  $\lambda = 2$  and 3 within the measured  $Q$  range, which is less than the fraction of proton number of the short pre-polymer PTE-50PA, 12.5 %. This result suggests that the stress concentration occurs on about 11 % monomers of the short strands in Hetero-gel.

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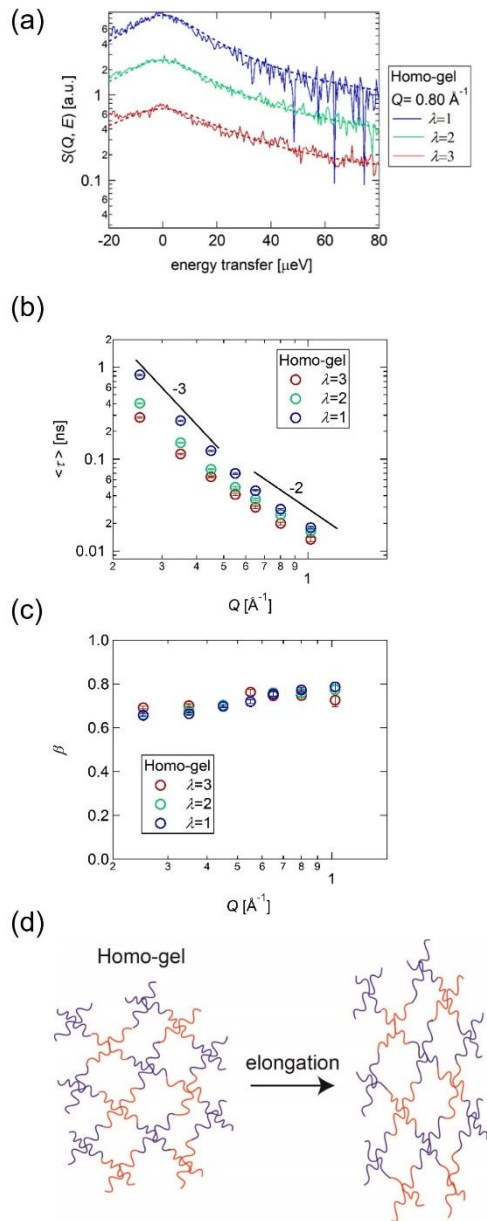


Figure 5. (a) Dynamic structure factor  $S(Q, \omega)$  of the Homo-gel. The solid lines are the fitting results.  $Q$  dependence of (b) average relaxation time and (c) stretching exponent  $\beta$  for Homo-gel at  $\lambda = 1, 2, 3$ . (d) Schematic illustration of deformation mechanism for Homo-gel.

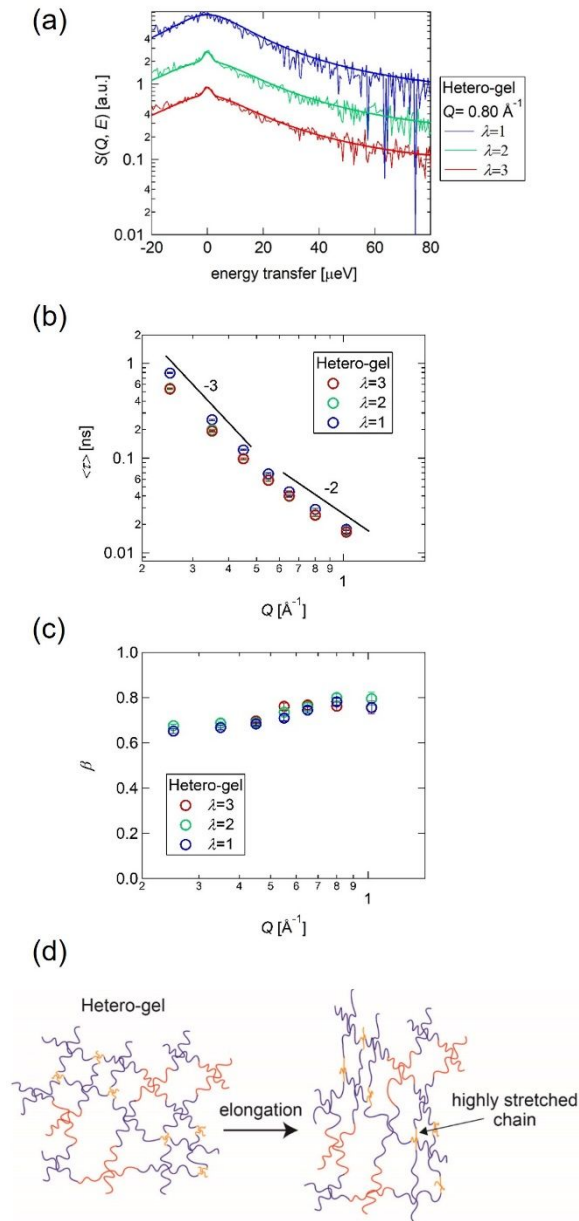


Figure 6. (a) Dynamic structure factor  $S(Q, \omega)$  of Hetero-gel. The solid lines are the fitting results.  $Q$  dependence of (b) average relaxation time and (c) stretching exponent  $\beta$  for Hetero-gel at  $\lambda = 1, 2, 3$ . (d) Schematic illustration of deformation mechanism for Hetero-gel.

#### 4. Conclusion

In this work, we investigated the segmental and monomer dynamics in the homogeneous and heterogeneous Tetra-PEG gels (Homo-gel and Hetero-gel) by QENS. Compared with the Tetra-PEG solutions, the un-deformed Tetra-PEG gels show about the same segmental and monomer dynamics. While the heterogeneity of the polymer networks does not influence the local chain dynamics in the un-deformed state, the inhomogeneity of the network structure is crucial for the local chain dynamics under stretching. Hetero-gel under stretching exhibits a small amount of elastic peak corresponding to a slow dynamics of highly stretched short strands, while for the Homo-gel, only a broad quasi-elastic component was observed. The existence of the highly stretched strands results in the smaller strain/stress at break for the heterogeneous gels. QENS measurements on deformed polymer gels and elastomers is quite useful to detect stress concentrations in the materials and deepen the understanding of the fracture mechanism.

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