

High-Strength Network Structure of Jungle-Gym Type Polyimide Gels Studied with Scanning Microscopic Light Scattering

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Abstract Latest high-strength gels overcome brittleness due to the inhomogeneities built in their network structure. However, the inhomogeneities still prevent precise characterization of their network structures by scattering methods. A new concept is to take advantage of the ensemble-averaged structure characterization with scanning microscopic light scattering (SMILS), in order to study the network structure and properties of inhomogeneous high-strength gels nondestructively in wide spatio-temporal ranges. In this study, two kinds of the jungle-gym type polyimide gels that have semi-rigid main-chains or rigid main-chains were synthesized in varying the preparing concentration and studied with SMILS. The optimal concentration of polyimide achieved ten times higher Young modulus than before.

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1 Introduction

Latest high-strength gels overcome weakness due to incomplete network structure, by different approaches to control the network structure. Okumura and Ito [1] synthesized slide-ring gels (SR gels) having figure-eight cross-links, which are able to slide along polymer chains and effectively relax their tension. Haraguchi and Takeshita [2] synthesized nanocomposite gels (NC gels) containing dispersed sheet-shape clay as a multifunctional crosslinker, which shows a resistance to extension as large as 1,000%. Gong et al. [3] synthesized double network gels (DN gels), containing 90% water, which exhibit a high Young's modulus (0.1–0.3 MPa) and large fracture strengths of more than 20 MPa. We also synthesized inter-crosslinking network gels (ICN gels), containing 97% water and exhibiting more than 60% increase in the ductility in comparison with normal gels [4, 5]. For each of these gels, the unique mechanisms for the excellent mechanical properties have been studied intensely. Differently from these gels, there is another approach to realize high-strength gels. That is the pursuit of homogeneous and complete network structure. He et al. [6], some of the present authors, developed a novel method of synthesizing polyimide gels with jungle-gym type homogeneous network structure, which exhibit a higher Young's modulus (35–40 MPa). Recently, Sakai et al. [7], synthesized a tetra-PEG gel having ideally homogeneous network structure form tetrahedron-like macromonomer, whose maximum breaking stress is typically 10 MPa. For these homogeneous gels, it is expected that the homogeneity of network structure should be important to achieve the highest strength. Thus the relation between the homogenous structure and the strength should be studied. Light scattering is a powerful method to analyze nanometer-scale structure of polymeric system. However, somewhat inhomogeneities still exist even in the homogeneous gels and prevent precise characterization of their network structures by scattering methods. A new concept is to take advantage of the ensemble-averaged structure characterization with scanning microscopic light scattering (SMILS), in order to study the structure and properties of inhomogeneous high-strength gels nondestructively in wide spatio-temporal ranges [8]. Previously, the gelation process of the jungle-gym type polyimide gels was studied with the SMILS [9]. In this study, two kinds of the jungle-gym type polyimide gels that have semi-rigid main-chains or rigid main-chains were synthesized in varying the preparing concentration and studied with SMILS. We found that the optimal concentration of polyimide achieved a quite higher Young modulus (320 MPa).

2 Experimental

2.1 Synthesis of Jungle-Gym Type Polyimide Gels

Materials: Pyromellitic dianhydride (PMDA) was purified by recrystallization from acetic anhydride, and dried at 120 °C in vacuum for 24 h. p-phenylene diamine

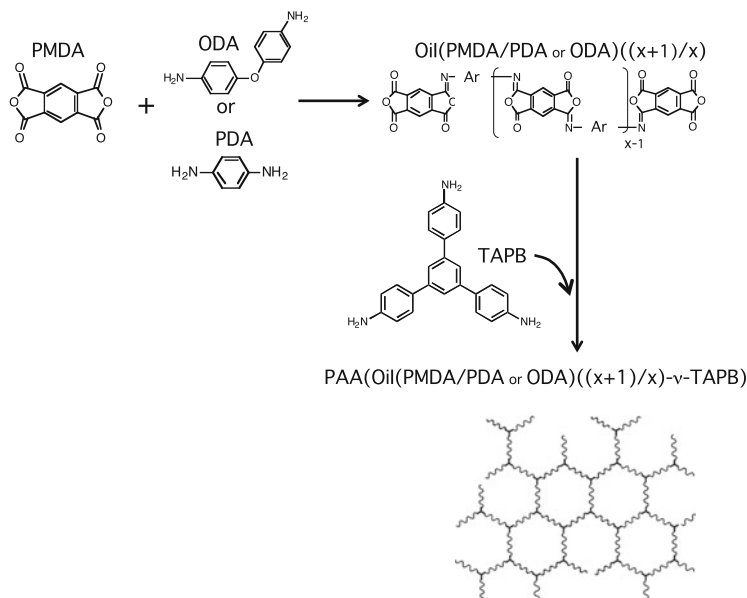
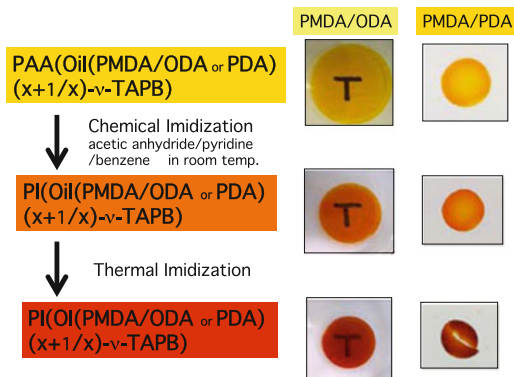


Fig. 1 Preparation scheme of jungle-gym type gels

(PDA) and 4,4-diaminodiphenyl ether (ODA) were purified by recrystallization from ethanol, and dried at 50 °C in vacuum for 24 h. *N*-methyl-2-pyrrolidone (NMP) and *N,N'*-dimethylacetamide (DMAc) and stored with molecular sieves. *N,N'*-dicyclohexylcarbodiimide (DCC) and the other chemicals were used without further purification. Oligoisoimide macromonomers: The scheme is shown in Fig. 1. Here, the number of repeating unit (the polymerization index) of the macromonomer was controlled by the molar ratio between PMDA and PDA in preparation. If one sets the ratio as $(x + 1) : x$, then the number of repeating unit becomes $2x + 1$. Here, we prepared the macromonomer at $x = 1, 3$, and 18 , thus the number became $3, 7$, and 37 . At first, PMDA was dissolved into NMP, and PDA was added slowly and NMP was added to prepare 10 wt%-solid reaction solution. Immediately, the increase of viscosity in the reaction solution was observed. However, the viscosity was decreased after stirring at room temperature for 24 h. The reaction mixture was diluted with 0.1 M LiCl/NMP to prepare 1 wt% solid solution. After stirring for 1 h, 5 wt% DCC/NMP solution was slowly added into the reaction mixture to make the ratio of DCC/PMDA to be 2, and stirred for 24 h. The solution color was changed from light brown to red brown, and became turbid. The solution was poured into 2-propanol. A dark yellow precipitate was collected by vacuum filtration, washed 2-propanol, and finally washed with benzene. The final slurry of benzene and product was freeze-dried and additionally dried at 40 °C in vacuum. This procedure yielded a dark yellow powder of a oligoisoimide, $\text{Oii(PMDA/PDA)((x + 1)/x)}$. Also, a bright yellow powder of $\text{Oii(PMDA/PDA)((x + 1)/x)}$ was similarly synthesized with a solvent DMAc in-stead of NMP. The reaction was checked by FT-IR.

Fig. 2 Appearances of prepared gels



Polyimide gels: In the previous paper [6], a new rigid and symmetric tri-functional amine, 1,3,5-tris(4-aminophenyl)benzene (TAPB) (Fig. 1), was synthesized. In the present study, the TAPB was also used as an end-crosslinker, to prepare jungle-gym type polyimide gels. In order to synthesize appropriate concentration, for example a wt%-solid concentration of polyimide gels in DMAc, the DMAc solution of a wt% oligoisoimide was prepared. Then, the DMAc solution of a wt% TAPB was added to the solution of oligoisoimide with a stoichiometric mole ratio (1:1) between the amino group of oligoisoimide and the terminal acid anhydride group of TAPB. The solution gelled after few minutes in room temperature, and then transparent as-prepared poly(amide acid) (PAA) gels, PAA(OiI(PMDA/PDA)) $((x + 1)/x)-v-TAPB$ and PAA(OiI(PMDA/ODA)) $((x + 1)/x)-v-TAPB$, were obtained. The colors of PMDA/PDA and PMDA/ODA gels were light brown and yellow, respectively, as shown in Fig. 2. The swollen PAA gels were dipped for 30 min in chemical imidization solution, which is a mixture of acetic anhydride, pyridine and benzene with 1:1:3 in volume ratio, and then transparent and orange colored gels, PI(OiI(PMDA/PDA)) $((x + 1)/x)-v-TAPB$ and PI(OiI(PMDA/ODA)) $((x + 1)/x)-v-TAPB$, were obtained. These gels were repeatedly (about 10 times) washed with a large amount of DMAc, and then the gels were gradually heated toward 200 °C for 4 h. Then transparent polyimide gels, PI(OI(PMDA/PDA)) $((x + 1)/x)-v-TAPB$ and PI(OI(PMDA/ODA)) $((x + 1)/x)-v-TAPB$, were obtained. The colors of these gels become darker than before heating. The reaction was checked by FT-IR, although the results are not shown here.

2.2 Scanning Microscopic Light Scattering (SMILS)

Dynamic light scattering measurement was performed at 30 °C in the scattering angle range of $\theta = 30^\circ-125^\circ$ with a SMILS apparatus [8]. With this apparatus (its schematic is shown in Fig. 3), many measurements for small scattering volume

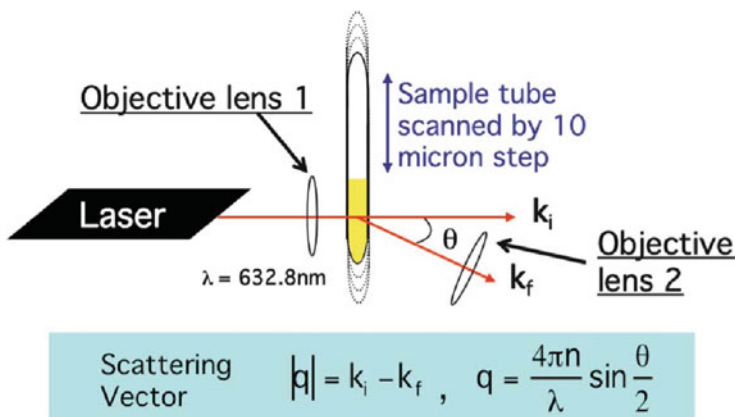


Fig. 3 Schematic of the scattering microscopic light scattering system

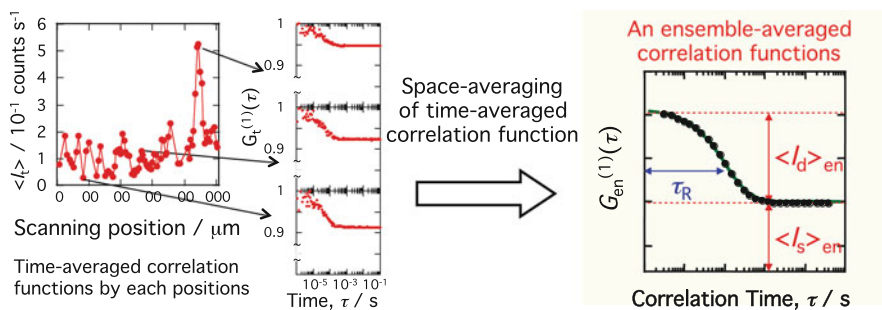


Fig. 4 Scheme to obtain an ensemble-averaged correlation function with the SMILS

can be successively performed at different positions in a sample. Hence, one can rigorously obtain a time- and space-averaged correlation function, i.e., an ensemble-averaged correlation function to overcome the non-ergodicity of inhomogeneous media, as shown in Fig. 4. The photon detection was carried out with a homodyne technique. For each sample, the time-averaged homodyne correlation functions $g_t^{(2)}(\mathbf{q}, \tau)$ were determined at over a 100 points, where \mathbf{q} is scattering vector and τ is correlation time. Then the ensemble-averaged heterodyne correlation function $g_{en}^{(1)}(\mathbf{q}, \tau)$ was calculated by using the following equation [10]

$$g_{en}^{(1)}(\mathbf{q}, \tau) = \frac{\left\langle \langle I \rangle_t \gamma^{-1} \sqrt{1 + g_t^{(2)}(\mathbf{q}, \tau) - g_t^{(2)}(\mathbf{q}, 0)} \right\rangle_{sp}}{\langle I \rangle_{en}} \quad (1)$$

where I is the scattering intensity and γ is an apparatus constant. In the present work, since we are interested mainly in the dynamics of fluctuation in gels, we

calculated the dynamic components of $g_{en}^{(1)}(\mathbf{q}, \tau)$ as

$$\begin{aligned} \Delta g_{en}^{(1)}(\mathbf{q}, \tau) &= \frac{g_{en}^{(1)}(\mathbf{q}, \tau) - g_{en}^{(1)}(\mathbf{q}, \infty)}{g_{en}^{(1)}(\mathbf{q}, 0) - g_{en}^{(1)}(\mathbf{q}, \infty)} \\ &= \frac{\left\langle \langle I \rangle_t \sqrt{1 + g_t^{(2)}(\mathbf{q}, \tau) - g_t^{(2)}(\mathbf{q}, 0)} \right\rangle_{sp} - \left\langle \langle I \rangle_t \sqrt{2 - g_t^{(2)}(\mathbf{q}, 0)} \right\rangle_{sp}}{\langle I \rangle_{en} - \left\langle \langle I \rangle_t \sqrt{2 - g_t^{(2)}(\mathbf{q}, 0)} \right\rangle} \end{aligned} \quad (2)$$

It is convenient to use this equation, since one has no need to consider the apparatus constant γ .

To analyze $\Delta g_{en}^{(1)}(\mathbf{q}, \tau)$, a relaxation time distribution was calculated numerically with inverse Laplace transform. In general, a monotonically decreasing correlation function can be expressed by the superposition of exponential functions as [8]

$$\Delta g_{en}^{(1)}(\tau) = N \sum_{i=1}^n P_{en} \exp(-\tau/\tau_{R,i}) \quad (3)$$

where $\tau_{R,i} = \tau_{R,min} \times (\tau_{R,max}/\tau_{R,min})^{(i-1)/n}$ ($i = 1, 2, \dots, n$) and is a normalized factor defined as $N = (1/n) \log(\tau_{R,max}/\tau_{R,min})$. Thus the nonlinear fitting with Eq. 3 to $\Delta g_{en}^{(1)}(\tau)$ was performed where the analytical condition was set as $\log(\tau_{R,min}) = -6$, $\log(\tau_{R,max}) = 1$, and $n = 51$.

3 Results and Discussion

In order to characterize the network structure through the analysis of the dynamic fluctuation, the ensemble-averaged correlation function $\Delta g_{en}^{(1)}(\tau)$ was obtained and then the relaxation time distribution $P_{en}(\mathbf{q}, \tau_R)$ was determined (not shown here). It was found that one main relaxation peak for each $P_{en}(\mathbf{q}, \tau_R)$, which can be assigned to cooperative diffusing (Brownian) motion of nanometer-scale network structure. It is often called gel mode. We tried to analyze the inhomogeneities of the network structure by fitting the following distribution function to $P_{en}(\mathbf{q}, \tau_R)$:

$$P_{en}(\mathbf{q}, \tau_R) = N \exp \left[-\frac{(\log \tau_R - \langle \log \tau_R \rangle)^2}{2\sigma^2} \right] \quad (4)$$

Then we obtained the relaxation time τ_R and determined the cooperative diffusion coefficient D_{coop} , by using the theoretical formula $\tau_R^{-1} = \mathbf{q}^2 D_{coop}$ [8]. Then, D_{coop} was plotted as a function of the preparing concentration of PAA gels, as shown in Fig. 5.

Fig. 5 Cooperative diffusion coefficient of the PAA gels as a function of the preparing concentration

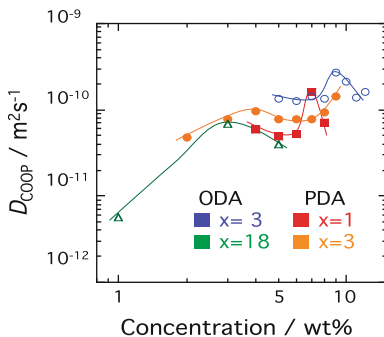
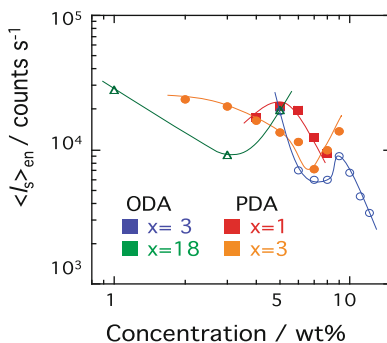


Fig. 6 Static component of ensemble-averaged intensity of the PAA gels as a function of the preparing concentration



We found that D_{coop} has a maximum value and it possibly corresponds to the smallest mesh size due to its homogeneous network structure. For rigid PMDA/PDA gels, 7 and 4 wt% may be optimal concentrations when $x = 1$ and 3. For semi-rigid PMDA/ODA gels, 9, 7, and 3 wt% may be optimal concentrations when $x = 3, 7,$ and 18 (the date of $x = 7$ is not shown here). Based on the Stokes-Einstein formula $D_{coop} = k_B T / 6 \pi \eta \xi$, the mesh size ξ was estimated as 0.9 nm ($x = 3, 9$ wt%), 1.5 nm ($x = 7, 7$ wt%) and 3.5 nm ($x = 18, 3$ wt%). If we compare these results at $x = 3$, the optimal concentration for the rigid gels 4 wt% is lower than for the semi-rigid gels 9 wt%. It implies that the main chain of the rigid gels is extended and forms the jungle-gym type network structure in the lower concentration. On the other hand, the main chain of the semi-rigid gels is little shrunken and forms the homogeneous network in the higher concentration. We found that the mesh size determined from $P_{en}(\mathbf{q}, \tau_R)$ and the static scattering intensity also depend on the preparing concentration and indicate the optimal concentration similarly. We also observed the scattering intensities as a function of the preparing concentration of PAA gels, as shown in Fig. 6. We consider the minimum of the static component of the intensity corresponds to the most homogeneous structure. The static intensity shows the similar behavior to the diffusion coefficient, however the detail behavior seems complex and should be studied further in future. Finally, the elastic properties of the polyimide gels swollen in DMAc were measured by Reometrics Solids Analyzer (RSAII, Reometrics Co.) at 0.16–16 Hz and at 20 °C

with parallel plates and compress mode. We prepared the PMDA/ODA polyimide gels at an optimal concentration $x = 7$ and 7 wt% and the samples was cut in the size of 3.2 mm in diameter and 1.8 mm in height. The optimal polyimide gels showed high Young moduli. The modulus of as-prepared poly(amide acid) PAA(OiI(PMDA/ODA)- ν -TAPB) gels, chemically imidized PI(OiI(PMDA/ODA)- ν -TAPB) and thermally full-imidized PI(OI(PMDA/ODA)- ν -TAPB) was 0.32, 13, and 320 MPa, respectively. Comparing to the previous modulus observed for the thermally imidized gels (0.1–35 MPa) [6], it becomes about ten times higher than before. It implies that the modulus of the polyimide gels strongly depend on the preparing concentration and the SMILS is convenient tool to find the optimal preparing concentration nondestructively.

4 Conclusion

Transparent jungle-gym type polyimide gels were developed by using both oligoisoimide macromonomers and two-step (chemical and thermal) imidizations. The optimum concentration, where as-prepared poly(amide acid) gels have the most homogeneous and jungle-gym type structure, was determined with SMILS.

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