

Synthesis of Novel Double Network Hydrogels via ATRP Initiated Radical Polymerization

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Synthesis of Novel Double Network Hydrogels *via* Atom Transfer Radical Polymerization

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Abstract

Novel double network (DN) hydrogels were prepared *via* atom transfer radical polymerization (ATRP) of the first network using two different initiators, and followed by ultraviolet (UV) photo-initiated polymerization for the second network. The first networks of DN hydrogels were prepared by using two different initiators; one is a one-side initiator, and the other is a double-side initiator. The mechanical properties of various DN gels, such as water content and compressive strength, were studied. The network structure of the DN hydrogels was also characterized by dynamic light scattering. Thus, we demonstrated that the ATRP method is useful to control the network structure of the first network for DN gels. Extensive inhomogeneous structure of the first network was obtained by ATRP method and increased both the swelling degree and softness of DN gels.

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Keywords

Double network hydrogels, polyelectrolyte gels, ATRP, swelling degree, fracture energy, dynamic light scattering

1. Introduction

Hydrogels are polymer networks swollen with a large amount of water. Normally, the water content is more than about 50–60% of the total weight when the term ‘gel’ is used. Recently, three new hydrogels with good mechanical performance have been developed: a topological (TP) gel [1], a nanocomposite (NC) gel [2], and a double network (DN) gel [3]. Thus, gels with a good mechanical performance might be open for wide applications in industry, including for load-bearing water absorbents, separation membranes, fuel cell membranes, in engineering fields, such as water-purity control system, optic and electronic devices, low friction gel

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machines, and in biomechanical fields, such as artificial cartilages, tendons, blood vessels, and other bio-tissues.

The DN gel is a kind of interpenetrated network gel that is synthesized *via* two-step network formation: the first step forms a highly cross-linked rigid polymer gel (first network), and the second step forms a loosely cross-linked network flexible polymer (second network). Generally, the method of synthesis that is applied for each step of network formation is photo-initiated polymerization. The DN gels synthesized in this way exhibit anomalously high mechanical strength only when the gel consists of polyelectrolyte gel as the first network and neutral polymer as the second network and the molar ratio of the first to the second component is a few dozen [3]. Such DN gels, containing about 90 wt% water, possess both hardness (elastic modulus of 0.3 MPa) and toughness (fracture stress of ~ 10 MPa).

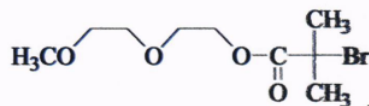
The mechanical strength of DN gels is so high that it is difficult to perform the quantitative evaluation of strength by the compress failure technique. Thus we tried to determine the fracture energy G of DN gels by tearing experiment [4]. From the tearing experiment of DN gels, we found the following important points about the anomalously high strength. The cross-linking densities of the two networks in free-radical polymerization are crucial parameters. The first network should be highly cross-linked, and the second network should be un-cross-linked or slightly cross-linked [5]. The fracture energy G increases as the cross-linking density of the second network decreases [4]. Further, for an un-cross-linked second network, the molecular weight of linear chain of the second network PAAm should be higher than a critical value of 10^6 for the large enhancement in G [6].

Concerning the chemical structure of DN gels, we have not clarified how the kind of polymerization reaction for the first network (polyelectrolyte gel) influences the mechanical properties of DN gels. Previously, we have always used the free-radical polymerization to prepare the DN gels. However, for more precise control of the chemical structure of the network, we should try to use other advanced polymerization techniques. With regard to this point, here we introduce an Atom Transfer Radical Polymerization (ATRP) [7–9] method to synthesize the first network of gel and follow this by photo-initiated polymerization for the second network. The first networks of DN gels are prepared by using two different initiators; one is one-side initiator, and the other is double-side initiator. The mechanical properties of various DN gels, such as water content and compressive strength, are investigated. The network structure of the DN gels is observed by dynamic light scattering. Then, we discuss the applicability of ATRP to the synthesis of DN gels.

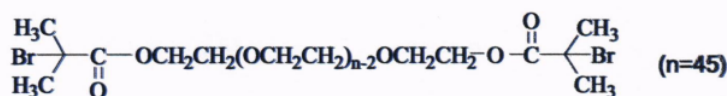
2. Experimental

2.1. Materials

Styrenesulfonic acid sodium salt (NaSS), 2-acrylamido-2-methylpropanesulfonic acid (AMPS), acrylamide (AAm), *N,N'*-methylenebis(acrylamide) (MBAA, cross-linker), 2-oxoglutaric acid (initiator), copper(I) bromide (CuBr), and bipyridyl



MEE-Br

PEG2000-Br₂

Scheme 1. Structure of initiators used in ATRP.

(Bpy) were used as purchased. Milli-Q treated distilled water was used to prepare all aqueous solutions.

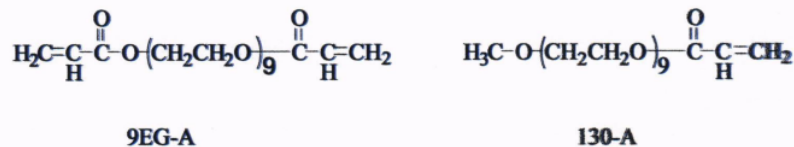
2.2. Synthesis of Initiators for ATRP

2.2.1. Synthesis of MEE-Br as One-Side Initiator

In a three-neck flask, 2-bromoisobutyryl chloride (1.15 ml, 10 mmol) and triethylamine (1.4 ml, 10 mmol) were mixed in THF (20 ml) at 0°C. A 30 ml THF solution of 2-(2-methoxy-ethoxy)-ethanol (MEE) (0.6 g, 5 mmol) was added dropwise. After this addition was complete, the reaction solution was allowed to warm to room temperature, and the reaction mixture was stirred for another 24 h. The reaction mixture was then filtered to remove the precipitated TEA, and the THF was removed using the rotary evaporator. The resulting yellow crude product was dissolved in water and extracted with diethyl ether. The diethyl ether layer was collected and dried over MgSO₄, and then the diethyl ether was removed under vacuum to obtain the yellow initiator MEE-Br (shown in Scheme 1), yield 82%. ¹H-NMR (CDCl₃, 400 MHz): δ = 4.34 (2H), 3.75–3.55 (6H), 3.38 (3H), 1.93 (6H).

2.2.2. Synthesis of PEG2000-Br₂ Macroinitiator Using PEG2000 as Double-Side Initiator [10, 11]

In a three-neck flask, 2-bromoisobutyryl chloride (1.15 ml, 10 mmol) and triethylamine (1.4 ml, 10 mmol) were mixed in THF (20 ml) at 0°C. To the formed yellow dispersion was added 100 ml solution of 10.0 g (2.5 mmol) of PEG2000 in the mixture of 90 ml dry THF and 10 ml dry CH₂Cl₂ dropwise during 2 h under dry nitrogen; subsequently, the temperature was allowed to rise to room temperature. The



Cross linker

Model compound

Scheme 2. Structure of cross-linker and model compound used in ATRP.

reaction was continued under stirring for 24 h. The solution was filtered, half of the solvent was evaporated, and the PEG macroinitiator was precipitated in cold diethyl ether. After dissolution in absolute ethanol, the solution was stored overnight to recrystallize the product. The macro-initiator was filtered, washed with cold ether, and dried in vacuum to obtain the PEG2000-Br₂ (shown in Scheme 1), yield 75%. ¹H-NMR (CDCl₃, 400 MHz): δ = 4.33 (4H), 3.75 (4H), 3.65 (172H), 1.95 (12H).

2.3. Estimation of Reactivity Ratio

The composition of gels is difficult to measure by the usual method used for linear copolymers. A model compound with only one vinyl end group was used instead of cross-linker, and the linear copolymer can be obtained. The composition of such copolymer can be determined easily.

In a test tube, NaSS monomer and 130-A (the model compound of cross-linker 9EG-A (shown in Scheme 2) was mixed in different molar ratio in H₂O/EG solution, ligand and initiator MEE-Br was added and degassed with argon; CuBr was added under argon. The polymerization was terminated by deposition in acetone at low conversion (<5%) of monomers. The copolymer obtained was washed by methanol to remove unreacted monomer and dried in vacuum. The composition of copolymer was determined by ¹H-NMR. The reactivity ratio was estimated by Fineman-Ross plot [12]. From the Fineman-Ross plot for NaSS/130-A copolymerization the monomer reactivity ratios were evaluated to be $r_{\text{NaSS}} = 0.38$ and $r_{130\text{-A}} = 0.021$.

2.4. Gel Preparation

2.4.1. Synthesis of First Networks (Single Network, SN) Gel

The first network gel was synthesized with ATRP of an aqueous solution of 1 M NaSS containing 4 mol% cross-linking agent (9EG-A), initiator (MEE-Br or PEG2000-Br₂) (NaSS/Br = 500), ligand, and catalyst (Cu/Bpy/Br = 1/2.5/1), and was polymerized in a reaction cell containing a pair of glass plates with 2 mm spacing for 24 h.

As a comparison gel, a first network gel was also synthesized via photo-initiated polymerization of an aqueous solution of 1 M NaSS containing 4 mol% cross-

linking agent (9EG-A), and 0.1 mol% initiator (2-oxoglutaric acid), in a reaction cell containing a pair of glass plates with 2 mm spacing using UV radiation for 8 h. Another first network gel was also prepared by photo-initiated polymerization of an aqueous solution of 1 M AMPS containing 4 mol% cross-linking agent (MBAA), and 0.1 mol% initiator (2-oxoglutaric acid), in a reaction cell containing a pair of glass plates with 2 mm spacing using UV radiation for 8 h.

2.4.2. Preparation of Double Network (DN) Gels

All of the first network gels (SN gels) were then immersed in an aqueous solution of 2 M AAm, containing 0.1 mol% MBAA and 0.1 mol% 2-oxoglutaric acid, for 2–3 days until equilibrium was reached, and then were polymerized by photo-initiated polymerization for 8 h. The second network was subsequently synthesized in the presence of the first network. All the above polymerizations were carried out in a glove box.

2.5. Measurements

2.5.1. Swelling Degree, q of the Gels

The amount of water contained in the gel was characterized by the swelling degree, q , which is defined as the weight ratio of the water or sodium chloride solutions with different concentrations of swollen sample to the dry sample. Swelling ratio $q = W_s/W_d$, where W_s and W_d denote the weight of swollen gels and dry gels, $\alpha = W_{as}/W_d$, where W_{as} and W_d denote the weight of gels as prepared and dry gels. Dry gels were obtained by drying in a vacuum until a constant weight was reached.

2.5.2. Mechanical Properties of the Gels

The compressive stress–strain measurements were performed on the gels swollen in water or 1 M NaCl solution for 7 days, using a tensile–compressive tester (Tensilon RTC-1310A, Orientec Company) with the original attachments (made by Arai Seisakusyo). A cylindrical gel sample of 9 mm diameter and 5 mm thickness was set on the lower plate and compressed by the upper plate of the attachment, which was connected to a load cell, at a strain of 10% thickness/min. The strain ratio, γ , is defined by $\Delta L/L$, where L is the initial thickness of the sample and ΔL is the change of the thickness. Compressive modulus was calculated from the stress–strain curve in a strain range of $0 < \gamma < 0.1$. Fracture stress σ was determined as the stress at which visible cracks appear in the samples. Data of σ are given as the average for at least five measurements.

The tear test for the DN gels was carried out using a commercial test machine (Tensilon RTC-1150A, Orientec). Gels were cut in a trouser-shape, which is standardized JIS-K6252 1/2 size ($w = 5\text{--}5.5$ mm; $d = 7.5$ mm; $L = 50$ mm; initial notch = 20 mm), with a gel cutting machine (Dumb Bell Co. Ltd.). The two arms of a test piece were cramped and pulled apart at a constant velocity of 500 mm/min, and the tearing force was recorded. Fracture energy, G , defined as the energy required to create a unit area of fracture surface, is calculated by the following

equation:

$$G = F_{av}/w,$$

where F_{av} is the average tearing force and w is the width of the gels.

2.5.3. Dynamic Light Scattering (DLS) Measurement of the Gels

Dynamic light scattering measurements were performed with the scanning microscopic light scattering system [13]. Dynamic light scattering experiments were carried out on a compact goniometer at respective angles of 40, 60, 90, 125°. A He-Ne laser with 22 mW (the wavelength in a vacuum; $\lambda = 632.8$ nm) was used as the beam through a cylindrical sample tube with 10 mm outer diameter. A typical measuring time at a position was 90 s. The temperature of the sample was kept at 30.0°C. Thirty points per sample were measured by the stepping motor with a step of 10 μ m moving the sample holder vertically. The dynamic component of ensemble-averaged correlation function was rigorously determined from the 30-point data and it was numerically transformed to relaxation-time distribution composed of two logarithmic Gaussian distributions (LGD) [14]. Then the two relaxation modes were quantitatively characterized. Based on the results of previous studies about the two modes [5, 14], the faster mode can be assigned to the cooperative diffusion mode of the second network in DN gels, which is related to the dynamically fluctuating motion of the second network. In the present study, we discuss especially the behavior of this fast mode of the second network because we focus on the sliding motion of the second network.

3. Results and Discussion

Four types of DN gels were prepared from the first network (SN) gels, which were synthesized by atom transfer radical polymerization (ATRP) and photo-initiated free radical polymerization using NaSS and AMPS monomers; this was followed by synthesis of the second network gel in the presence of the first network by photo-initiated polymerization technique using AAm monomers. In order to differentiate the gels, we named samples as follows; ATRP-NaSSBr and ATRP-NaSSBr₂ (or abbreviated as ATRPBr and ATRPBr₂ in figures) for the gels synthesized by ATRP with one-side and double-side initiators, and UV-NaSS and UV-AMPS for the gels synthesized by photo-initiated polymerization. Table 1 shows the component and the polymerization conditions of the gels. It is reported that the acrylamide based monomers are not satisfactorily reactive to ATRP [7–9]. Therefore, AMPS and MBAA were not used to synthesize the first network of DN gels, and only NaSS and 9EG-A were used as monomer and cross-linker, respectively, in ATRP.

3.1. Swelling Degree (q) of the Gels

A different synthesis process of the first network (SN) gels lead to a remarkable difference in the swelling degree, q , of the gels. In water, the SN gel prepared by ATRP showed higher q than that of prepared by photo-initiated polymerization (Fig. 1).

Table 1.
Preparation of DN gels

Sample name	First network			Second network	
	Monomer ^a	Cross-linker ^b	Initiator ^c	Monomer ^d	Initiator
ATRP-NaSSBr (abbr.: ATRPBr)	NaSS	9EG-A	MEE-Br	AAm	UV
ATRP-NaSSBr ₂ (abbr.: ATRPBr ₂)	NaSS	9EG-A	PEG2000-Br ₂		
UV-NaSS	NaSS	9EG-A	UV		
UV-AMPS	AMPS	MBAA	UV		

^a1 M concentration, ^b4 mol% of monomer, ^c0.1 wt% of monomer in photo-initiated polymerization both for first networks and second networks, and polymerized for 8 h; NaSS/Br = 500 in ATRP and polymerized for 24 h, and ^d2 M of concentration. UV = ultraviolet.

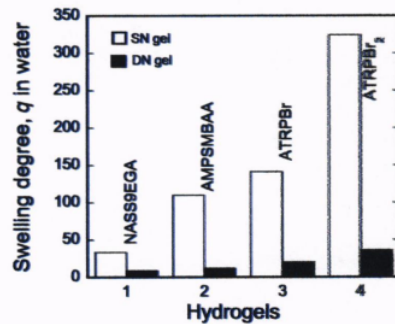


Figure 1. Swelling degree of first network (SN) and DN gels in water.

The highest q (324) was obtained on the sample synthesized by ATRP method using the double-side initiator of PEG2000-Br₂, ATRP-NaSSBr₂ gel, which was almost 10 times higher than that of UV-NaSS gel (33.6) or more than 2 times higher than that of ATRP-NaSSBr gel. The higher swelling degree of the gels prepared by the ATRP method was probably due to the characteristic mesh size and inhomogeneous structure of the gels, relatively larger than that of those prepared by photo-initiated polymerization. It should be noted that the inhomogeneous structure implies some kind of defect in the network structure due to the gelation reaction. In a previous study [15], Furukawa showed that any gel swollen in $q > 22$ contains an inhomogeneous structure due to the gelation reaction. The existence of the inhomogeneous structure in this condition was observed by DLS measurement [13].

In the DN gels, the q had a similar tendency to that of SN gels in water, where the higher the value of q in the SN gel, the higher the q in DN gels (Fig. 1). However, the penetration of the second network gels into the first network gels caused the q

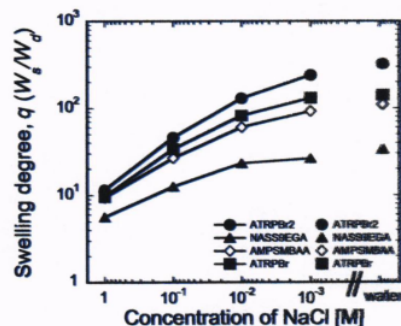


Figure 2. Swelling degree of first network (SN) gels in NaCl solution and water.

of all gels to be decreased drastically. The q of ATRP-NaSSBr₂ DN gel was 36.2, which was one-tenth of that of its SN gel and its net polymer content was only 2.8 wt%. This DN gel was swollen 3 times larger than that of the UV-NaSS DN gel. Drastic decrease of the q in the DN gel synthesized by ATRP was caused by easy penetration of the second network gel into the first network gel as a result of its extensive inhomogeneous structure.

In NaCl solution, the q of SN gels prepared by ATRP decreased drastically as the concentration of NaCl was increased from 10^{-3} M to 1 M due to shrinkage of the gels (Fig. 2). At high NaCl solution concentration (1 M), there was no significance difference in the q observed in the gels prepared by ATRP using one-side or double-side initiators.

3.2. Mechanical Properties of the Gels

Figures 3 and 4 show the relationship between the q and compressive properties of the SN gels in water and 1 M NaCl solutions. In water, fracture stress, σ , and compressive modulus, E , of SN gel, ATRP-NaSSBr and ATRP-NaSSBr₂ were about 4 times lower than that of UV-NaSS gel (Fig. 3(a) and 3(c)), but the fracture strain, λ_F showed the reverse tendency (Fig. 2(b)). Lowering of the σ_F and E was assumed to have been caused by higher values of the q of those gels. These indicated that gels obtained by ATRP were weaker and softer than that of obtained by photo-initiated polymerization. Similar compressive behavior was also observed when the SN gels were soaked in the 1 M NaCl solution (Fig. 4(a)–(c)). However, the σ_F and E of the gels improved significantly due to shrinkage in high salt concentration.

Generally, the σ_F and E of gel decrease as the q increases and show the power-law behavior in water (good solvent). However, ATRP-NaSSBr gel does not obey such a tendency. ATRP-NaSSBr gel was prepared using one-side initiator, MBEE-Br. It suggests that ATRP-NaSSBr gel has a structural defect, comparing to ATRP-NaSSBr₂ gel prepared using the two-side initiator, PEG2000-Br₂. Normally, the E of gel is in directly proportion to the cross-link density of the network: the sample

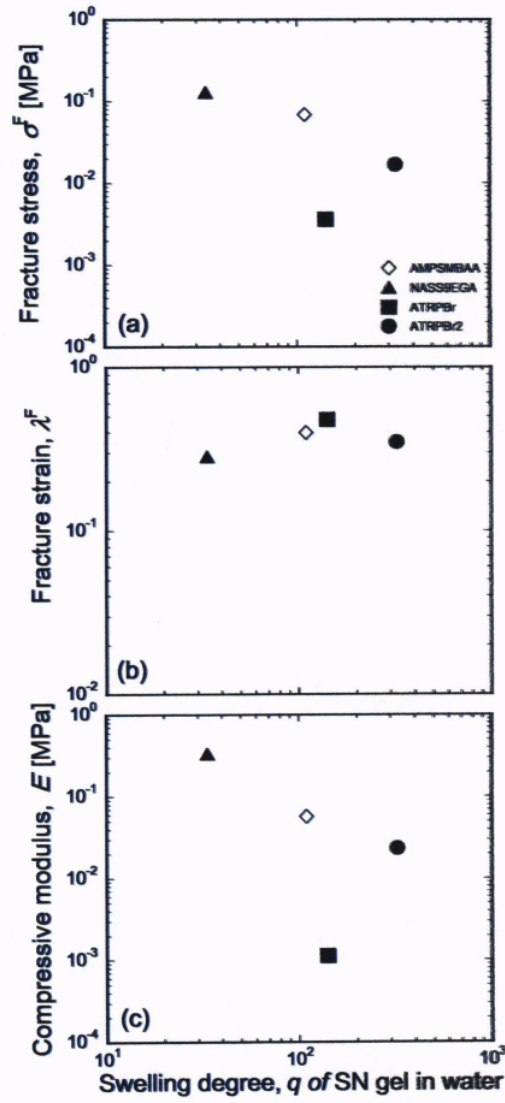


Figure 3. Relationship between compressive properties and swelling degree of the first networks (SN) gels in water: (a) fracture stress; (b) fracture strain; and (c) compressive modulus.

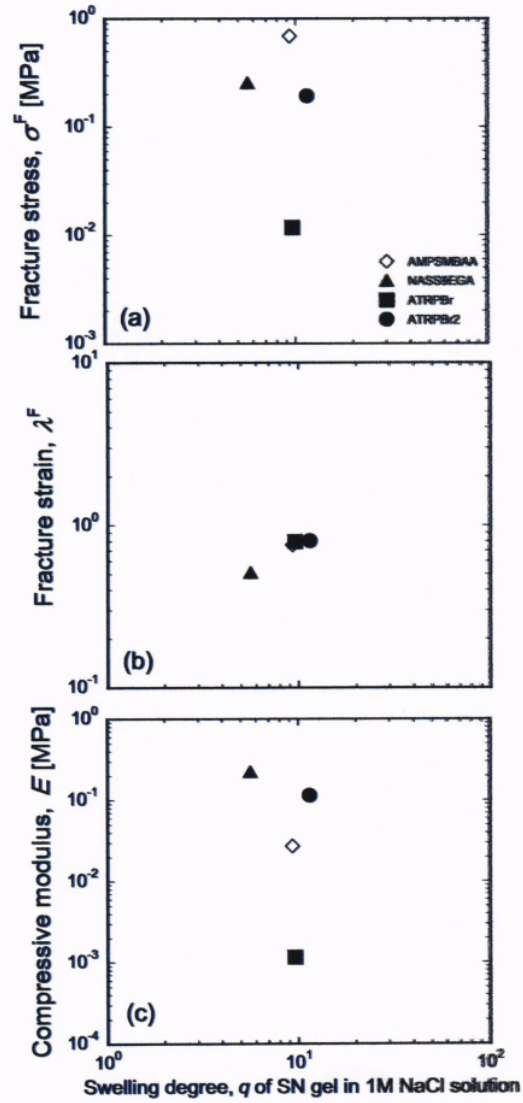


Figure 4. Relationship between compressive properties and swelling degree of the first networks (SN) gels in 1 M NaCl solution: (a) fracture stress; (b) fracture strain; and (c) compressive modulus.

ATRP-NaSSBr₂ has a higher cross-link density than the sample ATRP-NaSSBr, although in the same cross-linker concentration and the same monomer bromide molar ratio, except for the initiator. From the structure of initiators, the initiator PEG2000-Br₂, having an active site on both ends of the molecule, plays a role as cross-linker, resulting in a high cross-link density of gel. Thus, it should be noted that the network structure of SN gels can be controlled by ATRP and especially that the difference of ATRP initiator affects the network structure. The double-side initiator for ATRP is suitable for synthesizing highly swollen SN gel, being similar in tendency to usual SN gels.

Figure 5 shows the relationship between the q and compressive properties of the DN gels in water. Figure 5(a) shows remarkable improving of the σ properties of DN gel from its SN gel. By introducing the second network into the first network gel, the σ of DN prepared by ATRP, ATRP-NaSSBr increased more than 1000 times than its SN gel — from 0.0036 to 1.54 MPa — and for ATRP-NaSSBr₂ increased more than 100 times from 0.0167 to 2.03 MPa. However, these values were not so high compared to the σ of the DN gels of UV-NaSS and UN-AMPS prepared by photo-initiated polymerization due to the extensive inhomogeneous structure of its first network gels, except that it had a high strain ratio because of higher q (Fig. 5(b)). Interestingly, the E of ATRP-Br₂ did not change similar to that of SN gel; meanwhile, the E of ATRP-NaSSBr increased about 50 times compared with its SN gel. These E values were still very much lower than that of UV-NaSS, indicating that the ATRP DN gel was more elastic than that of UV-NaSS gel. Table 2 summarizes the swelling degree and mechanical properties of those DN gels.

The weaknesses of DN gels prepared by ATRP might be explained by the dynamic light scattering (DLS) measurement. In order to obtain the information about the network structure in swollen state, we analyzed the prepared gels by using DLS, as shown in Fig. 6. For all the DN gels, we observed both fast and slow modes as observed before for the usual high-strength DN gels [14]. In the previous study, we had found that, as the amount of the slow mode decreased compared to that of the fast mode, the mechanical strength improved. In the high-strength DN gels, the interaction between the first and the second networks is not static but tight due to the entanglement. In the present study, we found that the amount of the slow mode for the ATRP DN gels was larger than that of the usual DN gels. This was consistent with the mechanical strength of these gels. It means that in ATRP DN gels the entanglement between the first and the second networks was not tight due to the extensive inhomogeneous structure of the ATRP SN gels. In other words, there exists still the small molecular weight of the PAAm chain and there still exists also the non-entangled extensive inhomogeneous structure, which is not favorable to enhance the strength of the DN gel. To develop a stronger DN gel based on NaSS as monomer with ATRP, it is important to increase the concentration of monomer and to use a longer PAAm chain.

Finally, we know that by using ATRP, we can make another kind of first network structure which is different from general photo-initiated polymerization such

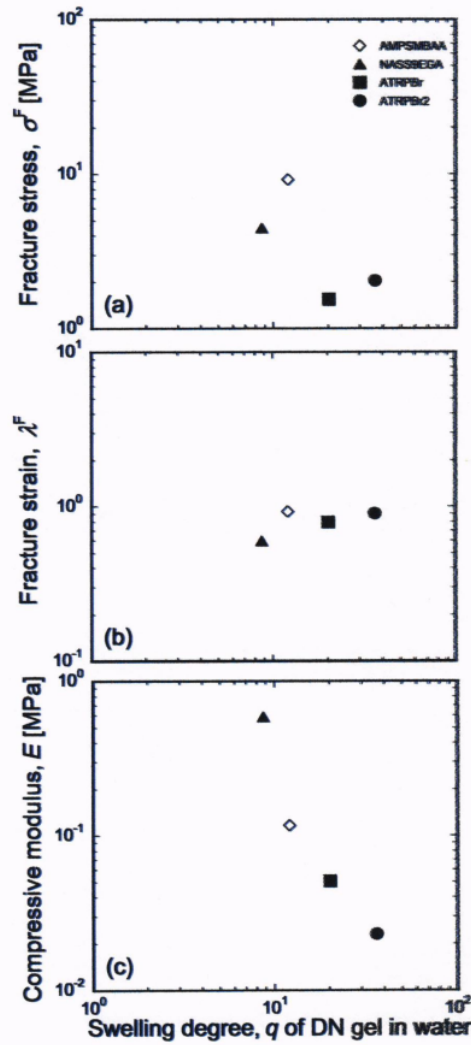


Figure 5. Relationship between compressive properties and swelling degree of the DN gels in water: (a) fracture stress; (b) fracture strain; and (c) compressive modulus.

as have extensive inhomogeneous size. Such structure influences very much the mechanical properties of DN gel: in this case the DN gels synthesized by ATRP become soft and elastic.

Table 2.
Mechanical properties of DN gels

Sample	α	q	Compressive modulus (MPa)	Fracture stress (MPa)	Strain ratio	Fracture energy (J/m^2)
ATRP-NaSSBr (abbr.: ATRPBr)	2.86	20.1	0.051	1.54	0.792	33
ATRP-NaSSBr ₂ (abbr.: ATRPBr ₂)	6.21	36.2	0.023	2.03	0.899	27.4
UV-NaSS	1.53	8.7	0.589	4.47	0.598	74.6
UV-AMPS	1.85	12.1	0.116	9.21	0.925	544

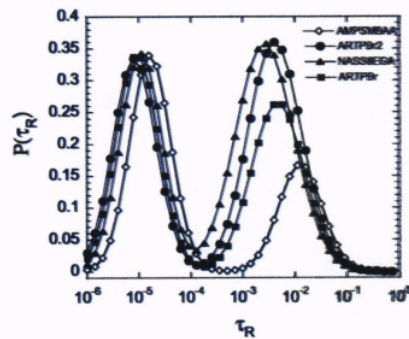


Figure 6. Relaxation-time distribution function $P(\tau_R)$ of various DN gels in water observed by DLS. Scattering angle is 40° . The solid curves are the logarithmic Gaussian distributions fitted to $P(\tau_R)$.

4. Conclusions

We showed that the ATRP method can be used to control the network structure of first network gels for DN gels. By using the ATRP method, an extensive inhomogeneous structure was introduced into the first network gel. The mechanical properties of ATRP first network gels were also improved by second network in DN gel. That means that the interpenetration of long liner chain as the second network into the first network structure with extensive inhomogeneous structure was a kind of universal method to realize the strong gels. The double-side initiator for ATRP was superior for synthesizing highly swollen DN gels. There remain some problems, such as that the size of the inhomogeneous structure in the first gels introduced by ATRP is too large to be improved by liner polymer chains of the second network. However, we think these problems can be overcome in future work and we hope that we can develop superiorly strong DN gels by controlling the first network structure with advanced polymerization technique as ATRP.

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