

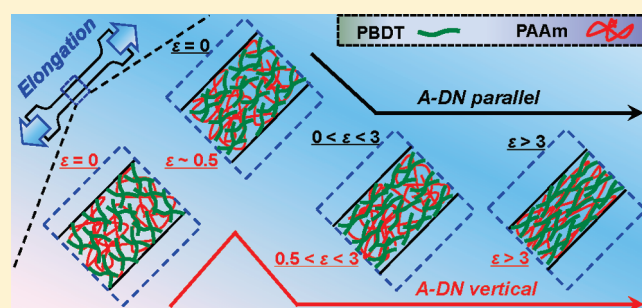
Strain-Induced Molecular Reorientation and Birefringence Reversion of a Robust, Anisotropic Double-Network Hydrogel

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ABSTRACT: A robust, macroscopically anisotropic double-network (A-DN) hydrogel has been developed by combining the first anisotropic, physically cross-linked network of semirigid poly(2,2'-disulfonyl-4,4'-benzidine terephthalamide) (PBDT) and the second chemically cross-linked network of flexible polyacrylamide (PAAm) through double-network technology. Owing to the cooperative orientation of the self-assembled bundle structure of semirigid PBDTs, the A-DN gel shows a very sensitive and strong birefringence change upon deformation, which is always dominated by PBDT for the wide strain range investigated ($\epsilon = 0-18$), regardless the fact that PAAm is in large excess. When the initial alignment of PBDT is vertical to the elongation direction, a birefringence reversion occurs at $\epsilon \sim 0.5$, indicating that the initial vertical alignment of PBDT is overwhelmed by the strain-induced parallel alignment, even at such a small strain due to the cooperative reorientation of PBDT.



INTRODUCTION

In recent decades, biomimetic and bioinspired hydrogels have received widespread attention because of their robust functions and potential applications in artificial tissues.¹ Most biotissues are in a soft, wet, gel-like state and have well-ordered structures that play a significant role in executing the functions of living organisms.² However, commonly synthesized hydrogels lack an ordered structure and have weak mechanical properties that limit their functionalities and applications in soft actuators, mechanical-optical sensors, and tissue engineering.³

There have been many efforts toward developing macroscopically ordered hydrogels by molecular self-assembly coupled with physical or chemical cross-linking; these gels usually incorporate additional functionalities.^{4,5} In a previous paper, we reported the synthesis of centimeter-scale anisotropic hydrogel by using a dialysis method initially developed by Dobashi and co-workers.⁶⁻⁸ Anisotropic hydrogel was obtained by the simple diffusion of a multivalent salt CaCl_2 into the semirigid polyanion poly(2,2'-disulfonyl-4,4'-benzidine terephthalamide) (PBDT) solution, where Ca^{2+} behaves as a physical cross-linker. We have found that the semirigid polyanion PBDTs make a reorientation at the Ca^{2+} diffusion flux driven by the complexation to form mesoscopic fibrous bundles that are staggered with slight directional preference parallel to the Ca^{2+} diffusion front (i.e., perpendicular to the diffusion direction).⁶

It should be interesting to elucidate how the physically cross-linked PBDT gel with staggered rigid bundles behaves under the elongation that usually induces molecular orientation transition and birefringence change in liquid crystalline (LC) elastomers.⁹

If the macroscopically anisotropic hydrogel with mechanical tunable birefringence can be obtained, it will process promising applications in materials science, such as in mechano-optical sensors.

Unfortunately, the physical PBDT gel is lacking stability and toughness, and it will be dissolved in a solution with high ionic strength or broken under a tensile strain larger than 80%.⁶ To improve the mechanical properties of physical LC gel, use of the double-network (DN) technology discovered by our group should be tremendously effective.¹⁰ The DN gels are typically composed of polyelectrolyte as the first network and a hydrophilic neutral polymer as the second network. In our current work, we synthesize the anisotropic double-network (A-DN) hydrogel by two steps: the first physical PBDT gel is developed by the dialysis of PBDT into an aqueous solution of Ca^{2+} , and the second network of flexible poly(acrylamide) (PAAm) is synthesized by photopolymerization after swelling the previous physical gel into the acrylamide precursor solution. The developed A-DN gel possesses both macroscopically anisotropic structure and robust mechanical properties.

We investigate the cooperative molecular orientation of the A-DN gel by observing the birefringence change during the elongation. The alignment of PBDT along the elongation direction is enhanced by the applied strain and exhibits positive

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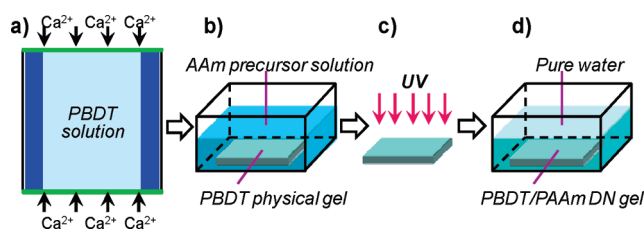


Figure 1. Scheme for the synthesis of an anisotropic double-network gel. The first network is a physically cross-linked LC gel synthesized by dialysis of PBDT solution in Ca^{2+} aqueous solution (a). The as-prepared physical gel is immersed into the precursor solution consisting of acrylamide monomer, chemical cross-linker, and photoinitiator (b). After UV initiated polymerization (c), the synthesized PBDT/PAAm DN gel is obtained and then swelled in a large amount of pure water to achieve equilibrium (d).

birefringence of PBDT, although the PAAm shows weak negative strain-induced birefringence. When the alignment of PBDT is vertical to the elongation direction, the molecular reorientation and birefringence inversion occur at a quite small strain, $\varepsilon \sim 0.5$, because the original preferential alignment of PBDT perpendicular to the elongation direction is overwhelmed by the strain-induced parallel molecular orientation. This strain-induced molecular reorientation and birefringence reversion originate from the specific bundles structure of PBDTs that are physically cross-linked by Ca^{2+} and staggered with weakly preferential orientation without being disturbed in the A-DN gel, leading to the molecular orientation and birefringence sensitive to the external strain.

EXPERIMENTAL SECTION

Synthesis of Anisotropic Double-Network Hydrogel. PBDT, a water-soluble semirigid polyanion, was synthesized by an interfacial polycondensation reaction.¹¹ The synthesized PBDT had a super-high weight-average molecular weight, $M_w \sim 2.1 \times 10^6$. The aqueous solutions of PBDT showed a significant low critical concentration of nematic liquid crystal, C_{LC}^* , of 2 wt %. The synthesis of anisotropic double-network (A-DN) gel was accomplished by two steps: the first anisotropic, physical gel was developed by a dialysis process, and the second network was synthesized by photopolymerization after swelling the previous physical gel into a precursor solution (Figure 1). One weight percent of PBDT solution was poured into a mold, consisting of a pair of parallel glass plates separated by a silicone spacer with a 1 mm thickness (Figure 1a). Two opposite sides were left open to permit uniaxial diffusion of multivalent cations into the mold that was wrapped by dialysis membranes (BX-100, Bel-Art Products). The mold containing the PBDT solution was dialyzed into 0.5 M CaCl_2 solution and gelled within 10 h; the platelike PBDT gel was obtained after 1 day in order to reach the diffusion equilibrium. This first physical gel was taken out from the mold and then immersed in a precursor solution containing 2 M acrylamide (AAM) (Junsei Chemical Co., Ltd.), 0.01 mol % (relative to the monomer) N,N' -methylenebisacrylamide (MBAA, used as the chemical cross-linker) (Tokyo Kasei Co., Ltd.), and 0.01 mol % 2-oxoglutaric acid (used as the initiator) (Wako Pure Chemical Industries, Ltd.) (Figure 1b) for 2 days. The polymerization of the second network was subsequently carried out under a nitrogen atmosphere with a UV lamp for 8 h (Figure 1c). The prepared gel, consisting of two independent polymer networks entangled with each other, was swelled in pure water for 1 week to achieve swelling equilibrium (Figure 1d).

Synthesis of Poly(acrylamide) Gel with and without Randomly Dispersed PBDT. The precursor solution of 2 M AAM, 2 mol % (relative to the monomer concentration) MBAA, and 0.01 mol % 2-oxoglutaric acid was poured into the reaction cell consisting of a pair

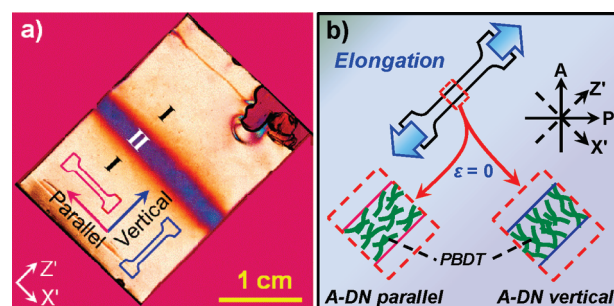


Figure 2. Optical microgram of the physical LC gel observed under crossed polarizers with 530 nm tint plate (a) and illustration of the sample preparation for the tensile test (b). I and II noted in part a indicate the outer region and inner region of the gel. Parallel and vertical noted in part a indicate that the sample and following elongation is parallel or perpendicular to the alignment of PBDT molecules, as shown in part b. In the illustration b, Ca^{2+} ions and PAAm chains are omitted for simplicity. A, analyzer; P, polarizer; X' , fast axis of the tint plate; Z' , slow axis of the tint plate.

of parallel glass plates with a spacing of 1 mm. The poly(acrylamide) (PAAm) gel was synthesized by photopolymerization at room temperature. Photopolymerization was carried out for 8 h under argon atmosphere. The as-prepared gels were immersed in a large amount of water for 1 week to attain equilibrium. The PAAm gel containing PBDT was synthesized in a similar way, of which 1 wt % PBDT was incorporated into the precursor solution. In this PBDT-containing PAAm gel, PBDT molecules did not form assembled structures and were randomly dispersed in the gel matrix.

Observation under Polarizing Optical Microscope (POM).

Liquid crystalline structures of the physical gel and A-DN gel were identified using a POM (Nikon, LV100POL); a 530 nm tint plate was applied to distinguish the PBDT molecular orientation in the synthesized gel. The overall image of the entire LC gels was obtained by stacking dozens of micrographs. The birefringence, Δn , was measured from the retardation values using a Berek compensator. The birefringence of gels during elongation was measured by POM after fixing the two ends of sample on a vernier caliper and elongating it to a certain strain.

Tensile Tests of A-DN Gels. Tensile mechanical properties were measured with a commercial test machine (Tensilon RTC-1150A, Orientec Co.). The gels after reaching equilibrium swelling in water were cut into a dumbbell shape standardized as the JIS-K6251-7 sizes (length, 35 mm; width, 6 mm; thickness, 3–4 mm; gauge length, 12 mm; inner width, 2 mm) with a gel cutting machine (Dumbbell Co., Ltd.). The sample length between two chucks was ~ 15 mm. Two kinds of samples were cut out from the A-DN gel in the directions parallel and perpendicular to the PBDT alignment direction (Figure 2). The stress was recorded while the sample gel was stretched at a constant rate of 100 mm/min. The elastic modulus of the gel was calculated by measuring the initial slope of the stress–strain curve ($\varepsilon < 0.1$).

RESULTS AND DISCUSSION

The 1 wt % PBDT aqueous solution is transparent and optically isotropic. After the dialysis process, the synthesized physical LC gel shows strong birefringence observed by POM (Figure 2a). The PBDT molecules orient perpendicular to the Ca^{2+} diffusion direction in the outer regions of the gel, whereas they align parallel to the diffusion direction in the narrow central region (details were described in the previous paper, ref 6). As described in the previous paper, PBDT and its assembled fibrous bundle are staggered in the gel and only possess weakly preferential molecular alignment.⁶

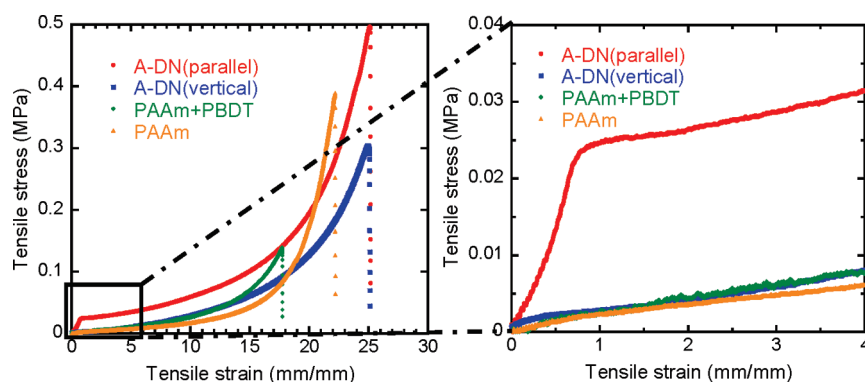


Figure 3. Stress–strain curves of A-DN gel in parallel and vertical direction, PBDT-containing PAAm gel, and PAAm gel.

Both the oriented structure and birefringence can be fully maintained after introducing the second network. The incorporation of the condensed, flexible PAAm chains greatly improves the mechanical properties of the physical PBDT gel without disturbing the staggered bundle structure of PBDT. The samples for tensile test are cut from the outer region of the A-DN gel in two directions, parallel and vertical to the alignment of PBDT molecules (Figure 2b) and are noted as A-DN parallel and A-DN vertical in the following part.

The stress–strain curve shows that the A-DN gels possess robust mechanical properties, especially excellent extensibility (Figure 3). The A-DN parallel sample exhibits a yield point at 25 kPa. On the other hand, the A-DN vertical sample, as well as the PAAm gel containing PBDT, does not have the yielding point but shows the similar curve as the PAAm gel. The elastic modulus, E , values of A-DN parallel and vertical are ~ 22 and ~ 6 kPa, respectively; the latter one is similar to the elastic modulus of the isotropic PAAm gels with and without randomly dispersed PBDT, ~ 4 kPa. The elastic modulus of A-DN gel is much smaller than that of physically cross-linked anisotropic PBDT gel with E of ~ 130 and ~ 50 kPa in parallel and vertical direction, respectively.⁶ Incorporating the second PAAm network leads the A-DN gel to swell slightly (~ 1.1 times of its original length) in water because of the high osmotic pressure of the loosely cross-linked PAAm network; this swelling of the PAAm network might partially destroy the physically cross-linked network of PBDT and thus decreases the elastic modulus. The existence of yielding point and relatively high elastic modulus in A-DN parallel sample is in agreement with the preferential alignment of PBDT and its fibrous bundle perpendicular to the diffusion direction.

The physical LC gel and A-DN gel exhibit very strong birefringence due to the oriented PBDT molecules. As elucidated previously, PBDT is an optically positive LC polymer, whereas PAAm shows a negative birefringence after the elongation-induced molecular orientation.^{5g,12,13} Therefore, it should be interesting to investigate the change of cooperative birefringence and the behavior of physically cross-linked staggered PBDT bundles during the tensile test of A-DN gel, of which elongation enhances the orientation of two polymers in line that have positive and negative birefringence, respectively. Figure 4a shows the birefringence of A-DN parallel and vertical gels, as well as PAAm gel with and without PBDT, after being elongated at a certain strain. The birefringence of both A-DN parallel and vertical samples increases with the increment of applied strain. Actually, the birefringence first increases dramatically with strain, ε , up to a transition point $\varepsilon_t \sim 3$ and then increases slightly with the further elongation. The

dramatic increment of birefringence of A-DN gel when $\varepsilon < \varepsilon_t$ and suppressed strain-enhanced birefringence when $\varepsilon > \varepsilon_t$ should relate to the strain-induced molecular alignment of PBDT and PAAm with opposite sign of the birefringence.^{9,13,14}

The original A-DN vertical sample shows a negative sign birefringence before elongation at $\varepsilon = 0$; however, the birefringence reverses to positive after a slight elongation at $\varepsilon > 0.2$ (Figure 4b). The birefringence reversion of the A-DN vertical gel is confirmed by the birefringent images observed under POM. The sample at $\varepsilon = 0$ and 1 shows negative and positive birefringence, respectively, since both of them are first white-gray colored and can be judged by insertion of the 530 nm tint plate (images D and F of Figure 4c). In terms of the birefringent colors, we found that PBDTs orient in northwest direction in image D and in southwest direction in image F of Figure 4c. That is to say, the slight elongation induces the molecular reorientation of PBDT and the reversion of birefringence. At the relatively small strain, that the strain-induced molecular orientation and birefringence of PAAm chains are negligible will be illustrated in the following part. It should be noted that image C in Figure 4c showed yellow birefringence because of the birefringence shifting into the second-order color rather than the birefringence reversion.

The essential origin of the apparent alignment reversion of PBDT in A-DN vertical sample comes from the staggered PBDT and its fibrous bundle with slightly preferential alignment. The preferential alignment of PBDT and its fibrous bundle is vertical to the elongation direction and easily surpassed by the alignment parallel to the elongation. On the other hand, the A-DN parallel sample with PBDT alignment parallel to the elongation has no alignment reversion of PBDT and therefore does not show the birefringence reversion.

To elucidate the effect of self-assembled structure and physical cross-linking of PBDT on the strain-induced molecular orientation, we further studied the strain-induced birefringence of PAAm gel containing randomly dispersed PBDTs (Figure 4d), without adding any multivalent cations. The PBDT-containing PAAm gel is optically isotropic at $\varepsilon = 0$ and shows weak positive birefringence at $2 < \varepsilon < 7$ because of the elongation-induced PBDT orientation to a certain degree.¹⁵ However, the increment of Δn with ε is much slower than that of A-DN gels. As a result, the birefringence of PBDT-containing PAAm gel, $\Delta n \sim 3 \times 10^{-5}$, is much weaker than that of A-DN gels, $\Delta n \sim 8 \times 10^{-4}$, at the same strain of $\varepsilon = 3$. Therefore, the abrupt birefringence change in A-DN gels is caused by the cooperative orientation of the physically cross-linked PBDT bundles. The molecular alignment reversion of A-DN vertical sample under a small strain is also

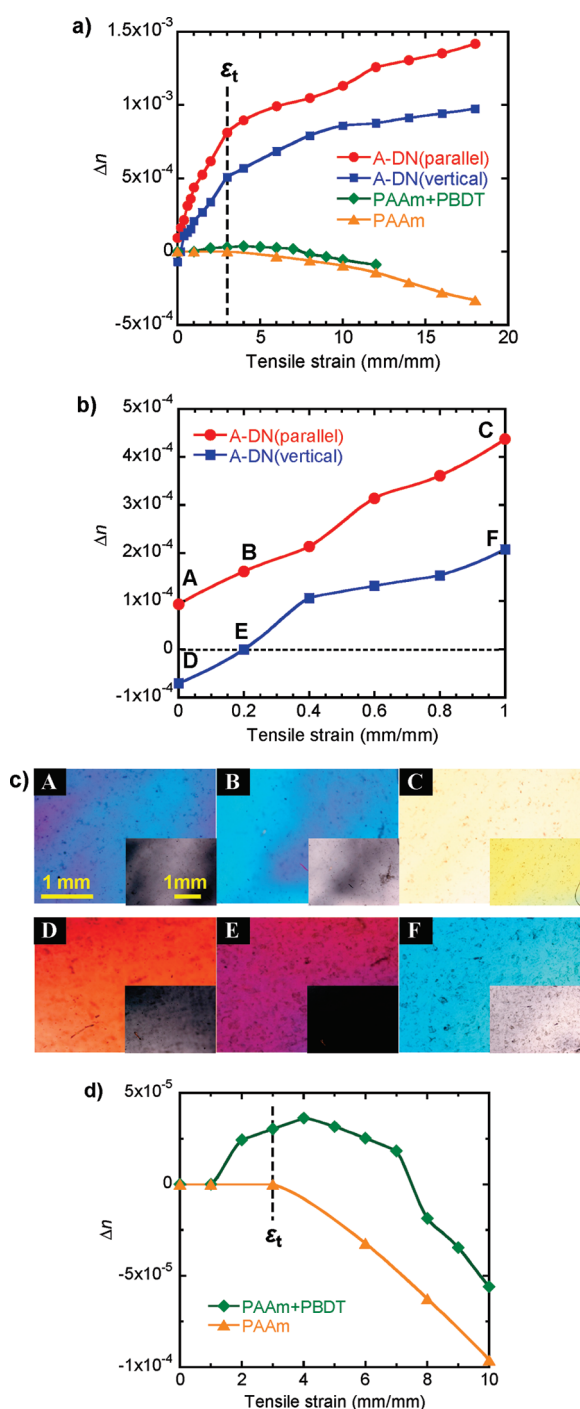


Figure 4. (a) Birefringence change of A-DN gel elongated along the direction parallel and vertical to PBDT alignment, PBDT-containing PAAm gel, and PAAm gel under various strains. (b) Enlarged plot to show the birefringence change of parallel and vertical A-DN gels with small strains ($\epsilon < 1$). (c) Optical micrographs of the A-DN gels observed under crossed polarizers with 530 nm tint plate. Micrographs A–F correspond to points A–F in part b, and the insets are the images observed under crossed polarizers without the tint plate. (d) Enlarged plot to show the birefringence change of PAAm gels with and without PBDT during the tensile test.

associated with the specifically staggered structure of PBDT and its fibrous bundle with slight orientation, rather than the complete reorientation of PBDT molecules from one direction to another direction.

Table 1. Birefringence of Parallel and Vertical A-DN Gels before, during ($\epsilon = 10$), and after the Elongation

sample	Δn		
	before ($\epsilon = 0$)	elongation ($\epsilon = 10$)	after ($\epsilon = 0$)
A-DN (parallel)	9.4×10^{-5}	1.1×10^{-3}	9.7×10^{-5}
A-DN (vertical)	-7.2×10^{-5}	8.6×10^{-4}	-5.5×10^{-5}

The strain-induced molecular alignment and birefringence of both A-DN parallel and vertical samples are reversible. The birefringence is much enhanced by the elongation; however, it can almost come back to its original state after release of the applied stress/strain (Table 1). After elongation, the birefringence of A-DN vertical ($\epsilon = 0$) slightly decreases and that of A-DN parallel slightly increases, suggesting that strain-induced alignment of PBDT along the elongation direction is slightly retained in the samples. The sample after elongation has the same shape as the original one, indicative of no residual strain due to the nature of the PAAm network. We speculate that the PBDT bundles do not slide out from the local PAAm network, even under a large strain. However, the elastic modulus of A-DN parallel sample after elongation test decreases to the level of PAAm gel, indicating the destruction of first physically cross-linking of PBDT molecules by the elongation.

The second network of PAAm, having larger quantity than the first network of PBDT (the monomeric repeating unit ratio and mass ratio of PAAm to PBDT are 99:1 and 27:1, respectively),⁷ should play a role in the birefringence change under elongation, since the applied strain should induce polymer chain alignment.^{9,13,14} Haraguchi and co-workers reported the birefringence reversion of nanocomposite hydrogels during uniaxial deformation, because the gel contains the opposite optical materials, i.e., positive exfoliated clay platelet and negative poly(*N*-isopropyl acrylamide).^{13c} However, we have not observed the birefringence reversion between the positive PBDT and negative PAAm, the two networks of the A-DN gel. The birefringence is always dominated by the PBDT in the A-DN gel, and the birefringence reversion in Figure 4b originates from the PBDT molecular reorientation of A-DN vertical gel under a small strain. This is different from the results for PBDT-containing PAAm gel that show weak positive birefringence at a certain range, $2 < \epsilon < 7$, corresponding to the strain-induced alignment of PBDT molecules.¹⁵ However, the birefringence decreases to negative value after further elongation. At that moment, the strain-induced alignment of PAAm chains with negative optical property plays a dominant role in the collective birefringence of the gel (Figure 4d). The PAAm gel without PBDT exhibits a monotonic decrement of birefringence from zero to negative value with the increment of strain when $\epsilon > 3$. These results coincide well with the birefringence of A-DN samples that changes from dramatic increment to slow further increment at approximately $\epsilon_t = 3$, as shown in Figure 4a.

We stress here that the strain-induced alignment and birefringence of PAAm chains are not so notable; Δn is less than 5×10^{-5} , even at a very large strain of $\epsilon = 15$, compared with 1×10^{-3} for A-DN gels at $\epsilon = 10$. The different enhancement extent of PBDT and PAAm causes the absence of the birefringence reversion in A-DN gel; indeed, the birefringence reversion occurs, despite being very weak, in the PBDT-containing PAAm gel during the elongation due to the competition of polymers with opposite birefringence (Figure 4d). We also stress that the strain-induced PBDT alignment and birefringence enhancement in the PBDT-containing

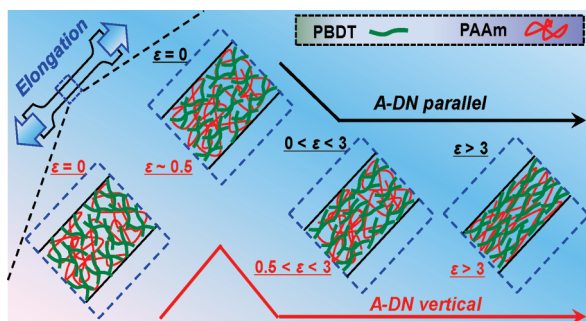


Figure 5. Illustration of the orientation change of PBDT and PAAm molecules in A-DN gels during the elongation. The PAAm chains in the original A-DN parallel and vertical samples are isotropic, whereas the PBDTs in A-DN parallel and vertical samples orient parallel and perpendicular to the elongation direction, respectively. During the elongation process, the alignment of PBDTs in A-DN parallel sample is dramatically enhanced when the strain $\varepsilon < 3$. Meanwhile, the PAAm chains are still in an isotropic state. Further increment of ε enhances orientation to align in the elongating direction for PBDT as well as PAAm chains. However, the strain-induced birefringence of PAAm is much weaker than that of PBDT molecules. Regarding the A-DN vertical sample, the initial orientation of PBDTs is perpendicular to the elongation direction that is overwhelmed by the strain-induced orientation along the elongating direction at $\varepsilon = 0.5$. Further increment of ε induces similar molecular orientation change to that of A-DN parallel sample.

PAAm gel are much less effective than that in A-DN gel. The PBDT molecules in A-DN gel are sensitive to external stress and strain because PBDTs forming mesoscopic fibrous bundles and being physically cross-linked by Ca^{2+} are easily stretched by the applied stress/strain. If the semirigid PBDTs form long and rigid fibrous bundles, under applied strain they should orient easily and cooperatively. In addition, the physical cross-linking of PBDTs by Ca^{2+} should make the deformation (strain) of the PAAm network act more effectively on the PBDT and its bundle, rendering their orientation along the elongation direction. In PBDT-containing PAAm gel, the above two points are absent; the strain-induced molecular orientation of randomly dispersed PBDT molecules should be much less effective.

On the basis of the above results, we propose an overall picture for the change of birefringence and molecular alignment in A-DN gel with the applied stress/strain (Figure 5). In the original state, PBDT and its fibrous bundle in A-DN parallel sample orient slightly parallel to the elongation direction, whereas the PAAm chains are isotropic. At the preliminary stage of elongation, $0 < \varepsilon < 3$, the alignment of PBDT and its fibrous bundle in A-DN parallel sample is dramatically enhanced. However, the PAAm chains are still in isotropic state; the strain-induced orientation is not notable for PAAm. As the strain increases further ($\varepsilon > 3$), the PBDT alignment gradually increases further. At this stage, the elongation also induces the alignment of PAAm chains. However, the strain-induced birefringence of PAAm is much weaker than that of PBDT molecules, due to the very flexible nature of PAAm. Therefore, the birefringence of the A-DN sample mainly attributes to the PBDT molecules. On the other hand, the initial alignment of PBDTs in A-DN vertical sample is perpendicular to the elongation direction. The weak orientation of PBDT and its fibrous bundle is overwhelmed by the strain-induced alignment along with the elongation direction when $\varepsilon > 0.2$. In this period, the birefringence inversion can be observed under POM, as shown in Figure 4b,c. The strain-induced PBDT alignment along the elongation

direction is enhanced further with the increment of ε , similar to that of A-DN parallel sample. When $\varepsilon > 3$, the strain-induced orientation of PAAm chains plays a role but is much weaker than that of PBDT, resulting in the modest increase in the collective birefringence of A-DN gel with the further increment of the strain. In the process of this strain-induced strong orientation of PBDT molecules in A-DN gel, the stacked bundle structure formed by Ca^{2+} cross-linking is found to be essential.

CONCLUSIONS

We have developed an anisotropic double-network hydrogel by integrating the first anisotropic, physically cross-linked network of semirigid PBDT with the second loosely cross-linked network of flexible PAAm. These A-DN gels possess robust mechanical properties, especially good extensibility. Due to the oriented structure of PBDT and its fibrous bundles, the elongation of the gel along with the alignment has a yielding point, whereas the sample perpendicular to the alignment does not. This gel has higher elastic modulus along the alignment of the PBDT than that of the perpendicular direction. Furthermore, we demonstrate that the birefringence of A-DN gel is enhanced by the elongation due to the strain-induced orientation of polymer chains. A-DN vertical sample shows a birefringence reversion at a slight strain, when the alignment of PBDT perpendicular to the elongation direction is overwhelmed by the strain-induced alignment along the elongation direction. At large strains, the strain-induced alignment of PAAm chains also plays a role; however, the birefringence of negative PAAm is much weaker than that of the positive PBDT, and thus the collective birefringence of the gel slowly increases further. By comparing with the behavior of PAAm gel containing randomly dispersed PBDTs, we conclude that the observed PBDT dominating birefringence change in A-DN gels is caused by the cooperative orientation of fibrous bundles of PBDT. This strain-induced molecular alignment and gel birefringence are reversible. The A-DN hydrogels, having both macroscopically optical anisotropy and robust mechanical properties, should play a crucial role in material sciences, such as artificial biotissues and stress-optical sensor.

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(15) In PBDT-containing PAAm hydrogel, the apparent positive birefringence is the collective birefringence of PBDT and PAAm. Actually, when $\varepsilon > 3$, PAAm chains are stretched by the applied stress/stain to exhibit negative birefringence, which exceeds the strain-induced positive birefringence of PBDT at $\varepsilon > 7$.