How to Choose a Secondary Interaction to Improve Stretchability of Associative Polymers?

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association improves the stretchability, and better improvement has been achieved for the triple hydrogen bonds. In comparison, the introduction of quadruple hydrogen bonds that are equally strong as the ionic association does not show this type of improvement. This result strongly indicates that there is an optimized strength ratio between the first (the stronger ionic) network and the secondary (the weaker hydrogen-bonding) network, i.e., the secondary network should be considerably weaker but still not too weaker than the first network. When this condition is satisfied,



continuous dissociation and association of the secondary network weaken the chain retraction after the strain-induced breakup of the first network, thereby suppressing the formation of defects or microscopic cracks that potentially grow into the macroscopic fracture.

1. INTRODUCTION

The stretchability of associative polymer is important in polymer processing, particularly when the dominant flow field is the elongational flow, e.g., in fiber spinning and membrane blowing processes.^{1–5} The stretchability of polymer melts and solutions, including both associative and nonassociative polymers, were examined intensively in the past ten years.^{6–22}

For associative polymers, extensive studies demonstrated that stretchability can be improved by changing the polymer backbone, the sticker species, and the degree of gelation.^{8,10,22} For example, Hassager, and co-workers⁸ found that unentangled associative networks based on poly(tetramethylene glycol) were brittle when the Weissenberg number was higher than one, but copolymerization with poly(ethylene glycol) greatly improved the extensibility. Huang and co-workers¹⁰ found that the stretchability of entangled poly(styrene-co-4vinylbenzoic acid) could be improved by neutralizing with "Jeffamine" type diamines having a plasticizing effect. Vlassopoulos and co-workers²² found that for 2-ureido-4[1H]pyrimidinone (UPy)-based associative polymers, the brittle-to-ductile transition occurred in parallel with a transition from shear strain hardening to shear strain thinning behavior.

Our previous studies have also been devoted to understanding the molecular-level mechanism of the brittle-toductile transition of unentangled associative polymers.^{23,24} To this end, the most conveniently tunable parameter is the number density of association groups that are usually referred to as "stickers".^{10,25–34} We examined a change in stretchability along with the sol-to-gel transition.²³ We found that the stretchability upon applying the "fast elongational flow" increased by decreasing the degree of gelation ε . Here, the fast elongational flow refers to the flow field where the Weissenberg number Wi, defined as a product of extension rate $\dot{\varepsilon}$ and terminal relaxation time τ_i is larger than 1. For those samples well above the gel point, the stretch ratio λ upon application of the fast elongational flow (Wi > 1) was well predicted by $\lambda = N_{bb}^{1/2}$, where N_{bb} is an average number of Kuhn segments per network strand. This stretch ratio could be rationalized by considering a strand with an unperturbed length $\sim N_{bb}^{1/2}$ that is stretched to its maximum length $\sim N_{bb}$. More importantly, we identified an extremely stretchable region near the gel point where the majority was the sol chains (and the gel network became the minority). The sample was stretched up to the limit of the equipment (i.e., a Hencky strain $\varepsilon_{\rm H}$ of 5 that corresponds to a stretch ratio of $\lambda = \exp(5) = 148$, which is much higher than $N_{\rm bb}^{1/2}$ without fracturing even upon application of a high extension rate with $Wi \sim 10$.

To explain this phenomenon, we proposed that the high stretchability was owing to the structural adjustment after the

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Figure 1. Chemical structures and expected linear viscoelasticity of the three types of double networks.

strain-induced dissociation. Namely, when the network strands were sparse, the strain-induced breakup was not intensive and thus the broken strand could find another partner to reassociate, and the continuous dissociation and reassociation along the stretch direction enabled the system to exhibit a pseudo-flow behavior without the macroscopic fracture. The denser network, in the opposite case, exhibited the macroscopic fracture at $\lambda = N_{\rm bb}^{1/2}$ because the strain-induced breakup was intensive when the network strands were stretched to their limit and the network structure could hardly be reconstructed.

In the molecular picture explained above, structural reconstruction is critical for the improvement of stretchability. Then, a natural question is: whether higher or lower chain mobility is more preferred for improving the stretchability? Recently, we designed a model system that enabled us to answer this question.²⁴ We used sulfonated polystyrene with two ionic groups per chain, on average, as the model system. Since dissociation of either of the two stickers belonging to the same chain would immediately lead to chain relaxation, the terminal relaxation time roughly equaled to the sticker dissociation time. We used mixed counterions that enabled us to tune the association energy in a wide range. We found that the brittle-to-ductile transition was consistently observed in a diagram constructed using two Weissenberg numbers, Wi and Wi_{R} , where the former and latter were defined with respect to the terminal relaxation time (~ion dissociation time) and the Rouse time, respectively. For the fast elongation with Wi >1 and $Wi_R < 1$, the sample was stretched up to a Hencky strain of 4 only when $Wi_{\rm R}$ was above a critical value. This result strongly suggested a larger Rouse time (but still smaller than $1/\dot{\varepsilon}$) and accordingly the lower intrinsic chain mobility was preferred for improving stretchability. We proposed that the strain-induced breakups would lead to the chain retraction for Wi > 1 and $Wi_{R} < 1$, and accordingly, a drop in the localized stress. The stress drop might lead to the unsteady flow and the formation of the defects (or microscopic cracks) that potentially grow into the macroscopic fracture. The larger

 $Wi_{\rm R}$ resulted in the stronger energy dissipation and the weaker retraction under the elongational flow, and thus, the brittle-to-ductile transition occurred at sufficiently large $Wi_{\rm R}$.

Although extensive studies explained above show that the brittle-to-ductile transition occurs through changing the polymer backbone, the sticker species or the degree of gelation, the more frequently faced problem in practice is to tune the stretchability for the associative polymers with fixed backbone and sticker species and without sacrificing the hardness. To this end, one frequently explored pathway is to introduce a secondary weaker association to "dissipate" the energy more efficiently.^{35–45}

In this study, we examine the mechanism of this strategy from the molecular level. We choose the ionomers that are intrinsically brittle as the first (the stronger) network, and three types of hydrogen bonds (dual, triple, and quadruple hydrogen bonds) as the secondary (the weaker) network to study the change in stretchability. The chemical structures of the double networks are shown in Figure 1. We find that the association strength of the hydrogen bonds changes systematically: The dual and triple hydrogen bonds are considerably weaker than, while the quadruple hydrogen bond is comparable to, the ionic association. More importantly, we find that the highest improvement of stretchability has been achieved using the triple hydrogen bonds as the secondary association. This result lends support to the molecular picture that the preferred secondary network should be considerably weaker than, but not too weaker than the first network. Under this condition, the continuous breakup and formation of the secondary network can be activated to effectively dissipate the energy as well as suppress the sudden chain retraction and stress drop after the strain-induced dissociation of the first network, thereby enabling network reconstruction during the elongational flow.

2. EXPERIMENTAL SECTION

2.1. Materials. The reactants *n*-isopropyl methacrylamide, 2-amino-4-hydroxy-6-methylpyrimidine, thymine, and melamine were

purchased from Macklin Reagent Co., Ltd. 3-bromo-1-propanol, triethylamine, methacryloyl chloride, tetrabutylammonium iodide, and 2-isocyanatoethyl methacrylate were supplied by Energy Chemical. Hexyl methacrylate (HMA, supplied by Aladdin) used as a monomer was passed through a column of basic alumina to remove the polymerization inhibitor. 2-cyanoprop-2-yl-dithiobenzoate (CPDB, purchased from Sinocompound Catalysts Co. Ltd.) was used as a chain transfer agent (CTA), and 2,2'-azobis(2-methylpropionitrile) (AIBN, J&K), used as an initiator, was recrystallized from ethanol before use. The solvents including dichloromethane (DCM), acetone, *n*-hexane, ethyl acetate, methanol, and chloroform (CHCl₃) were purchased from Beijing Chemical Reagents Co., (analytical purity); chloroform-*d* (CDCl₃), dry *N*,*N*-dimethylformamide (DMF), and dry dimethyl sulfoxide (DMSO) were purchased from Energy Chemical.

2.2. Synthesis and Characterization. Two monomers, 3-(thymin-1-yl) propyl methacrylate and 2-(2-ureido-4[1H]-6-methylpyrimidinone) ethyl methacrylate (UPy-MA), were synthesized according to the literature studies, 46,47 as explained in Schemes S1– S3 of the Supporting Information (SI). The pure ionomer samples were synthesized in our previous study.²³ The samples contain only hydrogen-bonding groups and both ionic and hydrogen-bonding groups (shown in Figure 1) were synthesized via reversible additionfragmentation chain transfer (RAFT) polymerization in this study. The predetermined amounts of monomers, including HMA, sodium 4-vinylbenzenesulfonate hydrate, and/or the hydrogen-bonding monomers, n-isopropyl methacrylamide, 3-(thymin-1-yl) propyl methacrylate, or UPy-MA, were dissolved in 10 mL of DMF, followed by the addition of 2-(2-cyanopropyl) dithiobenzoate (CPDB) as a chain transfer agent and AIBN as an initiator at a fixed molar ratio of 5:1. The solution was subjected to three freezepump-thaw circles for degassing, and then kept at 70 °C and reacted 24 h under nitrogen protection. After that, liquid nitrogen was applied to quench the reaction. The thawed liquids were put into a dialysis bag with molecular cutoff 1 kDa, and dialyzed against methanol for more than 5 days. The liquid in the dialysis bag was concentrated. For the samples including the monomer of 3-(thymin-1-yl) propyl methacrylate, an equivalent amount of melamine was introduced into the precursor to form triple hydrogen bonds according to the literature.⁴⁸ All samples were dried under vacuum at 80 °C more than one week before measurements.

The NMR spectra of samples above were collected on a Brucker AV 400-MHz spectrometer using chloroform-d as a solvent and trimethylsilane as an internal standard, and the results are shown in Figures S1–S3 of the SI. The elements of sulfur and nitrogen were determined by Vario El Cube elemental analyzer. The element sodium was measured using inductively coupled plasma optical emission spectroscopy (ICP-OES) analysis conducted with a Thermo iCAP spectrometer. A combination of S, N, and Na% obtained from the sulfur, nitrogen, and sodium elemental analyses enables us to determine simultaneously the number of ion-containing monomers per chain, the number of hydrogen-bonding monomers per chain, and the number average molecular weight, as explained below.

The results of S, N, and Na% are summarized in Tables 1 and 2. Sodium ions are attached to the ion-containing monomers, and sulfur

Table 1. Important Parameters of Samples Containing Either Ionic or Hydrogen-Bonding Groups

$M_{\rm n}~({\rm kg/mol})$	S%	N%	$p(q)^a$	$T_{g} (^{\circ}C)^{b}$	$\tau \text{ (ms)}^{c}$
10.9	0.588	0.68	4.3	-2.4	0.055
12.8	0.499	1.12	4.6	24	1.7
11.1	0.575	2.84	5.4	19	490
9.1	1.550		2.5	-7.0	1700
8.8	2.160		4.1	-1.1	5000
	M _n (kg/mol) 10.9 12.8 11.1 9.1 8.8	M _n (kg/mol) S% 10.9 0.588 12.8 0.499 11.1 0.575 9.1 1.550 8.8 2.160	M _n (kg/mol) S% N% 10.9 0.588 0.68 12.8 0.499 1.12 11.1 0.575 2.84 9.1 1.550 8.8 2.160	M_n (kg/mol)S%N% $p(q)^a$ 10.90.5880.684.312.80.4991.124.611.10.5752.845.49.11.5502.58.82.1604.1	M_n (kg/mol)S%N% $p(q)^a$ T_g (°C) ^b 10.90.5880.684.3-2.412.80.4991.124.62411.10.5752.845.4199.11.5502.5-7.08.82.1604.1-1.1

 ${}^{a}p$ and q are the number of stickers per chain for the hydrogenbonding polymer and ionomer, respectively. ${}^{b}T_{g}$ is determined by DSC. ${}^{c}\tau$ is determined from G' and G'' terminal tails at $T_{r} = 100$ °C. atoms are present in both the ion-containing monomers and one of the chain ends (two sulfur atoms originally in the RAFT agent CPDB). A combination of S and Na% enables us to determine the average number of the ion-containing monomers per chain q and the molecular weight M_n using

$$32(q+2)/M_{\rm p} = 8\%$$
 (1)

$$23q/M_{\rm p} = \rm Na\%$$

For the pure hydrogen-bonding samples, M_n can be calculated from eq 1 by allowing q = 0.

The nitrogen atoms are present in both the hydrogen-bonding monomers and one chain end (one nitrogen atom originally in the RAFT agent CPDB), and the average number of hydrogen-bonding monomers per chain p is determined using

$$14(pn_{\rm N}+1)/M_{\rm p} = N\%$$
 (3)

Here, $n_{\rm N}$ (= 1, 2, or 4) is the number of nitrogen atoms per hydrogen-bonding monomer. The important parameters obtained by analyzing S, Na, and N% using eqs 1–3 are summarized for the pure hydrogen-bonding samples, coded as #H-*p*, in Table 1 and for the samples containing both ionic and hydrogen-bonding groups, coded as #H-*p*&Na-*q*, in Table 2, where # (= 2, 3 or 4) indicates the number of hydrogen bonds per functional group. As a comparison, the two pure ionomer samples (with no hydrogen-bonding groups) in our previous study are coded as Na-*q*.²³

2.3. Measurements. 2.3.1. Differential Scanning Calorimetry (DSC). All DSC measurements were conducted using a DSC Q20 (TA Instruments, USA). The samples were tested in the temperature range of -70 to 120 °C. The data were collected during three heating runs with a heating rate of 20 °C/min. With the help of commercially available Universal Analysis software, the glass transition temperature (T_g) was determined by the second run, and reproducibility was confirmed in the third run. The results of T_g are summarized in Tables 1, 2 and Figure S5.

2.3.2. Shear Rheology. The frequency sweep and stress relaxation measurements were performed with an ARES-G2 rheometer (TA Instruments, USA) using 8 mm diameter parallel plates. Before measurements, all ionomer samples were kept in a vacuum oven at 120 °C and pure hydrogen-bonding samples were kept in a vacuum oven at 80 °C for at least one week. The frequency sweep measurements were conducted in a *T* range of 10–200 °C under the protection of highly purified nitrogen to prohibit oxidation and degradation. The stress relaxation measurement for sample 4H-6.0&Na-4.5 was completed at 120 °C with a fixed strain of $\gamma = 2\%$. In all shear rheology tests, the range of applied strain was kept in the linear regime as confirmed by the strain–sweep measurements.

2.3.3. Extensional Rheology. For all samples, the uniaxial extension tests were carried out using a filament stretch rheometer (VADER 1000; Rheo Filament, Denmark) which was designed by Prof. Hassager's group of Denmark Technology University. The samples were loaded on the rheometer in the temperature range of 150–180 °C under the protection of highly purified nitrogen. Within this scope of temperature, the samples can flow and easily fill up the gap between the cylindrical stainless steel plates of diameters of 4 or 6 mm. The measurements were conducted in the temperature range of 70–160 °C, where the elongational viscosity is above 10³ Pa·s at the extension rates $\dot{\varepsilon}_{\rm H} = 0.001-3 \text{ s}^{-1}$. Within the feedback control of the midfilament diameter, the results were collected at a constant rate $\dot{\varepsilon}_{\rm H}$.

3. RESULTS AND DISCUSSION

3.1. Linear Viscoelasticity. *3.1.1. LVE of Single-Network* Samples and Pure PHMA. In Figure 2, the (pseudo-) master curves of storage and loss moduli, G' and G'', reduced at reference temperature $T_r = 100$ °C for pure PHMA and the single-network samples, i.e., the hydrogen-bonding 2H-4.3, 3H-4.6, and 4H-5.4 samples, and the Na-2.5 ionomer sample are compared. The data of PHMA and Na-2.5 were reported in

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sample	$M_{\rm n}$ (kg/mol)	Na%	S%	N%	p ^a	q^{B}	$T_{g} (^{\circ}C)^{c}$	$\tau(s)^d$
2H-4.6&Na-2.0	12.7	0.359	1.005	0.62	4.6	2.0	19	2.2
3H-4.9&Na-2.2	10.6	0.478	1.271	1.44	4.9	2.2	30	2.2
4H-4.3&Na-2.5	10.4	0.561	1.398	2.47	4.3	2.5	48	320
2H-5.5&Na-4.0	14.9	0.616	1.288	0.61	5.5	4.0	27	17
3H-6.2&Na-4.6	14.3	0.749	1.491	1.32	6.2	4.6	53	17
4H-6.0&Na-4.5	11.9	0.873	1.754	2.95	6.0	4.5	69	9900

Table 2. Important Parameters of Samples Containing Both Ionic and Hydrogen-Bonding Groups

^{*a*}The number of hydrogen-bonding groups per chain. ^{*b*}The number of ionic groups per chain. ^{*c*} T_{g} is determined by DSC. ^{*d*} τ is determined from G' and G'' terminal tails at $T_r = 100$ °C.



Figure 2. Comparison of the (pseudo-) master curves of the storage and loss moduli, G' and G", obtained for pure PHMA, 2H-4.3, 3H-4.6, 4H-5.4, and Na-2.5 samples. All (pseudo-) master curves are reduced at $T_r = 100$ °C.

our previous study.²³ To obtain the (pseudo-) master curves, G' and G'' are multiplied by an intensity factor $b_{\rm T} = T_{\rm r}/T$, and the shift along the horizontal axis by a factor $a_{\rm T}$ to construct the (pseudo-) master curves. For the hydrogen-bonding 2H-4.3 and 3H-4.6 samples, the time-temperature superposition (tTs) holds approximately, and thus $a_{\rm T}$ can be easily chosen to obtain the master curves. (Although the FTIR spectra indicate that the number of hydrogen bonds changes slightly with T in the range of our LVE measurements, see Figure S4, this change appears to be too weak to lead to the failure of tTs.) In comparison, tTs does not work for the 4H-5.4 and Na-2.5 samples in the whole frequency range, where $a_{\rm T}$ is chosen to superpose the high- ω Rouse part of G' and G'' obtained at T < T_{rt} and the low- ω network-relaxation part of G' and G'' obtained at $T > T_r$. The pseudo-master curves thus constructed

can represent reasonably the relaxation mode distribution at

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 $T_{\rm r}$. The different thermorheological properties of the samples are probably owing partly to the different association strengths and also partly to the attractive interaction between the hydrogen-bonding groups and the ester groups of the polymer backbone. In particular, the association is not strong for 2H-4.3 and 3H-4.6, where the stickers can be regarded as the frictional dense sites and thus the tTs holds approximately. Nevertheless, the terminal relaxation time becomes similar for 4H-5.4 and Na-2.5, whereas the tTs holds much better for the former. We attribute this difference to the attractive interaction between the hydrogen-bonding groups and the ester groups of the polymer backbone for the former, leading to the delay of the whole system (both sticky and nonsticky monomers) rather than that of only the stickers, considering that the thermorheological complexity of associative polymers stems from different temperature dependences for the stickers and the nonsticky segments. This argument is supported by the observation that T_g values of all hydrogen-bonding polymers are higher than that of Na-2.5 (cf. Table 1 and Figure S5), and also by that the delay of the Rouse region (where $G' \sim 10^7$ Pa) with respect to that of PHMA is stronger for the hydrogenbonding samples, particularly for 3H-4.6 and 4H-5.4, than for Na-2.5 (cf. Figure 2).

Figure 3a compares the plots of $a_{\rm T}$ against $T - T_{\rm r}$ obtained for the samples shown in Figure 2. It is clear that the temperature dependence strengthens with increasing T_{g} summarized in Table 1, i.e., T_g follows the order pure PHMA < Na-2.5 < 2H-4.3 < 4H-5.4 < 3H-4.6 (cf. Table 1 and Figure S5). The slightly higher T_g of 3H-4.6 than that of 4H-5.4 has been confirmed with the repeated DSC measurements. The difference is also reflected in the slightly delayed Rouse region of 3H-4.6 compared to that of 4H-5.4 (cf. Figure 2), which may reflect that the functional groups of 3H-4.6 have stronger attractive interaction with the ester groups of the polymer backbone than those of 4H-5.4.

In Figure 3b, we choose a new isofrictional reference temperature $T_{iso} = T_g + 100$ °C and renormalize the shift factors. The plots of log a_{iso} against $T - T_{iso}$ of the PHMA, 2H-4.3, and 3H-4.6 are similar, which can be well described by the WLF equation

$$\log a_{\rm iso} = -7.64(T - T_{\rm iso})/(187 + T - T_{\rm iso}) \tag{4}$$

In comparison, the shift factors obtained for Na-2.5 are stronger than the prediction of the WLF equation at high T > $T_{\rm r}$, where the superposition is guided by the network-relaxation part of the modulus. (The shift factors of the 4H-5.4 sample show slightly stronger T dependence than the WLF prediction only at the highest T.) The network relaxation is governed by the dissociation of ionic groups that are associated with an



Figure 3. (a) Plots of $a_{\rm T}$ against $T - T_{\rm r}$ for the samples shown in Figure 2, with $T_{\rm r} = 100$ °C. (b) Plots of renormalized shift factors $a_{\rm iso}$ against $T - T_{\rm iso}$, where $T_{\rm iso}$ (= $T_{\rm g}$ + 100 °C) is the isofrictional temperature.

extra activation energy $E_{a'}$ thereby leading to a stronger temperature dependence than the segmental motion. Using T_{iso} as the new reference temperature, we can properly normalize the Rouse region of G' for all samples seen in Figure 2, as demonstrated in Figure S6 of the SI. (The failure of normalization for G'' in the Rouse region is attributable to the difference in the contribution of the glassy part of modulus therein.)

3.1.2. LVE of Double-Network Samples. Figure 4 compares the pseudo-master curves of storage and loss moduli, G' and G'', obtained for the Na-2.5 single-network ionomer sample (triangles) and three double-network samples, 2H-4.6&Na-2.0 (squares), 3H-4.9&Na-2.2 (spheres), and 4H-4.3&Na-2.5 (diamonds). The number densities of first and secondary networks are kept roughly the same, i.e., about two ioncontaining monomers and about five hydrogen-bonding monomers per chain, while the strength of the secondary network increases with the number of hydrogen bonds per functional group. The dashed curves represent the modulus of the pure hydrogen-bonding samples shown earlier in Figure 2. The pseudo-master curves of storage and loss moduli, G' and G'', are reduced at reference temperature $T_r = 100$ °C using the same protocol as for the single-network samples in Figure 3, with the shift factors compared in Figure S8.



Figure 4. Comparison of the pseudo-master curves of the storage and loss moduli, *G'* and *G''*, obtained for single-network sample Na-2.5 (triangles), and three double-network samples, 2H-4.6&Na-2.0 (squares), 3H-4.9&Na-2.2 (spheres), and 4H-4.3&Na-2.5 (diamonds). The dashed curves represent the modulus of the hydrogen-bonding samples shown earlier in Figure 2. All pseudo-master curves are reduced at $T_r = 100$ °C.

The master curves for 2H-4.3 and 3H-4.6 (dashed curves) can reasonably account for the high- ω relaxation process of their corresponding double-network samples, i.e., 2H-4.6&Na-2.0 and 3H-4.9&Na-2.2. Meanwhile, the terminal relaxation process of Na-2.5 is similar to the low- ω terminal relaxation processes of 2H-4.6&Na-2.0 and 3H-4.9&Na-2.2. These features suggest that the relaxation of the hydrogen bonds and that of the ionic groups are relatively independent for 2H-4.6&Na-2.0 and 3H-4.9&Na-2.2, and the latter process controls the terminal relaxation.

In contrast, the terminal relaxation of 4H-4.3&Na-2.5 (diamonds) is significantly more delayed than those of both the 4H-5.4 and Na-2.5 samples. One may think this result is due to the similar strength of the ionic and quadruple hydrogen-bonding groups, leading to an increase in the number of stickers that control the terminal relaxation time. Nevertheless, the sticky-Rouse mechanism^{32,49,50} that predicts the relaxation time being proportional to the square of the number of stickers gives a delay of terminal relaxation by a factor of only $\{(4.3+2.5)/2.5\}^2 = 10^{0.9}$ (~ one decade), which is much smaller than the delay of the terminal relaxation of 4H-4.3&Na-2.5 with respect to that of Na-2.5 seen in Figure 4, which is about two decades rather than one decade. Here, we suspect that the extra delay is due to a motional coupling effect among all stickers of 4H-4.3&Na-2.5. The coupling effect plays an ignorable role when the stickers are well separated, but a big role when the neighboring stickers are separated by the strand of a size smaller than the Kuhn length, where the strand becomes nonflexible. A number fraction of both the ionic and hydrogen-bonding stickers of 12% of 4H-4.3&Na-2.5 gives an average number of 8 (= 1/12%) monomers between two stickers. Considering that this number is smaller than the number of 10 monomers expected for one Kuhn segment, the coupling effect between the ionic and hydrogen-bonding stickers of similar strength could be responsible for the extra delay of the terminal relaxation. This coupling effect would be weaker for the terminal relaxation of 2H-4.6&Na-2.0 and 3H-4.9&Na-2.2 because the hydrogen bonds dissociate and reassociate at a frequency much faster than that of the ionic groups and so the ionic stickers "feel" less motional constraint from the hydrogen-bonding stickers.

Similar trends have been observed by increasing the number of ion-containing monomers from ~2 to ~4 and the number of hydrogen-bonding monomers from ~5 to ~6 (cf. Figure S7), including (1) for double-network samples with the dual- and triple-hydrogen-bonding stickers, i.e., 2H-5.5&Na-4.0 and 3H-6.2&Na-4.5, exhibit the terminal relaxation process similar to that of Na-4.1, and (2) 4H-6.0&Na-4.5 with quadruplehydrogen-bonding stickers shows much more delayed terminal relaxation process than that of Na-4.1. The latter observation is probably also owing to the strong coupling effect explained above because the number of ionic and hydrogen-bonding stickers of 4H-6.0&Na-4.5 becomes even larger than that of 4H-4.3&Na-2.5.

3.2. Extensional Rheology. Figure 5 summarizes the stress growth coefficients $\eta_{\rm E}^+$ against time *t* for the Na-*q* and #H-*p*&Na-*q* samples (shown earlier in Figure 4) obtained upon application of different extension rates $\dot{\varepsilon}_{\rm H}$ (= 0.001–3 s⁻¹) at different temperatures (from 70 to 140 °C). To avoid heavy overlap, the results obtained at lower temperatures are multiplied by an intensity factor as indicated (the number after the mark ×). The numbers associated with each curve are Weissenberg number $Wi = \dot{\varepsilon}_{\rm H} \tau$, with $\tau = [G'/\omega G'']_{\omega \to 0}$ being the terminal relaxation time (shown in Tables 1 and 2). The black and solid curves are calculated from $\eta_{\rm E,0}^+(t) = 3 \int_0^t G(t') dt'$, where $G(t') = \sum_{\rm p} g_{\rm p} \exp(-t'/\tau_{\rm p})$ is the relaxation modulus, with $\{g_{\rm p}, \tau_{\rm p}\}$ being calculated from fitting the pseudomaster curves shown earlier in Figure 4 with the multimode-Maxwell equation.⁵¹

For the Na-2.5, 2H-4.6&Na-2.0, and 3H-4.9&Na-2.2 samples, $\eta_{\rm E}^{+}(t, Wi)$ agrees well with the black solid line at a small Weissenberg number $Wi \ll 1$, but deviates strongly from the LVE envelope at a high Wi > 1, where strong hardening is observed and the plots of $\eta_{\rm E}^+$ against time become well above the LVE envelop. In comparison, $\eta_{\rm E}^+(t, Wi)$ of 4H-4.3&Na-2.5 shows strong hardening irrespective of Wi. The hardening for *Wi* \ll 1 indicates that the sample cannot flow freely even when the extension rate is much slower than the terminal relaxation determined by LVE; a similar feature (strain hardening for Wi \ll 1) is also seen for 4H-6.0&Na-4.5, as shown in Figure S9. This result could be related to the motional coupling among all hydrogen-bonding and ionic stickers, as explained earlier. The elongation flow may induce structural changes (e.g., the straininduced interchain association) that further strengthen the coupling effect, thereby restricting the chain motion.

For pure ionomer sample Na-2.5, slight strain hardening followed by the macroscopic fracture at $\varepsilon_{\rm H} < 2$ is seen at high Wi > 1 (indicated by the cross-marked symbol (\otimes)), which indicates the brittle nature upon application of the fast elongational flow. As discussed in our previous study,²³ the fracture is attributable to the dense gel network, where the strain-induced dissociation occurs tremendously when the network strands are stretched to their limit, where the broken stickers can hardly find the new partners along the stretch



Figure 5. Plots of the extensional stress growth coefficient $\eta_{\rm E}^+$ against time at different temperatures *T* for Na-*q* and #H-*p*&Na-*q* systems (shown earlier in Figure 4). In each panel, the data at different temperatures are shifted vertically by factors as indicated (following the mark ×) to avoid overlap. The numbers therein show the Weissenberg number (*Wi*) defined according to the linear viscoelastic terminal relaxation time. The cross-marked symbol (\otimes) indicates the sample fracture before reaching the preset strain ($\varepsilon_{\rm H} = 4$) during the measurement.

direction to reconstruct the network structure, thereby leading to the fracture.

The introduction of secondary stickers changes the stretchability. On the one hand, the 2H-4.6&Na-2.0 and 3H-4.9&Na-2.2 samples show improved stretchability compared with Na-2.5, and the improvement is more remarkable for 3H-4.9&Na-2.2. For example, both the samples 2H-4.6&Na-2.0 and 3H-4.9&Na-2.2 show an overshoot of $\eta_{\rm E}^+$ followed by the pseudo-yielding behavior (where the extensional stress decreases) at Wi > 1. However, the macroscopic fracture is observed after the $\eta_{\rm E}^+$ peak for 2H-4.6&Na-2.0 at Wi > 23, while no macroscopic fracture is observed for 3H-4.9&Na-2.2 that is stretched up to a preset strain $\varepsilon_{\rm H}$ = 4 at Wi as high as 170. On the other hand, the stretchability for 4H-4.3&Na-2.5 becomes even lower than that of Na-2.5. The poor extensibility for 4H-4.3&Na-2.5 is reminiscent of the single and broad network relaxation in Figure 4 that should reflect similar strengths of the quadruple hydrogen bonds and the ionic associations. Therefore, the reduced extensibility of 4H-4.3&Na-2.5 (compared with Na-2.5) should be partly due to the denser network and accordingly the decreased strand size. For 4H-4.3&Na-2.5, we argued that the strand size is even smaller than the Kuhn length if we consider the hydrogenbonding and ionic groups as equally strong stickers. Then, the poor extensibility even at $Wi \ll 1$ may be related to the motional-coupling effect between the hydrogen-bonding and ionic groups.

Figure 6 compares the stress versus strain curve obtained at high Wi > 1; for the samples in Figure 5, the dashed lines



Figure 6. True extensional stress $\sigma_{\rm E}$, plotted against the Hencky strain $\varepsilon_{\rm H\nu}$ for all measurements at Wi > 1 in Figure 5. The solid curves are expected from the neo-Hookean model, and the red vertical dashed line shows $\varepsilon_{\rm H} = 1.5$. The colored dashed curves are expected from a sum of the neo-Hookean model prediction and a dissipative part owing to the chain friction or dissociation/reassociation of hydrogen bonds.

represent $\varepsilon_{\rm H} = 1.5$, an average value for the Hencky strain of the overshoot seen for 3H-4.9&Na-2.2. The black solid curves represent predictions of the simplest neo-Hookean model $\sigma_{\rm E,neo-H} = G_{\rm eq}(\lambda^2 - 1/\lambda)$, where λ is the stretch ratio and $G_{\rm eq}$ is the equilibrium plateau modulus estimated as the value of G' at the valley of tan δ .⁵¹ The colored dashed curves are predicted after adding a dissipative part that stems from the chain friction or dissociation/reassociation of the hydrogen-bonding stickers, i.e., $\sigma_{\rm E} = \sigma_{\rm E,neo-H} + 3\eta_{0,r}\dot{\epsilon}_{\rm H}$, where $\eta_{0,r}$ is the zero-shear viscosity determined for the reference samples (i.e., PHMA, 2H-4.3, 3H-4.6, 4H-5.4). This choice is suitable if the elongational rate is much slower than the relaxation rate of the reference samples, as justified later in Figure 8.

This model is based on an assumption of Gaussian conformation with no FENE effect of the network strands having a fixed density. Thus, if the density of network strands increases or if the FENE effect starts to play a role, σ_E data would increase than expected. In contrast, if the density of network strands decreases during the elongation, we may expect that the σ_E data would drop below the neo-Hookean

prediction. In this study, $\sigma_{\rm E}$ of all samples is above the model prediction before the stress overshoot, but approaches or becomes lower than the model prediction after the stress overshoot, indicating strong strain-induced dissociations near the overshoot.

For Na-2.5, the $\sigma_{\rm E}$ data are close to the neo-Hookean prediction at low $\varepsilon_{\rm H}$. For Wi = 2.1, we can see a very weak overshoot before the macroscopic fracture at high $\varepsilon_{\rm H} > 1$. In comparison, the macroscopic fracture (with no overshoot) occurs at a lower $\varepsilon_{\rm H} < 1$ at Wi = 6.3. These features are attributed to a competition between the strain-induced dissociation and reassociation along the stretch direction, as discussed in our previous study.²³ If the latter process cannot capture the former process, the macroscopic fracture would occur. In the opposite case, the reassociation along the stretch direction (flow) along the stretch direction, thereby activating pseudo-yielding behavior after the overshoot.

For 2H-4.6&Na-2.0 and 3H-4.9&Na-2.2, the overshoot followed by the pseudo-yielding process is seen for all measurements with Wi > 1. The pseudo-yielding behavior is less abrupt for 3H-4.9&Na-2.2 than for 2H-4.6&Na-2.0. This feature is attributable to the more efficient suppressing of the chain retraction by the triple hydrogen bonds, which leads to the slower and weaker stress drop after the strain-induced dissociations of the ionic stickers. Correspondingly, a more stable elongational flow can be achieved for 3H-4.9&Na-2.2, allowing the sample to be extended to the preset Hencky strain of $\varepsilon_{\rm H} = 4$ even when Wi is as high as 170. In comparison, the samples are stretched to $\varepsilon_{\rm H} = 4$ only at $Wi \leq 12$ for 2H-4.6&Na-2.0, whereas macroscopic fracture occurs before $\varepsilon_{\rm H} = 4$ (and after the overshoot) for Wi of 23 or higher.

Similar trends have been revealed in samples with higher ion contents (cf. Figures S9 and S10) compared to the samples mentioned above. Namely, the improved stretchability is observed after introducing the dual- and triple-hydrogenbonding groups (for 2H-5.5&Na-4.0 and 3H-6.2&Na-4.6) and the improvement is more significant for the latter, while lower stretchability is observed after introducing the quadruple-hydrogen-bonding groups (for 4H-6.0&Na-4.5).

Figure 7 summarizes the peak stress $\sigma_{E,peak}$ and Hencky strain $\varepsilon_{H,peak}$ corresponding to the overshoot for Na-2.5, 2H-4.6&Na-2.0, and 3H-4.9&Na-2.2 samples. The $\varepsilon_{H,peak}$ values are very similar for all samples at Wi > 1 when the overshoot occurs, and decrease only slightly with increasing Wi. Meanwhile, $\sigma_{E,peak}$ increases with Wi by following a scaling relationship $\sigma_{E,peak} \sim Wi^{0.5}$ (dashed line in Figure 7b). The similar Wi dependences of $\varepsilon_{H,peak}$ and $\sigma_{E,peak}$ for Na-2.5, 2H-4.6&Na-2.0, and 3H-4.9&Na-2.2 suggest that these samples indeed have a similar density of ionic stickers that control the extensional stress before the overshoot. Nevertheless, the different stretchability of these samples should reflect the important role of the secondary hydrogen-bonding stickers, as discussed below.

3.3. Brittle-to-Ductile Transition and Dynamic Role of the Secondary Stickers. Figure 8 is a diagram of the stretchability of the Na-q (triangle symbols), 2H-p&Na-q(square symbols), and 3H-p&Na-q (sphere symbols) samples shown in Figures 5 and S9. The horizontal and vertical axes are chosen as the Weissenberg numbers, Wi_1 defined according to the terminal relaxation time of the focused ion-containing samples and Wi_2 defined according to the terminal relaxation time of the reference samples, i.e., pure PHMA, 2H-4.3, and



Figure 7. Plots of (a) the Hencky strain $\varepsilon_{\text{H,peak}}$ and (b) the peak stress $\sigma_{\text{E,peak}}$ at the overshoot against Weissenberg number Wi at Wi > 1. The dashed line in panel (a) indicates $\varepsilon_{\text{H,peak}} = 1.5$ (i.e., red dashed vertical lines in Figure 6). The dashed line in panel (b) represents the power law of $\sigma_{\text{E,peak}} \sim Wi^{0.5}$.

3H-4.6 whose relaxation times can be regarded as those of the ion-free chains. In this sense, Wi_2 is in a spirit similar to the Wi_R defined with respect to the Rouse time for pure ionomer samples (i.e., sulfonated polystyrene with different counterions) in our previous study.²⁴ The black dashed line (Wi_1 = Wi_2) represents the case where the first and secondary stickers are of the same strength, i.e., the case of 4H-4.3&Na-2.5 whose plots are not presented here because the fracture mechanism should be different. In this diagram, the green filled symbols indicate that the sample can be stretched without macroscopic fracture up to the set $\varepsilon_{\rm H}$ = 4 during the measurements, the red cross-marked symbols indicate the sample shows overshoot but the macroscopic fracture occurs below $\varepsilon_{\rm H}$ = 4, and the orange unfilled symbols represent the measurements during which the sample fracture occurs before the maximum stress has been achieved.

In Figure 8, we note three distinct regions with macroscopic behavior of double-network polymer samples and the ionomer samples from the literature,²³ i.e., melt fracture region before the overshoot (orange unfilled symbols), fracture after the overshoot (red cross-marked symbols), and no fracture up to $\varepsilon_{\rm H} = 4$ (green filled symbols), respectively.

For $Wi_1 < 0.2$ (vertical line), the extension rate is so slow that continuous dissociation and reassociation allow the sample to flow without melt fracture behavior during the elongation. For $Wi_1 > 0.2$, the high stretchability is achieved only above a critical Wi_2 . The introduction of the hydrogen-



Figure 8. Diagram based on Weissenberg numbers, W_{i_2} and W_{i_1} , for Na-q (triangle symbols), 2H-p&Na-q (square symbols), and 3H-p&Na-q (sphere symbols) samples shown in Figures 5 and S9. The orange unfilled and red cross-marked symbols represent the measurements during which the sample fracture occurs before and after η_E^+ exhibits a peak, respectively. The green filled symbols represent the measurements during which no fracture occurs up to the set Hencky strain of $\varepsilon_H = 4$. The triangle symbols represent the pure ionomer in our previous study,²³ and the square and sphere symbols represent double-network samples based on double- and triple-hydrogen bonds, respectively. The thin black dashed line represents $W_{i_1} = W_{i_2}$ The thick blue dashed lines indicate the brittle to ductile boundary.

bonding groups can increase Wi2 thereby improving the stretchability. It is likely that the continuous dissociation and association of the dual- and triple-hydrogen bonds occur during the elongational flow because Wi_2 is smaller than 0.1 for all elongational measurements of the samples based on them (cf. the upper limit of the vertical axis of Figure 8). The continuous dissociation/association of the hydrogen bonds would facilitate the energy dissipation and suppress the abrupt drop of local stress, thereby suppressing the formation of defects/voids that potentially grow into the macroscopic fracture. This mechanism is consistent with the mechanism suggested for the brittle-to-ductile transition that occurs at sufficiently a high Weissenberg number defined with respect to the Rouse time in our previous study for sulfonated polystyrene with different counterions,²⁴ considering that the characteristic time of the chain retraction after the strain-induced breakup of ionic groups would be close to the Rouse time for the single-network ionomer samples, but be close to the relaxation time of hydrogen-bonding chains for the doublenetwork samples in this study.

4. CONCLUDING REMARKS

In this study, we introduce three types of hydrogen bonds (dual-, triple-, and quadruple-hydrogen bonds) into the intrinsically brittle ionomer system. The dual and triple hydrogen bonds are much weaker than the ionic interaction, enabling the double network based on them to exhibit the twostep relaxation, where the fast and slow relaxation processes correspond to those of the hydrogen-bonding and ionic groups, respectively.

The focus of our current study is placed in a region where the Weissenberg number defined with respect to the slower and faster processes are larger and smaller than 1, respectively, where the elongational flow induces the breakup of the stronger stickers, while the dissociation/association of the weaker stickers faster than the flow field can occur continuously. We believe that the latter process plays important roles: it leads to more effective energy dissipation and it suppresses the chain retraction and accordingly the drop of localized stress after the strain-induced breakups of the stronger stickers, thereby suppressing the formation of defects/ voids that potentially grow into the macroscopic fracture. To realize these roles, the secondary (the weaker) stickers should be sufficiently strong but still considerably weaker than the first (the stronger) stickers. In the opposite case, if the first and secondary stickers become equally strong, we would have a similar Weissenberg number defined with respect to them. Then, the introduction of the secondary network would be akin to an increase of the network density and accordingly a decrease of the strand size, which should instead lower the ductility, as seen for the double-network samples based on the quadruple hydrogen bonds whose ductility are even worse than their mother ionomer samples. The results in this study should shed light on the molecular design of ductile double-network materials.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.macromol.1c01283.

Synthesis and characterization of monomer; FTIR of single hydrogen-bonding samples; DSC traces of the single- and double-network samples; linear viscoelasticity and extensional rheology measurements of Na-*q* and #H-*p*&Na-*q* samples with higher ion contents (PDF)

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Notes

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