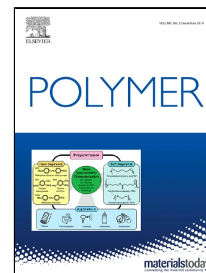


Journal Pre-proof

Cooperative dynamics of heuristic swelling and inhibitive micellization in double-network hydrogels by ionic dissociation of polyelectrolyte



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PII: S0032-3861(19)31045-6
DOI: <https://doi.org/10.1016/j.polymer.2019.122039>
Reference: JPOL 122039
To appear in: *Polymer*
Received Date: 05 October 2019
Accepted Date: 28 November 2019

Please cite this article as: Ziyu Xing, Haibao Lu, Mokarram Hossain, Yong Qing Fu, Jinsong Leng, Shanyi Du, Cooperative dynamics of heuristic swelling and inhibitive micellization in double-network hydrogels by ionic dissociation of polyelectrolyte, *Polymer* (2019), <https://doi.org/10.1016/j.polymer.2019.122039>

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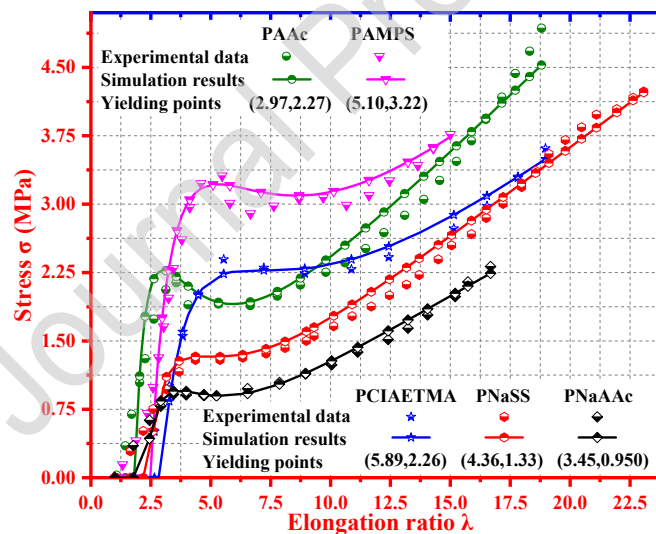
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A new cooperative model was proposed to explore the working mechanism of double network (DN) hydrogel undergoes heuristic swelling and inhibitive micellization, synchronously, by the ionic dissociation of polyelectrolyte.

Cooperative dynamics of heuristic swelling and inhibitive micellization in double-network hydrogels by ionic dissociation of polyelectrolyte

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Abstract: In this study, a cooperative model has been proposed for the double network (DN) hydrogel, which synchronously undergoes heuristic swelling and inhibitive micellization by the ionic dissociation of polyelectrolyte. Flory-Huggins solution theory is initially employed to identify the working mechanism of dielectric constants on swelling behavior of the DN hydrogel. Then a free-energy function is introduced to formulate the constitutive relationship of the DN hydrogels, in which the first hydrotropic network undergoes a heuristic swelling and the second hydrophobic network undergoes an inhibitive micellization. Finally, the proposed model has been verified using the experimental results reported in the literature. A good agreement between the **theoretical** results and experimental ones has been achieved. This study provides a fundamental approach to formulate the constitutive

relationship and to understand the cooperative dynamics of two types of networks in DN hydrogels induced by the polyelectrolyte.

Keywords: Double network (DN) hydrogels; ionic dissociation; free energy function

1. Introduction

Hydrogel is one of the most popular soft polymeric matters that exhibit a highly stretchable behavior in response to an externally mechanical loading [1-3]. It has highly absorbent polymeric networks and can contain over 90% water in it [4]. These stimulus-responsive hydrogels effectively pave the ways for their successful applications in artificial muscle, soft robots, and intelligent devices [5-7]. However, the conventional hydrogels are easily broken even at a low stress [8,9], and their mechanical properties are soft and weak [10,13-16].

Recently, double-network (DN) hydrogels have been proposed and attracted great attention due to their ultra-high mechanical strength and toughness [8-11]. These DN hydrogels are incorporated of two types of polymeric networks, which are referred to as the brittle and stretchable ones, respectively [10,11]. Experimental results reveal that the DN hydrogels have mechanical strengths of 1-10 MPa and strains of 1000% under the tensile stress, while their toughness values (e.g., tearing fracture energy) are as high as 100-1000 J/m² [10]. To further improve the mechanical properties of these soft materials, a tough and stretchable hybrid DN hydrogel has been synthesized and induced by the ionic dissociation of polyelectrolyte [12,16-22]. However, the working mechanisms of significantly improved mechanical properties of these polyelectrolyte

dissociated DN hydrogels are different from those of the conventional ones [23-25]. It is expected that the excellent mechanical properties are originated from the ionic interactions between polyelectrolyte networks and solvent molecules [26-30]. Therefore, it is necessary to investigate and explore the working mechanisms for these polyelectrolyte dissociated DN hydrogels.

When a polyelectrolyte dissociated DN hydrogel is able to swell, the dissolution degree of the hydrophobic network is far less than that of the polyelectrolyte (or hydrophilic) network. The hydrophobic network will undergo inhibitive micellization resulted from the swelling effects of the hydrophilic network. Due to the complexity of thermodynamics, in this study, we propose some theoretical models for the mechanical behavior of polyelectrolyte dissociated DN hydrogels which are based on the classical Flory-Huggins solution theory [31]. Initially, a free-energy equation of double networks is established according to the heuristic swelling and inhibitive micellization of two types of networks. Then the constitutive stress-strain relations are formulated for the DN hydrogels, whose cooperative dynamics has been identified as the driving force for their mechanical behavior. Finally, **theoretical** results with the proposed models are compared and verified using the experimental data reported in the literature.

2. Theoretical framework

The two types of networks in the DN hydrogels are mutually swollen by the solvent. However, one network is able to swell while the another one is able to micellize, as **illustrated** in **Figure 1**, resulting into a complexity in the free energy function of DN

hydrogels. Here, both the swelling effect and micellization effect are necessary to consider in the formulation of constitutive relationship for the DN hydrogels.

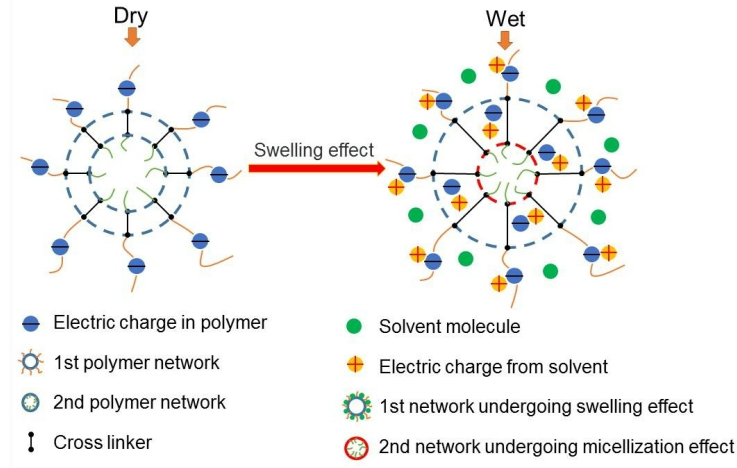


Fig. 1. Schematic diagram of the swelling and micellization behaviors of the two networks in DN hydrogel.

Huggins interactive parameter (χ) is often used to characterize the interaction between polymer and solvent by their molecular polarizabilities [32], which can be expressed as:

$$\begin{cases} \chi = \chi_{MS} - \frac{1}{2}(\chi_{MM} + \chi_{SS}) \\ \chi_{MS} = -k_e \alpha_M \alpha_S \\ \chi_{MM} = -k_e \alpha_M^2 \\ \chi_{SS} = -k_e \alpha_S^2 \end{cases} \quad (1)$$

where χ_{MS} is the Huggins interactive parameter between polymer and solvent, χ_{MM} is the interactive parameter between polymer macromolecules, χ_{SS} is the interactive parameter between solvent molecules, and k_e is the scaling constant [32]. Furthermore, α_M and α_S are the molecular polarizabilities of the polymer and solvent, respectively. Equation (1) can also be written as,

$$\chi = \frac{k_e}{2} (\alpha_M - \alpha_S)^2 \quad (2)$$

Molecular polarizability of the polymer can be experimentally determined by the dielectric constant (ε_M) of polymer, i.e., $\frac{\varepsilon_M - e}{\varepsilon_M + f} = \frac{N\alpha_M}{3C_0}$ [13]. Therefore, equation

(2) can be rewritten as,

$$\chi = \frac{k_e}{2}(\alpha_M - \alpha_S)^2 = \frac{k_e}{2}\left(\frac{3C_0}{N}\frac{\varepsilon_M - e}{\varepsilon_M + f} - \alpha_S\right)^2 = \frac{k_e\alpha_S^2}{2}\left(\frac{3C_0}{N\alpha_S}\frac{\varepsilon_M - e}{\varepsilon_M + f} - 1\right)^2 \quad (3)$$

where C_0 is the permittivity parameter, N is the number of molecules per unit volume, e and f are material constants. It should be noted that the proposed model of equation (3) is applicable for both single network (SN) and DN hydrogel, because the dielectric constant is determined by the whole hydrogel (for both DN or SN hydrogels), not determined by the network component.

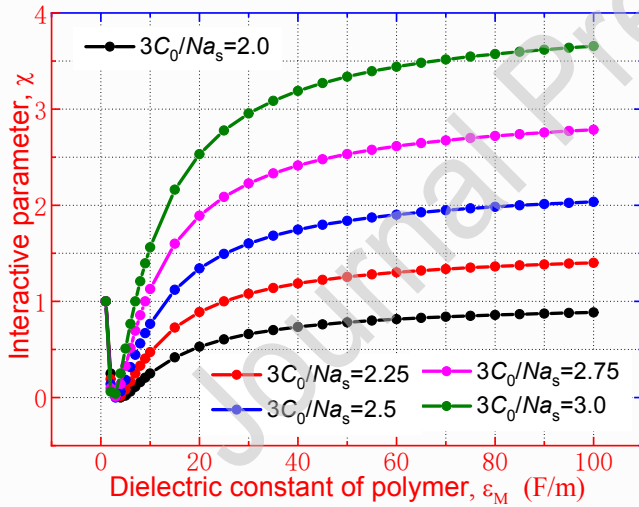


Fig. 2. Analytical results based on equation (3) for the interactive parameter (χ) as a

function of dielectric constant (ε) of polymer, where $\frac{3C_0}{N\alpha_S} = 2, 2.25, 2.5, 2.75$ and 3 .

Figure 2 plots the constitutive relationship of Huggins interactive parameters as a

function of dielectric constant of polymer, where the parameter $\frac{k_e\alpha_S^2}{2}$ is assumed to

be a constant as the solvent is fixed. For a given constant, e.g., $\frac{3C_0}{N\alpha_s}=2.0, 2.25, 2.5, 2.75$ or 3.0 , it is found that the interactive parameter is initially decreased by the increasing dielectric constant of polymer. However, it is then increased with a further increase in the dielectric constant, ε_M . These **theoretically calculated** results indicate that the interactive parameter (χ) is determined by the molecular polarizabilities of hydrogel (α_M) and solvent (α_s), as supported in equation (2). Therefore, the swelling behavior of the hydrogels can be designed by controlling the molecular polarizabilities according to the proposed model in equation (3).

Furthermore, χ is a dynamic parameter, which is determined by the fraction of solvent (ϕ_2) as [31],

$$\chi = B\phi_2 + C \quad (4)$$

where B and C are two coefficients. Here B is used to characterize the effect of weight fraction of solvent on the value of χ . It will be increased when there is a strong interaction between the polymer and solvent. C is a constant. Substituting equation (4) into (3), the swelling ratio (V/V_0) of hydrogel is obtained,

$$\frac{V}{V_0} = \frac{B}{\frac{k_e}{2}(\alpha_M - \alpha_s)^2 - C} - 1 = \frac{B}{\frac{k_e \alpha_s^2}{2} \left(\frac{3C_0}{N\alpha_s} \frac{\varepsilon_s - e}{\varepsilon_s + f} - 1 \right)^2 - C} - 1 \quad (5)$$

where, V is the swollen volume of hydrogel, V_0 is the volume of hydrogel in untreated state, ε_s is the dielectric constant of solvent.

To verify equations (5), the analytical results of swelling ratio as a function of dielectric constant have been plotted and compared with the experimental results reported in literature [12]. The results are shown in Figure 3. The parameters $B=9.952$

, $C=-0.52268$, $V_0=1$, $\frac{k_e \alpha_s^2}{2} = 6.2 \times 10^{-9}$, $\frac{3C_0}{N\alpha_s} = 9.327$, $e=21007$ and $f=-32.312$ are

used in equation (5). It is found that there is an inhibitive micellization effect for the DN hydrogels, where the swelling ratio is gradually decreased from 12.25 to the micellization ratio of 0.01 as the dielectric constant (ϵ_s) of solvent is increased from 0 F/m to 32.5 F/m. On the other hand, the swelling ratio is increased from -0.99 to 17.65 with an increase in dielectric constant (ϵ_s) of solvent from 32.5 F/m to 180 F/m. These **theoretical** results clearly reveal that the swelling behavior of the DN hydrogel is determined by the cooperative dynamics of heuristic swelling and inhibitive micellization of two types of networks. **If the values of these parameters are small, the fitting seems not good, which is mainly due to the small swelling ratio. When the swelling ratio is very small, the DN hydrogel is approximately a concentrated solution, while the proposed model is mainly originated from the dilute solution theory. Therefore, in this case, the simulation results of the proposed model do not fit well with the experimental results.**

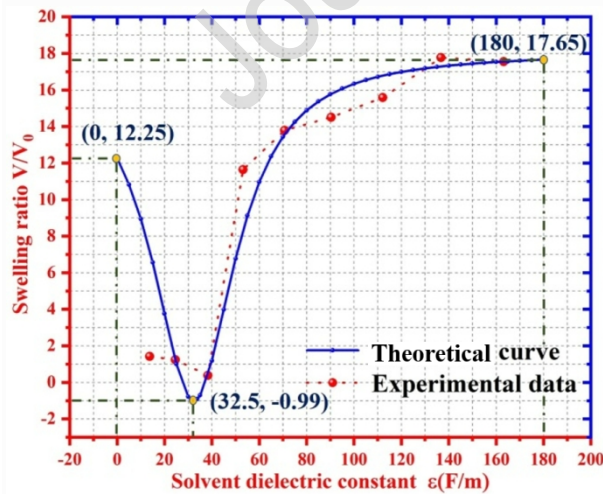


Fig. 3. Comparison of swelling ratio as a function of solvent dielectric constant between the experimental data [12] and **theoretical** results using equation (5).

DN hydrogel is incorporated into a hydrotropic network and a hydrophobic network, while the solvent is polyelectrolyte and undergoes an ionic dissociation, e.g., causing swelling of hydrogel in the water (or *N*-methyl formamide, NMF) solution containing LiCl solute [12]. Here the LiCl is dissociated into Li⁺ and Cl⁻ in the NMF or water, thus resulting in the swelling of the DN hydrogels.

If the DN hydrogel is incorporated into sodium salt and reacts with the Cl⁻ anions, equation (5) can be rewritten when we assume $\alpha_M = k_M C(\text{Cl}^-)$ [34,35]:

$$\frac{V}{V_0} = \frac{B}{\frac{k_e}{2}(\alpha_S - \alpha_M)^2 - C} - 1 = \frac{B}{\frac{k_e}{2}(\alpha_S - k_M C(\text{Cl}^-))^2 - C} - 1 \quad (6)$$

where $C(\text{Cl}^-)$ is the concentration of Cl⁻ anions. Here, the chemical equilibrium of the ionic dissociations can be expressed using,

$$\frac{C(\text{Na}^+)C(\text{Cl}^-)}{C_M} = K_a \quad (7)$$

where K_a is the chemical equilibrium constant. According to equation (7), the concentration of Cl⁻ anions can be obtained,

$$\Delta C(\text{Cl}^-) = \frac{C_0(\text{Na}^+) + C_0(\text{Cl}^-) + K_a - \sqrt{(C_0(\text{Na}^+) + C_0(\text{Cl}^-) + K_a)^2 - 4C_0(\text{Na}^+)C_0(\text{Cl}^-)}}{2} \quad (8)$$

Substituting equation (8) into (6), the swelling ratio is represented as,

$$\frac{V}{V_0} = \frac{B}{\frac{k_e(\alpha_S - k_M C_0(\text{Na}^+))^2}{2} \left[1 + \frac{k_M}{\alpha_S - k_M C_0(\text{Na}^+)} \Delta C(\text{Cl}^-) \right]^2 - C} - 1 \quad (9)$$

The analytical results of swelling ratio as a function of LiCl concentrations have been plotted and compared with the experimental results [12] as presented in Figure 4.

The parameters used in equation (9) have been listed in Table 1. With an increase in the concentration of LiCl, the dielectric constant of DN hydrogel is increased, thus

resulting in a decrease of the swelling ratio. It is revealed that the **theoretical** results fit well with the experimental data. Based on the theoretical results, for the DN hydrogels in the NMF solution, the swelling ratio is gradually decreased from 16 to 4.8 with an increase in the LiCl concentration from 1×10^{-4} mol to 1.0 mol. On the other hand, for the DN hydrogel in the water, the swelling ratio is gradually decreased from 19 to 4.0 with an increase in the LiCl concentration from 1×10^{-4} mol to 1.0 mol.

Table 1. Values of parameters used in equations (9) for the DN hydrogel with various concentrations of LiCl.

	$C_0(\text{Na}^+)$	K_a	$\frac{k_e(\alpha_S - k_M C_0(\text{Na}^+))^2}{2}$	$\frac{k_M}{\alpha_S - k_M C_0(\text{Na}^+)}$	B	C
NMF	0.021	0.163	3.54	9.28	9.553	3
Water	0.0003	0.091	10	20	1	10

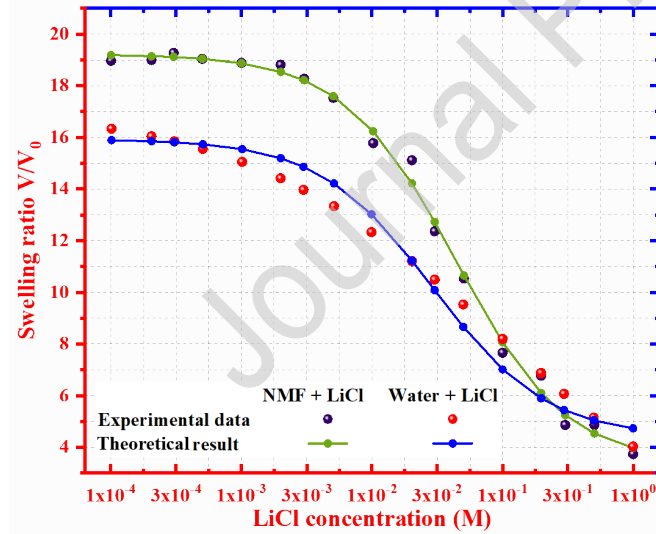


Fig. 4. Comparisons between the **theoretical** results using equation (9) with the experimental data [12] for DN hydrogel swollen by the NMF and water, which contain various weight concentrations of LiCl.

3. Modelling of cooperative dynamics in DN hydrogel

As mentioned earlier, in DN hydrogels, the two types of networks simultaneously undergo a distinct swelling behavior, resulting in a complex constitutive stress-strain relationship. Therefore, it is necessary to investigate the cooperative dynamics of heuristic swelling and inhibitive micellization in the DN hydrogel. According to Flory-Huggins theory [31], the free energy equation is initially employed to characterize the thermodynamics of DN hydrogels,

$$\Delta F_M = RT(n_1 \ln \phi_1 + n_2 \ln \phi_2 + \chi n_1 \phi_2) \quad (10)$$

where, ΔF_M is the mixing free energy, n_1 and ϕ_1 represent the amount and volume fraction of the solvent, respectively, n_2 and ϕ_2 represent the amount and volume fraction of the hydrogel, respectively. Therefore, the elastic free energy (ΔF_{el}) of the DN hydrogels is expressed as [31],

$$\Delta F_{el} = \frac{3\xi k_B T}{2} \left[\left(\frac{1}{\phi_2} \right)^{2/3} - 1 \right] \quad (11)$$

where k_B is the Boltzmann constant and ξ refers to the number of chains.

Free energy function of the hydrogel should be the sum of these two terms

$\Delta F = \Delta F_M + \Delta F_{el}$, while $\phi_1 = 1 - \phi_2 = \frac{V}{V + V_0}$, $V + V_0 = \lambda^3$ and $V_0 = \lambda_0^3$. Therefore,

the free energy function can be expressed as,

$$\Delta F = -RTn_1 \left[\ln \frac{\lambda^3 - \lambda_0^3}{\lambda^3} + \nu \frac{\lambda^3 - \lambda_0^3}{\lambda_0^3} \ln \frac{\lambda_0^3}{\lambda^3} + \left(B \frac{\lambda_0^3}{\lambda^3} + C \right) \frac{\lambda_0^3}{\lambda^3} \right] + \frac{3\xi k_B T}{2} \left[\frac{\lambda^2}{\lambda_0^2} - 1 \right] \quad (12)$$

where ν is the molar volume ratio of polymer to solvent, λ is the elongation ratio of the DN hydrogel.

It is necessary to further investigate micellization effect in the DN hydrogel. Micellization has been extensively studied in many types of block polymers, including the water-soluble block polymers [33]. The micelle radius (R_a) function can be expressed as [33],

$$R_a = k_a^{1/2} R = \left(\frac{1}{2} - \chi\right)^{1/5} k_a^{3/10} n^{3/5} F^{1/5} l \quad (13)$$

where, k_a is characteristic ratio of length, n is monomer number of a single arm, F is number of arms, and l is length of the arms. The swollen volume ratio (ΔV_{mic}) of the micelle is then obtained as:

$$\Delta V_{mic} = k_{mic} \left(\frac{1}{2} - \chi\right)^{3/5} = k_{mic} \left(\frac{1}{2} - B \frac{\lambda_0^3}{\lambda^3} - C\right)^{3/5} \quad (14)$$

where, k_{mic} is a scaling constant for the micelle [32].

The elastic free energy of micelle is therefore expressed as [31].

$$\Delta F_{el}^{mic} = \frac{3\xi kT}{2} \left[\left(\frac{1}{\phi_2}\right)^{2/3} - 1 \right] = \frac{3\xi kT}{2} (\Delta V_{mic}^{2/3} - 1) = \frac{3\xi kT}{2} \left[k_{mic}^{2/3} \left(\frac{1}{2} - B \frac{\lambda_0^3}{\lambda^3} - C\right)^{2/5} - 1 \right] \quad (15)$$

Combining equations (10), (11) and (15), the free energy function of the DN hydrogel is finally obtained:

$$\begin{aligned} \Delta F &= \Delta F_M + \Delta F_{el} + \Delta F_{el}^{mic} \\ &= -RTn_1 \left[\ln \frac{\lambda^3 - \lambda_0^3}{\lambda^3} + \nu \frac{\lambda_0^3}{\lambda^3 - \lambda_0^3} \ln \frac{\lambda_0^3}{\lambda^3} + \left(B \frac{\lambda_0^3}{\lambda^3} + C \right) \frac{\lambda_0^3}{\lambda^3} \right] \\ &\quad + \frac{3\xi kT}{2} \left[\frac{\lambda^2}{\lambda_0^2} + k_{mic}^{2/3} \left(\frac{1}{2} - B \frac{\lambda_0^3}{\lambda^3} - C\right)^{2/5} - 2 \right] \end{aligned} \quad (16)$$

According to the equation (16), the constitutive stress-strain relationship can therefore be expressed as:

$$\sigma = \frac{\partial \Delta F}{\partial \lambda} = -RTn_1 \left[\frac{\lambda_0^3}{\lambda(\lambda^3 - \lambda_0^3)} + 3\nu \left(\frac{3\lambda^2\lambda_0^3}{(\lambda^3 - \lambda_0^3)^2} \ln \frac{\lambda}{\lambda_0} - \frac{\lambda_0^3}{\lambda(\lambda^3 - \lambda_0^3)} \right) \right. \\ \left. - (6B \frac{\lambda_0^3}{\lambda^3} + 3C) \frac{\lambda_0^3}{\lambda^4} \right] + RTn_1 \frac{3\xi}{N_A n_1} \left[\frac{\lambda}{\lambda_0^2} + \frac{3k_{mic}^{2/3} B \lambda_0^3}{5\lambda^4} \left(\frac{1}{2} - B \frac{\lambda_0^3}{\lambda^3} - C \right)^{-3/5} \right] \quad (17)$$

According to equation (17), the capability of the DN hydrogels to resist to an external force is originated from a coupling effect of the two networks. The mechanical energy is transformed into mixed free energy and elastic free energy of the first hydrotropic network, whereas it is transformed into elastic free energy of the second hydrophobic network. Therefore, the mechanical performance of the DN hydrogels is resulted from a coupling effect from their two networks.

To verify the proposed model, the analytical results are plotted in Figure 5. The parameters used in equation (17) are listed in Table 2. As shown in Figure 5(a), it is found that the stress is dramatically increased from 0 MPa to 2.064 MPa as the dimensionless elongation ratio is increased from 1 to 1.155, at a given constant of $B=4.4$. Meanwhile, the maximum stress is increased from 1.364 MPa to 2.064 MPa, with an increase of the B from 3.6 to 4.4. These theoretical results imply that the stress is increased with an increase in the interactive parameter (χ), because the mixing of hydrogel and solvent becomes difficult. Therefore, more free energy is necessary to apply to the DN hydrogels at the same elongation ratio.

Table 2. Values of parameters used in equations (17).

	RTn_1	3ν	B	C	$\frac{3\xi}{N_A n_1}$	$\frac{9\xi B k_{mic}^{2/3}}{5N_A n_1}$
In Fig. 5(a)	0.5	1	/	2	4	2
In Fig. 5(b)	0.5	1	4	1.5	4	/

Analytical results of the stress as a function of elongation ratio at given values of $\frac{9\xi Bk_{mic}^{2/3}}{5N_A n_1} = 0, 1.6, 2, \text{ and } 2.4$ are plotted in Figure 5(b). The **theoretical** results show that the stress is dramatically increased from 0 MPa to 3.018 MPa as the elongation ratio is increased from 1 to 1.14. On the other hand, the maximum stress is increased from 1.454 MPa to 3.018 MPa, with an increase of the $\frac{9\xi Bk_{mic}^{2/3}}{5N_A n_1}$ from 0 to 2.4. These **theoretical** results clearly imply that the free energy function and the corresponding stress are both increased with an increase in the interactive parameter (χ), according to equations (4), (12) and (17). With an increase in the values of χ , the free energy is increased at the same elongation ratio of the hydrogel.

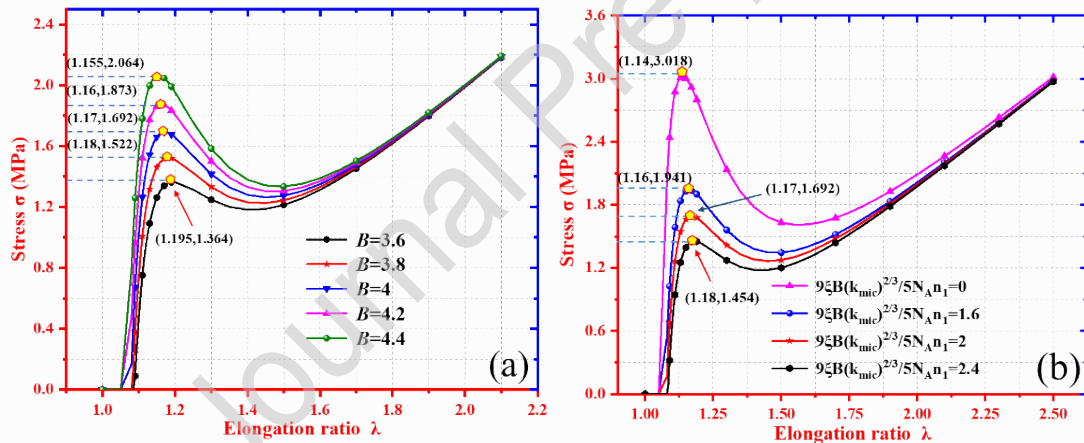


Fig. 5. **Theoretical** results of stress as a function of elongation ratio of DN hydrogel.

(a) At a given $B=3.6, 3.8, 4, 4.2$ and 4.4 . (b) At a given $\frac{9\xi Bk_{mic}^{2/3}}{5N_A n_1} = 0, 1.6, 2$ and 2.4 .

4. Experimental verification of mechanical behavior of DN hydrogel

To verify the proposed model, we have applied the experimental results for six groups of DN hydrogels reported in literature [12]. These six groups including (1) PNaAMPS (poly(2-acrylamido-2-methylpropanesulfonic acid sodium salt)) and PEA

(poly(ethyl acrylate)) DN hydrogel; (2) PAAc (Poly(acrylic acid)) and PEA (poly(ethyl acrylate)) DN hydrogel; (3) PAMPS (Poly(2-acrylamido-2-methylpropanesulfonic acid)) and PEA (poly(ethyl acrylate)) DN hydrogel; (4) PCIAETMA (Poly(2-acryloxyethyl trimethylammonium chloride)) and PEA (poly(ethyl acrylate)) DN hydrogel; (5) PNaSS (Poly(p-styrene sulfonic acid sodium salt)) and PEA (poly(ethyl acrylate)) DN hydrogel; (6) PNaSS (Poly(p-styrene sulfonic acid sodium salt)) and PEA (poly(ethyl acrylate)) DN hydrogel. The experimental results [12] have been used to compare with the analytical results. According to equation (17), the **theoretical** results of stress as a function of the elongation ratio have been plotted in Figure 6. It is found that the stress of DN hydrogels is gradually increased with the increase of the elongation ratio. The parameters used in the equation (17) have been listed in Table 3.

Table 3. Values of parameters used in equations (17) for DN hydrogels composed of various types of hydrotropic networks.

	RIn_1	3ν	B	C	$\frac{3\xi}{N_A n_1}$	$\frac{9\xi B k_{mic}^{2/3}}{5N_A n_1}$	λ'
PAAc	0.5	1	4	2	6.1	0.8	12
PAMPS	0.5	1	4.3	2.3	12	1.3	25
PCIAETMA	0.5	1	4.7	1.6	10.4	2.6	25
PNaSS	0.5	1	4	1.6	5.8	2.6	15
PNaAAc	0.5	1	3.6	1.5	3.5	2.2	12

It is revealed that the **theoretical** results are in good agreements with the experimental results of the DN hydrogels. Furthermore, the yielding behaviors of hydrogels have also been calculated, where the yielding points are ($\sigma=2.97$ MPa, λ

$=2.27$), ($\sigma=5.10$ MPa, $\lambda=3.22$), ($\sigma=5.89$ MPa, $\lambda=2.26$), ($\sigma=4.36$ MPa, $\lambda=1.33$) and ($\sigma=3.45$ MPa, $\lambda=0.95$) for the PAAc, PAMPS, PCIAETMA, PNaSS and PNaAAc networks, respectively.

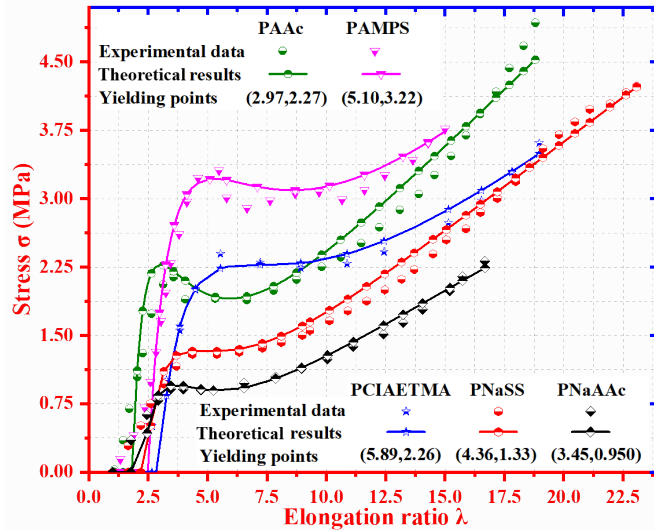


Fig. 6. Tensile stress-strain curves and **theoretical** prediction curves of DN hydrogels with different hydrotropic networks. The experimental data are derived from references [12].

Figure 7 illustrates the effect of weight concentration (f_{EA}) of hydrotropic network on the stress-strain relationship of DN hydrogels, where $f_{EA}=30, 40, 50$, and 60 . The used parameters in the theoretical analysis are listed in Table 4. As revealed from Figures 7(a), 7(b), 7(c) and 7(d), the **theoretical** results fit well with the experimental data of DN hydrogels with 30wt.%, 40wt.%, 50wt.%, and 60wt.% of hydrophobic network. The analytical results showed that the proposed model is able to characterize the constitutive stress-strain relationship of the DN hydrogel with various weight fractions of components. With an increase in the weight fraction of hydrophobic network from 30wt.%, 40wt.%, 50wt.% to 60wt.%, the yielding strain is gradually decreased from 5.35, 4.68, 4.48 to 4.46, while the yielding stress is decreased from

2.48 MPa, 2.23 MPa, 1.99 MPa to 1.99 MPa. These simulation results clearly reveal that the ability of DN hydrogel to resist external force is strongly determined by the density of polymer networks, e.g., resulting from the mixing free energy of hydrophobic network and water. Therefore, large free energy is necessary to enable the DN hydrogels swollen at the same elongation ratio, when the weight concentration of hydrotropic network is increased. Therefore, the proposed model is applicable to characterize and predict the effect of weight concentration of the components on the mechanical behaviors of DN hydrogels.

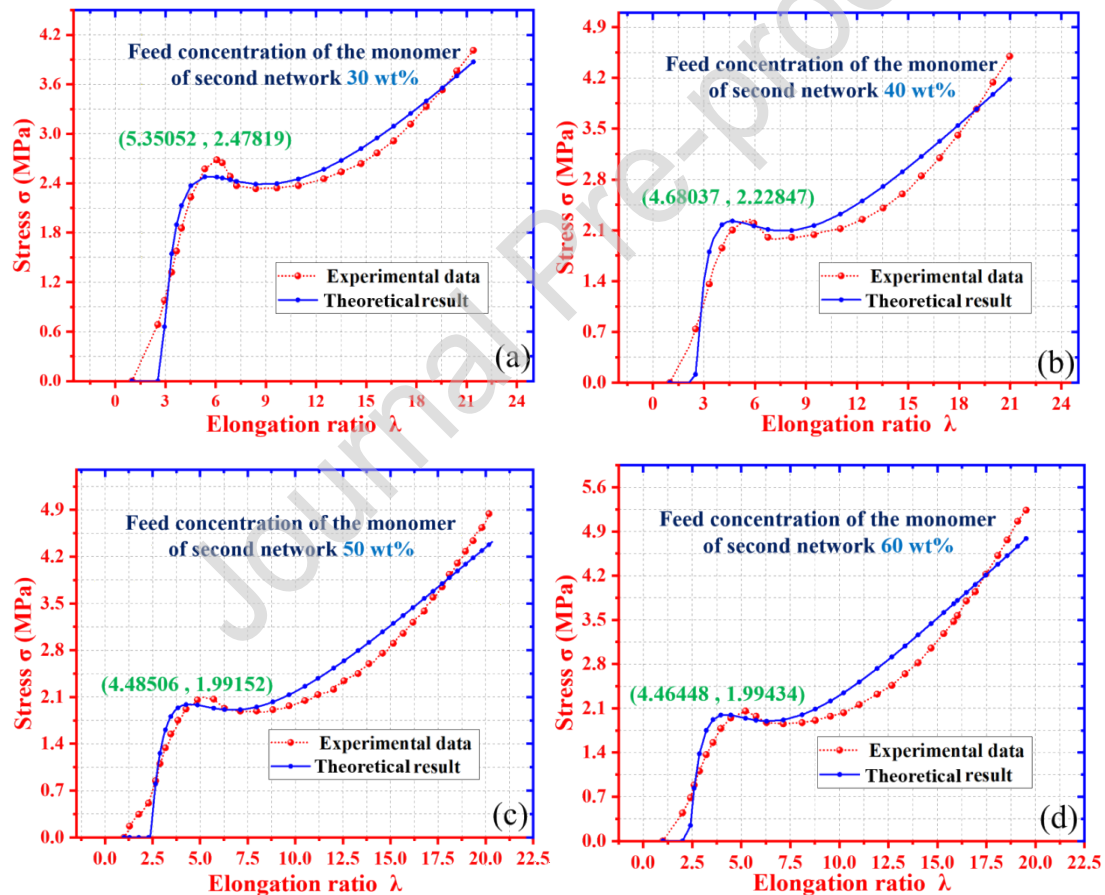


Fig. 7. Comparisons of theoretical results and experimental data [12] for the stress as a function of elongation ratio of DN hydrogel with various weight fractions of hydrotropic network.

Table 4. Values of parameters used in equations (17) for DN hydrogels incorporated of various weight concentration of hydrotropic network.

f_{EA}	RTn_1	3ν	B	C	$\frac{3\xi}{N_A n_1}$	$\frac{9\xi B k_{mic}^{2/3}}{5N_A n_1}$	λ'
30 wt%	0.5	1	4.8	2.2	9.8	2.8	26
40 wt%	0.5	1	6	2.4	8.4	4.6	22
50 wt%	0.5	1	6.5	2.4	9.4	5.4	20
60 wt%	0.5	1	8.2	3	10.8	7.2	20

4. Conclusion

In this study, we propose a constitutive model to study the mechanical behavior of the DN hydrogels, in which two types of networks synchronously undergo heuristic swelling and inhibitive micellization by the ionic dissociation of polyelectrolyte. It is demonstrated that the proposed framework is able to well predict mechanical behavior of DN hydrogels. It provides an effective approach to estimate and quantitatively separate the dependence of the stress-strain relationship on the dielectric constant, Huggins interactive parameter, dissociation of polyelectrolyte, and component concentration. The cooperative dynamics has been identified as the critical factor to determine the mechanical behaviors of DN hydrogels, which undergo the heuristic swelling and inhibitive micellization from these two types of networks, respectively. Finally, the analytical results have been verified by the experimental results. This study provides a fundamental approach to formulate the constitutive relationship and cooperative dynamics in DN hydrogels.

Acknowledgements

This work was financially supported by the National Natural Science Foundation of China (NSFC) under Grant No. 11672342 and 11725208, Newton Mobility Grant (IE161019) through Royal Society and NFSC.

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References

- [1] Lin P, Ma S H, Wang X L and Zhou F 2015 Molecularly engineered dual-crosslinked hydrogel with ultrahigh mechanical strength, toughness and good self-recovery *Adv. Mater.* **27** 2054-9
- [2] Hu Y, Du Z S, Deng X L, Wang T, Yang Z H, Zhou W Y and Wang C Y 2016 Dual physically cross-linked hydrogels with high stretchability, toughness, and good self-recoverability *Macromolecules* **49** 5660-8
- [3] Dai X Y, Zhang Y Y, Gao L N, Bai T, Wang W, Cui Y L and Liu W G 2015 A mechanically strong, highly stable, thermoplastic, and self-healable supramolecular polymer hydrogel *Adv. Mater.* **27** 3566-71
- [4] Yuk H W, Zhang T, Lin S T, Parada G A and Zhao X H 2016 Tough bonding of hydrogels to diverse non-porous surfaces *Nat. Mater.* **15** 190-6
- [5] Yang C, Liu Z, Chen C, Shi K, Zhang L, Ju X J, Wang W, Xie R and Chu L Y 2017 Reduced graphene oxide-containing smart hydrogels with excellent electro-response and mechanical properties for soft actuators *ACS Appl. Mater. Interfaces* **9** 15758-67
- [6] Fuhrer R, Athanassiou E K, Luechinger N A and Stark W J 2009 Crosslinking metal nanoparticles into the polymer backbone of hydrogels enables preparation of soft, magnetic field-driven actuators with muscle-like flexibility *Small* **5** 383-8

- [7] Zheng W J, An N, Yang J H, Zhou J X and Chen Y M 2015 Tough Al-alginate/Poly(N-isopropylacrylamide) hydrogel with tunable LCST for soft robotics *ACS Appl. Mater. Interfaces* **7** 1758-64
- [8] Webber R E, Creton C, Brown H R and Gong J P 2007 Large strain hysteresis and mullins effect of tough double-network hydrogels *Macromolecules* **40** 2919-27
- [9] Jang S S, Goddard W A and Kalani M Y S 2007 Mechanical and transport properties of the poly (ethylene oxide)-poly (acrylic acid) double network hydrogel from molecular dynamic simulations *J. Phys. Chem. B* **111** 1729-37
- [10] Kwon H J, Yasuda K, Ohmiya Y, Honma K, Chen Y M and Gong J P 2010 In vitro differentiation of chondrogenic ATDC5 cells is enhanced by culturing on synthetic hydrogels with various charge densities *Acta Biomater.* **6** 494-501
- [11] Gong J P, Katsuyama Y, Kurokawa T and Osada Y 2003 Double-network hydrogels with extremely high mechanical strength *Adv. Mater.* **15** 1155-8
- [12] Matsuda T, Nakajima T and Gong J P 2019 Fabrication of tough and stretchable hybrid double-network elastomers using ionic dissociation of polyelectrolyte in nonaqueous media *Chem. Mater.* **31** 3766-76
- [13] Gong J P 2010 Why are double network hydrogels so tough? *Soft Matter* **6** 2583-90
- [14] Yue Y F, Li X F, Kurokawa T and Gong J P 2016 Decoupling dual-stimuli responses in patterned lamellar hydrogels as photonic sensors *J. Mater. Chem. B.* **4** 4104-09

- [15] Szheng S J, Li Z Q and Liu Z S 2019 The inhomogeneous diffusion of chemically crosslinked Polyacrylamide hydrogel based on poroviscosity theory *Sci. China Technol. SC.* **62** 1375-1384
- [16] Zhao Y J, Zhao K Y, Li Y, Liu L, Zhang X X, Li J G, Chen M and Wang X L 2018 Enrichment of Cd²⁺ from water with a calcium alginate hydrogel filtration membrane *Sci. China Technol. SC.* **61** 438-445
- [17] Lu H B, Shi X J, Yu K and Fu Y Q 2019 A strategy for modelling mechanochemically induced unzipping and scission of chemical bonds in double-network polymer composite *Compos. Part B* **165** 456-66
- [18] Koetting M C and Peters J T 2015 Stimulus-responsive hydrogels: Theory, modern advances, and applications *Mat. Sci. Eng. R* **93** 1-49
- [19] Hong W, Zhao X H and Suo Z G 2010 Large deformation and electrochemistry of polyelectrolyte gels *J. Mech. Phys. Solids* **58** 558-77
- [20] Marcombe R and Cai S Q 2010 A theory of constrained swelling of a pH-sensitive hydrogel *Soft Matter* **6** 784-93
- [21] Li J Y, Suo Z G and Vlassak J J 2014 A model of ideal elastomeric gels for polyelectrolyte gels *Soft Matter* **10** 2582-90
- [22] Basak D and Ghosh S 2013 PH-regulated controlled swelling and sustained release from the core functionalized amphiphilic block copolymer micelle *ACS Macro Lett.* **2** 799-804

- [23] Dopieralski P, Ribas-Arino J, Anjukandi P, Krupicka M and Marx D 2017 Unexpected mechanochemical complexity in the mechanistic scenarios of disulfide bond reduction in alkaline solution *Nat. Chem.* **9** 164-70
- [24] Ducrot E, Chen Y, Bulters M, Sijbesma R P and Creton C 2014 Toughening elastomers with sacrificial bonds and watching them break *Science* **344** 186-9
- [25] Diesendruck C E, Peterson G I, Kulik H J, Kaitz J A, Mar B D, May P A, White S R, Martínez T J, Boydston A J and Moore J S 2014 Mechanically triggered heterolytic unzipping of a low-ceiling-temperature polymer *Nat. Chem.* **6** 623-8
- [26] Zhang H J, Sun TL, Zhang A K, Nakajima T, Nonoyama T, Kurokawa T, Ito O, Ishitobi H and Gong J P 2016 Tough physical double-network hydrogels based on amphiphilic triblock copolymers *Adv. Mater.* **28** 4884-90
- [27] Na Y H, Tanaka Y, Kawauchi Y, Furukawa H, Sumiyoshi T and Gong J P 2006 Necking phenomenon of double-network gels *Macromolecules* **39** 4641-5
- [28] Nakajima T, Kurokawa T, Ahmed S, Wu W L and Gong J P 2013 Characterization of internal fracture process of double network hydrogels under uniaxial elongation *Soft Matter* **9** 1955-66
- [29] Zheng W J, Liu Z Q, Xu F, Gao J, Chen Y M, Gong J P and Osada Y 2015 In vitro platelet adhesion of PNaAMPS/PAAm and PNaAMPS/PDMAAm double-network hydrogels *Macromol. Chem. Phys.* **216** 641-9
- [30] Matsuda T, Nakajima T, Fukuda Y, Hong W, Sakai T, Kurokawa T, Chung U I and Gong J P 2016 Yielding criteria of double network hydrogels *Macromolecules* **49** 1865-72

- [31] He M J, Zhang H D, Chen W X and Dong X X 2006 Polymer physics Shanghai: Fudan Press
- [32] Gennes P G 1979 Scaling concepts in polymer physics. Ithaca and London :Cornell University Press
- [33] Marzio E A D and Guttman C M 1989 A simple treatment of the collapse transition in star molecules *J. Phys. Chem.* **93** 7004-9
- [34] Wheatle B K, Fuentes E F 2019 Influence of host polarity on correlating salt concentration, molecular weight and molar conductivity in polymer electrolytes *ACS Macro Lett.* **8** 888-92
- [35] Wheatle B K, Lynd N A 2018 Effect of polymer polarity on ion transport: A competition between ion aggregation and polymer segmental dynamics *ACS Macro Lett.* **7** 1149-54

Tables caption

Table 1. Values of parameters used in equations (9) for the DN hydrogel with various concentrations of LiCl.

Table 2. Values of parameters used in equations (17).

Table 3. Values of parameters used in equations (17) for DN hydrogels composed of various types of hydrotropic networks.

Table 4. Values of parameters used in equations (17) for DN hydrogels incorporated of various weight concentration of hydrotropic network.

Figures caption

Fig. 1. Schematic diagram of the swelling and micellization behaviors of the two networks in DN hydrogel.

Fig. 2. Analytical results based on equation (3) for the interactive parameter (χ) as a function of dielectric constant (ε) of polymer, where $\frac{3C_0}{N\alpha_s} = 2, 2.25, 2.5, 2.75$ and 3.

Fig. 3. Comparison of swelling ratio as a function of solvent dielectric constant between the experimental data [12] and **theoretical** results using equation (5).

Fig. 4. Comparisons between the **theoretical** results using equation (9) with the experimental data [12] for DN hydrogel swollen by the NMF and water, which contain various weight concentrations of LiCl.

Fig. 5. **Theoretical** results of stress as a function of elongation ratio of DN hydrogel.

(a) At a given $B=3.6, 3.8, 4, 4.2$ and 4.4 . (b) At a given $\frac{9\xi Bk_{mic}^{2/3}}{5N_A n_1} = 0, 1.6, 2$ and 2.4 .

Fig. 6. Tensile stress-strain curves and theoretical prediction curves of DN hydrogels with different hydrotropic networks. The experimental data are derived from references [12].

Fig. 7. Comparisons of **theoretical** results and experimental data [12] for the stress as a function of elongation ratio of DN hydrogel with various weight fractions of hydrotropic network.

Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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Author Contributions Section:

Ziyu Xing: Investigation and Writing- Original draft preparation;

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Mokarram Hossain: Conceptualization and Writing- Original draft preparation;

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Highlights:

- A cooperative model has been proposed for the DN hydrogel, which synchronously undergoes heuristic swelling and inhibitive micellization.
- By combination of Flory-Huggins solution theory, a free-energy function is introduced to formulate the constitutive relationship of the DN hydrogels,
- This study provides a fundamental approach to formulate the constitutive relationship for the cooperative dynamics in DN hydrogels.

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