

Rheological kinetics of thermo-sensitive supramolecular assemblies from poly(*N*-isopropyl acrylamide) and adenine-functionalized poly(ethylene oxide) stabilized by complementary multiple hydrogen bonds

Hui-Wang Cui^{1,2,*} and Shiao-Wei Kuo¹

¹Department of Materials and Optoelectronic Science, National Sun Yat-Sen University, Kaohsiung 804, Taiwan

²Institute of Scientific and Industrial Research, Osaka University, Ibaraki 565-0047, Osaka, Japan

(Received November 2, 2013; final revision received February 1, 2014; accepted February 4, 2014)

In this study, we synthesized a poly(*N*-isopropylacrylamide) (PNIPAm) through the polymerization of *N*-isopropylacrylamide in distilled water with azodiisobutyronitrile as the initiator and a bisadenine-functionalized poly(ethylene oxide) (A-PEO-A) from the reaction of adenine with a difunctionalized toluenesulfonyl-PEO. When blended together in distilled water, PNIPAm and A-PEO-A formed supramolecular aggregates stabilized through complementary multiple hydrogen bonds between the amide groups of PNIPAm and the adenine units of A-PEO-A. Agrawal integral equation and rheometry revealed the rheological kinetics of supramolecular assemblies, which were influenced significantly by the spherical micelles, large associated aggregates of spherical micelles, network structures, and toroid structures formed in aqueous solutions.

Keywords: supramolecule, hydrogen bond, rheology

Introduction

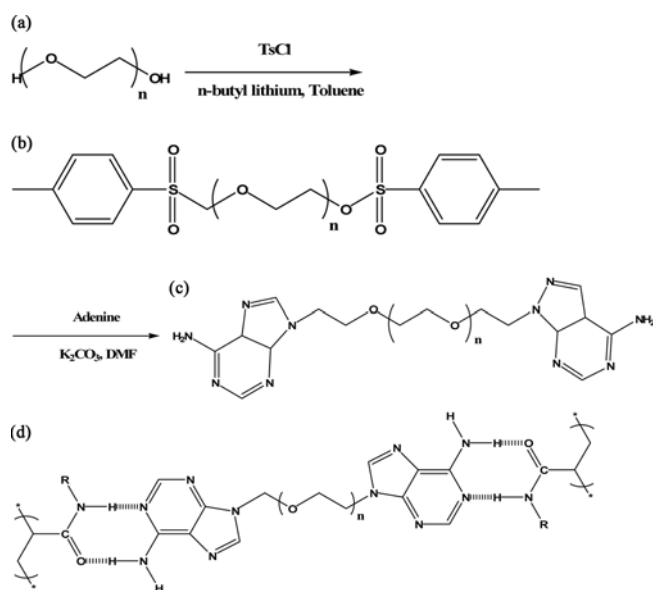
Poly(*N*-isopropylacrylamide) (PNIPAm) is one of the most widely studied thermo-responsive polymers. How to change, improve, and control the lower critical solution temperature (LCST) of PNIPAm has been a hot research topic in experiment, theory, and applications (Schmidt *et al.*, 2008; Cao *et al.*, 2010; Du and Qian, 2011; Liu *et al.*, 2012; Sun *et al.*, 2012). A major approach is to synthesize hetero-arm star (Li *et al.*, 2009), double brush-shaped (Luo *et al.*, 2012), and H-shaped pentablock (Li *et al.*, 2010) copolymers from PNIPAm and poly(ethylene oxide) (PEO) (Li *et al.*, 2009, Li *et al.*, 2010; Chen *et al.*, 2011; Kuo *et al.*, 2012), ring-opening (Chen *et al.*, 2011), atom transfer radical (Tu *et al.*, 2009; Li *et al.*, 2010; Mei *et al.*, 2010; Chen *et al.*, 2011; Lai *et al.*, 2011; Kuo *et al.*, 2012), single-electron-transfer living radical (Li *et al.*, 2010), free radical (Chen *et al.*, 2005a, 2005b, 2006a, 2006b), and reversible addition fragmentation transfer (Yan *et al.*, 2008; Lee *et al.*, 2010) polymerizations. These approaches usually require a combination of two or more polymerizations to prepare high performed copolymers, but such polymerizations are really complex and time-consuming.

In a previous study, we investigated the use of complementary multiple hydrogen bonds (for brevity, CMHB) between amide groups of PNIPAm and adenine (A) units to form supramolecular assemblies through simple blending (Cui *et al.*, 2014). We firstly synthesized A-difunctionalized PEO (A-PEO-A) [Scheme 1c] from the reaction of adenine with difunctionalized toluenesulfonyl-PEO [Scheme 1b] and PNIPAm from the polymerization of *N*-

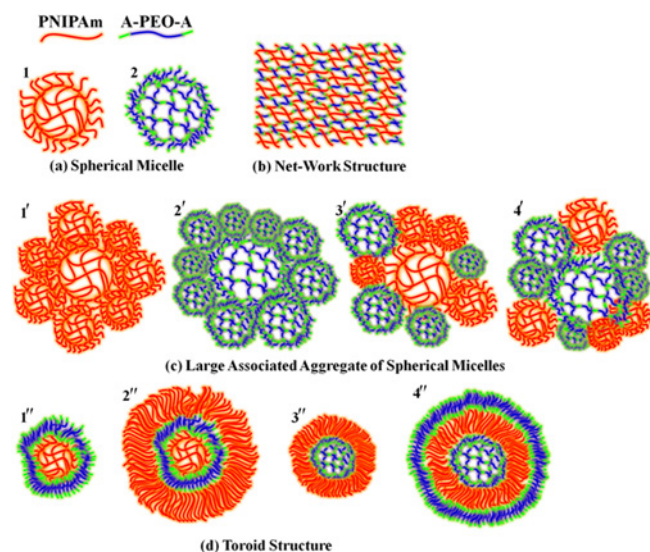
isopropylacrylamide (NIPAm) in distilled water with azodiisobutyronitrile (AIBN) as the initiator. We then mixed PNIPAm with A-PEO-A in distilled water using a blending method. The CMHB formed between amide groups of PNIPAm and adenine units of A-PEO-A led to the development of a supramolecular system in the aqueous solution [Scheme 1d]. The supramolecular assemblies featured spherical micelles [Scheme 2a], network structures [Scheme 2b], large associated aggregates of spherical micelles [Scheme 2c], and core-shell and core-shell-shell toroid structures [Scheme 2d]. The presence of these structures improved greatly the thermo-sensitive properties of PNIPAm/A-PEO-A blends with the LCST up to 40.3°C, exhibiting good film-forming, high degree of gelation, toughness, elasticity, and flexibility.

To further investigate the rheological properties of these supramolecular assemblies, in the present work, we initially attempted to apply Agrawal integral equation (see Appendix A). The rheological kinetics with variations of elastic and viscous moduli is based on the curing of resins obtained from the modulus variations by using dynamic torsion vibration method and Avrami-Erofeev equation (Zou *et al.*, 2003; Yao *et al.*, 2004). It determines the reaction mechanism (e.g., CMHB), and we obtain the activation energy E and pre-exponential factor A by applying rheological analysis with physical changes or chemical reactions. Kinetics is important in theory, production, and applications (Brown, 2001; Gabbott, 2007; Menzel and Prime, 2009), which can be studied by several methods, e.g., model-fitting method and model-free method by determining reaction models and pre-exponential factors (Vyazovkin *et al.*, 2011). In this study, we measured the changes of elastic and viscous mod-

*Corresponding author: cuihuiwang@hotmail.com



Scheme 1. Chemical structures of (a) PEO, (b) TsCl-PEO, (c) A-PEO-A, and (d) multiple hydrogen bonding interactions between amide groups of PNIPAm and adenine groups of A-PEO-A.



Scheme 2. (Color online) Possible morphologies of pure PNIPAm, pure A-PEO-A, and supramolecular complexes formed from PNIPAm/A-PEO-A blends: (a) spherical micelles, (b) network structure, (c) large associated aggregates of spherical micelles, and (d) toroid structures.

uli of PNIPAm/A-PEO-A blends in heating conditions, from which we obtained their rheological kinetics using Agrawal integral equation. It is possible to give guidance for designs and processing conditions of PNIPAm and relevant polymers, understanding the relationship between structures and rheological properties.

Table 1. Experimental design of PNIPAm/A-PEO-A complexes.

Molar ratio	1:0	1:0.4	1:1	1:2	1:4	0:1
PNIPAm (g)	0.01	0.01	0.01	0.01	0.01	-
A-PEO-A (g)	-	0.04	0.1	0.2	0.4	0.01
Distilled water (ml)	10	10	10	10	10	10
Concentration (mg/ml)	1	5	11	21	41	1

Experiments

We obtained NIPAm from Tokyo Chemical Industry (Japan) and n-butyllithium in hexane from Chemetall (Taiwan). AIBN, PEO ($M_w=2000$), and potassium carbonate were purchased from Showa Chemical, and p-toluenesulfonyl chloride, adenine (A), *N,N*-dimethylformamide, toluene, diethyl ether, dichloromethane, tetrahydrofuran, and magnesium sulfate ($MgSO_4$) were purchased from Sigma-Aldrich. PEO-TsCl, A-PEO-A, and PNIPAm were synthesized according to the previous report (Cui *et al.*, 2014), as shown in Scheme 1. To prepare the supramolecular assemblies, PNIPAm (0.01 g, 0.1 mmol) was blended with various amounts of A-PEO-A (Table 1) in distilled water (10 mL) to form supramolecular complexes stabilized through CMHB [Scheme 1d]. When the supramolecular complexes had become homogeneous, they were dried to constant weight at room temperature, forming the powdery samples. Their elastic modulus (G') and viscous modulus (G'') were studied using Physica MCR 301 Rheometer (Anton Paar) from 25 to 50°C at a rate of 2 °C/min. The amplitude γ was 0.5 % and the angular frequency (ω) was 10 s⁻¹.

Results and Discussion

The rheological kinetics of PNIPAm/A-PEO-A complexes was expressed using the simplified Agrawal integral equation (Agrawal, 1987; Sladkov, 2002)

$$\ln\left[\frac{G(a)}{T^2}\right] = \ln\left(\frac{AR}{\beta E}\right) - \frac{E}{RT}. \quad (1)$$

Here, $G(a)$ is the mechanism function that reflects a relationship between the reaction rate and the reaction conversional rate, T is the temperature, R is the universal gas constant (8.314 J/mol·K), β is the heating rate at 2 K/min, E (kJ/mol) is the activation energy defined as the minimum energy that must be input to a chemical system, containing potential reactants, and A (1/min) is the pre-exponential factor only determined by the reaction nature and independent on the reaction temperature and concentration in the system. The relative modulus a is calculated by

$$a = \frac{G'_{onset} - G'}{G'_{onset} - G'_{offset}} \quad \text{or} \quad a = \frac{G''_{onset} - G''}{G''_{onset} - G''_{offset}} \quad (2)$$

where G'_{onset} and G'_{offset} are the elastic modulus at onset and offset temperatures, and G''_{onset} and G''_{offset} are the viscous

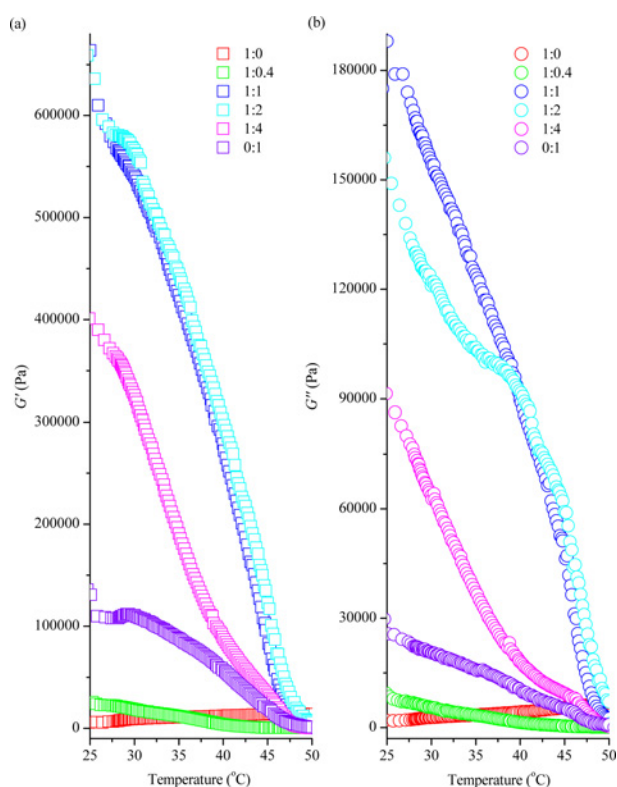


Fig. 1. (Color online) (a) Elastic modulus (G' , \square) and (b) viscous modulus (G'' , \circ) of PNIPAm/A-PEO-A complexes at different molar ratios.

modulus at onset and offset temperatures, respectively.

$\ln[G(a)/T^2]$ and $1/T$ will be in a linear relationship using a proper $G(a)$. E is obtained from the linear slope and A from the linear intercept. According to the simplified Agrawal integral equation, T and a in the rheological variations (Fig. 1) were linearly fit using a trial-and-error method (Halab-Kessira and Ricard, 1999; Hu and Shi, 2001; Woo *et al.*, 2007). We obtained fitting results from elastic and viscous moduli, but those are not presented here. Based on linearly dependent coefficient (r), the optimized results were obtained (Table 2), which represented the rheological kinetics of PNIPAm/A-PEO-A complexes.

In these kinetic parameters, $G(a)$ is the kinetics mechanism function to illustrate the rheological process. If $G(a)$ is different, the linear fit equation, r , E , and A definitely different. The LCSTs at various PNIPAm/A-PEO-A molar ratios were 34.8 (1:0, pure PNIPAm), 36.1 (1:0.4), 37.4 (1:1), 39.4 (1:2), and 40.3°C (1:4). The LCST for pure A-PEO-A (0:1) was not detected within the tested temperature range (25–50°C). Both hydrodynamic diameters for PNIPAm and A-PEO-A were approximately 85 nm. Those of PNIPAm/A-PEO-A mixtures increased with increasing blend ratio as approximately 100 (1:0.4), 125 (1:1), 360 (1:2), and 735 nm (1:4). The values of G' for the blends at various molar ratios were 727 kPa (1:0.4),

Table 2. Rheological kinetics of PNIPAm/A-PEO-A complexes.

PNIPAm/ A-PEO-A (Molar ratios)	$G(a)$	E (kJ/mol)	A (1/min)
1:0	$\square, \circ [(1-a)^{-1/3}-1]^2$	\square 263.01 \circ 250.11	\square 2.79×10^{43} \circ 3.87×10^{42}
1:0.4	$\square, \circ [1-(1-a)^{1/3}]^2$	\square 226.32 \circ 158.23	\square 6.49×10^{36} \circ 1.99×10^{25}
1:1	$\square, \circ [1-(1-a)^{1/3}]^2$	\square 210.85 \circ 206.73	\square 5.31×10^{33} \circ 7.90×10^{32}
1:2	$\square, \circ [1-(1-a)^{1/3}]^2$	\square 220.26 \circ 160.02	\square 1.64×10^{35} \circ 8.33×10^{24}
1:4	$\square, \circ [1-(1-a)^{1/3}]^2$	\square 223.66 \circ 170.33	\square 1.19×10^{36} \circ 1.38×10^{27}
0:1	$\square, \circ [1-(1-a)^{1/2}]^2$	\square 176.02 \circ 137.46	\square 1.26×10^{28} \circ 5.01×10^{21}

\square determined from G' , \circ determined from G''

838 kPa (1:1), 371 kPa (1:2), and 131 kPa (1:4); corresponding values of G'' were 158, 149, 91.4, and 29.8 kPa, respectively (Cui *et al.*, 2014). They are influenced extremely by $G(a)$. PNIPAm/A-PEO-A complexes at molar ratio of 1:0 consisted of small spherical micelles [Scheme 2a, label 1] and their large associated aggregates [Scheme 2c, label 1'] from linear PNIPAm molecules at molar ratio of 0:1 [Scheme 2a, label 2; Scheme 2c, label 2'].

As Table 2 shows, $G(a)$ of $[(1-a)^{-1/3}-1]^2$ (Zhuralev-Lesokin-Tempelmann equation) represented the rheological process of PNIPAm at molar ratio of 1:0 for PNIPAm/A-PEO-A complexes; the mechanism was three-dimensional diffusion (3D). $G(a)$ of $[1-(1-a)^{1/2}]^2$ (Jander equation) represented the rheological process of A-PEO-A at molar ratio of 0:1 for PNIPAm/A-PEO-A complexes with the mechanism of two-dimensional diffusion (2D).

Apparently, $G(a)$ for those PNIPAm/A-PEO-A complexes at molar ratios of 1:0.4, 1:1, 1:2, and 1:4 was the same because of the CMHB formed between the amide groups of PNIPAm and the adenine units of A-PEO-A. Table 2 shows Jander equation of $[1-(1-a)^{1/3}]^2$. The mechanism was three-dimensional diffusion, spherical symmetry (3D, D_3), decelerating shaped $a-t$ curve. During the increasing temperature procedure, macromolecular chains absorbed heat, which released the entanglements and increased the distances between/among macromolecular chains. Meanwhile, the intermolecular force decreased. In addition, this was also often accompanied by the destruction and rupture of macromolecular chains. Actually, this process was a movement for macromolecules from a relatively regular arrangement to a disordered arrangement. The modulus transition from high to low values and PNIPAm/A-PEO-A complexes from solid to viscous fluid

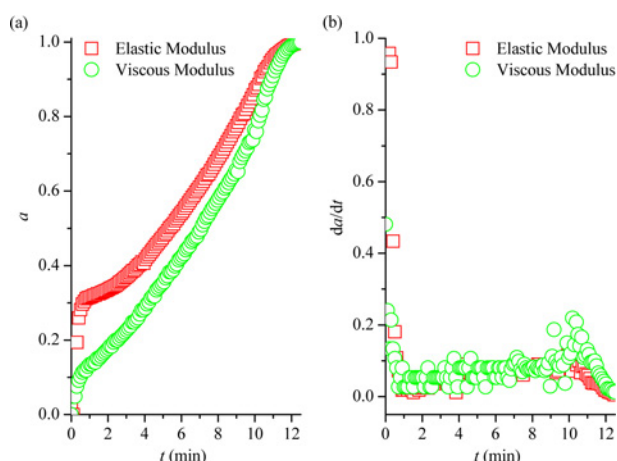


Fig. 2. (Color online) (a) Decelerating shaped $a-t$ curve and (b) da/dt curve of PNIPAm/A-PEO-A complexes at molar ratio of 1:1.

state both reflected this movement macroscopically. Transferring heat and mass in this movement was anisotropic and led to the disordered movement of macromolecules in all directions. This model is 3D, D_3 .

Fig. 2 shows the decelerating shaped $a-t$ curve and da/dt curve of PNIPAm/A-PEO-A complexes at molar ratio of 1:1. Apparently, as t (time) lengthened, a (relative modulus) increased slowly, not so fast as that at initial t (Fig. 2a). The da/dt presented high values at initial t and low values at next t (Fig. 2b), which also showed evidences for the decelerating shaped $a-t$ curve. In this study, PNIPAm/A-PEO-A complexes at molar ratio of 1:0.4 had a simple network structure, and that at molar ratio of 1:1 a complex one [Scheme 2b]; while those at molar ratios of 1:2 and 1:4 had single toroid structure and multiple toroid structure [Scheme 2d] (Cui *et al.*, 2014; Han *et al.*, 2013; Hirsh *et al.*, 2013; Hsu *et al.*, 2013; Shin *et al.*, 2013). In other words, $G(a)$ represented the rheological process of PNIPAm/A-PEO-A complexes at these molar ratios. In addition, it can be seen that $G(a)$ obtained from G' and G'' was the same for a PNIPAm/A-PEO-A complex at the same molar ratio, which also showed $G(a)$ represented the related rheological processes clearly. For example, $G(a)$ obtained from G' and G'' was Jander equation of $[1-(1-a)^{1/3}]^2$ for PNIPAm/A-PEO-A complex at molar ratio of 1:1, Zhuralev-Lesokin-Tempelmann equation of $[(1-a)^{-1/3}-1]^2$ for linear PNIPAm, and Jander equation of $[1-(1-a)^{1/2}]^2$ for linear A-PEO-A.

E is the required minimum energy of molecules from a reactant state to an activated state in a chemical reaction. In a rheological process, it is the different energy between the onset and offset points. A is a constant determined by the reaction essence and does not have any relationship to the reaction temperature and concentration in the system. E and A always have a same variation trend. PNIPAm and

A-PEO-A had high crystallinity and brittleness. The former was a white crystal at room temperature and had to require high energy to undergo a slight variation of elastic and viscous moduli. The latter was a viscous light yellow crystal at room temperature and just required low energy to undergo a slight variation of elastic and viscous moduli. The CMHB formed between the amide groups of PNIPAm and the adenine units of A-PEO-A gave PNIPAm/A-PEO-A complexes with a high degree of gelation, good toughness, elasticity, and flexibility (Cui *et al.*, 2014), so they underwent significant variations of elastic and viscous moduli using neither too high nor too low energies. As Fig. 1 shows, G' of PNIPAm/A-PEO-A complexes at molar ratios of 1:0.4, 1:1, 1:2, and 1:4 was higher than those at molar ratios of 1:0 (PNIPAm) and 0:1 (A-PEO-A). As Table 2 shows, E were 263.01 (obtained from G') and 250.11 (obtained from G'') kJ/mol for PNIPAm/A-PEO-A complex at molar ratio of 1:0, and 176.02 (obtained from G') and 137.46 (obtained from G'') kJ/mol for PNIPAm/A-PEO-A complex at molar ratio of 0:1. E obtained from elastic modulus were 226.32, 210.85, 220.26, and 223.66 kJ/mol, and that obtained from viscous modulus were 158.23, 206.73, 160.02, and 170.33 kJ/mol, for PNIPAm/A-PEO-A complexes at molar ratios of 1:0.4, 1:1, 1:2, and 1:4, respectively. Apparently, E of PNIPAm/A-PEO-A complexes at molar ratios of 1:0.4, 1:1, 1:2, and 1:4 was lower than that at molar ratio of 1:0 (PNIPAm) and higher than that at molar ratio of 0:1 (A-PEO-A). About PNIPAm/A-PEO-A complexes at molar ratios 1:0.4, 1:1, 1:2, and 1:4, E did not have a regular variation trend as elastic and viscous moduli did because they not only had the network structures [Scheme 2b] and toroid structures [Scheme 2d, but also contained small PNIPAm spherical micelles [Scheme 2a, label 1], small A-PEO-A spherical micelles [Scheme 2a, label 2], large associated aggregates from small spherical micelles [Scheme 2c, label 1' and 2'], and their mixed large associated aggregates [Scheme 2c, label 3' and 4']. It also can be seen that E determined through elastic modulus was higher than that determined through viscous modulus as that the elastic modulus was higher than the viscous modulus. For example, at molar ratio of 1:1, PNIPAm/A-PEO-A complex showed a higher E at 210.85 kJ/mol obtained from elastic modulus than that at 206.73 kJ/mol obtained from viscous modulus. This may be caused by the hysteresis phenomenon between elastic modulus and viscous modulus. As mentioned above, A varied accordingly with the variations of E (Table 2).

The kinetic compensation effect, a linear relationship between $\ln A$ and E , explains that A compensates to the change of E partly (Hu and Shi, 2001; Marcilla *et al.*, 2007; Yip *et al.*, 2011; Barrie, 2012a, 2012b): $\ln A = KE + Q$, where K and Q are the kinetic compensation effect parameters calculated from the linear fit between E and A .

Table 3. Kinetic compensation effect equations of PNIPAm/A-PEO-A complexes.

PNIPAm/A-PEO-A (Molar ratios)	Kinetic compensation effect equation	
1:0	□ $\ln A=0.0004E+0.5724$	○ $\ln A=0.0004E-1.2911$
1:0.4	□ $\ln A=0.0004E-1.6143$	○ $\ln A=0.0004E-3.5672$
1:1	□ $\ln A=0.0004E-1.3908$	○ $\ln A=0.0004E-2.8390$
1:2	□ $\ln A=0.0004E-1.6403$	○ $\ln A=0.0004E-2.8462$
1:4	□ $\ln A=0.0004E-1.6773$	○ $\ln A=0.0004E-3.2889$
0:1	□ $\ln A=0.0004E-0.7406$	○ $\ln A=0.0004E+1.1958$

□determined from G' , ○determined from G''

Table 3 shows the kinetic compensation effect equations of PNIPAm/A-PEO-A complexes. PNIPAm and A-PEO-A both were crystals with high crystallinity and brittleness. They developed the CMHB to form supramolecular assemblies of PNIPAm/A-PEO-A at molar ratios of 1:0.4, 1:1, 1:2, and 1:4. Thus, K was the same at 0.0004, indicating rheological properties and processes were the same. Similarly to E and A , Q had a close relationship to the small spherical micelles [Scheme 2a], large associated aggregates of small spherical micelles [Scheme 2c], network structures [Scheme 2b], and toroid structures [Scheme 2d]. The Q varied accordingly with E and A . Because K and Q are not influenced by experimental factors, the kinetic compensation effect equations can explain the rheological processes and reveal the rheological essences of PNIPAm/A-PEO-A complexes.

Conclusions

In this study, we prepared supramolecular complexes from PNIPAm/A-PEO-A blends in distilled water, stabilized through the CMHB between the amide groups of PNIPAm and the A units in A-PEO-A. The supramolecular assemblies featured spherical micelles, large associated aggregates of spherical micelles, network structures, and core-shell and core-shell-shell toroidal structures. The rheological kinetics, obtained from the variations of elastic and viscous moduli using Agrawal integral equation, had a close relationship to these supramolecular structures.

Appendix A. Agrawal Integral Equation

The Agrawal integral equation used for modeling nonisothermal reactions is obtained independently by solving the exponential temperature integral by Simpson's and Trapezoidal rule. Compared to others, it shows higher accuracy. For example, Coats-Redfern equation deviates by less than 1% from the exact solution for $E/RT > 23$ and by less than 10% for $E/RT > 6$; Gorbachev equation deviates by less than 0.1% for $E/RT > 41$ and by less than 1%

for $E/RT > 11$; Agrawal equation deviates by less than 0.1% for $E/RT > 7$. These equations are analysis methods (or fitting methods). Simpson law $G(a) = a^n$, Valensi equation $G(a) = a + (1-a)\ln(1-a)$, and Avrami-Erofeev equation $G(a) = [-\ln(1-a)]^n$ are obtained from Agrawal equation by fitting T and a .

References

- Agrawal, R.K., 1987, *J. Therm. Anal.* **32**, 149-156.
 Barrie, P.J., 2012a, *Phys. Chem. Chem. Phys.* **14**, 318-326.
 Barrie, P.J., 2012b, *Phys. Chem. Chem. Phys.* **14**, 327-336.
 Brown, M.E., 2001, *Introduction to Thermal Analysis: Techniques and Applications (Hot Topics in Thermal Analysis and Calorimetry)*, Springer, New York.
 Cao, C.W., et al., 2010, *Macromolecules* **43**, 9511-9521.
 Chen, H.W., et al., 2005a, *Macromolecules* **38**, 4403-4408.
 Chen, H.W., et al., 2005b, *Macromolecules* **38**, 8045-8050.
 Chen, H.W., et al., 2006a, *J. Colloid Interf. Sci.* **298**, 991-995.
 Chen, H.W., et al., 2006b, *Polymer* **47**, 8367-8373.
 Chen, J.C., et al., 2011, *J. Phys. Chem. B* **115**, 14947-14955.
 Cui, H.W., et al., 2014, *Euro. Polym. J.* **50**, 168-176.
 Du, H.B. and X.H. Qian, 2011, *J. Polym. Sci. Part B* **49**, 1112-1122.
 Gabbott, P., 2007, *Principles and applications of thermal analysis*, Wiley-Blackwell, New York.
 Halab-Kessira, L. and A. Ricard, 1999, *Eur. Polym. J.* **35**, 1065-1071.
 Han, J.H., et al., 2013, *J. Am. Chem. Soc.* **135**, 3736-3739.
 Hirsh, A.D., et al., 2013, *J. Comput. Nonlin. Dynamics* **8**, 031001.
 Hsu, C.Y., et al., 2013, *Macromol. Rapid Commun.* **34**, 689-694.
 Hu, R.Z. and Q.Z. Shi, 2001, *Thermal analysis kinetics*, Science Press, Beijing.
 Kuo, S.W., et al., 2012, *J. Nanomater.* 749732.
 Lai, C.T., et al., 2011, *Macromolecules* **44**, 6546-6556.
 Lee, H.N., et al., 2010, *Macromolecules* **43**, 9522-9528.
 Li, J., et al., 2009, *J. Polym. Sci. Part A* **47**, 1450-1462.
 Li, L.Y., et al., *J. Polym. Sci. Part A* **48**, 5018-5029.
 Liu, X.B., et al., 2012, *Macromolecules* **45**, 4830-4838.
 Luo, Y.L., et al., 2012, *J. Polym. Sci. Part A* **50**, 2053-2067.
 Marcilla, A., et al., 2007, *Ind. Eng. Chem. Res.* **46**, 4382-4389.
 Mei, A.X., et al., 2010, *Macromolecules* **43**, 7312-7320.
 Menzel, J.D. and R. Prime Bruce, 2009, *Thermal analysis of polymers, fundamentals and applications*, Wiley-Blackwell, New York.
 Schmidt, S., et al., 2008, *Polymer* **49**, 749-756.
 Shin, S., et al., 2013, *J. Am. Chem. Soc.* **135**, 2156-2159.
 Sladkov, I.B., 2002, *Russ. J. Appl. Chem.* **75**, 1770-1773.
 Sun, S.T., et al., 2012, *Soft Matter* **8**, 3980-3987.
 Tu, C.W., et al., 2009, *Polymer* **50**, 2958-2966.
 Vyazovkin, S., et al., 2011, *Thermochim. Acta* **520**, 1-19.
 Woo, M.W., et al., 2007, *Dry Technol.* **25**, 1741-1747.
 Yan, J.J., et al., 2008, *Macromolecules* **41**, 4908-4913.
 Yao, Y., et al., 2004, *J. Func. Polym.* **17**, 515-520.
 Yip, K., et al., 2011, *Proc. Combust. Inst.* **33**, 1755-1762.
 Zou, G., et al., 2003, *Chem. Res. Chinese U.* **24**, 537-540.