Rheological Test for the Homogeneity of Aqueous Blends of Associative Polymer Network and Entangled Linear Polymer

Takamitsu CHIBA*, Takuya KATASHIMA**, Osamu URAKAWA*†, and Tadashi INOUE*

*Department of Macromolecular Science, Graduate School of Science, Osaka University, Toyonaka, Osaka 560-0043, Japan
**Present address: Department of Bioengineering, School of Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan
(Received : December 20, 2019)

Linear viscoelastic behavior has been examined for the mixtures of a transient network and entangled linear polymers in aqueous solutions. We have found that the aqueous blends of hydrophobically ethoxylated urethane (HEUR) and sodium polyacrylate (PAANa) become transparent solutions and look homogeneous. To examine the molecular level homogeneity of this mixture, we analyze the linear viscoelastic spectra as functions of the volume fraction of PAANa, \( \phi_P \), at fixed HEUR concentrations, especially focusing on the plateau modulus, \( G_{N,mix} \) of the mixtures. The increase in \( G_{N,mix} \) by increasing \( \phi_P \) is assumed to be due to the formation of the hetero-entanglement between HEUR and PAANa, and the contribution of the hetero-entanglement on the plateau modulus, \( G_{0,N,H-P} \), can be estimated by using the Wu’s model. We have obtained the result that all the data can be explained in terms of a single \( G_{0,N,H-P} \) value, strongly supporting the view that the HEUR and PAANa chains are homogeneously mixed and interpenetrated each other in the mixed aqueous solutions.

Key Words: HEUR / Sodium polyacrylate / Transient network / Homogeneity / Hetero-entanglement

1. INTRODUCTION

Hydrophobically ethoxylated urethane (HEUR) consists of the hydrophilic linear main chain (poly(ethylene oxide)) and hydrophobic moieties chemically attached to the both chain ends. HEUR is one of telechelic type associative polymers and has been widely used as rheology modifiers in water-born coatings. Because of their unique association structure and rheological behaviors, many studies have been pursued to understand the relationship between their structure and rheological properties. For the industrial application of HEURs, the control of viscoelastic profiles under elongational and shear flows in both linear and nonlinear regions is needed. The addition of various surfactants to HEUR solutions is known to be one way to modify the rheological properties through the interaction between HEUR and surfactant molecules. As another approach, the addition of water soluble polymers in which only the one chain end was hydrophobically modified, is also reported. However, both studies are intended to change the stability of the associated structure of HEUR. We think that the addition of water soluble long flexible polymers causes another effect: the formation of hetero-entanglements between the HEUR network and linear polymers. This can be a new option to modify the rheology of HEUR solutions in a different direction.

Since HEUR forms associating network structure, mixing other high molecular weight polymers often results in phase separation, even if water is mixed as the third component. Actually, in our preliminary experiments, we found that poly(vinyl alcohol) with the molar mass \( M = 8.8 \times 10^4 \text{ g mol}^{-1} \) and poly(ethylene oxide) with \( M = 5 \times 10^5 \text{ g mol}^{-1} \) did not form homogeneous mixtures with HEUR in aqueous solutions, but the blend of sodium poly(acrylic acid) (PAANa) and HEUR became a transparent aqueous solution. Therefore, in this study we have conducted rheological tests to examine the molecular level homogeneity of this mixed system. Wu reported a theoretical equation to explain the plateau modulus of miscible blends. The extension of his equation to ternary solutions allows us to analyze the concentration dependence of the plateau modulus in HEUR / PAANa aqueous solutions and to estimate the molar mass of the hetero-entanglement. Here, we show that this analysis is useful to confirm the molecular level uniformity of entangled polymer blend solutions including temporary cross-linking networks.
2. EXPERIMENTAL

2.1 Sample Preparation

A hydrophobically modified ethoxylated urethane sample was kindly supplied by ADEKA. Its characterization details have been reported previously[^10]. The weight average molar mass, \( M_w \), and the polydispersity index represented by the ratio of the weight to number averaged molar masses (\( M_w/M_n \)) were \( M_w = 3.5 \times 10^4 \) g/mol and \( M_w/M_n = 3.7 \), respectively. Sodium polyacrylate (PAANa) with the molar mass of \( 4.3 \times 10^6 \) g/mol was purchased from Wako Chemicals.

For the preparation of HEUR/PAANa aqueous solutions, prescribed amounts of HEUR, PAANa and distilled water were mixed together and stirred at least for 1 week and left standing for more than 2 months until the mixture had become transparent. The neat HEUR and PAANa solutions were prepared in the similar way but the waiting time for the solutions to look homogeneous was shorter, less than 1 week. The volume fractions of HEUR and PAANa components in both binary and ternary solutions, \( \phi_H \) and \( \phi_P \), were respectively set to be \( \phi_H = 0.014 \sim 0.019 \) and \( \phi_P = 0.0038 \sim 0.015 \).

2.2 Linear Viscoelastic Measurement

For the dynamic viscoelastic and stress relaxation measurements, a stress rheometer MCR301 (Anton Paar) equipped with a cone-plate fixture of 25 mm diameter was used. The angular frequency, \( \omega \), sweep tests were carried out from \( \omega = 0.01 \) to 100 s\(^{-1} \) at 25 ºC. The oscillatory shear strain amplitude, \( \gamma \), for all the tests was 0.1, which was in the range of linear viscoelasticity. To observe the longer relaxation time component, stress relaxation measurements up to \( 10^3 \) s were conducted by applying a step strain with \( \gamma = 0.3 \), which was also confirmed to be in the linear response region.

3. RESULTS AND DISCUSSION

3.1 Linear Viscoelastic Spectrum

Figure 1 shows the complex shear moduli, \( G' (\omega) \) (= \( G' (\omega) + iG'' (\omega) \)), where \( i \) is the imaginary unit, for the HEUR solutions (a) and the PAANa solutions (b) as functions of \( \omega \). The storage and loss moduli, \( G'_H (\omega) \) and \( G''_H (\omega) \), of the HEUR solutions can be well represented by the Maxwell model (solid curves in Fig. 1) given by the following equation.

\[
G''_H (\omega) = G_N H \frac{\omega^2 \tau_H}{1 + \omega^2 \tau_H^2}, \quad G'_H (\omega) = G_N H \frac{\omega \tau_H}{1 + \omega^2 \tau_H^2} \quad (1)
\]

Here, \( G_N H \) is the modulus and \( \tau_H \) is the relaxation time of the transient network of HEUR. This result is consistent with the previous studies[^1,5,8-10,15], and can be explained in the framework of the classical transient network theory[^17,18]. The theoretical models for transient networks assume that the viscoelastic relaxation is caused by the detachment of the bridged chains from the hydrophobically associated cores. They premise that each network strand obeys the Gaussian statistic and relaxes instantaneously to the equilibrium state after the dissociation of the hydrophobic chain end from the hydrophobically associated core. This mechanism is considered to be responsible for a single relaxation (Maxwellian) behavior observed through dynamic viscoelastic measurements.

On the other hand, as shown in Fig. 1 (b), the shapes of \( G'_P (\omega) \) and \( G''_P (\omega) \) for the PAANa solutions are broader than those of the HEUR solutions, meaning the broader relaxation time distribution for the PAANa solutions. These broad shape spectra are typical for entangled polymers with broad molecular weight distributions.

Fig. 1 Frequency dependence of \( G' \) (open) and \( G'' \) (filled) for (a) HEUR, and (b) PAANa solutions with various concentrations measured at 25 ºC. The solid curves in (a) are the \( G' \) and \( G'' \) calculated by the Maxwell model, and those in (b) are guide for the eye.
Figure 2 shows the $\omega$ dependence of the shear complex moduli for the mixed systems with fixed $\phi_H (= 0.014)$ and various volume fractions of PAANa, $\phi_P = 0.0038 \sim 0.015$. With increasing $\phi_P$, the $G'$ spectra shift upward, while the $\tan \delta (= G''/G')$ values at low $\omega$ decrease. The decrease in $\tan \delta$ can be related to the existence of a slow relaxation mode which is more pronounced at higher $\phi_P$. Actually, $G'$ and $G''$ in the low frequency region, especially at $\log(\omega/s^{-1}) < 0$, do not show typical terminal relaxation behavior of $G' \sim \omega^2$, $G'' \sim \omega$, and $\tan \delta \sim \omega^{-1}$ for the mixed systems: the absolute values of the power low exponents are smaller than the typical terminal values especially for $G'$ and $\tan \delta$ indicating the presence of the unrelaxed modes. Regarding such a slow relaxation mode, the following two possibilities can be considered: (1) just the appearance of the PAANa relaxation in the low $\omega$ region, and/or (2) the appearance of an extra slow relaxation originating from the phase separated domains if the system is phase-separated. To see the slow relaxation mode more precisely, the relaxation moduli, $G(t)$, measured for long time intervals ($t = 10^{-2} \sim 10^3$ s) are shown in Fig. 3(a). For comparison the data of PAANa solutions are also shown in Fig. 3(b). By looking at the $G(t)$ data in the wide time span, two step type relaxation can be clearly recognized for the mixed solutions. By comparing the data shown in Fig. 3 (a) and (b), the slow relaxation component of the mixed systems observed in the long time region almost corresponds to the terminal relaxation of the PAANa aqueous solutions. This means that the fast and slow relaxation components can be mainly ascribed to the relaxation of the HEUR component and that of the PAANa component, respectively. This result could deny the possibility of phase separation in these samples, because for phase-separated systems, extra-relaxation component with the relaxation time longer than the chain relaxation and/or a power law type decay in $G(t)$ will be observed. Moreover, the data reproducibility for both the $G'(\omega)$ and $G(t)$ curves shown in Figs. 2 and 3 were also very good. Judging from those results, we can say that there is no phase-separated structure in these solutions with the spatial size larger than the polymer chain size. Regarding the component contributions in the observed viscoelastic spectra shown in Figs. 2 and 3, we will discuss it in detail by using the modified stress optical rule in near future.

The three $G'(\omega)$ spectra for the HEUR, PAANa, and mixed solutions are compared in Fig. 4 at the typical concentrations: $\phi_H = 0.014$ and $\phi_P = 0.015$. The plateau modulus ($G'$ in the high frequency region) of the mixed system is larger than those of the HEUR and PAANa solutions, and the frequency of the mixed system at which the $G''$ curve has a peak is smaller than those of the HEUR and PAANa solutions. This result could deny the possibility of phase separation in these samples, because for phase-separated systems, extra-relaxation component with the relaxation time longer than the chain relaxation and/or a power law type decay in $G(t)$ will be observed. Moreover, the data reproducibility for both the $G'(\omega)$ and $G(t)$ curves shown in Figs. 2 and 3 were also very good. Judging from those results, we can say that there is no phase-separated structure in these solutions with the spatial size larger than the polymer chain size. Regarding the component contributions in the observed viscoelastic spectra shown in Figs. 2 and 3, we will discuss it in detail by using the modified stress optical rule in near future.

The three $G'(\omega)$ spectra for the HEUR, PAANa, and mixed solutions are compared in Fig. 4 at the typical concentrations: $\phi_H = 0.014$ and $\phi_P = 0.015$. The plateau modulus ($G'$ in the high frequency region) of the mixed system is larger than those of the HEUR and PAANa solutions, and the frequency of the mixed system at which the $G''$ curve has a peak is smaller than those of the HEUR and PAANa solutions. This result could deny the possibility of phase separation in these samples, because for phase-separated systems, extra-relaxation component with the relaxation time longer than the chain relaxation and/or a power law type decay in $G(t)$ will be observed. Moreover, the data reproducibility for both the $G'(\omega)$ and $G(t)$ curves shown in Figs. 2 and 3 were also very good. Judging from those results, we can say that there is no phase-separated structure in these solutions with the spatial size larger than the polymer chain size. Regarding the component contributions in the observed viscoelastic spectra shown in Figs. 2 and 3, we will discuss it in detail by using the modified stress optical rule in near future.

Fig. 2  Frequency dependence of $G'$ (open symbol), $G''$ (filled symbol), and $\tan \delta$ (gray filled symbol) for the mixed systems with various $\phi_P$ at fixed $\phi_H (= 0.014)$ measured at 25 °C. The solid, dashed, and dotted curves are guide for the eye.

Fig. 3  Time dependence of relaxation modulus (a) for the mixed systems with various $\phi_P$ at fixed $\phi_H (= 0.014)$, and (b) for neat PAANa aqueous solutions with various $\phi_P$ measured at 25 °C.
maximum is lower than that of the neat HEUR solution. We think that these results are caused by the increase in the entanglement density, which may be due to the formation of the hetero-entanglement between the HEUR and PAANa chains. In the next section, we will analyze the entanglement densities based on the Wu’s model to examine the homogeneity of the mixed solutions at the entanglement molecular size.

### 3.2 Concentration Dependence of Plateau Modulus

For the data shown in Fig. 2, we approximately regard the values of $G'$ at $\omega = 100 \text{ s}^{-1}$ as the plateau modulus, $G_{N,\text{mix}}$, of the mixed solutions. Thus determined $G_{N,\text{mix}}$ values as a function of $\phi_p$ are shown in Fig. 5. The values of the neat PAANa solutions, $G_{N,P}$, were also determined in the same way and plotted against $\phi_p$ in the same figure. It is seen that the $\phi_p$ dependence of $G_{N,\text{mix}}$ is weaker than that of $G_{N,P}$.

Generally the plateau modulus, $G_N$, of a single component polymer solution in the entangled state is given by\(^{16, 22}\)

$$G_N = \frac{\phi \rho RT}{M_e(\phi)} = \phi^2 G_0^N$$

(2)

where $\phi$ is the volume fraction of the polymer, $\rho$ is the density of the polymer in melt, $M_e(\phi)$ is the molar mass between the entanglement points at the polymer volume fraction equal to $\phi$, $M_{e,melt}$ is the entanglement molar mass in melt, and $G_0^N (= \rho RT/M_{e,melt})$ is the modulus at $\phi = 1$. It is seen that for the neat PAANa solutions the proportionality between $G_{N,P}$ and $\phi_p^2$ as given by Eq.(2) holds.

The $G_{N,\text{mix}}$ of the mixed solution is written by the sum of three contributions from HEUR, PAANa, and the cross-term.

$$G_{N,\text{mix}} = G_{N,H} + G_{N,P} + G_{N,H-P}$$

(3)

These three terms represent the moduli originating from the temporal network of HEUR ($G_{N,H}$), the homo-entanglement of PAANa chains ($G_{N,P}$), and the hetero-entanglement between HEUR and PAANa ($G_{N,H-P}$), respectively. While the $G_{N,H}$ term is determined by the association structure of HEUR, the $G_{N,P}$ and $G_{N,H-P}$ terms are determined by the entanglement effect, and thus can be written by the similar expression with Eq.(2) using two component volume fractions, $\phi_H$ and $\phi_P$.

According to Wu\(^{16}\), the following expression for the mixed system can be written.

$$G_{N,\text{mix}} = G_{N,H} + \phi_H^2 G_{N,P}^0 + 2\phi_H \phi_P G_{N,H-P}^0$$

(4)

Here $G_{N,P}$ and $G_{N,H-P}$ are the moduli in the molten state determined by the homo-entanglements and the hetero-entanglements, respectively. Since HEUR is associated through hydrophobic interaction and PAANa is dissolved in the ionized state in the aqueous solutions, it will not be feasible to make the solution in the molten state ($\phi_H + \phi_P = 1$) with keeping several interactions to be the same as in the solution system. Therefore, the $G_{N,P}$ and $G_{N,H-P}$ values are virtual parameters. However, to examine how the modulus depends on the concentrations, Eq.(4) is useful. In this equation, we left the term of $G_{N,H}$ as it is, although the Wu’s original equation expresses this term as $\phi_H^2 G_{N,H}^0$. This is because the modulus of the HEUR component is not determined by a simple binary contact, but
by the hydrophobic association of the telechelic chain ends. We assume that regarding the first term of Eq.(4) as constant is permissible if the temporary network structure of the HEUR component is fixed. In this study, the $\phi_H$ value is fixed so that the $G_{N,H}$ term is also fixed: $G_{N,H} = 1.5 \times 10^2$, $2.5 \times 10^2$, and $3.1 \times 10^2$ Pa at $\phi_H = 0.014$, 0.017, and 0.019, respectively. The $G_{N,P}$ and $G_{N,H-P}$ terms in Eq.(4) can be further rewritten(6) using the same expressions with Eq.(2) as follows.

$$G_{b,P}^0 = \frac{\rho RT}{M_{m,H-P}}$$ $$G_{b,H-P}^0 = \frac{\sqrt{\rho \theta_T RT}}{M_{m,H-P}}$$

Here, $M_{m,H-P}$ and $M_{m,H-P}$ are the average entanglement molecular masses between homo-entanglement points formed by two PAANa chains and hetero-entanglement points formed by the HEUR and PAANa chains in the melts, respectively. These are also virtual parameters considered under the assumption that all the interactions acting in aqueous solutions are preserved even in the molten state.

The $G_{N,P}^0$ value can be determined from the data of PAANa solutions shown in Fig. 1 as $G_{N,P}^0 = 4.0 \times 10^5$ Pa. Regarding the $G_{N,H-P}^0$ value, this was used as an adjustable parameter to fit the data of $G_{N,mix} (\phi_H)$, from which the hetero-entanglement molecular mass could be obtained. The fitting result by Eq.(4) is also shown in Fig. 5 with the black solid line along with each component contributions, $G_{N,H}$, $G_{N,P}$, and $G_{N,mix}$ which were determined as the functional forms given in Eq.(4). It is seen that Eq.(4) including only one adjustable parameter ($G_{N,H-P}^0$) can fit the $G_{N,mix}$ data well. The obtained value of $G_{N,H-P}^0$ is $3.5 \times 10^5$ Pa, from which the $M_{m,H-P}$ value is calculated to be $8.3 \times 10^3$ g mol$^{-1}$. This estimated molar mass is a virtual value in the molten state. However, by comparing it with the values for PAANa and poly(ethylene oxide) (PEO) which is a main part of HEUR, we can see the entanglement probability of dissimilar chains as proposed by Wu(6). The reason why we use the $M_{o}$ of PEO as a counterpart of HEUR is as follows. The $G_{N,H-P}$ term in $G_{N,mix}$ comes from the formation of hetero-entanglements between the network strands of HEUR and the PAANa chain in the aqueous solution. In the elastically responding region at a high frequency ($\omega = 100$ s$^{-1}$), the HEUR network can be considered as a permanent one consisting of PEO chains (3 dimensionally cross-linked PEO network), and thus the hetero-entanglement can be simply regarded as the entanglement between the PEO chain and the PAANa chain. For this reason, $M_{m,PEO}$ is used as a guide to represent the entanglement probability of HEUR strands.

The estimated molar mass ($M_{m,H-P} = 8.3 \times 10^3$ g mol$^{-1}$) by using Eq.(4) is higher than $M_{m,PEO} (= 7.5 \times 10^3$ g mol$^{-1}$) determined from the data of the PAANa solutions and the reported value for PEO, $M_{m,PEO} = 1.6 \times 10^3$ g mol$^{-1}$). The relationship of $M_{m,H-P} > M_{m,PEO}$ suggests that the hetero-entanglement is less favorable than the homo-entanglements. Moreover, the result shown in Fig. 5 indicates that the plateau modulus of the mixed systems consisting of a transient network and linear polymers can be explained by considering the effect of the hetero-entanglement.

For the $G' (\omega)$ spectra of the other two HEUR concentrations ($\phi_H = 0.017$ and 0.019), the increase of the high frequency plateau modulus with increasing $\phi_H$ was also observed. Figure 6 shows all the results of the $\phi_H$ dependence of $G_{N,mix}$ which were determined as $G' (\omega)$ at $\omega = 00$ s$^{-1}$ from the $G' (\omega)$ data. The fitting curves given by Eq.(4) are also shown. The parameters involved in Eq.(4) are $G_{N,H}$, $G_{N,P}$, and $G_{N,H-P}$, and all the values are already known: the $G_{N,H}$ and $G_{N,P}$ values have been determined from the data of the neat HEUR and PAANa solutions, and the $G_{N,H-P}$ value has also been determined in Fig. 4 using the data of $\phi_H = 0.014$. The results shown in Fig. 6 (the agreement between the data and the fit curves for all the solutions) indicates the validity of Eq.(4). Furthermore, the fact that a single set of parameters in Eq.(4) can explain the concentration dependence of the plateau values for all the solutions with different $\phi_H$ strongly suggests that this ternary system is homogeneously mixed in the spatial scale of the entanglement: the temporary network of HEUR and the entangled PAANa chains are well interpenetrated each other at all concentrations examined in this study.

Fig. 6 Relationship between $G_{N,mix}$ and $\phi_H$ for HEUR / PAANa aqueous solutions with three different HEUR concentrations ($\phi_H = 0.014$, 0.017, and 0.019). Thick solid lines represent the calculated results with Eq. (4) in which the same $G_{N,H-P}$ value ($3.5 \times 10^5$ Pa) was used.
4. CONCLUSION

In order to verify the miscibility of HEUR / PAANa aqueous solutions, we conducted linear viscoelastic measurements on the mixed aqueous systems of transient networks and entangled linear polymers, HEUR / PAANa, with the fixed HEUR concentrations ($\phi_H = 0.014, 0.017, \text{ and } 0.019$) and varying the PAANa concentration ($\phi_P = 0.0038 \sim 0.015$).

For the concentration dependence of the plateau modulus, the Wu’s equation could reasonably represent the data. The only fitting parameter was the hetero-entanglement plateau modulus, $G_0^{N,H-P}$, or the corresponding molar mass, $M_{e,melt,H-P} = \sqrt{\rho_H \rho_P RT / G_0^{N,H-P}}$, in the molten state of the HEUR / PAANa mixture, which were determined to be $G_0^{N,H-P} = 3.5 \times 10^5 \text{ Pa}$ and $M_{e,melt,H-P} = 8.3 \times 10^3 \text{ g mol}^{-1}$ as a virtual parameter assuming all the interactions, such as hydrophobic interaction and ionic interaction acting in aqueous solutions to be the same in the molten state. The $M_{e,melt,H-P}$ value was higher than those of the components (HEUR and PAANa) suggesting the less favorable hetero-entanglement formation than the homo-entanglements. However, from the result that the same value of $M_{e,melt,H-P}$ or $G_0^{N,H-P}$ could reproduce the plateau moduli of all the mixed solutions with different $\phi_H$ and $\phi_P$, we have concluded that the HEUR network and PAANa chains are well interpenetrated (mixed) each other in the aqueous solution.

ACKNOWLEDGMENTS

This work was partially supported by JSPS KAKENHI Grant Number 16H04204 & JP19H0277 and ImPACT Program of Council for Science, Technology and Innovation (Cabinet Office, Government of Japan). We wish to thank ADEKA Co., Ltd. for the supply of HEUR samples.

REFERENCES

1) Winnik MA, Yekta A, Curr Opin Colloid In, 2, 424 (1997).
2) Elliott PT, Mahli DM, Glass JE, J Coat Technol Res, 4, 351 (2007).
3) Schwab FG, Adv Chem Ser, 213, 369 (1986).
4) Ishida S, Koike K, Journal of Japan Coating Technology Association, 53, 90 (2018).
5) Annable T, Buscall R, Ettenlae R, Whittlestone D, Journal of Rheology, 37, 695 (1993).
6) Rao BH, Uemura Y, Dyke L, Macdonald PM, Macromolecules, 28, 531 (1995).
7) Uemura Y, Macdonald PM, Macromolecules, 29, 63 (1996).
8) Uneyama T, Suzuki S, Watanabe H, Phys Rev E, 86, 031802 (2012).
9) Tripathi A, Tam KC, McKinley GH, Macromolecules, 39, 1981 (2006).
10) Ohnishi M, Katashima T, Nakahata M, Urakawa O, Nihon Reoroji Gakkaishi, 47, 133 (2019).
11) Zhang KW, Xu B, Winnik MA, Macdonald PM, Journal of Physical Chemistry B, 100, 9834 (1996).
12) Dai S, Tam KC, Jenkins RD, Journal of Physical Chemistry B, 105, 10189 (2001).
13) Dai S, Tam KC, Jenkins RD, Macromolecules, 34, 4673 (2001).
14) Zinn T, Willner L, Knudsen KD, Lund R, Macromolecules, 50, 7321 (2017).
15) Annable T, Ettenlae R, Macromolecules, 27, 5616 (1994).
16) Wu SH, Polymer, 28, 1144 (1987).
17) Yamamoto M, J Phys Soc Jpn, 11, 413 (1956).
18) Green MS, Tobolsky AV, Journal of Chemical Physics, 14, 80 (1946).
19) Vlassopoulos D, Rheologica Acta, 35, 556 (1996).
20) Vinckier I, Laun HM, Rheologica Acta, 38, 274 (1999).
21) Inoue T, Okamoto H, Osaki K, Macromolecules, 24, 5670 (1991).
22) Ferry JD, “Viscoelastic Properties of Polymers, 4th. ed.”, (1980), Wiley, New York.
23) Fetters LJ, Lohse DJ, Richter D, Witten TA, Zirkel A, Macromolecules, 27, 4639 (1994).