Rheological Behavior of Weakly Associated Polymers

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Viscoelastic terminal relaxation behavior of unentangled polymers having hydrogen bonding moieties was examined. Specifically, partially saponified poly(vinyl acetate), i.e., poly(vinyl acetate-co–vinyl alcohol) with various hydroxyl (OH) group contents, \( f_{\text{OH}} \), was used as a model polymer. Formation of hydrogen bonds due to the presence of the OH groups resulted in the increase of both the glass transition temperature, \( T_g \), and the terminal relaxation time, \( \tau_w \). For the viscoelastic spectra of all the samples, time-temperature superposition principle approximately held. The shift factors could be expressed by the universal Williams Landel Ferry equation by setting appropriate reference temperatures, \( T_r^* \). Comparison of \( \tau_w \) under an iso-frictional condition (at \( T_r^* \)) revealed the formation of aggregates of constituent polymers. By considering the distribution of the aggregation numbers predicted by the mean field percolation model the viscoelastic spectra could be reproduced when \( f_{\text{OH}} \leq 0.28 \). However, for the samples with \( f_{\text{OH}} = 0.35 \) and 0.37, an extra relaxation component was found to exist in addition to the prediction of the percolation model.

Key Words: Associating polymer / Hydrogen bond / Rouse model / Percolation / Complex shear modulus

1. INTRODUCTION

Structures formed in polymeric materials through inter-molecular association such as hydrogen (H-) bonds affect their physical properties\(^1\). Since typical energies of H-bonds\(^2\) are 5–30 kJ mol\(^{-1}\), slightly higher than the thermal energy (~2.5 kJ mol\(^{-1}\) at room temperature), the association structure formed by H-bonding can be thermally destroyed and easily regenerated. In other words, thermplasticity is preserved even though the polymer network structure cross-linked by H-bonding exists. In that sense, this interaction is easy to use in controlling physical properties of polymer materials. In many cases, the formation of H-bonds decreases the free volume so that the glass transition temperature \( T_g \) increases\(^1, 3, 4\). At the same time, the global polymer chain motion is retarded due to the intermolecular association\(^5\). Furthermore, because the lifetime of the hydrogen bonds depends on temperature, which may be different from the temperature dependence of the free volume fraction related to the \( T_g \), the time temperature superposition principle (TTS) does not necessarily hold\(^6\). In the case that the TTS holds in a certain range of temperature, the H-bonding structure does not change at these temperatures or all the H-bonding structure has already broken, i.e., the lifetime of the H-bonding aggregate is much longer or shorter than the measurement time scale. On the other hand, in the case of the TTS failure, the association structure changes by changing temperature.

Previously, we investigated rheological behaviors of partially saponified poly(vinyl acetate), i.e., poly(vinyl acetate-co–vinyl alcohol), (P(VA-OH)), as a model hydrogen bonding system and reported both cases where the TTS held or not\(^3\). For the samples with low vinyl alcohol content (molar fraction), \( f_{\text{OH}} \leq 0.37 \), the TTS held, but for the samples of high \( f_{\text{OH}} \geq 0.57 \), in which network structures were formed through the inter chain H-bonding, the TTS broke down especially in the low frequency plateau region corresponding to the H-bonding network structure. In our previous paper\(^2\), we examined the latter case in detail including the time evolution and memory effect of the association structure after changing temperature. In this paper, the dynamic viscoelastic spectra of P(VA-OH)s with \( f_{\text{OH}} \leq 0.37 \) (in the case that TTS holds) have been reanalyzed based on the Rouse model assuming the associating structure expected by the mean field percolation model. The maximum association number of polymer chain can be extracted by this analysis. Moreover, since for the high \( f_{\text{OH}} \) samples we found the necessity of adding an extra relaxation mode to the percolation model in order to fit the
viscoelastic spectra, the possible mechanism for this relaxation mode is also discussed.

2. EXPERIMENTAL

Poly(vinyl acetate), (PVAc) was purchased from Aldrich Chemicals and used after the reprecipitation purification from methanol (solvent) / water (non-solvent). The weight average molecular weight was determined to be $M_w = 1.2 \times 10^4$ from the intrinsic viscosity of the THF solution, and the molecular weight distribution was determined to be $M_w/M_n = 1.77$ by size exclusion chromatography equipped with refractive index detector (Tosoh Corp.)³. The random copolymers of vinyl acetate and vinyl alcohol, (PVAc-OH) with various OH contents were synthesized through the saponification reaction of the PVAc by using NaOH following the method previously reported⁸ ⁹. The degrees of saponification $f_{OH}$ were determined by $^1H$-NMR measurements⁹. Table I shows the characteristics of the samples used in this study. The details of the characterization was described elsewhere⁵ ⁷.

Glass transition temperatures, $T_g$, were measured with differential scanning calorimetry (DSC 6220, EXSTAR-6000, Seiko Instruments) with the heating rate of 10 Kmin⁻¹. The results are also shown in Table I.

Dynamic viscoelastic measurements were carried out with the stress rheometer (Rheometrics, Inc. SR-200) in the temperature range of 60–150 °C and the angular frequency $\omega$ range of 0.001–500 rad/s.

3. RESULTS AND DISCUSSION

3.1 Viscoelastic Spectra of P(VA-OH)s in Melt

The master curves of the complex shear modulus, $G^\prime (\omega) = G' (\omega) + iG'' (\omega)$, where $G'$ is the storage modulus and $G''$ is the loss modulus, as functions of the angular frequency, $\omega$, for all the samples are shown in Fig. 1. The reference temperature, $T_0$, was 351.7 K. As can be seen in these data, the time temperature superposition principle worked well. Since the molecular weight of PVAc ($M_w = 1.2 \times 10^4$) is less than the characteristic molecular weight for entanglement, i.e. less than the twice of the entanglement molecular weight, $M_e (= 6944)^{10}$, the viscoelastic spectra can be compared with the Rouse model prediction given by the following equation¹¹.

$$G^* = G' + iG'' = \frac{\rho RT}{M_w} \sum_{k=1}^{N_0} \frac{\omega \tau_k / k^2}{1 + i\omega \tau_k / k^2}$$  \hspace{1cm} (1)

Here, $\rho$ is the density (= 1.0 g cm⁻³), $R$ is the gas constant, $N_0$ is the degree of polymerization, $k$ is the mode number (a natural number) from 1 to $N_0$, and $\tau_k$ is the relaxation time of the first (slowest) mode. The fitting result for the PVAc data is shown by the solid lines in this figure. The parameter to reproduce the $G'(\omega)$ and $G''(\omega)$ spectra is only the $\tau_1 (= 0.03$ s for PVAc). However, the intensity factor in Eq.(1), $\rho RT/M_w$, should be slightly changed to attain a reasonable fit. Specifically, the molecular weight $M_w$ was changed to be $2.0 \times 10^4$ instead of $1.2 \times 10^4$. We think that the broadness of the molecular weight distribution (MWD)¹² ($M_d/M_w = 1.77$) and/or the weak emergence of long-time term¹²,¹³ will be the cause of the need of this modification. In this paper, we assume that such non-idealities are approximately compensated by modifying the intensity factor and hereafter this factor is also used to reproduce the $G^*$ data of P(VA-OH) samples.

All the solid curves in Fig.1 are the fitted results by the Rouse model (with fixed intensity factor and only by adjusting $\tau_1$. It is seen that $G'(\omega)$ and $G''(\omega)$ for the low $f_{OH}$ samples is well described by Eq.(1). In contrast, for the high $f_{OH}$ samples ($f_{OH} \geq 0.35$), deviation from the solid curve is seen at low $\omega$ region. This will be due to the interchain aggregation with long lifetime because the number of interchain H-bonds increases with increasing the OH content as reported previously³. Concerning the specificity of the samples with $f_{OH} \geq 0.35$, we note that anomalies were observed for the neutron scattering profiles due to the concentration fluctuation in the P(VA-OH35) / poly(ethylene oxide) (PEO) blend⁷. Because of the large number of H-bonding sites for the P(VA-OH35) sample, the formation of the intermolecular H-bonds between P(VA-OH) and PEO was considered to suppress the concentration fluctuation more strongly than the prediction of the random phase approximation theory.

From the viscoelastic spectra shown in Fig. 1, the terminal (secondary average) relaxation time, $\tau_\infty$, was determined from the cross point frequency ($= 1/\tau_\infty$) of the two asymptotic lines for $G'(-\omega^2)$ and $G''(-\omega^2)$ at low $\omega$. It is noted that the $\tau_\infty$
the Rouse model prediction. The reference temperature is 351.7 K.

of the Rouse model and the first mode relaxation time, \( \tau_1 \), are close but not equal. The relationship between them is given by \( \tau_a = (\sigma^2/15)\tau_1 \). However, this relation did not exactly hold because of the imperfect agreement in \( G'(\omega) \) spectra between the experimental data and the fitted one by the Rouse model. For example, \( \tau_a = 0.030 \) s obtained by the Rouse fitting corresponds to \( \tau_1 = 0.020 \) s while the experimentally observed one was \( \tau_a = 0.034 \) s. Figure 2 shows the \( f_{OH} \) dependence of the \( \tau_a \) (directly determined from the \( G' \) data) at \( T = 351.7 \) K (filled circles). It is seen that the terminal relaxation slows down with increasing \( f_{OH} \) especially at \( f_{OH} = 0.35 \) and 0.37 probably by the influence of hydrogen bonding.

### 3.2 WLF Analysis

The shift factors, \( \alpha_T \), to construct the master curves for all the samples are shown in Fig. 3(a). The solid curves represent the fit by the following Williams Landel Ferry (WLF) equation:

\[
\log a_T = -\frac{C_2 (T - T_r)}{C_2 + (T - T_r)}
\]

(2)

Here \( T_r \) is the reference temperature set to be 351.7 K, and \( C_1 \), \( C_2 \) are the constants which were determined to fit each data and are given in Table II. In the determination of these parameters, we assumed that the shapes of \( \log a_T \) vs. \( T \) curves are the same for all the samples. The WLF equation with \( (C_1, C_2) = (C_{10}, C_{20}) \) to fit the PVAc data was used as a standard curve and shifted to fit on the other samples’ \( \log a_T \) curves. This procedure is equivalent to choose one particular point \( (T = T'_r) \) of the WLF equation for PVAc to move it to the reference temperature (357.1 K) position. Namely, instead of using two parameters \((C_1, C_2)\) in Eq.(2), one particular temperature, \( T'_r \), was chosen to fit the data and then the values of \( (C_1, C_2) \) were calculated from the following relation:

\[
C_1 = \frac{c_1^0 c_2^0}{c_2^0 - (T_r - T'_r)} , \quad C_2 = c_2^0 - (T_r - T'_r)
\]

(3)

As already shown in Fig. 3(a) this procedure worked well. Fig. 3(b) shows the superposed shift factors drawn by using a new reference temperatures, \( T'_r = 351.7 \) K + (351.7 K – \( T'_r \)). The values of \( T'_r \) are also shown in Table II. Thus determined \( T'_r \) is compared with \( T_r \) measured by DSC in Fig. 4. In this plot, the deviation from the straight line with slope unity is seen. If the friction factor for the polymer chain dynamics is simply determined by the free volume fraction, \( i.e. \ T_i \), a proportional relationship between these quantities should hold. The failure of this proportionality might be related to the thermo-rheological complexity usually observed in the vicinity of \( T_g \) for the global and segmental dynamics of
polymers. If the degree of this complexity depends on the degree of H-bonding (if the complexity becomes weaker by the H-bond formation), we think that the result of Fig. 4 could be explained.

For the data shown in Fig. 2, the difference in the frictional coefficients can be corrected by simply comparing the \( \tau_w \) data at \( T = T_r^* \). The open symbols in Fig. 2 shows thus corrected \( \tau_w \). It is seen that the \( \tau_w \) under the iso-frictional condition still depends on \( f_{OH} \) even though the dependence becomes weaker by this correction. In the following sections, we will discuss the reason why such \( f_{OH} \) dependence in \( \tau_w \) and also the shape change of \( G^* \) spectra (deviation from the Rouse spectrum) appear.

3.3 Percolation Model of the Rouse Chain

The main reason for the deviation from the Rouse model concerning the \( G'(\omega) \) and \( \tau_w \) with the increase of \( f_{OH} \) is considered to be the formation of the associated structure of P(VA-OH) chains through the intermolecular hydrogen bonding. To consider the association structure and its dynamics, in this section, the mean field percolation model of the Rouse chain is explained.

The Mean field model of gelation can be represented by a bond percolation on the Bethe lattice. The functionality of the monomers (percolating units corresponding to single chains in the case of P(VA-OH)), \( f \), can be taken into account by adopting it for the lattice structure (\( f \)-branched lattice). All lattice sites are occupied by monomers and the possible bonds between neighboring monomers are formed with probability \( p \). Near the gel point the number density of \( N \)-mers, \( n(N) \), is written as

\[
n(N) = \frac{f}{\sqrt{2\pi}(f-1)(f-2)} N^{-\frac{5}{2}} \exp \left( -\frac{N}{N^*} \right) \tag{4}\]

Here \( N^* \) is the cutoff (maximum) aggregation number of the monomers given by
\[ N^* = \{(f - 1)p - 1\}^{-2} \]  

(5)

The parameters \( p, f, \) and \( N' \) are not independent and the parameter to determine the shape of the distribution function is either \( p \) or \( N' \) because the front factor involving \( f \) in Eq.(4) can be deleted by the normalization (Eq.(6)).

Consider the crosslinking of linear precursor chains with degree of polymerization \( N_0 \) and functionality \( f(>>1) \) in the melt. This case is known to be one type of gelation for polymer, which are the same as those defined in Eq.(1), and with degree of polymerization \( N_0 \) and functionality \( f \) being very large and the critical gel point which is given as \( 1/(f - 1) \) becomes very low. In this case all the deviations from the mean field theory, such as the loop formation and excluded volume effect become negligible.

Viscoelastic spectra for associative branching chains can be calculated by using the number density distribution function \( n(N) \) given by Eq.(4) and the Rouse model\(^{23}\), if the dynamics of all the associated chains with several sizes are independent and entanglement effect does not appear.

\[ G^*(\omega) = \frac{\sum_{N=1}^N N^* \left[ \frac{n(N)^{\alpha_{RT}} t_{k,N}^{N_0} + \omega t_{k,N}^{N}}{1 + \omega t_{k,N}^{N}} \right]}{\sum_{N=1}^N N^* \left[ \frac{n(N)^{\alpha_{RT}} t_{k,N}^{N_0} + \omega t_{k,N}^{N}}{1 + \omega t_{k,N}^{N}} \right]} \]

(6)

\[ t_{k,N} = \tau_{k,N} \left( \frac{N_0 N}{k} \right)^{(d_f+2)/3} = \tau_1 \left( \frac{N}{k} \right)^{(d_f+2)/3} \]

(7)

Here \( N_0 \) is the degree of polymerization, \( \tau_{k,N} \) and \( \tau_1 \) are the shortest and the longest relaxation times of the precursor polymer, which are the same as those defined in Eq.(1), and \( d_f \) is the fractal dimension of the branched chain, respectively. In the case of the Bethe lattice (mean field), the fractal dimension of branched chain is known to be 4 and the space dimension to be 6, so that the Rouse type scaling \( t_{r,N} \sim (N/k)^{2/3} \) holds.

### 3.4 Fitting Results by Percolation Rouse Model

In the molten P(VA-OH)s, hydrogen bonds formed between OH groups cause the interchain association\(^5\). Therefore, for the system of the P(VA-OH) which have large number of functionality \( f \), the mean field approximation might work well. Figs. 5 and 6 show the same \( G^* \) data as in Fig. 1 (but compared at \( T = T_* \)) along with the fitted results by Eq.(6). As explained in the previous section, for the pure PVAc, the Rouse model prediction corresponding to the case of \( N^* = 1 \) in Eq.(6) can fit the data fairly well with one parameter \( \tau_1 (= 0.03 \) s). However, as shown by the dash-dotted lines in Fig. 5, the \( G^* \) of P(VA-OH) with \( f_{OH} \leq 0.28 \) cannot be represented by the Rouse model with the same \( \tau_1 (\propto \tau_*) \) value. (In Fig. 1, we used \( \tau_1 \) as a fitting parameter.) The slight deviation from the Rouse curve for these samples is equivalent to the result that the \( \tau_* \) is not constant and weakly dependent on \( f_{OH} \) even compared at \( T = T_* \). As already shown in Fig. 2. We use Eq.(6) to fit the data by introducing a new fitting parameter, \( \gamma \) the cutoff aggregation number \( N' \). As shown in Fig. 5, Eq.(6) with \( N' = 2, 3, \) and 4 for \( f_{OH} = 0.10, 0.18, \) and 0.28, respectively, gave good agreements (solid curves in Fig. 5). On the other hand, in the case of \( f_{OH} = 0.35 \) and 0.37, this equation failed to fit the data as shown by dashed curves in Fig. 6. The deviations are seen in the following two points: [1] The slope \( u \) of the power law relation at high frequency, \( i.e. \ G(\omega) - G'(\omega) - \omega^u \), is slightly lower than the Rouse model exponent \( (u = 1/2) \), and [2] in the low frequency region, addition of extra relaxation mode to the Eq.(6) is necessary to fit the data. The possible reasons for these deviations will be discussed in the next paragraph. Further to see the low \( \omega \) deviation observed for high \( f_{OH} \) samples, the \( \tau_* \) values were determined from the fitted \( G^* \) spectra by the Rouse percolation model (Eq.(6)) for all samples. The values compared at \( T = T_* \) are shown in Fig. 2. It can be seen that the agreement with the data for the low \( f_{OH} \) samples \( (f_{OH} \leq 0.28) \) is reasonable but there is a large discrepancy for the high \( f_{OH} \) samples \( (f_{OH} \geq 0.35) \). This discrepancy means that the strong increase of the terminal relaxation times at \( f_{OH} \geq 0.35 \) is due to the appearance of the extra relaxation mode.

Concerning the high-\( \omega \) deviation [1], observed for the high \( f_{OH} \) samples (Fig. 6), we think that the emergence of the entanglement effect will be responsible. The reason we think so is that the power law exponent of the shear modulus for chemically branched polymers is reported to decrease near the critical point when the entanglement effect appears\(^{24}\). Concerning the low-\( \omega \) deviation [2], addition of the extra relaxation component simply represented by the Maxwell model (Eq.(8)), can reproduce the experimental data well as already shown in Fig. 6.

\[ G^*(\omega) = \frac{G_D \omega^2 \tau_D^2}{1 + \omega^2 \tau_D^2} + \frac{i \sigma_D \omega \tau_D}{1 + \omega^2 \tau_D^2} \]

(8)

The \( G_D \) and \( \tau_D \) values are listed in Table III along with the \( N' \) values. As one possibility, this extra mode may be due to the formation of large sized aggregates which cannot be expressed by Eq.(6). As another possibility, we think that this is related to the dissociation of the network structure. If the
formation of network-like aggregates at these \( f_{\text{OH}} \) occurs and the lifetime of such a network structure is not so long, then the relaxation process corresponding to the dissociation of the network strand will be observable. The Sticky Rouse model proposed by Rubinstein and Semenov actually predicts the appearance of the Maxwell type relaxation corresponding to the lifetime of the temporary network structure.\(^{6, 25, 26} \) For the parameters of the extra relaxation mode, \( G_M \) and \( \tau_M \), of the two samples, listed in Table III are not so different, maybe because of the small difference in \( f_{\text{OH}} \). The validity of these numerical values could be judged by obtaining further data of different \( f_{\text{OH}} \) in the future.

4. CONCLUSION

Viscoelastic behavior was examined for a series of P(VA-OH) samples in melts under iso-frictional condition by using the mean field percolation theory of the Rouse chain. To obtain the appropriate reference temperatures, \( T'_r \), the viscoelastic shift factors were analyzed based on the universal WLF equation. The obtained \( T'_r \) was strongly correlated with the glass transition temperature, \( T_g \). However, the relation between \( T'_r \) and \( T_g \) slightly deviated from the proportional relationship.

The shape of the complex modulus \( G' \) of PVAc was represented by the Rouse model, but for those of P(VA-OH) at \( T = T'_r \), the simple Rouse model did not work. The mean-field-Rouse-percolation model could reproduce the data of \( f_{\text{OH}} \leq 0.28 \) and the maximum numbers of chain association \( N^* \) were determined. For the samples with \( f_{\text{OH}} \geq 0.35 \), deviations from this model appeared at both high and low \( \omega \) regions. At high \( \omega \), the power law exponent, \( u \), in \( G' \) and \( G'' \) represented by the Rouse model. For those of P(VA-OH) at \( T = T'_r \), the simple Rouse model did not work. The mean-field-Rouse-percolation model could reproduce the data of \( f_{\text{OH}} \leq 0.28 \) and the maximum numbers of chain association \( N^* \) were determined. For the samples with \( f_{\text{OH}} \geq 0.35 \), deviations from this model appeared at both high and low \( \omega \) regions.

Table III  Parameters to fit the \( G' \) spectra for P(VA-OH) samples.

| Code            | \( N^* \) | \( G_M / \text{Pa} \) | \( \tau_M / \text{s} \) |
|-----------------|-----------|-----------------------|------------------------|
| P(VA-OH10)      | 2         |                       |                        |
| P(VA-OH18)      | 3         |                       |                        |
| P(VA-OH28)      | 4         |                       |                        |
| P(VA-OH35)      | 4 \( \quad 50 \) | 10.4                  |                        |
| P(VA-OH37)      | 6 \( \quad 85 \) | 9.4                   |                        |

Fig. 5. Storage modulus \( G' \) (open symbols) and loss modulus \( G'' \) (closed symbols) for P(VA-OH)s with \( f_{\text{OH}} = 0.10, 0.18, \) and 0.28 compared at \( T = T'_r \). The dash-dotted lines are the simple Rouse curve with fixed \( \tau_1 (= 0.03 \text{ s}) \). The solid curves are the fitted results with Eq. (6).

Fig. 6. Storage modulus (open symbols) and loss modulus (closed symbols) for P(VA-OH35) and P(VA-OH37). The dash-dotted curves are the Rouse spectra with \( \tau_1 = 0.03 \text{ s} \) and the dashed curves are the fitted results with Eq.(6). The dotted lines represent the Maxwell relaxation of \( G' \) and \( G'' \) and the solid lines are the final fit curves (Eq. (6) + Maxwell relaxation).
$G''(G''\sim G''\sim \omega^\nu)$ was smaller compared to the Rouse exponent ($\nu = 1/2$). This deviation was ascribed to the emergence of weak entanglement effect. At low $\omega$, addition of extra-relaxation mode to the Rouse percolation model was necessary to fit the $G''$ data of $f_{OH} \geq 0.35$. The extra mode was represented by the Maxwell model with a single relaxation time and considered to be due to the large sized aggregates unpredictable with the percolation model and/or the dissociation of H-bonding network.

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**REFERENCES**

1) Kuo SW, “Hydrogen Bonding in Polymer Materials” (2018), Wiley-VCH, Weinheim.
2) Jeffry GA, “An Introduction to Hydrogen Bonding” (1997), Oxford University Press, NY
3) Urakawa O, Shimizu A, Fujita M, Tasaka S, Inoue T, Polym J, 49, 223 (2017).
4) Kuo SW, Chang FC, Macromolecules, 34, 7737 (2001).
5) Noro A, Matsushita Y, Lodge TP, Macromolecules, 41, 5839 (2008).
6) Zhang Z, Liu C, Cao X, Gao L, Chen Q, Macromolecules, 49, 9192 (2016).
7) Urakawa O, Ikuta H, Nobukawa S, Shikata T, J Polym Sci Part B Polym Phys, 46, 2556 (2008).
8) Minsk LM, Priest WJ, Kenyon WO, J Am Chem Soc, 63, 2715 (1941).
9) Moritani T, Fujiwara Y, Macromolecules, 10, 532 (1977).
10) Fetters LJ, Lohse DJ, Richter D, Witten TA, Zirkel A, Macromolecules, 27, 4639 (1994).
11) Rouse PE, J Chem Phys, 21, 1272 (1953).
12) Morishima K, Inoue T, Nihon Reoroji Gakkaishi (J Soc Rheol Jpn), 41, 151 (2013).
13) Osaki K, Inoue T, Uematsu T, J Polym Sci Part B Polym Phys, 39, 211 (2001).
14) Watanabe H, Prog Polym Sci, 24, 1253 (1999).
15) Ferry JD, “Viscoelastic Properties of Polymers”, 3rd ed. (1980), John Wiley & Sons Inc, NY.
16) Urakawa O, Ujii T, Adachi K, J Non Cryst Solids, 352, 5042 (2006).
17) Plazek DJ, J Phys Chem, 69, 3480 (1965).
18) Inoue T, Onogi T, Yao ML, Osaki K, J Polym Sci Part B Polym Phys, 37, 389 (1999).
19) Urakawa O, Yamanaka M, Tomie S, Inoue T, Shikata T, Adachi K, J Chem Phys, 148, 034904 (2018).
20) Stauffer D, Aharony A, “Introduction to Percolation Theory” (1994), Taylor & Francis, London.
21) Rubinstein M, Colby RH, “Polymer Physics” (2003), Oxford University Press Inc, NY.
22) de Gennes PG, “Scaling Concepts in Polymer Physics” (1979), Cornell University Press, London.
23) Maji S, Urakawa O, Inoue T, Polym J, 46, 584 (2014).
24) Lusignan CP, Mourey TH, Wilson JC, Colby RH, Phys Rev E, 60, 5657 (1999).
25) Rubinstein M, Semenov AN, Macromolecules, 31, 1386 (1998).
26) Chen Q, Huang CW, Weiss RA, Colby RH, Macromolecules, 48, 1221 (2015).