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Viscoelastic Behavior of Supramolecular Polymeric Systems Consisting of N,N',N'' -Tris(3,7-dimethyloctyl)benzene-1,3,5-tricarboxamide and n -AlkanesToshiyuki Shikata,^{*,†} Daisuke Ogata,[†] and Kenji Hanabusa[‡]*Department of Macromolecular Science, Osaka University, Toyonaka, Osaka 560-0043, Japan, and Graduate School of Science and Engineering, Shinshu University, Ueda, Nagano 386-8567, Japan**Received: April 29, 2003; In Final Form: October 1, 2003*

Viscoelastic behavior of supramolecular polymeric systems, so-called organogels, consisting of N,N',N'' -tris(3,7-dimethyloctyl)benzene-1,3,5-tricarboxamide (DO₃B) and n -alkanes (C_{*n*}) such as decane ($n = 10$), dodecane ($n = 12$), and tetradecane ($n = 14$) was examined varying the concentration of DO₃B (c) with temperature ranging from 20 to 50 °C. It is widely accepted that DO₃B forms long columnar supramolecular structure in nonpolar solvents like C_{*n*} due to intermolecular hydrogen bonding between amide groups. The obtained storage and loss moduli as functions of frequency for DO₃B/C_{*n*} were simple and well described with a Maxwell model possessing only one set of a relaxation time (τ) and strength (G_N) just like those in aqueous threadlike micellar systems formed by some surfactants. The value of G_N is proportional to c^2 as observed in fully entangled linear flexible polymer systems. The value of τ slightly decreases with increasing the value of c contrary to the behavior of the polymer systems. The activation energy of τ was determined to be 32 ± 2 kJ mol⁻¹ irrespective of the sort of solvents and was different from those of the viscosity for each solvent. These strongly suggest that columnar, flexible supramolecular polymeric structure is generated in DO₃B/C_{*n*} and densely entangles each other to show the pronounced viscoelasticity as well as in the polymer systems, whereas a mechanism for entanglement release is not similar to that in the polymer systems, but to that in aqueous threadlike micellar systems.

Introduction

Recently, a number of kinds of chemical reagents, the so-called *gelators* that can transform low viscous organic liquids into gels or gellike viscoelastic substances, *organogels*, have been synthesized.^{1–3} In organogels, enormously large *supramolecular polymers* are developed by gelator molecules in general. The amount of gelators that is necessary to make systems gel or gellike is less than a few percent in many cases. Some gelators form two-dimensional sheetlike supramolecular structures^{1–6} utilizing strong intermolecular interactions such as hydrogen bonding between functional groups like an amide, carboxyl, and hydroxyl group; consequently, the formed sheetlike supramolecular structure develops into three-dimensional network structure to make systems gels or gellike substances. Other gelators form one-dimensional columnar or ribbony supramolecular polymeric structure^{1,2,7–10} also utilizing intermolecular interaction. Since the formed one-dimensional supramolecular polymeric structure finally forms three-dimensional networks due to entangling each other or branching of themselves and/or bundles of them, gels or gellike substances are obtained in this case as well as the former case. Moreover, many different types of supramolecular structures making systems gel or gellike other than these two have been also reported.^{1,2,11–13}

Whether a prepared system is a real gel or not has been the most important point of discussion for a long period, so that mechanical or viscoelastic features of organogels have not been mentioned so much. Many organogels have been tested and judged by simply turning over vials containing them. Viscoelastic behavior of an organogel strongly depends on which type of supramolecular structure is generated in the organogel. General information and consideration on viscoelastic behavior of three-dimensional networks formed by sheetlike components is not so much gathered as we can employ to discuss the viscoelastic behavior of organogels developing in the two-dimensional fashion. On the other hand, at present, enough information and consideration of viscoelastic behavior of three-dimensional networks formed by one-dimensional components, for example, linear flexible^{14,15} and rigid polymers,^{16,17} and threadlike surfactant micelles^{18–22} formed in aqueous solution have been gathered to apply to organogels developing in a one-dimensional fashion.

Terech et al.^{7,8} and López et al.⁹ studied the viscoelastic behavior of a decalin solution of bicopper tetracarboxylate, in which solute or gelator molecules form one-dimensional columnar supramolecular polymers caused by organometallic coordination chemical bonding from oxygen to copper. The obtained viscoelasticity for the system is dependent on temperature and is simply described with a Maxwell model possessing only one set of a relaxation time (τ) and strength (G_N) below a certain transition temperature. Because the dependencies of τ and G_N on gelator concentration (c) for the system, $\tau \propto c^{1.5-2.0}$

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and $G_N \propto c^{2.0}$, are similar to those predicted by a living polymer model proposed by Cates et al.;^{23–25} $\tau \propto c^{1.4–1.5}$ and $G_N \propto c^{2.0–2.3}$, they conclude the columnar supramolecular structure has a thermally equilibrated molecular weight distribution maintained by scission and recombination reaction between gelator molecules in the supramolecular structure.

Hirschberg et al.¹⁰ studied the viscoelastic behavior of chloroform solution of telechelic oligo(dimethylsiloxane) with two ureidopyrimidone (UPy) units. The gelator forms enormously long one-dimensional associations, namely a supramolecular polymer, due to intermolecular hydrogen bonding between two UPy units, and the zero-shear viscosity (η_0) for the system dramatically increases with c in proportion to $c^{3.9}$, for which the concentration dependence is not so different from that predicted by the living polymer model;^{23–25} $\eta_0 \sim c^{3.5–3.7}$. Consequently, they conclude that the system also obeys the living polymer model.

As described above, the viscoelastic behavior reported for organogels, in which gelator molecules form a supramolecular polymeric structure, developed in a one-dimensional fashion, is likely explained by the living polymer model assuming the scission and recombination reaction between gelator molecules in the formed supramolecular polymeric structure.

However, we recently found a different type of viscoelastic behavior for an organogel system in which gelator molecules form one-dimensional columnar supramolecular polymers that show pronounced viscoelasticity due to entanglement between them. One gelator molecule employed in this study is N,N',N'' -tris(3,7-dimethyloctyl)benzene-1,3,5-tricarboxamide (DO₃B), and the solvents were n -alkanes (C_n) such as decane (C₁₀), dodecane (C₁₂), and tetradecane (C₁₄). Hanabusa et al.²⁶ have already reported that DO₃B is able to make gellike substances in solution of many kinds of nonpolar solvents, such as hexane and cyclohexane. In particular, a solution of DO₃B in cyclohexane at 30 g L⁻¹ shows a high viscosity, 20 Pa s at 20 °C. The obtained viscoelasticities in this study for organogels DO₃B/ C_n do not obey the prediction by the living polymer model^{23–25} in contrast with the facts observed in reported organogels.^{7–10} In this paper, we report the viscoelasticities of the DO₃B/ C_n systems in detail as functions of the concentration of the gelator, c , and temperature. Furthermore, the obtained viscoelastic parameters such as a relaxation time and strength of the DO₃B/ C_n systems will be discussed in conjunction with the conceived supramolecular polymeric structure formed with the gelator, DO₃B.

Experimental Section

Materials. DO₃B was synthesized from 1,3,5-benzenetricarbonyl trichloride and 3,7-dimethyloctylamine and was purified by recrystallization.^{26–28} Solvent molecules, C₁₀, C₁₂, and C₁₄, were purchased from Wako Pure Chemical Industries, Ltd. (Osaka, Japan), and were used without further purification.

The concentration of DO₃B, c , of the prepared systems, DO₃B/C₁₀, DO₃B/C₁₂, and DO₃B/C₁₄, ranged from 3.0 to 30 g L⁻¹. To prepare homogeneous clear sample solutions, the solution temperature was raised to about 70 °C and still highly viscoelastic sample solutions even at that temperature were stirred gently by a spatula. Then the solutions were sealed and kept standing at room temperature for more than 10 h prior to viscoelastic measurements.

Method. Dynamic viscoelastic measurements for sample solutions were carried out in a frequency (ω) range from 1×10^{-3} to 1×10^2 rad s⁻¹ using a stress controlled rheometer (Reologica DAR-100, Lund) equipped with a cone and plate

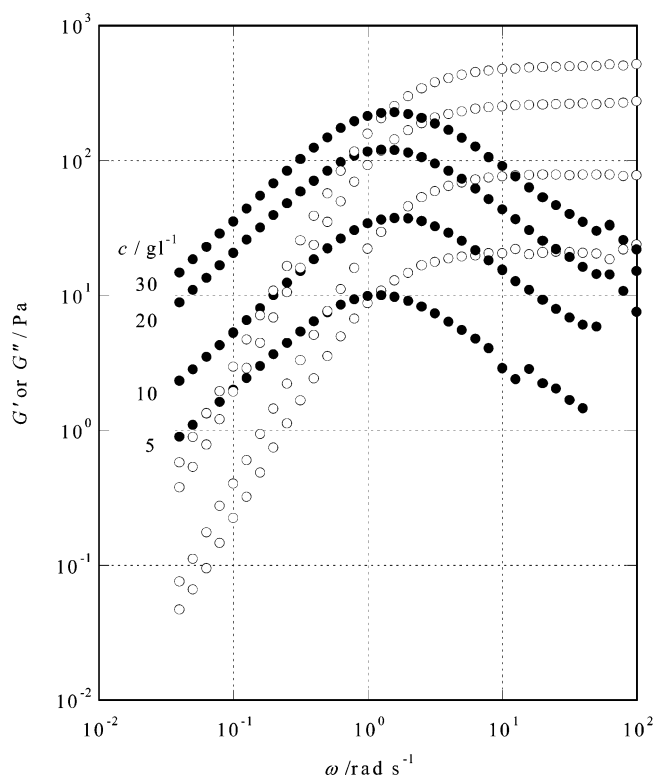


Figure 1. Frequency, ω , dependency of storage and loss moduli, G' and G'' , for a DO₃B/C₁₀ system with various concentrations, c , at 20 °C.

geometry. Measurement temperature was ranged from 20 to 50 °C by using circulating thermostated water. Storage and loss moduli (G' and G'') were determined as functions of ω varying the value of shear stress, and G' and G'' data which obeyed the linear viscoelasticity were accepted.

Results

Concentration Dependence. Frequency, ω , dependencies of G' and G'' for the DO₃B/C₁₀ system at 20 °C are shown in Figure 1 as a typical example for all the DO₃B/ C_n system examined. In a high ω region, G' approaches to a constant plateau value, G_N , dependent on c , while G'' decreases with increasing ω , keeping a slope of about -0.8 in double-logarithmic plots; $G'' \propto \omega^{-0.8}$. This means that the system shows almost pure elastic behavior in a higher ω region. On the other hand, in a low ω region, the value of G'' , proportional to ω , is always greater than that of G' ; proportional to ω^2 , therefore, the system behaves as a viscous liquid in a lower ω region. According to the linear viscoelasticity, the zero-shear viscosity is given as $\eta_0 = \lim_{\omega \rightarrow 0} (G''/\omega)$, so that the value of η_0 for the system can be determined very precisely in the lower ω region.

In many cases, when the maximum of a G'' curve is found at a frequency ω_M , an apparent viscoelastic relaxation time is roughly or approximately calculated to be $\tau_A = \omega_M^{-1}$. However, if the viscoelasticity of a mentioned system is reasonably described with a Maxwell model possessing only one set of the relaxation time, τ , and strength, G_N , as given by eq 1, the ω_M^{-1} value is identical with τ . As we describe next, since the viscoelasticity shown in Figure 1 is reasonably described with the Maxwell model, the evaluated ω_M^{-1} value exactly coincides with the relaxation time, τ .

$$G' = \frac{G_N \omega^2 \tau^2}{1 + \omega^2 \tau^2} \quad G'' = \frac{G_N \omega \tau}{1 + \omega^2 \tau^2} \quad (1)$$

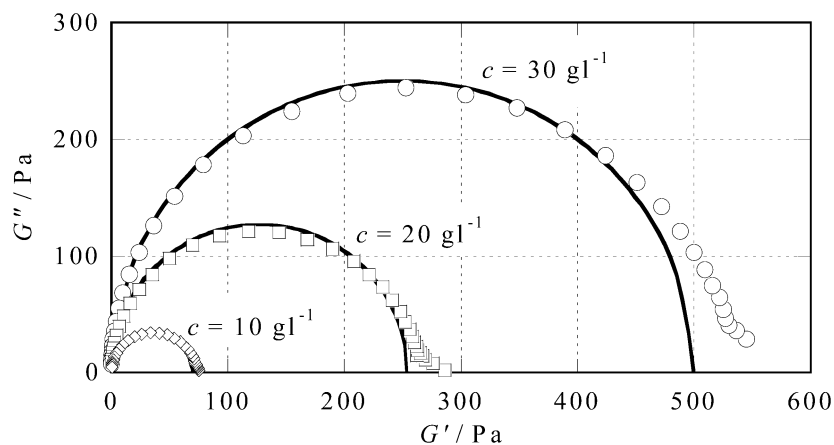


Figure 2. Relationship between G'' and G' for the $\text{DO}_3\text{B}/\text{C}_{10}$ system with $c = 30, 20$, and 10 g L^{-1} at 20°C . Solid lines represent semicircles with radii of $G_N/2$ evaluated from Figure 1.

It is well-known that a linear plot between G'' and G' , a so-called Cole–Cole plot, for the viscoelasticity of the Maxwell model exhibits a semicircle with a radius of $G_N/2$. Some G' and G'' data in Figure 1 are replotted in Figure 2 in the manner of the Cole–Cole plot. The solid lines in the figure imply semicircles with radii of $G_N/2$ evaluated from Figure 1. Agreement between the predicated semicircles and experimental data looks reasonably good. Therefore, we conclude the viscoelasticity of the organogel systems, $\text{DO}_3\text{B}/\text{C}_n$, to be well described with the Maxwell model as well as that of an organogel system, a decalin solution of bicopper tetracarboxylate, in which long, one-dimensional supramolecular polymeric structure develops,^{7–9} and of aqueous threadlike micellar solutions containing enormously long flexible threadlike micelles.^{18–22}

The obtained G_N values at 20°C for each $\text{DO}_3\text{B}/\text{C}_n$ are plotted as functions of c in Figure 3 on a double-logarithmic scale. A relationship of $G_N \propto c^2$ is obtained irrespective of the sort of solvents since the slope of the solid line in Figure 3 is 2.0. Because the same relationship as $G_N \propto c^2$ is widely recognized in entangled linear flexible polymer solutions,^{14,15} the reason for the elasticity in the $\text{DO}_3\text{B}/\text{C}_n$ systems is likely the entanglement effect between long, flexible supramolecular polymeric structures formed in the systems. The difference in the sort of solvents does not affect the characteristics of the formed supramolecular structure since the magnitude of G_N is essentially independent of it. If some characteristics of the formed structure such as flexibility and/or persistence length change depending on the sort of solvents, the number density of entanglement points (ν_e) in the system is more or less affected by the sort of solvents even at the same c .^{14,15} According to the rubber elasticity,²⁹ which is the essential basis of viscoelasticity of fully entangled polymer systems, G_N is proportional to ν_e ; therefore, a change in the flexibility and/or persistence length of the formed supramolecular structure would be reflected in a difference in the magnitude of G_N . It is worth noting that the organogel, a decalin solution of bicopper tetracarboxylate,^{7–9} and aqueous threadlike micellar solutions^{18,22} also exhibit the same relationship as $G_N \propto c^2$.

The concentration, c , dependence of relaxation time, τ , at 20°C for the $\text{DO}_3\text{B}/\text{C}_n$ systems is plotted in Figure 4. Because the obtained data are a little scattered, experimentally determined error bars are attached to each data for the $\text{DO}_3\text{B}/\text{C}_{10}$ system. It seems that the value of τ slightly decreases with increasing c irrespective of the sort of solvents. This involves that τ is not an increasing function of c in the $\text{DO}_3\text{B}/\text{C}_n$ systems. This

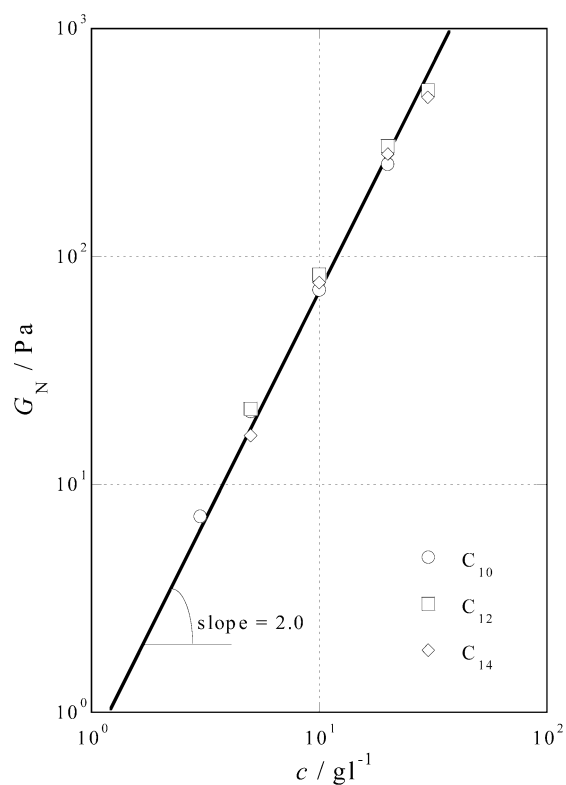


Figure 3. Relationship between G_N and c for the $\text{DO}_3\text{B}/\text{C}_n$ ($n = 10$, n -decane; $n = 12$, n -dodecane; $n = 14$, n -tetradecane) systems at 20°C in a double-logarithmic scale.

behavior of τ is in definitely contradiction to that of entangled polymer systems in which the value of τ or the longest relaxation time is always a steep increasing function of the concentration of polymers, c_p .^{14,15} Thus, a mechanism for the longest relaxation mode that is directly related to entanglement release in the $\text{DO}_3\text{B}/\text{C}_n$ systems is not governed by a *reptation mode*¹⁵ which is widely accepted in fully entangled polymer systems with finite molecular weights. Moreover, it is reported that the organogel, Decalin solution of bicopper tetracarboxylate,^{7–9} shows the relationship of $\tau \propto c^{1.6 \pm 0.1}$ which is close to the prediction of the living polymer model supposing the scission and recombination reaction of supramolecular polymeric structure.^{23–25} Consequently, the living polymer model cannot explain the relationship between τ and c for the $\text{DO}_3\text{B}/\text{C}_n$ systems at all.

The concentration, c , dependence of the zero-shear viscosity, η_0 , at 20°C for the $\text{DO}_3\text{B}/\text{C}_n$ systems is exhibited in Figure 5

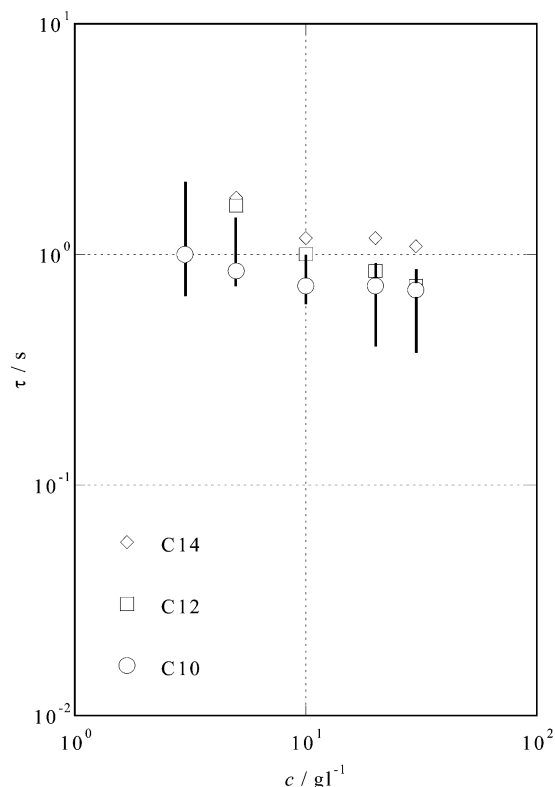


Figure 4. Relationship between τ and c for the $\text{DO}_3\text{B}/\text{C}_n$ systems at 20 °C in a double-logarithmic scale.

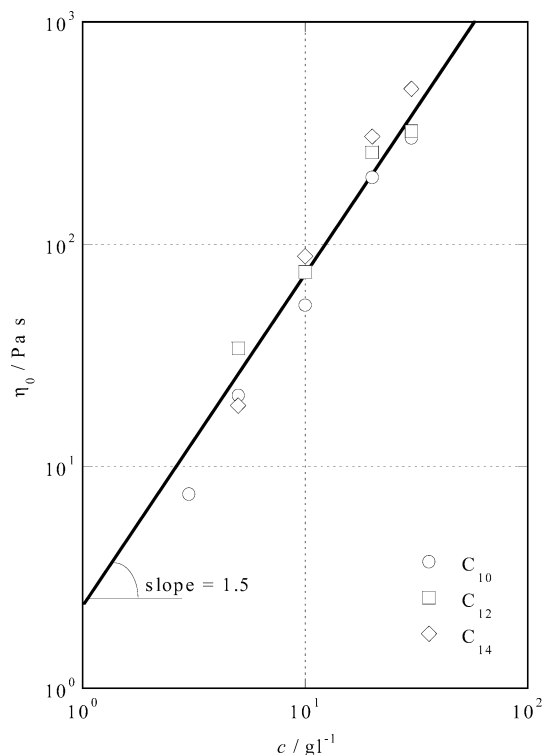


Figure 5. Relationship between η_0 and c for the $\text{DO}_3\text{B}/\text{C}_n$ systems at 20 °C in a double-logarithmic scale.

in a double-logarithmic scale. The slope of a solid line in the figure is evaluated to be 1.5 ± 0.1 ; therefore, the relationship of $\eta_0 \propto c^{1.5 \pm 0.1}$ is obtained for the $\text{DO}_3\text{B}/\text{C}_n$ systems. The exponent of 1.5 ± 0.1 is much smaller than the value predicted by the living polymer model;^{23–25} $\eta_0 \propto c^{3.5–3.7}$. Thus, we might conclude that the mechanism for entanglement release between the formed long, columnar supramolecular polymeric structure

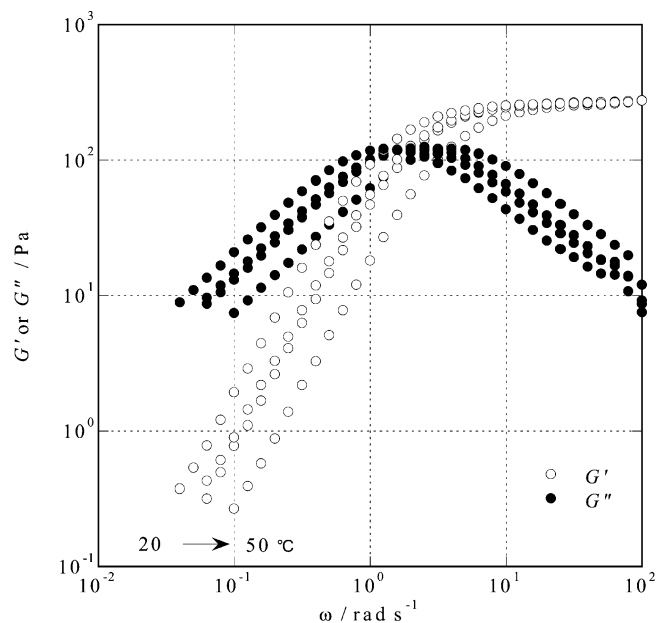


Figure 6. Dependence of G' and G'' on ω for the $\text{DO}_3\text{B}/\text{C}_{10}$ system with $c = 20 \text{ g L}^{-1}$ at various temperatures from 20 to 50 °C.

in the $\text{DO}_3\text{B}/\text{C}_n$ systems is controlled neither by the reptation mode¹⁵ nor the living polymer model.^{23–25} The columnar supramolecular structure in the systems likely possesses another entanglement release mechanism.

Temperature Dependence. Figure 6 shows the dependence of G' and G'' on ω at several temperatures ranging from 20 to 50 °C for the $\text{DO}_3\text{B}/\text{C}_{10}$ system at $c = 20 \text{ g L}^{-1}$ as a typical example. The magnitude of G_N that is identical with a constant value of G' in a higher ω region looks to be independent of temperature in the range examined. However, since the maximum frequency, ω_M , at which G'' shows the maximum shifts toward a higher ω region without changing the shape of ω dependence of G'' curves, the relaxation time, τ , shortens with increasing temperature.

In general, the elasticity of rubberlike systems consisting of long chainlike molecules or substances keeping micro-Brownian motion, such as the $\text{DO}_3\text{B}/\text{C}_n$ systems, results from the entropic origin. In the case, the magnitude of G_N is proportional to the absolute temperature (T). The reason the magnitude of G_N does not increase with temperature as seen in Figure 6 is possibly that the temperature range examined is not wide enough to detect the increase clearly and the increase is compensated for by the depression of the density of the system with increasing temperature.

The activation energy (E^*) of the relaxation time, τ , can be evaluated from the slope of a semilogarithmic plot between τ^{-1} and T^{-1} , a so-called Arrhenius plot, as seen in Figure 7A. The value of E^* is determined to be $32 \pm 2 \text{ kJ mol}^{-1}$ for the $\text{DO}_3\text{B}/\text{C}_{10}$ system irrespective of c . Figure 7B shows the Arrhenius plot between τ^{-1} and T^{-1} for each $\text{DO}_3\text{B}/\text{C}_n$ system at $c = 10 \text{ g L}^{-1}$. Slopes of solid lines in Figure 7B look identical with each other for every system, and the value of E^* is evaluated to be $32 \pm 2 \text{ kJ mol}^{-1}$ again, irrespective of the sort of solvent. Because the activation energy of viscosities for C_{10} , C_{12} , and C_{14} are evaluated to be 11.1, 12.6, and 13.8 kJ mol^{-1} ,³⁰ respectively, the value of E^* for the $\text{DO}_3\text{B}/\text{C}_n$ systems is not correlated to those essentially.

Discussion

Phantom Crossing Model. Because neither the reptation mode nor living polymer model is suitable for the $\text{DO}_3\text{B}/\text{C}_n$

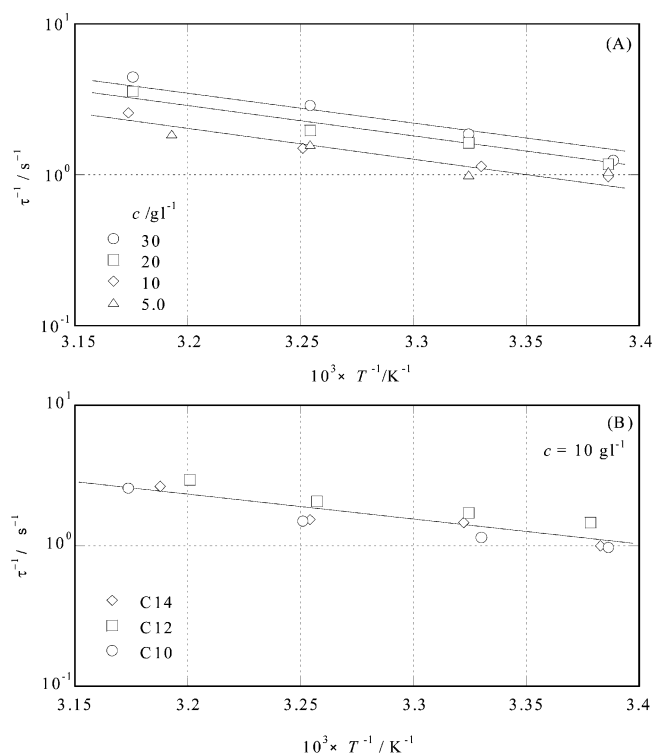


Figure 7. (A) Temperature, T , dependence of τ for the $\text{DO}_3\text{B}/\text{C}_{10}$ system with various c from 5 to 30 g L^{-1} . (B) Dependence of τ on T for the $\text{DO}_3\text{B}/\text{C}_n$ ($n = 10, 12$, and 14) systems at $c = 10 \text{ g L}^{-1}$.

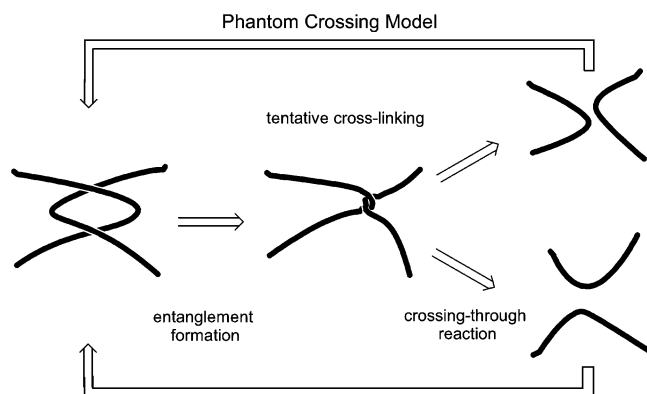


Figure 8. Schematic representation of a *phantom crossing model* for an entanglement release mechanism in chainlike substances.

systems, we here introduce another relaxation model called a *phantom crossing model*^{19,22} which has been proposed to explain the entanglement release mechanism in aqueous threadlike micellar systems.^{18–22} In the model, it is assumed that two distinct flexible chainlike substances such as threadlike micelles make an entanglement point of which lifetime is τ_1 , then two chainlike substances cross through each other at the entanglement point just like a phantom as depicted schematically in Figure 8. The viscoelastic behavior of the *phantom crossing model* is perfectly described with a Maxwell model possessing a relaxation time, τ , identical with τ_1 and a relaxation strength proportional to the squared concentration of the chainlike substances.¹⁹ The *phantom crossing model* is essentially identical with the *phantom network model* proposed by Yamamoto³¹ and Lodge³² more than 4 decades ago to explain the viscoelasticity of entangled flexible polymer chain systems, which is not able to reveal the relationship between the relaxation time and molecular weight and broad relaxation spectra for the systems.

In the case of threadlike micelles, a *crossing-through reaction* in the phantom crossing model (see Figure 8) is quite realistic

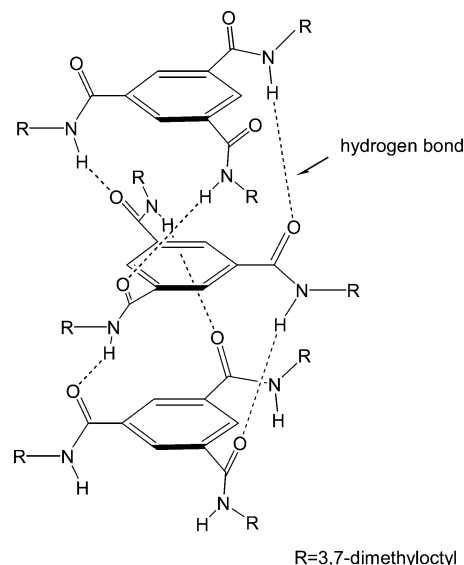


Figure 9. Schematic representation of a columnar supramolecular polymeric structure proposed for organogels consisting of a gelator, DO_3B , in nonpolar solvents.

because the micelles are not formed by covalent chemical bonding but are formed by relatively weak intermolecular interaction between constituent surfactant and additive molecules. As we discuss in the next section, intermolecular interaction working in the columnar supramolecular polymeric structure formed in the $\text{DO}_3\text{B}/\text{C}_n$ systems is hydrogen bonding between two amide groups. If exchange of hydrogen bonding occurs between distinct two columnar supramolecular structure at an entanglement point, the crossing-through reaction of the supramolecular structure like a phantom is possible also in the $\text{DO}_3\text{B}/\text{C}_n$ systems. Thus, we here insist that the phantom crossing model is essential for the viscoelastic behavior in the $\text{DO}_3\text{B}/\text{C}_n$ systems.

The phantom crossing model does not contain the molecular weight of chainlike substances but has only a lifetime of the entanglement point, τ_1 ($=\tau$), as a molecular parameter controlling viscoelastic relaxation time, τ . Therefore, the activation energy, E^* , of τ directly corresponds to that of the lifetime of the entanglement point, τ_1 , in the $\text{DO}_3\text{B}/\text{C}_n$ systems.

Conceived Supramolecular Structure. The supramolecular structure formed by DO_3B in nonpolar solvents has been proposed as schematically shown in Figure 9 based on crystal structure^{2,33} formed by an analogue of DO_3B with shorter side chains, N,N',N'' -tris(2-methoxyethyl)benzene-1,3,5-tricarboxamide. The proposed supramolecular polymeric structure is a helical column sustained by strong 3-fold hydrogen bonding²⁶ between amide groups and by relatively weak intermolecular interaction caused by π - π stacking between central benzene rings. Brunsveld et al.³⁴ reported that achiral compounds with a benzene-1,3,5-tricarboxamide frame form an equimolar mixture of left-handed and right-handed helical columns in solution, whereas addition of a small amount of chiral compounds bearing homo-chiral side chains such as N,N',N'' -tris((*S*)-3,7-dimethyloctyl)benzene-1,3,5-tricarboxamide to solutions of achiral compounds with the benzene-1,3,5-tricarboxamide frame remarkably induces one helicity.

Because DO_3B used in this study was synthesized from a racemic mixture of (*R*)- and (*S*)-3,7-dimethyloctylamine, DO_3B does not bear homochiral side chains. Then, the formed columnar supramolecular structure in the $\text{DO}_3\text{B}/\text{C}_n$ systems is an equimolar mixture of left-handed and right-handed helical columns as schematically shown in Figure 10. This is easily

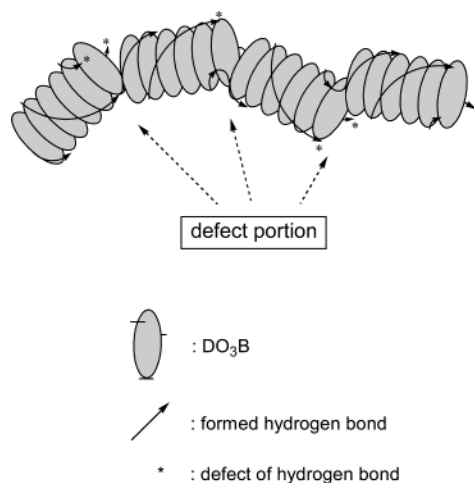


Figure 10. Conceptual depiction of the conceived higher order supramolecular structure in the $\text{DO}_3\text{B}/\text{C}_n$ systems. The right-handed and left-handed helical columns formed by DO_3B are mixed at an equimolar composition. A defect portion at which the helicity of the formed column changes keeps defects in hydrogen bonding.

confirmed by the fact that CD spectra for the $\text{DO}_3\text{B}/\text{C}_n$ systems show no detectable Cotton effect. A short columnar portion consisting of one helicity, a left-handed or right-handed helix, contains perfect 3-fold hydrogen bonding between amide groups without defects and should keep a relatively high rigidity, while a defect portion at which the helicity changes must contain defects in hydrogen bonding. This involves the defect portion in the columnar supramolecular structure being an origin for the high flexibility of the formed columnar structure, which behaves as flexible polymer-like chains from viscoelastic aspects described above.

The defect portion in the columnar supramolecular polymeric structure has another important role that is necessary for the crossing-through reaction in the entanglement release mechanism to take place. A defect portion keeps one or two free amide groups which are able to create hydrogen bonding with other free amide groups belonging to different defect portions. When two defect portions approach each other and create an entanglement point, free amide groups belonging to the two defect portions create new hydrogen bonding to make a tentative cross-linking point. Since the formed entanglement or tentative cross-linking point has higher energy than that of defect portions without cross-linking due to the steric hindrance between contacting side chains, some hydrogen bonds at the cross-linking point disappear after their lifetime, τ_1 , so that the entangled columnar structure separates into two distinct columns. This process is essentially identical with the passing-through reaction in the phantom crossing model useful in the aqueous threadlike micellar systems (Figure 8).

The $\text{DO}_3\text{B}/\text{C}_n$ systems contain no catalytic reagents which are able to accelerate the passing-through reaction dramatically such as a salicylate anion in aqueous threadlike micellar solutions consisting of cetyltrimethylammonium bromide (CTAB) and sodium salicylate (NaSal), CTAB:NaSal/W;¹⁹ therefore, the obtained τ value corresponds to the intrinsic lifetime of the entanglement point, τ_1 , in the systems, which should be less dependent on c via the simplest conjecture. The reason for the decreasing in τ with increasing c as seen in Figure 4 is not clear at present; however, the number of terminals of the formed supramolecular polymers is possibly dependent on c and is related to the value of τ in the $\text{DO}_3\text{B}/\text{C}_n$ systems.

It is interesting to compare the magnitude of G_N for the $\text{DO}_3\text{B}/\text{C}_n$ systems with that for aqueous threadlike micellar systems

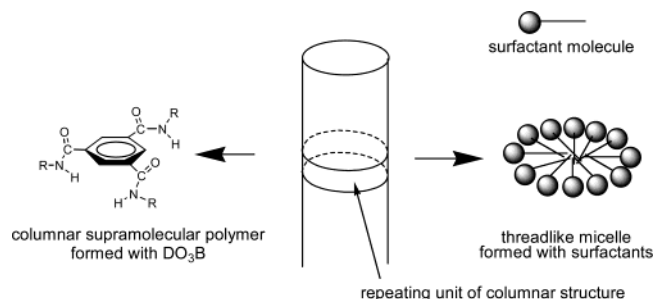


Figure 11. Schematic representation of repeating units for the conceived columnar supramolecular polymer formed in the $\text{DO}_3\text{B}/\text{C}_n$ systems (left) and threadlike micelles formed in a CTAB:NaSal/W system (right). The thickness of repeating units is roughly estimated to be 0.4 nm for the supramolecular polymer³³ and 0.9 nm for the threadlike micelle,³⁵ respectively.

such as CTAB:NaSal/W because the conceived structure for threadlike micelles is completely different from that for the supramolecular polymeric structure in the $\text{DO}_3\text{B}/\text{C}_n$ systems as shown schematically in Figure 10. The threadlike micelle has 15–20 CTAB molecules in its cross section,³⁵ while the columnar supramolecular polymeric structure has only one gelator molecule in its cross section. This difference in the two columnar structures lead to the fact that the total contour length (λ_c) of the columnar supramolecular polymeric structure formed in the $\text{DO}_3\text{B}/\text{C}_n$ systems is much longer, e.g., 10–15 times longer via very rough estimation, than that of the threadlike micelle in the CTAB:NaSal/W system at the same molar concentration.

The number density of entanglement point, ν_e , is proportional to the square of λ_c for the formed columnar supramolecular polymeric structure or threadlike micelles in precise expression. Then, the experimental magnitude of G_N ($\propto \lambda_c^2$) for the $\text{DO}_3\text{B}/\text{C}_n$ systems is about 200 times as large as that of the CTAB:NaSal/W system at the same molar concentration. Since a proportional constant connecting ν_e and λ_c^2 depends on values of the radius and persistence length of the columnar supramolecular polymeric structure and we do not know both the values in the $\text{DO}_3\text{B}/\text{C}_n$ systems at present, the comparison of the G_N values between the two systems only qualitatively suggests a difference in the value of λ_c . However, such a large number as 200 found in a ratio of the G_N values at the same molar concentration obviously reflects structural differences between the columnar supramolecular polymers in the $\text{DO}_3\text{B}/\text{C}_n$ systems and threadlike micelles as shown in Figure 11.

Finally, we expect that experimental investigation using scattering techniques like X-ray, neutron, and light scattering providing structural characteristics of the formed supramolecular polymeric structures, such as a radius and persistence length, will support the validity of the speculation based on the phantom crossing model taking account of the presence of defect portions in the columnar supramolecular polymeric structure.

References and Notes

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