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Controlled Large Macrodipoles in a Supramolecular Polymer of Tri-3,7-dimethyloctyl-*cis*-1,3,5-cyclohexanetricarboxamide in *n*-Decane

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Herein, we report evidence that highly controlled large macrodipoles are present in the supramolecular polymer of tri-3,7-dimethyloctyl-*cis*-1,3,5-cyclohexanetricarboxamide (DO_3CH) formed in *n*-decane (C_{10}) due to 3-fold hydrogen bonds. In nonpolar solvents, C_3-type organo-gelators such as DO_3CH form enormously long supramolecular polymers that exhibit remarkable viscoelasticity.[1,2] It has been proposed that the supramolecular structure of DO_3CH in nonpolar solvents consists of a straight column sustained by 3-fold hydrogen bonds between amide groups[1−5] (Figure 1). A striking characteristic of the supramolecular structure of DO_3CH is the presence of electric macrodipoles resulting from the fixed direction of hydrogen bonds. Large macrodipoles created as the sum of dipoles in DO_3CH may also be generated in columns such as α-helixes of proteins.[6]

Recently, many organo-gelators have been synthesized, and they have generated great interest among scientists because of the fascinating mechanical and structural properties of their gels. One of the C_3-type organo-gelators, *N*,*N*′,*N*″-tris(3,7-dimethyloctyl)benzene-1,3,5-tricarboxamide (DO_3B), which has a phenyl ring as a central backbone instead of cyclohexane, forms long supramolecular polymers in nonpolar solvents, and its gels exhibit remarkable viscoelasticity due to entanglements between the formed supramolecular polymers.[1,2,5] The proposed supramolecular structure of DO_3B consists of a helical column sustained by 3-fold hydrogen bonds between amide groups, rather than a straight column (Figure 1). When DO_3B does not bear homochiral (*S*)- or (*R*)-3,7-dimethyloctylamine side chains, but instead has a racemic mixture of the two forms, its supramolecules consist of an equimolar mixture of left- and right-handed helical columns.[7−11] Defective parts connecting left- and right-handed columns in a contiguous sequence result from failure to form hydrogen bonds, which may be the reason for the flexibility of the supramolecular polymer and may play an essential role in the entanglement release mechanism governing viscoelasticity that can be described with a single relaxation time.[11]

The supramolecular structure of DO_3B is responsible for formation of macrodipoles due to the fixed direction of its hydrogen bonds: $C{=}O\cdots H{-}N$. The overall electric dipole of the three $C{=}O$ groups forming the 3-fold hydrogen bond in every DO_3B is fixed in the same direction perpendicular to the phenyl rings in both the left- and right-handed columns (Figure 1). In a study of the dielectric behavior of an organo-gel system, DO_3B/C_{10}, a Debye-type single relaxation behavior was observed.[12] The obtained relaxation time of DO_3B/C_{10} is about 3 times as long as its mechanical relaxation time, irrespective of the concentration (c) of DO_3B, and its relaxation strength is proportional to $c^{\sim 0.8}$.[12] These findings suggest that macrodipoles (i.e., supramolecular columns) are connected by defective parts in a head-to-tail manner to create total macrodipoles between entanglement points, and that the dipolar sequence is conserved in the entanglement release process that controls the mechanical relaxation.[11,12] About 2 decays ago, Jadżyn et al.[13] also reported the presence of macrodipoles in supramolecular polymeric systems of *sym*-dialkylureas in nonpolar solvents due to the hydrogen bond formation. Some reports[14,15] were published on the switching behavior of mesophases of columnar supramolecular systems at the onset of electric field, which should be related to macrodipoles generated along supramolecular polymers in the systems.

Because the supramolecular polymer of DO_3CH in C_{10} has a straight columnar structure, rather than a helical columnar structure, it is not necessary to consider the helix inversion of supramolecular columns at defective parts, even in samples consisting of DO_3CH bearing a racemic mixture of side chains. Thus, in the present study, we restricted analysis to the dipolar sequence of contiguous supramolecular polymers containing macrodipoles. Figure 2a shows the angular frequency, ω, and dependence of storage and loss shear moduli, G' and G'', for DO_3CH/C_{10} at 25°C in the linear response regime.[16] Although it is not clear whether G' and G'' curves contain at least two relaxation modes in a c range less than 7 mM, two distinct relaxation modes were clearly observed in a c range higher than 15 mM. Hence, we assume that G' and G'' curves for the system can be expressed simply as the sum of two kinds of Maxwell elements,[16] with mechanical relaxation times of τ_{m1} and (<) τ_{m2}:

$$G' = \frac{G_1\omega^2{\tau_{m1}}^2}{1+\omega^2{\tau_{m1}}^2} + \frac{G_2\omega^2{\tau_{m2}}^2}{1+\omega^2{\tau_{m2}}^2}, \qquad G'' = \frac{G_1\omega\tau_{m1}}{1+\omega^2{\tau_{m1}}^2} + \frac{G_2\omega\tau_{m2}}{1+\omega^2{\tau_{m2}}^2} \quad (1)$$

where G_1 and G_2 represent shear moduli corresponding to the respective relaxation times. By decomposing G' and G'' curves into two modes using eq 1, the parameters τ_{m1}, τ_{m2}, G_1, and G_2 can be determined reasonably, and relationships such as $G_1 \propto c^2$ and $G_2 \propto c^{\sim 1.3}$ can be obtained.[16] The relationship $G_1 \propto c^2$, which has also been observed in DO_3B/C_{10},[11] which exhibits a single relaxation mode, commonly holds for flexible polymer systems with full entanglement and strong viscoelasticity.[17,18] In contrast, the relationship $G_2 \propto c^{\sim 1.3}$ has been observed in suspensions of stiff rods in viscous media.[18−20] These viscoelastic behaviors describe a situation in which the supramolecular polymer in DO_3CH/C_{10} has

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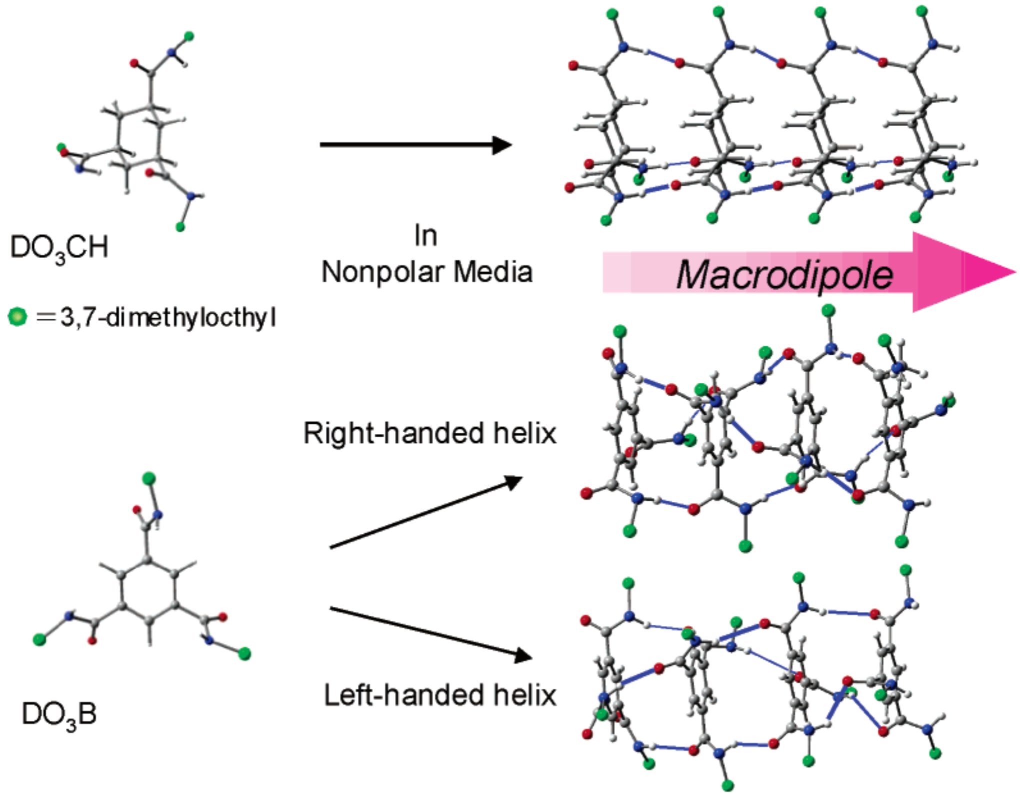

Figure 1. Schematic depiction of proposed supramolecular polymers in organo-gel systems of DO_3CH/C_{10} (straight columnar structure[3,4] sustained by 3-fold hydrogen bonding) and DO_3B/C_{10} (helical columnar structure[5] sustained by 3-fold hydrogen bonding). Blue solid lines in the supramolecular structures represent the hydrogen bonds.

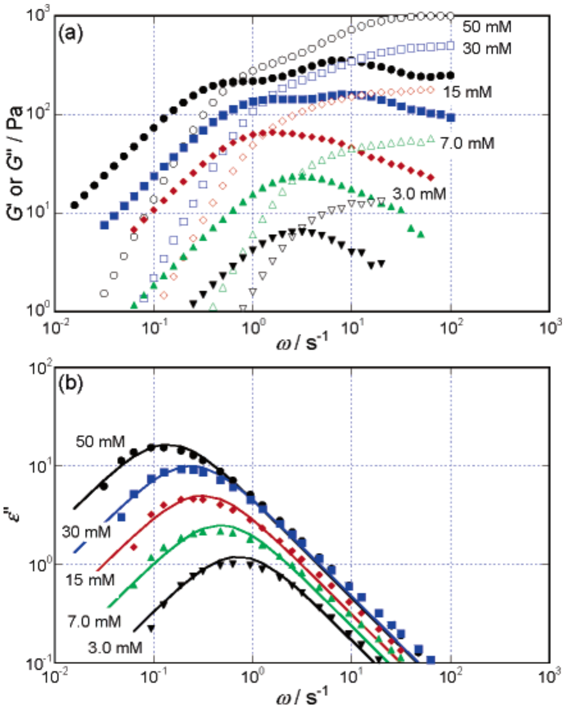

Figure 2. (a) ω dependence of G' (open symbols) and G'' (closed symbols) for the organo-gel system of DO_3CH/C_{10} with various c values at 25 °C. (b) Relationship between ϵ'' and ω for the organo-gel samples in (a). Solid lines represent fit curves using eq 2.

an alternating sequence of stiff rod columnar parts and flexible chain parts consisting of shorter columns connected by defective parts that fail to form hydrogen bonds. There should be three types of entanglements in such systems: between flexible chain parts (c−c), between flexible chain and rod parts (c−r), and between rod parts (r−r). In a previous study,[16] we found that the short relaxation time (τ_{m1}, around 0.1 s) is due to a c−c entanglement release mode irrespective of the c value, which is governed by a phantom crossing mechanism owing to exchange of hydrogen bonds using free amide groups of defective parts at entanglement points. When there are no r−r entanglements because the c value is <7 mM, the value of τ_{m2} (around 0.5 s) is due to a c−r entanglement release mode, i.e., rotation of rod parts in a relaxing matrix of entangling flexible chain parts. At c > 7 mM, τ_{m2} is due to an r−r entanglement release mode, i.e., rotation of rod parts fully entangling each other.

Figure 2b shows the ω dependence of the imaginary part (ϵ'') of electric permittivity for DO_3CH/C_{10} at 25 °C. The obtained ϵ'' and the real part (ϵ', not shown) curves are perfectly expressed by a Debye-type relaxation function (eq 2) with only one set of dielectric parameters: relaxation time (τ_d), strength ($\Delta\epsilon$), and high-frequency limiting permittivity (ϵ_{inf}). However, the system retains two mechanical relaxation times, as described above. Thus, we conclude that the supramolecular polymer that forms in DO_3CH/C_{10} generates large macrodipoles that obey the Debye-type relaxation function.[21]

$$\epsilon' = \frac{\Delta\epsilon}{1+\omega^2{\tau_d}^2} + \epsilon_{inf}, \quad \epsilon'' = \frac{\Delta\epsilon\omega\tau_d}{1+\omega^2{\tau_d}^2} \tag{2}$$

Figure 3, which shows the c dependencies of $\Delta\epsilon$, ϵ_{inf}, τ_d, τ_{m1}, and τ_{m2} for the system, suggests that the value of $\Delta\epsilon$ is perfectly proportional to c and that τ_d retains the relationship $\tau_d = 3\tau_{m2}$ over the c range examined, whereas τ_d appears to be independent of τ_{m1}. This

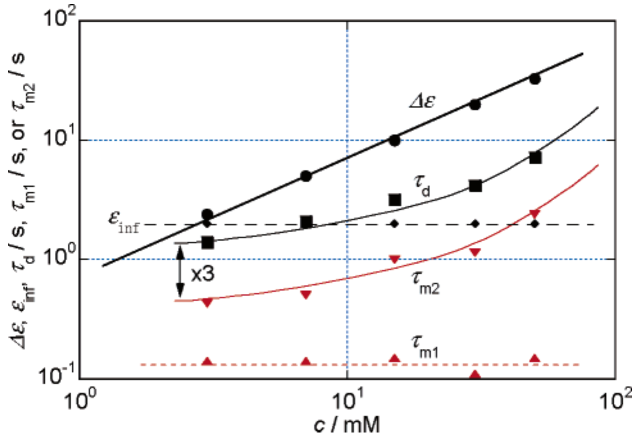

Figure 3. c dependencies of $\Delta\epsilon$, ϵ_{inf}, τ_d, τ_{m1}, and τ_{m2} for the DO_3CH/C_{10} organo-gel samples in Figure 2.

indicates that the mechanical relaxation mode of τ_{m1} related to the c−c entanglement release mode is not affected by the dielectric relaxation process, but the τ_{m2} mode is detectable as the τ_d mode in distinct measurements. From a theoretical point of view,[22] the dielectric relaxation time attributed to the rotational diffusion mode of particles suspended in media is 3 times as long as the mechanical relaxation time due to a difference in the rank of the observed spherical harmonic function between the two measurement methods. The reason for the slow dielectric relaxation, relative to the entanglement release mechanism of flexible networks of supramolecular polymers in the DO_3B/C_{10} system,[12] is the nature of the dipolar head-to-tail sequence of supramolecular helical columns. However, the dipolar sequence of shorter columns connected by defective parts in flexible chain parts of DO_3CH/C_{10} may retain a random or alternating arrangement, eliminating large dipole moments between entanglement points.

The relationship $\Delta\epsilon \propto c$ implies that the product of the number density of long, stiff rod parts (ν) and the square average of magnitude of macrodipoles ($\langle\mu^2\rangle$) for the rod parts is proportional to c; i.e., $\Delta\epsilon \propto \nu\langle\mu^2\rangle$. Moreover, the observed single dielectric relaxation mode strongly suggests that the distribution of length of the stiff rod parts (λ) is also clearly defined, irrespective of the c value. Because the value of $|\mu|$ is simply proportional to λ for stiff rods (Figure 1), the relationship $\nu\langle\lambda^2\rangle \propto c$ holds for the system. Also, previous theoretical and experimental examinations[18−20] of the mechanical behavior of stiff rod suspensions in viscous media indicate that G_2 is proportional to $\nu^{1-1.4}$. Therefore, the relationship $G_2 \propto c^{\sim 1.3}$ described above suggests that the relationship $\nu \propto c$ approximately holds for DO_3CH/C_{10}. Consideration of mechanical behavior, assuming the relationship $\nu \propto c$, has successfully explained the c dependence of τ_{m2} in the range of $c > 7$ mM.[16] Consequently, we can conclude that the average value of λ (i.e., the number of DO_3CH molecules in stiff rod parts) is maintained at a precisely controlled value irrespective of c in the examined range of c values.

Addition of a hydrogen bond breaker or exchanger, such as 3,7-dimethyl-1-octanol (DOAL), to DO_3CH/C_{10} provides useful information about the large macrodipoles along stiff rod parts of the supramolecular polymer. In the present study, the presence of DOAL effectively prevented formation of hydrogen bonds between amide groups of different DO_3CH molecules. Figure 4 shows the ω dependence of ϵ'' for DO_3CH:DOAL/C_{10} systems, varying the ratio of the concentration of DOAL to c ($c_{AL}c^{-1}$) from 0 to 10 at $c = 30$ mM. The system clearly retains Debye-type single relaxation behavior, and the relaxation frequency ($\omega_d = \tau_d^{-1}$) clearly increases with increasing $c_{AL}c^{-1}$, finally reaching the saturation value of 30 s^{-1} at $c_{AL}c^{-1} > 6$. The arrows in Figure 4 that represent reciprocals of 3 times the values of related mechanical relaxation times, $(3\tau_{m2})^{-1}$, coincide well with the ω_d values. Because the magnitude of G_2 (not shown) for the system remains constant irrespective of $c_{AL}c^{-1}$, ν also remains essentially constant. Thus, a slight decrease in $\Delta\epsilon$ ($= 2\epsilon''$ at ω_d) until $c_{AL}c^{-1} = 4$ leads to a slight decrease in the λ value induced by the addition of DOAL. These findings indicate that addition of DOAL accelerates the rate-determining process (the c−c entanglement release mode), and consequently accelerates the r−r entanglement release mode, but does not greatly influence λ of the stiff rod parts of the supramolecular polymer.

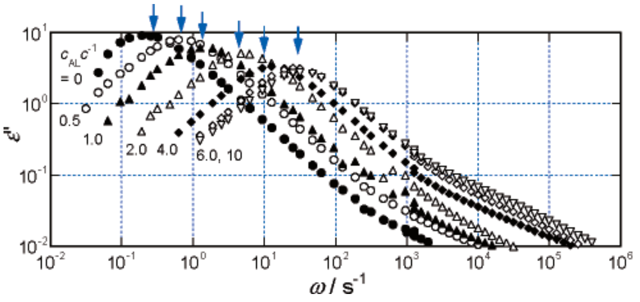

Figure 4. Dependence of ϵ'' on ω for the DO_3CH:DOAL/C_{10} system at various $c_{AL}c^{-1}$ values; $c = 30$ mM and 25 °C. Arrows represent the reciprocals of 3 times the values of corresponding mechanical relaxation times, $(3\tau_{m2})^{-1}$, for the same system at each $c_{AL}c^{-1}$.

At last, the macrodipoles are generated along long columnar parts of the supramolecular polymer and behave as stiff rods rotating in viscoelastic media. The magnitude of the macrodipole is proportional to the number of DO_3CH molecules in the column and appears to remain at a precisely controlled constant irrespective of the concentration, c. The controlled large macrodipoles observed in the present study appear to have considerable potential for a wide range of industrial applications, as new materials for use in electrooptical or electromechanical devices. We are currently studying the absolute value of the dipole moment of macrodipoles in the supramolecular polymer of DO_3CH/C_{10}.

Experimental Section. DO_3CH was synthesized from *cis*-1,3,5-cyclohexanetricarbonyl trichloride and 3,7-dimethyloctylamine using conventional reaction methods and was purified by recrystallization.[3] C_{10} (purity >99%) was purchased from Tokyo Kasei Kogyo Co. Ltd. (Tokyo) and was used without further purification. Dynamic viscoelastic measurements were performed using a stress-controlled rheometer (Reologica DAR-100, Lund) with a cone-and-plate geometry with a diameter and cone angle of 40 mm and 4.0°, respectively.

Dielectric measurements were performed at 25 °C using three systems[12] over an ω range of 10^{-2}−2×10^{10} s^{-1}. For the lowest ω values (10^{-2}−10^4), we used a homemade measuring system with a fast Fourier transform analyzer (Hitachi, VC-2440, Tokyo) based on a precise impedance analysis technique.[23] For ω ranges of 10^2−6×10^6 s^{-1} and 6×10^6−2×10^{10} s^{-1}, we used two different LCR meters: Hewlett-Packard 4284A (Palo Alto) and Agilent Technologies 4287A (Palo Alto), respectively. Real and imaginary parts of electric permittivities, ϵ' and ϵ'', were calculated from the electric capacitance and conductance of a sample as functions of ω.[12,21]

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