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Large macro-dipoles generated in a supramolecular polymer of *N*,*N*′,*N*″-tris(3,7-dimethyloctyl) benzene-1,3,5-tricarboxamide in *n*-decane

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Abstract

A supramolecular polymer formed by *N*,*N*′,*N*″-tris(3,7-dimethyloctyl)benzene-1,3,5-tricarboxamide (DO_3B) in *n*-decane (C_{10}) possesses large macro-dipoles naturally generated by three-fold inter-molecular hydrogen bonding aligned along its helical columnar structure connected by defective portions, which are DO_3B molecules containing failure in the hydrogen bond formation, in the order of head to tail arrangement without dipole inversion like type-A polymers.

Keywords: Dielectric relaxation; Viscoelasticity; Supramolecular polymer

Herein, we report a crucial evidence that a supramolecular polymer formed by *N*,*N*′,*N*″-tris(3,7-dimethyloctyl)benzene-1,3,5-tricarboxamide (DO_3B) in *n*-decane (C_{10}) keeps large macro-dipoles naturally generated by three-fold inter-molecular hydrogen bonding aligned along its helical columnar structure.

It is well known that DO_3B, one of C_3-type organo-gelators, forms enormously long supramolecular polymers in non-polar solvents such as C_{10}, which exhibit remarkable viscoelasticity due to entanglements between themselves [1,2]. Based on the crystal structure of an analogue of DO_3B with shorter side-chains [1,3], it has been proposed that the supramolecular structure of DO_3B in non-polar solvents consists of helical columns sustained by three-fold hydrogen bonds [1–4] between the amide groups, as depicted in Scheme 1. When DO_3B does not exclusively bear homo-chiral (*S*)- or (*R*)-3,7-dimethyloctylamine, but rather bears a racemic mixture of these groups as side-chains, the columnar supramolecules of DO_3B consist of an equimolar mixture of left- and right-handed helical columns. This equimolar composition of helicity is confirmed by the observation that circular dichroism (CD) spectra for the DO_3B/C_{10} system [4–6] do not exhibit Cotton Effects. However, addition of (*S*)DO_3B bearing only (*S*)-type side chains to the system induces a marked excess of left- or right-handed helicity, resulting in significant Cotton Effects in CD spectra [5–7].

Defective portions, which are DO_3B monomers containing failure in the hydrogen bond formation in the supramolecular polymer, connect mixtures of left- and right-handed columns in a contiguous sequence. The defective portion may account for the flexibility of the supramolecular polymer and may play a decisive role in the entanglement release mechanism due to the exchange of hydrogen bonds at entanglement points [2]. Because the DO_3B/C_{10} system [2] has only one mechanical relaxation mode as a Maxwell element [8], with strength and time of G_N and τ_m, the storage and loss moduli of the system, G' and G'', depend on ω as expressed in Eq. (1).

$$G' = \frac{G_N\omega^2\tau_m^2}{1+\omega^2\tau_m^2} \quad G'' = \frac{G_N\omega\tau_m}{1+\omega^2\tau_m^2} \tag{1}$$

Another striking characteristic of the supramolecular structure of DO_3B in non-polar solvents is the formation of electric summed dipoles or macro-dipoles due to the fixed direction of hydrogen bonds: N–H···O=C. Because the overall

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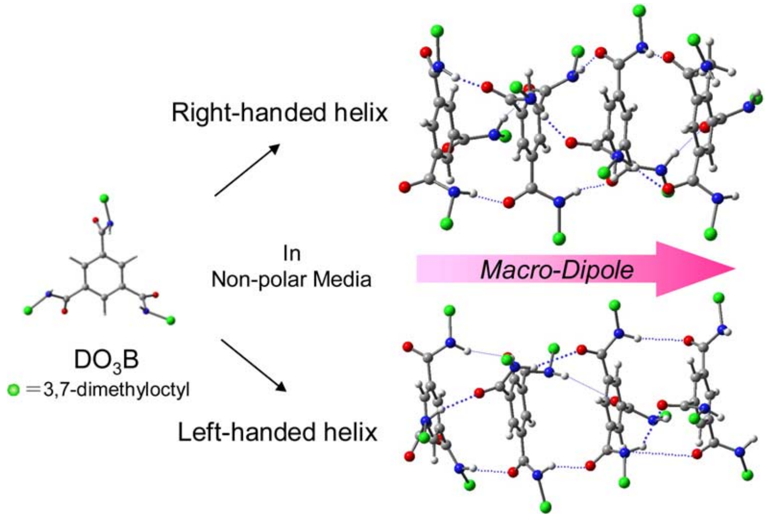


Scheme 1. Proposed supramolecular polymeric structures [1–3] of DO$_3$B in non-polar solvents. Thin dotted lines linking N–H and O=C groups represent hydrogen bonds.

electric dipole of the three amide groups forming the three-fold hydrogen bond in every DO$_3$B monomer is fixed in the direction keeping a component perpendicular to the benzene rings in both the left- and right-handed columns, large macro-dipoles that consist of the sum total of dipoles in every DO$_3$B monomer are generated in each column (Scheme 1), as in α-helixes of proteins [9]. When directions of the three-fold hydrogen bonds in supramolecular polymers of DO$_3$B are identical with each other, those of macro-dipoles coincide irrespective of the helicity. However, there have been few studies of such macro-dipoles in the supramolecular polymer of DO$_3$B or its analogues in non-polar solvents.

Here, we discuss evidence indicating that macro-dipoles are present in the supramolecular polymer in the DO$_3$B/C$_{10}$ system, based on the results of conventional dielectric relaxation measurements over a wide frequency range, in which viscoelastic relaxation was also observed. Also, we discuss the sequence and orientation of macro-dipoles in contiguous supramolecular polymers and a mechanism for dielectric relaxation in the system, including a comparison between dielectric and viscoelastic relaxation behavior. About 2 decades ago, Jadżyn et al. [10] reported leading work on the dielectric relaxation behavior of supramolecular polymeric systems consisting of *sym*-dialkylureas in non-polar solvents due to the hydrogen bond formation. Some reports [11,12] were also published on the switching behavior of meso-phases of columnar supramolecular systems at the onset of electric field, which should be related to the presence of macro-dipoles along supramolecular polymers in the systems.

In the present study, we observed dielectric spectra, the imaginary part of electric permittivity (ε'') vs angular frequency (ω), for a highly viscoelastic DO$_3$B/C$_{10}$ system at several DO$_3$B concentrations (c) determined at 25 °C as shown in Fig. 1. Those spectra clearly show dielectric relaxation modes, the strengths of which depend on c, around the peak frequency of ε'' at $\omega_{\mathrm{P}} = 7\times10^{-2}\ \mathrm{s}^{-1}$, irrespective of c values. Fig. 2 shows the relationship between c and the magnitude of relaxation strength ($\Delta\varepsilon$), based on the peak heights of ε'' curves at ω_{P}, on a double-logarithmic scale. Because the relaxation modes at ω_{P} are sharp, the magnitude of $\Delta\varepsilon$ calculated from the height of ε'' is similar to the magnitude obtained from a step-wise increment in a curve of the real part of permittivity (ε'). When a system has only 1 dielectric relaxation mode with a strength and time of $\Delta\varepsilon$ and τ_{d}, respectively, we observe the relationships given by Eq. (2)

$$\varepsilon' = \frac{\Delta\varepsilon}{1+\omega^2\tau_{\mathrm{d}}^2} + \varepsilon_\infty \qquad \varepsilon'' = \frac{\Delta\varepsilon\omega\tau_{\mathrm{d}}}{1+\omega^2\tau_{\mathrm{d}}^2} \tag{2}$$

where ε_∞ represents the high frequency limiting value for ε' [13]. In this case, $\Delta\varepsilon = \varepsilon'(0) - \varepsilon_\infty = 2\varepsilon''(\tau_{\mathrm{d}}^{-1})$. The slope of the curve in Fig. 2 suggests the relationship $\Delta\varepsilon \propto c^{0.8}$. Because C$_{10}$ did not exhibit dielectric relaxation in any of the ω region examined, we doubtless conclude that the supramolecular polymer in the system possesses large macro-dipoles and maintains distinctive relaxation of the summed or individual macro-dipoles at ω_{P}.

The dielectric relaxation time, τ_{d}, calculated from ω_{P}^{-1} is 2–3 times as long as the (longest) mechanical relaxation time (τ_{m}) determined from viscoelastic measurements [2]. In general, the equation $\tau_{\mathrm{d}} = 3\tau_{\mathrm{m}}$ holds even in the same

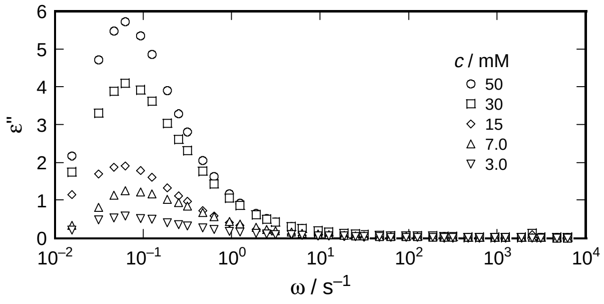


Fig. 1. Dependence of the imaginary part of electric permittivity (dielectric loss factor), ε'', on angular frequency, ω, for DO$_3$B/C$_{10}$ at several concentrations, c, of DO$_3$B at 25 °C.

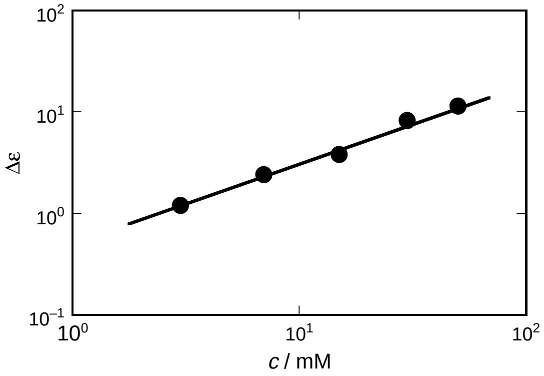


Fig. 2. Relationship between c and the magnitude of relaxation strength, $\Delta\varepsilon$, for the relaxation mode estimated from the heights of ε'' peaks in Fig. 1. The slope of a solid line is evaluated to be 0.8.

rotational motion of rigid rod particles, due to the difference in the rank of observed spherical harmonic functions depending on the measured parameters [14]. Moreover, it has been known that flexible polymer chains bearing dipoles aligned parallel along their backbones classified as type-A polymers [15] show the relationship $\tau_d = 2\tau_m$ in the unentangled condition [16]. Therefore, the finding of $\tau_d = 2\tau_m \sim 3\tau_m$ in the system strongly suggests that the (slowest) viscoelastic relaxation mode, which has been assigned to a passing-through (phantom crossing) process between supramolecular polymers at entanglement points caused by exchange of hydrogen bonds [2,6], is directly related to the dielectric relaxation as in both rod and flexible type-A polymer systems. Such a hypothesis can easily be verified by experiments in which τ_m and τ_d are systematically controlled by addition of a strong hydrogen bond breaker or exchanger of the supramolecular polymer, such as 3,7-dimethyl-1-octanol (DOAL). The value of τ_d markedly decreases with increasing the concentration (c_{AL}) of DOAL, with a slight decrease in relaxation strength, $\Delta\varepsilon$, until $c_{AL}c^{-1} \sim 2$ as seen in Fig. 3. The values of τ_m, which are calculated from the reciprocals of the peak frequencies of G'' curves (cf. Eq. (1)), also decrease with increasing $c_{AL}c^{-1}$, maintaining a single mechanical relaxation mode, and τ_m becomes too short to be determined at $c_{AL}c^{-1} \geq 6$ as observed in Fig. 4. The arrows in Fig. 3 show $(3\tau_m)^{-1}$ at some $c_{AL}c^{-1}$ values. The relationship $\tau_d = 2\tau_m – 3\tau_m$ holds well also in the system containing DOAL at $c_{AL}c^{-1} < 4$.

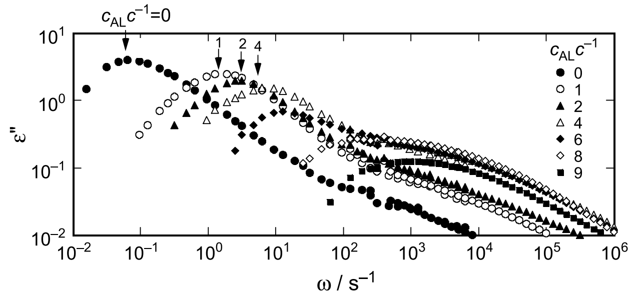


Fig. 3. Dependence of ε'' on ω for DO$_3$B:DOAL/C$_{10}$ at $c = 30$ mM and several DOAL concentrations, c_{AL}, from $c_{AL}c^{-1} = 0$–9, at 25 °C. Arrows in the figure represent the reciprocals of three times mechanical relaxation times, $(3\tau_m)^{-1}$, of some solutions, determined from Fig. 4.

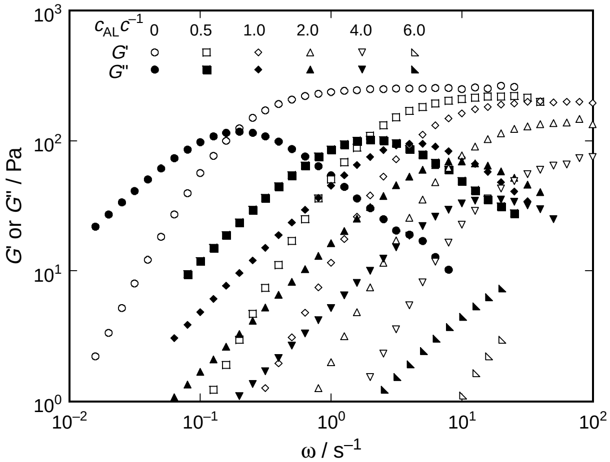
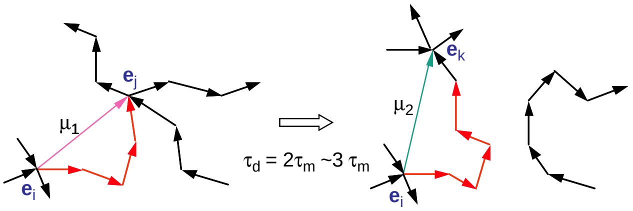


Fig. 4. Dependence of storage and loss moduli, G' and G'', on ω for DO$_3$B:DOAL/C$_{10}$ at $c = 30$ mM and varying $c_{AL}c^{-1} = 0$–6.

It is likely that the addition of a small amount of DOAL to the system only accelerates the passing-through process at entanglement points, due to activation of defective portions of the supramolecular polymer. However, addition of an excessive amount of DOAL ($c_{AL}c^{-1} \geq 8$) induces dismantling of the supramolecular polymer into small fragments or individual DO$_3$B monomers hydrogen bonded by DOAL. A broad dielectric relaxation mode observed around $\omega = 10^3$ s^{-1} at $c_{AL}c^{-1} = 9$ is assigned to the rotational relaxation modes of small fragments of supramolecular polymers which consist of a few number of macro-dipoles and are not so long enough to entangle each other, because fully hydrogen bonded DO$_3$B monomers by DOAL possibly obtained at $c_{AL}c^{-1} = 10$ scarcely show dielectric relaxation around $\omega = 10^3$ s^{-1} and a relaxation mode attributed to the rotation of hydroxyl groups of excess DOAL is observed at $\omega > 2 \times 10^{10}$ s^{-1}.

Given the sequence of directions of macro-dipoles in a contiguous supramolecular polymer, random orientation is easily excluded because the slowest relaxation mode corresponding to the entanglement release is mainly observed as described above. In the case of random orientation, faster relaxation modes related to higher harmonics of bending motions occurring in the supramolecular polymer between entanglement points would be preferentially detectable. Thus, macro-dipoles are connected by defective portions in the order of head to tail arrangement along the supramolecular polymer like type-A polymers [15] as schematically depicted in Scheme 2 with short arrows representing macro-dipoles generated in each column, i.e. helical columns formed by DO$_3$B (Scheme 1). Unless the order of head to tail arrangement of macro-dipoles is conserved at every entanglement release process, it disappears after several entanglement release processes. Therefore, we may conclude that dipole inversion scarcely occurs at entanglement release processes.

Time dependency of the total dipole moment between entanglement points, long arrows in Scheme 2, indicated by the sum of constituent macro-dipoles reflects the dynamics of the



Scheme 2. Each short arrow represents a macro-dipole generated along a supramolecular column such as helical columns formed with DO_3B depicted in Scheme 1. The total dipole, $\boldsymbol{\mu}_1$, defined as the sum of macro-dipoles between two entanglement points, e_i and e_j, alters to $\boldsymbol{\mu}_2$ due to the entanglement release and creation caused by the passing-through process [2] at e_i and e_k, respectively.

entanglement release process in the system. We propose a mechanism for dielectric relaxation caused by the entanglement release process. The vector of the total dipole, $\boldsymbol{\mu}_1$, defined between two entanglement points changes to $\boldsymbol{\mu}_2$ after the passing-through process at the entanglement point, e_j, associating the creation of a new entanglement point, e_k, as schematically depicted in Scheme 2. Then, the system relaxes dielectrically and also mechanically. Since the passing-through process at entanglement points is the slowest relaxation mode, there exist a number of faster bending modes in supramolecular polymer strands between entanglement points resulting from thermal motions of individual constituent columns bearing macro-dipoles. These faster modes between entanglements involving orientational relaxation of constituent columns are responsible for mechanical relaxation behavior, whereas the modes do not provide dielectric relaxation in type-A polymers when both the entanglement points are tightly fixed spatially. The presence of the faster mechanical relaxation modes are recognized as slight deviation of G'' data from the relationship $G'' \propto \omega^{-1}$ (Eq. (1)) in an ω range much higher than τ_m^{-1} as observed in Fig. 4. If entanglement points formed by the supramolecular polymer are not fixed spatially, but involve fluctuation with a certain time constant shorter rather than τ_d, the fluctuation of entanglement points results in that of the magnitudes of total dipoles between entanglement points and also of the orientation of constituent columns. Consequently, the spatial fluctuation of entanglement points is possibly responsible for relaxation modes observed in higher ω ranges in addition to the slowest single relaxation modes (Eqs. (1) and (2)) in both the dielectric and mechanical relaxation behavior seen in Figs. 3 and 4.

According to standard dielectric theory [13], the magnitude of dielectric relaxation strength, $\Delta\varepsilon$, is proportional to the product of number density (n) of dipolar particles and the square of their dipole moment, $\boldsymbol{\mu}^2$. As shown below, the fundamental features of entanglement networks for ordinary flexible polymer systems [8,18] can be applied to the DO_3B/C_{10} system, therefore, the relationship $\Delta\varepsilon \propto c^{0.8\text{–}1.0}$, which is the same as the above result, is obtained using the relevant relationships, $n \propto c^2$ and $\boldsymbol{\mu}^2 \propto c^{-1.0\ \text{to}\ -1.2}$, naturally derived for the supramolecular polymers of DO_3B.

Because the viscoelasticity of the DO_3B/C_{10} system [2] is well described by a formulation that is valid for ordinary entangling flexible polymer solution in a semi-dilute regime, the number density (ν) of polymer strands between entanglement points (i.e. dielectric particles) proportional to G_N is described by the relationship $\nu(\propto n) \propto c^2$. The contour length of the polymer strand (L_e) between entanglement points, which is proportional to molar mass between entanglement points, is calculated to be $L_e \propto c^{-1}$ [8,17]. Because this relationship has been confirmed perfectly in the DO_3B/C_{10} system [2], i.e. the relationship $G_N \propto cRT/L_e \propto c^2$ has been found for the system; R and T means the gas constant and absolute temperature, respectively, regarding the supramolecular polymer formed in the system as a flexible polymer chain is valid without doubt. The magnitude of the dipole moment of a type-A polymer strand is proportional to its end-to-end distance, i.e. entanglement spacing (R_e) in this case, as described by the formula $|\boldsymbol{\mu}|\ (\propto R_e \propto L_e^{0.5\text{–}0.6}) \propto c^{-0.5\ \text{to}\ -0.6}$. The exponent depends on the quality of the solvent, C_{10}, for the supramolecular polymer of DO_3B [8,17]. These relationships lead to $\Delta\varepsilon \propto c^{0.8\text{–}1.0}$ obtained above.

The essential microscopic motion in the supramolecular polymer of DO_3B to the dielectric relaxation is the rotation of the total dipole with the average magnitude of $|\boldsymbol{\mu}| \propto L_e^{0.5\text{–}0.6}$, which is promoted by the passing-through process at entanglement points. This looks like the rotational motion of a type-A polymer with the $|\boldsymbol{\mu}|$ dissolved in a liquid medium, C_{10}, and spatially (and loosely) pinned down at two terminals for a lifetime equivalent to τ_d.

Recently, we also investigated dielectric behavior of a highly viscoelastic supramolecular polymeric system of tri-3,7-dimethyloctyl-*cis*-1,3,5-cyclohexanetricarboxamide (DO_3CH) dissolved in C_{10} [18]. In the DO_3CH/C_{10} system, the formed long supramolecular polymer consists of an alternating sequence of straight columnar parts behaving as stiff rods and flexible columns. Large macro-dipoles are generated only along stiff rod parts, whereas very little macro-dipole remains along flexible columns presumably due to frequent dipole inversion. The magnitude of the macro-dipole in the stiff rod part appears to remain at a constant value irrespective of c. Difference in dipolar characteristics related to supramolecular polymeric structures between DO_3B/C_{10} and DO_3CH/C_{10} definitely results from that in the three-fold hydrogen bond formation in the helical (DO_3B/C_{10}) and straight manner (DO_3CH/C_{10}) [3,18].

We are currently conducting further quantitative analysis of the unique dielectric behavior observed in the present study.

1. Experimental section

Dielectric measurements were performed over an ω range of 10^{-2} to $2\times10^{10}\ \mathrm{s}^{-1}$ at 25 °C using three systems. In the lowest ω region (10^{-2}–10^4), we used a home made system with a current amplifier (428, Keithley, Cleveland) and a fast Fourier transform analyzer (VC-2440, Hitachi, Tokyo), which was constructed based on a precise impedance analysis technique [19]. For ω ranges of 10^2–$6\times10^6\ \mathrm{s}^{-1}$ and 6×10^6–$2\times10^{10}\ \mathrm{s}^{-1}$, we used a 4284A Precision LCR meter (Hewlett Packard, Palo Alto) and a 4287A RFLCR meter

(Agilent Technologies, Palo Alto), respectively. Real and imaginary parts of electric permittivities, ε' and ε'', were determined from capacitance and conductance as functions of ω.

Dynamic viscoelastic measurements were performed at 25 °C with ω ranging from 10^{-2} to $10^{2}\ \mathrm{s}^{-1}$, using a DAR100 stress rheometer (Reologica, Lund) equipped with a cone-and-plate geometry with a diameter and cone angle of 4.0 mm and 4.0°, respectively, to determine G' and G'' as functions of ω.

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