Sol–Gel Transition of Organogels Observed by Terahertz Spectroscopy

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Abstract

Terahertz (THz) absorption spectra of organogels consisting of (1*R*,2*R*)-1,2-bis(dodecanoylamino)cyclohexane/2-nitrophenyl octyl ether (RR-BDC/NPOE) and RR-BDC/*n*-dodecane were measured by Fourier-transform far-infrared (FT-FIR) spectroscopy. The vibrational peaks of the gels were observed at the same frequencies as those of the pure gelator, suggesting that the intermolecular structure around the N–H...O=C hydrogen bond is maintained in the gel phase. Temperature-dependent spectroscopy showed a drastic spectral change at the sol–gel transition temperature, in which the vibrational peak at 3.5 THz disappears and a new peak appears at 2.9 THz. The change in THz vibrational frequency is indicative of the structural collapse of the hydrogen-bonded fibrous architecture in the sol phase.

Keywords

Terahertz spectroscopy, Organogel, Sol–gel transition

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3 The development of spectroscopic techniques in the terahertz (10^{12} Hz; THz) frequency
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6 region over the past decade has enabled the rapid and precise measurement of low-frequency
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9 vibrational spectra.[1, 2] Since the absorption bands of organic molecules in the frequency
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12 region of 1.0–3.0 THz ($33\text{--}100\text{ cm}^{-1}$) originate mainly from intermolecular vibrational
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15 motions,[3, 4] THz spectroscopy directly reflects both their intermolecular conformations and
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18 intermolecular interactions such as hydrogen bonding. As the physical and chemical properties
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21 of macromolecules such as polymers, proteins, and DNA originate in their higher-order
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24 conformations, THz spectroscopy is anticipated for use as a new tool for observing the
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27 conformations of those materials.
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32 We have investigated the THz spectra of polyhydroxybutyrate (PHB) and observed the
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35 vibrational mode of $\text{C}\text{--}\text{H}\cdots\text{O}=\text{C}$ hydrogen bonds between molecular chains at 2.3 THz, and the
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38 skeletal vibrational modes of the molecular chains at both 2.5 and 2.9 THz.[5, 6] Those
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41 assignments were made by using the polarization dependence of the vibrational intensities of the
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44 stretched PHB samples, in which the crystal axes are aligned. We have also developed a
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47 computational calculation method based on density functional theory (Cartesian coordinate
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50 tensor transfer method) to simulate the THz spectra of polymers, and have confirmed those
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53 assignments.[7] Since the vibrational modes observed in the THz spectra were fingerprints of
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3 higher-order polymeric structures, the conformational changes experienced by polymers, such as
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6 phase transitions, can be monitored by THz spectroscopy.[8-10] For example, the intensity
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9 change in hydrogen-bond vibrations during the isothermal crystallization of PHB shows direct
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12 evidence of the two-step crystallization of the lamellar crystals.[11] Recently, we have studied
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15 Nylon 6 and observed the fingerprint peak of the α form at 6.6 THz.[12] The intensity of the
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18 peak was observed to change at 160 °C during variable-temperature spectroscopy, which is
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21 clearly indicative of the phase transition from its α -crystalline form to a pseudo-hexagonal form
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25 (the so-called Brill transition).
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29 In this paper, we describe our study of the THz absorption spectra of organogels.
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33 Organogels consist of a three-dimensional gelator network produced through self-assembly due
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36 to non-covalent interactions, and form a viscoelastic gel phase by absorbing a large amount of
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39 solvent molecules, as shown in Figure 1. The gel network collapses as temperature is increased;
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42 the gel phase is subsequently transformed into the sol phase at the sol–gel transition temperature.
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45 To understand the origin of the physical and chemical properties of such gels, information about
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48 the supramolecular structure of the gelator is required. However, commonly used methods, such
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51 as wide-angle X-ray scattering (WAXS), do not provide enough information related to the gelator
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structure since its fibrous structure is not crystalline. Conventionally, structural information has been obtained by small angle X-ray scattering (SAXS) or atomic force microscopy.

In this study, (1*R*,2*R*)-1,2-bis(dodecanoylamino)cyclohexane (RR-BDC) was used as a gelator. By analogy with similar gelators,[13] RR-BDC is expected to form long fibrous structures constructed of N–H···O=C hydrogen bonds. The RR-BDC gelator material was dissolved in 2-nitrophenyl octyl ether (NPOE) at concentrations of 10 wt% and 20 wt%, and *n*-dodecane was also used as solvent at a concentration of 10 wt%. To obtain a uniform sample thickness, we prepared the gels and measured their absorption spectra in a sample cell made of a highly resistive Si material, which is transparent in the THz frequency region; the cell employed in the present study is depicted in Figure 2. The thickness of the sample was about 0.8 mm for RR-BDC/*n*-dodecane and about 2.4 mm for RR-BDC/ NPOE. The gel samples were heated to 150 °C in the cell to completely melt the gelator and subsequently cooled down to room temperature. The spectra of pure NPOE and *n*-dodecane were also measured. THz absorption spectra were measured using a Fourier-transform far-infrared (FT-FIR) spectrometer (JASCO FARIS) in the frequency range of 1.0–10 THz with a frequency resolution of 0.06 THz. The sample cell was placed in a temperature-controlled heating stage (LINKAM 19113L) and its temperature was increased from 25 to 140 °C. The THz absorption spectrum of pure RR-BDC

was also observed by measurement of an RR-BDC pellet made by pressing a powder sample at 20 kg/cm² for 10 min.

FIG. 1. Schematic figure of the gel and sol structures, and the chemical structures of the gelator and solvents.

FIG. 2. Schematic figure of (a) the gel sampling technique, and (b) a photograph of the sample cell.

Figure 3 shows the absorption spectra of (a) RR-BDC/NPOE 20 wt%, (b) NPOE, (c) RR-BDC/*n*-dodecane 10 wt%, and (d) *n*-dodecane in the Si cell, as well as (e) the pure RR-BDC pellet, all of which were obtained at 25 °C. Pure RR-BDC shows absorption peaks at 2.4, 3.4, 4.3, 5.1, 6.7, 7.3, and 8.4 THz. These peaks are also observed in the spectra of both RR-BDC/NPOE and RR-BDC/*n*-dodecane. The absorption of *n*-dodecane is quite weak because the molecule has no permanent dipole moment, and the spectrum shows quite weak absorption (about 0.3 cm^{-1}) in the frequency region from 3–10 THz due to intermolecular dispersion interactions. In contrast, the spectrum of NPOE shows intense absorption bands at

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3 1.4, 2.0, 7.6, and 8.7 THz. These absorption bands are most likely due to the intermolecular
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6 vibrations between NPOE molecules and rotational relaxation (Debye relaxation) of NPOE. For
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9 convenience, these absorption bands are superposed in the absorption spectrum of
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FIG. 3. THz absorption spectra of (a) RR-BDC/NPOE 20 wt%, (b) NPOE, (c) RR-BDC/*n*-dodecane 10 wt%, and (d) *n*-dodecane in a Si cell, and (e) the RR-BDC pellet.

To remove the absorptions associated with solvents from the gel spectra, we calculated the corresponding differential spectra. According to Beer's law, the absorbance of a sample α_{gel} is the sum of the absorption of the gelator α_{RR-BDC} , that of solvent $\alpha_{solvent}$, and the absorption induced by the interaction between gelator and solvents α_{int} , normalized by sample thickness,

$$\alpha_{gel} = x\alpha_{RR-BDC} + (1-x)\alpha_{solvent} + x(1-x)\alpha_{int} \quad (1)$$

where x is the molar fraction of the gelator. The differential spectra were calculated by the following equation,

$$\Delta\alpha = \alpha_{RR-BDC} + (1-x)\alpha_{int} = \frac{\alpha_{gel} - (1-x)\alpha_{solvent}}{x} \quad (2)$$

By assuming that the interactions between gelator and solvents are negligibly small, we establish that the differential absorption intensity $\Delta\alpha$ is equal to α_{RR-BDC} . Figure 4 shows the differential spectra of (a) RR-BDC/NPOE 10 wt%, (b) RR-BDC/NPOE 20 wt%, and (c) RR-BDC/*n*-dodecane 10 wt% obtained using Eq. (2), and trace (d) shows the absorption spectrum of pure RR-BDC. It is clearly seen that all the spectra in Fig. 4 show similar features, displaying absorption peaks at 3.4, 4.3, 5.1, 6.7, 7.3, and 8.4 THz; nevertheless, the signal-to-noise ratio of the spectrum of RR-BDC/NPOE is not as good as the result of subtracting the intense absorptions

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3 of NPOE. Especially, the spectral features of RR-BDC/*n*-dodecane 10 wt% are quite similar to
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6 those of pure RR-BDC (See traces (c) and (d) in Figure 4). Since the THz vibrational spectrum is
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9 highly dependent on the intermolecular conformations,[3, 4] this result suggests that the
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12 intermolecular structure of RR-BDC in the gel phase (c) is close to that in the pure sample (d).
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15 The only difference between (c) and (d) is the spectral linewidth of the vibrational bands, which
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18 are slightly broadened in the gel phase, showing that vibrational relaxation times in the gel phase
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21 are faster than those in the solid phase due to the presence of solvents surrounding the gelator.
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FIG. 4. Differential spectra of (a) RR-BDC/NPOE 10 wt%, (b) RR-BDC/NPOE 20 wt%, and (c) RR-BDC/*n*-dodecane 10 wt% obtained using Eq. (1), and (d) the absorption spectrum of pure RR-BDC. The units of traces (a)–(c) are in cm^{-1} , and that of (d) is in arbitrary units.

The explicit structure of the RR-BDC gel is not well known, but on the basis of the known structure of a similar molecule, *trans*-((1*S*,2*S*)-bis(ureidododecyl)cyclohexane), the gelator is expected to take a fibrous structure via one-dimensional stacking due to the N–H···O=C hydrogen bonds.[13] It has been previously established that polymers containing N–H···O=C hydrogen bonding show intense absorption bands around 3 THz.[14] For example, the low-frequency vibrational mode of polyurethane was observed around 3.2 THz.[15, 16] Frank et al. have measured the far-infrared absorption spectra of a series of polyamides (Nylon 2, 4, 6, 8, 10, and 12) and found that all spectra show a vibrational band structure between 3.0 to 3.3 THz.[17] We have also observed a similar band structure in the spectra of other Nylons (Nylon 6/6 and Nylon 11).[12] Since the frequencies of those bands are observed to be independent of the intermolecular conformations, they have been assigned to the hydrogen bond vibration between N–H and C=O groups.[15] Recently, Onishi et al. have performed DFT calculations using the Cartesian coordinate tensor transfer method in their investigations of the low-frequency

vibrational modes of Nylon 6 and assigned the mode at 3 THz as the vibration of the methylene chain coupled with the out-of-plane N–H...O=C hydrogen bond.[18] Therefore, the similar absorption features observed at 3.5 THz in the spectra of pure RR-BDC and gels are assigned to be vibrational modes related to the intermolecular N–H...O=C hydrogen bond between RR-BDC molecules.

Figure 5 shows the temperature-dependent THz spectra of RR-BDC/*n*-dodecane 10 wt% at varying temperatures. As the temperature is increased, the vibrational band at 3.5 THz is broadened and a new absorption band appears at 2.9 THz. Moreover, the peaks from 6 to 9 THz are weakened and frequency-shifted. These spectral changes suggest that the conformational change occurs at a higher temperature. To separate the overlapped peaks at 2.9 and 3.5 THz, the spectra were fitted to Gaussian line-shape functions using the least-squares fitting method in order to obtain the integrated intensities of the overlapped bands (Figure 6). It is clearly shown that the intensity of the peak at 3.5 THz begins decreasing at 100 °C, whereas that at 2.9 THz increases instead. This drastic spectral change occurs in the temperature range of 100–130 °C. Differential scanning calorimetry (DSC) was also performed for this sample, and an endothermic peak was observed at 102 °C, which shows the sol-gel transition temperature.

FIG. 5. Temperature dependence of the differential absorption intensity $\Delta\alpha$ of RR-BDC/*n*-dodecane 10 wt% from 25 to 140 °C.

FIG. 6. Integrated absorption intensities of the vibrational bands at 2.9 and 3.5 THz, respectively, obtained by least-squares fitting of the spectra in Fig. 5 by the Gaussian line-shape function.

The drastic change observed in the THz spectra indicates that an intermolecular structural change in the gelator occurs at the sol–gel transition temperature. The decrease in intensity of the band at 3.5 THz shows that the one-dimensional fibrous structure of the gelator collapses at higher temperatures. On the other hand, an increase in intensity of the new band at 2.9 THz suggests the appearance of another structure in the sol phase. The lowering of the

vibrational frequency from 3.5 to 2.9 THz suggests that the N–H...O=C hydrogen bond in the sol phase is weaker than that in the gel phase. The linewidth of the band at 2.9 THz was about 1.5 THz at room temperature, which is narrower than that of the intermolecular vibrational band of hydrogen-bonded liquids (about 5.4 THz (H₂O) for example[19]), suggesting that the intermolecular conformation in the sol phase is ordered and maintains an intermolecular structure between the gelator and solvents.

In conclusion, the THz absorption spectra of organogels RR-BDC/NPOE and RR-BDC/*n*-dodecane were observed in this study. The vibrational peaks of the gels were observed at the same frequencies as those of the pure gelator, suggesting that the intermolecular structure around the N–H...O=C hydrogen bond is maintained in the gel phase. The temperature-dependent absorption spectra showed a spectral change at the sol–gel transition temperature, in which the vibrational peak at 3.5 THz disappeared and a new peak arose at 2.9 THz, indicating that the hydrogen bonded fibrous structure collapses in the sol phase. THz spectra provide a rich source of information about the intermolecular conformations and intermolecular interactions of gels. This technique may have a potential to become a novel tool for investigating soft materials.

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