Article

Dielectric Relaxation of Guest Molecules in a Clathrate Structure of Syndiotactic Polystyrene

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ABSTRACT: Structure and dynamics of semicrystalline polymer films composed of syndiotactic polystyrene (sPS) and 2-butanone were examined through X-ray diffraction, polarized FTIR, and dielectric relaxation measurements. The X-ray and FTIR measurements revealed its crystal structure to be δ-clathrate containing 2-butanone molecules inside. The carbonyl group of 2-butanone in the crystal was found to orient preferentially parallel to the ac plane of the crystal through the polarized ATR FTIR measurements. Dielectric measurements were also conducted on these film samples to see only the relaxation dynamics of 2-butanone thanks to the high dielectric intensity of 2-butanone compared to sPS. Two relaxation modes denoted by slow and fast modes appeared. The former was assigned to the motion of 2-butanone molecules entrapped in the cavities of the crystalline (δ-form) and the latter to those in the amorphous region. We focused on the slow mode in order to elucidate the specific dynamics of the guest molecule confined in the crystalline region. The relaxation time of the slow mode was about 4 orders of magnitude longer than that of liquid 2-butanone. This suggests that the dynamics of guest molecules is highly restricted due to the high barrier to conformational and/or orientational change of the guest molecule in the cavity of δ-crystal. Furthermore, the dielectric intensity $\Delta\varepsilon$ of the slow mode was much smaller than the one calculated from that of bulk liquid 2-butanone and the guest concentration in the crystalline region (the intensity was only 10% of the estimated value from the bulk liquid data). This result also indicates that the free rotational motion of 2-butanone molecules is restricted inside the crystal. This will be consistently related to the weak uniplanar orientation of the carbonyl group of 2-butanone parallel to the *ac* plane revealed by the X-ray and polarized ATR FTIR measurements.
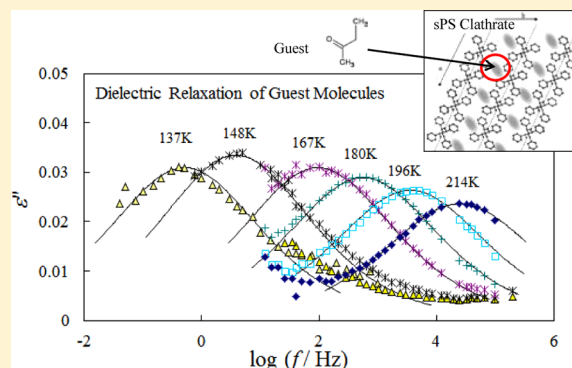
INTRODUCTION

Syndiotactic polystyrene (sPS) has a unique and fascinating property of forming cocrystalline structures with a variety of low mass molecules. This nature of sPS has attracted the attention of researchers and active research is going on concerning the structure and properties of the cocrystalline structures. It has been recognized that the cocrystalline structure has a significant potential for new kinds of functional materials by loading functional molecules into the crystalline region.

The cocrystalline structures of sPS can be classified into four major groups;[1−9] the monoclinic δ-clathrate and intercalate cocrystals, the orthorhombic ε-clathrate cocrystal, and the triclinic δ-clathrate cocrystal. In all cases, sPS takes a helical $(T_2G_2)_2$ (T and G stand for trans and gauche, respectively) conformation in the crystalline region. The δ-clathrate and intercalate cocrystals have a common structural feature; the guest molecules are confined in the space sandwiched by the polymer sheets consisting of right- and left-handed $(T_2G_2)_2$ helices. In the δ-clathrate cocrystal there are generally two guest molecules per unit cell and each guest is isolated in a cage defined by ten phenyl groups,[1−3] whereas the intercalate complex contains four guest molecules per unit cell, which are arranged contiguously in the direction along the sPS helices within a wider interspace between the polymer sheets.[4,5] On

the other hand, in the ε-clathrate complex, the guest molecules are confined in the channel defined by six $(T_2G_2)_2$ helices which passes through the unit cells along the c axis.[6,7] As for the recently reported triclinic δ-clathrate complex, there are two kinds of structures: one contains two guest molecules per unit cell similarly in the case of the monoclinic δ-clathrate and the other contains one guest molecule. The bigger cavities in the latter adopt bulky compounds.[8,9]

Many different kinds of organic compound have already been incorporated into the four kinds of cocrystalline structures such as dye,[10] fluorescent,[11,12] photoreactive,[13,14] paramagnetic,[15,16] highly polar[7] molecules, and so on. The combination of such organic compounds with the polymer crystalline region would provide several benefits, which the combination with the amorphous region does not have. It will prevent or at least retard the dissipation and aggregation of doped molecules and make them arrange periodically and separate into individual rooms. The orientation of molecules will be possibly made by controlling the arrangement of the polymer crystalline region. Furthermore, the molecules entrapped in the cavities might

exhibit unique characteristics which they do not exhibit in amorphous polymer media or in their pure states.

The environment of the cavity has a significant influence on the conformation and dynamical properties of the entrapped molecules.[17−23] In some cases, guest molecules take a specific conformation predominantly from several preferable conformations. Highly restricted molecular motions are also confirmed. It seems that such restriction by the surrounding polymers affects the response of the entrapped molecules to the external stimuli, such as the application of electric and magnetic fields. The response behavior is of course determined by the molecular motion of the guest molecule inside the crystal, so that the profound and general knowledge of guest dynamics would give clues to develop new polymer-crystalline functional materials by doping functional low-molecular compounds into sPS crystalline region.

In order to elucidate the dynamics of polar guest molecules, dielectric relaxation spectroscopy was used in this study. We investigated, as a first step, the dielectric properties of 2-butanone having a polar carbonyl group encapsulated in sPS δ-clathrate and clarified how the molecular dynamics was modified by the confinement effect from the comparison with that in the bulk liquid.

■ EXPERIMENTAL SECTION

Samples. sPS was supplied by Idemitsu Petrochemical Co. Ltd. The weight-average molecular weight M_w was 17.9k and molecular weight distribution index M_w/M_n was 3.08. Atactic polystyrene aPS (Toporex GP550−51) of M_w = 246 000 and M_w/M_n = 1.92, was supplied by Mitsui Chemical Co., Ltd. Chloroform (98%) and 2-butanone (99%) were purchased from Nakarai Tesque and used without further purification.

Sample Film Preparation. Syndiotactic polystyrene (sPS) films with thicknesses of 25 and 75 μm, were prepared by casting sPS/chloroform solutions on a flat glass plate. The films were soaked in 2-butanone (methyl ethyl ketone) for more than one day at room temperature. During this process, guest exchange took place and 2-butanone molecules were replaced with chloroform and incorporated into the crystalline region of the films. The degree of crystallinity of film samples prepared by this method was estimated to be about 42% by using IR spectral data.[24]

For dielectric measurements, gold electrodes were sputtered onto both sides of a film using an ion sputter apparatus (E-1010, Hitachi, Japan) under vacuum at room temperature. The time necessary for the sputtering was about 5 min. During this procedure, a certain amount of 2-butanone will be removed from the film. The concentrations of 2-butanone that remained in the film were determined by thermogravimeteric analysis (Seiko Instruments Inc., TG/DTA6200 thermobalance) after dielectric measurements.

Measurement. The electrode-deposited film was set in dielectric sample chamber purged with nitrogen gas, and dielectric measurements were carried out with an LCR meter (QuadTech, 7100 or 7600) at several frequencies (12 Hz to ∼100 kHz and 10 Hz to ∼3 MHz, respectively) in the heating scan at a rate of 0.33 K min^{-1} from 80 to 320 K. For the frequency dispersion measurements at constant temperature in a wide range of frequency covering 10 mHz to 100 kHz, two instruments, the aforementioned LCR meter (QuadTech, 7100) and a homemade apparatus consisting of a current amplifier (Keithley, 428) and an FFT analyzer (Hitachi, VC-2440), were employed. In dielectric measurements the

temperature was controlled within ±0.2 K. For the measurements of bulk liquid 2-butanone at room temperature in a frequency range from 3 MHz to 50 GHz, two RF LCR meters (Agilent Technologies, 4287A and N5032C) were used.

Dielectric measurements were also conducted on mixtures of atactic polystyrene (aPS)/2-butanone in which the concentration of 2-butanone was below 10 wt %, in order to examine the guest dynamics in the amorphous region. In this case, samples for the measurements were prepared by pouring a 2-butanone solution of aPS (about 50%) into a dish shaped dielectric cell and then by letting the solvent 2-butanone evaporate for a while. After that the cell was sealed and kept in the oven regulated at 80 °C for 1 h to minimize the concentration gradient in the sample. The concentration of the remaining 2-butanone in the sample was determined by measuring the weight loss during this process. The dielectric cell was set in a chamber for temperature-dependent measurement and cooled to 80 K, and then dielectric measurements were conducted upon heating at a rate of 0.33 K min^{-1}.

In order to examine the thermal transition behavior (e.g., glass transition and vaporization of 2-butanone) of sPS/2-butanone mixtures, differential scanning calorimeter (Seiko Instruments Inc., DSC 6220, EXSTAR-6000) and thermogravimeteric analysis apparatus (Seiko Instruments Inc., TG/DTA6200 thermobalance) were used. Both measurements were conducted in a nitrogen atmosphere at a heating rate of 10 K/min.

The clathrate structure of sPS/2-butanone was confirmed by X-ray diffractometry and IR spectroscopy. In order to get the information about the orientation of the carbonyl group of 2-butanone, a uniaxially drawn clathrate sample was also prepared by exposing an 4-times-drawn glass sPS film to toluene vapor first and then to 2-butanone vapor.

Polarized transmission IR spectra and polarized ATR IR spectra were taken at a resolution of 2 cm^{-1} with a JASCO FT/IR-510 spectrometer equipped with a D-TGS detector and a JASCO FT/IR-610 spectrometer equipped with a MCT and D-TGS detector. For polarized ATR IR measurements, a JASCO PR500 wire-grid polarizer, a JASCO ATR 500 M attachment, and an internal reflection element (KRS-5) with wedge angle of 45° were employed. The number of accumulation cycles was 32 to 64. X-ray diffraction patterns in reflection mode were measured over a 2θ range of 2 to 40° at 0.5°/min with a step of 0.05° with a Rigaku RINT-2000 diffractometer equipped with a cupper X-ray tube for generating Cu Kα radiation (40 kV and 40 mA), a graphite monochromator, and with a scintillation counter. Finely chopped sPS films were used as powder samples to avoid the orientation effect. In order to obtain information about the crystallite orientation against the film surface, X-ray measurements were carried out with a film placed perpendicularly to the scattering vector.

■ RESULTS AND DISCUSSION

Sample Condition. After being subjected to the guest exchange process, sPS films showed no C−H deformation band due to the original guest CHCl$_3$ at 1219 cm^{-1} in the IR spectrum. Instead the bands due to 2-butanone, such as an intense band of C=O stretching at 1720 cm^{-1}, were observed. Figure 1 shows X-ray diffraction diagrams taken after the exchange treatment. The powder sample shows the 010 and $\overline{2}$10 reflections characteristic of sPS cocrystal structures at 8.0° and 9.9°, slightly different from their positions 8.2° and 10.2° in the starting sPS/CHCl$_3$ cocrystal. The slight shift of the 010
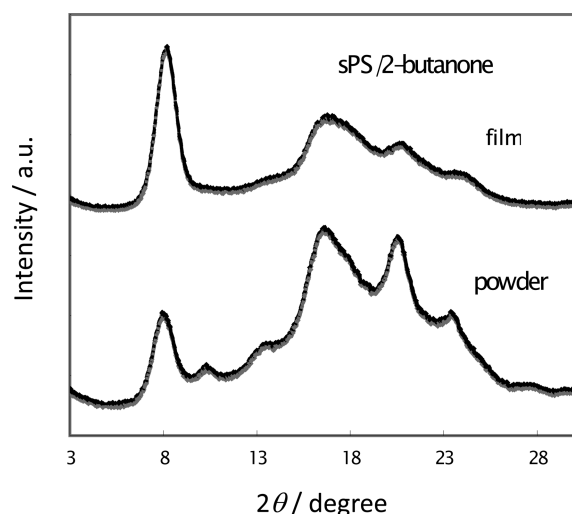
Figure 1. X-ray diffraction patterns obtained by an automatic powder diffractometer for a film and a powder sample of sPS/2-butanone cocrystal.

reflection corresponds to an expansion of the distance between polymer sheets from 1.08 to 1.11 nm. From these data, it is confirmed that the original guest chloroform is almost replaced with 2-butanene by the guest exchange procedure and sPS/2-butanone cocrystal is formed as δ-clathrate structure where 2-butanone is trapped in a cavity between sPS polymer sheets.

In the X-ray diffractogram taken with a film sample of sPS/2-butanone cocrystal, the 010 and $\overline{2}$10 reflections are very conspicuous and obscure respectively. This is a common feature for the starting sPS/CHCl$_3$ cocrystal whose ac plane tends to align parallel to the film surface.[25] In other words, there is a tendency that the sPS chain axis aligns parallel to the film surface and the polymer sheets are stacked perpendicularly to it. The X-ray result indicates that the uniplanar orientation remains unchanged during the course of guest exchange. Consequently, it can be said that the ac plane of sPS/2-butanone cocrystal is set preferentially parallel to the electrodes for dielectric relaxation measurements.

The uniplanar orientation is confirmed also by polarized ATR IR spectroscopy, whose absorption intensities with p and s polarizations, A_p and A_s, are related to the in-plane and out-of-plane extinction coefficients, $k_{\parallel}$ and $k_{\perp}$, as follows.[26]

$$A_p = c^A(k_{\parallel} + \alpha k_{\perp}) \tag{1}$$

$$A_s = c^A(\beta k_{\parallel}) \tag{2}$$

Here, c^A is a constant and α and β are parameters determined by incident angle θ and refractive indices of prism and sample, n_1 and n_2. In the present experimental conditions of $\theta = 45°$, $n_1 = 2.4$, and $n_2 = 1.57$, α and β are estimated to be 6.3 and 3.7, respectively, meaning that the IR active modes having a substantial transition moment component perpendicular to the film surface are emphasized in p-polarized spectra and the in-plane modes are emphasized in s-polarized spectra. As shown in Figure 2, some vibrational modes parallel and perpendicular to the ac plane[27] appear more intensely in s-polarized and p-polarized spectra, respectively, which is consistent with the ac uniplanar orientation indicated by X-ray diffractometry.

The polarized ATR IR spectra provide orientational information not only about the crystallites but also about the carbonyl group of 2-butanone, as shown in Figure 3. The band due to the C=O stretch of guest 2-butanone at 1719 cm^{-1} is stronger in s polarization, whereas the 1600 and 1583 cm^{-1} bands due to phenyl C=C stretch of host sPS are obviously stronger in p polarization. In the case of isotropic samples, that is, $k_{\parallel} = k_{\perp}$, the relation of $A_p = 2A_s$ is obtained from eqs 1 and 2. Therefore, the larger intensity in s polarization means that the in-plane component $k_{\parallel}$ is obviously larger than the perpendicular component $k_{\perp}$ as to the C=O stretch band; $k_{\parallel}$ is estimated to be around three times $k_{\perp}$, suggesting that the C=O bond is highly aligned to the film surface.

Polarized transmission IR spectra taken with a drawn sample can add further information; the C=O stretch band appears much larger in the parallel polarization, as shown in Figure 3b. In a drawn sample, it can be said that the c axis is aligned to the draw direction and the a and b axes are set perpendicular to it. Simply assuming the uniaxial orientation, the absorption intensities in parallel and perpendicular polarizations, $A_{\parallel}^d$ and $A_{\perp}^d$, can be related to the parallel and perpendicular extinction coefficients, $k_{\parallel}^d$ and $k_{\perp}^d$, of the drawn sample, and the two coefficients can be further related to the three extinction
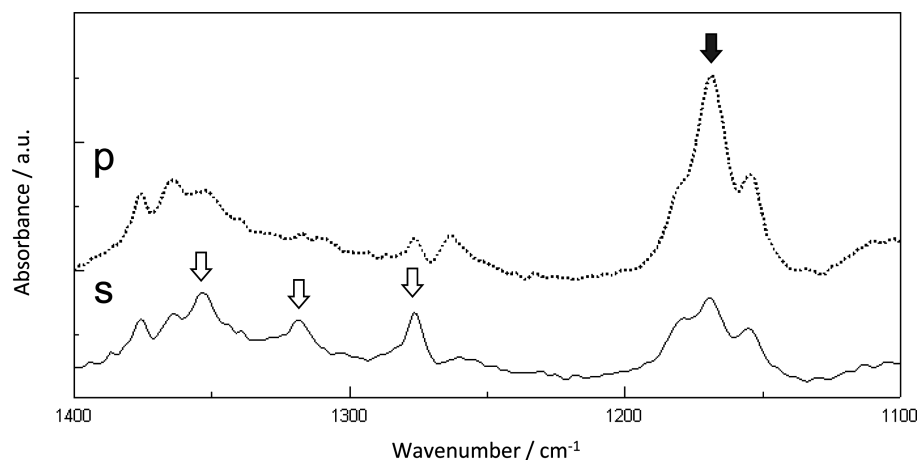

Figure 2. Polarized ATR IR spectra taken with p and s polarization. The p spectrum was shifted upward to avoid overlapping. The black arrow indicates the bands due to the out-of-(ac)-plane modes related to the phenyl ring deformations, and the white arrows indicate the ones due to the in-(ac)-plane modes related to the vibration of backbone chain internal coordinates.[27]
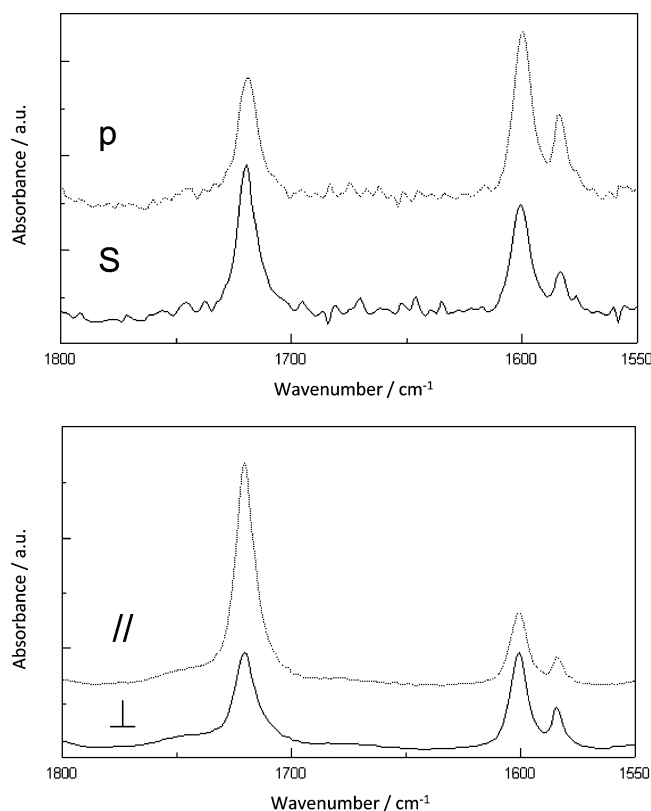
Figure 3. Polarized ATR IR spectra of a uniplanarly oriented sPS clathrate film taken with p and s polarizations (top) and polarized transmission IR spectra of a uniaxially oriented film.

coefficients based on the crystal structure, k_a, k_{b*}, and k_c, as follows:

$$A_{\parallel}^d = c^T k_{\parallel}^d = c^T k_c \tag{3}$$

$$A_{\perp}^d = c^T k_{\perp}^d = c^T\{(k_a + k_{b*})/2\} \tag{4}$$

Here, c^T is a constant, k_a and k_c are the coefficients parallel to the a and c ($\parallel$ chain axis) axes, and k_{b*} is the one parallel to the normal (the b* axis) of the ac plane. Similarly, eqs 1 and 2 can be rewritten with k_a, k_{b*}, and k_c

$$A_p = c^A\left\{\left(\frac{1}{2}\right)(k_a + k_c) + \alpha k_{b*}\right\} \tag{5}$$

$$A_s = c^A\left\{\left(\frac{\beta}{2}\right)(k_a + k_c)\right\} \tag{6}$$

Applying the absorption intensity of the C=O band into eqs 3−6, two ratios of extinction coefficients, k_a/k_c and k_{b*}/k_c, are estimated to be 0.72 and 0.29, from which the angles of the transition moment of C=O band to the a, b*, and c axes can be calculated as 55°, 77°, and 38°, respectively. Although there must be imperfection in the uniplanar and uniaxial orientations of sPS crystallites in the employed samples and the influence of the imperfection on absorption intensities has not been included in the present crude evaluation, the results obtained at least indicate that the carbonyl group of a guest 2-butanone in the cavity is anisotropically orientated; in average the C=O bonds tend to orient parallel to the ac plane judging from the angles described above. This means that the cavity in the δ-

crystal gives an orientational potential field to the guest 2-butanone molecules inside it.

Glass Transition of sPS/2-Butanone Mixtures. Figure 4 shows the DSC and TGA traces of sPS/2-butanone film
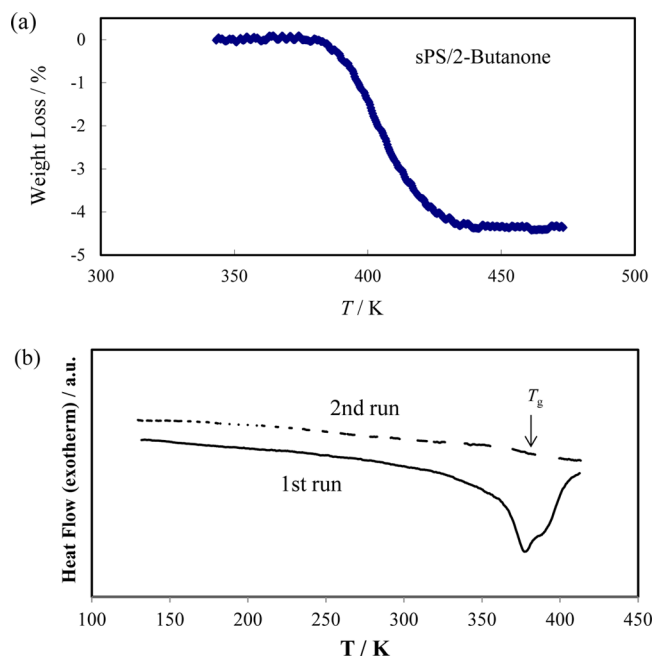

Figure 4. (a) Temperature dependence of the weight loss for a sPS/2-butanone film with 25 μm thickness obtained by theremogravimetric analysis and (b) the differential scanning calorimetry curves (first run and second run) of the similar sample. The glass transition temperature, T_g, is indicated by the arrow.

prepared by the aforementioned guest exchange method. TGA result shows that the weight loss due to the vaporization of 2-butanone starts around 380 K. This phenomenon can also be seen in the first-run measurement of DSC: the endothermic peak appear around 380 K. Because of this large thermal flow, glass transition of the mixture could not be accurately detected. However small change in the baseline can be seen for the DSC trace starting from about 320−330 K. This might be due to the glass transition in the amorphous region of the sPS/2-butanone mixture. It is too ambiguous to determine the T_g value, however, what we can say from these data is that there is no detectable thermal transition below 320 K for the sPS/2-butanone system.

After heating the sample to 420 K, the second scan of DSC was carried out from 125 to 420 K at the same heating rate. The result is also shown in the figure. It is seen that the endothermic peak disappears and T_g at around 375 K corresponding to that in the amorphous region of sPS can be detected, which means almost all 2-butanone molecules evaporate upon heating to around 420 K.

Dielectric Relaxation of Guest Molecules in a Semi-crystalline sPS. In order to observe the dynamics of guest molecules in the δ-clathrate structure, we investigated dielectric relaxation behavior below 320 K which is lower than both the glass transition temperature T_g of the amorphous phase in sPS/2-butanone (>320 K) and vaporization temperature of 2-butanone (380 K). The scanned temperature region is also below the transition temperature of the crystal structure from δ to γ (390 K) and the melting temperature T_m (543 K) of sPS.

The temperature dependence of the dielectric loss ε'' at various frequencies is shown in Figure 5 for the 75 μm thick sPS/2-
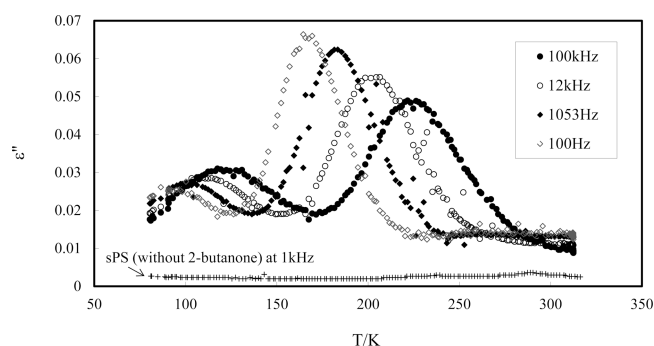

Figure 5. . Temperature dependence of dielectric loss ε'' for 2-butanone incorporated sPS film at various frequencies indicated in the legend. For comparison, the dielectric data of sPS (δ-form) without guest molecule is shown.

butanone film. For comparison, the ε'' data of the sPS film casted from the chloroform solution and dried under vacuum for one day at about 350 K is shown. It is seen that two relaxation peaks clearly appear for the sPS/2-butanone mixture, whereas pure sPS does not exhibit observable dielectric relaxation process at these temperatures.[28] Therefore, the two relaxation peaks in the sPS/2-butanone system can be ascribed to the motion of 2-butanone molecules. Concerning the possibility that 2-butanone evaporates during the temperature scan (up to 320 K), we found that it could be negligible, since the (second-run) dielectric data taken after the first-run measurements during which temperature increased to 320 K almost coincided with the first-run data. The observed two relaxation modes at low and high temperatures are denoted here as "fast" and "slow" modes, respectively.

It is considered that there are two environments for guest molecules dissolved in the sPS film: one is in the crystalline region and the other is in the amorphous region. According to the previous studies extensively made for different low mass guest molecules, clathrate guests have higher stability than those in the amorphous region.[23,24] Therefore, those in the amorphous region will be easier to vaporize under vacuum.

After the temperature scan, the sample cell was cooled to the room temperature and the chamber was depressurized by a vacuum pump at about 0.1 Pa for a certain period. Then after purging nitrogen gas again, temperature scan measurements were carried out again from 80 to 320 K. We repeated this procedure several times. All of the results are shown in Figure 6. It is seen that the observed two relaxation peaks decrease their intensities with vacuum time, meaning that 2-butanone molecules were gradually removed during the depressurization. In the figure, the result of one-third thickness film (25 μm) vacuum-dried for 1 h is also shown. For the thinner films the evaporation of 2-butanone will be faster, and thus the height of ε'' peak for this sample is the lowest.

The heights of the ε'' peaks measured at 12kHz for thick film were plotted against the vacuuming time in Figure 7. This figure clearly shows that the decreasing rate of the fast mode is higher than that of the slow mode. Since 2-butanone in the clathrate state is more stable than in the amorphous PS, the fast and slow modes could be ascribed to the molecular motion of 2-butanone in the crystalline and amorphous regions, respectively.
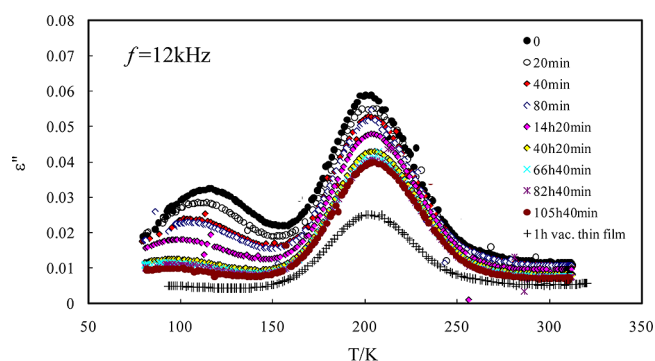

Figure 6. Dielectric loss ε'' measured at f = 12 kHz for SPS/n-butanone mixture at various vacuuming times which are shown in the legend.
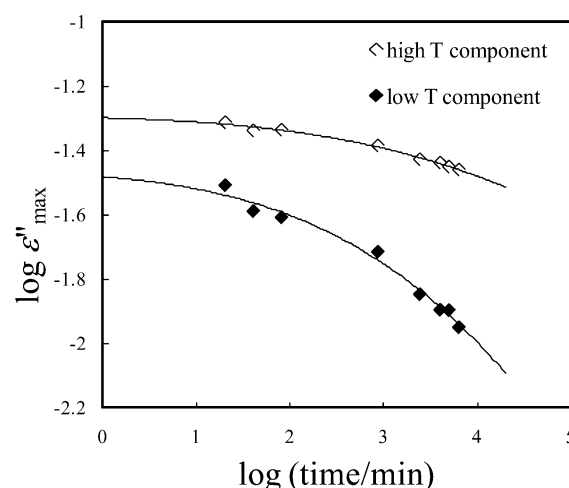

Figure 7. Time dependence of the ε'' values at the two (high and low temperature) peaks.

In order to confirm the above-mentioned assignment, dielectric measurements were also conducted on the 2-butanone/atactic-PS mixtures in which the 2-butanone dynamics only in the amorphous matrix can be detected because of the lack of crystalline region. Figure 8 shows the temperature dependence of ε'' for aPS/2-butanone mixtures with various 2-butanone concentrations. It is seen that a single
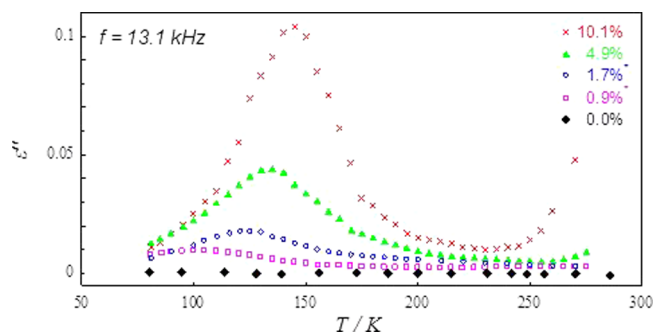

Figure 8. Temperature dependence of dielectric loss ε'' for 2-butanone/aPS mixtures with various 2-butanone concentrations. The concentration values higher than 4.9% were estimated by weighting. The values less than 1.7% could not be determined by weighting due to the limited accuracy, so that they were estimated, as a reference, from the height of the ε'' peak, ε_{max}'', assuming the proportionality between the concentration and the ε_{max}''.

peak is observed at any concentrations, and this peak seems to correspond to the fast mode in Figure 6 judging from the peak temperature. Therefore, the aforementioned assignment of both modes is validated.

Estimation of 2-Butanone Concentration. In order to estimate the concentration of 2-butanone in the sPS film, we made thermogravimetric (TG) analysis for the thin (25 μm thick) sPS/2-butanone film, after the dielectric measurements. The TG and the dielectric data were already shown in Figures 4a and 6, respectively. This sample did not show the fast mode relaxation, so that almost all of the 2-butanone molecules are considered to exist in the crystalline phase. The TG result shown in Figure 4 indicated that the 25 μm thick sPS sample contained 4.4−4.6 wt % 2-butanone. From the comparison of dielectric intensities, $\Delta\varepsilon$, of the slow mode for the thick film samples, 2-butanone content in the crystalline phase varies from 12 wt % (for as prepared sample) to 7 wt % (for the finally dried sample) assuming the proportionality of $\Delta\varepsilon$ and the concentration of 2-butanone.

Similarly it is also possible to determine the concentration in the amorphous region from the dielectric intensities of the fast mode based on the data of the aPS/2-butanone system shown in Figure 7. Assuming the proportionality, the concentration in the amorphous region for the 75 μm thick sPS film can be determined to be 3 wt % (for as prepared sample) and to be 1 wt % (for the finally dried sample).

Temperature and Concentration Dependence of Relaxation Times. The variation of the vacuum time shown in Figure 6 can be regarded as the concentration variation in the sPS/2-butanone system. Interestingly, the peak temperature of the slow mode does not change, whereas that of the fast mode decreases with decreasing 2-butanone content. The former result is understandable given that there are enough vacant spaces in the crystal structure to incorporate 2-butanone molecules. In contrast, the latter result is anomalous considering the general plasticization phenomena of amorphous polymer glasses. This behavior can also be seen in the aPS system shown in Figure 8. Since the fast mode appears far below the glass transition temperature, the motion of 2-butanone is considered to be highly restricted and localized. In such case the cooperative motion between 2-butanone and the PS segment will be unlikely to occur. With lowering the 2-butanone concentration (resulting in more isolation of 2-butanone molecules in glassy amorphous sPS), the decoupling in molecular motion between components will be more enhanced, and thus the dynamical contrast increases, i.e., the motion of the PS matrix becomes slower and that of 2-butanone speeds up. This causes the shift of the peak temperature of the fast mode to the lower T side. This kind of phenomena was already reported and well-known for miscible polymer blends with high dynamic asymmetry, such as aPS/poly(vinyl methyl ether) (PVME).[29] In that system segmental dynamics of dilute PVME, which is the mobile component having lower T_g, became faster with decreasing the PVME concentration.

For the analysis of the slow mode relaxation, ε'' data of the thin sPS/2-butanone film are again shown as a function of frequency in Figure 9. These data were fitted with the Cole−Cole function[30] given by

$$\varepsilon^*(\omega) = \varepsilon' - i\varepsilon'' = \varepsilon_\infty + \frac{\Delta\varepsilon}{1 + (i2\pi f\tau)^\alpha} \qquad (7)$$
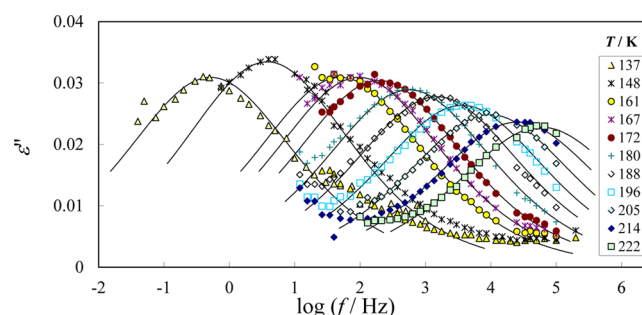

Figure 9. Frequency dependence of dielectric loss ε'' at various temperatures. The solid curves represent the fit by Cole−Cole function given by eq 1 with $\alpha = 0.45$.

Here, τ is the relaxation time, $\Delta\varepsilon$ is the relaxation strength, and α is the symmetric broadening parameter. All of the data could be represented by this equation with constant α (=0.47) meaning that the shape of the ε'' curve is almost independent of temperature. However it is noted that small deviation is seen for the low temperature data at the high frequency tails suggesting that the relaxation time distribution changes slightly with temperature.

The slow mode relaxation time determined from the fitting with eq 7 is shown as a function of reciprocal of temperature in Figure 10. For the fast mode, since the similar fitting procedure
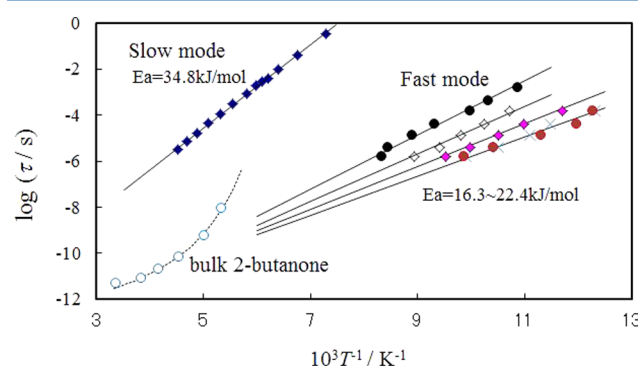

Figure 10. Arrhenius plot of slow and fast mode of 2-butanone in sPS clathrate structure. For comparison the data of liquid 2-butanone are shown.

was difficult to employ due to the less accuracy coming from the lower intensity and the broader ε'' spectra, isochronal ε'' curves shown in Figure 6 were used instead to determine the T dependence of τ. The data set of ε'' peak temperature T_{max} and measured frequency f converted to the relaxation time τ ($=(2\pi f)^{-1}$) are plotted in Figure 10 with the form of $\log \tau$ vs T_{max}^{-1}.

The data with different vacuuming time t_v (i.e., different content of 2-butanone) are shown for the fast mode because they were dependent on t_v. It is seen that both relaxation times of the slow and fast modes obey the following Arrhenius type temperature dependence in the T range examined.

$$\tau = \tau_0 \exp\left(\frac{E_a}{RT}\right) \qquad (8)$$

Here τ_0 is the relaxation time at high limiting temperature, E_a is the activation energy, and R is the gas constant. The E_a value obtained was 34.8 kJ mol^{-1} for the slow mode and 16.3−22.4 kJ mol^{-1} (increasing with 2-butanone content) for the fast mode.
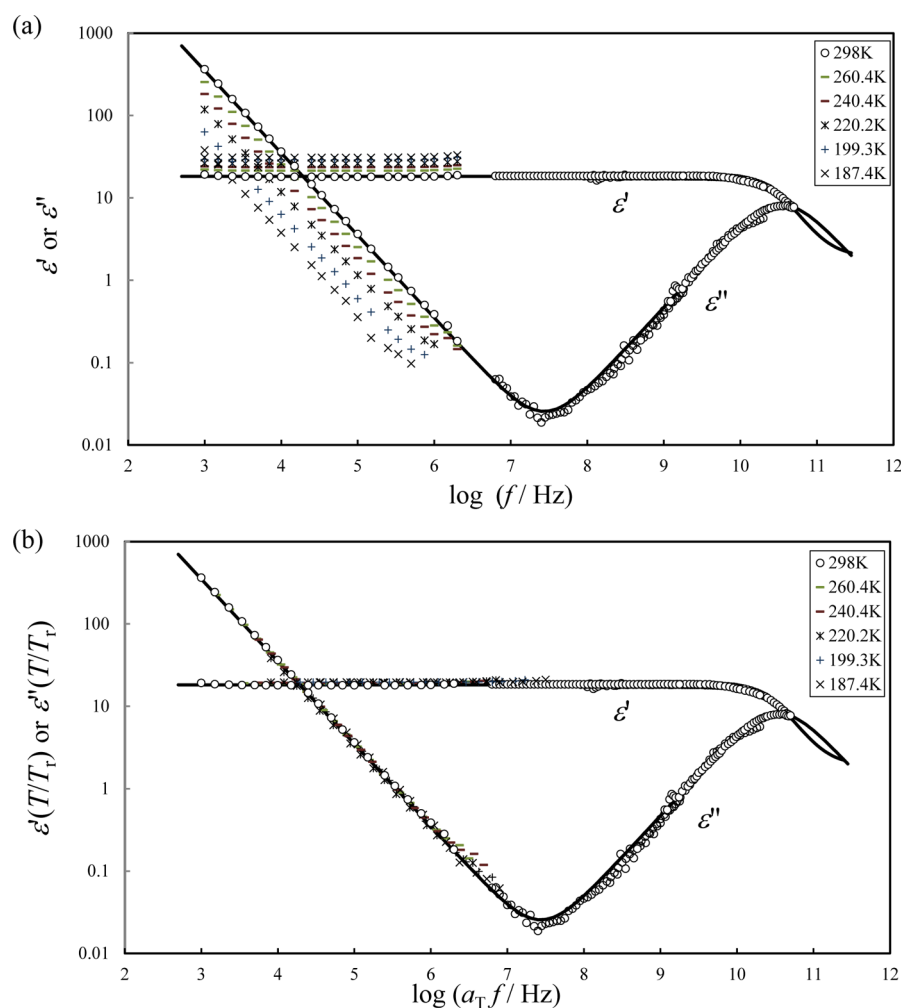
Figure 11. Dielectric constant ε' and loss ε'' spectra of bulk *n*-butanone at several temperatures (a), and superposed master curve at 298 K (b). The numbers in the legend indicate the temperatures.

The smaller value of E_a for the fast mode at the lower concentration suggests that the motion of 2-butanone molecule in the amorphous region are more highly decoupled from the motion of the amorphous part of PS as the concentration decreases. The Arrhenius behavior of the fast mode is also similar to the PS/PVME miscible systems.[29] On the other hand, E_a of the slow mode is independent of the concentration. It means that the guest molecules in the clathrate structure are isolated and do not affect each other in terms of their dynamics. In this case, the guest dynamics will be mostly determined by the (dynamic) interaction with the cavity wall composed of the phenyl groups of sPS chains.

Comparison with Liquid 2-Butanone. In order to determine the relaxation rates of 2-butnone molecule in the bulk liquid, we conducted high frequency measurement for liquid 2-butanone up to 50 GHz at room temperature (298 K). The result is shown in Figure 11a with white circles. The relaxation peak in the ε'' observed at around 10^{11} Hz corresponds to the rotational motion of 2-butanone and the increase of the ε'' at low frequency is due to the ionic conductivity. Polar impurity in liquid 2-butanone will be responsible for this low frequency response. Because at low temperatures only the low frequency data (10 Hz to 1 MHz) were available with our apparatus, the frequency−temperature superposition principle was used to determine the temperature

dependence of the relaxation time through the shift factor a_T. The assumption made here is that the rotational motion of 2-butanone molecule and the diffusion of polar impurities have the same temperature dependence. The composite curves are shown in Figure 11b. Here the vertical shift factor were assumed to be T/T_r, where T_r is the reference temperature (in this case 298 K), since dielectric constant is proportional to T^{-1}. Thus obtained composite ε' and ε'' curves were fitted by the following equation and the results are shown by the solid curves.

$$\varepsilon^*(\omega) = \varepsilon_\infty + \frac{\Delta\varepsilon}{1 + i2\pi f\tau} + \frac{\sigma}{i2\pi f\varepsilon_0} \qquad (9)$$

Here, σ and ε_0 are the conductivity and permittivity of vacuum, respectively. This equation is the sum of a Debye function and the conductivity term (last term). From this fitting, the values, $\Delta\varepsilon = 16.3$ and $\tau = 4.56$ ps, were obtained. The temperature dependence of the relaxation time is given by $\tau/ps = 4.56a_T$ and shown in Figure 10. It can be inferred that the relaxation time of fast mode, τ_{fast}, is comparable with the bulk liquid (τ_{liquid}) at around room temperature by assuming the Arrhenius equation and becomes shorter than the τ_{liquid} with decreasing temperature. On the other hand, that of slow mode, τ_{slow}, is about 4 orders of magnitudes longer than the τ_{liquid} at room temperature.

Kremer et al.[31] examined the dynamics of small molecules confined in zeolitic and nanoporous hosts and concluded that the guest dynamics is determined by the counterbalance between surface and confinement effects. Surface effects cause a decrease, whereas confinement effects are characterized by an apparent increase of the mobility due to the decrease of the amplitude of molecular motion by the special restriction. By using their terminology, the dynamics of 2-butanone molecules in the amorphous region is mostly determined by the confinement effect, since there is no specific (chemical) interaction like hydrogen bonding between 2-butanone and sPS. In contrast, the slow mode is largely slowed and thus will be governed by the surface effect (interaction with the cavity wall). However the interaction is not the chemical one but is probably due to the stabilizing force to a specific conformation and orientation for the guest 2-butanone in the cocrystalline structure. The X-ray and ATR FTIR results as explained in the previous section also support this view. It is very interesting that, even taking the stable cocrystalline structure, the guest molecule still exhibits dielectric relaxation. It means that the guest 2-butanone molecule will be loosely confined in a specific orientation and conformation with local energy minimum but have a room for the rotational motion inside the cavity.

Further Analysis of the Molecular Motion of 2-butanone in a Clathrate Structure. In order to see how the molecular motion is restricted in a clathrate structure, here we analyze the dielectric intensity data which reflect both the concentration of 2-butanone and the degree of spatial restriction for the molecular motion. Since the molecular motion in a liquid state is free without strong spatial restriction, the dielectric relaxation spectra of bulk liquid 2-butanone shown in Figure 5 can be well represented by the single Debye function given in eq 9. Dielectric intensity $\Delta\varepsilon$ is generally proportional to ϕ_{butanone}/T, where ϕ_{butanone} is the volume fraction of 2-butanone molecules and T is the absolute temperature. The ratio of $\Delta\varepsilon$ between sPS/2-butanone (thin film data) and bulk liquid systems ($\Delta\varepsilon_{\text{clathrate}}/\Delta\varepsilon_{\text{liquid}}$) estimated as 0.54% should correspond to the volume fraction of 2-butanone if the molecular motion is the same in both states. However, the concentration of 2-butanone in the sPS/2-butanone film determined by TG measurement was 4.4−4.6 wt % (∼5.4−5.6 vol. %), which is ten times larger than the $\Delta\varepsilon_{\text{clathrate}}/\Delta\varepsilon_{\text{liquid}}$ value. This means that the dielectric relaxation of 2-butanone in the crystalline phase is highly depressed (the dielectric data exhibits only 10% intensity) compared to that in the liquid state. As described in the previous section, the *ac* plane of the δ crystal tends to align parallel to the electrode surface (perpendicular to the electric field direction for dielectric measurements) and the polar C=O group of 2-butanone weakly align to this plane (perpendicular to the electric field direction). Therefore, it is natural to think that the rotational motion of the C=O group is restricted within a limited angle around the direction parallel to the ac plane and thus the dielectric intensity will become smaller than the case of free isotropic rotation like in the liquid state. We think this will be one reason why the dielectric intensity of the slow mode is highly suppressed.

Dielectric intensity of the fast mode is also smaller compared to that for the bulk liquid: the intensity factor is about one-third of that calculated from the data of bulk liquid. The full rotational motion of the guest molecules are not allowed either even in the isotropic amorphous phase below T_g, possibly because the limited free space will be allowed for the guest motion, meaning the restricted orientation of the dipole under an electric field. In this case, as reported by Nobukawa et al,[32] the relaxation intensity and the relaxation time becomes smaller and shorter, respectively, with decreasing temperature below T_g.

Concerning the higher suppression of the dielectric intensity for the crystalline region than that for the amorphous region, there will be two causes. One is the anisotropic orientation of crystalline region formed in the film shaped samples and the other will be the anisotropic potential field that the cavity of the δ-form provides to guest 2-butanone molecules accompanied by the interaction with the cavity wall.

■ CONCLUSION

We examined the dielectric relaxation behavior of 2-butanone molecules in the clathrate sPS films below the glass transition temperature and found that two relaxation (fast and slow) modes appeared. These two modes were assigned to the rotational motion of 2-butanone molecules in the amorphous and the crystalline regions, respectively.

The relaxation times of both modes followed the Arrhenius equation with activation energies E_a = 34.8 kJ mol^{-1} (independent of 2-butanone concentration) for the slow mode and E_a = 16.3−22.4 kJ mol^{-1} (the higher the 2-butanone concentration, the higher the E_a values) for the fast mode. The relaxation time of the slow mode was 4 orders of magnitude longer than that of the bulk liquid 2-butanone at temperatures above 187.4 K, whereas the fast mode showed a shorter relaxation time. This means that the dynamics of the guest molecule in the clathrate structure is highly restricted.

The ATR-FTIR and X-ray diffraction data indicated that the carbonyl groups of 2-butanone in the clathrate crystal weakly align parallel to the electrode surface and thus perpendicular to the electric field. Furthermore, the smaller dielectric intensity of 2-butanone in the crystalline region relative to the bulk liquid suggested that the dynamics of guest 2-butanone molecules in the cavity of the δ-form was restricted by the anisotropic potential field which the ordered sPS molecules surrounding the cavity will provide.

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Notes
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■ REFERENCES

(1) Chatani, Y.; Shimane, Y.; Inagaki, T.; Ijitsu, T.; Yukinari, T.; Shikuma, H. *Polymer* **1993**, *34*, 1620−1625.
(2) Chatani, Y.; Shimane, Y.; Inagaki, T.; Shikuma, H. *Polymer* **1993**, *34*, 4841−4845.
(3) De Rosa, C.; Rizzo, P.; De Ballesteros, O. R.; Petraccone, V.; Guerra, G. *Polymer* **1999**, *40*, 2103−2110.

(4) Petraccone, V.; Tarallo, O.; Venditto, V.; Guerra, G. *Macromolecules* **2005**, *38*, 6965−6971.

(5) Tarallo, O.; Petraccone, V.; Venditto, V.; Guerra, G. *Polymer* **2006**, *47*, 2402−2410.

(6) Albunia, A. R.; Rizzo, P.; Guerra, G. *Chem. Mater.* **2009**, *21*, 3370−3375.

(7) Tarallo, O.; Schiavone, M. M.; Petraccone, V.; Daniel, C.; Rizzo, P.; Guerra, G. *Macromolecules* **2010**, *43*, 1455−1466.

(8) Tarallo, O.; Petraccone, V.; Albunia, A. R.; Daniel, C.; Guerra, G. *Macromolecules* **2010**, *43*, 8549−8558.

(9) Tarallo, O.; Petraccone, V.; Daniel, C.; Guerra, G. *Cryst. Eng. Commun.* **2009**, *11*, 2381−2390.

(10) Uda, Y.; Kaneko, F.; Tanigaki, N.; Kawaguchi, T. *Adv. Mater.* **2005**, *17*, 1846−1850.

(11) Itagaki, H.; Sago, T.; Uematsu, M.; Yoshioka, G.; Correa, A.; Venditto, V.; Guerra, G. *Macromolecules* **2008**, *41*, 9156−9164.

(12) De Mauro, A. G. D.; Carotenuto, M.; Venditto, T. V.; Petraccone, V.; Scoponi, M.; Guerra, G. *Chem. Mater.* **2007**, *19*, 6041−6046.

(13) D'Aniello, C.; Musto, P.; Venditto, V.; Guerra, G. *J. Mater. Chem.* **2007**, *17*, 531−535.

(14) Stegmaier, P.; Del Mauro, A. D.; Venditto, V.; Guerra, G. *Adv. Mater.* **2005**, *17*, 1166−1168.

(15) Kaneko, F.; Uda, Y.; Kajiwara, A.; Tanigaki, N. *Macromol. Rapid Commun.* **2006**, *27*, 1643−1647.

(16) Albunia, A. R.; D'Aniello, C.; Guerra, G.; Gatteschi, D.; Mannini, M.; Sorace, L. *Chem. Mater.* **2009**, *21*, 4750−4752.

(17) De Rosa, C.; Rizzo, P.; de Ballesteros, O. R.; Petraccone, V.; Guerra, G. *Polymer* **1999**, *40*, 2103−2110.

(18) Musto, P.; Manzari, M.; Guerra, G. *Macromolecules* **2000**, *33*, 143−149.

(19) Albunia, A. R.; Graf, R.; Grassi, A.; Guerra, G.; Spiess, H. W. *Macromolecules* **2009**, *42*, 4929−4931.

(20) Tamai, T.; Fukuta, M. *Chem. Phys. Lett.* **2003**, *371*, 620−625.

(21) Trezza, E.; Grassi, A. *Macromol. Rapid Commun.* **2001**, *23*, 260−263.

(22) Albunia, A. R.; Graf, R.; Guerra, G.; Spiess, H. W. *Macromol. Chem. Phys.* **2005**, *206*, 715−724.

(23) Kaneko, F.; Uda, Y.; Kawaguchi, T.; Ute, K.; Yamamuro, O. *Macromol. Symp.* **2006**, *242*, 113−119.

(24) Uda, Y.; Kaneko, F.; Kawaguchi, T. *Macromolecules* **2005**, *38*, 3320−3326.

(25) Rizzo, P.; Lamberti, M.; Albunia, A. R.; De Ballesteros, O. R.; Guerra, G. *Macromolecules* **2002**, *35*, 5854−5860.

(26) Flournoy, P. A.; Schaffers, W. J. *Spectrochim. Acta* **1966**, *22*, 5−13.

(27) Torres, F. J.; Civalleri, B.; Meyer, A.; Musto, P.; Albunia, A.; Rizzo, P.; Guerra, G. *J. Phys. Chem. B* **2009**, *113*, 5059−5071.

(28) Yano, O.; Wada, Y. *J. Polym. Sci., Part A-2* **1971**, *9*, 669−686.

(29) Lorthioir, C.; Alegria, A.; Colmenero, J. *Phys. Rev. E* **2003**, *68*, 31805−1−31805−9.

(30) Cole, K. S.; Cole, R. H. *J. Chem. Phys.* **1941**, *9*, 341−351.

(31) Kremer, F.; Huwe, A.; Amdt, M.; Behrens, P.; Schwieger, W. *J. Phys. Condens. Matter* **1999**, *11*, A175−A188.

(32) Nobukawa, S.; Urakawa, O.; Shikata, T.; Inoue, T. *Macromolecules* **2011**, *44*, 8324−8332.

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