VARIABLE-TEMPERATURE STUDY OF A GEL-SPUN ULTRA-HIGH MOLECULAR-MASS POLYETHYLENE FIBER BY SOLID STATE NMR

Jinlong Cheng*, Matilda Fone*, Yigang Fu** and Wei Chen**

*Raychem Corporation, 300 Constitution Drive, Menlo Park, CA 94025
**Department of Chemistry, University of Tennessee, Knoxville, TN 37996, USA

Dedicated to Professor Bernhard Wunderlich on the occasion of his 65th birthday

Abstract

Solid-state ^{13}C nuclear magnetic resonance (^{13}C NMR) methods have been applied to study a gel-spun ultra-high molecular-mass polyethylene fiber. The mass fractions of the crystalline (orthorhombic and monoclinic), intermediate, and amorphous phases have been determined at temperatures between 296 and 413 K. The mobility of the polymer chains in the crystalline and the intermediate phases have been measured within the same temperature range, 296–413 K. Discussions on the chain conformation and the rate of motion are carried out based on the ^{13}C chemical shift and spin-lattice relaxation time, respectively.

Introduction

The relationship between solid-state morphology and properties has been a topic for many investigations [1–4]. Many morphological researches utilize the crystalline-amorphous two-phase model and have shown that this traditional concept can be improved. A third phase has been introduced based on the various experimental evidences [5–7]. This third phase is termed the intermediate phase in this work. It was demonstrated by Wunderlich and coworkers [8] that the inclusion of the intermediate phase can lead to a more satisfactory explanation on the structure-property relationship in the PE fibers.

The operational definition of the intermediate phase by solid state NMR, DSC, and wide angle X-ray diffraction (WAXD) have been introduced by examining the chain conformation and mobility [9]. It could be shown by solid state ^{13}C NMR that the intermediate phase is a region in which the carbon–carbon bonds adopt, on the average, all-*trans* conformation and are more mobile than

those in the crystalline state. Consequently, the intermediate phase often yields less heat on fusion because of its greater mobility, but scatters X-ray in a similar fashion as the crystalline phase because of similar chain conformation (all-*trans*).

In addition, a quantitative method has also been established for the determination of the mass fractions of the crystalline, the intermediate, and the amorphous phases in melt-crystallized polyethylenes [9]. Initial success of applying such a concept and quantitative method at ambient temperature for the structure-property study of PE fibers has been noted [8, 10]. In this work the temperature, which is the most important independent variable in thermal analysis, is varied to follow the fusion process of the gel-spun PE fiber.

Experimental

The original fiber sample was supplied by Allied Signal Inc., and provided to us by the Advanced THermal AnalysiS (ATHAS) lab, led by Professor Bernhard Wunderlich at the University of Tennessee. The polyethylene has a molecular mass of greater than 10^6. The fiber is gel-spun. The physical properties are listed in Table 1. The details of the processing history were unfortunately not available to us. A second sample was prepared to study the pressure effect on the monoclinic phase. The original sample was compressed under 0.7 Gpa for 60 min.

Table 1 The physical properties of the polyethylene fiber[a]

Sample	Modulus/GPa	Tenacity/GPa	Density/Mg m^{-3}	Crystallinity/%
PE-I	179	3.9	0.964	80

The ^{13}C NMR experiments were performed on a Chemagnetics CMX-200 spectrometer, operating at 200 MHz for ^1H and 50 MHz for ^{13}C. The probe is a magic-angle-spinning (MAS) design and accommodates the cylindrical sample rotor (7.5 mm in diameter). The 90° pulse-widths for ^{13}C and ^1H are 4.0 and 3.5 µs, respectively. The fiber sample was packed isotropically in the central portion of the sapphire rotor (one-third of the rotor volume) and spun at 4 kHz (±5 Hz). This is to minimize the temperature gradient and *rf* inhomogeneity over the sample region inside the rotor. The sample was allowed to equilibrate for at least 20 min at each temperature before the measurement. The temperature at the sample was calibrated using ethylene glycol. Probe tuning for matching the impedance before observation of NMR signals is always performed to ensure optimal and reproducible performance.

The current NMR method on the determinations of mass fractions of the all-*trans* components (including the orthorhombic and the intermediate phases) and
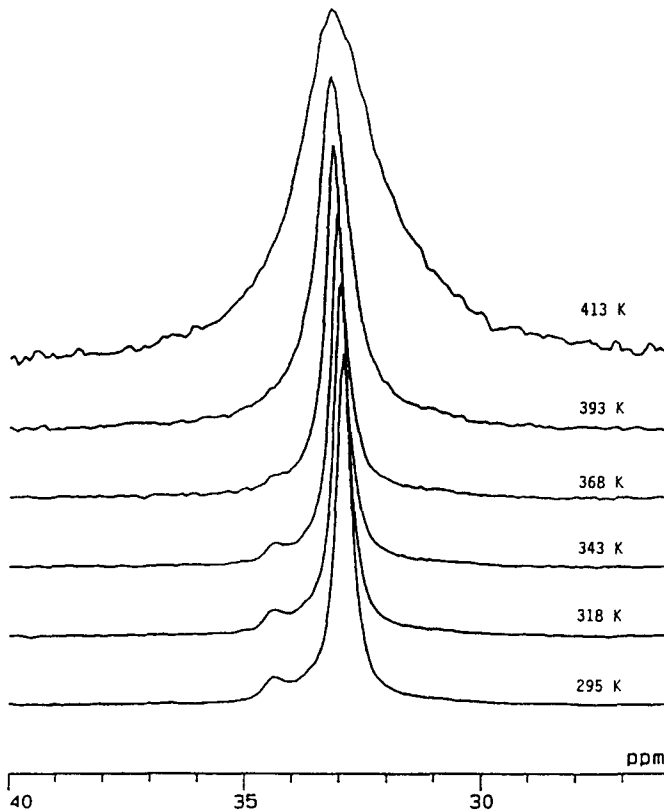
Fig. 1 50 MHz ^{13}C CP-MAS NMR spectra of a gel-spun PE fiber at temperatures shown. The contact times are 1.5, 4.0, 2.0, 2.0, 0.35, and 0.10 ms in the order of temperature increasing. The main peak at about 33 ppm contains contributions from the orthorhombic crystalline phase and an intermediate phase with the latter having greater mobility. The weak peak at about 34.4 ppm is attributed to the monoclinic phase. The amorphous peak (31 ppm) cannot be observed under the CP-MAS conditions

the amorphous phase have been documented [9, 10]. The method involves curve fitting of two peaks (one all-*trans* peak at 33.0 ppm and one amorphous peak at 31.2 ppm) for each variable contact time of the cross-polarization and magic-angle-spinning spectra. The results are subsequently corrected for the different values of proton spin-lattice relaxation time in the rotating frame (T_{1pH}) for the different phases. The 33.0 ppm peak is further separated into the crystalline and the intermediate phases with the measurement of ^{13}C spin-lattice relaxation times using saturation-recovery with broad-band decoupling of protons. There is a difference in mobility by one to two orders of magnitude between the crystal and the intermediate phases [9].

The unique feature in the ^{13}C CP-MAS NMR spectra of PE fibers is the existence of an additional resonance at 34.4 ppm, which is 1.4 ppm downfield relative to the major peak of the orthorhombic phase (33.0 ppm). The 34.4 ppm peak is attributed to the monoclinic phase. The mass fraction of the monoclinic phase is obtained by curve fitting to the 34.4 ppm peak in the same way as for the orthorhombic peak (33.0 ppm).

Results

Figure 1 shows the variable-temperature ^{13}C CP-MAS NMR spectra. The contact time was chosen differently at each temperature in order to represent the corrected intensities of the different phases. Based on Fig. 1 the chemical shift and the linewidth can be obtained as a function of temperature. The results are listed in Table 2.

Table 2 Variable-temperature solid-state ^{13}C NMR measurements of the polyethylene fiber[a]

Temperature/K	295	318	343	368	393	413
Chemical shift of orthorhombic crystal δ_{orth}/ppm	32.92	32.98	33.05	33.14	33.16	33.20
Chemical shift of monoclinic crystal δ_{mono}/ppm	34.32	34.34	34.35	34.4		
Linewidth of orthorhombic crystal W_{orth}/Hz	19.0	19.1	19.2	22.0	38.4	96.0
Spin-lattice relaxation time of orthorhombic crystal T_{1C}^{orth}/s	375	302	267	250	120	72.4
Spin-lattice relaxation time of the intermediate phase T_{1C}^{int}/s	10.0	7.3	6.1	7.5	6.5	6.2
Rotating frame ^{1}H spin-lattice relaxation time for the orthorhombic phase $T_{1\rho H}^{orth}$/ms	130	101	48.1	13.0	2.76	1.07
Rotating frame ^{1}H spin-lattice relaxation time for the monoclinic phase $T_{1\rho H}^{mono}$/ms	53.1	41.4	22.9	8.0		
Mass fraction of orthorhombic crystalline phase X_{orth}/%	78.0	80.1	81.0	82.7	74.7	71.6
Mass fraction of intermediate phase X_{int}/%	14.8	13.7	15.6	15.4	25.3	28.4
Mass fraction of monoclinic phase X_{mono}/%	7.2	6.2	3.4	1.9	0	0

[a] Sample was provided by the ATHAS lab, also see Ref. [8]

The variable contact time experiment was performed at temperatures of 295, 318, 343, 368, 393 and 413 K. The relationship between the signal intensity and the contact time was measured to yield proton spin-lattice relaxation time in the rotating frame, T_{1pH}, for the various phases. The T_{1pH} data are shown in Table 2. The variable contact time spectra were also used to yield the mass fractions of the orthorhombic and the monoclinic phases. The mass fractions are proportional to the peak areas after correction is made using the T_{1pH} data [9].

For the fiber sample studied in this work, the amorphous peak could not be observed under the normal CP-MAS conditions. Selective observation of the amorphous phase is possible by using pulse sequences, such as Bloch decay with sufficiently short recycle delay, which detects preferably the mobile ^{13}C atoms (having short T_1) in the amorphous phase. Figure 2 shows two MAS
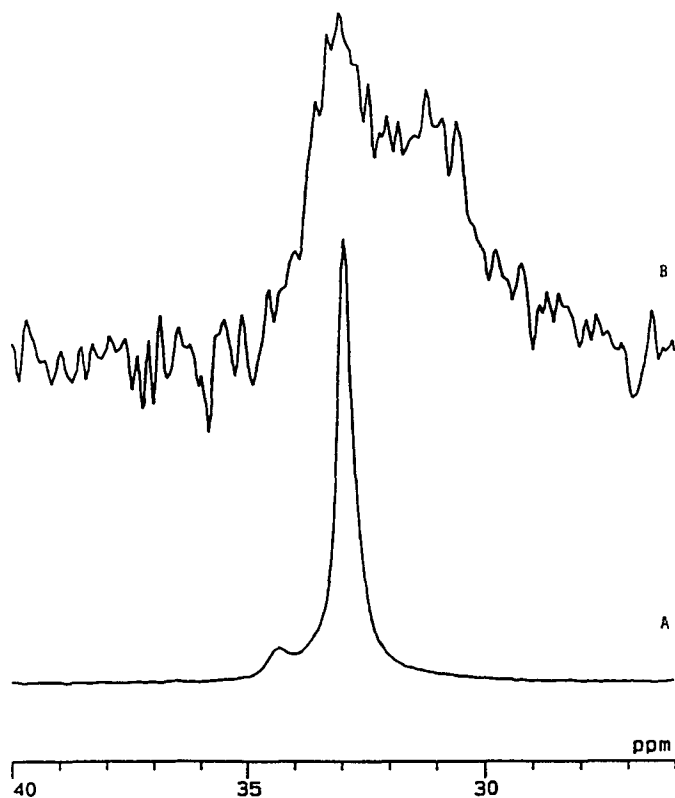

Fig. 2 50 MHz ^{13}C MAS NMR spectra of a gel-spun PE fiber at 295 K. Spectrum A was measured with CP-MAS using a contact time of 1.5 ms. The spectrum B was obtained with Bloch decay using a recycle time of 1 s and 90° pulse width (4 μs). The amorphous signal at about 31 ppm is enhanced by approximately two orders of magnitude in the Bloch decay spectrum

spectra, one is obtained with the Bloch decay using a recycle delay of 1 s (Spectrum B), and the other is obtained with CP (Spectrum A). It is estimated, based on the peak areas and the spin-lattice relaxation times of the ^{13}C, that the mass fraction of the amorphous phase falls below the error limit of the current method (< 1 %).

In order to separate the intermediate phase from the orthorhombic crystalline phase, the ^{13}C spin-lattice relaxation times were measured using saturation-recovery method. Figure 3 shows the ^{13}C NMR spectra obtained by increasing the recovery time from 0.001 s (bottom) to 450 s (top). The change of integrated signal intensity as a function of recovery time is plotted in Fig. 4 (filled circles). The recovery time was chosen between 1.0 and 450 s in Fig. 4. Since the T_1 of carbon atoms in the amorphous phase is about 0.2 s, within the recovery-time given above the amorphous signal has recovered fully and will have hardly any effect on the measurements of the intermediate and the crystalline
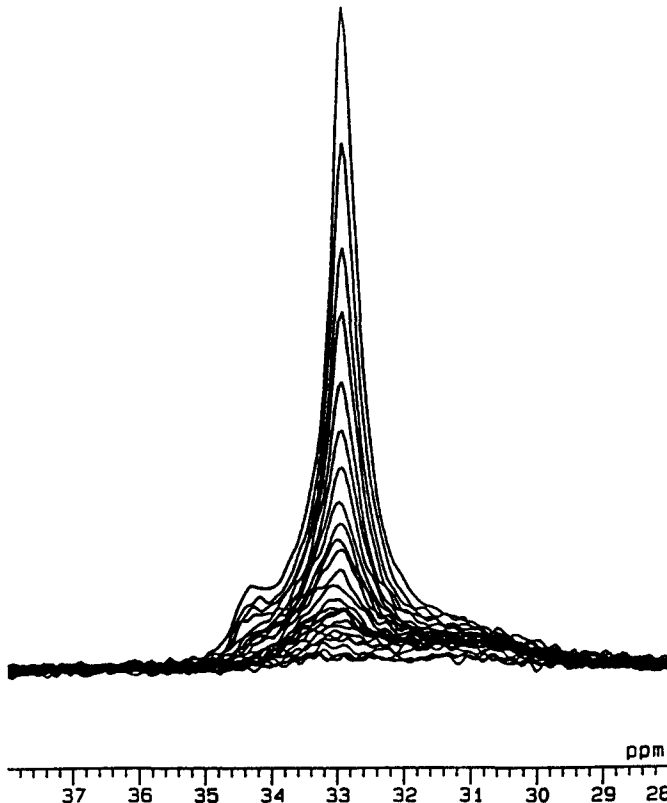

Fig. 3 50 MHz ^{13}C NMR spectra measured at 295 K with saturation-recovery using recovery-delays (from bottom to top): 0.07, 0.1, 0.15, 0.3, 0.5, 0.7, 1.0, 1.5, 1.8, 2.5, 3.0, 3.5, 4, 5, 7.0, 10, 15, 20, 25, 35, 50, 70, 100, 150, 200, 300 and 450 s

phases. The experimental data points (filled circles) in Fig. 4 cannot be fitted with a single exponential equation. An equation of two exponential terms $(1 - e^{\tau/T_1})$ can improve the correlation coefficient to at least 0.995, as demonstrated by Curve X in Fig. 4 (Curve X = Curve A + Curve B). The term that has a shorter T_{1C} (Curve B in Fig. 4) is naturally attributed to the intermediate phase, and the longer T_{1C} (Curve A in Fig. 4) to the crystalline phase. Results of T_{1C} are listed in Table 2. The mass ratio between the intermediate phase and the crystalline phase can be obtained using the pre-exponential constants of the respective exponential-terms. Table 2 lists results for mass fractions of the orthorhombic, monoclinic, and intermediate phases.
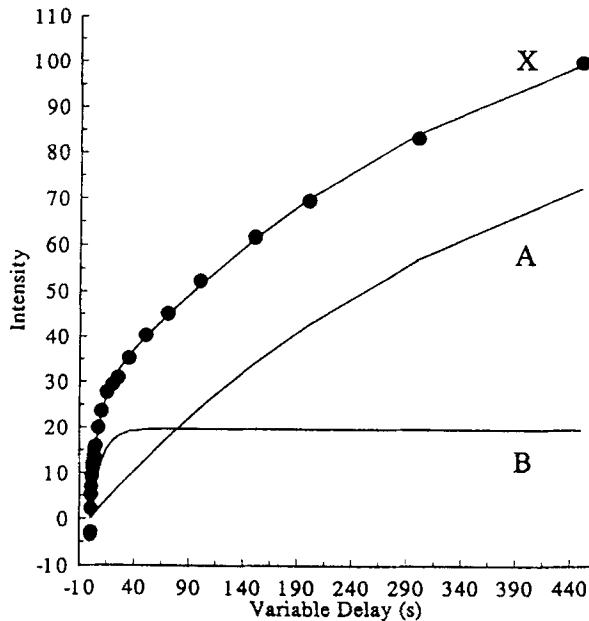

Fig. 4 Curve fitting of the integrated intensity data as a function of recovery delay. Filled circles are the measured intensities for the orthorhombic/intermediate peak (33 ppm). Lines A and B are single exponential function of the form $1 - \exp(-\tau/T_1)$, and curve X is the linear combination of A and B

Discussions

The monoclinic phase

The monoclinic peak can be observed clearly at 34.4 ppm between 295 and 368 K. The mass fraction of the monoclinic phase is about 7% at 295 K and decreases gradually to less than 2% at about 373 K. At higher temperatures, the monoclinic phase disappears completely. Subsequent cooling of the same sam-

ple cannot recover the monoclinic form. The same trend was also observed by wide-angle X-ray diffraction [8].

The origin of the monoclinic form was believed to arise from a unique packing [12, 13] in which the planes of the zig-zag, all-*trans* chains are parallel to one another, as in *n*-alkanes in n-C_XH_{2X+2} with 6≤X(even) <26, whose unit cells are triclinic and contain one chain per unit cell. During the process of fiber-making, the deformation of polyethylene under certain conditions leads to the formation of a distinct, metastable crystalline phase, namely the monoclinic phase, in addition to the usual orthorhombic crystalline phase. Indications of a monoclinic phase have been observed in drawn samples with residual strains in the range of 0.2–1.7, in samples that had been stretched and kept under tension at constant strain, and in stretched samples that subsequently have been allowed to contract. The formation of this phase is partially reversible and stabilized by the presence of external stresses [13]. Figure 5 shows the ^{13}C NMR results on the effect of compression on the monoclinic phase. Spectrum A is the same as that shown in Fig. 1 at 295 K, Spectrum B was obtained with the same sample after compression under 0.7 Gpa for 60 min. The monoclinic phase (34.4 ppm) increases from 7 to 23%.
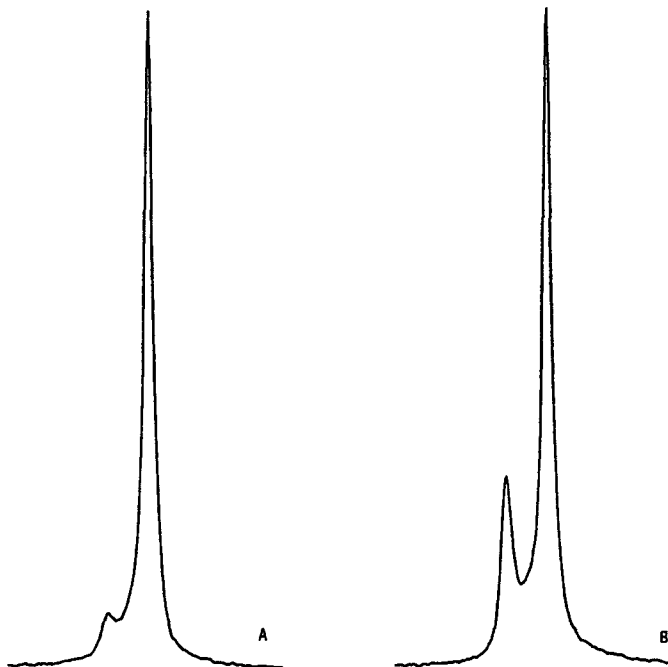

Fig. 5 50 MHz ^{13}C CP-MAS NMR spectra measured at 295 K with contact time of 1.5 ms. A: original fiber, B: compressed under 0.7 Gpa for 30 min. The monoclinic phase increases from 7% in A to 23% in B

As the temperature is increased, the polymer chains gain enough mobility to release the tension or stress that creates the monoclinic phase, and eliminate the monoclinic phase. Figure 1 shows that the monoclinic phase (34.4 ppm) disappears completely at 393 K.

The intermediate and orthorhombic crystalline phases

The intermediate and the crystalline phases show the same ^{13}C chemical shift of 33.0 ppm. The reason is that the average conformation of the polymer chains in the intermediate phase is similar to that of the crystalline state, i.e., *trans*. The two phases are, however, drastically different in terms of mobility. As shown by their ^{13}C T_{1C} data in Table 2, the difference is 1–2 orders of magnitude.

The orthorhombic crystalline phase

The orthorhombic crystalline phase was identified by the chemical shift of 33.0 ppm, (superimposed with the intermediate phase) and by its slow motion as indicated by its ^{13}C T_{1C} in Table 2. The rate of short-range molecular motion in the MHz range can be estimated based on the ^{13}C T_1 data listed in Table 2. The relationship between the measured T_{1C} and motional rate is given by the common equation for spin-lattice relaxation *via* dipole-dipole interaction [14]. The calculation shows that the motion in the crystalline phase is rather slow: the rate is about 3 kHz at 295 K and increases to 15 kHz at 413 K. In comparison to the proton decoupling field, which is about 70 kHz in this work, the motion is too slow to cause any change in the spectral linewidth.

The intermediate phase

The variable temperature ^{13}C NMR spectra of the PE fiber show, however, a significant line broadening for the 33.0 ppm peak when temperature is increased to 393 K (see Fig. 1 and Table 2 for the linewidths). Since the increase in the linewidth are not associated with the crystalline phase because of its sluggish motion, attention should be naturally focused on the motion of the intermediate phase. One of the possible causes for line broadening is conformational disordering (inhomogeneous line-broadening). The conformational disordering should, however, also cause an increase in the *gauche* content, and consequently cause the chemical shift move up-field (becomes smaller). As shown in Fig. 1 and Table 2, the chemical shift is still basically the same even at 413 K (33.2 ppm), the conformational disordering in the polyethylene chains of the intermediate phase can be excluded.

To sort out the mechanism of line broadening at 393 K and above, the motion in the intermediate phase should be examined. Using the equation for the ^{13}C spin-lattice relaxation of dipole-dipole interaction [14], the rate of motion in the

intermediate phase can be shown to increase from 110 kHz at 295 K to 180 kHz at 413 K. These rates are much greater than the decoupling field (70 kHz). The rapid motion, on the other hand, is not isotropic in geometry due to the restriction by the crystal structure. It is well known that rapid and asymmetric motion causes line broadening due to incomplete motional averaging (so-called homogeneous line broadening). In order to narrow the residual linewidth (motionally broadened line), a decoupling field (expressed in Hz) stronger than the motional rate should be applied, which requires a proton 90° pulse width less than 1.4 μs and is impossible for the current NMR setup.

The answer to an unsolved problem, revealed some decades ago by Wunderlich et al. in a series of study on the heat capacity of polyethylene crystal [15], maybe better understood now. The experimental heat capacity for the assumed crystalline phase is always greater than the calculated, vibration-only heat capacity at temperatures much below the isotropization. The extra heat capacity contribution is now attributed to the well excited large-amplitude motion (other than vibrations) in the *intermediate phase*, in which the motional rate increases on heating as shown in this work.

The peak of the crystalline and the intermediate phases shifts slightly downfield as the temperature is increased as shown in Table 2. The downfield shift is generally associated with a deshielding of the ^{13}C nuclei. Since the amplitude of the observed deshielding (about 0.2 ppm) is much less than the expected value for any conformational change of the polymer chain, change of chain packing or expansion of crystal should be considered.

Mass fractions

The mass fraction for the crystalline phase undergoes a slight increase between 295 and 368 K, and then a relatively large decrease when temperature is increased to 398 and 413 K (Table 2). On the other hand, the intermediate phase shows a steady increase when temperature is increased to 413 K. It is clear that at temperatures close to the melting point, the molecules in the crystalline phase, especially those in the smaller crystallites, become mobile and behave the same motionally as those in the intermediate phase.

Conclusions

The mass fraction of the amorphous in the fiber studied in this work is within the error limit of the current NMR method, which is about 1%. The fiber contains a monoclinic phase of about 7% at 296 K, which decreases gradually to less than 2% when temperature is increased to 373 K. The monoclinic phase can be enhanced significantly if the fiber sample is subsequently compressed.

The orthorhombic crystalline phase, on the other hand, undergoes a slight increase from 78% at 296 K to 83% at 368 K, and then a sharp decrease to 75% at 393 K and to 72% at 413 K. The intermediate phase shows a constant mass fraction of about 15% from between 298 K and 368 K, and a sharp increase to 25.3% and 28.4% when temperature is increased to 393 K and 413 K, respectively. This indicates a conservation of mass fractions between the crystalline and intermediate phases at the high temperature region.

In addition, it has been identified that even at temperatures close to isotropization no significant conformational disordering occurs in the orthorhombic phases, but the content of the mobile intermediate phase has increased significantly.

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