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Dielectric study of the main-chain liquid-crystal polyesters poly(alkyl terephthaloyl-bis-4-oxybenzoate)s and poly(alkyl-4,4′-diphenoxy terephthalate)s[1]

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Abstract

Two analogous series of thermotropic main-chain polyesters, poly(alkyl-4,4′-diphenoxy terephthalate)s and poly(alkyl terephthaloyl-bis-4-oxybenzoate)s, have been analyzed by dielectric techniques. Analysis of the dielectric properties as a function of temperature and frequency show three main processes, termed α, β and β^*. The α transition has been associated with the glass transition of the amorphous phase. The low-temperature processes β and β^* have been related to the local motion of internal and external polar groups in the mesogenic unit. The activation energy and dielectric strength values associated with these relaxations have been determined, and a very important effect of the crystalline order on these parameters has been observed. The effect of the thermal history on the dielectric behaviour has also been studied. © 1998 Elsevier Science Ltd. All rights reserved.

Keywords: Liquid crystal; Thermotropic polyester; Dielectric analysis

1. Introduction

Thermotropic polyesters have received a great deal of attention in the last few years as engineering polymers [1]. These materials offer good processability conditions and excellent mechanical properties along with the possibility of reinforcement of the matrix in blends with thermoplastic resins. Industrial and academic research has been focused on understanding the structure–property relationship in order to tailor appropriate chemical structures with suitable properties of technological interest [2].

Investigation of the relaxational behaviour is an important aspect of this study as the molecular mobility plays an essential role in the formation of the mesomorphic structure [3]. However, detailed work has been carried out in just a few cases [3–18], due to the fact that main-chain liquid-crystal polymers often exhibit very complex behaviour. In particular, the low- temperature transitions in these materials are strongly dependent on the chemical structure and the thermal treatment.

Dielectric spectroscopy is a powerful technique for investigating the molecular dynamics of polymers [19] in general, and specifically of liquid-crystal polymers [3–12]. Dielectric analysis can be performed over a wider frequency range than dynamic mechanical analysis, thus providing complementary information to the latter method.

Most of the reported dielectric analyses of main-chain liquid-crystal polymers relate to either rigid or semirigid copolyesters. In the first case, copolyesters based on 4-hydroxybenzoic acid with comonomers of naphthoic acid [6,7] and biphenol terephthalate [8,9] have been described. In most of these rigid systems, a high-temperature relaxation related to the glass transition is observed along with two low-temperature processes identified as local modes associated with the naphthyl and phenyl moieties.

In the second case, copolymers of poly(*p*-hydroxybenzoic acid) (PHB) and semirigid comonomers such as poly(ethylene terephthalate) (PET) and poly(ethylene 2,6-naphthalenedicarboxylate) (PEN) have recently been analyzed [10–12]. Two relaxation processes have been clearly distinguished: the α relaxation, related to the glass transition of the amorphous polymer, and a subglass process assigned to local motions of ester groups attached to both sides of the aromatic rings.

However, only a few studies [3–5] have dealt with the dielectric analysis of both thermotropic polyethers and

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[1] In memory of Professor Jose M. Gómez Fatou

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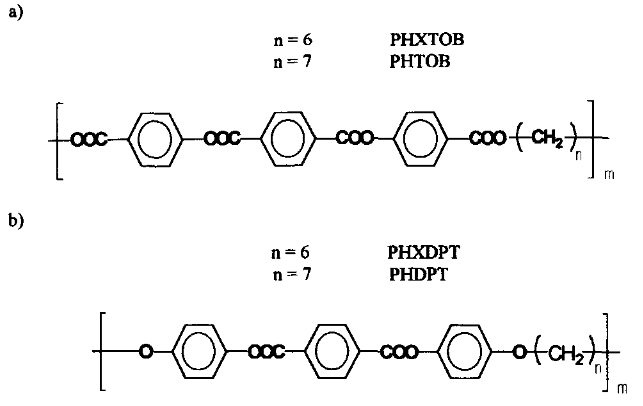

Fig. 1. Structure and nomenclature of (a) poly(alkyl terephthaloyl-bis-4-oxybenzoate)s, and (b) poly(alkyl 4,4′-diphenoxy terephthalate)s.

Table 1
Thermal transitions and thermodynamic parameters of the polymers studied

Sample	T_1[a] (°C)	T_i[b] (°C)	ΔH_1 (J g^{-1})	ΔH_i (J g^{-1})	Mesophase[c]
PHXDPT	255	360	36	–	S–N
PHXTOB	249	325	22	–	N
PHDPT	162	203	37.4	3.73	N
PHTOB	175	295	10.3	13.0	S

[a] Crystal–mesophase transition
[b] Mesophase–isotropic transition
[c] S, smectic; N, nematic

polyesters. Therefore, the main objective of this research is the analysis of two analogous series of main-chain liquid-crystal polymers with structures shown in Fig. 1. For this purpose, we have investigated the relaxation behaviour, using dielectric techniques, of two series of thermotropic polyesters: poly(alkyl terephthaloyl-bis-4-oxybenzoate) and poly(alkyl-4,4′-diphenoxy terephthalate) with six and seven methylene groups in the flexible spacer, in order to correlate the observed spectra with the intramolecular motion.

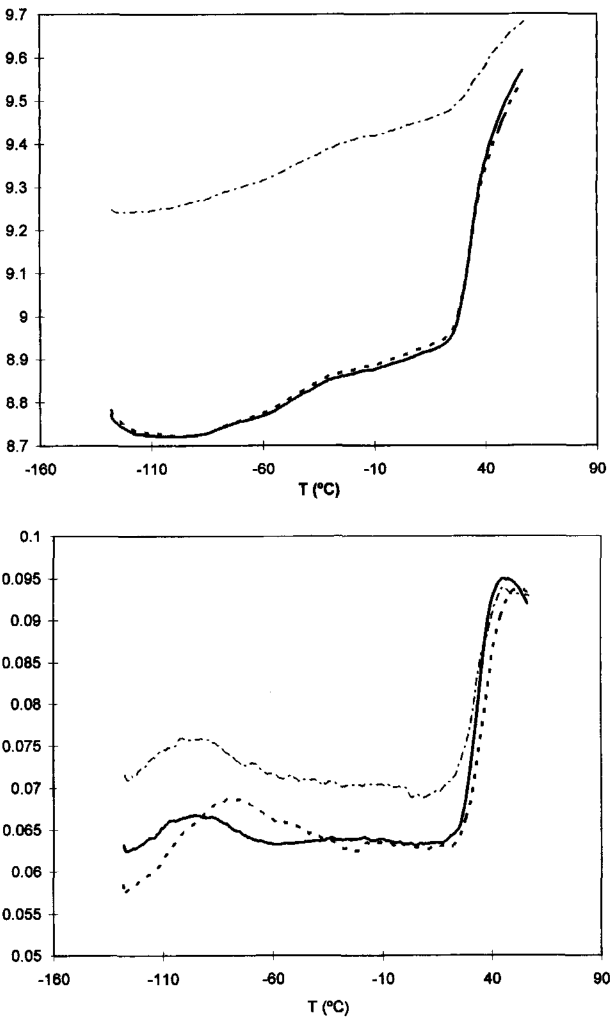

Fig. 2. The (a) ε′ and (b) ε″ dielectric plots of PHDPT as a function of temperature, measured at (– • –) 500 Hz, (————) 1 kHz and (— — —) 10 kHz.

2. Experimental

The synthesis and thermal characterization of these polyesters have been described previously [20–22]. The crystallinity values were estimated from the corresponding wide-angle X-ray diffraction data.

Dielectric relaxation measurements were performed using a Seiko Instruments DES100 dielectric module, and the results were evaluated using MAS5700 MA Station 3.0 software. A detailed description of the spectrometer and the enhancement in resolution obtained with this equipment in some polymeric materials has been given elsewhere [23,24]. The experiments were carried out at a constant frequency (between 10 and 5×10^4 Hz) in the temperature range from − 130 to 150°C, using a heating rate of 2°C min^{-1}. The samples were prepared as films by compression moulding from the mesophase and cooled down to room temperature. The corresponding X-ray diffraction patterns did not show any changes in the observed reflections indicating the absence of orientational effects in the prepared films.

The complex moduli and the corresponding storage and loss moduli were measured using a TA dynamic mechanical thermal analyzer (DMA) apparatus working in the flexural bending mode at frequencies of 0.1, 0.5 and 1 Hz in the temperature range from − 150 to 150°C employing a heating rate of 5°C min^{-1}.

3. Results and discussion

The thermotropic behaviour of the four polyesters under investigation has been studied previously by calorimetric, microscopic and X-ray diffraction techniques [20–22]. Their thermodynamic parameters are summarized in Table 1. These results indicate that the systems are semicrystalline polymers, showing at least three main transitions: the glass transition, T_g; a thermotropic transition

Table 2
Summary of dielectric data

Parameter	PHXDPT				PHXTOB				PHDPT				PHTOB			
Frequency (Hz)	10^2	5×10^2	10^3	10^4	10^1	10^2	10^3	10^4	5×10^2	10^3	10^4	10^5	5×10^2	10^3	10^4	5×10^4
T_α (°C)	72	74	78	83	–	–	–	–	46	47	53	57	48	45	52	60
T_β (°C)	−40	−35	−24	1	−17	−26	−18	−5	−8	−12	−3	2	−40	−32	−29	−4
T_{β^*}	–	−125	−116	–	−58	−65	−62	−55	−95	−95	−81	−57	−73	−70	−42	−42
E_a α (kJ mol^{-1})	394				–				365				286			
E_a β (kJ mol^{-1})	54				108				208				73			
E_a β^* (kJ mol^{-1})	–				–				42				–			
$\Delta\epsilon_\alpha^a$	0.264				–				0.64				0.90			
$\Delta\epsilon_\beta^a$	0.021				0.23				0.14				0.24			
$\Delta\epsilon_{\beta^*}{}^a$	–				–				0.065				–			
Crystallinity (%)	41				25				38				23			

[a] $\nu = 1$ kHz

from the crystal to the mesophase, T_1; and, finally, a transition from the mesophase to the isotropic melt, T_i.

The dielectric constant, ϵ', the loss, ϵ'', and the loss tangent, tan δ have been analyzed as a function of temperature and frequency for all the polymers studied. The corresponding ϵ' and ϵ'' plots for poly(heptamethylene-4,4′ diphenoxy terephthalate) (PHDPT) are shown in Fig. 2 as an example. All the samples displayed two relaxation processes, respectively referred to as α and β, in order of decreasing temperature. The dielectric data for all these relaxation processes are summarized in Table 2. The temperatures at which the maxima appear at the indicated frequencies have been obtained from the dielectric loss data (ϵ''). The corresponding values associated with the low-temperature relaxation process were estimated by curve fitting using Peakfit 3.11B/601432 software. It is observed that the maxima of all the transitions shift to higher temperatures with increasing frequency, following a general tendency in polymers.

The relaxation strength values $\Delta\epsilon = \epsilon_r - \epsilon_u$, where ϵ_r and ϵ_u are the relaxed and unrelaxed dielectric permittivities, respectively, are also included in Table 2. The relaxation strength is related to the number of dipoles and the extent of the dipole motion involved in the relaxation processes. The relaxation strength was estimated by a graphical procedure previously reported [5,6] and recently applied to copolyesters [12], as the difference in dielectric permittivity between the high- and low-temperature sides of the transition obtained from the ϵ' versus T isochronal plots.

The α transition observed at the highest temperature by dielectric methods can be assigned to the main glass transition of the amorphous system. This transition is hidden in the corresponding spectra of the polyester poly(hexamethylene terephthaloyl-bis-4-oxybenzoate) (PHXTOB) by sharp increases in the dielectric constant ϵ' and the loss tangent tan δ related to the onset of ionic conduction. The temperature associated with this transition could be estimated by dynamic mechanical measurements. The corresponding DMA diagrams of an original sample of poly(hexamethylene-4,4′ diphenoxy terephthalate) (PHXDPT) are shown in Fig. 3. The sample cooled from the mesophase showed a pronounced maximum in the loss modulus at 85°C, identified as the α transition of the material, along with another transition observed in the lower temperature range.

The T_α values included in Table 2 are very similar for the polyesters PHDPT and poly(heptamethylene terephthaloyl-bis-4-oxybenzoate) (PHTOB). These data apparently indicated that T_α was not very much affected by structural changes in the mesogenic unit, such as the replacement of an ether by an ester bond between the mesogenic unit and the flexible spacer, but it was strongly dependent on the nature of the flexible spacer. As is shown in Table 2, T_α increased with decreasing length of the spacer. This behaviour can be expected for the glass transition because of the reduction in the chain flexibility, as is observed for conventional polymers.

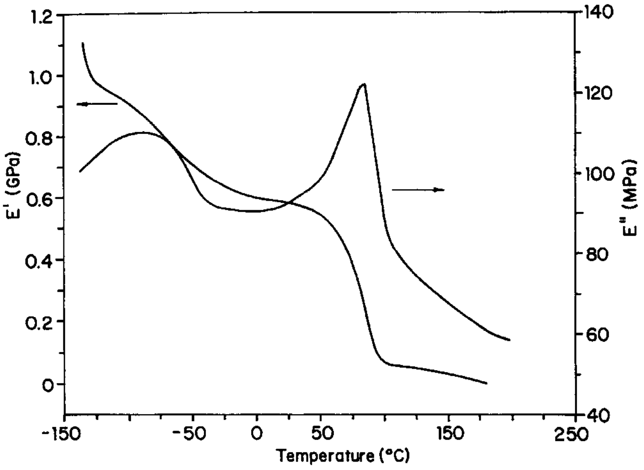

Fig. 3. DMA curves of PHXTOB as a function of temperature, at 0.1 Hz.

The analysis of the temperature dependence of the relaxation time for the relaxations that appear at temperatures $T \geq T_g$ have been assumed to obey a Vogel–Fulcher-type relationship by several authors [12,15,25,26], while the lower temperature transitions can be described by the Arrhenius equation [19]. From the experimental data obtained in this work, it is not possible to discriminate the nature of the relaxation from the fit of either the Vogel or the Arrhenius equation. For this reason, the activation energies for both the α and β transitions were calculated using the Arrhenius approximation, for comparative purposes. The logarithm of the frequency was plotted *versus* the reciprocal temperature of the maxima obtained from the isochronal diagrams, and the corresponding energy values are shown in Table 2. In any case, it is important to remark that the energy values presented in this work have only a comparative value due to the small range of experimentally analyzed frequencies.

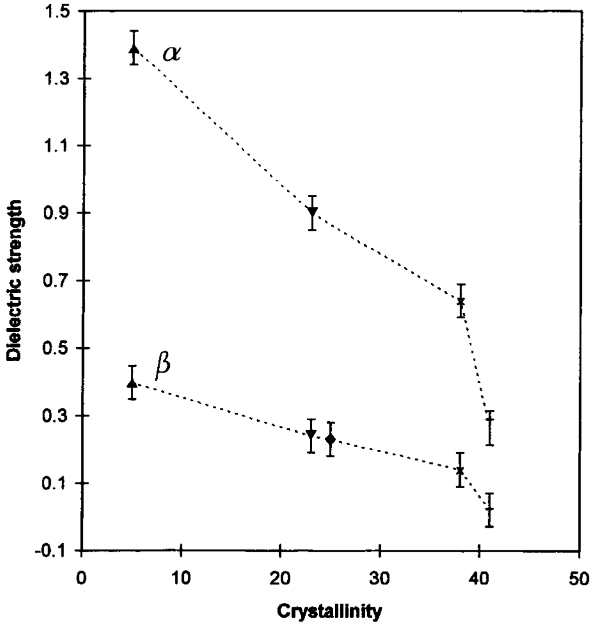

Fig. 4. Dielectric strength values for the α and β transition *versus* percentage crystallinity for (▲) PHTOB quenched from the mesophase, (▼) PHTOB, (◆) PHXTOB, (×) PHDPT, and (+) PHXDPT. The line is drawn to guide the eye.

The values of the activation energy obtained for the α transition were similar to those reported for dielectric studies of other series of polyesters with analogous structures and different substitutions in the spacer or in the mesogenic unit [27]. The E_a data for the transition could be correlated with the corresponding crystallinity data reported in Table 2, as is clearly observed for the two polyesters with a heptamethylene spacer. It is a general fact for semicrystalline systems that the glass transition related to the amorphous phase is strongly dependent on the levels of crystallinity [28].

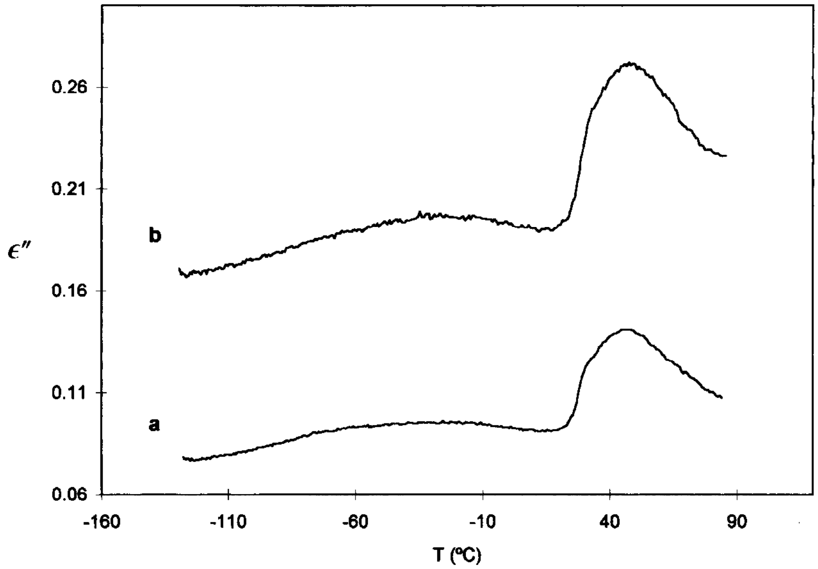

Fig. 5. Isochronal dielectric plot of PHTOB as function of temperature measured at 1 kHz for (a) an original sample (b) a sample quenched from the mesophase.

An effect of the degree of crystallinity on the relaxation strength values could be also observed (Table 2). The relaxation strength, $\Delta\epsilon$, is a function of the number of dipoles, N, the effective dipole moment, μ, and the correlation factor, g, related to the inter- and intrachain dipole correlation, following the Fröhlich equation [29]

$$\Delta\epsilon \propto g(T)\mu^2(T)N/T \tag{1}$$

A general decrease in $\Delta\epsilon$ was observed when the crystalline order increased due to a reduction in the number of dipoles involved in the process, which is restricted to the amorphous phase. This behaviour has been observed in the results obtained in this work for the α and β transitions, as shown in Fig. 4, and shows a good correlation with dielectric studies of poly(ethylene terephthalate) [30] and several thermotropic copolyesters previously reported [6,12].

Dielectric studies of PHTOB quenched from the mesophase seem to confirm this behaviour. As was previously reported [21], the thermotropic behaviour of this polyester is strongly sensitive to its thermal history. The original material contains all three phases: amorphous, crystalline and liquid crystal. In the quenched sample, the mesomorphic state can be isolated and only a small amount of crystalline material is observed. The dielectric spectra of these samples as a function of temperature are shown in Fig. 5. Although the α relaxation is observed at the same temperature and has a similar shape in the quenched sample as in the melt-crystallized sample, in contrast to other results for thermotropic copolyesters with a glass transition related to the amorphous phase and a glass transition related to a liquid-crystal phase, the dielectric strength value obtained for this latter relaxation ($\Delta\epsilon = 1.391$) is considerably higher than that reported in Table 2 for the melt-crystallized sample. This behaviour is also observed in the β process, along with other differences related to the shape of this low-temperature relaxation, as is shown in Fig. 5.

Moreover, the activation energy and dielectric strength values associated with the β transition are lower than those reported for the amorphous glass transition. These data are consistent with the assignment of the β process as a local mode, and they are in the range expected for the local motion of ester groups, as has been pointed out by different authors [6,7,11,12,27]. The influence of the thermal history on the low-temperature transition indicated above are in good agreement with previous results for PHTOB obtained by vibrational spectroscopy [31]. These studies demonstrated that several bands in the Raman spectra of this polyester, assigned to ester bonds, are closely related to the crystalline order in the material and experimental sharp changes in intensity have been detected as the crystals rearrange to adopt a liquid-crystal structure.

The motion of the carboxyl groups responsible for this low- temperature relaxation can be restricted by the adjacent aromatic rings or can be accompanied by flipping movements of these phenyl groups [32–34]. In spite of the local character attributed to the β relaxation, the dynamics of the process can be considerably influenced by the existence of liquid-crystal properties in the polymeric system due to changes in the free volume of the chain motions [16].

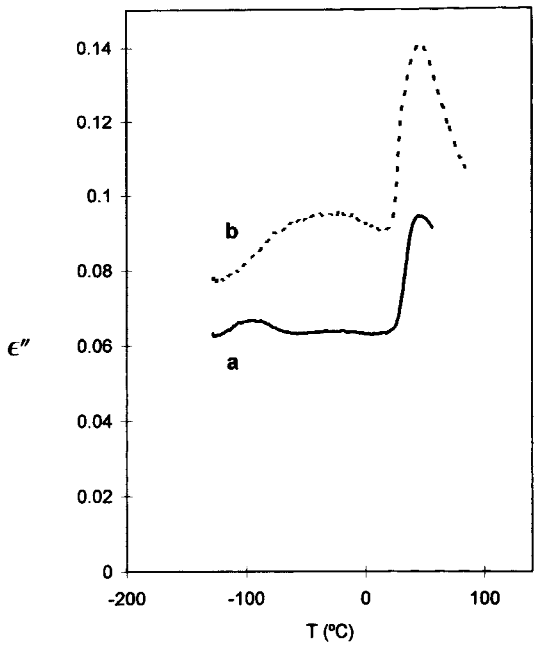

Fig. 6. Isochronal dielectric plot as a function of temperature mesured at 1 kHz for (a) PHDPT, and (b) PHTOB.

Previous studies of other members of the TOB series with oxyethylene spacers [14]. using dynamic mechanical analysis and thermally stimulated depolarization techniques have demonstrated that the β low-temperature relaxation is a complex process which can be decomposed into two different processes. Similar results have been obtained from dielectric measurements performed on several polyesters [3,4]. As the central and peripheral –COO groups have different environments, the relaxation that appears at lower temperature is associated with the motion of external carbonyl groups, as they are connected to flexible spacers with more conformational freedom. The higher temperature process is determined by the internal –COO groups of the mesogenic units whose motion is restricted by the adjacent aromatic units. We have also drawn the same conclusions in a study of the relaxation behaviour of poly(tetramethylene terephthaloyl-bis-oxybenzoate) (P4TOB) by introducing different types of substitution in the spacer and in the mesogenic unit [15,27].

Our present results also follow this pattern. Two overlapping relaxations β and β^* are observed in the low-temperature range of the isochronal plots obtained for the polyesters with ester interconnected bonds between the mesogen and the spacer (Fig. 6*b*). The lower temperature process β^* is detected separately from the β relaxation in the corresponding plots for the analogous series with ether bonds, Fig. 6*a*. Both processes, β and β^*, must originate from the polar groups contained in the mesogenic unit.

The type of interconnecting group between the mesogen and the flexible spacer has an important effect in the intensity and position of the β^* relaxation. For this reason, this process can be related to the mobility of the peripheral polar groups of the mesogen, while the higher temperature process β is a consequence of the reorientation of the –COO groups in the central part of the mesogenic unit. This β^* transition is more intense, and its temperature maxima shift to lower temperatures for the polyesters with ether bonds, as can be observed in Table 2. This behaviour can be explained as being due to the higher flexibility of the C–O interconnecting bond that allows conformational changes to occur at lower energy, as has been described by several authors [35–39].

4. Conclusions

The polymers analyzed show an α transition at the highest temperatures, which has been assigned to the main glass transition. This relaxation is affected by the crystallinity levels and the chain flexibility. Two relaxations, β and β^*, have been observed in the low- temperature range, which seem to have originated from the polar groups included in the mesogenic unit. Meanwhile the β process can be related to the mobility of internal –COO groups of the mesogenic unit, the lower-temperature process β^* is a consequence of the reorientation of the peripheral groups of the mesogen. This transition is more intense and appears at a lower temperature in the polyesters with ether interconnecting groups between the mesogen and the spacer due to the higher flexibility of these bonds.

The crystallinity order leads to an important increase in the dielectric strength values associated with the α and β relaxations because of a reduction in the dipole motion. This effect is particularly important in PHTOB where crystalline or anisotropic phases can be isolated depending on the thermal treatment.

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