

Thermal analysis of complex relaxation processes in poly(desaminotyrosyl-tyrosine arylates)

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Abstract

The goal of this study is to better understand the thermal characteristics and molecular behavior of two poly(desaminotyrosyl-tyrosine arylates). These two polymers were chosen from a combinatorial library of polymers developed by changing the type and size of the two substitutable chain locations. The objective of this work was to describe the origin of the complex relaxation processes that have been observed by thermal analysis methods. DSC, TMA and TSC studies were conducted on poly(desaminotyrosyl-tyrosine dodecyl dodecanedioate), poly(DT 12,10), and poly(desaminotyrosyl-tyrosine ethyl succinate), poly(DT 2,2), in film and fiber form. DSC experiments on poly(DT 2,2) show only a glass transition at about 80 °C which is characteristic of an amorphous polymer. The DSC of poly(DT 12,10) shows multiple thermal events indicative of a more complex internal structure. The thermally stimulated current (TSC) analysis results for poly(DT 2,2) indicate a region of molecular mobility at about 80 °C consistent with the T_g from DSC. For poly(DT 12,10) there is a dipole relaxation process observed at about 40 °C. An additional region of mobility at 60 °C for poly(DT 12,10) fibers is observed. The comparison of conventional TSC with a modified TSC procedure suggests that this process represents a spontaneous reorganization of the internal structure of the solid. The comparison of DSC and TSC results suggests that poly(DT 12,10) has two distinct modes of organization with a transition between these modes at about 60 °C. Previously published results indicate that solid state structure formation is related to two different modes of hydrogen bonding in the internal structure of the solid.

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1. Introduction

1.1. Objective

Biomaterials are synthetic materials that are used in medical devices in order to replace, support or heal tissue. A biomaterials' ability to achieve success depends on its properties and the body's acceptance of the material. As the implant is placed in the body it must not invoke immunological and toxic responses. How the material is placed in the body and what its properties and functions are must be predetermined.

The biological acceptability of an implant material and its ability to perform the desired function are dependent on the bulk and surface properties of the implant. Thus before a material is implanted in the body, an extensive characterization of its physical properties must be conducted. These properties include mechanical and thermal behavior, biodegradability as well as the changes of these properties as the material ages under biological conditions. This characterization process is an important step in understanding the initial and long-term behavior of the material. This study involves the thermal characterization of two specific polymers synthesized by Kohn for biomedical applications [1–3].

The two polymers that have been chosen for study are representative of desaminotyrosyl-tyrosine monomers incorporated

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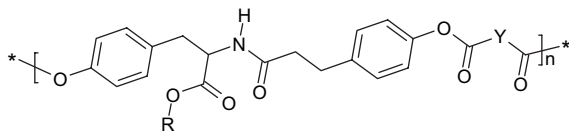


Fig. 1. Backbone chemical structure of poly(desaminotyrosyl-tyrosine arylates).

into a combinatorially designed library of polyesters. The library is synthesized by varying the number of methylene groups at two different sites. One substitution site is in the side chain and the other site is in the backbone, as shown in Fig. 1. The polymers studied will be referred as poly(R,Y). In this study, the two polymers chosen were poly(DTE succinate) and poly(DTD dodecanedioate). Poly(DTE succinate) will be referred as poly(DT 2,2) and poly(DTD dodecanedioate) will be referred as poly(DT 12,10). For poly(DT 2,2) the representations for R and Y are R: $-\text{CH}_2-\text{CH}_3$ and Y: $-(\text{CH}_2)_2-$. For poly(DT 12,10) the R and Y representations are R: $-(\text{CH}_2)_{11}-\text{CH}_3$ and Y: $-(\text{CH}_2)_{10}-$. The DT refers to the backbone composition that is desaminotyrosyl-tyrosine based. These two polymers were chosen because they represented two extreme substitution architectures. Previous studies conducted on polymers in the combinatorial library have suggested a relationship between lengths of the methylene chains at these two locations to the nature of the molecular organization [4]. These studies have shown that when the methylene groups at these substitution sites are short in length the material is amorphous. As the methylene groups at R and Y increase in length, the material is no longer strictly amorphous and a certain non-crystalline organization is observed in the solid state. This study is aimed at better understanding the nature of the internal structure using these two polymers as representatives of short and long methylene chain lengths. Conventional thermal analysis methods have been employed. In addition, a dielectric technique, thermally stimulated current, TSC, has been used to probe the behavior of these materials.

2. Experimental

In this section we describe the various techniques that were used to evaluate the behavior of these materials. In addition to the experiments performed in our laboratory, the authors acknowledge X-ray data that were provided by Dr. J. Schuut at the Center for Biomaterials, Rutgers University, Piscataway, New Jersey.

2.1. Differential scanning calorimetry (DSC)

Differential scanning calorimetric experiments were carried out using a TA Instruments Q100. The basic protocol involved using the heat–cool–heat option in the instrument setup software which cycled the temperature between a low temperature limit and a high temperature limit. The initial heating was employed ostensibly to eliminate previous thermal history of the sample. The subsequent cooling and heating of the segments were done to identify thermal transitions in the

polymers. A heating and cooling rates of $7^\circ\text{C}/\text{min}$ were chosen to match that used for TSC experiments described below.

Several different temperature limits were used in the heat–cool–heat program to evaluate the response of the polymer samples to various high temperature limits. Experiments on poly(DT 12,10) were conducted to see the effect of multiple heating cycles. For these experiments five consecutive heat–cool–heat cycles were carried out on poly(DT 12,10) between 0°C and 90°C . A similar program of five consecutive heat–cool–heat cycles with a temperature range of 0 – 120°C was employed. A sequence of heat–cool–heat runs were conducted on poly(DT 12,10) in which the same sample was heated from 0°C and the high temperature limit of the temperature program varied from 70°C to 120°C . The changes in thermal events of a sample were observed as it is heated progressively to higher temperatures.

2.2. Thermally stimulated current (TSC)

Although thermally stimulated current (TSC) is not as widely used as DSC, it is a highly sensitive thermal analysis technique that can provide information that can complement what is extracted from DSC. Thermally stimulated current is a general term that applies to the measurement of current that originates from the temperature induced relaxation motion of charges that are displaced by the application of a static electric field. In molecular systems there are typically either dipolar structural features or a molecular asymmetry that results in a net dipole. In either case, the displacement current of a relaxing dipole as a function of temperature represents a direct probe of the molecular scale mobility as a function of the input of thermal energy. A fairly comprehensive description of the technique is provided in the seminal review by Turnhout et al. [5]. For these materials, thermally stimulated current analysis was conducted using two different protocols: thermally stimulated polarization current (TSPC) and thermally stimulated depolarization current (TSDC). Both modes were able to reveal the molecular scale mobility in both poly(DT 12,10) and poly(DT 2,2). These experiments were conducted on a TherMold TSC/RMA Model 9000 using fiber specimens and film specimens of nominal thickness 0.15 – 0.20 mm.

2.2.1. Thermally stimulated polarization current (TSPC)

Thermally stimulated polarization current (TSPC) specifies that current observed as dipolar structures orient in response to the presence of a static field as the temperature is increased. In this experimental protocol, a film specimen is placed between the instrument electrodes and the temperature is linearly increased at $7^\circ\text{C}/\text{min}$, while a specified voltage is applied. The temperature range used for poly(DT 2,2) was 30 – 110°C , and for poly(DT 12,10) was 0 – 90°C . As the internal energy increases, and the molecules gain mobility, the polar structures will align to the applied field. It is the displacement of these polar groups as they align which is detected as a polarization current. Fig. 2 illustrates the profile of a TSPC experiment.

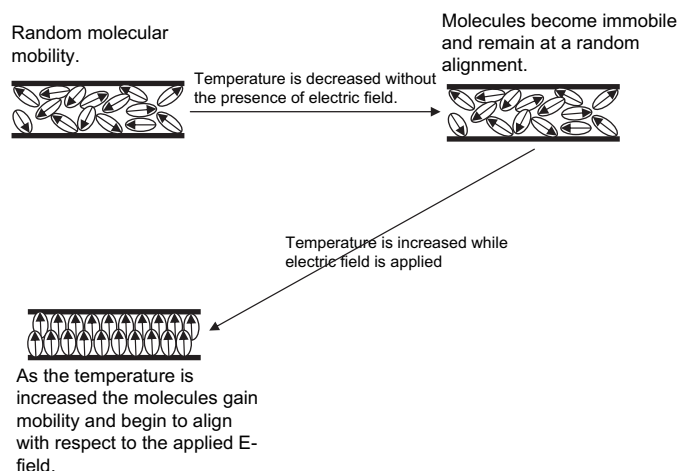


Fig. 2. The schematic of TSPC.

2.2.2. Thermally stimulated depolarization current (TSDC)

Three different variations of the TSDC technique are employed. Fig. 3 illustrates the experimental profile for a conventional depolarization experiment. In the first segment, the temperature is raised high enough to induce molecular mobility. Typically this is at, near or above the glass transition, T_g . This temperature is called the polarization temperature, T_p . At this temperature, the polarization voltage is turned on to some value, E_p , and the temperature is held for some period of time, t_p . After the polarization segment, the sample is rapidly cooled during segment 2, with the field on, to a lower temperature, T_0 , where mobility is suppressed and held there during segment 3 for a period of time, t_0 , with the voltage off. The suppressed mobility at this lower temperature will quench the dipolar alignment in the specimen. In segment 4, the specimen is heated at $7^\circ\text{C}/\text{min}$ from T_0 to the final temperature, T_f , with no voltage. It is during this segment that the dipoles that were oriented during the previous polarization segment fall away from that orientation and generate a depolarization current that is detected by the instrument.

Normally, during a conventional TSDC no attempt is made to detect current during the cooling in segment 2, because the field holds the dipoles in alignment as described above. However, as a variation of conventional TSDC, if current is detected during this cooling segment, this current can only arise from spontaneous reorganization processes. Performing TSDC experiments and monitoring the current during the cooling segment allow spontaneous reorganization processes to be observed on cooling

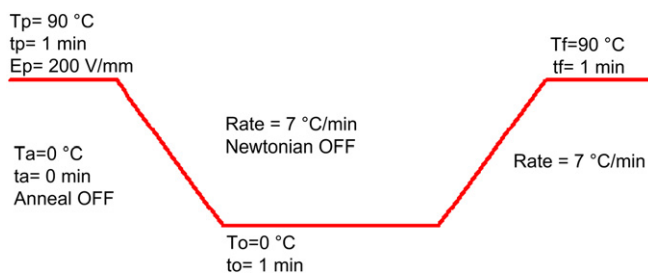


Fig. 3. TSDC mode 1.

and dipole relaxation processes to be observed in the same specimen on heating in segment 4, Fig. 3.

2.3. Thermomechanical analysis (TMA)

Thermomechanical measurements were carried out on TA Instruments 2940. In these experiments, TMA was used to measure the dimensional change of the fiber samples as a function of temperature. The observation of dimensional change was made on a 12 mm length of the fiber. These specimens were heated from -60°C to 120°C at $5^\circ\text{C}/\text{min}$ with an applied load of 0.05 N. Liquid nitrogen was used as a coolant to initially lower the temperature.

2.4. Film and fiber sample preparation

Poly(DT 2,2) and poly(DT 12,10) polymers were received from Advanced Material Design, Piscataway, New Jersey. The samples were in powder form and were made into film and fibers in our laboratory. Films were formed by compression molding at 140°C using a Carver press. After compression molding, the samples were cooled to ambient temperature. After the formation of films, the samples were stored in a desiccator. Fibers were spun with a James plunger fed micromelt spinner, fitted with a single hole, $750\ \mu\text{m}$ diameter spinnerette [6]. The melt spinning temperature was typically between 130°C and 140°C . Fibers of different diameters could be spun by varying the take-up speed. For this study, poly(DT 2,2) fiber diameter was $67\ \mu\text{m}$, and poly(DT 12,10) fiber diameter was $140\ \mu\text{m}$.

3. Results

In this section we present the experimental data that were obtained using various thermal analysis techniques.

3.1. X-ray diffraction of poly(DT 2,2) and poly(DT 12,10) films

X-ray diffraction pattern of the two polyarylate films is shown in Fig. 4. In poly(DT 2,2) film (Fig. 4(a)), one broad peak was observed at about 20° of its 2θ angle. The d -spacing is approximately $4.7\ \text{\AA}$, and the value corresponds to the van der Waals peak which is the average value of non-chemically bonded interatomic spacing. The two-dimensional image also shows amorphous halo that is the reflection of the high angle peak.

The spectrum of poly(DT 12,10) film (Fig. 4(b)) showed two peaks. One is the van der Waals peak that is identical to poly(DT 2,2). The other peak is the low angle peak observed at around 3° of the 2θ angle. The peak is relatively sharper than the van der Waals peak, and the two-dimensional image shows more intense ring than the amorphous halo. Regarding the difference in the chemical structure between these two polymers, it is considered that the low angle peak is caused by the long aliphatic chains in poly(DT 12,10). As only single peak was shown in the X-ray diffraction pattern of poly(DT 12,10), there is some level of organization of the internal structure at

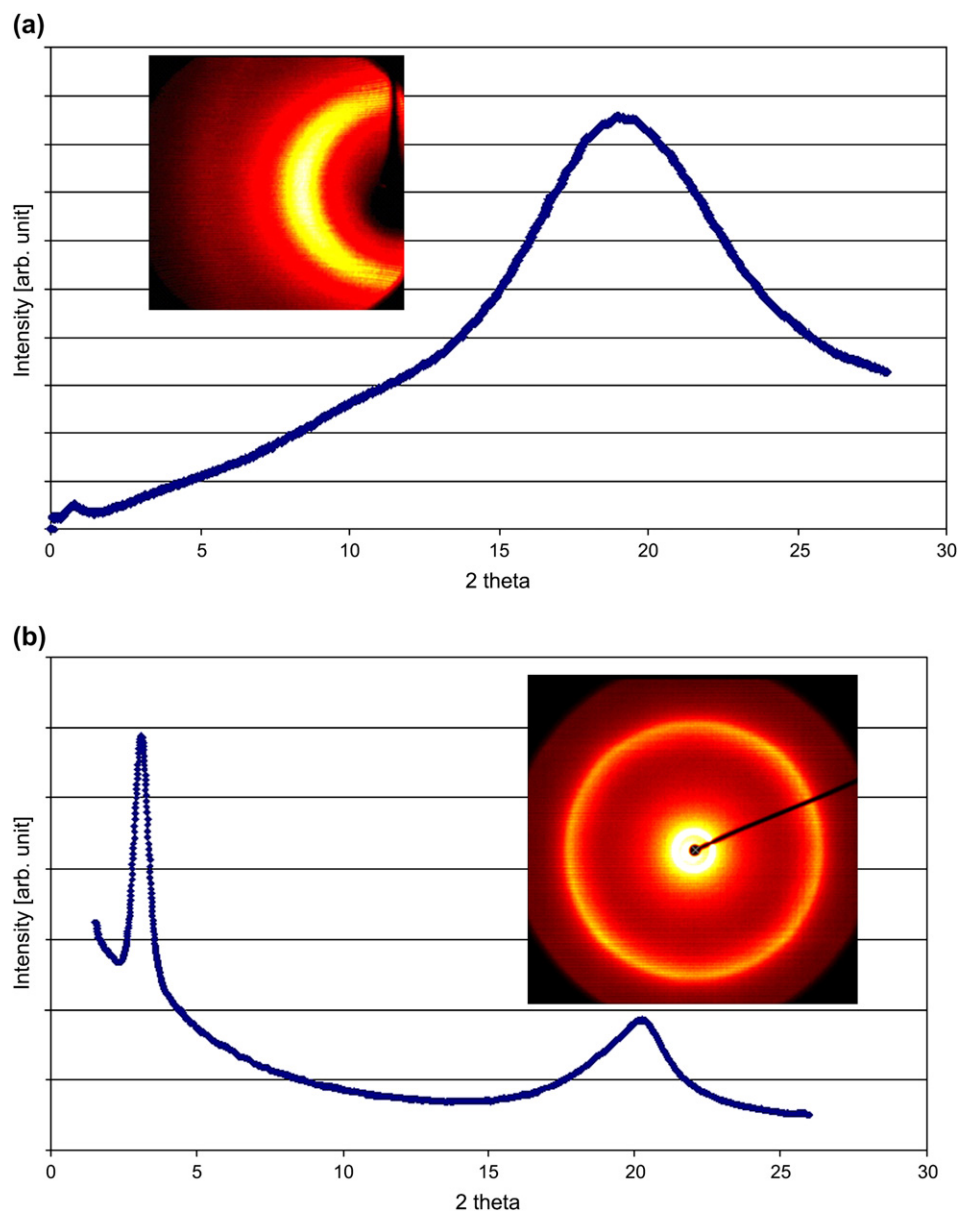


Fig. 4. X-ray scattering data of: (a) poly(DT 2,2) and (b) poly(DT 12,10).

the molecular scale, but that organization does not appear to have the three dimensional periodicity characteristic of typical crystalline structure. It should be more likely considered as non-crystalline, complex amorphous system caused by the co-existence of different types of density structure or a mesogenic polymer structure that is between semi-crystalline and amorphous structure. This point has been examined in our laboratory and will be discussed in detail in future reports.

3.2. Thermal transitions by differential scanning calorimetry (DSC)

Various DSC experiments were conducted to understand the thermal transitions of poly(DT 2,2) and poly(DT 12,10). Fig. 5 shows the results of temperature scans between $-20\text{ }^{\circ}\text{C}$ and $140\text{ }^{\circ}\text{C}$ on samples of poly(DT 2,2) film.

Fig. 6 shows the DSC results for poly(DT 12,10) film between $-20\text{ }^{\circ}\text{C}$ and $140\text{ }^{\circ}\text{C}$. For this material the results are more complex. Four thermal features can be identified for the poly(DT 12,10) specimens. A weak low temperature feature is observed that occurs between $39\text{ }^{\circ}\text{C}$ and $41\text{ }^{\circ}\text{C}$. A shallow, high temperature feature occurs between $85\text{ }^{\circ}\text{C}$ and $87\text{ }^{\circ}\text{C}$. In the temperature region between these extremes, a distinct endothermic feature is observed at about $55\text{ }^{\circ}\text{C}$ and a less distinct feature is observed at about $67\text{ }^{\circ}\text{C}$.

The DSC results clearly indicate that the behavior of poly(DT 12,10) is more complex than that of poly(DT 2,2). This phenomenon was examined by further DSC experiments. Fig. 5 shows a heat-cool-heat cycle between $-20\text{ }^{\circ}\text{C}$ and $140\text{ }^{\circ}\text{C}$ for poly(DT 2,2) in which only the glass transition between $78\text{ }^{\circ}\text{C}$ and $82\text{ }^{\circ}\text{C}$ can be reproducibly observed. Fig. 7 shows a heat-cool cycle between $-20\text{ }^{\circ}\text{C}$ and $140\text{ }^{\circ}\text{C}$ for

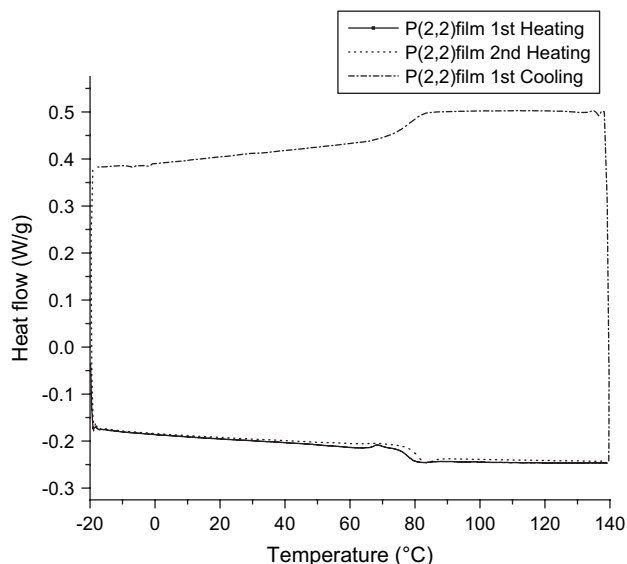


Fig. 5. DSC results for poly(DT 2,2) at 55 °C.

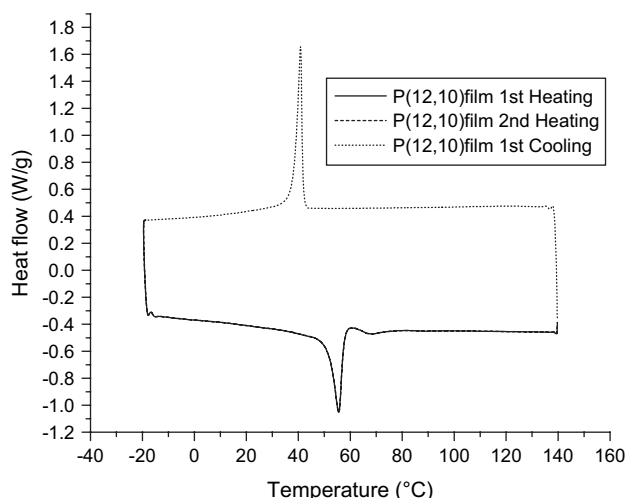


Fig. 6. DSC results for poly(DT 12,10) at 55 °C.

poly(DT 12,10) repeated five times. Successive heatings show similar behavior. On cooling, a sharp exotherm at about 41 °C is observed which is highly reproducible.

Fig. 8 illustrates the behavior of poly(DT 12,10) when subjected to five consecutive heat–cool cycles between 0 °C and 90 °C. Lowering the maximum temperature results in a successive attenuation of the endothermic peak observed on heating and the exothermic peak observed on cooling. It should also be noted that although the peaks diminish in intensity on successive cycles, if allowed to sit at room temperature for 24 h, the original peak intensity will return.

As a final illustration of the complexity of the thermal behavior of poly(DT 12,10), Fig. 9 shows the DSC results for a repetitive heat–cool experiment where on each successive cycle the maximum temperature was increased in increments of 10 °C from 70 °C to 120 °C. Clearly as the maximum temperature increases, there are changes in the behavior of the

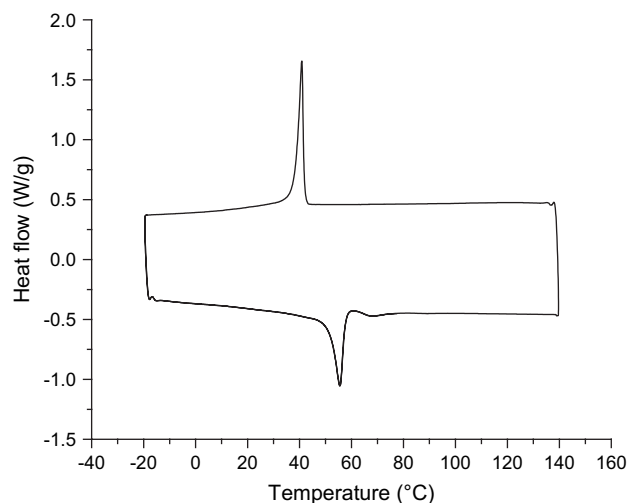


Fig. 7. DSC results for poly(DT 12,10) five heat–cool cycles between –20 °C and 140 °C.

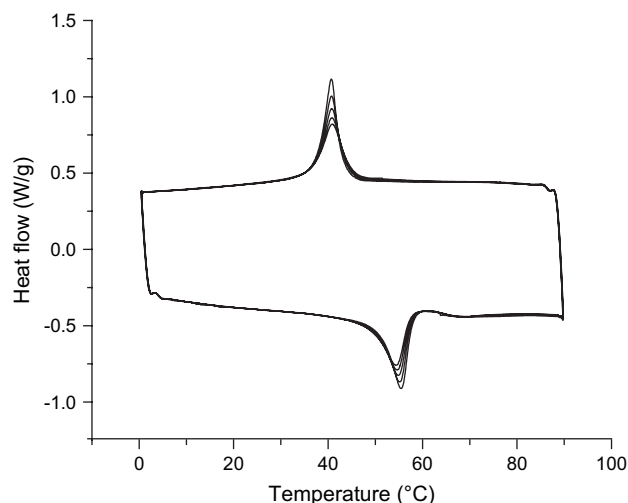


Fig. 8. DSC results for poly(DT 12,10) five heat–cool cycles between 0 °C and 90 °C.

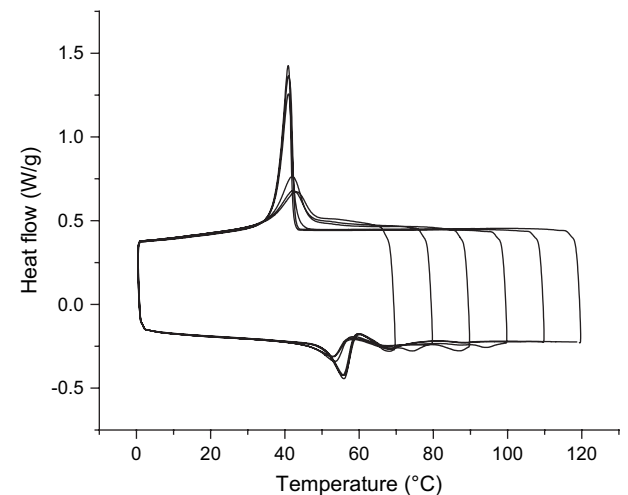


Fig. 9. DSC results for poly(DT 12,10) repetitive heat–cool cycles with increasing maximum temperature.

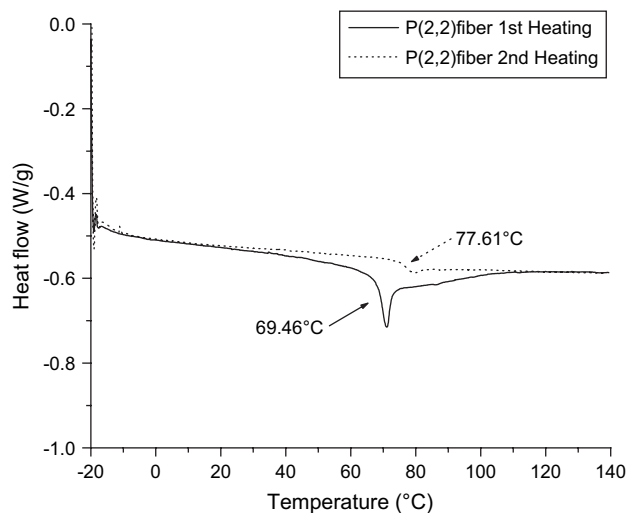


Fig. 10. DSC results for poly(DT 2,2) fibers.

DSC endotherm on heating, and changes in the exotherm on cooling.

Fibers made from poly(DT 2,2) and poly(DT 12,10) were also subjected to DSC analysis. Fig. 10 shows the DSC results for poly(DT 2,2) fiber on two successive heatings between -20°C and 140°C . Only the glass transition can be observed. On the first heating, the T_g is estimated at about 69°C and there is evidence of enthalpic recovery. On the second heating, the T_g is shifted upward to about 78°C , and the enthalpic recovery is no longer observable. Fig. 11 shows the DSC results from two successive heatings for fiber made from poly(DT 12,10). On the first heating the position of the four peak features observed nominally correspond to what was observed for the film samples, but they appear much sharper than the film sample. On the second heating, the low temperature and high temperature features become more subtle in appearance and are more similar to what was observed in the film sample.

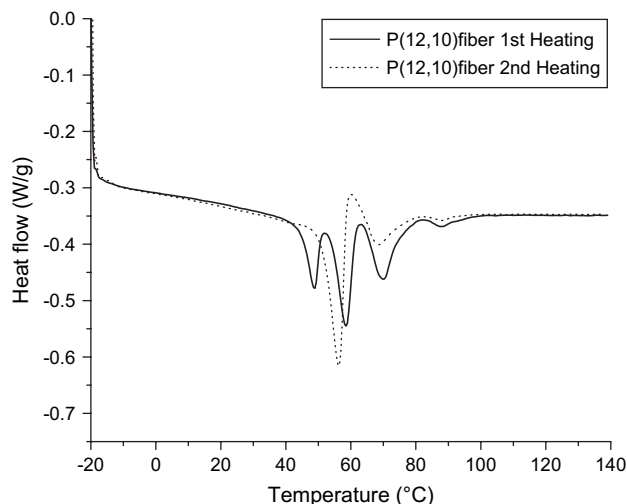


Fig. 11. DSC results for poly(DT 12,10) fibers.

3.3. Dimensional change in fibers by thermomechanical analysis (TMA)

TMA experiments were performed on as-spun poly(DT 2,2) and poly(DT 12,10) in order to determine whether the striking difference in the DSC behavior of these two fibers was reflected in their thermomechanical behavior. Fig. 12 shows the TMA results of poly(DT 2,2) fiber from -60°C to 120°C . From -60° to about 80°C there is a monotonic increase in fiber length, indicating a positive thermal expansion. At 80°C there is a large change in the rate of the increase in length indicative of what is typically called “softening” of the solid material. This “softening” is the result of the on-set of the glass transition. After this “softening” event there is a rapid loss of mechanical integrity, and under the applied load of 0.05 N the fiber extends to the limit of the instrument.

The situation for poly(DT 12,10) is observably different as illustrated in Fig. 13. From -20°C to 20°C there is a decrease in fiber length, indicating a negative thermal expansion. Qualitatively, this behavior is similar to what can often be observed as entropic shrinkage in oriented fibers [9]. It represents the decrease in chain end-to-end distance as a consequence of thermally induced rotational relaxations occurring in the oriented polymer chains. At about 43°C there is the on-set of a “softening” phenomenon that is usually associated with the glass transition. Unlike the poly(DT 2,2) fiber, the poly(DT 12,10) fiber does not rapidly lose its mechanical integrity over a short temperature range. Instead, the rate of extension of the fiber specimen varies over the temperature range of 43°C to about 90°C . For this material, the loss of mechanical integrity is a more complex process occurring over a wide temperature range.

3.4. Molecular motion by thermally stimulated current (TSC)

As a dielectric technique that responds to the motion of dipolar structures, TSC provides a direct probe of molecular dynamics and complements the information provided by

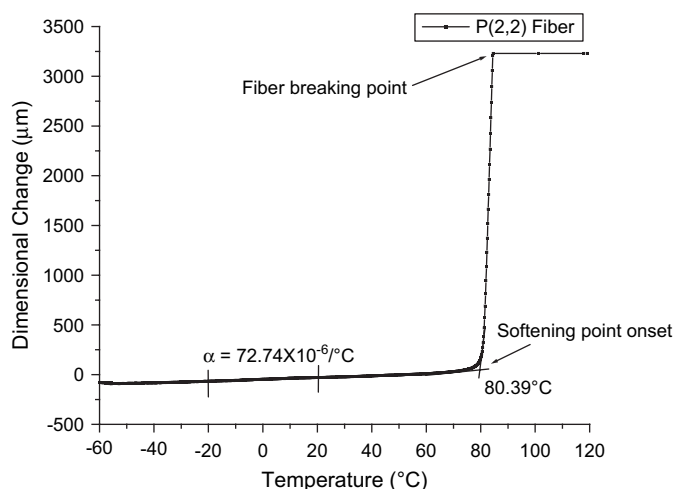


Fig. 12. TMA results for poly(DT 2,2) fibers.

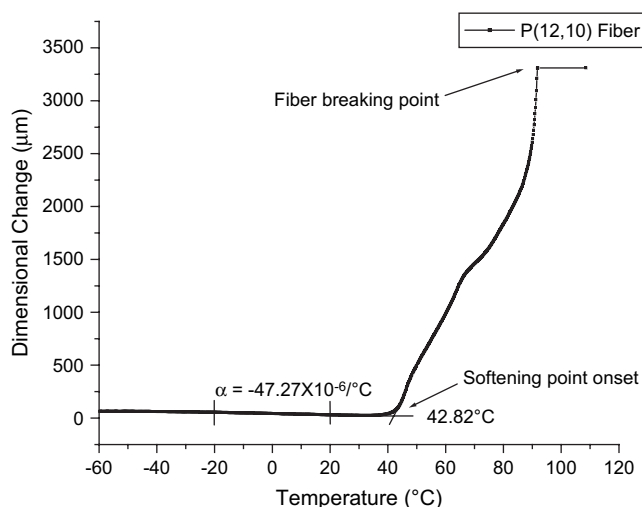


Fig. 13. TMA results for poly(DT 12,10) fibers.

DSC. Basically, DSC is a calorimetric method that measures a heat flow associated with thermodynamic transitions such as crystallization and melting, and changes in the state of motion such as that associated with the glass transition. TSC can be simply described as a non-calorimetric method that measures the current produced when charged structures such as dipoles move under the influence of temperature and electric field [10].

TSPC and TSDC experiments were performed for each sample. Positive current peaks are generated in the TSDC experiments. Negative current peaks are generated in the TSPC experiments. For TSPC the observed current is the result of polarization, and for TSDC the observed current is depolarization. The signals are mirror images of each other if they represent the same dipole relaxation process occurring in both the polarization and depolarization modes. For poly(DT 2,2), Fig. 14 provides a comparison of the results of TSDC experiments (positive peaks) done at 100 V, 200 V, 300 V and 400 V with TSPC experiments (negative peaks) done at the same voltages for films of poly(DT 2,2). Nominally, the TSPC peaks are a negative reflection of the TSDC peaks, and the position of both positive and negative peaks is at about 80 °C. The

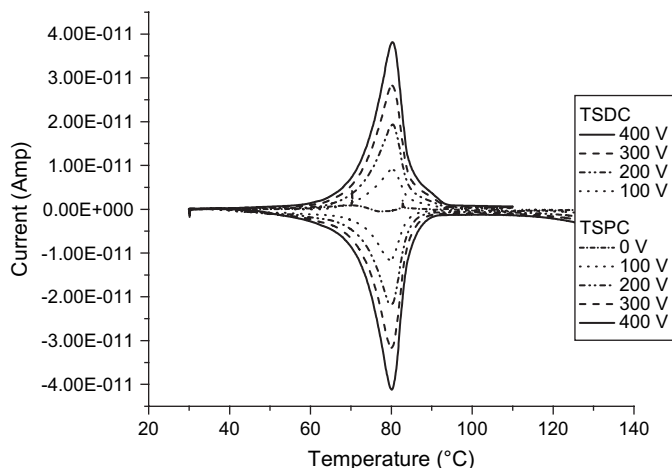


Fig. 14. TSDC/TSPC results for poly(DT 2,2) films.

magnitudes of the TSDC peaks as well as the TSPC peaks are a linear function of the voltage that was used to generate the peaks. This linear behavior along with the TSDC/TSPC negative reflection is indicative of a dipole relaxation process which is responsible for the observed current peaks [9]. Since the position of the peaks is nominally similar to what has been previously observed as the T_g from DSC and TMA experiments, this peak is taken to be the dipolar relaxation manifestation of the glass transition for poly(DT 2,2). It represents the current produced by the motion of the molecular dipoles at the on-set of structural relaxation at T_g .

Fig. 15 shows TSC results for similar TSPC/TSDC experiments performed on films of poly(DT 12,10). As has been observed in other thermal analysis results, the TSPC and TSDC behaviors of this material are more complex than that of poly(DT 2,2). For poly(DT 12,10) there is a low temperature shoulder centered near 20 °C, a large peak at about 40 °C and a sharp feature at about 60 °C. The magnitudes of the low temperature shoulder and the large peak are linearly related to the field, but the sharp feature at 60 °C is not. The implication of this is that the processes represented by the shoulder and the large peak are dipole relaxations that are influenced by the electric field, and that the feature at 60 °C represents a dipolar motion that occurs spontaneously and does not require the presence of a field for it to be observed.

For as-molded poly(DT 12,10) film, the sharp feature at about 60 °C (Fig. 21) has been tentatively assigned to a process that occurs spontaneously as the temperature is increased. In order to examine this further, a modified TSDC procedure was used. As described in Section 2, in a typical TSDC experiment, the current is measured only during the heating segment with the field off. In the modified TSDC experiment (see Section 2.2.2), the current is measured during cooling when the field is on and also during heating when the field is off. During the initial polarization, the current detected during cooling cannot be due to dipolar relaxations since the dipoles are immobilized as a result of the applied field. Any current detected while cooling can only be the result of a spontaneous reorganization of the dipoles. Using this modified procedure, the

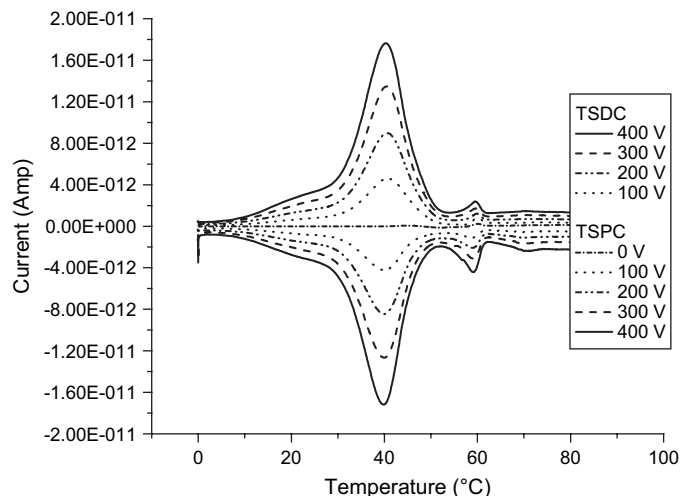


Fig. 15. TSDC/TSPC results for poly(DT 12,10) films.

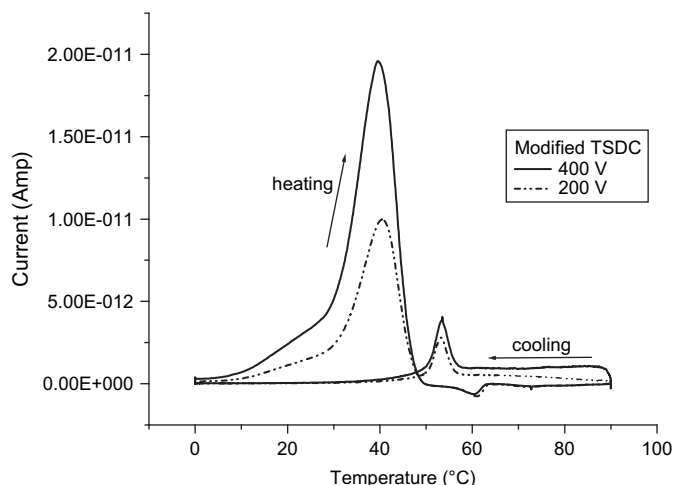


Fig. 16. Modified TSDC results for poly(DT 12,10) films on cooling and heating.

same specimen of as-molded poly(DT 12,10) film was run twice, once at 200 V and once at 400 V. Fig. 16 shows the results using this modified TSDC procedure. On cooling with the field on and the dipoles immobilized, a sharp feature is observed at about 53 °C. On heating with the field off, the relaxation process at 40 °C is observed along with the high temperature sharp feature at about 60 °C.

Additional TSC studies were conducted on poly(DT 12,10) fibers to evaluate the effect of processing on the thermal events that have been observed. TSDC and modified TSDC experiments were carried out on poly(DT 12,10) fiber. Fig. 17 shows the result of the depolarization experiments done at 100 V, 200 V, 300 V and 400 V. When compared with the results of similar depolarization experiments for poly(DT 12,10) film (positive peaks in Fig. 15), it is observed that in addition to the relaxation peak at 40 °C, there is a large relaxation peak at about 58 °C in the fiber depolarization current profiles that is not present in the film depolarization current profiles. Further, the peak at 58 °C that is present in the fiber sample linearly varies in magnitude with the magnitude of the applied

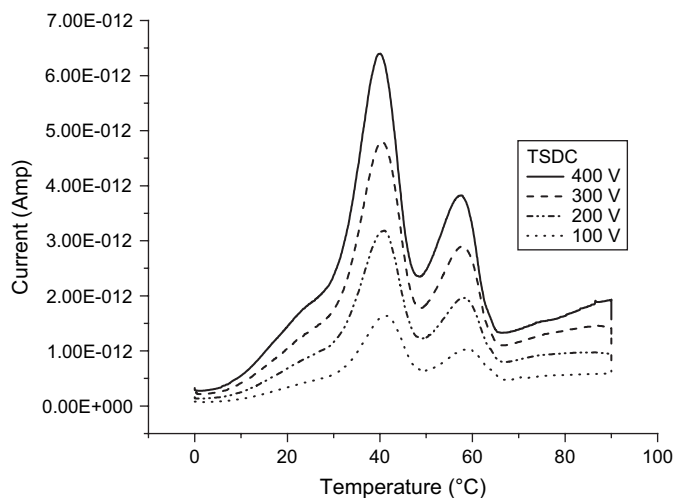


Fig. 17. TSDC results for poly(DT 12,10) fibers at multiple voltages.

voltage. This indicates that the peak represents a field induced dipole relaxation process.

Using the modified TSDC protocol, it was previously shown that for poly(DT 12,10) film there was a sharp feature at about 60 °C that was the result of spontaneous reorganization of the solid state structure (Fig. 16). Fig. 18 shows the results of using that same modified TSDC protocol on poly(DT 12,10) fibers. On cooling with the field on and the dipoles immobilized, there is still evidence of a spontaneous reorganization at about 52 °C. On heating with the field off, the two dipole relaxation peaks at 40 °C and 58 °C can be observed.

3.5. Optical microscopy (OM) in fibers and films

The optical pattern of poly(DT 2,2) and poly(DT 12,10) fiber samples were observed as a function of temperature with optical microscope on a hot stage. Figs. 19 and 20 show the change of optical pattern as a function of temperature in poly(DT 2,2) and poly(DT 12,10) fiber, respectively. In both materials, the difference in optical pattern was observed along the fiber axis and the structure of the pattern becomes more distinct as the temperature approaches about 65 °C. The pattern then becomes less distinct with further increase in temperature. This presence of birefringence indicates that both polymer samples obtained some level of orientation during the spinning process. Both samples lose the birefringence above about 80 °C.

The optical pattern of poly(DT 12,10) film sample was observed as a function of temperature. In the previous study [4], the smectic-like optical pattern was observed in poly(DT 12,10) film. In this study, the change of the pattern was observed during heating and cooling the sample, and the result was compared with DSC result (Fig. 21). The film sample was initially heated up to 120 °C to remove all the process history. When it was cooled down, the optical pattern reappeared at about 40 °C, where the sharp exothermic peak appears in DSC, and the pattern became more distinct as it cooled down. Once it was cooled down, the sample was heated up again. During the

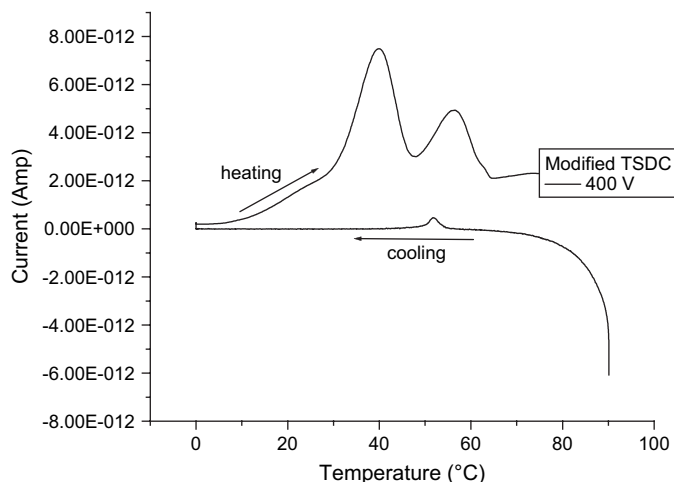


Fig. 18. Modified TSDC results for poly(DT 12,10) fibers on cooling and heating.

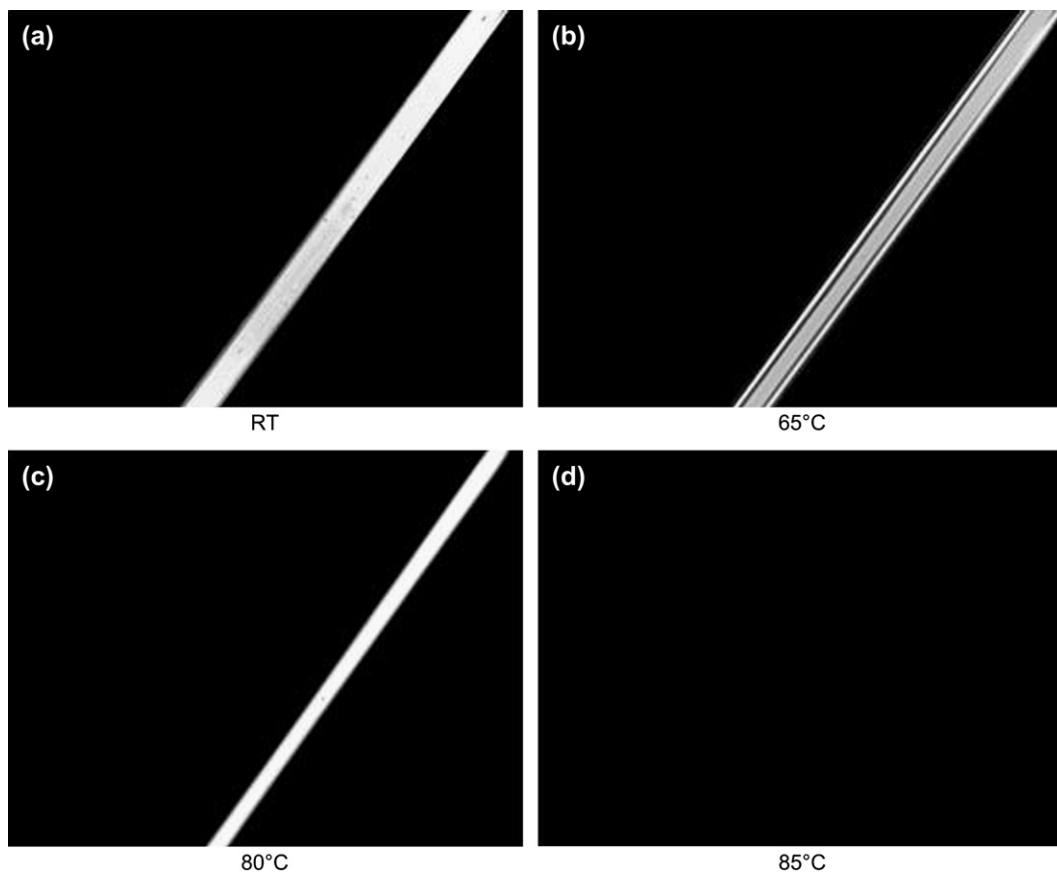


Fig. 19. Optical pattern of poly(DT 2,2) fiber on hot stage.

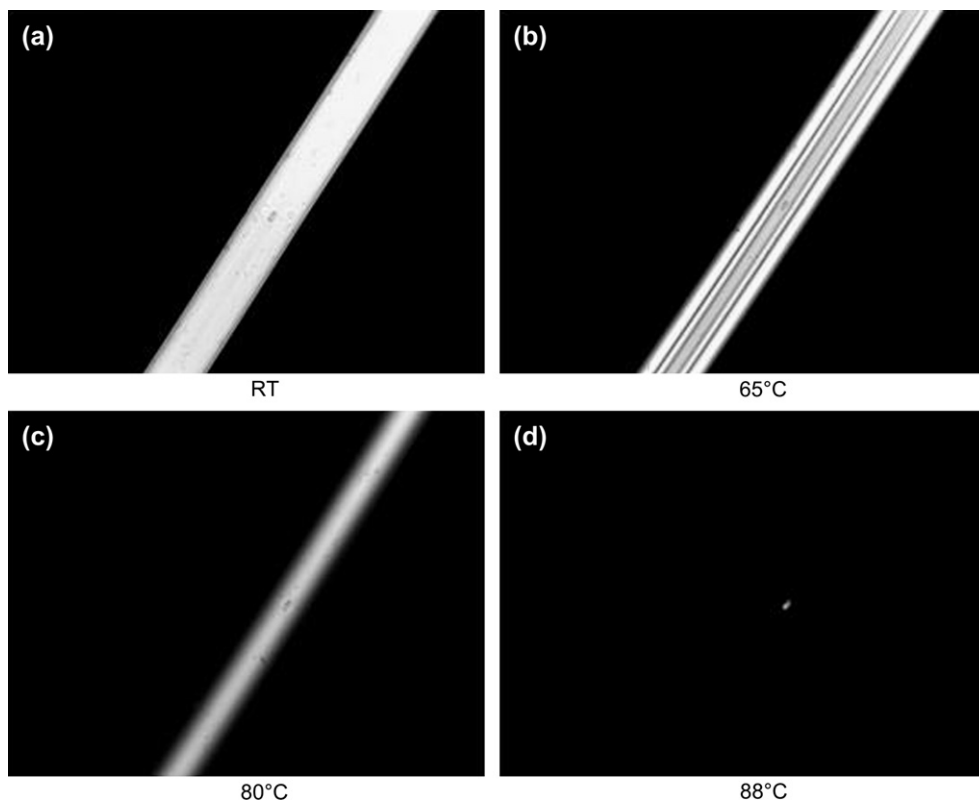


Fig. 20. Optical pattern of poly(DT 12,10) fiber on hot stage.

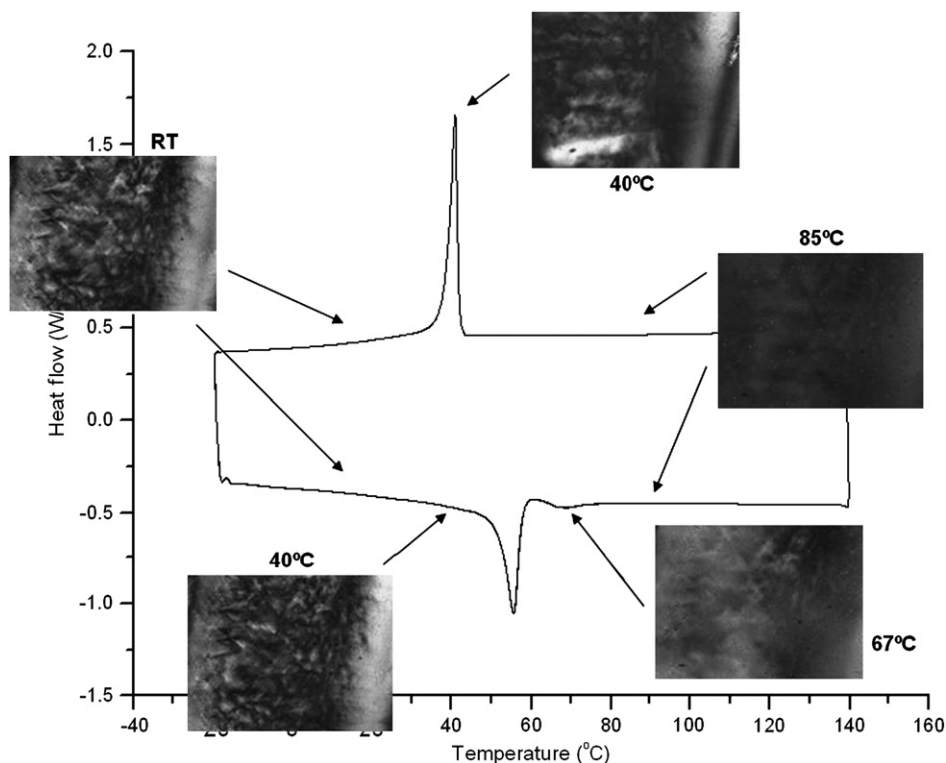


Fig. 21. Overlay of optical pattern and DSC of poly(DT 12,10) film.

heating process, the optical pattern became blurred above the temperature where the main endothermic peak appears in DSC, and the birefringence was lost after above 80 °C.

4. Discussion

In this section we describe what appears to be the relationship between the results from the various methods of analysis. These relationships provide information about internal configuration of the solid and the nature of the temperature dependent relaxations that take place in the material.

4.1. Comparison of DSC, TSC and optical results for film samples

The only feature that is observed in the DSC for the as-molded poly(DT 2,2) film is the change in heat capacity at about 80 °C on heating. This behavior is what would be expected from an amorphous polymer. This event can be confidently assigned to the glass transition for poly(DT 2,2). The position of the dipole relaxation peak at 80 °C in the TSC results for poly(DT 2,2) shown in Fig. 14 suggests that this peak is related to the glass transition observed for this material in DSC. The situation with poly(DT 12,10) is quite different. First of all, in the DSC of poly(DT 12,10) as-molded film in Fig. 6 there is no distinctive change in heat capacity that can be identified as a glass transition. The shallow feature that occurs between 39 °C and 40 °C in the DSC appears to correspond to the large dipole relaxation peak observed in the TSPC/TSDC experiments as shown in Fig. 15. Further, the

large endotherm in the DSC results occurring at about 60 °C appears to correspond to the TSC peak in the same temperature range that was identified as a spontaneous reorganization process using the modified TSDC procedure in Fig. 16. We have previously reported that FTIR results indicate that a temperature dependent reconfiguration of the hydrogen bonds does occur in these materials [4]. In more recent FTIR work, we have found that the temperature of hydrogen bond reconfiguration is in the range 55–60 °C [11]. The suggestion is that what is observed as a spontaneous reorganization in the TSC and as a distinct endotherm in the DSC results corresponds to the hydrogen bond reconfiguration as observed in FTIR results in the temperature range 55–60 °C. These results indicate that in poly(DT 12,10) there is a low temperature mode of solid state organization and a high temperature mode of solid state organization, with a transition between these two modes at 55–60 °C. For convenience, the label “A” is given to the lower temperature mode of organization, and the label “B” is given to the high temperature mode of organization.

The fact that the shallow feature that occurs in DSC between 30 °C and 40 °C in poly(DT 12,10) corresponds to a large dipole relaxation peak in the TSPC/TSDC experiments, suggests something specific about the molecular process responsible for the observations by these two techniques. The weak thermal response indicates that only a small amount of thermal energy is absorbed for by this process, and/or only a small heat capacity change occurs. On the other hand, the large depolarization current observed indicates that the motion of a substantial number of dipolar structures is initiated in the

temperature range. Responses of this type can be observed in nematic liquid crystal polymers where large scale, cooperative segmental motion that would result in the loss of nematic order is restricted. Relaxations are constrained to occur by rotational motions of structural units [12]. The thermal energy required to initiate rotational motion will depend on how tightly aggregated the rotating structures are, and if indeed there is no long range segmental motion, there will be only a small change in heat capacity that may not be detected in DSC experiments. The rotational motion of a dipolar structure, however, can produce a substantial dipole relaxation current, without any measurable change in heat capacity [12]. Based on this assessment, in poly(DT 12,10) the shallow thermal event that appears at about 40 °C in the DSC corresponds to the large dipolar relaxation event that appears in TSPC/TSDC results, and represents a rotational relaxation process occurring in the A-mode of solid state organization.

For as-molded poly(DT 12,10) film, in addition to the two thermal events discussed above, there is a shallow event in the DSC at about 67 °C and a weak high temperature feature between 85 °C and 87 °C. Comparing the DSC results to the optical results (Fig. 21), it appears that any structure that is detectable by the birefringent quality of the optical micrographs is lost in the vicinity of 85 °C. The transition between the A-mode and the B-mode of organization occurs in the range of 55–60 °C. As a consequence, in the temperature region between 60 °C and 85 °C the poly(DT 12,10) material is in the B-mode of organization. The loss of optical texture at 85 °C suggests that at that temperature the material loses any organization that can produce birefringence. The shallow thermal event at that temperature in the DSC is taken to represent the thermal energy absorption that results in the destruction of the B-mode of organization. This presumably leads to the formation of a nominally unorganized state of aggregation, which for convenience, is designated the “U-mode” of organization.

The weak thermal event at 67 °C in the DSC of as-molded film is qualitatively similar to what is observed at 40 °C. The persistence of optical texture at 67 °C indicates that a detectable extent of the B-mode of organization is present at this temperature. There is no corresponding TSC signal at this temperature for the film. The similarity between the 67 °C DSC event and the 40 °C DSC event along with the persistence of organization suggests that the 67 °C event is also a rotational relaxation occurring in the B-mode. The fact that there is no corresponding TSC signal indicates that this rotation does not involve dipoles. This event, then, is assigned to localized rotational relaxations of methylene units in the polymer structure.

In summary, this analysis leads to the assertion that the observed thermal events in the poly(DT 12,10) material is a consequence of multiple modes of organization in the solid state. Poly(DT 12,10) allowed to equilibrate at room temperature will exist in the A-mode of organization as determined by the arrangement of the hydrogen bonds. As temperature is increased, the macromolecules will undergo a localized rotational relaxation at about 40 °C that involves dipolar

structures, and which preserves the A-mode organization. A further increase in temperature from 55 ° to 60 °C results in a transition from A-mode organization to B-mode organization as determined by a thermally induced rearrangement of the hydrogen bonds as observed in FTIR. At 67–70 °C a localized rotational relaxation of methylene structural elements occurs which preserves the B-mode of organization. At about 85 °C there is a transition from the B-mode to an unorganized mode of aggregation, the U-mode.

4.2. Comparison of DSC, TSC and optical results for fiber samples

Fiber samples of poly(DT 2,2) and poly(DT 12,10) were prepared in order to evaluate the effect of molecular orientation on the behavior of these materials [6]. The DSC results for poly(DT 2,2) and poly(DT 12,10) fibers are shown in Figs. 10 and 11, respectively. Because fiber structure is lost on heating to high temperatures, only the first heating in these results can be taken as representative of native fiber behavior.

For the poly(DT 2,2) fiber, the first DSC scan shows only a glass transition with evidence of enthalpic relaxation in the vicinity of 69 °C. There is subtle evidence of a broad endothermic process that extends 15–20 °C above the end of the enthalpic relaxation event. Optical microscopy as a function of temperature shows that the poly(DT 2,2) fiber shows birefringence that reflects the macromolecular orientation induced by the fiber spinning process. According to the birefringence results, the orientation is not fully lost at 69 °C, which is the glass transition event. Instead there appears to be a gradual loss of orientation as the filament is heated. Total loss of birefringence occurs in the region between 80 °C and 90 °C. This gradual loss of orientation may account for the subtle endothermic process that is observed.

Similar to what is observed in poly(DT 12,10) film, the first DSC scan of poly(DT 12,10) fiber shows four endothermic events. Table 1 compares the positions of these four peaks in film and fiber.

From the previous discussion, Peak 1 would represent the rotational relaxation process occurring in the A-mode, Peak 2 would represent the spontaneous reorganization from the A-mode to the B-mode, Peak 3 would represent the rotational relaxation process occurring in the B-mode, and Peak 4 would represent the transition from the B-mode to the unorganized mode. Assuming that each peak corresponds to similar molecular processes, the activation energies of these processes are increased in the fiber relative to the film, as indicated by the shift to higher temperatures in the fiber material. This could reflect a higher barrier to structural relaxation imposed by

Table 1
DSC thermal events peak positions

	DSC (°C)			
	Peak 1	Peak 2	Peak 3	Peak 4
Poly(DT 12,10) film	41	55	67	85
Poly(DT 12,10) fiber	49	58	70	88

a closer packing arrangement that is achieved in the fiber. Not only are the DSC peaks shifted to higher temperature in the poly(DT 12,10) fiber, but also the peaks at 49 °C and 70 °C are sharper and more well developed in the fiber than they appear in the film.

Fig. 17 shows the TSDC of poly(DT 12,10) fiber. Because of the need to polarize the dipoles and to perform multiple runs on a single fiber specimen in order to verify that the process is a dipole relaxation process, the native fiber behavior may not have been captured. The high temperature limit of the experiment was kept at 90 °C, which was low enough for the material to retain its fiber shape. The results are clearly reproducible and different from the film material. While there is a dipole relaxation peak slightly above 40 °C in the fiber as in the film, there is a dipole relaxation peak just below 60 °C in the fiber TSDC that is not present in the film TSDC. Since the film and fiber are chemically the same material, this difference can only arise because of a difference in the internal state of aggregation. Fig. 18 confirms that by immobilizing the dipoles, the spontaneous reorganization assigned to hydrogen bond reorganization can still be observed in the fiber. The occurrence of the TSDC peak just below 60 °C in the fiber suggests that the rotational relaxation processes that are initiated at this temperature in the fiber are more extensive than in the film in the sense that they involve dipolar structures that were not mobile in the film. This is a clear indication of a difference in the state of aggregation between the film and the fiber.

The thermal analysis results indicate that there are two distinct modes of solid state organization in poly(DT 12,10), which have been designated the A-mode and B-mode. The A-mode, stable at temperatures lower than 55–58 °C, is transformed above that to the B-mode. This temperature dependent transition from one mode of organization to another is reversible, although it is mediated by the kinetics of transformation. The thermally induced, reversible transition of one mode of organization to another is frequently observed in crystalline materials as enantiotropic polymorphism [13].

Based on the observations that have been described from the TSC and the DSC results for poly(DT 12,10), a free energy diagram has been formulated to account for these results that is identical to the free energy diagram for enantiotropic polymorphism. Fig. 22 models the temperature induced changes in solid state organization for poly(DT 12,10).

At low temperature, the equilibrium solid state configuration is the A-mode. As the temperature is increased, there is a rotational relaxation that occurs with the preservation of the A-mode configuration at Event 1. This would correspond to Peak 1 in Table 1. At progressively higher temperature there is a reorganization of the solid state configuration from A-mode to B-mode shown as Event 2 in this diagram and corresponds to Peak 2 in Table 1. With increasing temperature there is a rotational relaxation process that occurs with the preservation of the B-mode configuration at Event 3, which corresponds to Peak 3 in Table 1. At higher temperatures the B-mode of solid state is disrupted and transforms to what is presumed to be an unorganized mode of solid state

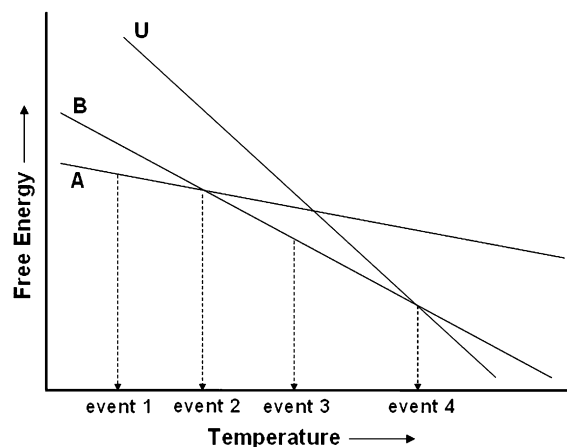


Fig. 22. Free energy diagram for poly(DT 12,10).

aggregation, the U-mode. That transformation is indicated as Event 4 in the diagram and corresponds to Peak 4 in Table 1. While this diagram has the same general features as used to describe enantiotropic polymorphism in crystalline materials, in the case of poly(DT 12,10), the polymorphic forms refer to the two distinct modes of hydrogen bonding in a non-crystalline material. Considering this, the behavior of poly(DT 12,10) represents an example of polyamorphism as described by Angell [14].

4.3. Comparison of DSC and TMA results for fiber samples

The possibility of distinct multiple states of aggregation might be expected to have some influence on the mechanical behavior of the solid. A straightforward method to assess this possibility is to observe the difference in the thermomechanical behavior of poly(DT 2,2) fiber versus poly(DT 12,10) fiber. Figs. 12 and 13 show the TMA results for poly(DT 2,2) and poly(DT 12,10), respectively. A careful examination of the low temperature regions of these two TMA traces reveals that for poly(DT 2,2) between -20 °C and 20 °C the linear expansion is about $73 \mu\text{m}/^\circ\text{C}$, while for poly(DT 12,10) the linear expansion is about $-47 \mu\text{m}/^\circ\text{C}$. The large difference in these values suggests a difference in the mechanistic response of the fiber to increased thermal energy. The birefringence observed in both fiber materials as indicated by Figs. 19 and 20 provide evidence that there is molecular orientation in both fibers. It is not unusual to observe a negative linear expansion in oriented fibers. This is typically observed as fiber shrinkage. The origin of this phenomenon is the shortening of the end-to-end distance in the oriented polymer as a result of the conformational relaxations occurring along the chain as temperature is increased [9]. In the case of poly(DT 2,2) this process likely occurs, but the structure of the solid state also allows for interchain slippage, which would result in the positive linear expansion. For poly(DT 12,10) the interchain connectivity provided by the hydrogen bonding inhibits interchain slippage and facilitates the thermally induced chain contraction to be transmitted through

the filament and be observed as a negative linear expansion. This is consistent with what is observed at higher temperatures. At the glass transition temperature of 80 °C, poly(DT 2,2) rapidly loses its mechanical integrity over a very short temperature range. Above this temperature, there are no modes of intermolecular connectivity that inhibit the chains from slipping past each other in a rapid failure process. Poly(DT 12,10), on the other hand, starts to lose its mechanical integrity at about 43 °C but does not completely fail until about 90 °C. Over that temperature range there is a complex process of failure as reflected in the shape of the TMA curve. For this fiber there are modes of intermolecular connectivity related to the hydrogen bonding that inhibit the chains from slipping past each other. The failure process for poly(DT 12,10) is more complex because it requires that enough thermal energy must be put into the solid system to overcome each of these modes of connectivity.

Fig. 23 overlays the DSC and TMA results for poly(DT 12,10). It is immediately obvious that temperature over which the complex TMA failure process occurs is the same temperature range over which the multiple DSC events are observed. The implication is that, indeed, as indicated in the previous discussion, the thermal events represent relaxations and reorganizations that are occurring in the solid state, and further, that these processes influence the mechanical integrity of the material.

4.4. Multiple DSC scans of poly(DT 12,10) film

Fig. 8 shows the behavior of poly(DT 12,10) film when subjected to five consecutive heat–cool cycles between 0 °C and 90 °C. It is clear that the event represented by the exotherm between 42 °C and 43 °C on cooling and the endotherm between 54 °C and 57 °C on heating is progressively attenuated on successive heat–cool cycles. From Table 1 it is internally consistent to assign this peak to the spontaneous reorganization from the A-mode to the B-mode on heating,

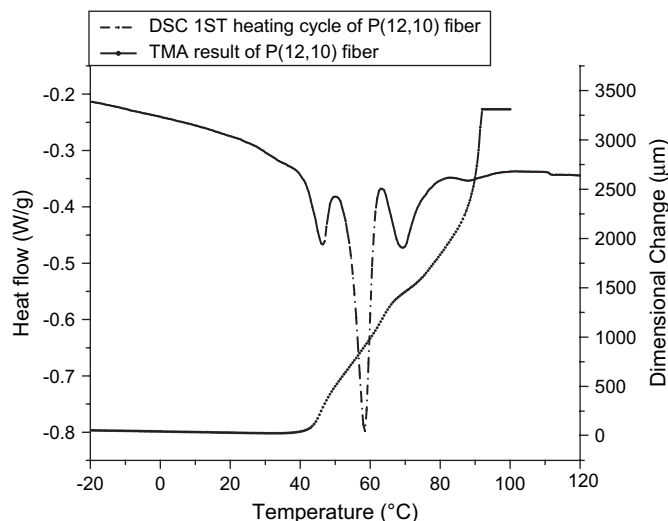


Fig. 23. Overlay of poly(DT 12,10) fiber DSC and TMA.

and from the B-mode to the A-mode on cooling. Given this assignment, this behavior can be interpreted in terms of the limiting kinetics of the transition from one mode of organization to the other. Consider that the experiment shown in Fig. 8 can be mapped onto the free energy diagram in Fig. 22 by raising and lowering the temperature from some temperature below Event 1 to some higher temperature that approaches but may not exceed Event 4. The rotational relaxation that can occur near 40 °C is too subtle to observe in this specimen. On the first heating, the largest endothermic peak is observed; likewise, on the first cooling, the largest exothermic peak is observed. If it is allowed that the kinetics of conversion are slow relative to the heating and cooling rate, the conversion from A-mode to B-mode will be incomplete on heating, and, similarly, the conversion from B-mode to A-mode will be incomplete on cooling. The result of this will be a progressive buildup of solid structure organized in B-mode relative to A-mode. As the amount of B-mode in the solid structure increases, the amount of A-mode which is transformed to B-mode diminishes. The consequence of this will be a progressive diminution of the magnitude of the exotherm that represents the transition from A-mode to B-mode simply because there is a decrease in the fraction of A-mode.

With this interpretation, an interesting possibility emerges. If the exotherm observed on cooling represents the transition from B-mode to A-mode, then if the solid is taken to a temperature above the transition from B-mode to U-mode, then it maybe possible to observe a different exotherm as the material relaxes from U-mode to a lower free energy mode. Fig. 9 shows the results for multiple scan DSC experiments where the upper limit temperature is successively increased by 10 °C on each successive run starting from an upper limit of 70 °C to an upper limit of 120 °C. As the upper limit temperature increases, the exotherm that is observed on cooling transforms from being broad with low peak heat flow and total heat flow of about 0.7 W/g to being rather sharp with a high peak heat flow and a total heat flow of about 1.2 W/g when the maximum temperature of the heating reaches 100 °C. This is consistent with a change in the nature of the event that takes place on cooling.

In Fig. 8, the event occurring on cooling is the partial conversion of solid organized in the B-mode to the A-mode configuration. As long as the highest temperature is kept at or below 90 °C the conversion remains between these two modes of organization. As the level of B-mode builds up, there is less A-mode to transform, and the magnitude of the peak representing this solid state transformation decreases. If the temperature of heating is taken above 90 °C, from Table 1, B-mode is transformed to U-mode. On cooling the material heated to 100 °C, the exotherm that is observed represents the transition of material from U-mode to a lower free energy configuration. The sharp exotherm that is observed at about 41 °C on cooling and the endotherm that is observed at about 56 °C on subsequent heating suggest that when cooled from an upper limit temperature of 100 °C or higher, the material transforms from the supercooled U-mode to the lower free energy A-mode solid state configuration.

5. Conclusion

Based on the relationship between the observations from the various thermal techniques, and the interpretation that we have outlined in Section 4, the following conclusions are reached.

5.1. Hydrogen bonding and the complex relaxations in poly(DT 12,10)

The presence of a specific temperature dependent modes of hydrogen bonding in the poly(DT 12,10) strongly influences its physical behavior compared to what is observed for poly(DT 2,2). By examining the relationship between the DSC and TSC results for poly(DT 12,10), the thermally induced relaxation events in poly(DT 12,10) have been interpreted in terms of the changes in the mode of hydrogen bonding in the internal structure of this material as observed using a variety of thermal analysis methods. For convenience, the lower temperature mode of organization in poly(DT 12,10) has been designated the A-mode. The higher temperature mode of organization has been designated the B-mode. For poly(DT 12,10) films and fibers, the thermal event observed in the DSC in the range 41–49 °C is assigned to a rotational relaxation that preserves the A-mode. The event observed in the range 55–58 °C is assigned to the spontaneous reorganization of the internal structure from the A-mode to the B-mode. The event observed at 67–70 °C is assigned to a rotational relaxation that preserves the B-mode. The event observed in the range 85–88 °C is assigned to the thermally induced transition from the B-mode to a configuration without distinct organization, a configuration that is designated the U-mode.

5.2. Polyamorphism

The behavior of poly(DT 12,10) invokes the Angell [14] notion of polyamorphism, that is, a non-crystalline solid

with multiple modes of aggregation. The thermodynamic behavior of this material is expected to be similar to enantiotropic polymorphism observed in polymorphic crystalline material. One distinction between the behavior of poly(DT 12,10) and strict enantiotropic polymorphism is the presence of localized rotational relaxations in the two polymorphic, non-crystalline phases.

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