

*Dedicated to Prof. Edith A. Turi in recognition of her leadership in education*

## **THERMAL PROPERTIES OF THE POLYAMIDE FROM 2-METHYLPENTAMETHYLENEDIAMINE AND DODECANEDIOIC ACID**

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### **Abstract**

The polyamide from 2-methylpentamethylenediamine and dodecanedioic acid (MPMD-12) has been studied by differential scanning calorimetry, dynamic mechanical analysis, dielectric analysis, X-ray crystallography, and simultaneous small and wide-angle X-ray scattering using synchrotron radiation. The polymer exhibits polymorphism which is shown to be associated with the incorporation of the branched diamine. At relatively low temperatures, the crystal structure is similar to the gamma form which has been found in many other polyamides. At higher temperatures, a new delta form appears in which the diamine moiety adopts a bent conformation. In this form, the chains follow a zig-zag pattern with two chemical repeats units per crystallographic repeat with a shortening of about 10% along the *c*-axis.

**Keywords:** branched diamine, crystal structures, dielectric properties, dodecanedioic acid, mechanic properties, 2-methylpentamethylenediamine, modulated DSC, polyamides, polymorphism, SAXS, Synchrotron X-ray, WAXD

### **Introduction**

2-methylpentamethylenediamine (MPMD) (CAS Registry No. 15520-10-2) is an isomer of hexamethylene diamine (HMD) [1]. It is sold under the trade name, Dytex<sup>®</sup>-A. Since MPMD contains an asymmetric carbon atom, it has two stereo isomers, which are presumed to be present in equal quantities. Moreover, since the diamine can enter a polymer chain from either end, the methyl group can be on either the second or the fourth carbon atom. Thus, the methyl groups are presumed to be distributed at random among four positions in the polymer segments.

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The properties of nylon MPMD-6 and copolymers with nylon 66 have been described by Stouffer *et al.* [2]. The polymer derived from MPMD and terephthalic acid (MPMD-T) has been described by Menczel *et al.* [3] under the designation nylon M5T.

The present paper is concerned with nylon MPMD-12 that is derived from MPMD and dodecanedioic acid (CAS Registry No. 693-23-2). Some aspects of this polymer have been described in a paper by Keating *et al.* [4]. It can be used for powder coating and heat sealable films as well as oriented fibers.

## Experimental

The synthesis of the polymer and the X-ray diffraction experiments were done as described in [4]. The differential scanning calorimetric experiments were done using TA Instruments 2920 standard and temperature-modulated DSC and the dynamic mechanical measurements were done using Seiko Instruments DMS 210 in tension mode.

The dielectric measurements were taken in the parallel plate geometry. Films were clamped between phosphor bronze disc electrodes (16 mm diameter) in a custom built variable temperature dielectric cell using liquid nitrogen cooling and electrical heating in conjunction with a Lake Shore Cryotronics model DRC 82C temperature controller. The dielectric data (primarily the dielectric dissipation factor) were collected with a C. Andeen Associates Impedance Measuring Bridge (model CCA-85) with 17 frequencies covering the range 10 to 100 kHz plus a PC. During the dielectric scans, the temperature was ramped upwards at  $0.5^{\circ}\text{C min}^{-1}$ . Prior to the dielectric scans, the samples were either dried (for example, by heating in the dry-nitrogen swept dielectric cell) or humidified by storage in a desiccator over appropriate saturated salt solutions.

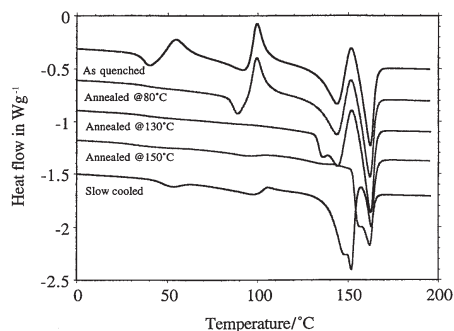
Simultaneous small-angle X-ray scattering (SAXS) and wide-angle X-ray diffraction (WAXD) were carried out at the X3A2 beamline in the National Synchrotron Light Source (NSLS) at the Brookhaven National Laboratory (BNL) [6–9]. The wavelength used was 1.28 Å. Two linear position sensitive detectors (Mbraun) connected in series were used to record the simultaneous SAXS and WAXD profile. The chosen data collection time per frame was 30 s. An evacuated flight was used for the SAXS detection with a sample to detector distance of 1190 mm. The WAXD detector covered an angular range from 12 to  $32^{\circ}$  in 2-theta. A dual chamber temperature was used for the melting study with a heating rate of  $2^{\circ}\text{C min}^{-1}$ . An unoriented pressed film of MPMD-12 was quenched from the melt to an amorphous state and stored for several days at room temperature prior to the measurement. A small percentage of crystallinity was found in the measured sample as a result of this annealing below  $T_g$ .

## Results and discussion

### Calorimetry

Samples were examined by differential scanning calorimetry (DSC) at a heating rate of  $10^{\circ}\text{C min}^{-1}$  after quenching from the melt with liquid nitrogen. In some cases, a

preliminary scan was run to a selected annealing temperature at which the sample was held for ten minutes.



**Fig. 1** DSC scans for samples of MPMD-12 with various thermal histories

As shown in Fig. 1, the glass transition of a freshly quenched sample is seen at 35°C followed by crystallization exotherms at 55 and 100°C and melting endotherms at 144 and 162°C. There is a small endotherm between the exotherms and a small exotherm between the endotherms, indicating that some melting and recrystallization may have occurred in these regions. The fact that the overall areas above and below the baseline are essentially equal demonstrates that the sample was amorphous at the beginning of the scan. It has been found that when a quenched sample is annealed overnight at room temperature, some crystallization occurs even though the material is below its glass temperature.

When a quenched sample is annealed at a given temperature, the peaks at lower temperatures are eliminated in a subsequent DSC scan, because the corresponding thermal events have already occurred. This is also shown in Fig. 1. For a sample annealed at 80°C, only the second exotherm and the two endotherms are present. A sample annealed at 130°C shows only the endotherms. For a sample annealed at 150°C, only the second endotherm is present. The scan for each annealed sample exhibits an additional endotherm a few degrees above the annealing temperature. This is characteristic of many polymers and it attributed to the melting of small, imperfect crystals which were formed during annealing. A scan from a sample, which had been cooled slowly from the melt, contained a large endotherm at 152°C and a smaller endotherm at 164°C.

As reported in [4], a study of crystallization kinetics found that the half time for crystallization showed two minima in the region of the endotherms for the quenched sample in Fig. 1. The shortest half times were a little more than one minute, which is consistent with the ease with which the polymer can be quenched from the melt to an amorphous state.

Further insights into the thermal events can be obtained through modulated or dynamic DSC in which a cyclic temperature fluctuation is superposed on the usual temperature ramp. The experiment was carried out at amplitude of  $\pm 0.5^\circ\text{C}$ , a period

of 60 s, and an underlying heating rate of  $5^{\circ}\text{C min}^{-1}$  from ambient to  $180^{\circ}\text{C}$ . Thus, the sinusoidal heating rate varied between  $2$  and  $8^{\circ}\text{C min}^{-1}$  with an average of  $5^{\circ}\text{C min}^{-1}$ . This technique has been used in the study of MPMD-T [3].

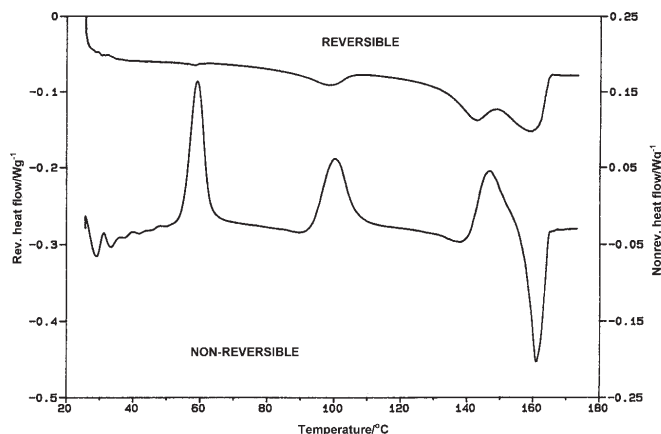


Fig. 2 Temperature-modulated DSC scans for quenched MPMD-12

The separated reversible and non-reversible data are plotted in Fig. 2 for a sample of MPMD-12, which had been quenched from the melt. The first crystallization exotherm at  $59^{\circ}\text{C}$  is present only in the non-reversible curve. The second exotherm at  $100^{\circ}\text{C}$  in the non-reversible curve is accompanied by a somewhat smaller endotherm at  $98^{\circ}\text{C}$  in the reversible curve. This indicates the partial melting of the existing crystal form and the formation of a new form. At this point, both forms coexist. The slight offset of the peak temperatures of the melting and crystallization activities is due to the phase lag of these events with the designated temperature modulation, which determines the event to be either in phase (reversible) or out-of-phase (non-reversible). The local melting of the first form occurs, followed by the formation of the second form in the next half cycle of modulation.

The endothermic peak at  $143^{\circ}\text{C}$  in the reversible curve is followed closely by an exothermic peak in the non-reversible curve at  $147^{\circ}\text{C}$ . It appears that as in the region of  $100^{\circ}\text{C}$ , the partial melting of one crystal form is followed closely by the formation of another. The final endotherm appears in both curves, at  $159^{\circ}\text{C}$  in the reversible curve and as a somewhat sharper peak at  $161^{\circ}\text{C}$  in the non-reversible curve. Both curves return to the baseline at  $165^{\circ}\text{C}$ .

DSC scans from oriented fibers of MPMD-12 do not generally show the multiple peaks which are characteristic of the unoriented polymer. As shown in Fig. 4 of [4], most fibers are characterized by a single, sharp endothermic peak. The exception was a fiber, which had been heat treated at  $135^{\circ}\text{C}$ , which is in the middle of the transition from one crystal form to another. The scan from that fiber contained two sharp endothermic peaks. We conclude that in the oriented fibers, unlike the unoriented polymer, the crystal-crystal transitions cannot take place within the time-scale of a

temperature ramp of  $10^{\circ}\text{C min}^{-1}$ . However, the transformation can occur during an overnight isothermal treatment.

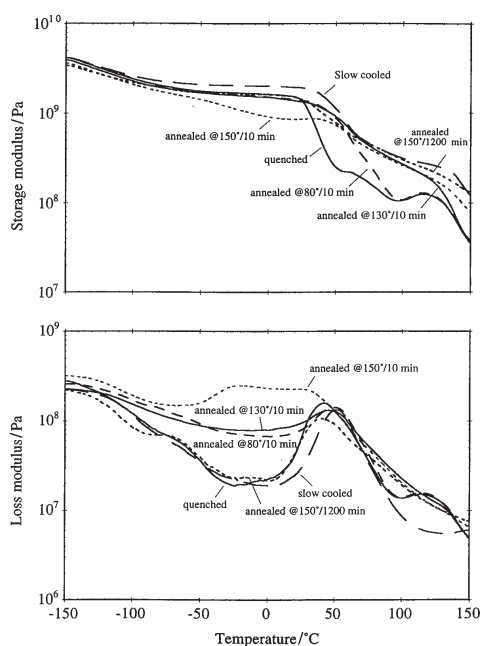
MPMD-12 is isomeric with Nylon 612, and the sequence of chain atoms is similar to that in Nylon 512. Those polymers cannot be readily quenched from the melt to an amorphous state, and their DSC scans exhibit a single, relatively sharp melting endotherm without the multiple exo and endothermal peaks which are characteristics of MPMD-12 [4].

### Mechanical properties

Most viscoelastic relaxations in polymers are properties of the amorphous regions. However, crystalline transitions can also be reflected in the mechanical behavior. The storage modulus ( $E'$ ) and the loss modulus ( $E''$ ) measured by dynamic mechanical analysis (DMA) at a frequency of 1 Hz for samples of MPMD-12 after various thermal treatments are plotted against temperature in Fig. 3.

The storage modulus of the quenched sample decreased at the glass transition at  $42^{\circ}\text{C}$  and showed increases at about  $60$  and  $120^{\circ}\text{C}$  near the temperatures of the two crystallization exotherms. The loss modulus had a major peak at the glass transitions and a secondary peak at about  $115^{\circ}\text{C}$ .

The sample, which had been annealed at  $80^{\circ}\text{C}$ , had a higher storage modulus between the glass transition at  $100^{\circ}\text{C}$  and again an increase near  $120^{\circ}\text{C}$ . Samples annealed at higher temperatures had still high storage moduli above the glass transition.



**Fig. 3** Dynamic mechanical properties of MPMD-12 measured at a frequency of 1 Hz. Top: storage modulus. Bottom: loss modulus

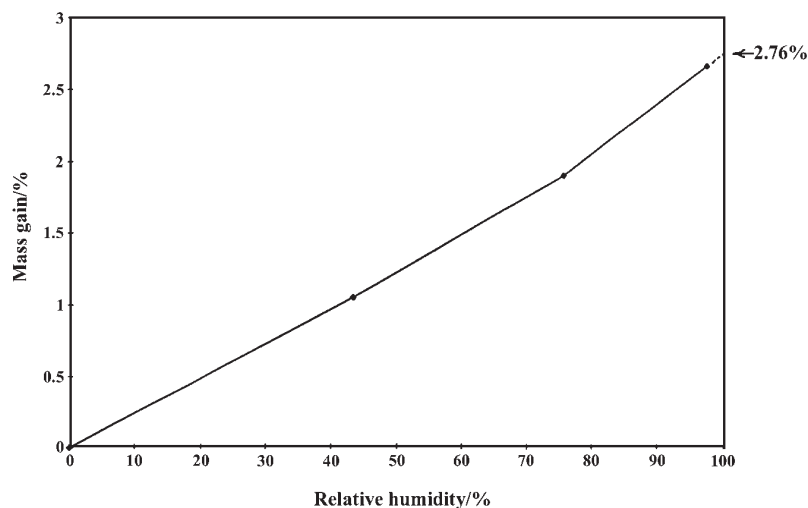


Fig. 4 Mass gain of MPMD-12 vs. relative humidity

The peak associated with the glass transition is the major feature in the loss modulus for all samples, although it is shifted to somewhat higher temperatures by annealing. The sample which had been annealed for 10 min at 150°C had a reduced storage modulus at temperatures between about -60 and +50°C and a double maximum in the loss modulus at about -25 and +30°C. These features were not present in a sample which had been annealed at 150°C for 1200 min. Clearly, 10 min at this temperature is not sufficient to produce a fully ordered state.

A sample, which had been cooled slowly from the melt, had the highest storage modulus and a relatively low loss modulus at most temperatures. All samples showed a small maximum in the loss modulus near -120°C where the gamma relaxation is generally seen in polymers having sequences of four or more methylene groups.

### Dielectric properties

The dielectric constant of MPMD-12 is about 3.7, which is similar to those of other dry nylons at room temperature [1]. At a frequency of 1 kHz, the maximum in the dissipation factor corresponding to the alpha relaxation or glass transition occurs at 68°C, and the gamma relaxation which is attributed to local motions of the hydrocarbon chain segments is observed at -60°C. There is a shoulder near 0°C, which is attributed to the beta relaxation, a feature, which becomes more prominent in nylons, which have absorbed water.

The dependence of the mass gain at equilibrium on the relative humidity is shown in Fig. 4. The mass gain at 97% RH is 2.76%, and the relationship is almost linear. The peak temperatures for the alpha relaxation at various relative humidities and frequencies are shown in the Table 1.

**Table 1** Temperature for the dielectric alpha relaxation/°C

% RH	10 Hz	100 Hz	1 kHz	10 kHz	100 kHz
0	55.4	59.8	67.3	77.5	90.9
43.2	37.1	–	50.0	59.4	77.9
97.3	10.0	16.6	24.3	36.7	52.0

The amount by which this temperature decreases between 0 and 97% RH decreases with increasing frequency from 45°C at 10 Hz to 39°C at 100 kHz. This is equivalent to a decrease in the apparent activation energy from 77 kcal mol<sup>-1</sup> in the dry sample to 50 kcal mol<sup>-1</sup> at 97% RH.

The effect of relative humidity on the mass gain and the temperature of the alpha relaxation in MPMD-12 is much less than in nylon 66 or nylon 6 but is comparable to that for the isomeric polymer, nylon 612 [1]. These properties in nylons are primarily determined by the concentration of amide groups in the polymer chain.

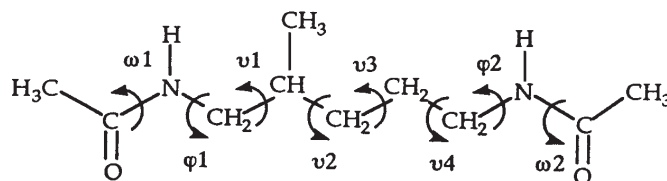
As in the case of the dynamic mechanical relaxations, most dielectric relaxations in polymers are properties of the amorphous regions, although the presence of crystallinity may shift the glass transition or alpha relaxation to higher temperatures. As was found for MPMD-6 [2], the principle effect of the methyl branches in MPMD-12 is a small increase in the temperature of the gamma relaxation.

### *Crystallography*

We have found polymorphism in polyamides based on MPMD and aliphatic diacids containing either an even or odd number of carbon atoms (e.g. MPMD-6, MPMD-10, MPMD-12, MPMD-7, and MPMD-9). In MPMD-T, three crystalline phases have been observed [3]. Since polymorphism does not occur in analogous polyamides based on pentamethylene diamine or hexamethylene diamine, this feature is clearly related to the presence of the methyl side group. Many aliphatic polyamides have a conformation close to the planar zigzag found in polyethylene. However, if an odd-even polyamide such as MPMD-12 is to have all its hydrogen bonds in a single plane, there must be a 180° twist in the diamine moiety. There is also the problem of crowding between the atoms of the amide group and the methyl side group on the number two carbon atom.

Valuable insights into these issues can be gained from ab initio quantum mechanical studies on the diacetamide of MPMD by Alemán and Puiggali [5]. Their designations for the bonds in the mainchain of this model compound are shown in Fig. 5. The bonds,  $v_3$  and  $v_4$ , which connect pairs of CH<sub>2</sub> groups were assumed to be trans. It was found that the bonds  $\omega_1$  and  $\omega_2$  within the amide groups deviate at least slightly from planarity. The most favorable conformation for  $\phi_1$  and  $\phi_2$  were found to be skew, neither trans nor gauche. Changing  $v_1$  from trans to gauche reduced the clash between the amide oxygen and the methyl side group. As shown in Fig. 5, several conformations have fairly close energy levels. The barriers between them are relatively low, indicating that there is a good deal of flexibility within the diamine moiety.

Studies by X-ray diffraction have shown that at relatively low temperatures MPMD-12 forms a crystal with a two-chain orthorhombic unit cell ( $a=5.00$  Å,



$\omega_1$	$\phi_1$	$\nu_1$	$\nu_2$	$\omega_2$	$\phi_2$	$\Delta E$
-178.7	-120.0	-172.2	171.7	-120.0	-179.6	0.0
172.6	120.0	-175.6	168.4	120.0	176.0	0.2
-170.1	60.0	-175.5	171.0	60.0	-169.2	1.0
-170.7	180.0	-170.5	172.4	180.0	179.7	1.3
169.2	-60.0	-65.5	167.2	-150.0	168.4	1.6

**Fig. 5** Low energy conformations for the diacetamide of MPMD: from Alemán and Puigallí [5], used with permission

$b=8.66 \text{ \AA}$ ,  $c=21.7 \text{ \AA}$ ) having chains located at the corner and center of the unit cell and a fiber repeat corresponding to a single chemical repeat unit.

Unlike nylon 66 in which the amide groups are coplanar, the planes of the amide groups are rotated  $60^\circ$  to each other, allowing the chain in the center of the unit cell to hydrogen bond to the four corner chains. The MPMD moiety adopts an extended chain conformation with the amide group near the methyl branch rotated approximately  $90^\circ$  from the position in nylon 66 to remove steric compression caused by the methyl group. This structure has many of the characteristics of the gamma structure which has been found in a number of nylons such as 55 and 65, and we have given it that designation [4].

At higher temperatures, MPMD-12 adopts a completely different structure characterized by a one-chain monoclinic unit cell ( $a=5.74 \text{ \AA}$ ,  $b=4.86 \text{ \AA}$ ,  $c=38.95 \text{ \AA}$ ,  $\gamma=120.5^\circ$ ). The fiber repeat consists of two chemical repeats related by a  $2_1$  helical operation. The chain adopts a zig-zag conformation consisting of extended diacid moieties with MPMD moieties in a bent conformation that allows the chain to change direction. The amide groups are oriented normal to the plane of the zig-zag and hydrogen bond to an equivalent chain related by simple translation. We will call this structure which is very different from those observed in non-branched aliphatic polyamides the delta form.

The conversions from the gamma to the delta form are accompanied by a shrinkage of 10% in the  $c$  (fiber axis) direction. The projected chemical repeat decreases from  $21.7 \text{ \AA}$  in the gamma form to  $19.5 \text{ \AA}$  ( $38.95 \text{ \AA}/2$ ) in the delta form. In fibers held under modest tension, this transformation can take place without loss of orientation. However, the macroscopic shrinkage is much greater than in proportion to the change in the projected chemical repeat in the crystal. In fact, if one attempts to hold a fiber at constant length during the transformation, it will break.

As was reported in [4], for fibers held under tension overnight at various temperatures, the gamma-delta transformation takes place between  $125$  and  $140^\circ\text{C}$ .



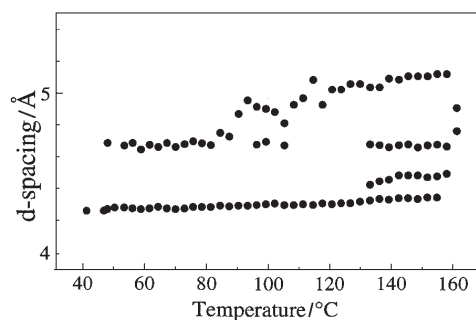
Referring back to the DSC curve for the quenched sample of unoriented MPMD-12 in Fig. 1, we wish to know which of the endotherms corresponds to the exotherm at 55°C and which to the exotherm at 100°C. The samples annealed at 80 and 150°C each contain a single form. If they are the same, the lower temperature exotherm must correspond to the higher temperature endotherm, and the higher temperature exotherm must correspond to the lower temperature endotherm. If not, the opposite must be true, and lower corresponds to lower and higher to higher.

Fortunately, three orders of meridional diffraction are observed as illustrated in Fig. 3 of [4]. As expected for an amorphous polymer, a scan from a quenched sample showed no such peaks. For the sample, which had been annealed at 80°C, the second and third order peaks corresponded closely to the gamma form. Equally clearly, the peaks for the slow cooled sample and that annealed at 150°C belong to the shortened delta form. The positions of the peaks in the diffraction pattern from the sample annealed at 130°C suggest that both forms were present in this sample. From these observations, we conclude that the exotherm at 55°C and the endotherm at 144°C are associated with the gamma form, while the exotherm at 100°C and the endotherm at 162°C are associated with the delta form.

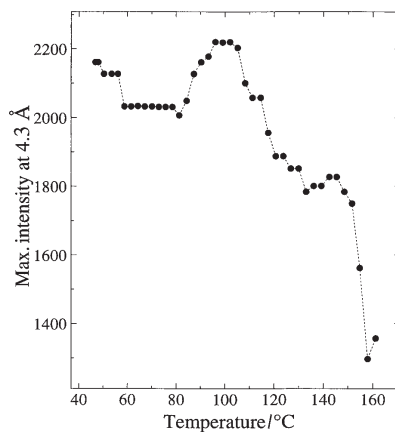
It should be noted, however, that a different conclusion was reached in [4] largely based on DSC scans from oriented fibers and the thermal history of films after isothermal crystallization. It should also be recognized that, as discussed with respect to Fig. 2, there is clear evidence of partial melting of the gamma form and recrystallization as the delta form in the regions of the 100° and 144°C transitions.

#### *Synchrotron experiments*

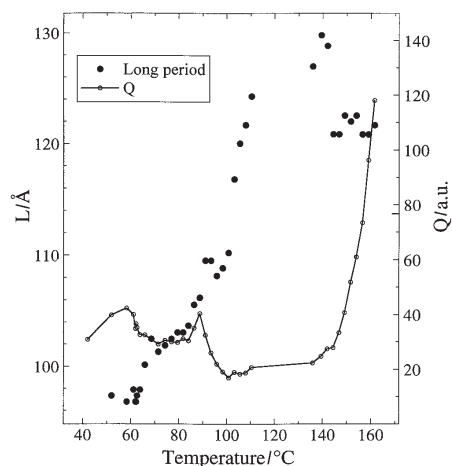
The SAXS data were analyzed by the method of correction function [10]. With this method (after determining the Porod constant and correlating the liquid scattering and finite interference between the scattering phases), we can calculate several morphological variables including the long period ( $L$ ), lamellar thickness ( $L_c$ ), amorphous layer thickness ( $L_a$ ), and the scattering invariant ( $Q$ ), assuming that the system follows a two-phase lamellar stacks model. Only the values of  $L$  and  $Q$  will be reported here. For the WAXD data, the integrated intensities, peak positions, and peak



**Fig. 6** Values of the  $d$ -spacings determined from the WAXD profiles during the heating of a quenched sample at  $2^{\circ}\text{C min}^{-1}$



**Fig. 7** Diffraction intensity at the  $d$ -spacing of  $4.7 \text{ \AA}$  determined from the WAXD profiles during the heating of a quenched sample at  $2^\circ\text{C min}^{-1}$



**Fig. 8** Values of the long period  $L$  and invariant  $Q$  determined from the SAXS profiles during the heating of a quenched sample at  $2^\circ\text{C min}^{-1}$

widths for the crystal reflection peaks and amorphous background were calculated by a deconvolution method (all peaks were chosen to be Gaussian) using program GRAMS/21 Spectral Notebook™ (Galactic Industries Corporation).

The values of the  $d$ -spacing determined from the peak positions in the WAXD profiles during heating are shown in Fig. 6. At temperatures below about  $80^\circ\text{C}$ , three  $d$ -spacing ( $8.6$ ,  $4.7$  and  $4.3 \text{ \AA}$ ) are seen. These values are consistent with the parameters for the gamma crystal form discussed earlier. In the region near the exotherm at  $100^\circ\text{C}$ , the spacing at  $4.7 \text{ \AA}$  increased to about  $4.9 \text{ \AA}$  and continued to increase somewhat with rising temperature. In the region of the first endotherm near  $144^\circ\text{C}$ , the spacing at  $8.6 \text{ \AA}$  disappeared. Between about  $133$  and  $158^\circ\text{C}$  where the delta crystal form is most prominent,

additional peaks appeared between 4 and 5 Å. Finally, all crystalline peaks disappeared in the region of the second endotherm near 160°C.

The maximum intensity of the peak at a  $d$ -spacing of 4.7 Å is plotted vs. temperature in Fig. 7. Maxima are associated with the exotherm and endotherm combinations indicating partial melting and recrystallization near 100 and 145°C. As expected, the intensity falls away as the final melting point is approached.

The long period ( $L$ ) and the invariant ( $Q$ ) from the SAXS data are plotted vs. temperature in Fig. 8. The long period increases steadily from 97 Å at 60°C to 130 Å at 140°C and then decreases to 122 Å as the final melting point is approached. The corresponding decrease in the lamellar ( $L_c$ ) from 97 to 83 Å corresponds to the differences in the unit thickness cell  $c$ -parameters between the gamma and delta crystal structures. In each case, the lamellar thickness is equivalent to about 4.2 chemical repeat units. The invariant ( $Q$ ) is indicative of the variation of density within the sample and inhibits maxima in the regions where crystallographic changes occur. The major peak is seen at the final melting point, and secondary peaks occur near 60 and 90°C near the exotherms, which were observed by DSC.

## Conclusions

Like other polyamides based on 2-methylpentamethylenediamine, MPMD-12 can be quenched to an amorphous state. Crystallization is relatively slow and leads to multiple crystalline states depending on the thermal history. Because of the relatively low concentration of amide groups, both the sorption of water and the melting point are lower than those of most polyamides.

This combination of properties leads to a number of applications which are related to the polymer's adhesive properties. An important example is powder coating for which no primer is required. Other applications include heat-sealable films, heat or ultrasonic fusible filaments or fibers, and bubble insulation film.

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