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# POLYMORPHISM IN POLYAMIDE OF DYTEK®-A AND DODECANEDIOIC ACID

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## Abstract

Our X-ray work of Dytek®-A, 2-methyl-pentamethylenediamine, containing polyamides shows polymorphism, whereas the polyamides with linear diamines do not. The polyamide of Dytek®-A and dodecanedioic acid, MPMD-12, is singled out for discussion and compared with the unbranched analogs of polyamides 6,12 and 5,12. Due to the presence of the $-CH_3$ side group in the 2-position of the diamine, the polyamide MPMD-12 exhibits two stable crystal conformations. The new δ polymorph is not seen in linear polyamides 6,12 and 5,12.

Studies by DSC polyamide MPMD-12 clearly illustrates at least two crystal forms, γ and δ, coexisting over a wide temperature range, and the isolation of each phase is possible by controlling temperature and time. The DMA modulus in the temperature region between the glass transition (or alpha relaxation) and melting transition shows strong dependence on the thermal history as demonstated in a study of crystallization kinetics.

**Keywords:** branched diamine, melting, polyamides, polymorphism, transformation, WXRD

## Introduction

2-Methyl-pentamethylenediamine (MPMD) (CAS Registry No. 15520-10-2), an isomer of hexamethylene diamine (HMD), is sold under the trade name, Dytek®-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 the polymer chain from either end, the methyl group can be on either the second or the fourth carbon atom. Thus, the methyl groups are to be distributed at random among four positions in the polymer segments.

The driving force for polymorphic transformation in polyamides is the optimization of hydrogen bonding in addition to the standard consideration of group conformation and crystallization rate [1]. The properties of polyamide MPMD-6 and copolymers with polyamide 66 have been described by Stouffer *et al.* [2]. The polyamide derived from MPMD and terephthalic acid (MPMD-T) has been described by Menczel *et al.* under the designation Nylon M5T [3].

In this paper we describe the structure, physical transitions and end use properties as well as the dynamics of the crystallization and lamellae thickening effect,

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polymorphism and thermal properties of the polyamide MPMD-12, which is derived from MPMD (Dytek®-A) and dodecanedioic acid (CAS Registry No. 693-23-2). The polyamides 5,12 and 6,12 are used to standardize the properties of the unbranched analog of similar diamine backbone carbon skeleton or total diamine carbon. A more complete account of the investigation including properties other than those discussed here will be attempted at a later time.

## Experimental

### *Materials and preparation*

The polyamide MPMD-12 was prepared by heating a salt solution in an autoclave containing 37.5 g dodecanedioic acid, 19.1 g 2-methyl-pentamethylenediamine and 35 g water. The pressure control was set for 250 psig and the solution was heated to 250°C with agitation. After reaching 250°C, the pressure was reduced to atmosphere over one h while increasing the temperature to 280°C. The polyamide was finished in 45 min. The number average molecular mass, *Mn*, was 18000 as measured by end group analysis. Polyamides 5,12 and 6,12 were prepared similarly with the appropriate salt solutions.

As-spun fibers of the polyamide MPMD-12 were annealed overnight under moderate tension at 60, 70, 80, 90, 100, 110, 125, 130, 135, 140, 145, 150 and 175°C for wide-angle X-ray analyses (WXRD) at ambient conditions. A stock amorphous film was also prepared by quenching the melt-pressed polyamide MPMD-12 in a cold second press and stored in a dry box for DSC and DMA analyses. The crystalline MPMD-12 films were prepared by annealing at 80, 130 and 150°C for 10 min each for DMA analyses. One additional MPMD-12 film was annealed at 150°C for 10 h for the reason will be discussed below.

### *X-ray diffraction*

X-ray diffractometry scans were collected at room temperature in the symmetrical transmission mode using an automated Philips diffractometer and CuK$_\alpha$ radiation. Data were collected in a fixed time mode with a step size of 0.05° and run from $2\theta=2°$ to 45° in the meridonal and equatorial directions.

### *DSC for melting and the kinetics of isothermal crystallization*

Crystallization kinetics was studied by heating 10 mg of the polyamide in Perkin-Elmer DSC7 at 50 K min$^{-1}$ rate to 250°C. After holding for 3 min at the melt temperature, the specimen was rapidly cooled at 200 K min$^{-1}$ to a crystallization temperature between 80 and 160°C and held there until crystallization was completed. The time required varied from 15 to 600 min. The crystallization between 35 and 80°C was carried out by quenching the polyamide from the melt first to liquid nitrogen temperature and transferring to a sitting cold cell at 5°C. After holding for 3 min at 5°C, the specimen was rapidly heated at 200 K min$^{-1}$ to the crystallization temperature and held there till completion. The halftimes at the peak positions were regarded as a measure of the rates of crystallization at the holding temperatures. All dynamic scans for probing thermal behavior of MPMD-12 at various stages of heat treatment were carried out in a TA Instruments 2920 DSC at the standard 10 K min$^{-1}$.

### *Dynamic mechanical analysis*

A film 10×10×0.12 mm was scanned in Seiko Instruments DMS 210 in the tensile mode from –150 to 150°C at 2 K $\text{min}^{-1}$ and 6 frequencies (1, 2, 3, 5, 10, 20 Hz). The amplitude was at 10 μm and the film tension was set to attenuate automatically with temperature from an initial force of 100 to a minimum of 5 g.

## Results and discussion

### *Polyamide MPMD-12*

Designing specialty aliphatic polyamides is made possible from a large selection of diacids and diamines. Polyamide MPMD-12, 2-methyl-pentamethylene dodecanedioamide, combines nylon's hardness and strength with olefinic adhesion and flexibility. Because of the optical activity and asymmetry of the Dytek®-A moiety, the incorporation of this diamine moiety produces an inherently disordered structure. Figure 1 displays DSC scans of MPMD-12, 5-12 and 6-12. While the quenched linear polyamides show single melting transitions and very minute cold crystallization, MPMD-12 shows complicated cold crystallization transitions at 55 and 100°C and a partial melting transition in-between at 92°C, followed by crystal melting transitions at 144 and 162°C and a crystal reorganizing event between them at 151°C. It appears that heat treatments between the thermal events at 80, 130 and 150°C can simplify the analyses. We have found that all polyamides, both aliphatic and aromatic, containing MPMD show similar polymorphism.

### *The γ-form structure*

All even-odd, odd-even and odd-odd nylons as well as the even nylons containing more than seven carbon atoms crystallize in the γ crystal form [1]. As spun fibers of MPMD-12, and fibers heat treated under tension at low temperature (≤125°C) are observed to associate in the γ phase. Figure 2a shows the fiber diffraction pattern of a MPMD-12 fiber bundle heat treated at 120°C overnight. (The diffraction pattern was collected at room temperature.) The pattern shows a series of meridional reflec-

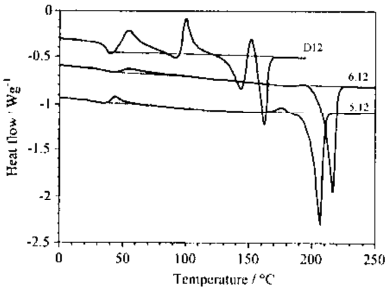

**Fig. 1** DSC scan of quenched polyamide MPMD-12: two crystallization peaks, two melting peaks and crystal γ-δ transformation transient peaks as compared to single melting peaks of polyamides 6,12 and 5,12

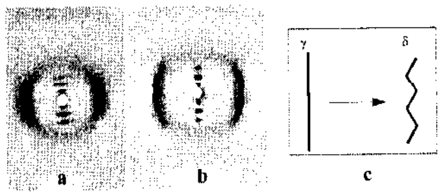

**Fig. 2** Fiber diffraction patterns of (a) the γ crystal form and (b) the δ* crystal form, (c) schematics of chain conformations

tions and a single broad equatorial reflection. The pattern was indexed for a two chain orthorhombic unit cell with dimensions $a$=5.00, $b$=8.66, $c$(fiber repeat)=22.1 Å with a single chemical residue in each chain fragment.

### *The δ-form structure*

The fiber diffraction pattern collected from the same MPMD-12 fiber bundle after heat treatment overnight at 150°C is shown in Fig. 2b. (Diffraction pattern was collected at room temperature.) In addition to the series of three sharp meridional reflections, the pattern shows 20+ (independent) general reflections. The MPMD-12 adopts a two-fold helix conformation and packs in a one chain monoclinic unit cell with dimensions $a$=5.74, $b$=4.86, $c$(fiber axis)=39.98 Å, γ=120.5°. While the γ polymorph has diffracted intensity concentrated on the equator, in this new δ polymorph, the intensity is concentrated in a four-point pattern indicating a zig-zag conformation (Fig. 2c). This mode of packing/chain conformation has not been observed in linear polyamides. As expected, this transition is accompanied by decrease in the projected chemical repeat length from 22.1 in the γ form to 20 Å (=39.98 Å/2) in the δ form.

### *The γ–δ transformation with temperature*

The meridional diffractometry scans from the same fiber bundle after heat treatment under tension at 120 (γ phase) and 150°C (δ phase) are shown in Fig. 3. The positions and relative intensities of the meridional reflections are different in the two phases. The positions of the reflection were determined and the projected chemical repeat was determined by a least squares refinement for each sample.

The projected chemical repeat distance determined for a series of heat treatment temperatures is shown in Fig. 4 The γ–δ transition in constrained fibers (overnight heat treatment) occurs between 125 and 140°C. The projected chemical repeat of MPMD-12 is 22.1 in the γ form and 20.0 Å in the δ form. The γ phase is found in fibers annealed between ambient and 125°C. The melting point of the extended rod-like orthorhombic γ forrn of polyamide MPMD-12 is 159°C. The DSC scans of the fibers were taken after completion of X-ray experiments and shown in insets to Fig. 4. The melting point of the δ form of polyamide D12 varies with annealing temperature due to lamellae thickening. It melts at 145°C in the 135°-annealed fiber, at 151°C in 145°-annealed fiber, at 164°C in the 150°-annealed fiber and at 169°C in the 175°-annealed fiber. The presence of both the γ and δ forms were found between 125 and 140°C (the inset in Fig. 4. is a 135°-annealed).

However, the mixture of γ and δ forms can be obtained at as low as 95°C as suggested in DSC dynamic temperature profile in Fig. 1 when unoriented polyamide

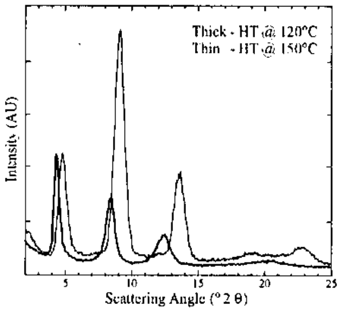

**Fig. 3** The meridional diffraction of MPMD-12 fiber $\gamma$ crystal form heat treated under tension at 120°C and $\delta$ crystal form at 150°C

MPMD-12 was analyzed. The heat flux signals in DSC can follow the transient events, i.e. cold crystallization, melting-recrystallization, solid-solid transformation, which are useful for tracking the crystal evolution and their agreement with crystal structures from WAXD in case of the same thermal history. Figure 5, a series DSC scans follow the thermal history of heat treated unoriented polyamide MPMD-12 and the transformation of form $\gamma$ to form $\delta$. The top curve in Fig. 5 shows that MPMD-12 crystallizes in $\gamma$ form at 55 and in $\delta$ form at 100°C. Before reaching 95°C, there is only $\gamma$ form. Between 95 and 140°C, $\gamma$ and $\delta$ forms are present in different ratios. We believe the metastable rod-like $\gamma$ form of the film melts at 161°C, agreeing well with but slightly higher than the 159°C melting of the constrained $\gamma$ form fiber (Fig. 4). This melting peak, crystallized at a range of temperatures, stays constant at 161°C, and the peak intensity decreases with increase of the crystallization temperature. The stable zigzag $\delta$ form melts at 144°C when it is crystallized at 100°C. This melting point increases to 151°C when it is annealed at 140°C due to the lamellae thickening effect. However, the recrystallization of polyamide MPMD-12 annealed at 150°C, which is exactly the melting point of thickened form $\delta$, will need very long time at least 10 h to reconstruct the crystal form. The lamellae of the newly formed $\delta$ crystals after long annealing time would be substantially thickened to be melted at 164°C. One experiment of 160°C annealing shows a melting peak at 168°C. We observed the same effect in constrained MPMD-12 fibers (Fig. 4).

### *Isothermal crystallization and isolation of $\gamma$–$\beta$ forms*

The annealing time of MPMD-12 films for complete recrystallization between 40 and 150°C was guided by the isothermal crystallization half time study. The critical $\gamma$–$\delta$ conversion information given in Fig. 5 complements the crystallization kinetic data in Fig. 6. The mixture of two forms is readily expected at temperature between 95 and 140°C, the polymorphism of polyamide D12 is apparent: the recrystallization half-times of the pure $\gamma$ form at low temperatures are long; the mixture of $\gamma$ and $\delta$ forms is obtainable at 100–130°C in half-times of 2–3 min. The half-time increases below 100 and above 130°C. In Fig. 6, the two crystallization curves intersect at about 95°C; both the $\gamma$ and $\delta$ forms of MPMD-12 are present in same ratio regardless whether it has been recrystallized for 25 or 600 min. The pure $\gamma$ form is obtainable simply by sitting days at ambient temperature or annealing no higher than 80°C,

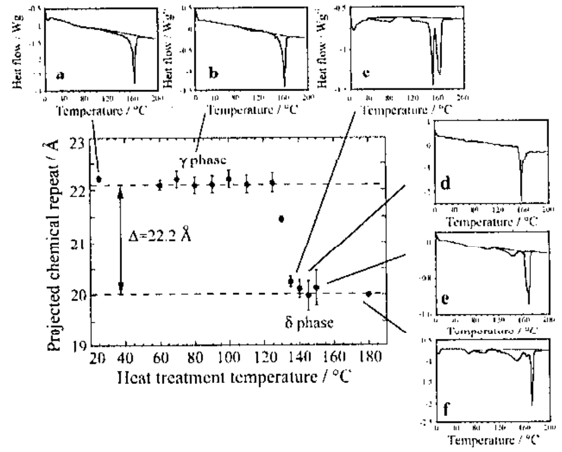

**Fig. 4** The projected chemical repeats in Å at heat treatment temperatures in °C. The DSC insets are the melting points of MPMD-12 γ form and δ form taken after X-ray experiments a) As-spun fiber constrained; Fiber annealed at b) 80°C; c) 135°C; d) 145°C; e) 150°C; f) 175°C overnight/constrained

where as the pure δ form needs 10 h recrystallization at 150°C. This δ form melts at a substantially higher temperature ($T_m$=164°C) than those which exist in mixed two γ–δ forms ($T_m$=144–151°C) described before. We could call it δ* form because of its unique X-ray deflection pattern and substantially thickened lamellar structure.

### *DMA modulus dependence on polymorphism of MPMD-12*

The storage modulus ($E'$) is a measurement of material stiffness. Based on the crystallization program we learned from controlling annealing temperature and time, the modulus profiles of the MPMD-12 in the amorphous form as well as the γ and δ forms are compared by DMA in Fig. 7. The modulus drops above 25°C is the beginning of the α relaxation. The mid-points of the modulus drops $T$ α is the glass transition seen in DSC as step transitions. As expected, the forms are not distinguishable from one another below 25°C. However, above 25°C the morphology of MPMD-12 at various states is quite clear. The amorphous MPMD-12 film has the lowest glass transition temperature at 42°C in the mechanical loss spectrum and goes through two stages of crystallization where the modulus is seen to increase at 60°C for the formation of γ form and at 120°C for the δ form.

The film of the pure γ form obtained from crystallization at 80°C for 10 min shows a slightly higher glass transition at 49°C and further crystallization of the δ form is seen in this curve at 120°C. The film of mixed γ form and δ form, obtained from crystallization at 130°C for 10 min, shows a higher modulus than the amorphous film and the film of pure γ form. We knew that 10 min would be sufficiently long for MPMD-12 crystals to reach their full crystallinity at 130°C. The $T_g$ of this heat-treated film with mixed crystal forms is at 46°C. The isolation of pure δ form, the δ* form to be precise, can be accomplished by annealing at 150°C for at least

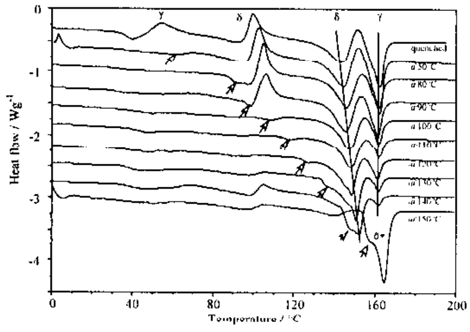

Fig. 5 DSC scans of fully crystallized polyamide MPMD-12 at indicated temperatures: the melting point of the γ form stays constant and decreases in intensity with temperature; the melting point of the δ form increases with annealing temperature

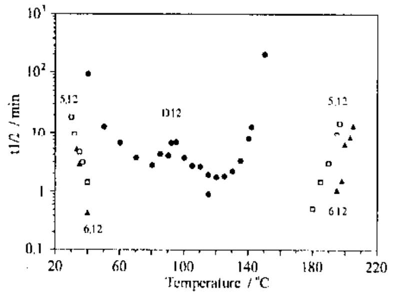

Fig. 6 The isothermal recrystallization halftimes of polyamide MPMD-12 (•) between 40 and 150°C, polyamides 5,12 (▲) and 6,12 (□) between 30 and 210°C

10 h. As mentioned before, 150°C is also the melting point of γ form of a certain lamellar thickness. Therefore, the modulus of the film annealed for only 10 min at 150°C is very low, because the δ form is not yet constructed, and the amount of γ form present is relatively small at this temperature. In fact, the melting point is 162°C recorded in DSC after annealing polyamide MPMD-12 at 150°C for 10 min, indicating that only the γ form is present. After 10 h recrystallization time and the formation of the δ form, however, the modulus tops even the 130°C-annealed MPMD-12 polyamide film. The $T_g$ is seen at 40°C for this film. The modulus at various stages of film morphology satisfies scientific curiosity, yet a best process temperature has to be selected based on economy and film properties.

## *Polyamides 5,12 and 6,12*

The conformation of polyamide 5,12 fiber adopts a rod-like γ extended chain crystal. The observed fiber repeat is 20.12 Å in this case. The recrystallization from melt state of polyamide 5,12 film is fast in a much wider range of temperatures as compared to MPMD-12 (Fig. 6). Only a small fraction of polyamide 5,12 can be

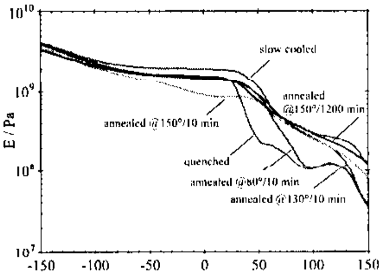

**Fig. 7** The storage modulus curves of MPMD-12 films after quenching and various heat treatments taken at frequency of 1 Hz. Keys are given on the graph

quenched as amorphous phase (Fig. 1). The $T_g$ is 52°C and the melting temperature which is 206°C when PA-5,12 is quenched from the melt, increases slightly to 209°C when it is annealed at 195–197°C for 25 min due to lamellae thickening effect. The storage moduli recorded from –150 to 150°C are very similar when the films were quenched or annealed at 80, or at 150°C.

The conformation of polyamide 6,12 is also a rod-like extended chain crystal. The recrystallization rate of PA-6,12 is even faster than PA-5,12 (Figs 1 and 6). The $T_g$ is 60°C and the melting temperature is 216°C when PA-6,12 is quenched from the melt, and increases slightly to 219°C when it is annealed at 203–205°C for 25 min. The storage moduli are very similar regardless of the treatment conditions.

## Conclusions

The polyamide MPMD-12 fiber shows γ and δ crystal forms, whereas the linear 6,12 and 5,12 are only in the γ form responding to heat treatment. The transformation can be illustrated simply as conversion of a rod-like to zigzag conformation (Fig. 2c) driven by optimization of hydrogen bonding to accommodate the methyl group. The melting point of the stable δ form is slightly lower than the metastable γ form. The isolation of the pure γ and δ forms are possible by annealing. The modulus of MPMD-12 films depends on the heat treatment, i.e. the presence of the γ, δ and mixed forms.

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