

# Changes in Structure of PA6 During Processing

B. JURKOWSKI,<sup>1</sup> Y. A. OLKHOV,<sup>2</sup> K. KELAR,<sup>1</sup> O. M. OLKHOVA<sup>2</sup>

<sup>1</sup> Plastic and Rubber Processing Division, Poznan University of Technology, Piotrowo 3, 61-138 Poznan, Poland

<sup>2</sup> Institute of the Problems of Chemical Physics, Russian Academy of Sciences, Chernogolovka, Moscow Region, Russia

Received 1 August 1999; accepted 1 September 1999

**ABSTRACT:** Using thermomechanical analysis, the molecular weight distribution and relaxation transitions were investigated in commercial PA6 and in this polymer after passage through an extruder with a static mixer. A diblock or triblock amorphous structure and a crystalline portion in the studied PA6 were found. These amorphous structures differ in the glass transition temperatures by 80–180°C. There was a principal difference in the topological and molecular structures of PA6 depending on the processing conditions—number of cycles and shear rates. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 80: 2361–2368, 2001

**Key words:** compounding; melt mixing; PA6; TMA; topological structure; MWD

## INTRODUCTION

The properties of a polymer depend on the molecular and topological structures of its physical and/or chemical intermolecular interactions. Transformation of these structures during processing is the usual case. In our laboratory, a prototype static mixer was designed, which allows one to control the processes of the mechanochemical grafting of polymers and the blending of immiscible polymers under defined shear stresses.<sup>1–4</sup> To understand better why the processing conditions (number of processing cycles and shear rates during melt-mixing) influence the properties of the polymer, it is necessary to know what changes there are in the structure of the polymer's network. The method of thermomechanical analysis (TMA) of solid polymers was used to evaluate the molecular and topological structures without degradation of their intermolecular junctions.<sup>5–12</sup> In previous articles,<sup>3,4,9,10,12–16</sup> small parts of this complex problem were studied. It could be expected that the presence of different

depths of degradation of the mixed particular elements of the polymer structures resulted from the simultaneous action of heat and shearing stresses during processing, depending on the applied shear stress and the number of passages through the static mixer. This degradation could be reflected in changes in the molecular and topological structures of the polymer. Polyamide is a very important engineering plastic and it is often melt-mixed with other polymers. Also, as a thermoplastic material, it is many times reprocessed. These change the polyamide structure and the related properties. These phenomena have not been fully understood up to now. The aim of this work was to investigate some changes in the molecular and topological structures of polyamide 6 (PA6) at different processing conditions, for example, with a temperature about 230°C, shearing forces, and the presence of some oxygen.

## METHODOLOGY

The adopted method is based on measurements of the sample deformation under a very low load and at a temperature which varies against time, giving the thermomechanical curve (TMC). From

Correspondence to: B. Jurkowski (Boleslaw.Jurkowski@put.poznan.pl).

*Journal of Applied Polymer Science*, Vol. 80, 2361–2368 (2001)  
© 2001 John Wiley & Sons, Inc.

this curve, the glass transition temperature,  $T_g$ , and the temperature at the beginning of the molecular flow,  $T_f$ , were evaluated. This methodology of measurements and calculations of the molecular weight distribution (MWD), the crystallinity degree, and the share of blocks with different thermal properties was described in detail in refs. 5–12.

## EXPERIMENTAL

### Materials

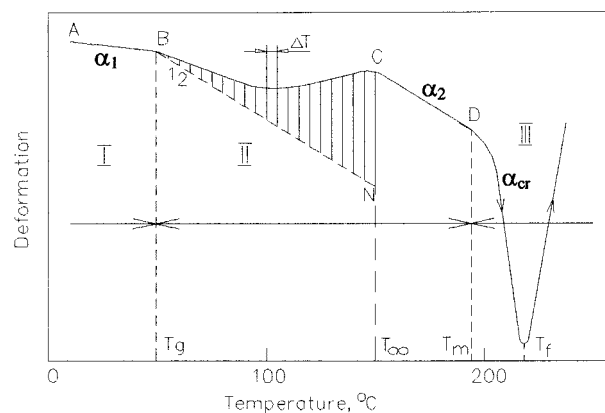
In this study, PA6 (Tarnamid T-27) with a density of  $1.12 \text{ g/cm}^3$ , a melting point of  $220^\circ\text{C}$ , and an MFI ( $220^\circ\text{C}$ ;  $21.1\text{N}$ ) =  $23.4 \text{ g/10 min}$ , made by the Nitrogen Chemistry Plant (Tarnów, Poland), was used. PA6 was dried before use in a vacuum oven at  $80^\circ\text{C}$  for 48 h.

### Sample Preparation

PA6 was mixed using laboratory equipment based on a modified Brabender plastograph. A static mixer was attached to the extruder of the plastograph to allow the mixing of components in controlled conditions and to obtain very fine dispersions of the molten polymers.<sup>9,13</sup> For a shearing rate of  $29 \text{ s}^{-1}$ , mixing discs of 1.1-mm diameter were used, whereas for a shearing rate of  $16 \text{ s}^{-1}$ , holes of 1.9-mm diameter were made.<sup>4</sup> The length of the static mixer was 120 mm. The rates at which the molten batch was moving through the static mixer were so selected that the batch was in the nitrogen atmosphere in the regions heated up to  $185^\circ\text{C}$  for about 4 min. The process runs at a maximal temperature in the body of the extruder's head of  $220 \pm 5^\circ\text{C}$ . The product as a string was cooled in air to room temperature.

### Methodology of Testing

The polymer string was cut to form cylindrical tablets 2–6 mm in diameter and 1–6 mm in thickness. The samples were put into the heating chamber of the thermomechanical device UIP-70M made by the Russian Academy of Sciences in order to be frozen without pressing under a scanning rate of  $2\text{--}10^\circ\text{C/min}$  to a temperature of  $-100^\circ\text{C}$ . After that, the sample was stored for 10–15 min to stabilize the temperature. A quartz rod with a tip having a radius of 2 mm that pressed a 0.2-g sample was accepted as a pseudodilatometric load. The rod was moved down to contact the surface sample and, further,



**Figure 1** TMC for the virgin tested PA6: (I) zone of the glassy state; (II) zone of the amorphous block; (III) zone of the crystalline portion;  $T_g$ , the glass transition temperature for the amorphous block;  $T_\infty$ , temperature of the beginning of a plateau of high elasticity;  $T_m$ , temperature of the beginning of melting of the crystalline portion;  $T_f$ , temperature of the beginning of flow of the crystalline portion;  $\alpha_1$ , coefficient of linear thermal expansion in the glassy state;  $\alpha_2$ , coefficient of linear thermal expansion in a high-elastic state;  $\alpha_{cr}$ , coefficient of linear thermal expansion of the crystalline portion.

the sample was defrosted with a rate of  $5^\circ\text{C/min}$ . Here, a result of the thermal expansion and the thermomechanical and molecular flow of the sample is understood as deformation. An example of the calculation used was shown in refs. 9 and 10.

## RESULTS AND DISCUSSION

### Virgin Polyamide

The TMC of virgin PA6 is shown in Figure 1. Here, the sectional shading of the transitional zone of the TMC is used as one procedure for dividing the temperature interval  $T_g - T_\infty$  into  $n$  smaller intervals  $\Delta T$  ( $3\text{--}5^\circ\text{C}$  wide) during the molecular parameter calculation of the polymer tested and also of designing the differential function of the MWD. The shape of this TMC is typical for a semicrystalline structure of the sample of polymers. The zone of the glassy state of its amorphous block (the straight line  $AB$ ) is visible up to  $T_g = 55^\circ\text{C}$ . Above this temperature, at point  $B$ , starts the accumulation of the high-elastic thermomechanical deformation and permanent lowering of the modulus of the physical network of the sample that is in the thermal field, which is variable against time (the curve  $BC$ ). This deformation process runs until  $136^\circ\text{C}$ , when the transi-

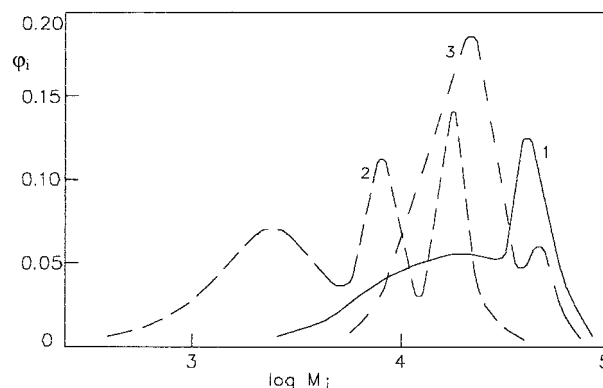
tional zone of the TMC ends. This part of the TMC, being the fencing of all the deformation jumps, resulted from the lowering of the elasticity modulus of the physical network after the successive, as the molecular weight of the homologs between the junctions grows, transfer all the macromolecules into the flowing state ("sol state"). This zone of the TMC reflects a pseudointegral function of the MWD of the chains between the junctions of a crosslinked or pseudocrosslinked polymer.<sup>10,17</sup>

The temperature at point *C* begins a plateau of high-elastic deformation of the amorphous polyamide that resulted from the growth of the free volume  $V_f$ . A rate of deformation is equal to the coefficient of the linear thermal expansion  $\alpha_2 = 16.7 \times 10^{-5} \text{ deg}^{-1}$ . A respective parameter for a glassy state is  $\alpha_1 = 8.76 \times 10^{-5} \text{ deg}^{-1}$ . The ratio of these coefficients, which equals about 2, is essentially lower than is critical (equal to about 7) to differentiate the amorphous from the crystalline structures<sup>18</sup>.

At point *D* on the TMC, a rapid growth was found of the accumulation rate of expansion in expense of the process of melting of a crystalline portion of PA6, which starts at 194°C. This rate of accumulation is equal to  $\alpha_{cr} = 360 \times 10^{-5} \text{ deg}^{-1}$  and  $\alpha_{cr}/\alpha_1 = 41.1$ . The process of the molecular flow of the polymer starts at a temperature of 212°C.

The molecular weight characteristics of the chains creating the amorphous structure of polyamide, calculated based on analysis of the transitional zone of the TMC,<sup>10</sup> were  $\bar{M}_n = 28,500$  (the number-average molecular weight between the junctions of a pseudonetwork),  $\bar{M}_w = 40,800$  (the weight-average molecular weight between the junctions of a pseudonetwork), and the coefficient of polydispersity  $K = \bar{M}_w/\bar{M}_n = 1.43$ . These molecular weights were determined in the bulk. As a result, they could not be correlated with those obtained by measurements in a solution. Figure 2(curve 1) shows the MWD of an amorphous portion of the virgin polyamide. A crystalline portion has a molecular weight of about 1000 and a weight ratio of an amorphous to a crystalline portion of 0.11/0.89, which was evaluated based on the presumption<sup>10</sup> that the total deformation is the sum of its constituents.

In our previous article,<sup>19</sup> another topological structure of such a polyamide was observed. It was characterized as a ratio of the linear thermal expansion coefficients in a plateau of high elasticity of the high-temperature block to a value in the glassy state  $< 6$ , which informed us that the



**Figure 2** (1) MWD of the chains between the junctions in the amorphous block of virgin PA6 and (2) this PA6 after passage through the single-screw extruder and (3) through the single-screw extruder equipped with the static mixer with holes 1.9 mm in size.

system studied had a polyblock amorphous structure. Now, we have a case when such a ratio  $\alpha_{cr}/\alpha_1 = 41.1$ , which evidences that the second topological block could be accepted as having a crystalline nature, because it is over the critical value,<sup>18</sup> which is equal to about 7. The reason for the difference is postulated to be a result of the thermal and stress history in particular points of the tested samples because the TMA method is very sensitive to such outer impacts.

#### Polyamide Structure After One Passage Through the Extruder

The PA6 topological structure after a single passage through the extruder is not changed substantially. However, noticeable changes occur in the molecular structure of its blocks. Also, some temperatures of the relaxation transitions were changed. The molecular characteristics of the amorphous and crystalline structures after this technological operation were substantially changed. In the amorphous block, they were reduced, reaching magnitudes of  $\bar{M}_n = 6400$  and  $\bar{M}_w = 10,000$ . Melt-mixing of PA6, with a screw, resulted in drawing into the crystalline portion its macromolecules with a higher molecular weight from the amorphous one. It affects the mixing with shorter chains, which increases the polydispersity in the crystalline portion. As the result, the coefficient of polydispersity  $K = 1.56$ . The MWD's shape was changed from unimodal into trimodal [Fig. 2(curve 2)].

The content of the crystalline portion decreased from 89 to 55 wt %. The molecular weight of this fraction substantially increased, reaching

a value of about 1 million. The melting of the crystalline portion starts at the temperature of  $T_m = 51^\circ\text{C}$  and a flow begins at the temperature of  $T_f = 196^\circ\text{C}$ . All these facts evidence the essential redistribution of macromolecules included in these structures. As a result, it caused a substantial growth of the flexibility of parts of the macromolecules included in the amorphous block ( $T_g = -64^\circ\text{C}$ ) and some reduction of the compactness of the crystalline portion. This is reflected in that the value of  $\Delta T = T_f - T_m$  increases to  $140^\circ\text{C}$ , which is much higher than that ( $20^\circ\text{C}$ ) for a virgin polymer. It should be mentioned that a very low ( $-125^\circ\text{C}$ ) glass transition temperature for PA6 was also found many years ago by other authors.<sup>20</sup>

### Polyamide Structure After One Passage Through the Extruder with the Static Mixer (Holes 1.9 mm)

As it was for the case when the polyamide was processed passing one time through the single-screw extruder, after a single passage through the extruder equipped with the static mixer (holes 1.9 mm in diameter), the polymer preserved its semicrystalline structure. However, the molecular characteristics in the blocks and temperatures of the relaxation transformations change in a similar manner as in the above-described case. The weight ratio of the amorphous-to-crystalline portion was 0.52:48, meaning that it is preserved practically the same as it was after a single passage through the extruder alone, when the ratio was 0.45:0.55.

The flexibility of macromolecules in a pseudonetworked structure of the amorphous block is intermediate between those in the virgin polymer and such a polymer after processing through a single-screw extruder alone, and the glass transition temperature was equal to  $-15^\circ\text{C}$  (Table I). The temperature at the beginning of melting of the crystalline portion decreased from  $194^\circ\text{C}$  for the virgin PA6 to  $74^\circ\text{C}$ . A new structural attribute in a structure of the crystalline part of the polymer was observed. There, two crystalline structures with different levels of arrangements were found (Fig. 3). Their temperatures at the beginning of both the melting and the flow had the following magnitudes: For the first one,  $T'_m = 74^\circ\text{C}$ ,  $T'_f = 109^\circ\text{C}$ , and the resulting  $\Delta T' = T'_f - T'_m = 35^\circ\text{C}$ , and for the second one,  $T''_m = 133^\circ\text{C}$ ,  $T''_f = 144^\circ\text{C}$ , and the resulting  $\Delta T'' = T''_f - T''_m = 11^\circ\text{C}$ . These structures have approximately the same weight ratios.

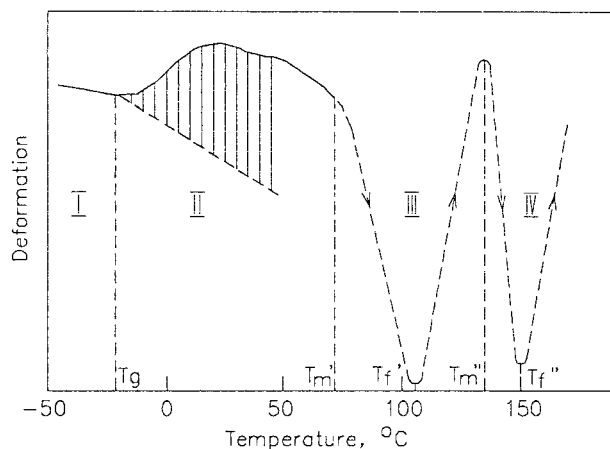
The molecular weight characteristics of the chains between the junctions of the amorphous

**Table I Properties of PA6 After Different Stages of Processing**

Stage of Processing	Low-temperature Block				High-temperature Blocks				Crystalline Portion				
	$T_g$ ( $^\circ\text{C}$ )	$\bar{M}_n$	$\bar{M}_w$	$K$	$\phi_1$	$T_g$ ( $^\circ\text{C}$ )	$\bar{M}_n$	$\bar{M}_w$	$K$	$\phi_2$	$T_m$ ( $^\circ\text{C}$ )	$T_f$ ( $^\circ\text{C}$ )	$\phi_{cr}$
Initial stage (virgin polyamide)	—	—	—	—	0	55	28,500	40,800	1.43	0.11	194	216	0.89
After a single passage through the extruder	-64	6400	10,100	1.56	0.45	—	—	—	—	0	51	196	0.55
Static mixer 1.9 mm	-15	20,060	27,600	1.38	0.53	—	—	—	—	0	74/133	109/144	0.48
Static mixer 1.1 mm	-22	3200	4300	1.34	0.13	99	3460	35,050	10.1	0.87	—	162	0
Static mixer 1.1, two passages	-11	5100	8000	1.57	0.18	137	125,200	414,000	3.31	0.82	—	154	0
Static mixer 1.1 mm, three passages	-67	10,800	16,000	1.48	0.43	123/192	9900/Kuhn	22,500/Kuhn	2.27/—	0.02/0.55	—	202	0
Static mixer 1.1 mm, four passages	-15	9100	15,900	1.75	0.64	107/139	2300/23,100	3100/39,100	1.35/1.69	0.18/0.18	—	196	0

$T_g$ , glass transition temperature;  $\bar{M}_n$ , number-average molecular weight;  $\bar{M}_w$ , weight-average molecular weight;  $K = \bar{M}_w/\bar{M}_n$ , polydispersity coefficient of the chains;  $T_m$ , temperature of the beginning of melting of the crystalline portion;  $T_f$ , temperature of the beginning of flow of the crystalline portion;  $\phi$ , weight shares of the block, Kuhn-Kuhn's segment.





**Figure 3** TMC for PA6 passed through the single-screw extruder equipped with the static mixer with holes 1.9 mm in size: (I) zone of the glassy state; (II) zone of the amorphous block; (III) zone of the first crystalline structure; (IV) zone of the second crystalline structure;  $T_g$ , glass transition temperature for the amorphous block;  $T_m'$ , temperature of the beginning of melting of the first crystalline structure;  $T_m''$ , temperature of the beginning of melting of the second crystalline structure;  $T_f'$ , temperature of the beginning of flow of the first crystalline structure;  $T_f''$ , temperature of the beginning of flow of the second crystalline structure.

block<sup>10</sup> are  $\bar{M}_n = 20,060$  and  $\bar{M}_w = 27,600$ . As the result, the coefficient of polydispersity  $K = 1.38$ . Now, the MWD has some (5–10 wt %) low molecular weight admixtures, which are shown in Figure 2 (curve 3).

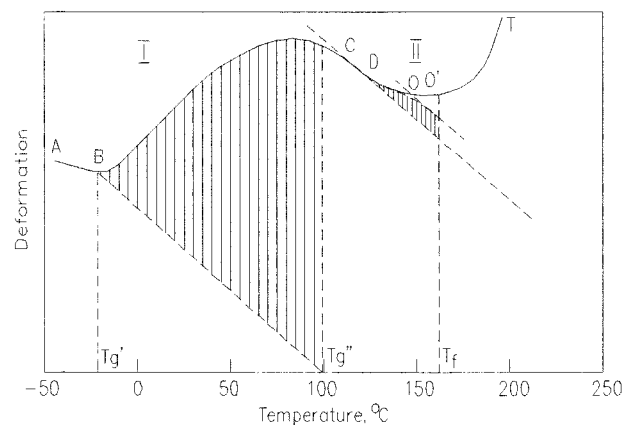
#### Polyamide Structure After One Passage Through the Extruder with the Static Mixer (Holes 1.1 mm)

The topological structure of polyamide after one passage through the extruder with the static mixer with holes of 1.1 mm in diameter is principally different from that described above for processing using a static mixer with larger holes. It is transformed from a semicrystalline structure in the virgin polymer into a completely amorphous diblock topological structure after one passage through the extruder with the static mixer (Fig. 4). In this case, the flowing melt was pressed through the smallest holes of the static mixer, causing high shearing stresses, which destroy the crystalline portion completely. Also, possible degradation of the macromolecules, lowering their molecular weight, could be expected. This was confirmed by the experimental data (Table I). From the TMC of the polymer, it was observed that a straight-line segment of a plateau of high

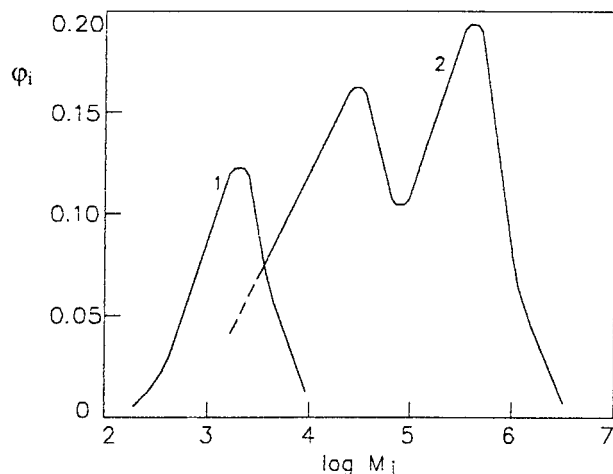
elasticity (the straight line  $CD$ ), if the temperature increases, is transformed into a zone of penetration deformation (the curve  $DO'$ ) of a high-temperature amorphous block. It is different from that for a virgin PA6 (Fig. 1) when it was transformed into the curve describing the melting process of the crystalline portion. At the temperature at point  $C$ , the process of defrosting of the segmental mobility of the most-polar fragments of polyamide chains begins ( $T_g'$ ), which creates a structure of a pseudonetwork of a low-temperature block. Accumulation of the thermomechanical deformation in the transitional zone of a high-temperature block (curve  $CD$ ), as was shown earlier, terminates not at point  $O$ , but 3–5°C higher in point  $O'$  at a temperature  $T_f'$ . The drawing method of the real coordinates of the pseudointegral curve of the MWD in this block (curve  $DO'$ ) was described in ref. 5.

The process of the molecular flow of polyamide starts at a temperature at point  $O$  and is displayed as curve  $OT$ . In this way, one passage through the extruder with the static mixer with holes of 1.1 mm in a diameter is sufficient to homogenize molten PA6, practically causing its transformation fully into the amorphous state, meaning that it suppresses its recrystallization after melt-mixing.

The transition temperatures for low- and high-temperature amorphous blocks were equal to  $T_g' = -22^\circ\text{C}$  and  $T_g'' = 99^\circ\text{C}$ , respectively. These blocks have a weight ratio of 0.87:0.13. The mo-



**Figure 4** TMC for PA6 passed through the single-screw extruder equipped with the static mixer with holes 1.1 mm in size: (I) zone of the low-temperature amorphous block; (II) zone of the high-temperature amorphous block;  $T_g'$ , glass transition temperature for the low-temperature amorphous block;  $T_g''$ , glass transition temperature for the high-temperature amorphous block.



**Figure 5** (1) MWD of the chains in the low-temperature block and (2) linear fragments of the high-temperature block polyamide.

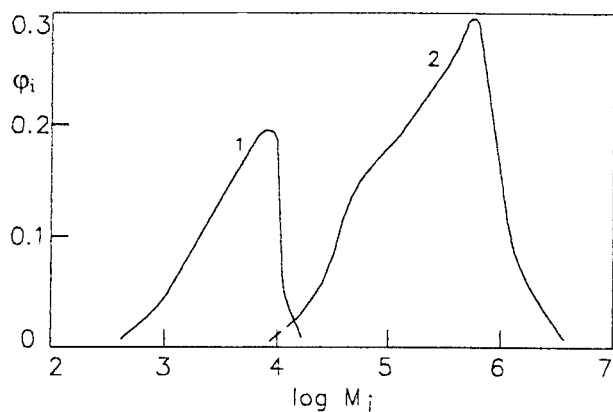
molecular weight characteristics of the chains between the junctions of the pseudonetworked amorphous low-temperature block are  $\bar{M}_n = 3200$  and  $\bar{M}_w = 4300$ . As the result, the coefficient of polydispersity  $K' = 1.34$ . These characteristics for the linear fragments of macromolecules in the high-temperature block are  $\bar{M}_n = 3460$  and  $\bar{M}_w = 35,050$ . Because of this, the coefficient of polydispersity  $K'' = 10.1$ . The abnormally high magnitude of the coefficient of polydispersity evidenced after a single passage of the molten polyamide through the static mixer in addition to the molecular homogenization according to their intermolecular interactions indicates that some mechanochemical processes also took place. These processes probably resulted in the high molecular branching. The MWD of this material is shown in Figure 5.

#### Polyamide Structure After Two Passages Through the Extruder with the Static Mixer (Holes 1.1 mm)

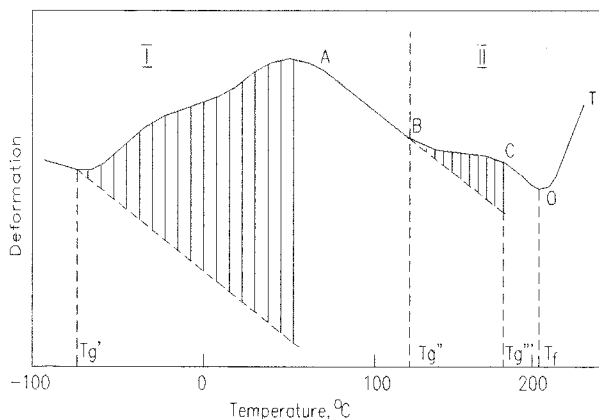
Two passages through the extruder with the above-discussed static mixer having holes of 1.1 mm in diameter did not result in substantial changes to the topological structure of the polymer tested. As it was for one passage through the extruder, the polyamide here also had an amorphous structure with a bimodal MWD (Fig. 6). Also, it is now impossible to obtain the full homogenization of the diphillic structure of the virgin polyamide. Some disorder of the most-polar fragments of the chains, creating a crystalline portion in the virgin polymer and transformation of it into the high-temperature amorphous block, was obtained.

After the second passage through the extruder, the quantitative ratio of the amorphous blocks (0.82:0.18) was changed slightly in comparison with the case of a single passage through the extruder. Also, the remaining molecular characteristics were noticeably changed, namely, the second processing cycle resulted, in our opinion, not only in the redistribution of parts of the macromolecules of different polarity between the blocks, but also in the mechanochemical transformation of the chains. Both of these processes result in the growth of the mobility of fragments of the chains in a structure of the blocks. This results in a noticeable decreasing of their transition temperatures:  $T'_g = -11^\circ\text{C}$  and  $T''_g = 137^\circ\text{C}$ , respectively. Simultaneously, it is followed by some increase in the molecular weight characteristics of the chains between the junctions of the pseudonetworked most-polar high-temperature amorphous block.

A noticeable increase in the "crosslinking degree" in a pseudonetworked structure of the low-temperature amorphous block was observed. The molecular weight characteristics now are  $\bar{M}_n = 5100$  and  $\bar{M}_w = 8000$ . As the result, the coefficient of polydispersity  $K' = 1.57$ . These characteristics for linear fragments of the chains in a high-temperature block are  $\bar{M}_n = 125,200$ ,  $\bar{M}_w = 414,000$ , and, as the result,  $K'' = 3.31$ . The lowering of the  $K$  value from 10.1 after one passage through the static mixer to 3.31 after two passages evidences the reduction in the branching degree of the chain fragments, creating the high-temperature block. The MWD curves for these blocks are shown in Figure 6.



**Figure 6** (1) MWD of the chains in the low-temperature block and (2) linear fragments of the high-temperature block of polyamide after two passages through the single-screw extruder equipped with the static mixer with holes 1.1 mm in size.



**Figure 7** TMC for PA6 passed three times through the single-screw extruder equipped with the static mixer with holes 1.1 mm in size: (I) zone of the low-temperature amorphous block; (II) zone of the high-temperature amorphous block;  $T'_{g'}$ , the glass transition temperature for the low-temperature amorphous block;  $T'_{g''}$ , glass transition temperature for the high-temperature amorphous block;  $T_f$ , temperature of the beginning of the flow.

#### Polyamide Structure After Three Passages Through the Extruder with the Static Mixer (Holes 1.1 mm)

The separation of the fragments of macromolecules in the amorphous blocks that resulted from the differences in polarity observed in PA6 after two passages was strengthened after three passages through the extruder with the static mixer. As a result, the topological polymer's amorphous structure was transformed from diblock to triblock (Fig. 7). Now, two high-temperature pseudocrosslinked blocks were created, the chains of which have different polarity and their two transition temperatures were  $T'_{g'} = 123^\circ\text{C}$  and  $T'_{g''} = 192^\circ\text{C}$ . It is assumed now that the fragments of the macromolecules of polyamide with the lowest polarity were introduced into the network of the low-temperature block as chains between the junctions. The glass transition temperature of this block was  $T'_{g'} = -67^\circ\text{C}$ . The junctions of the network of this block in the temperature interval of a plateau of high elasticity (the straight line *AB*) were created by fragments of the chains of the first high-temperature block that was in a glassy state which resulted from their higher polarity than that between the junctions. At  $T'_{g''}$ , they start to defrost. As a result, there is an accumulation of the thermomechanical deformation as the temperature of the sample increases. This is the result of the successive transformations of more and more molecular weight

homologs between the junctions into the sol state. Here, it created the transitional zone of the TMC.

It is assumed that the pseudonetworked structure of the second high-temperature block, as for the first one, is created by the most-polar fragments of the chains of polyamide. Their molecular weight is directly proportional, as it was in the latter block, to the magnitude of  $\Delta T = T_f - T'_{g''}$ . The TMC of this block is characteristic for linear polymers—the curve *COT*. The lack of a straight line of a high elastic expansion and the transfer of macromolecules from the glassy state into the flowing state is characteristic for the flow of non-polymeric liquids with a molecular weight equal to Kuhn's segment.

The weight share of material having a molecular weight equal to Kuhn's segment after three passages through the extruder with the static mixer did not exceed 2%. The weight ratio of the remaining blocks—the low temperature to the first high temperature—is equal to 0.43:0.55. The molecular weight characteristics of the chains between the junctions in a pseudonetwork are  $\bar{M}_n = 10,800$ ,  $\bar{M}_w = 16,000$ , and, as the result,  $K' = 1.48$ , and  $\bar{M}_n = 9900$ ,  $\bar{M}_w = 22,500$ , and, as the result,  $K'' = 2.27$ .

#### Polyamide Structure After Four Passages Through the Extruder with the Static Mixer (Holes 1.1 mm)

The topological structure of PA6 after four passages through the extruder with the static mixer is principally unchanged in comparison with that of three passages, meaning that a structure with three amorphous blocks is preserved. However, separation of the macromolecules into these blocks of different polarity, having, typically, for polymers glassy, high-elastic, and viscoelastic states, now was slightly more pronounced.

The second high-temperature block after the previous processing regime (three passages) had two states only—glassy and viscoelastic. Because of this, it could not be accepted as a typical polymer structure. After four passages through the extruder with the static mixer, this structure now is different. It has glassy, high-elastic, and viscoelastic states as is typical for polymers. Simultaneously, the weight ratio of this block in PA6 increased. The weight ratios of these blocks is now equal to 0.64:0.18:0.18.

The molecular mobility of the chains in a pseudonetwork of a low-temperature block was noticeably reduced in comparison with such a property of PA6 molecules after three passages through the static mixer. It resulted from the

removal of the fragments of the chains with lower polarity from its structure or from the creation of a spatial pseudonetwork, which disturbed the intermolecular interactions. The glass transition temperature of this low-temperature block increased until  $-15^{\circ}\text{C}$ . Also, in the remaining blocks, it was decreased as the result of the reduction in the polarity of the chain fragments contained.

The molecular weight characteristics of these blocks changed as follows for a low-temperature amorphous block:  $\bar{M}_n = 9100$  and  $\bar{M}_w = 15,900$ . As the result, the coefficient of polydispersity  $K' = 1.75$ . These characteristics for the first high-temperature block were  $\bar{M}_n = 2300$ ,  $\bar{M}_w = 3100$ , and, as the result,  $K' = 1.35$ . For the second high-temperature block, it was  $\bar{M}_n = 23,100$ ,  $\bar{M}_w = 39,100$ , and, as the result,  $K' = 1.69$ .

The properties of all the tested samples of polyamide after different processing conditions are collected in Table I. From these data, it is concluded that some ways of processing PA6 affect the transition temperatures of topological blocks and the temperatures at the beginning of the molecular flow. These characteristics were very sensitive to the size of the holes in the static mixer (changing the shear rates) and the number of processing cycles. Because of this, it could be reasonable to conduct further experiments to study the properties of PA6 versus the shear rate and the number of processing cycles.

## CONCLUSIONS

A diblock or triblock amorphous topological structure and a crystalline portion of a studied PA6 independent of the number of processing cycles and for two shear rates during melt-mixing were observed. The number of topological structures (one amorphous and one crystalline) in the virgin PA6 and in it after a single passage through the extruder and also after one passage through the extruder with the static mixer with holes 1.9 mm in diameter was preserved. However, the molecular characteristics of the chains in the topological blocks and the temperatures of the relaxation transitions were changed.

The topological structure of PA6 after one, two, three, and four passages through the extruder

with the static mixer with the holes 1.1 mm in diameter (when higher shear stresses were applied) was transformed from a semicrystalline structure into a completely amorphous complex structure. These amorphous topological blocks differ substantially in the glass transition temperatures. It suggests that they have different compaction and related solubility of ingredients molten during the compounding and/or processing of complex polymer blends and result in the homogeneity of processed reactive blends.

## REFERENCES

- Jurkowski, B.; Urbanowicz, R.; Szostak, M. Pol. Patent 168 449, 1992.
- Jurkowski, B.; Urbanowicz, R.; Szostak, M. Pol. Patent 168 416, 1992.
- Pesetskii, S. S.; Jurkowski, B.; Krivoguz, Yu. M.; Urbanowicz, R. *J Appl Polym Sci* 1997, 65, 1493.
- Jurkowski, B.; Kelar, K.; Ciesielska, D. *J Appl Polym Sci* 1998, 69, 719.
- Olkhov, Y. A.; Irzhak, V. I.; Baturin, S. M. Rus. Patent 1 763 952, Oct. 27, 1989.
- Baturin, S. M.; Olkhov, Y. A. *Tech Machinebuilding (in Russian)* 1995, 4(6), 20.
- Olkhov, Y. A.; Baturin, S. M.; Irzhak, V. I. *Polym Sci USSR A* 1996, 38, 5, 1.
- Jurkowska, B.; Olkhov, Y. A.; Jurkowski, B.; Olkhova, O. M. *J Appl Polym Sci* 1999, 71, 729.
- Olkhov, Y. A.; Jurkowski, B. *J Appl Polym Sci* 1997, 65, 499.
- Jurkowska, B.; Olkhov, Y. A.; Jurkowski, B. *J Appl Polym Sci* 1999, 74, 490.
- Olkhov, Y. A.; Smirnova, T. N.; Kotova, N. F.; Bublikanova, N. N. *Chim Vysokich Energii* 1995, 4(6), 20.
- Jurkowska, B.; Olkhov, Y. A.; Jurkowski, B. *J Appl Polym Sci* 1998, 68, 2159.
- Kelar, K.; Jurkowski, B. *Polymer* 1999, 41, 1055.
- Jurkowski, B.; Kelar, K.; Ciesielska, D.; Urbanowicz, R. *Kautschuk Gummi Kunstst* 1994, 44, 642.
- Kelar, K.; Ciesielska, D.; Jurkowski, B. *Polimery* 1995, 40, 298.
- Kelar, K.; Jurkowski, B.; Ciesielska, D. *Polimery* 1997, 42, 549.
- Olkhov, Y. A.; Irzhak, V. I. *Polym Sci B* 1998, 40, 357.
- Olkhov, Y. A.; Gorbushkina, G. A.; Baturin, S. M. Rus. Patent N1 713 359 A1, Sept. 11, 1989.
- Jurkowski, B.; Olkhov, Y. A. *J Appl Polym Sci* 1997, 65, 1807.
- Schmieder, K.; Wolf, K. *Kolloid-Z* 1953, 134, 149.