

Enhancing the Drawability of a Polyester by Copolymerization with a Second Type of Crystallizable Block

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ABSTRACT: A polyester-amide segmented block copolymer with short monodisperse amide segments was synthesized along with its neat polyester counterpart. The copolymer, containing 10 wt % amide, displayed a T_g and T_m for the polyester phase as well as a high T_m corresponding to the polyamide. The high-melting amide segments enhanced the dimensional stability of the copolymer and also considerably increased the crystallization rate of the polyester segments. As compared to the neat polyester, the polyester-amide block copolymer could be drawn at higher temperatures and to higher draw ratios. The maximum draw ratio for this copolymer was obtained just a few

degrees below the melting temperature of the polyester segments, and as a result of these higher draw ratios, the fracture stresses were higher. In conclusion, a short monodisperse amide segment in a polyester-amide block copolymer increased the crystallization rate of the polyester, enhanced the dimensional stability, allowed a higher maximum draw ratio, and raised the fracture strength. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 119: 23–30, 2011

Key words: polyester; polyamide; monodisperse; poly(hexamethylene terephthalate); drawing; properties; nucleation; crystallization

INTRODUCTION

The copolymerization of polyesters nearly always lowers the crystallinity, dimensional stability, and the melting temperature.^{1–4} Copolymers of polyester and polyamides demonstrate this effect too, but if their structures are “isomorphic” the lowering of the crystallinity is less significant and a certain increase in melting temperature can be observed.^{5,6} However, such “isomorphic” copolymers have not been seen to display a cocrystallization of the ester and amide units and can thus not be designated truly isomorphic.

A special case of polyester-diamide copolymers concerns materials in which the amide is a monodisperse diamide with a length of only 1.5 repeat units.^{7–11} Copolymers of poly(ethylene terephthalate) (PET),^{9,10} poly(butylene terephthalate) (PBT),^{7,8} and poly(hexamethylene terephthalate) (PHT)¹¹ comprising diamide units of similar structure have been found to display enhanced crystallinities, dimensional stabilities, and melting temperatures as opposed to their neat polyester counterparts. These polyester-amide

copolymers had a single glass transition temperature (T_g) and one melting temperature (T_m). Moreover, increasing the diamide content in such PET, PBT, and PHT copolymers raised the glass transition temperature, the melting temperature, and also the crystallization rate.

The rate of crystallization is often quantified by the value of undercooling ($T_m - T_c$) as determined in DSC experiments at a scan rate of 20°C/min. Upon modification of PET with 10 wt % diamide units, the $T_m - T_c$ value has been seen to decrease from 56 to 49°C,⁹ and the corresponding decrease for PBT was from 36 to 30°C.⁸ The diamide units had a crystal structure differing from that of the polyester and were expected to crystallize adjacent to the polyester segments.⁸ The crystallization temperature of the short diamide segments was too low for them to crystallize before the crystallization of the ester units.

Bis-ester-tetra-amides TxTxT based on a diamine with a methylene length of x and terephthalic acid units (T) are mono-disperse amide segments with an elevated melting temperature.^{12–14} It can be expected that a copolymer of a polyester with such high-melting amide segments should display a single T_g and two melting temperatures. Poly(tetra methylene oxide)-TxTxT block copolymers have three-phase structure; however, the poly(tetra methylene oxide) (PTMO) segments have a melting temperature near

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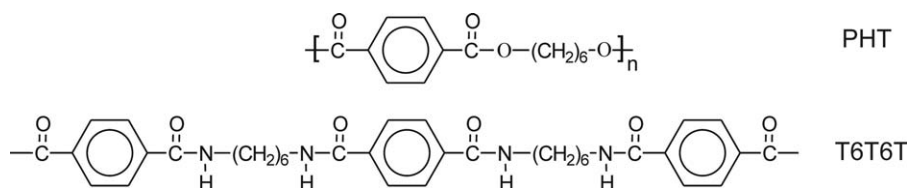


Figure 1 Chemical structures of PHT and T6T6T.

room temperature.^{12–14} The behavior of PTMO-TxTxT might be indicative of the properties of the polyester-TxTxT copolymer.

The TxTxT units in the PTMO-TxTxT copolymers crystallized very fast and fully even at concentrations below 10 wt %. Moreover, TxTxT displayed a high-dimensional stability already at concentrations as low as a few wt %^{12–14}. Copolymers of PTMO and monodisperse hard segments demonstrated a high drawability and excellent tensile properties,^{13,15–17} and optimal tensile properties were found at temperatures in the neighborhood of the T_m of the PTMO, at which the strongest strain hardening response could be observed.¹⁵ Thus, an orientation of these PTMO-amide copolymers could best be done very near the melting temperature of the PTMO. The fracture properties of the copolymers increased strongly with the molecular weight of the copolymers.^{13,17}

Orientation of polyesters is often carried out in steps and the maximum orientation is achieved at a temperature some 20–30°C below the melting temperature of the material.^{18–20} Nearer to the melting temperature, drawing is possible; however, the draw ratio becomes reduced as the drawline stabilization is lost.

This study involved copolymers of PHT and T6T6T segments. As can be seen in Figure 1, the monodisperse T6T6T segment is based on 2.5 repeat units of poly(hexamethylene terephthalamide). The PHT does not have a high-melting temperature (147°C), and the melting temperature of the T6T6T segments was expected to be above 200°C.^{12–14} One objective of the investigation was to determine whether this polyester-tetra-amide copolymer had two melting temperatures, i.e., one for the polyester, and one for the tetra-amide segments. Also, if the polyester and the tetra-amide had “isomorphic structures”, like with PHT and T6T6T, whether the early crystallizing amide segments influenced the polyester melting temperature. Furthermore, whether it would be possible to orient the polyester-amide at a higher temperature and to a higher draw ratio in the presence of the high-melting amide phase, similarly to PTMO-tetra-amide copolymers.

EXPERIMENTAL

Dimethyl terephthalate (DMT) and hexanediol (HDO) were purchased from Merck. Tetra-isopropyl orthotitanate $\text{Ti}(\text{i-OCH}_3)_4$ was also obtained from Merck and was diluted in anhydrous *m*-xylene to 0.05 mol %. T6T6T-dimethyl was synthesized according to a procedure described elsewhere and the resultant product had a melting temperature of 316°C and a heat of fusion of 129 J/g.¹²

PHT polymerization

A 250 mL three-necked, straight-walled stainless steel reactor, equipped with a nitrogen inlet/outlet, magnetic stirrer, and condenser unit, was charged with 39.1 g of DMT, 61.9 g of HDO (2.6× excess), and 0.27 g of $\text{Ti}(\text{i-OCH}_3)_4$ catalyst in toluene. The reaction flask was placed in an oil bath, heated to 180°C, and kept at this temperature for 60 min during which time methanol boiled off. The reaction mass was then further heated to 250°C in 75 min, and once the temperature was reached, a low vacuum (15 mbar) was applied for 60 min followed by a high vacuum (0.1 mbar) for 120 min. Subsequently, the flask was cooled, and the polymer removed and ground to fine particles.

PHT-T6T6T₁₀ polymerization

A 250 mL three-necked, straight-walled stainless steel reactor, equipped with a nitrogen inlet/outlet, magnetic stirrer, and condenser unit, was charged with 35.2 g of DMT, 172 g of HDO (8× excess), 6.04 g of T6T6T-dimethyl, and 0.27 g of $\text{Ti}(\text{i-OCH}_3)_4$ catalyst in toluene. The reaction flask was placed in an oil bath, heated to 180°C, and reacted for 60 min at this temperature. During this time, the reaction mass became homogenous and methanol boiled off. The reaction mass was then further heated to 250°C in 75 min, and at this temperature, a low vacuum (15 mbar) was applied for 60 min. Now, the excess HDO boiled off. In the last step, the reaction temperature was increased to 260°C and the vacuum was lowered to 0.1 mbar for 120 min. Subsequently, the flask was cooled, and the polymer removed and

ground into fine particles. The so-obtained copolymer was postcondensed in an oven at 170°C for 24 h at a vacuum of 0.1 mbar.

Viscometry

Solution viscosities were measured at a concentration of 0.1 g/dL in a mixture of phenol/1,1,2,2-tetrachloroethane (1 : 1 molar ratio) at 25°C using a capillary Ubbelohde type 1B viscometer. From the obtained results, the inherent viscosities were calculated.

Fourier transform infrared spectroscopy

Fourier transform infrared spectroscopy (FTIR) spectra were recorded on a Nicolet 20SXB FTR spectrometer with a resolution of 4 cm⁻¹. The polymer was dissolved in hexafluoro isopropanol (0.3 wt %) and drops were added to pressed KBr tablets.

Nuclear magnetic resonance

¹H NMR spectra of the polymers were recorded on a Bruker Spectrometer at 300 MHz, and deuterated trifluoro acetic acid was used as a solvent.

Differential scanning calorimetry

Differential scanning calorimetry (DSC) spectra were recorded on a Perkin Elmer DCS7 apparatus, equipped with a PE7700 computer and Tas-7 software. Approximately 5 mg samples of the dried polymer were scanned at a heating and cooling rate of 20°C/min. The temperatures at the maximum of the melting and crystallization peaks were taken as the transition temperatures.

Dynamic mechanical thermal analysis

Samples for Dynamic mechanical thermal analysis (DMTA) (70 mm × 9 mm × 2 mm) were prepared on an Arburg-H manual injection molding machine with a barrel temperature of 280°C. Before use, the samples were dried in a vacuum oven at 70°C overnight. The torsion behavior (G'' and G' versus temperature) was studied at a frequency of 1 Hz, a strain of 0.1%, and with a heating rate of 1°C/min using a Myrenne ATM3 torsion pendulum. The glass transition temperature (T_g) was expressed as the temperature where the loss modulus G'' displayed a maximum, and the flow temperature (T_{flow}) was defined as the temperature where the storage modulus G' reached 0.5 MPa.

Extrusion

The dried polymer powder was processed into threads with the use of a 4-cc DSM Res RD11H co-rotating twin-screw mini extruder. The extruder had a barrel temperature of 275°C and the screw speed was set to 30 rpm. The threads were wound at a speed of 30 m/min, and the thickness (linear mass density) of the treads was expressed in dtex (1 dtex = g/10⁴ m).

Drawing

The drawing was performed on a Zwick universal tensile tester equipped with a 500 N load cell at an (initial) strain rate of 0.01 s⁻¹. The drawing was carried out in two steps: first at 30°C, just above the T_g of PHT to a factor four and the second at various temperatures in a hot gas (N₂) oven. Before and after the drawing, the dtex (g/10⁴ m) was determined, and from these values, the draw ratio was calculated.

Tensile testing

The tensile properties were determined at room temperature on a Zwick universal tensile tester equipped with a 500 N load cell at a strain rate of 0.01 s⁻¹.

RESULTS AND DISCUSSION

PHT and the copolymer of PHT with 10 wt % of T6T6T (PHT-T6T6T₁₀) units were synthesized on a 45 g scale in a melt polymerization process. Their synthesis routes are given in Figure 2. The T6T6T represented two and a half repeat units of PA-6T as can be seen in Figure 1. Trans-amidation or esteramide trans-reactions were not expected to take place, which would signify that the T6T6T units were stable during the polymerization and melt processing.²¹

The melt synthesis of PHT-T6T6T₁₀ was conducted in the presence of excess HDO to dissolve the T6T6T-dimethyl at the onset of the polymerization. As a similar viscosity for PHT and PHT-T6T6T₁₀ was preferred, the PHT-T6T6T₁₀ was postcondensed at 170°C for 24 h under vacuum. Following this, both polymers had an inherent viscosity of 0.81 (Table I). This was not a high value but sufficient enough for injection molding and extrusion.

H¹ NMR

The H¹ NMR spectrogram of PHT displayed three peaks at 1.64, 1.94, and 4.50 ppm, corresponding to the methylene protons of the HDO, and one at

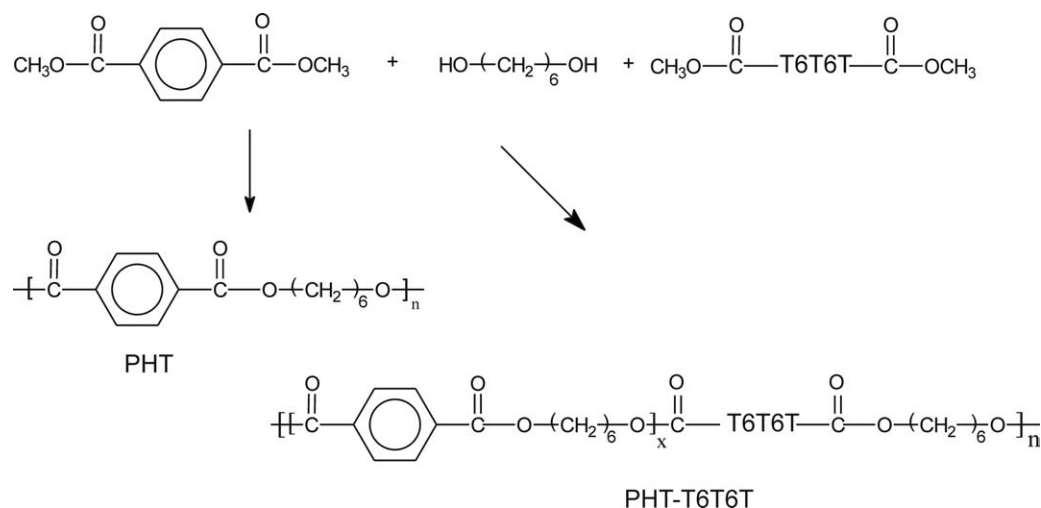


Figure 2 Synthesis routes of PHT and PHT-T6T6T.

8.17 ppm, assigned to the terephthalate protons. The ratio of all these peaks was 1. The PHT-T6T6T₁₀ presented additional peaks for the methylene protons of the hexamethylene diamine (HMDA): shoulders at 1.58 and 1.82, a peak at 3.65 ppm, and a terephthalamide triple peak at 7.8–7.9 ppm. Based on the integrals of the 4.50 ppm HDO and 3.65 ppm HMDA peaks, the concentration of HMDA, when compared to the HDO + HMDA in the copolymers, was found to be ~ 8.0 mol %, which corresponded to 10.1 wt % T6T6T in the copolymer. The concentration of T6T6T in the copolymer was in good agreement with the weighed-in amounts.

FTIR

The FTIR spectrum for PHT and PHT-T6T6T₁₀ in the 400–4000 cm⁻¹ region is given in Figure 3(a). With regard to the T6T6T segments, an NH band can be seen at 3300 cm⁻¹, amide I bands at 1625–1670 cm⁻¹, and an amide II band at 1527 cm⁻¹. As presented in Figure 3, the carbonyl band region 1600–1800 cm⁻¹ was enlarged. The polyester PHT had an ester carbonyl band at 1720 cm⁻¹. Next to the carbonyl band of the ester groups, the PHT-T6T6T₁₀ FTIR spectrum also displayed bands corresponding to the amide groups. The amide carbonyl bands were weak as the amide concentration was low. Moreover, this band was sensitive to the packing. The crystalline amide

band appeared at 1640 cm⁻¹, while the amorphous carbonyl was seen at 1670 cm⁻¹. The amide crystalline carbonyl band was unusually broad and present at a higher wave length than in the starting compound (i.e., T6T6T-dimethyl, 1625 cm⁻¹) or in the polyether-T6T6T copolymers (1625 cm⁻¹).¹² This suggested that the crystalline packing of T6T6T in PHT-T6T6T₁₀ was less than ideal. The T6T6T crystallinity could be determined by integrating the crystalline and the amorphous amide carbonyl peaks, and was found to be ~ 55%. Although this was relatively high, it was not as high as in the polyether-T6T6T copolymers (85–90 %).²²

DSC

As the T6T6T and PHT had similar repeat units (cf. Fig. 1), they might have isomorphous structures or the T6T6T units should at least be able to be built into the PHT crystalline phase without much disturbance. This would increase the melting temperature of the polyester. It is known that polyamides and polyesters described as isomorphous are in fact not truly so.^{5,6} Copolymers of PHT and the diamide T6T displayed a melting transition that increased with the amide content.¹¹

The synthesized PHT had a melting temperature of 147°C and a heat of fusion of 37 J/g and these values corresponded well with those found in the

TABLE I
Thermal Properties of PHT and PHT-T6T6T₁₀ As Obtained by DSC and DMTA

	η_{inh} (dl/g)	DSC							DMTA			
		T_{m1} (°C)	ΔH_{m1} (J/g)	T_{c1} (°C)	$T_{m1} - T_{c1}$ (°C)	T_{m2} (°C)	ΔH_{m2} (J/g)	T_{c2} (°C)	$T_{m2} - T_{c2}$ (°C)	T_g (°C)	$T_{\text{flow}1}$ (°C)	$T_{\text{flow}2}$ (°C)
PHT	0.81	147	37	111	36	–	–	–	–	25	145	–
PHT-T6T6T	0.81	145	23	118	27	229	6	211	16	25	150	(195)

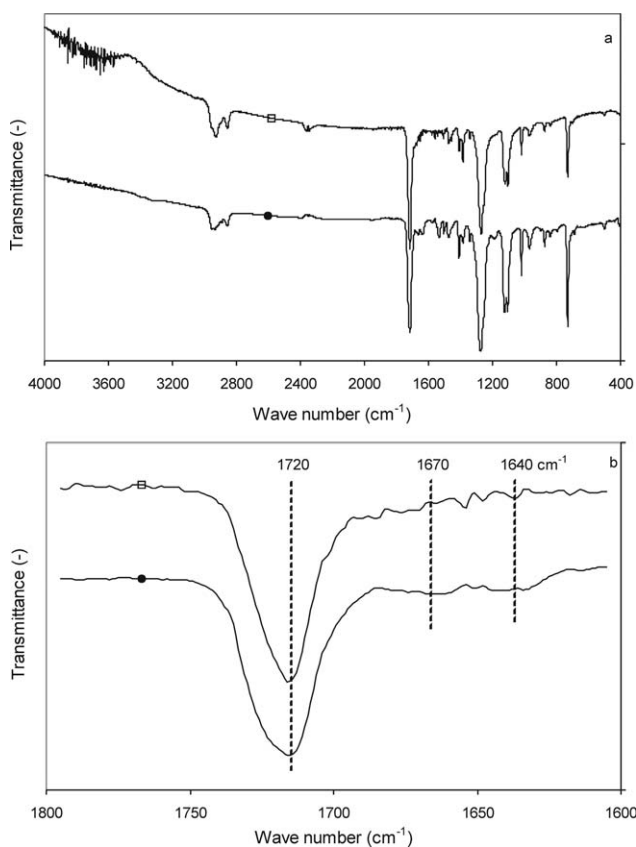


Figure 3 FTIR spectra in the wavelength range 400–4000 cm^{-1} (a) and of carbonyl bands in 1600–1800 cm^{-1} region (b): \square , PHT; \bullet , PHT-T6T6T₁₀.

literature.^{2,11,23,24} The PHT-T6T6T₁₀ displayed two melting transitions: one at 145°C and another at 229°C, and the heat of fusion was 23 and 6 J/g, respectively. Thus, by copolymerizing PHT with T6T6T, it was possible to obtain a system with two melting temperatures. Surprisingly enough, the PHT melting transition was not increased, despite the structural similarity of PHT and T6T6T.

On cooling, the crystallization temperature (T_c) of PHT occurred at 111°C for the neat polymer and at 118°C for PHT-T6T6T₁₀. The under cooling ($T_m - T_c$) of PHT caused by the presence of T6T6T, decreased from 36 to 27°C, and was more significant than for the polyesters modified with diamide units (6°C). The tetra-amide units thus had a very strong nucleating effect on the polyester crystallization.

The undercooling ($T_m - T_c$) for the T6T6T segments in the copolymer was only 16°C, suggesting an extremely fast crystallization of the T6T6T segment. Upon cooling, the T6T6T segment crystallized well before the start of the PHT crystallization. The T6T6T crystals nucleated the PHT crystallization, but as the melting temperature of the PHT did not increase, the T6T6T segments were not part of the

PHT crystalline structure. This behavior differed from that of polyester-diamide copolymers.^{7–11}

DMTA

The thermal transitions were also studied by DMTA, and Figure 4 shows the storage and loss moduli as functions of temperature for PHT and PHT-T6T6T₁₀. The PHT had a glass transition temperature (T_g) at 25°C and a flow temperature (T_{flow}) at 145°C. The T_{flow} obtained at 1°C/min was similar to the T_m as measured by DSC at 20°C/min (147°C). The PHT-T6T6T₁₀ displayed a T_g at 25°C, a $T_{\text{flow}1}$ at 150°C, and a $T_{\text{flow}2}$ at 195°C. The fact that the T_g values of PHT and PHT-T6T6T₁₀ were identical signified that very few T6T6T segments were dissolved in the PHT amorphous phase. Furthermore, it was not possible to observe a T_g corresponding to a pure T6T6T phase.

The PHT melting temperatures ($T_{\text{flow}1}$) obtained by DMTA were similar to the T_m values as measured by DSC. For PHT-T6T6T, the $T_{\text{flow}1}$ was only slightly higher than the T_m obtained by DSC. The melting temperature of the T6T6T segments could not be determined by DMTA as the modulus at temperatures above 150°C was too low and the measurement stopped before the melting transition had been reached.

The shear modulus of PHT-T6T6T₁₀ in the temperature range between the T_m of the PHT and that of T6T6T was little dependant on temperature and had a value of ~ 1 MPa.

At room temperature, the PHT-T6T6T₁₀ copolymer system thus had three phases: an amorphous PHT phase, a crystalline PHT phase and a crystalline T6T6T phase. This was similar to PTMO-T6T6T copolymers with the exception that the T_g and T_m values of the PHT phase were higher than for PTMO.

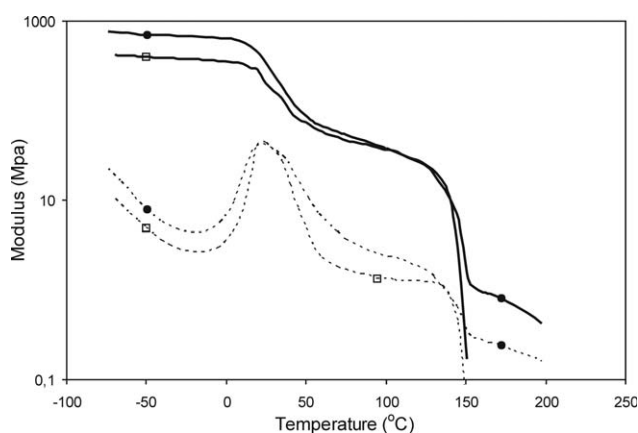


Figure 4 The storage modulus (G') (solid lines) and loss modulus (G'') (dashed lines) as functions of temperature: \square , PHT; \bullet , PHT-T6T6T₁₀.

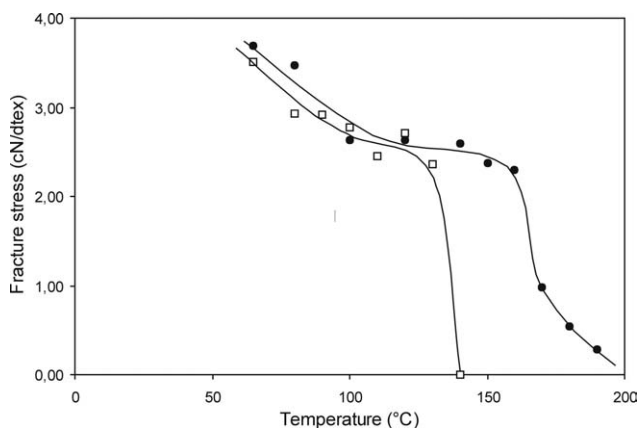


Figure 5 The fracture stress as a function of temperature for the predrawn samples: □, PHT; ●, PHT-T6T6T.

Drawing process

Threads of the polymers were extruded with a 3-cc mini extruder, cooled in the air, and wound at a speed of ~ 30 m/min. The threads were not very homogenous and displayed thicknesses in the range 30–100 dtex. As the polyesters demonstrated a strong tendency toward necking, the threads were first drawn a factor 4 at 30°C, which was just above the T_g of PHT. These predrawn samples were subsequently strained to fracture at various temperatures, and Figure 5 presents the resultant fracture stress as a function of the temperature. The fracture stress of PHT decreased gradually upto 130°C and at 140°C it failed to bear the stress any longer. The PHT-T6T6T₁₀ could resist a reasonable stress up to 160°C above which the fracture stress dropped sharply. At 200°C, the fracture stress was approximately zero. The T6T6T units in the PHT-T6T6T₁₀ clearly increased the temperature at which the polymer could continue to bear a reasonable load.

In a next stage, oriented samples were fabricated by a two-step process. The samples were first drawn a factor 4 at 30°C after which further drawing was carried out at a variety of temperatures. The drawing was performed upto 90% of the pre-determined fracture stress at the temperature in question (cf. Fig. 5) and then cooled under strain. By measuring the new tex of the drawn samples, it was possible to determine the draw ratio as a function of the drawing temperature and this is presented in Figure 6. The maximum draw ratio for PHT was a factor 5.6 at 110°C. At temperatures above 120°C, PHT-T6T6T₁₀ displayed a higher draw ratio with a maximum of 7.4 at 140–160°C. At temperatures above 160°C, the drawing process on PHT-T6T6T₁₀ was not further improved. As opposed to PHT, the PHT-T6T6T₁₀ copolymer could be drawn at a higher temperature and thereby achieve a higher draw ratio.

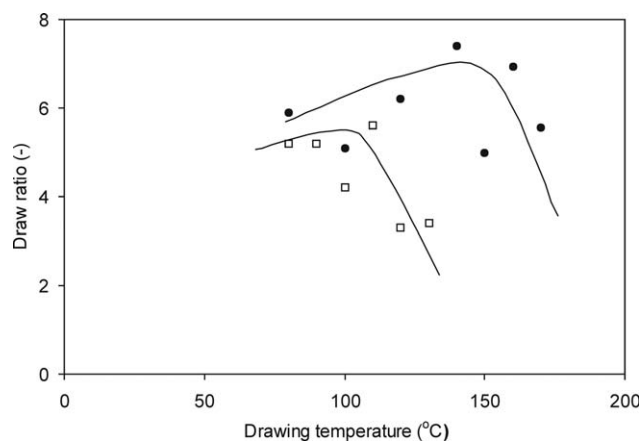


Figure 6 The draw ratio as a function of the drawing temperature. □, PHT; ●, PHT-T6T6T.

It was further studied whether the PHT melting temperature increased upon drawing. Figure 7 displays DSC traces of both unoriented and oriented samples of the PHT and PHT-T6T6T polymers. The melting temperature for the unoriented PHT was 147°C, whereas for the oriented sample drawn at 120°C it was 149°C. The melting temperature of PHT thus increased by two degrees upon drawing at 120°C. Consequently, the T_m of PHT was little affected by the drawing process and the heat treatment at 120°C. This was not surprising because annealing is known not to increase the PHT T_m much.²⁵

The T_m of the PHT phase in the PHT-T6T6T₁₀ copolymer was also measured after drawing (Fig. 7). The melting temperature of the PHT phase in the unoriented PHT-T6T6T was 145°C and increased to 161°C after drawing at 80°C. Furthermore, drawing of PHT-T6T6T at 120°C and 150°C increased the T_m

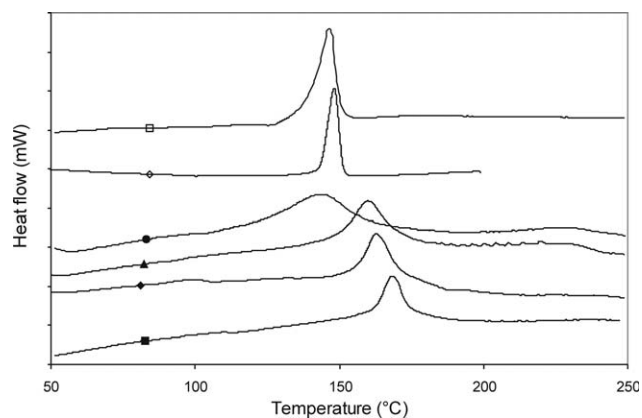


Figure 7 DSC traces of the PHT and PHT-T6T6T polymers: □, PHT unoriented; ◇, PHT drawn at 120°C. ●, PHT-T6T6T unoriented; ▲, PHT-T6T6T drawn at 80°C. ◆, PHT-T6T6T drawn at 120°C. ■, PHT-T6T6T drawn at 150°C.

even further: to 164°C and 170°C, respectively. This significant increase in the T_m of the PHT-phase in the PHT-T6T6T copolymer was not because of the orientation or to the heat treatment during this process, as no similar effect was observed for the neat PHT. Instead, the effect must be the result of a cocrystallization of PHT and T6T6T during the drawing process. Moreover, the maximum drawing temperature at 160°C was very near the melting temperature of the oriented PHT (170°C). At temperatures higher than 170°C, a high draw ratio could not be obtained. Some T6T6T segments must have taken part in the PHT crystallization and these cocrystallized segments were suspected to have been the noncrystalline T6T6T dissolved or dispersed in the PHT matrix. The T_m of the T6T6T crystallites also increased upon drawing from 229 to 238°C. Although T6T6T crystallites gave sufficient dimensional stability for drawing at a higher temperature, a PHT crystalline phase was still required to obtain a high draw ratio. A similar drawing behavior was found for the PTMO-diamide copolymers, where the optimum fracture strains and fracture stresses were obtained very near the melting temperature of PTMO.¹⁶

In the presence of the T6T6T segments, two crystalline phases were present, and because of the increased dimensional stability as a result of the T6T6T crystals, the drawing process of the polyester could now be performed at a temperature just below the PHT melting temperature. As the PHT melting temperature in PHT-T6T6T increased upon drawing, the optimum drawing temperature might have been higher if the drawing had been carried out in multiple steps, and the temperature for the final steps had been increased with the increasing T_m of PHT.

Tensile properties

The oriented samples, obtained by drawing to 90% of their fracture stress at various temperatures, were tensile tested at room temperature, and Figure 8 presents the fracture stress as a function of the draw ratio. The fracture stress was found to increase linearly with the draw ratio, and the draw ratio dependence was similar for PHT and PHT-T6T6T. The PHT and PHT-T6T6T samples drawn at temperatures higher than 110°C and 160°C, respectively, gave rise to scattered data. However, the PHT-T6T6T samples could be drawn at more elevated temperatures and to higher draw ratios, thereby giving rise to materials with higher strengths. If a draw ratio of 20 could have been obtained, as for the PTMO-diamide copolymers, then a fracture stress of ~ 100 cN/dtex would be expected, corresponding to very strong polyester fibers.

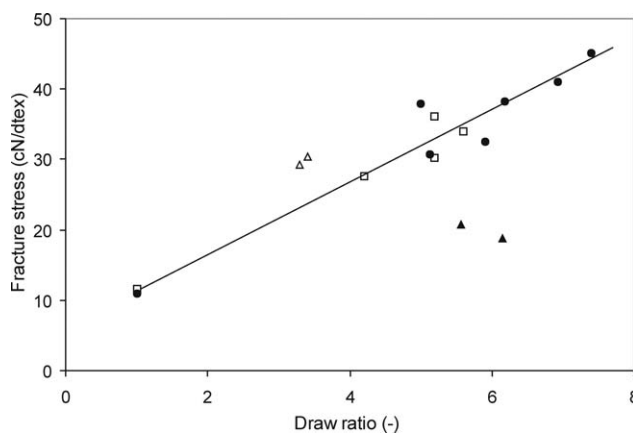


Figure 8 The fracture stress as a function of the draw ratio: □, PHT 20–110 °C; △, PHT 120–130°C; ●, PHT-T6T6T 20–160°C; ▲, PHT-T6T6T 170–180°C.

The fracture strains of the oriented PHT samples were 11%, to be compared with about 15% for the oriented PHT-T6T6T₁₀ samples. An exception was the sample drawn at 180°C, which displayed a fracture strain of 23%. Thus, for T6T6T not only did the maximum fracture stresses increase but also the fracture strains were higher.

CONCLUSIONS

The PHT-T6T6T copolymers had a three-phase structure and presented melting temperatures for both the PHT and T6T6T segments. In the unoriented state, the melting temperature of the PHT was unaffected by the presence of the T6T6T units, and cocrystallization effects between the PHT and T6T6T segments were thus not observed. However, the T6T6T segments had a considerable nucleating effect on the PHT crystallization, and the T6T6T crystalline phase increased the dimensional stability of the copolymer.

Despite the relatively low molecular weights of the studied polymers, threads of these materials could be drawn reasonably well. The draw ratio increased with the drawing temperature and the maximum draw ratio for PHT occurred at 110°C, whereas for the PHT-T6T6T it took place at 160°C. On drawing PHT-T6T6T, the PHT melting temperature was found to increase. The higher maximum drawing temperature of PHT-T6T6T must have been because of this increased PHT melting temperature and to the fact that drawing nearer the PHT melting temperature was now possible as a result of the presence of the T6T6T crystallites. The ability of the PHT phase to crystallize on straining was thus essential for achieving a high draw ratio. The strain hardening process stabilized the drawn threads.

Very high draw ratios (i.e., a factor 20) of the PTMO-amide copolymers have yet to be obtained. With a higher molecular weight of the polyester-amide copolymers, a further improvement in their properties can be expected. The concentration of amide units in the studied copolymer was 10 wt % but it is not unlikely that this concentration can be lowered while maintaining a sufficient dimensional stability for a high drawing behavior. The enhancement in drawability in the presence of a second crystalline phase can probably also be applied to other polyesters, such as PBT and PET, and possibly also to other fiber-forming polymers, such as nylon and POM.

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