



## Segmented copolymers of uniform tetra-amide units and poly(phenylene oxide): 2. Crystallisation behaviour

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### Abstract

The crystallisation behaviour of copolymers of telechelic poly(2,6-dimethyl-1,4-phenylene ether) segments with terephthalic methyl ester endgroups (PPE-2T), 13 wt% crystallisable tetra-amide segments of uniform length units (two-and-a-half repeating unit of nylon-6,T) and dodecanediol (C12) was studied. The crystallisation rate of the T6T6T units was found to be very high despite the high  $T_g/T_m$  ratio. The supercooling ( $T_m - T_c$ ) as measured by DSC is 18 °C at a cooling rate of 20 °C/min. WAXD has elucidated that the tetra-amide units remain organised in the melt.

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**Keywords:** Poly(phenylene oxide); Tetra-amide; Segmented copolymer

### 1. Introduction

Copolymers of telechelic poly(2,6-dimethyl-1,4-phenylene ether) segments and crystallisable tetra-amide segments of uniform length (two-and-a-half repeating unit of nylon-6,T, called T6T6T) with dodecanediol (C12) as an extender can be made via a polycondensation reaction in the melt [1]. These PPE/C12/T6T6T copolymers are semi-crystalline materials with a  $T_g$  around 170 °C, a melting temperature of 264–270 °C and a  $T_g/T_m$  ratio above 0.8. The modulus is high up to the  $T_g$ , which is not achievable in a blend of PPE and polyamide that has a glass transition of the semi-crystalline polyamide phase at 70 °C. The most probable morphology of the PPE/C12/T6T6T copolymers is that of long crystalline nano-ribbons in the amorphous matrix. The materials have good solvent resistance, low water absorption and good processability.

Thus far the crystallisation behaviour was not studied in detail. Dynamic mechanical analysis (DMA) has shown that these high  $T_g$  segmented copolymers are semi-crystalline materials, which is very surprising. With increasing  $T_g/T_m$  ratio, the window of crystallisation is decreased and the rate and extent of crystallisation of semi-crystalline polymers is

known to decrease dramatically [2,3]. Despite the high  $T_g/T_m$  ratio, the T6T6T crystallinity is only 25–40% lower than that of PTMO/T6T6T (polytetramethylene oxide) that have a low  $T_g$  of –65 °C [1,4].

The aim of this work is to study the crystallisation behaviour of uniform T6T6T segments in high  $T_g$  PPE/C12/T6T6T copolymers using DSC and WAXD techniques.

### 2. Experimental

#### 2.1. Materials

PPE/C12/T6T6T copolymers were synthesized by polycondensation (transesterification) using PPE-2T, T6T6T-dimethyl and 1,12-dodecanediol (C12) as was described before [1]. The PPE-2T segments are telechelic difunctional PPE endcapped with terephthalic methyl ester groups [5]. T6T6T-dimethyl is the uniform tetra-amide segments based on two-and-a-half repeating unit of hexamethylene terephthalamide (nylon-6,T) with methyl ester endgroups [6]. Two copolymers with inherent viscosity ( $\eta_{inh}$ ) of 0.41 and 0.52 dl/g (in 50/50 phenol/1,1,2,2-tetrachloroethane) and 13 wt% T6T6T were used.

Pure PPE (PPO-803<sup>®</sup>) with a number average molecular weight of 11.000 g/mol (inherent viscosity is 0.37 dl/g (in

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Table 1

Melting and crystallisation behaviour of PPE/C12/T6T6T with 13 wt% T6T6T and two different inherent viscosities [1]

$\eta_{\text{inh}}$ (dl/g)	$T_{\text{m}}(\text{peak})$ (°C)	$\Delta H_{\text{m}}$ (J/g)	$\Delta H_{\text{m}}$ (J/g T6T6T)	$x_{\text{c}}$ (%)	$T_{\text{c}}(\text{peak})$ (°C)	$T_{\text{m}} - T_{\text{c}}(\text{peak})$ (°C)	$\Delta H_{\text{c}}$ (J/g)
0.41	268	14	109	70	250	18	13
0.52	264	12	93	60	241	23	12

chloroform) was obtained from GE Plastics (The Netherlands). For PPE this molecular weight is high enough for good properties.

## 2.2. DSC

DSC spectra (at least on 5 samples) were recorded on a Perkin Elmer DSC7 apparatus, equipped with a PE7700 computer and TAS-7 software. Dried samples of 5–10 mg polymer in aluminium pans were measured with a heating rate of 20 °C/min and different cooling rates (5–160 °C/min). The samples were heated to 300 °C, kept at that temperature for 2 min, cooled to 100 °C and reheated to 300 °C. The (peak) melting temperature and enthalpy were obtained from the second heating scan. The crystallisation temperature was defined as the maximum of the peak in the cooling scan. For comparison with other data the onset of the crystallisation peak was determined as well.

To account for the thermal lag between a point in the sample and the calorimeter furnace, the recorded temperatures in non-isothermal crystallisation experiments must be corrected. For Perkin Elmer DSC7 with aluminium pans the actual temperature was calculated from the display temperature and cooling rate  $\lambda$  (°C/min) with Eq. (1) [7,8].

$$T_{\text{actual}} = T_{\text{display}} + 0.089\lambda \quad [^{\circ}\text{C}] \quad (1)$$

## 2.3. WAXD

X-ray diffraction data of melt-pressed samples were collected with a Philips PW3710 based X'Pert-1 diffractometer in Bragg–Brentano geometry, using a  $\Theta$  compensating divergence slit (12.5 mm length). Diffraction data collection was performed at room temperature, using a low-background spinning (1 r/s) specimen holder. Cu  $K_{\alpha 1}$  radiation of 1.54056 Å was obtained using a curved graphite monochromator. The data were collected in a range of  $2\Theta = 4$ – $60^{\circ}$ .

Melt-pressed samples of  $10 \times 15 \times 1 \text{ mm}^3$  were prepared from an injection moulded test bar in a mould at 300 °C for 5 min with a pressure of 10 bar, after which the samples were slowly cooled with 5 °C/min. Melt-pressed samples of  $\sim 0.1$  mm thickness were prepared from polymer powder between two Teflon sheets (5 min at 300 °C, 10 bar), after which the thin film was directly quenched in ice–water (corresponding cooling rate estimated at  $>100$  °C/s).

## 2.4. WAXD as function of temperature

Diffraction patterns at different temperatures were obtained using a Philips X'Pert-MPD diffractometer. With a curved graphite monochromator Cu  $K_{\alpha 1}$  radiation of 1.54056 Å was obtained. Melt-pressed samples of approximately 1 mm thickness were mounted in a sample holder in an Anton Paar HTK-16 temperature chamber. The measurements were carried out in nitrogen atmosphere and the heating and cooling rate were 2 °C/min. The data were collected in a range of  $2\Theta = 4$ – $60^{\circ}$ . The experiment started with a measurement at room temperature and then the temperature was raised to 175 °C and further to 300 °C with a measurement every 25 °C. Measurements were also performed during cooling with the same temperature steps.

## 3. Results and discussion

### 3.1. DSC

With DSC the melting and crystallisation behaviour of PPE/C12/T6T6T with 13 wt% uniform T6T6T [1] was studied in a 20 °C/min heating and cooling cycle.

#### 3.1.1. Molecular weight

The crystallisation behaviour of PPE/C12/T6T6T polymers with 13 wt% uniform T6T6T with different molecular weights (inherent viscosity) was studied. The peak melting temperature ( $T_{\text{m}}(\text{peak})$ ), melting enthalpy ( $\Delta H_{\text{m}}$ ), calculated crystallinity ( $x_{\text{c}}$ ), peak crystallisation temperature ( $T_{\text{c}}(\text{peak})$ ), supercooling ( $T_{\text{m}} - T_{\text{c}}(\text{peak})$ ) and crystallisation enthalpy ( $\Delta H_{\text{c}}$ ) are given in Table 1. The data were corrected for the thermal lag. For a cooling rate of 20 °C/min the thermal lag is  $\sim 2$  °C [7,8] (Eq. (1)).

With increasing molecular weight the melting temperature and enthalpy decrease a little. Polymers with a lower melting temperature at a constant amide content have a lower crystallinity. The solvent effect of the amorphous phase increases when the degree of crystallinity decreases and therefore the melting temperature decreases with decreasing crystallinity [9]. When the molecular weight increases the viscosity of the melt increases and therefore crystallisation is suppressed.

The peak melting temperature as measured by DSC is 268 °C with an enthalpy of 14 J/g (109 J/g T6T6T) at an inherent viscosity of  $\sim 0.41$  dl/g. The supercooling is only 18 °C. The  $T_{\text{m}}$  of T6T6T-dimethyl is 303 °C with an

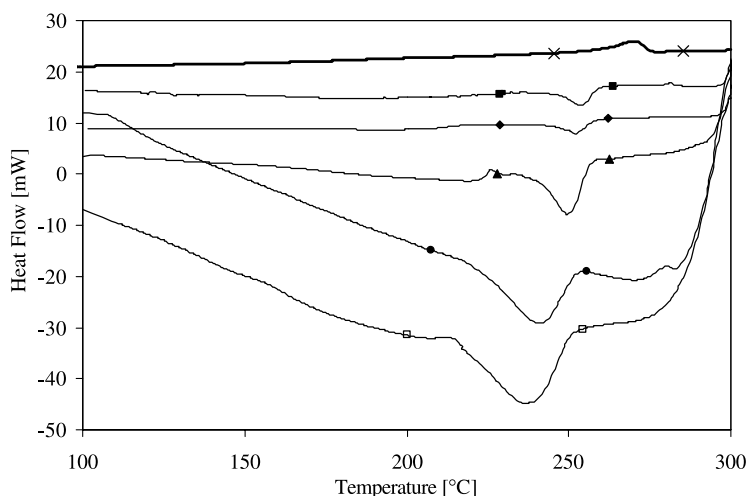


Fig. 1. Melting and crystallisation curves (after correction) of PPE/C12/T6T6T with 13 wt% T6T6T (0.42 dl/g) as measured by DSC at different rates: (×) +20 °C/min; (■) –10 °C/min; (◆) –20 °C/min; (▲) –40 °C/min; (●) –80 °C/min; (□) –120 °C/min.

enthalpy of 152 J/g [6]. When it is assumed that the melting enthalpy of T6T6T in the copolymer and T6T6T-dimethyl are comparable it can be calculated that about 70% of the T6T6T has crystallised. This value corresponds nicely to the calculated crystallinity from the rubber modulus in DMA of 75% relatively to PTMO/T6T6T copolymers [1]. At an inherent viscosity of 0.52 dl/g the melting and crystallisation temperature and enthalpy decrease, while the supercooling increases. The crystallinity of T6T6T as calculated from the melting enthalpy of T6T6T-dimethyl is ~60%, which was also calculated from DMA.

Furthermore these data corroborate the results of dynamic mechanical analysis. The rate of crystallisation of these segmented copolymers is dependent on the molecular weight of the polymer and therefore the crystallinity of T6T6T decreases with increasing molecular weight.

### 3.1.2. Cooling rate

The crystallisation of the polymer with an inherent viscosity of 0.42 dl/g was studied at different cooling rates. The data were corrected for the thermal lag. For low cooling rates (5–10 °C/min) the thermal lag is less than 1 °C [7,8] (Eq. (1)). At higher cooling rates (above 50 °C/min) the error in the temperature increases because of a delay in the

heat transfer to the sample in the DSC pan. At 160 °C/min the thermal lag increases to 14 °C/min.

The corrected crystallisation data as measured by DSC are given in Fig. 1. The onset ( $T_c(\text{onset})$ ) and peak crystallisation temperature ( $T_c(\text{peak})$ ) at different cooling rates are given in Table 2. The relative crystallinity as a function of the corrected temperature at different cooling rates is given in Fig. 2.

The crystallisation peak shifts to lower temperatures and becomes broader when the cooling rate increases. At all cooling rates the onset of crystallisation is sharp, while the peak broadens at the end.

The supercooling values of 15–38 °C ( $T_m(\text{peak}) - T_c(\text{peak})$ ) at cooling rates of 5–160 °C are very low. Other semi-crystalline polymers such as PBT or nylon-4,6 that are known to crystallise fast have higher supercooling values.

The temperature at which 50% of the crystallisation is reached is given as a function of temperature in Fig. 3. The temperature of 50% crystallisation decreases linearly with increasing cooling rate. These data show how the cooling rate influences the rate of crystallisation of T6T6T.

A simple method to characterise the crystallisability of polymers and their sensitivity towards processing conditions, mainly cooling rates, was proposed by Nadkarni et al

Table 2

Crystallisation temperature at different cooling rates for PPE/C12/T6T6T with 13 wt% T6T6T and  $\eta_{\text{inh}} = 0.42$  dl/g that has a peak melting temperature of 268 °C

Cooling rate (°C/min)	$T_c(\text{onset})$ (°C)	$T_m(\text{peak}) - T_c(\text{onset})$ (°C)	$T_c(\text{peak})$ (°C)	$T_m(\text{peak}) - T_c(\text{peak})$ (°C)
5	257	11	253	15
10	256	12	252	16
20	255	13	250	18
40	254	14	248	20
80	252	16	241	27
120	251	17	236	32
160	244	24	230	38

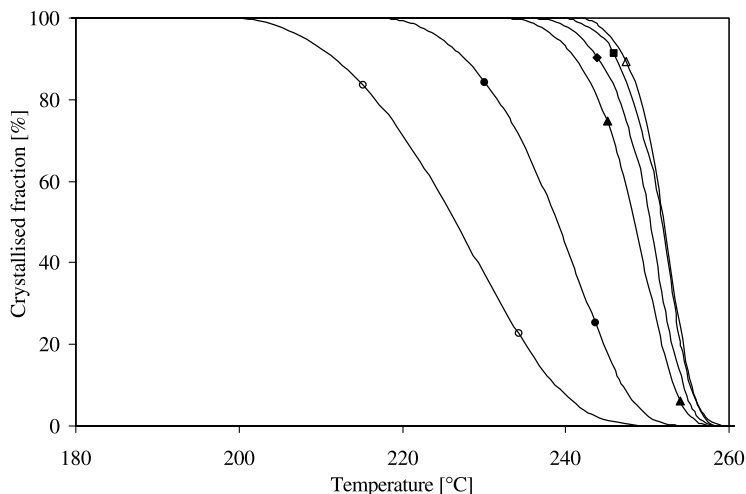


Fig. 2. Corrected crystallised fraction of PPE/C12/T6T6T with 13 wt% T6T6T (0.42 dl/g) as measured by DSC at different cooling rates: ( $\Delta$ ),  $-5^\circ\text{C}/\text{min}$ ; ( $\blacksquare$ ),  $-10^\circ\text{C}/\text{min}$ ; ( $\blacklozenge$ ),  $-20^\circ\text{C}/\text{min}$ ; ( $\blacktriangle$ ),  $-40^\circ\text{C}/\text{min}$ ; ( $\bullet$ ),  $-80^\circ\text{C}/\text{min}$ ; ( $\circ$ ),  $-160^\circ\text{C}/\text{min}$ .

[10,11]. The variation of the supercooling  $\Delta T(T_{m,\text{peak}} - T_{c,\text{onset}})$  with cooling rate ( $\lambda$ ) can be fitted to a linear equation (Eq. (2)).

$$\Delta T = P\lambda + \Delta T^0 \quad [^\circ\text{C}] \quad (2)$$

The degree of supercooling required in the limit of zero cooling rate ( $\Delta T^0$ ) signifies the inherent crystallisability of the polymer. This value is related to the thermodynamic driving force for nucleation. The slope  $P$  ([min]) of this line is a process sensitivity factor that accounts for kinetic effects. The variation of the degree of supercooling with cooling rate indicates the ability of polymer molecules to respond to thermal changes. For the data in Table 2 the slope  $P$  is 0.07 min and  $\Delta T^0 = 11^\circ\text{C}$ . These values are very low and confirm the fast crystallisation of T6T6T in these copolymers.

The rate of crystallisation as expressed by Eq. (2) of the PPE/C12/T6T6T copolymer is compared with several other polymers (Table 3). To compare the  $P$  and  $\Delta T^0$  values the

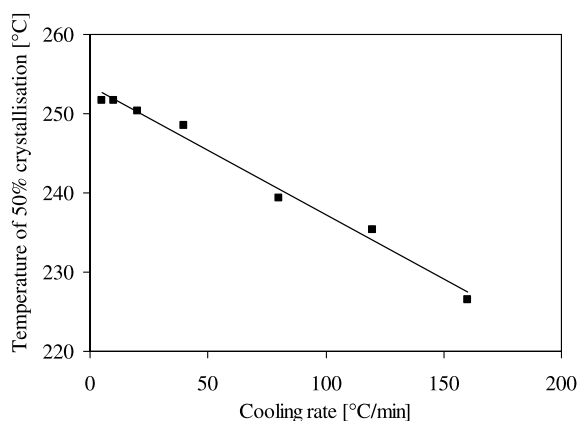


Fig. 3. Temperature at which 50% of the crystallisation of PPE/C12/T6T6T with 13 wt% T6T6T (0.42 dl/g) is completed as a function of cooling rate as measured by DSC.

supercooling were now calculated as  $T_{m,\text{peak}} - T_{c,\text{peak}}$  because  $T_{c,\text{onset}}$  data are not available. Therefore the values of  $P$  and  $\Delta T^0$  are larger for PPE/C12/T6T6T than mentioned above. From Table 3 it can be seen that the crystallisation of PPE/C12/T6T6T is very fast and less sensitive to changes in cooling rate compared to polyamides and polyesters. This is remarkable bearing in mind that our copolymer has a high  $T_g/T_m$  ratio.

It was not possible to determine isothermal crystallisation data that can be used in the Avrami equation. [16] to calculate the rate of crystallisation because the crystallisation was too fast. Ozawa derived a non-isothermal crystallisation kinetics model for crystallisation at a constant cooling rate by extending the Avrami equation [8,11,17]. According to this theory, the relative crystallinity  $\theta$  at temperature  $T$  can be calculated with Eq. (3).

$$\theta(T) = 1 - \exp\left[\frac{-K^*(T)}{\lambda^n}\right] \quad (3)$$

In this equation  $\lambda$  is the cooling rate,  $n$  is the Avrami exponent and  $K^*(T)$  is the cooling crystallisation function at temperature  $T$  for non-isothermal crystallisation. The  $K^*$  is related to the overall crystallisation rate and indicates how fast crystallisation occurs.

After rewriting and taking the logarithm of the Ozawa

Table 3  
Slope  $P$  and intercept  $\Delta T^0$  for several polymers using  $\Delta T = T_{m,\text{peak}} - T_{c,\text{peak}}$

	$P$ (min)	$\Delta T^0$ ( $^\circ\text{C}$ )
PPE/C12/T6T6T	0.15	15
Nylon-4,6 [12,13]	0.28	24
Nylon-6 [12,13]	0.55	33
PBT [13–15]	0.40	26
PET [14]	1.3	40

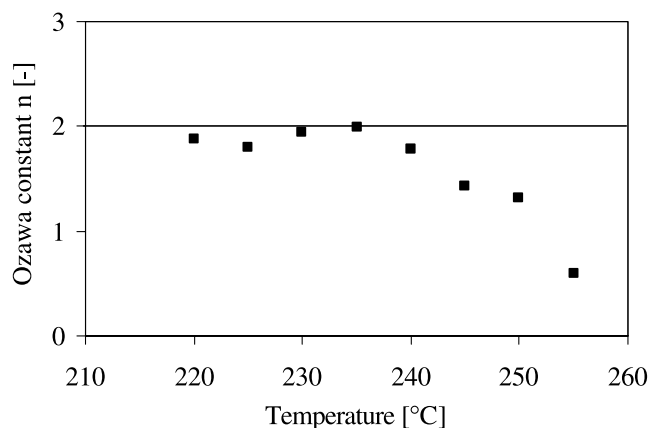


Fig. 4. Ozawa constant  $n$  as a function of temperature as calculated by Eq. (4).

equation, Eq. (4) is obtained:

$$\log\{-\ln[1-\theta(T)]\} = \log K^*(T) - n \log \lambda \quad (4)$$

The value of  $n$  at a certain temperature can be obtained as the slope of a straight line of a plot of the left term of Eq. (4) versus  $\log \lambda$ . When Eq. (4) is applied to the data of Fig. 2 at different temperatures the value of  $n$  as a function of temperature can be calculated. The results are given in Fig. 4.

The Ozawa or Avrami constant  $n$  has a value of 2 below 240 °C. Above 240 °C the value of  $n$  is lower, but these data are not so reliable because the error in the relative crystallinity is very high at low cooling rates as the crystallisation peak becomes very small. A value of 2 for  $n$  is indicative for 1-dimensional crystal growth with sporadic nucleation and contact as the rate determining step [18]. When  $n$  decreases to 1.5 diffusion becomes the rate determining step and for  $n = 1$  the nucleation mode becomes simultaneous.

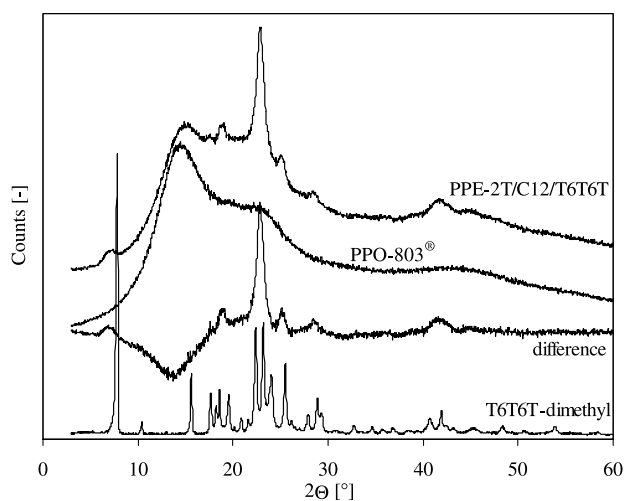


Fig. 5. WAXD data of PPE/C12/T6T6T, PPO-803<sup>®</sup> and PPO-803<sup>®</sup> subtracted from PPE-2T/C12/T6T6T (difference) compared to T6T6T-dimethyl [6].

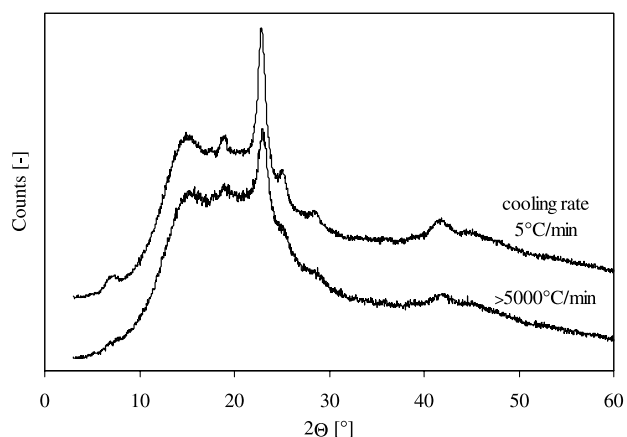


Fig. 6. WAXD data two PPE/C12/T6T6T melt-pressed sample at 300 °C for 5 min; one with a thickness of 1 mm and a cooling rate of 5 °C/min and one with a thickness of 0.1 mm that was quenched in an ice–water bath (> 100 °C/s or ~ 5000 °C/min).

### 3.2. WAXD

The crystalline structure of PPE/C12/T6T6T with 13 wt% uniform T6T6T (0.41 dl/g) was studied with WAXD. A melt-pressed sample of 1 mm thickness was prepared in a press at 300 °C during 5 min with a pressure of 10 bar. Then the sample was cooled down under pressure with a cooling rate of 5 °C/min. The strip that was obtained was slightly transparent. A similar strip of PPO-803<sup>®</sup> was prepared according to the same procedure. This strip was transparent. In Fig. 5 the data of the WAXD experiment on these two strips are given. The difference between the semi-crystalline PPE/C12/T6T6T and the amorphous PPO-803<sup>®</sup> data is given in this figure as well. The data are compared with the WAXD spectrum of the T6T6T-dimethyl segment [6].

PPE/C12/T6T6T shows a number of small peaks at  $2\theta = 8, 19, 25, 29$  and  $42^\circ$ . There is one large peak at  $2\theta = 23^\circ$ . These peaks become better visible when the spectrum of the amorphous PPO-803<sup>®</sup> is subtracted from the spectrum of the copolymer. In this way the amorphous contribution to the spectrum can roughly be filtered out. It is clear that the peaks that can be found in the spectrum of the copolymer correspond nicely with a peak or a group of peaks of T6T6T-dimethyl [6]. Peaks of T6T6T can be found at the same positions in the WAXD figure for T6T6T-PTMO [4]. This suggests that the crystalline structure of T6T6T in PPE and PTMO is comparable.

It was expected that crystallinity would be absent at very high cooling rates. The effect of very high cooling rates on the crystalline structure was studied on a melt-pressed (5 min at 300 °C) film of 0.1 mm thickness that was quenched in ice–water. The polymer film was prepared between two Teflon sheets and was fluid up to the moment that it was quenched in the ice–water bath. The cooling rate therefore was estimated at > 100 °C/s. This thin polymer

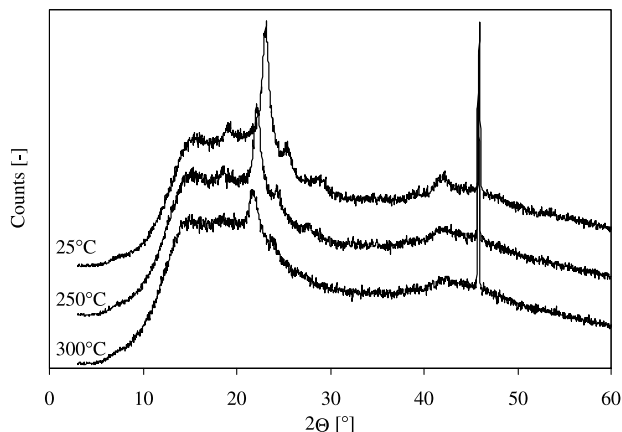


Fig. 7. WAXD data for a measurement on PPE/C12/T6T6T (13 wt%) at different temperatures; room temperature, 250 and 300 °C as indicated in the figure.

film was transparent. The expectation was that this film was amorphous.

The WAXD data of this quenched film are compared with the melt-pressed sample of PPE/C12/T6T6T of 1 mm thickness that was obtained after cooling with 5 °C/min in Fig. 6.

WAXD data show that the quenched sample shows crystalline order despite the very high cooling rate. The peak height of the main peak at  $2\theta = 23^\circ$  is reduced to 60% of the peak in the sample that was cooled with 5 °C/min. This can be explained by the fact that the T6T6T units remain largely ordered in the melt and as a result can form ordered structures after fast cooling.

The influence of temperature on the crystalline structure of T6T6T in PPE-2T/C12/T6T6T with 13 wt% uniform T6T6T was studied by WAXD as well. A melt-pressed sample of 1 mm thickness (at 300 °C, cooling rate of 5 °C/min) was used for this measurement. The experiment started with a measurement at room temperature and then the temperature was raised to 175 °C and further to 300 °C with a measurement every 25 °C. The sample was measured

during cooling with the same temperature steps. The heating and cooling rate were 2 °C/min.

The results after heating to 250 and 300 °C are given in Fig. 7 together with the data for a measurement at room temperature. The relative peak height of the peak at  $2\theta = 22\text{--}23^\circ$  is given in Fig. 8 with the peak height at 25 °C at the beginning of the experiment set at 100%.

The peak at  $2\theta = 22\text{--}23^\circ$  shifts to lower position and decreases in height when the temperature is increased. This indicates an increase in crystal dimensions and a decrease in crystalline order with increasing temperature respectively.

It is remarkable that the crystalline order at 25 °C is higher than that at 175 °C with heating as well as cooling. The  $T_g$  of this polymer as determined by DMA is 180 °C, which means that the modulus of this polymer is high up to this temperature. Nevertheless the order is decreasing (upon heating) or increasing (upon cooling) a little between room temperature and the  $T_g$ .

At 300 °C, which is well above the melting temperature of  $\sim 268^\circ\text{C}$ , the peak at  $2\theta = 22\text{--}23^\circ$  has still 30% of its original height. So in the melt there is still an ordered T6T6T fraction present. This is probably an ordered T6T6T phase in which the length of the hydrogen bonds is increased and the distance between the T6T6T units is larger than in crystalline T6T6T. For copolymers of PTMO and aromatic di-amide units [19] it was found by IR experiments that the di-amide units remain hydrogen bonded in the melt and that the average hydrogen bond strength decreases with increasing temperature. In the melt these di-amide units are thought to form a smectic crystalline structure.

#### 4. Conclusions

Copolymerisation of PPE with uniform, crystallisable T6T6T units and dodecanediol as an extender is a good method to obtain a semi-crystalline material with a very high  $T_g/T_{\text{flow}}$  ratio. It is particular that the T6T6T units can actually crystallise in these copolymers despite the very

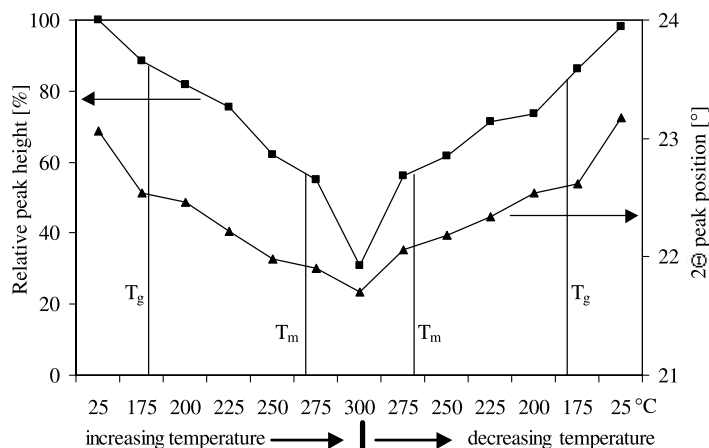


Fig. 8. Relative peak height (■) and  $2\theta$  peak position (▲) of the crystalline peak at  $2\theta = 22\text{--}23^\circ$ .

high  $T_g/T_{\text{flow}}$  ratio above 0.8 and low hard segment concentration (13 wt%).

The molecular weight of the product seems to have a large effect on the rate of crystallisation of the polymer. With DSC it was measured that the temperature of crystallisation decreases a little while the supercooling increases strongly when the molecular weight increases. From DMA and DSC it was calculated that the crystallinity of T6T6T in the copolymers is between 60 and 75%. The rate of crystallisation decreases dramatically when the cooling rate increases. However with WAXD it was shown that even at very high cooling rates (quenching) ordered T6T6T is still present. Also the copolymer contains ordered T6T6T above its melting temperature (at 300 °C). These results indicate that the tetraamide units remain organised in the melt.

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