

Synthesis and Properties of Segmented Copolymers of Polyphenylene Ether and Tetra-Amide Units

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Summary: Copolymers of telechelic poly(2,6-dimethyl-1,4-phenylene ether) segments with terephthalic methyl ester endgroups (PPE-2T, 3100 g/mol), uniform crystallizable tetra-amide units based on nylon-6,T (T6T6T, 13 wt%) and dodecanediol (C12) as an extender were made via a polycondensation reaction. The PPE-2T/C12/T6T6T copolymers are semi-crystalline materials with a glass transition temperature (T_g) of 169°C, a melting temperature (T_m) of 268°C and a very high T_g/T_m ratio of 0.82. The modulus is high up to the T_g and the modulus in the rubbery plateau after injection moulding is 10 MPa. The materials are slightly transparent and have good solvent resistance, low water absorption and good processability. With DSC it was calculated that the crystallinity of T6T6T in the copolymer is around 70%. The undercooling (T_m-T_c) as measured by DSC is 18°C at a cooling rate of 20°C/min. With WAXD it was shown that the tetra-amide units remain partially organized in the melt.

Keywords: crystallization, high temperature materials, mechanical properties, poly(2,6-dimethyl-1,4-phenylene ether), segmented copolymers

Introduction

Poly(2,6-dimethyl-1,4-phenylene ether) (PPE)^[1-3] or PPO is a linear amorphous polymer with a glass temperature of approximately 215°C.^[4] PPE has excellent properties such as high toughness, high dimensional stability, good flame retardation and low moisture uptake. However, PPE has a low solvent resistance and poor processability. To obtain solvent resistance, some crystallinity is necessary. The solvent resistance and processability of PPE can be improved by blending with a semi-crystalline polymer, for example polyamide-6,6 (Noryl-GTX®). However both polymers phase separate easily and the polyamide phase is semi-crystalline with a T_g around 70°C. A high polyamide content (~40%) is needed and the modulus of the blend is only high up to ~50°C instead of 200°C. Some blockcopolymers of PPE and

polyamide-6 are known,^[5-8] however the crystallization of the polyamide is slow and incomplete and thus the materials are hardly crystalline. The rate of crystallization of the polyamide is decreased by the high viscosity of PPE.^[9,10]

A new polymer system based on PPE segments and fast crystallizing uniform amide units that is a segmented copolymer is described in this article. Uniform di-amide units were found to crystallize very fast and complete upon cooling from the melt in a copolymer with poly(tetramethylene oxide) that has a T_g of -65°C .^[11-13] However the melting temperature is not so high. A higher melting temperature can be obtained with tetra-amide units.^[14,15] For fast crystallization and good phase separation it is important that the crystallizable units have uniform length.^[16-19]

The structure of segmented copolymers of PPE-2T segments^[20] and tetra-amide units (T6T6T-dimethyl)^[15] that are linked via dodecanediol is shown in Figure 1. These polymers are made via polycondensation. PPE-2T is bifunctional PPE with terephthalic methyl ester endgroups and a molecular weight of ~ 3100 g/mol [20]. T6T6T-dimethyl is a tetra-amide segment with terephthalic methyl ester endgroups that is based on two-and-a-half repeating unit of nylon-6,6.^[15] The length of this segment (without the endgroups) is ~ 4 nm.

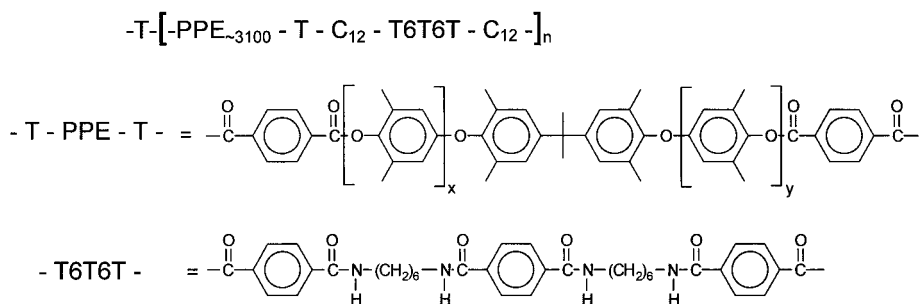


Fig. 1. Schematic structure of a PPE-2T/C12/T6T6T copolymer.

It is expected that the morphology of segmented copolymers based on PPE and uniform tetra-amide units is comparable with that of PTMO/(DMT) with uniform di-amide units.^[21] A model for the crystalline structure of segmented copolymers that contain a low content (<20 wt%) of

fast crystallizing short uniform amide segments is given in Figure 2.^[21] The uniform amide crystalline segments crystallize into threads or ribbon-like structures (C) of ~4 nm thickness with high aspect ratio and some will be amorphous (B) and mixed with the amorphous PPE phase (A).^[21-23] The length of the crystalline ribbons can be 100-500 nm, as was measured by AFM experiments.^[21] When the crystalline content is low the copolymer is transparent. At high amide contents (>30 wt%) spherulitic structures can be formed and transparency will be lost.^[23] Possibly the amide units are still ordered in the melt.^[24-26] It is thought that crystallization of T6T6T takes place from these ordered T6T6T in the melt upon cooling. However, due to the high T_g of PPE, crystallization is incomplete and some T6T6T will be amorphous.

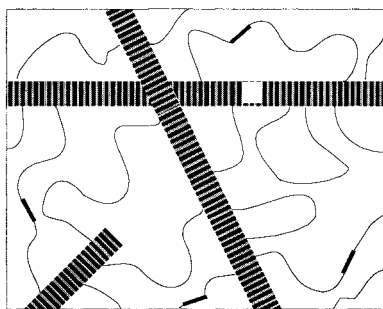


Fig. 2. Schematic representation of the morphology of crystallised segmented copolymers with uniform crystallizable segments: A = amorphous phase; B = amorphous crystallizable segments; C = crystalline ribbons.

In this review the synthesis and structure-property relationships of a segmented copolymer based on PPE-2T, dodecanediol and 13 wt% of T6T6T-dimethyl are described. The goal of this work is to obtain a semi-crystalline material with a high glass transition temperature ($>150^\circ\text{C}$) and a high T_g/T_m ratio above 0.8 ($T_m < 300^\circ\text{C}$). The synthesis and results of thermal-mechanical analysis, DSC, WAXD, water absorption and rheology experiments will be discussed successively.

Experimental

Materials. 1,12-Dodecanediol (C12), tetraisopropyl orthotitanate ($\text{Ti}(\text{i-OC}_3\text{H}_7)_4$) and N-methyl-2-pyrrolidone (NMP) were purchased from Merck. PPO-803[®] (11.000 g/mol) and Noryl-GTX[®] (GTX914) were obtained from GE Plastics (The Netherlands). All chemicals were used as received. T6T6T-dimethyl^[15] and PPE-2T of 3100 g/mol ($573 \mu\text{mol OCH}_3/\text{gram}$)^[20] were synthesized as described before.

Polymer Synthesis. The PPE-2T/C12/T6T6T copolymer was synthesized via a polycondensation reaction. The reaction was carried out in a 50 ml glass reactor with a nitrogen inlet and mechanical stirrer. The vessel was loaded with PPE-2T (10.0 g, 5.73 mmol OCH_3), dodecanediol (1.15 g, 5.73 mmol), T6T6T-dimethyl (1.97 g, 2.87 mmol), 20 ml NMP and catalyst solution (0.6 ml of 0.05M $\text{Ti}(\text{i-OC}_3\text{H}_7)_4$ in m-xylene). This mixture was first heated in an oil bath to 180°C under nitrogen flow. Then the temperature was raised in steps: 30 min 180°C, 30 min 220°C, 60 min 250°C and 60 min 280°C. The pressure was then carefully reduced ($P < 20$ mbar) to distil off the remaining NMP and then further reduced ($P < 1$ mbar) for 60 minutes. Finally, the vessel was allowed to slowly cool to room temperature whilst maintaining the low pressure. Then the polymer was cut out of the reactor and crushed.

Viscometry. The inherent viscosity of the polymers was determined with a capillary Ubbelohde type 1B at 25°C, using a polymer solution with a concentration of 0.1 g/dl in phenol/1,1,2,2-tetrachloroethane (50/50, mol/mol).

Dynamical Mechanical Analysis (DMA). Samples for the DMA test (70x9x2 mm) were prepared on an Arburg-H manual injection molding machine and dried in a vacuum oven at 80°C overnight. The torsion behavior was studied at a frequency of 1 Hz, a strain of 0.1% and a heating rate of 1°C/min using a Myrenne ATM3 torsion pendulum. The storage modulus G' and loss modulus G'' were measured as a function of temperature starting at -100°C. The glass transition temperature (T_g) was expressed as the temperature at which the loss modulus G'' has a maximum. The modulus of the rubbery plateau was determined at 40°C above the T_g . The flow temperature (T_{flow}) was defined as the temperature where the storage modulus G' reaches 0.5 MPa. The flow temperature is close to the melting temperature (T_m).

Differential Scanning Calorimetry (DSC). DSC spectra 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 aluminum pans were measured with a heating and cooling rate of 20°C/min. The samples were heated to 300°C, kept at that temperature for 2 minutes, cooled to 100°C and reheated to 300°C. The (peak) melting temperature and enthalpy were obtained from the second heating scan. The crystallization temperature was defined as the maximum of the peak in the cooling scan.

Wide Angle X-ray Diffraction (WAXD) as Function of Temperature. Diffraction patterns at different temperatures were obtained using a Philips X'Pert-MPD diffractometer (curved graphite monochromator $\text{CuK}\alpha_1$, radiation of 1.54056 Å). 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 $2\Theta = 4\text{--}60^\circ$.

Water Absorption. The absorption of water was measured as the weight gain after conditioning. DMA test bars were dried at 70°C in a vacuum oven for several days and weighed (w_0). Then the samples were conditioned in a desiccator over water at room temperature for 28 days (100% RH). The samples were reweighed after 7 and 28 days (w). The water absorption (in %) was calculated as $(w - w_0)/w_0 \times 100\%$.

Melt Viscosity. The melt viscosity was measured using a Kayeness capillary flow rheometer at 300°C. The length and diameter of the capillary were 20.32 and 1.016 mm respectively. The diameter of the barrel was 9.525 mm. The pressure was measured at different flow rates by applying varying piston speeds of 10, 20, 50, 100, 130, 200 and 500 mm/min (shear rates of 115, 230, 576, 1154, 1499, 2304 and 5760 sec^{-1} respectively).

Results and Discussion

Synthesis. Copolymers of PPE-2T, dodecanediol (C12) and T6T6T-dimethyl were made via a polycondensation reaction with a maximum temperature of 280°C. During the first part of the reaction NMP was used as a solvent because of the high melting temperature of the tetra-amide segment. The melting temperature of T6T6T-dimethyl is 303°C.^[15] After one hour at 250°C, the reaction had progressed enough to allow the final part of the reaction to be performed in the melt. Most of the NMP was stripped off at 280°C. During the last hour a vacuum of <1 mbar was applied to strip off any methanol formed and to obtain polymers with high molecular

weights. For copolymers with T6T6T-dimethyl as crystallizable segment the reaction mixture was gradually transferred from a clear solution into a clear melt. The clear melt indicates that melt phasing or liquid-liquid demixing between both segments is absent or only present at a nano-scale level.

The copolymer has an inherent viscosity of 0.41 dl/g ($M_n \sim 15,000$ g/mol) which is higher than that of PPO-803[®] ($M_n = 11,000$ g/mol). A molecular weight above 10,000 g/mol is preferred for good toughness of the material.

Thermal-mechanical properties. The thermal-mechanical properties of segmented copolymers based on PPE-2T, dodecanediol and T6T6T-dimethyl were measured by DMA. The polymers were injection molded (with an unheated mold) into bars and dried in a vacuum oven at 80°C. The test bars are slightly transparent. When the material is transparent this indicates that no spherulites are present.^[23] Light scattering also occurs when phase separated domains with a size above 100 nm are present. Apparently such domains are not present in PPE-2T/C12/T6T6T with 13 wt% T6T6T.

Table 1. Properties of the PPE-2T/C12/T6T6T copolymers.

	T6T6T content [wt%]	η_{inh} [dl/g]	T_g [°C]	G' (at T_g + 40°C) [MPa]	T_{flow} [°C]	T_g/T_{flow} [-]
PPE-2T ^a	-	0.18 ^b	168 ^c	-	-	-
PPO-803 [®]	-	0.37 ^b	200	-	222	-
PPE-2T/C12	0	0.31 ^b	169	-	193	-
PPE-2T/C12/T6T6T	13	0.41	169	10	269	0.82

(a), bimodal product made by one-pot synthesis (3100 g/mol);^[20]

(b), chloroform was used as a solvent instead of phenol/tetrachloroethane;

(c), measured by DSC instead of DMA;

(d), properties of test bar after heat treatment in a press (10 bar) for 5 minutes at 240°C and then slowly (5°C/min) cooled down to room temperature.

In Figure 3 the storage and loss moduli as measured by DMA are given for the PPE-2T/C12/T6T6T and amorphous PPE-2T/C12 copolymer compared to pure PPE (PPO-803[®]). The results are summarized in Table 1.

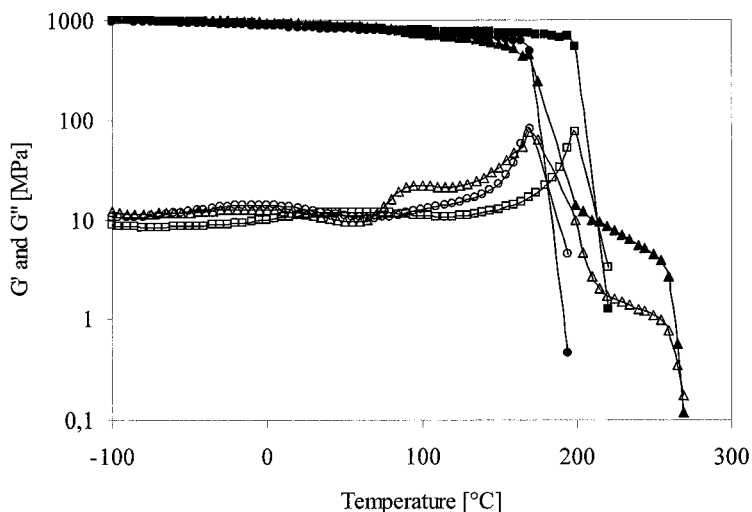


Fig. 3. Storage (solid symbols) and loss (open symbols) modulus of: (▲, Δ), PPE-2T/C12/T6T6T (13 wt%); (●, ○), PPE-2T/C12; (■, □), PPO-803®.

PPO-803® has a high and constant modulus up to the T_g at 200°C. The amorphous PPE-2T/C12 copolymer has a high and constant modulus up to the T_g at 169°C. The T_g is decreased compared to pure PPE because of incorporation of the flexible dodecanediol.^[27]

The copolymer of PPE-2T, dodecanediol and T6T6T-dimethyl is a semi-crystalline material. It shows a rubbery plateau above the glass transition temperature of the amorphous PPE phase. This result is very surprising, because the T_g/T_{flow} ratio is very high (~ 0.82). The modulus is high and constant up to the T_g of 169°C. However the modulus drops somewhat above 70°C and the loss modulus shows a peak around 100°C. This small effect can possibly be attributed to a glass transition in the (semi-crystalline) T6T6T phase. The T_g of nylon-6,T is 125°C.^[28] So the peak in the loss modulus at 100°C in the copolymer with T6T6T is probably originating from a T6T6T/C12 phase that has a little lower T_g than pure nylon-6,T.

The rubber modulus of the copolymer with 13 wt% T6T6T is 10 MPa and the flow temperature is 269°C. The flow temperature is sharp, which indicates that crystalline ribbons with a constant thickness are present. Compared to the commercial blend Noryl-GTX®, PPE-2T/C12/T6T6T has a higher modulus between 50 and 200°C. The T_g and T_m are comparable.

DSC. With DSC the melting and crystallization behavior of PPE-2T/C12/T6T6T with 13 wt% uniform T6T6T was studied. The T_m of T6T6T in the copolymer is 268°C and the enthalpy of melting is 14 J/g, which corresponds to 109 J/g T6T6T. From the enthalpy of melting of T6T6T-dimethyl (152 J/g)^[15] it can roughly be calculated that the crystallinity of T6T6T is around 70%. The crystallization temperature is 250°C and thus the undercooling is only 18°C, which indicates that the crystallization of T6T6T is very fast.

WAXD. The crystalline structure of PPE-2T/C12/T6T6T with 13 wt% T6T6T was studied with WAXD. A melt-pressed sample of 1 mm thickness was prepared in a press at 300°C during 5 minutes with a pressure of 10 bar (cooling rate 5°C/min). The WAXD spectrum was measured at room temperature and at 300°C (Figure 4).

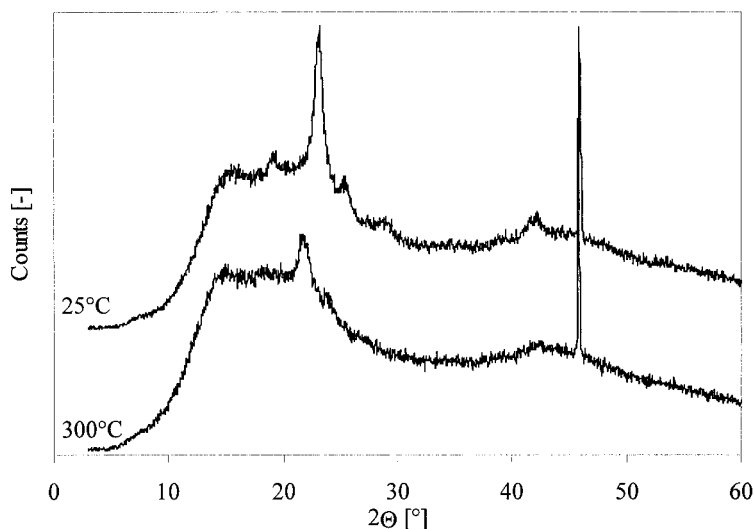


Fig. 4. WAXD data for PPE-2T/C12/T6T6T (13 wt%) at 25 and 300°C.

The main 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. 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 phase present. In this phase 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(DMT) and di-amide units^[24-26] 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.

Water Absorption. The water absorption of DMA test bars of PPE-2T/C12/T6T6T with 13 wt% uniform T6T6T was measured. The water absorption is compared with that of Noryl-GTX[®] and PPO-803[®]. The results are given in Table 2.

PPO-803[®] has a very low water absorption of 0.24% after one week. The water absorption of the PPE-2T/C12/T6T6T copolymer is 0.48% after one week. The water absorption does not increase further after 7 days. The water absorption of Noryl-GTX[®] is 2.1% after 7 days and 3.3% after 28 days. PPE-2T/C12/T6T6T copolymer with 13 wt% T6T6T has a lower water absorption than Noryl-GTX[®]. Polyamides are known to have high water absorption. The new copolymer has a lower polyamide content (about 3 times) and the crystallinity of the polyamide phase is higher than in Noryl-GTX[®]. Crystalline polyamide adsorbs less water than amorphous polyamide.

Table 2. Water absorption of PPE-2T/C12/T6T6T with 13 wt% uniform T6T6T compared to Noryl-GTX[®] and PPO-803[®] (20°C, 100% RH).

	7 days [%]	28 days [%]
PPE-2T/C12/T6T6T	0.48	0.48
Noryl-GTX [®]	2.1	3.3
PPO-803 [®]	0.24	0.24

Rheology. The melt viscosity of PPE-2T/C12/T6T6T with 13 wt% uniform T6T6T (~15.000 g/mol) was studied using a capillary flow rheometer at 300°C. The data of the copolymer are compared with that of Noryl-GTX[®] (GTX914) and PPO-803[®] in Figure 5.

The melt viscosity of PPO-803[®] is very high. By blending with polyamide as in Noryl-GTX[®] the processability is improved a lot. At 300°C the PPE-2T/C12/T6T6T copolymers have a much lower melt viscosity than Noryl-GTX[®]. The melt viscosity increases slightly with increasing molecular weight. It can be concluded that the processability of a copolymer of PPE and T6T6T with only 13 wt% of T6T6T is much better than that of PPO-803[®] and Noryl-GTX[®].

with 40 wt% of polyamide.

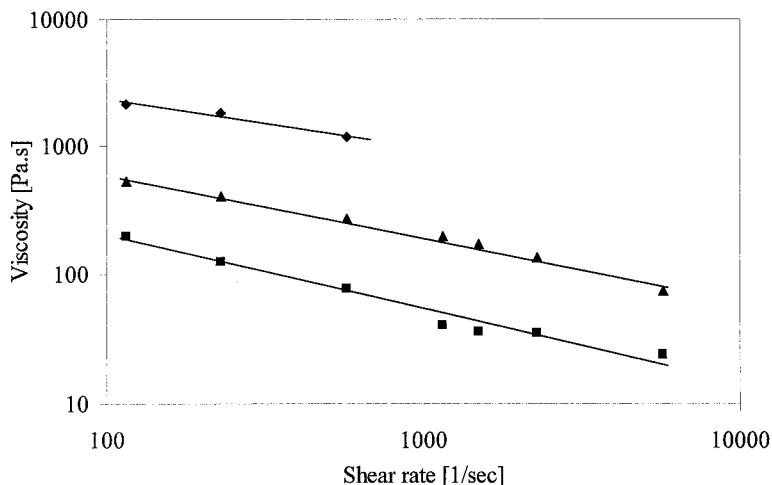


Figure 5: Melt viscosity at 300°C as a function of shear rate: (■), PPE-2T/C12/T6T6T (13 wt%, ~15000 g/mol); (▲), Noryl-GTX®; (◆), PPO-803® (11.000 g/mol).

Conclusions

Copolymerisation of PPE with uniform crystallizable T6T6T units and dodecanediol as an extender is a good method to obtain a semi-crystalline material with a very high T_g/T_m ratio, good solvent resistance and good processability. The copolymer that contains only 13 wt% of T6T6T has a T_g of 169°C and T_{flow} of 269°C ($T_m = 268^\circ\text{C}$). The polymer has a high and constant modulus up to the T_g . The modulus in the rubbery plateau is 10 MPa. It is very particular that the T6T6T units can actually crystallize in these copolymers despite the very high T_g/T_{flow} ratio of 0.82 and low hard segment concentration. The crystallinity of T6T6T is around 70%. The undercooling as measured by DSC is 18°C, which indicates that the crystallization is very fast. The crystallization is facilitated by ordering of T6T6T in the melt.

The PPE-2T/C12/T6T6T copolymers are interesting for applications where a high modulus up to the T_g of PPE is essential in combination with good solvent resistance and good processability. The segmented copolymers can also be useful as compatibilizer for blends of

PPE with polyamide. This method can also be useful to modify other high T_g amorphous polymers such as polycarbonate.

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