

Segmented copolymers of uniform tetra-amide units and poly(phenylene oxide). Part 4. Influence of the extender

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Abstract

Copolymers of telechelic poly(2,6-dimethyl-1,4-phenylene ether) (PPE) segments, uniform crystallisable tetra-amide units (T6T6T, 6–15 wt%) and different diols (C2–C36, polytetramethylene oxide) as an extender were synthesised. The telechelic PPE segment was end-functionalised with terephthalic ester groups and had a molecular weight of 3100 g/mol. The coupling between the PPE segment and the T6T6T unit was made with diols. The influence of the length and flexibility of the diol-extender and the concentration of the T6T6T units were studied on the thermal (DSC) and thermal–mechanical (DMA) properties of the copolymers. A crystalline T6T6T phase in the copolymers was evident from 9 wt% onwards. The length of diol extender had an effect on the glass transition temperature of the PPE phase, the crystallinity of the T6T6T segments and modulus above the glass transition temperature. With ethylene glycol the T_g of the copolymer was high but the crystallinity of the T6T6T rather low. With dodecanediol or hexanediol as an extender the T_g s of the PPE phase were somewhat lower, but the crystallinities of the T6T6T segments higher. With C36 and polytetramethylene oxide diols, the T_g were strongly decreased and broad and the modulus above the glass transition temperature not so high.

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1. Introduction

Segmented copolymers consisting of amorphous poly(2,6-dimethyl-1,4-phenylene ether) (PPE; also called polyphenylene oxide, PPO) segments and crystallisable tetra-amide units (T6T6T, two-and-a-half repeating unit of nylon-6,T; up to 20 wt%) with dodecanediol as an extender have a homogenous melt [1–3]. Surprisingly, these copolymers are semi-crystalline materials with a high T_g (170–180 °C), a not too high melting temperature of ~260–275 °C and as a result have an extremely high T_g/T_m ratio (>0.8). This is very particular because normally crystallisation is very slow at such high T_g/T_m ratios [4,5]. It was concluded that the crystallisation of the T6T6T units in these copolymers is extremely fast and that these units already order in the melt

[2]. The copolymers have good processability, good solvent resistance and low water absorption.

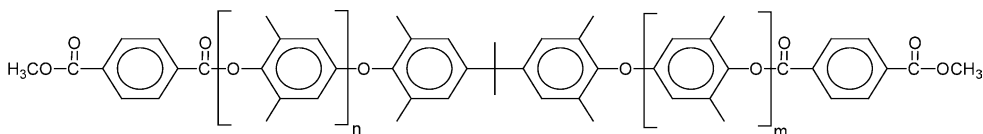
In particular at crystallisation temperatures near the T_g of the system, the crystallisation process is very sensitive to molecular weight and processing conditions. The PPE used was end functionalised with terephthalic ester groups (PPE-2T) [6]. Thus far PPE-2T (Fig. 1) and tetra-amide (T6T6T-dimethyl (Fig. 2) [7]) were copolymerised in a polycondensation reaction with dodecanediol (C12) as an extender. It will be interesting to study the effect of the type of diol on the thermal–mechanical behaviour of these copolymers and particular on the modulus above the PPE T_g , which is a function crystallinity of the T6T6T units. In the copolymer of PPE-2T with just diols the glass transition temperature of these copolymers decreases with increasing diol length [8]. The diols are situated between two PPE units (Fig. 3), between the PPE and T6T6T (Fig. 4) or between two T6T6T units (Fig. 5). In the system with a molar ratio of T6T6T/PPE of less than 1, studied here, the amount of diols between two T6T6T units (Fig. 5) is expected to be small.

Long flexible diols allows amide segment to order easily, but lower the T_g of the PPE phase. Very short diol extenders limit the mobility of the amide segments in the copolymer,

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T-PPE-T

Fig. 1. End capped poly(phenylene ether) oligomer.

but lower the PPE T_g less. With a decreasing T_g the window of crystallisation ($T_g - T_m$) might increase.

The aim of the present work was to investigate the influence of the length (flexibility) of the diol extender and the concentration of T6T6T units on the glass transition temperature of the PPE phase, modulus above this temperature and the crystallinity of the T6T6T units.

2. Experimental

2.1. Materials

1,2-Ethandiol, 1,6-hexanediol, 1,12-dodecanediol and *N*-methyl-2-pyrrolidone (NMP) were purchased from Merck. Tetraisopropyl orthotitanate ($\text{Ti}(i\text{-OC}_3\text{H}_7)_4$), obtained from Merck, was diluted in anhydrous *m*-xylene (0.05 M), obtained from Fluka. C36-Dimerised fatty diol (C36-diol) was obtained from Uniquema, Gouda (The Netherlands). Poly(tetramethylene-oxide) (PTMO₁₀₀₀, $M_n = 1000$ g/mol) was provided by DuPont. PPO-803[®] (11,000 g/mol) was obtained from GE Plastics (The Netherlands). All chemicals were used as received. The PPE/diol/T6T6T copolymers were synthesised according to the method described in Ref. [1]. T6T6T-dimethyl was synthesised as described before and has >98% uniformity [7]. The telechelic PPE-2T with terephthalic ester end-groups (PPE-2T, ~ 3100 g/mol, 573 μmol OCH₃/gram) were prepared by redistribution (depolymerisation) of PPO-803[®] according to the one-pot method [6]. These PPE-2T segments have a bimodal molecular weight distribution because part of the starting PPO-803[®] cannot be depolymerised [6,9]. The bimodal PPE-2T contains a depolymerised low molecular weight fraction ($M_n \sim 2000$ g/mol) with two reactive groups and a high molecular weight fraction with only one or no reactive endgroups ($M_n \sim 10,000$ g/mol).

2.2. Viscometry

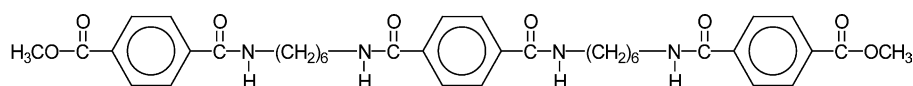
The inherent viscosity of the polymers was calculated from diluted solution viscosity measurements with a capillary Ubbelohde type 1B at 25 °C, using a polymer solution with a concentration of 0.1 g/dl in phenol/1,1,2,2-tetrachloroethane (50/50, mol/mol).

2.3. DMA

Samples for the DMA test ($70 \times 9 \times 2$ mm³) were prepared on an Arburg-H manual injection moulding machine. Before use, the samples were dried in a vacuum oven at 80 °C overnight. The torsion behaviour 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. Due to the very high damping of PPE at the T_g the G'' maximum was not always accurate to determine and may in some samples have been 0–10 °C lower than the G'' maximum temperature. The modulus of the rubbery plateau was determined at 40 °C above the T_g . The crystallinity was calculated from the modulus in the rubbery plateau using the method described in Refs. [1,10]. The flow temperature (T_{flow}) was defined as the temperature where the storage modulus G' reached 0.5 MPa. The flow temperature indicates the onset of melting. When the T_{flow} is sharp it is only a few degrees below the melting temperature (T_m) and the T_g/T_{flow} ratio (K/K) is about the same as the T_g/T_m ratio.

2.4. 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 aluminium pans were measured with a heating and cooling rate of 20 °C/min. The samples were heated to 300 °C, kept at that



T6T6T-dimethyl

Fig. 2. Bis ester hexamethylene terephthalamide tetra-amide.

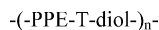


Fig. 3. Poly(phenylene ether ester).

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.

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 λ (°C/min) with Eq. (1) [11, 12].

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

3. Results and discussion

All the studied segments copolymers based on PPE-2T, a diol and T6T6T-dimethyl could be obtained with an inherent viscosity of at least 0.29 g/dl (Table 1), which is close to the value for PPO-803[®] (0.37 g/dl). Although the chemical composition of the copolymers is different from pure PPE, the inherent viscosities are a good indication of whether a high molecular weight copolymer was obtained. The thermal–mechanical properties of series of copolymers based on PPE-2T (~3100 g/mol) and varying T6T6T content (0–20 wt%) with different diols as extender (PTMO₁₀₀₀, C36-diol, dodecanediol [1–3], hexanediol and ethanediol), will be discussed successively. The effect of the diol length on the thermal behaviour, in particular the undercooling ($T_m - T_c$) for crystallisation, was studied with DSC.

3.1. Thermal–mechanical properties

The thermal–mechanical properties of the copolymers were studied by DMA as this method is very sensitive to changes in the amorphous and crystalline phase (Table 1). The T6T6T content was calculated, not counting the ester carbonyl, as the carbonyl group does not take part in the crystallisation [1,13]. It is assumed that the uniformity of the T6T6T units (>98%) is preserved during the polymerisation reaction [1,10].

3.1.1. Series 1: PTMO₁₀₀₀

A copolymer with PTMO₁₀₀₀ as extender between PPE-

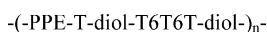


Fig. 4. Poly(phenylene ether–tetra-amide) copolymer).

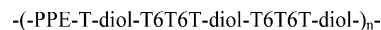


Fig. 5. Poly(phenylene ether–tetra-amide) copolymer with extended tetra-amide segments.

2T and T6T6T-dimethyl, with 9 wt% T6T6T was synthesized. In this copolymer the PPE-2T and T6T6T-dimethyl endgroup concentrations are equal. However, as a result of the random reaction of PTMO₁₀₀₀ with PPE-2T and T6T6T-dimethyl there will also be PPE units that are linked directly to other PPE units (Fig. 3) as well as T6T6T units that are coupled with PTMO₁₀₀₀ to form extended T6T6T units (Fig. 5). Extended T6T6T (Fig. 5) is not likely to crystallise in fully extended form, as PTMO₁₀₀₀ is too long and flexible for that. In absence of the fully extended form of the extended T6T6T a sharp melting temperature of crystallised T6T6T can be expected. The PPE/PTMO₁₀₀₀/T6T6T copolymer has an inherent viscosity of 0.53 dl/g, which is a high value. The test bars of the copolymers in this series are not transparent, indicating that phase separation has taken place. The PPE and the PTMO₁₀₀₀ segments already partly demixes. The PPE/PTMO₁₀₀₀/T6T6T copolymer, with a higher PTMO content (Table 1) and T6T6T units also demixes. The T6T6T units might have partly crystallised in the PPE phase and partly be present in the phase separated PTMO particles. The storage and loss modulus are given for the T6T6T containing copolymer and the amorphous PPE/PTMO₁₀₀₀ copolymer [8] (Fig. 6).

The amorphous polyether–ester copolymer based on PPE-2T/PTMO₁₀₀₀ has a high and constant modulus up to the T_g at 115 °C. The PPE/PTMO₁₀₀₀/T6T6T copolymers contain about twice the amount of PTMO₁₀₀₀ compared to the amorphous PPE/PTMO₁₀₀₀ copolymer (Table 1). The modulus decreases gradually with temperature and the T_g transition is broad. Even two transitions are apparent at –50 and 165 °C. This suggests a (partial) phase separation between PPE and PTMO₁₀₀₀, due to incompatibility of these two segments [8]. The low modulus at room temperature even suggests that the PTMO phase is (partly) cocontinuous. As a result of this phase separation the copolymers are not transparent.

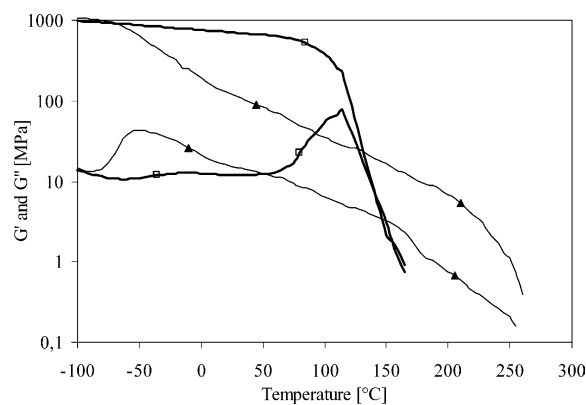
Fig. 6. Storage and loss modulus for copolymers with PTMO₁₀₀₀ as extender, T6T6T content: (□), 0 wt%; (▲), 9 wt%.

Table 1
Properties of the PPE/T6T6T copolymers with varying extender between PPE and T6T6T

	T6T6T content (wt%)	Diol content (wt%)	η_{inh} (dl/g)	T_g (°C)	G' (at $T_g + 40$ °C) (MPa)	T_{flow} (°C)	T_g/T_{flow} (-)	T6T6T crystallinity ^a (%)
Starting materials								
PPO-803 [®]	–	–	0.37 ^b	200	–	222	–	–
PPE-2T ^c	–	–	0.17 ^b	173 ^d	–	–	–	–
Series 1: PTMO ₁₀₀₀								
PPE/PTMO ₁₀₀₀	0	24	0.50	115	–	165	–	–
PPE/PTMO ₁₀₀₀ /T6T6T	9	35	0.54	165 ^e	1	260	0.82	< 10
Series 2: C36-diol								
PPE/C36 [8]	0	15	0.55	140	–	180	–	–
PPE/C36/T6T6T	6	19	0.53	135	0.7	225	0.82	< 10
PPE/C36/T6T6T	8	21	0.57	130	2.0	267	0.75	22
PPE/C36/T6T6T	10	22	0.60	128	2.2	267	0.74	23
PPE/C36/T6T6T	11	23	0.65	126	2.2	266	0.74	21
Series 3: Dodecanediol [1–3]								
PPE/C12	0	5.4	0.31	169	–	193	–	–
PPE/C12/T6T6T	6	7.0	0.32	173	–	209	–	–
PPE/C12/T6T6T	8	7.5	0.53	179	4	263	0.84	59
PPE/C12/T6T6T	10	8.0	0.56	179	6	266	0.84	71
PPE/C12/T6T6T	13	8.8	0.41	169	10	269	0.82	76
PPE/C12/T6T6T	15	9.4	0.47	179	12	267	0.84	69
Series 4: Hexanediol								
PPE/C6	0	3.7	0.30	185	0	210	–	–
PPE/C6/T6T6T	7	4.8	0.33	184	0	228	–	–
PPE/C6/T6T6T	9	5.1	0.33	178	1	236	0.89	< 10
PPE/C6/T6T6T	11	5.5	0.32	183	4	263	0.85	48
PPE/C6/T6T6T	14	5.9	0.37	184	4	266	0.85	37
Series 5: Ethanediol								
PPE/C2	0	1.9	0.36	190	0	217	–	–
PPE/C2/T6T6T	7	2.6	0.29	188	0	220	–	–
PPE/C2/T6T6T	9	2.8	0.30	185	1	232 ^f	0.91	< 10
PPE/C2/T6T6T	11	3.0	0.31	188	2	261 ^f	0.86	16
PPE/C2/T6T6T	14	3.2	0.30	189	2	278 ^f	0.84	13

^a T6T6T crystallinity determination Section 2.

^b Chloroform was used as a solvent instead of phenol/1,1,2,2-tetrachloroethane.

^c Bimodal PPE-2T (3100 g/mol) made by one-pot synthesis [6].

^d Measured by DSC instead of DMA.

^e The T_g of the PPE rich phase is given instead of the maximum of G'' .

^f The flow temperature is not well defined because there is not a sharp decrease in modulus.

The copolymer shows above 165 °C a rubbery plateau as a result of the crystalline of T6T6T units. A flow temperature of ~260 °C is obtained and the rubber modulus is around 1 MPa. From this low modulus it can be estimated that only small amount of T6T6T present that has crystallised. In this estimation the modulus-crystalline amide content relationship for PTMO-T6T6T was used as described in Section 2 [2,10]. This high temperature modulus is much lower than for PPE/C12/T6T6T [2]. It can be concluded that PTMO₁₀₀₀ at high contents easily phase separate from the PPE segments and that as a result the crystallinity of the T6T6T segments is very low.

3.1.2. Series 2: C36-diol

In a series PPE/C36/T6T6T copolymers with C36-diol (Fig. 7) as extender between PPE-2T and T6T6T-dimethyl the T6T6T content was varied between 6 and 11 wt%.

In the copolymer with 11 wt% T6T6T the PPE-2T and

T6T6T-dimethyl endgroup concentrations are equal. As a result there will be next to the alternating copolymer (Fig. 4), some PPE units that are linked directly to other PPE units (Fig. 3) as well as T6T6T units that are coupled with C36-diol to form extended T6T6T units (Fig. 5). The T6T6T extended with these diol units, T6T6T–C36–T6T6T, are not expected to crystallise in an extended form as, therefore, the C36-diol too long and too irregular (Fig. 7). The copolymers based on C36-diol all have high inherent viscosities (0.53–0.65 dl/g). The test bars of the copolymers of this series are not transparent. This suggests that PPE and C36 segments are not fully compatible. In Fig. 8, the storage and loss modulus as measured by DMA are given for the copolymers with C36-diol as an extender.

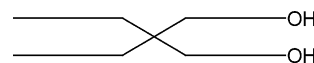


Fig. 7. Structure of C36-diol dimerised fatty diol.

With increasing T6T6T content the modulus in the temperature range of 50–150 °C decreases, however, the modulus above 150 °C increases. The lowering of the modulus below 150 °C seems to be due to the increasing C36-diol and the increasing T6T6T content (Table 1). Next to the glass transition of the PPE-phase a second transition can be observed at about 80 °C, which increases in size with T6T6T content. This transition might be of an amorphous C36–T6T6T–C36 phase, this as the T_g of pure nylon-6, T is 125 °C [15] and for C12–T6T6T–C12 of 100 °C [1–3].

With increasing T6T6T content the rubber modulus (above 150 °C) and flow temperature increase. This is due to the crystalline T6T6T segments. However, the modulus in the rubbery plateau decreases with temperature and T_{flow} are not sharp. These results suggest that PPE and C36 segments were partly phase separated and some of the T6T6T units are expected to be in the C36–T6T6T–C36 phase. Due to the presence of the phase separated amorphous C36–T6T6T–C36 domains the copolymers are not transparent.

From the modulus at $T_g + 40$ °C an estimation of the T6T6T crystallinity can be obtained and was in these copolymers around 20% (Table 1). This is rather low and might be due to the phase separated structure as we have seen for the copolymers with PTMO₁₀₀₀. An other effect is the high molecular weight of these copolymers, a strong molecular weight effect in the crystallisation was seen before [1–3].

3.1.3. Series 3: Dodecanediol

Copolymers of PPE-2T (~3100 g/mol) and uniform T6T6T-dimethyl with dodecanediol (C12) as an extender were described before [1–3] (Table 1). The polymers had high solution viscosities and were thus of a high molecular weight (Table 1). The copolymers were transparent suggesting that now no or little liquid–liquid demixing had taken place. However, in the DMA graph still a small transition was observed at 80–100 °C [10]. This transition can as indicated above be ascribed to C12–T6T6T–C12 segments that have phase separated. As the materials are transparent, the molecular weights high and the loss peak in the DMA low, the amount of the liquid–liquid demixed phase must be small and of a sub micron size. These copolymers had a high T_g (170–180 °C) and a well-developed rubbery plateau when more than 8 wt% T6T6T was incorporated. With increasing T6T6T content the rubbery plateau (4–13 MPa) and flow temperature (260–275 °C) increased. The calculated crystallinity of the uniform T6T6T units (Section 2) in these copolymers was between 50 and 80%.

3.1.4. Series 4: Hexanediol

In series 4, hexanediol was used as an extender and the T6T6T content was varied from 7 to 14 wt%. With 14 wt% T6T6T the PPE-2T and T6T6T-dimethyl endgroup concentrations are equal. The copolymers based on hexanediol all have low inherent viscosities of 0.30–0.37 dl/g. The loss

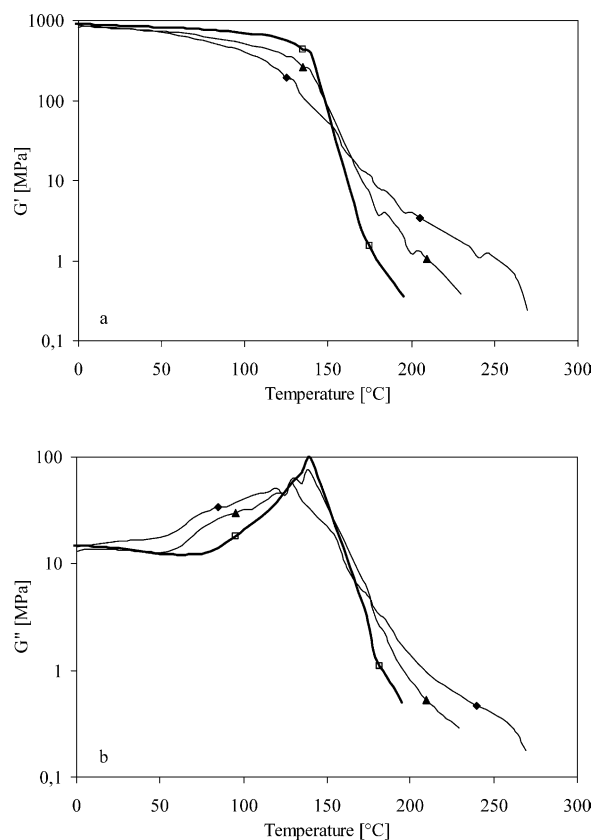


Fig. 8. Storage (a) and loss (b) modulus for copolymers of PPE-2T and T6T6T-dimethyl with C36-diol as an extender, T6T6T content: (□), 0 wt%; (▲), 6 wt%; (◆), 11 wt%.

hexanediol during the reaction by evaporation is probably responsible for this. The DMA test bars of the PPE/C6/T6T6T polymers were transparent, this probably to the low diol content as a result of the lower molecular weight of hexanediol than with PTMO₁₀₀₀ and C36 (Table 1). The storage modulus as measured by DMA is given in Fig. 9.

With hexanediol as extender a rubbery plateau is obtained for copolymers with 11 and 14 wt% T6T6T. With 9 wt% T6T6T or less no rubbery plateau is observed. The T_g and the T_{flow} are sharp. The T_g is a few degrees higher than with dodecanediol as its contents is lower and its flexibility higher. The presence of a sharp flow temperature indicates that no C6-extended T6T6T units (Fig. 9) have crystallised.

The rubber modulus and flow temperature increase with increasing T6T6T content. The rubber modulus and flow temperature are the same for the copolymers with 11 and 14 wt% T6T6T and thus the degree of crystallinity of these copolymers is comparable. The calculated crystallinity of T6T6T in the copolymer with 11 wt% T6T6T is 48% and with 14 wt% T6T6T 37%. These crystallinities are lower than for the PPE/C12/T6T6T copolymers [Table 1]. Possibly at higher C6–T6T6T–C6 contents and/or the presence of C6–T6T6T–C6–T6T6T–C6 units in this copolymer is responsible for this behaviour.

In the loss modulus (not given) there is a peak around 100 °C due to an amorphous C6–T6T6T–C6 phase, comparable to the PPE/C12/T6T6T copolymers, see above and this close to the T_g of nylon-6, T of 125 °C [14]. As a result of this transition the modulus decreases at this temperature. The peak in the loss modulus at ~100 °C is larger for the copolymer with 14 wt% T6T6T, and this suggests a higher amorphous C6–T6T6T–C6 content. Despite the presence of some amorphous C6–T6T6T–C6 domains, the PPE/C6/T6T6T copolymers are transparent (as were the copolymers with C12 as an extender), indicating that these domains are small.

3.1.5. Series 5: Ethanediol

In polymer series 5, ethanediol was used as an extender and the T6T6T content was varied from 0 to 14 wt%. With 14 wt% T6T6T, the PPE-2T and T6T6T-dimethyl endgroup concentration are equal. The ethanediol content in these copolymers is due to its small size low (Table 1). The copolymers based on ethanediol all have low inherent viscosities (0.29–0.36 dl/g). The problem of evaporation of ethanediol during the reaction might have been the reason for this and further optimisation of the reaction conditions is necessary. The copolymers of this series were transparent. The storage modulus as measured by DMA (Fig. 10).

The modulus remains almost constant up to the glass transition temperature and the T_g changes little with increasing T6T6T content. The rubber modulus (above the T_g) and flow temperature increase with increasing T6T6T content. The modulus at these high temperatures is, however, rather low and thus the crystallinity of T6T6T units is in these copolymers less than 20%. This is much lower than in copolymers with C12 or C6 as extender. This indicates that the length and thus the flexibility of the diol that links the PPE-2T and T6T6T segment is important for the rate and extent of crystallisation of T6T6T. If also some C2–T6T6T–C2–T6T6T–C2 segments are present, the centre C2 is too short to chain fold and this segment is expected to crystallise in its extended form. These crystallites have a higher lamellar thickness and thus a higher

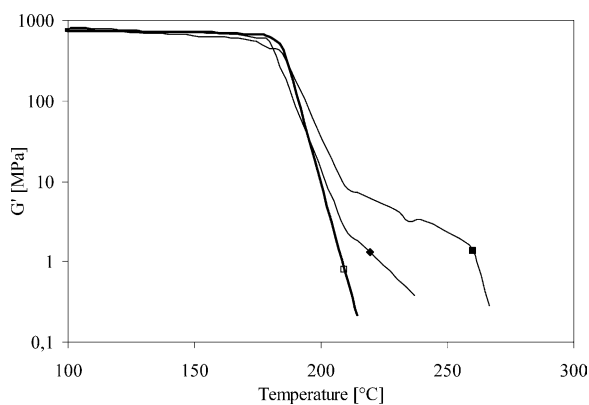


Fig. 9. Storage modulus for PPE/C6/T6T6T copolymers with different amounts of T6T6T: (□), 0 wt%; (◆), 9 wt%; (■), 14 wt%.

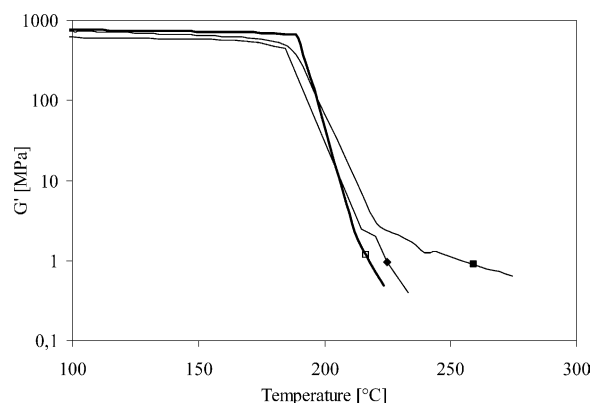


Fig. 10. Storage modulus for PPE/C2/T6T6T copolymers with different amounts of T6T6T: (□), 0 wt%; (◆), 9 wt%; (■), 14 wt%.

melting temperature [15]. As a result, the copolymers should show a melting range without a sharp flow temperature.

3.2. Comparison of extenders

The influence of the type and length of the extender between PPE and T6T6T segment influences the phase separation, the T_g of the amorphous phase and the crystallisation of the T6T6T units. The storage modulus of different PPE/diol/T6T6T copolymers with 11 wt% T6T6T (9 wt% for PTMO₁₀₀₀) of series 1–5 are compared Fig. 11.

With increasing length of the diol extender between PPE and T6T6T the T_g of the PPE phase decreases and becomes less sharp. So in these copolymers a part of the diol units is mixed with the amorphous PPE phase. This behaviour was also found in absence of T6T6T units [8].

At the same time, a second transition was observed probably of a liquid–liquid demixed diol–T6T6T–diol phase. With increasing diol length (content) the transition is

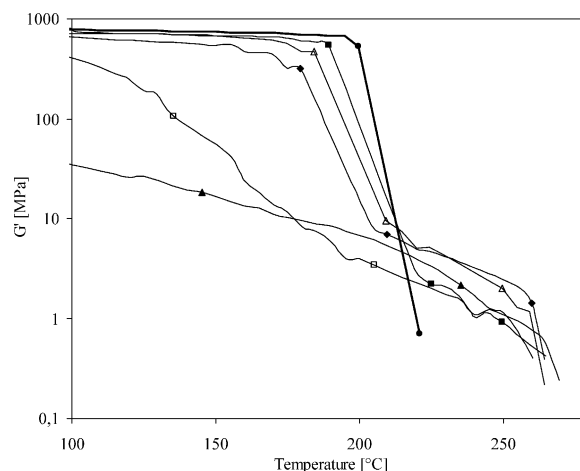


Fig. 11. Storage modulus for PPE/diol/T6T6T copolymers with different diols as flexible link between PPE and T6T6T and 11 wt% T6T6T (series 1–5): (▲), PTMO₁₀₀₀ (9 wt% T6T6T); (□), C36; (◆), C12; (△), C6; (■), C2; (●), PPO-803[®].

Table 2
DSC results for copolymers of series 2–5 with 11 wt% T6T6T

	T_m (°C)	ΔH_m (J/g)	ΔH_m (J/g T6T6T)	Cryst. ^a (%)	T_c (°C)	ΔH_c (J/g)	$T_m - T_c$ (°C)
PPE/C2/T6T6T ^b	249	1	9	< 10	239	– 1	10
PPE/C6/T6T6T	267	9	82	54	250	– 7	17
PPE/C12/T6T6T [2]	267	10	91	60	249	– 11	18
PPE/C36/T6T6T	277	10	91	60	259	– 9	18

^a The crystallinity of T6T6T was calculated with the enthalpy of melting of T6T6T-dimethyl (152 J/g) [7].

^b For ethanediol the melting and crystallisation peaks were very broad.

stronger and at a lower temperature. With PTMO₁₀₀₀ and C36 the samples were also not transparent.

The rubber modulus (above the T_g) has the highest values for C12 and decreasing with both increasing and decreasing length. The T6T6T crystallinities are thus expected to be highest with the C12 extender. This difference in crystallinity cannot be ascribed to a molecular weight effect, because, for example the molecular weight of the copolymers with ethanediol as an extender is lower than with hexanediol or dodecanediol. The crystallinity is important for the mechanical properties, the dimensional stability and the solvent resistance of the material. C12 seem to be an optimum length of the diol for easy crystallisation of the T6T6T units. Shorter diols decreases the flexibility necessary for crystallisation, longer diols promote liquid–liquid demixing. As was found before, the flow temperature is little influenced by the degree of T6T6T crystallinity [3]. The T_g/T_{flow} ratio of these copolymers are all high.

3.3. DSC

With DSC the melting temperature and enthalpy and crystallisation temperature and enthalpy were measured for copolymers of series 2–5 with 11 wt% T6T6T. The results (after correction for the thermal lag [2,11,12]) are given in Table 2.

The crystallinity of T6T6T units in these copolymers was calculated with an enthalpy of 150 J/g for the T6T6T unit [7]. The crystallinity of T6T6T in PPE/C2/T6T6T is very low (<10%), the melting and crystallisation peaks were also broad. The crystallinity of T6T6T in the copolymers with C6–C36 as extender is between 54 and 60%. With DMA such a high crystallinity was only observed for C12 (Table 1). The difference of the DSC and DMA crystallinities for the other copolymers are as yet unexplained.

The undercooling ($T_m - T_c$) is for the PPE/T6T6T copolymers with C6–C36 as an extender, at approximately 18 °C, which is a low value, indicates fast crystallisation. With C2 an undercooling of only 10 °C was found, but this is probably due to the difficulty in determining the peak temperature of the melting and crystallisation peak for this copolymer.

4. Conclusions

The influence of the diol extender length and the T6T6T content on the thermal–mechanical properties of PPE/diol/T6T6T copolymers were studied. The diols studied were C2, C6, C12, C36 and PTMO₁₀₀₀ and with their increasing length their content increased. The T6T6T content was increased 0 to about 14 wt%, at which content the molar ratio of PPE-2T and T6T6T was one. The function of the T6T6T is to crystallise and thereby increasing the mechanical properties, the dimensional stability and the solvent resistance of the material. The function of the diol-extender is to couple the PPE-2T segments with the T6T6T units, but has as side effects a lowering of the PPE T_g , a formation of an extra amorphous phase, and an influence on the T6T6T crystallisation due to its flexible structure.

Based on the DSC results the crystallinity of the T6T6T units in these copolymers is high despite its high T_g/T_m ratio (0.84). However, these high crystallinities do not always lead to high moduli in the rubbery region (above the T_g). As yet it is not clear why this is so. Certainly with long diols partial liquid–liquid demixing of a diol–T6T6T–diol phase seems to take place. The T_g of this phase is at about 80–100 °C and as a result of this is the modulus of the copolymer at temperatures below the T_g of the PPE phase lowered. The PPE–diol–T6T6T copolymer with a C12 diol extender had the highest modulus in the rubbery region combined with being transparent.

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