Segmented Copolymers of Uniform Tetra-amide Units and Poly(Phenylene Oxide) by Direct Coupling

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ABSTRACT: Segmented copolymers with telechelic poly (2,6-dimethyl-1,4-phenylene ether) (PPE) segments and crystallizable bisester tetra-amide units (two-and-a-half repeating unit of nylon-6,T) were studied. The copolymers were synthesized by reacting bifunctional PPE with hydroxylic end groups with an average molecular weight of 3500 g/mol and bisester tetra-amide units via an ester polycondensation reaction. The bisester tetra-amide units had phenolic ester groups. By replacing part of the bisester tetra-amide units with diphenyl terephthalate units (DPT), the concentration of tetra-amide units in the copolymer was varied from 0 to 11 wt%. Polymers were also prepared from bifunctional PPE, DPT, and a diaminediamide (6T6-diamine). The thermal and thermal mechanical pro-

perties were studied by DSC and DMA and compared with a copolymer with flexible spacer groups between the PPE and the T6T6T. The copolymers had a high T_g of 180–200°C and a melting temperature that increased with amide content of 220–265°C. The melting temperature was sharp with monodisperse amide segments. The $T_m - T_c$ was 39°C, which suggests a fast, but not very fast, crystallization. The crystallinity of the amide was $\sim$ 20%. The copolymers are semicrystalline materials with a high T_g and a high T_g/T_m ratio ($>$ 0.8). © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 103: 512–518, 2007

Key words: PPE; PPO; segmented copolymer monodisperse; tetra-amide

INTRODUCTION

Segmented copolymers consisting of amorphous poly(2,6-dimethyl-1,4-phenylene ether) (PPE) (also called PPO) segments, crystallizable tetra-amide units (up to 20 wt %), and spacer groups (-spacer-T-PPE-T-spacer-T6T6T-) have been studied.[1–3] The monodisperse tetra-amide units T6T6T are two and a half repeat units of PA-6,T. The copolymers are semicrystalline materials with a high T_g (170–180°C) combined with a not too high melting temperature (260–275°C) and have thus an extremely high T_g/T_m ratio ($>$ 0.8). This is very particular because crystallization is normally absent in (co)polymers with a high T_g/T_m ratio.[4,5] The uniform length T6T6T segments form ribbon-like crystalline structures with a very high aspect ratio dispersed in the amorphous matrix.[6–9] The copolymers undergo melt processing well and have good solvent resistance and low water absorption. Increasing the spacer group length decreases the T_g of the system a bit, but increases the storage modulus between T_g and T_m.[10] However very long spacer units ($M_n > 1000$ g/mol) are immiscible with

the PPE phase and form a separate amorphous phase.[10] The optimum spacer length seems to be C6—C12.

It is interesting to study whether high-molecular-weight PPE-T6T6T copolymers can be made without spacer units and what the properties of these copolymers are. Without spacer units, the copolymer synthesis is in less steps and thus simpler.

The starting telechelic PPE has two hydroxylic groups (PPE-2OH) (Fig. 1) and a molecular weight of 3500 g/mol.[11] These phenolic hydroxylic end groups can be reacted with ester groups. As the reactivity of the phenolic hydroxylic group in PPE is low, the used ester group should be very reactive, like a phenolic ester. Polymerization is possible of PPE-2OH, and diphenyl terephthalate (DPT) or diphenyl ester of T6T6T (T6T6T-diphenyl) are used (Fig. 1).[12] As T6T6T-diphenyl is a high melting compound (312°C[12]) and the polymerization temperature is 280°C, a solvent is needed in the initial stage of the reaction. Another route is to react PPE-2OH with diphenyl terephthalate (DPT) and a diamine-diamide (6T6-diamine).[12] As DPT and 6T6-diamine are not very high melting materials, this reaction can be carried out, in principle, in the absence of a solvent. Also in this way it is not necessary to synthesize first T6T6T-diphenyl. However a side effect of this route is that the amide units prepared are on average tetra-amide (T(6T)₂) but not anymore monodisperse

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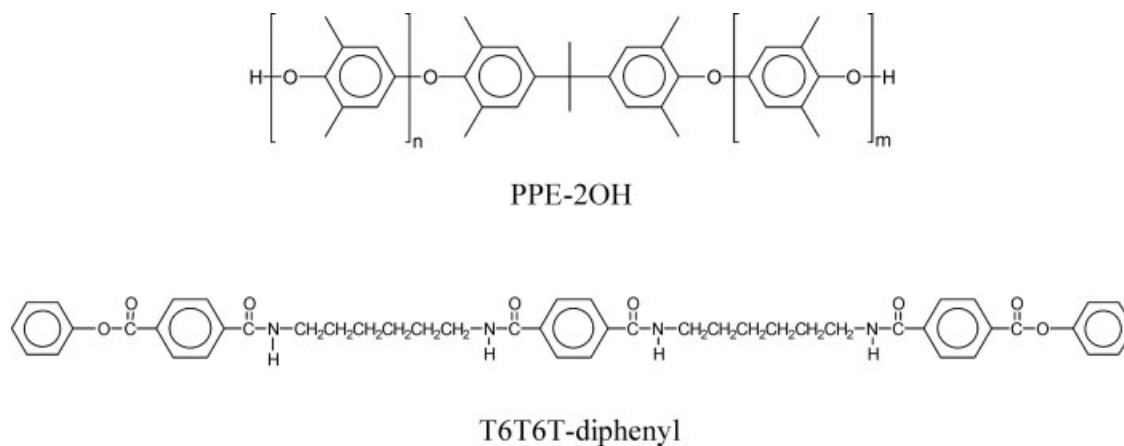
Figure 1 Molecular structure of PPE-2OH and T6T6T-diphenyl.

in length. Next to T6T6T also T6T6T6T6T and T6T6-T6T6T6T6T, etc., can be formed.

The aim of the present work is to study the synthesis and properties of (-PPE-T6T6T-) segmented copolymers based on difunctional PPE segments (PPE-2OH) and T6T6T-diphenyl or 6T6-diamine/DPT. The T6T6T content in the copolymers could be varied by replacing some of the T6T6T-diphenyl with DPT. The DPT extends the PPE to -PPE-T-PPE- and thereby increases the segment length between T6T6T segments. The copolymers were analyzed by viscometry and DSC. The thermal mechanical behavior of the copolymers was studied by DMA: the glass transition temperature, the melting temperature, and modulus in the $T_g - T_m$ region. The properties were compared with a (-spacer-T-PPE-T-spacer-T6T6T-) copolymer having C12 spacer units.

EXPERIMENTAL

Materials

N-methyl-2-pyrrolidone (NMP) was purchased from Merck. Tetraisopropyl orthotitanate (Ti(i-OC$_3$H$_7$)$_4$), obtained from Merck, was diluted in anhydrous m-xylene (0.05M), obtained from Fluka. A poly(2,6-dimethyl-1,4-phenylene ether), PPO-803® (11,000 g/mol), was obtained from GE Plastics (The Netherlands). Telechelic PPE-2OH with a number average molecular weight of 3500 g/mol and 450 μmol OH/g was made according to Krijgsman et al.[11] The telechelic PPE-2OH is obtained by a depolymerization or redistribution reaction of high molecular weight PPE (PPO-803®). As this starting PPE contained chains that cannot take part in the redistribution reaction, the crude redistributed PPE-2OH contains some unreacted PPE chains and as a result of this PPE-2OH has a bimodal molecular weight distribution. All chemicals were used as received. Uniform

T6T6T-diphenyl (> 95% uniform), 6T6-diamine, and diphenyl terephthalate (DPT) were synthesized as described before.[12]

Synthesis of -PPE-T6T6T- copolymers

The preparation of an alternating segmented block copolymer of PPE-2OH and T6T6T-diphenyl is given as an example. For copolymers with lower T6T6T contents, part of the T6T6T-diphenyl was replaced by DPT to retain stoichiometry and high molecular weight. The polymerization procedure for PPE-T6T6T starting from PPE-2OH, DPT and 6T6 was also similar.

The reaction was carried out in a 50-mL glass reactor with a nitrogen inlet and mechanical stirrer. The vessel was loaded with PPE-2OH (10.0 g, 4.50 mmol OH), T6T6T-diphenyl (1.82 g, 2.25 mmol), 20 ml NMP, and catalyst solution (0.6 mL of 0.05 M Ti(i-OC$_3$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 120 min 280°C. Subsequently, the pressure was then carefully reduced ($P < 20$ mbar) to distil off the remaining NMP in 60 min and then further reduced (< 1 mbar) for 60 min. Finally, the vessel was allowed to slowly cool to room temperature while maintaining the low pressure. The polymer was then removed from the reactor and powdered.

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).

Dynamic mechanical analysis

Samples for dynamic mechanical analysis (DMA) test ($70 \times 9 \times 2$ mm³) were prepared on an Arburg-H manual injection molding machine. Before use, the samples were dried overnight in a vacuum oven at 80°C. The DMA behavior in torsion 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. This maximum is 0–10°C lower than the actual glass transition temperature, because with this DMA apparatus it was not possible to measure a few points around the T_g due to the very high damping. 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' 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. The crystallinity was estimated from the modulus in the rubbery plateau using the method described in.[1,9] The effect crystalline of T6T6T content on the modulus of PPE-T6T6T copolymers is comparable with that in PTMO-T6T6T.[2,9] The estimated crystallinities are calculated with eqs. (1) and (2):

$$\log G' = \log G_o' + \text{T6T6T (crystalline)} * B \qquad (1)$$

$$X_c = \frac{\text{T6T6T (crystalline)}}{\text{T6T6T (total)}} \qquad (2)$$

$$X_c = \frac{\log G' - \log G_o'}{B * \text{T6T6T (total)}} \qquad (3)$$

where G'_o is 1.3 MPa, and B is 9.44.[2,9]

Differential scanning calorimetry

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 min, 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.

To account for the thermal lag between a point in the sample and the calorimeter furnace, the recorded

temperatures in non-isothermal crystallization experiments must be corrected. For Perkin-Elmer DSC7 with aluminum pans the actual temperature was calculated from the display temperature and cooling rate λ (°C/min) with eq. (4)[14,15]

$$T_{actual} = T_{display} + 0.089\lambda \; [°C] \qquad (4)$$

RESULTS AND DISCUSSION

The bifunctional PPE telechelic with hydroxylic endgroups (PPE-2OH) was reacted with DPT and T6T6T-diphenyl. The used PPE-2OH had a number average molecular weight of 3500 g/mol. Because of the aromatic nature and steric hindrance of the 2,6-dimethyl groups, the phenolic endgroups have a low reactivity. Also present in PPE are Mannich base type OH-endgroups, which are expected to have a very low reactivity.[11,16] In view of this was the final reaction step in the polymerization carried out at 280°C: 2 hours atmospheric, one hour at a low vacuum (< 20 mbar) and one hour at high vacuum (< 1 mbar). Two series of segmented block copolymers were studied. In series 1, monodisperse T6T6T-diphenyl and DPT units were used. In series 2 the copolymerization was with diaminediamide 6T6 and DPT. Some properties are summarized in Table I.

The T6T6T content was calculated, assuming that the ester carbonyl does not crystallize and belongs to the amorphous phase.[17] For the polymers that were made with T6T6T-diphenyl it is assumed that the uniformity of the T6T6T units is preserved during the polymerization reaction.[1,9] It is expected that amide segments in the copolymers synthesized with DPT and 6T6 have a less monodisperse character.

Series 1: PPE-T6T6T/T

From PPE-2OH and T6T6T,-diphenyl copolymers were prepared with varying T6T6T content (11–0%). The T6T6T content was changed by replacing T6T6T-diphenyl units with DPT. The DPT forms a terephthalate (T) linkage between PPE segments (-PPE-T-PPE-). The copolymer without T6T6T is -PPE-T- and the copolymer without DPT is -PPE-T6T6T-. If both T6T6T and DPT are used the copolymer is abbreviated as -PPE-T6T6T/T-. The copolymers were obtained by a solution/melt polymerization and had relative high inherent viscosities (0.31–0.38 dL/g) despite the low reactivity of the phenolic endgroups of PPE-2OH. Increasing the DPT content did not seem to have an effect on the inherent viscosities. The reactivity of the T6T6T-diphenyl is thus not lower than DPT and the miscibility of T6T6T-diphenyl with PPE-2OH not a problem. The copolymers were transparent.

TABLE I
Properties of the PPE-T6T6T Copolymers with Difunctional PPE Segments (Mn 3500 g/mol)

	T6T6T (wt %)	h_{inh} (dL/g)	T_g (°C)	G' (at T_g + 40°C) (MPa)	T_{flow} (°C)	T_g/T_{flow} (−)	Calc. cryst. (%)[d]
Starting materials							
PPO-803[®a]	–	0.37[b]	200	–	222	–	–
PPE-2OH	–	0.19[b]	182[c]	–	–	–	–
Series 1: -PPE-T6T6T/T-							
-PPE-T-	0	0.33	195	0	220	–	–
-PPE-T6T6T/T-	7	0.31	183	0	230	–	–
-PPE-T6T6T/T-	9	0.38	183	2.3	262	0.85	30
-PPE-T6T6T/T-	10	0.35	188	1.6	251	0.88	10
-PPE-T6T6T-	11	0.34	183	1.6	254	0.87	10
Series 2: -PPE-T(6T)₂/T-							
-PPE-T-	0	0.33	195	0	220	–	–
-PPE-T(6T)₂/T-	7	0.40	188	0	235	–	–
-PPE-T(6T)₂/T-	9	0.37	192	2.2	284[e]	0.83	25
-PPE-T(6T)₂-	11	0.42	188	2.0	264[e]	0.86	20
-PPE-T(6T)₂.₅-	14	0.44	193	1.8	290[e]	0.83	15

[a] PPO-803[®] is a high-molecular-weight PPE (Mn 11,000).
[b] Chloroform was used as a solvent instead of phenol/1,1,2,2-tetrachloroethane.
[c] Measured by DSC instead of DMA.
[d] Estimated crystallinity from the storage modulus at T_g + 40°C [eq. (3)].
[e] Flow temperature is not well defined because there is not a sharp decrease in modulus.

The melting behavior of the copolymers was studied by DSC. As the T6T6T contents were low only measurable results could be obtained for the 11 wt % T6T6T copolymer. The melting temperature was at 261°C and the crystallization temperature at 222°C. The $T_m - T_c$ difference is 39°C, which suggests a fast, but not very fast, crystallization. For a very fast crystallization $T_m - T_c$ difference should have been less than 30°C.[2] The heats of melting and crystallization were hardly measurable and were about 1 J/g.

The copolymers could be injection molded into bars and these were tested by DMA (Fig. 2, Table I). The samples had not given a heat treatment. The PPE-T copolymer (0% T6T6T) is an amorphous material that is not expecting to crystallize. This copolymer has a T_g at 195°C and a flow temperature (T_{flow}) of 220°C. Increasing the T6T6T content decreases the T_g to 183°C and increases the T_{flow} to 250–260°C. As the T_g of the copolymers with T6T6T is lower than that of the amorphous copolymer PPE-T, some T6T6T units are mixed with the amorphous PPE phase. The loss modulus (G'') of the PPE-T6T6T/T copolymers shows a shoulder at ∼ 130°C that increases with T6T6T content. The shoulder in the loss modulus can be ascribed to the presence to an amorphous T6T6T phase.

The flow temperature increases with T6T6T content due to crystallized T6T6T segments. The crystallized T6T6T segments thus increases the dimensional stability of the copolymers, and possibly the solvent resistance as well. The shear storage modulus (G') at 40°C above T_g increases with T6T6T content to about

2 MPa. From the height of the storage modulus the T6T6T crystallinities can be estimated with eq. (3). The copolymers with 9–11 wt % T6T6T have on average an estimated crystallinity of 20%. The noncrystallized T6T6T segments are expected to be partly present the PPE phase, as judged from the lowered T_g and partly as a separate T6T6T phase as judged from the shoulder in the loss modulus graph at 130°C.

Series 2: PPE-T(6T)₂/T

In series 2, PPE-T(6T)₂/T copolymers were made in from PPE-2OH, 6T6-diamine and diphenyl terephthalate (DPT). The T(6T)₂ segments were formed during the reaction. If lower -T(6T)₂- contents were used the PPE was extended with excess DPT to -PPE-T-PPE-. The 6T6-diamine has a melting temperature of 178°C and this is much lower that the melting temperature of T6T6T-diphenyl (312°C).[12] Therefore, at 180–280°C a solvent is not needed and the polymerization can in principle be performed in the melt. However, in this study NMP was used as a solvent like in series 1. A disadvantage of synthesis of T(6T)₂ during the polymerization reaction is that next to T6T6T segments T6T6T6T6T and T6T6T6T6T6T segments can also be formed. Thus, now there will be a length distribution in the T(6T)₂ units. With 11 wt % of T6T6T, the 6T6-diamine and PPE-2OH endgroup concentrations are equal. With 14 wt % of T(6T)ₙ units, the average repeat length n is larger than 2, on
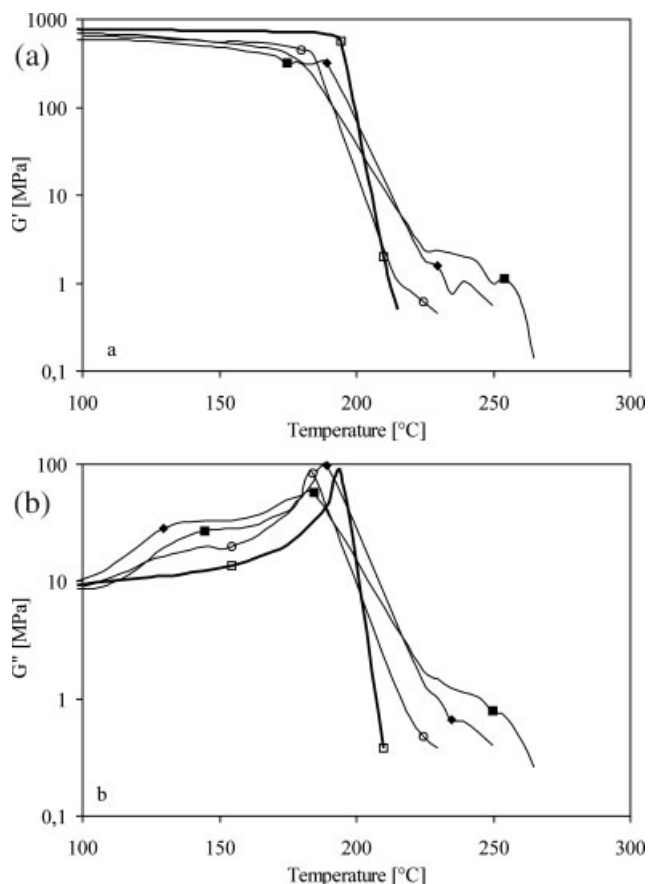
Figure 2 Storage (a) and loss (b) modulus of -PPE-T6T6T/T- copolymers with different amounts of T6T6T: □, 0 wt %; ○, 7 wt %; ■, 9 wt %; ◆, 10 wt %.

average 2.5, and the concentration of amide segments with $n \geq 4$ will be increased.

The inherent viscosities of the copolymers of series 2 was 0.37–0.44 dL/g, which is somewhat higher than that of series 1. The copolymers of series 2 were transparent. The copolymers could well be injection molded and the DMA properties studied (Table I, Fig. 3).

In these copolymers, the T_gs were slightly lower than that of PPE-T, and in the loss modulus curve a shoulder at 130°C was observed. Apparently part of the amide units had not crystallized. With increasing $T(6T)_2$ content, the storage modulus above the T_g increased gradually with temperature and also the flow temperatures. The flow transition was for these copolymers not sharp. For $T(6T)_n$ units with a distribution of lengths the melting transition is broad.[18,19] The storage modulus above the T_g of the copolymer is very sensitive to the crystallinity in copolymers.[2,9] The shear storage modulus at $T_g + 40°C$ was for copolymers with an amide contents of 9–14 wt % at ∼ 2 MPa. With eq. (3), the crystallinity of the amides segments was estimated to be 20%.

Influence of spacer unit and amide dispersity

The copolymers of series 1 and 2 had no spacer units between the PPE and the amide segments. Spacer units for crystallizable segments increase the chain flexibility during crystallization and with that increases the crystallization rate and the crystallinity. The crystallization rate is also thought to depend on the polydispersity of the crystallizable segments. However, how critical this polydispersity for the $T(6T)_2$ segments is little known.

For the -PPE-T-spacer-T6T6T-spacer-T- copolymers, the optimum spacer length was C6—C12[10] and the copolymer with the C12 spacer unit is here taken for comparison (Tables II and III). Copolymers without spacer units require fewer steps to prepare but probably decrease the crystallization rate and crystallinity.

The melting temperature and crystallization behavior of the copolymers is studied by DSC at a scan rate of 20°C/min (Table II). The (-PPE-T-spacer-T6T6T-spacer-T-) and (-PPE-T6T6T-) both with 10–11 wt % T6T6T are compared.

The melting temperatures as measured by DSC are near one and another and correspond with the flow
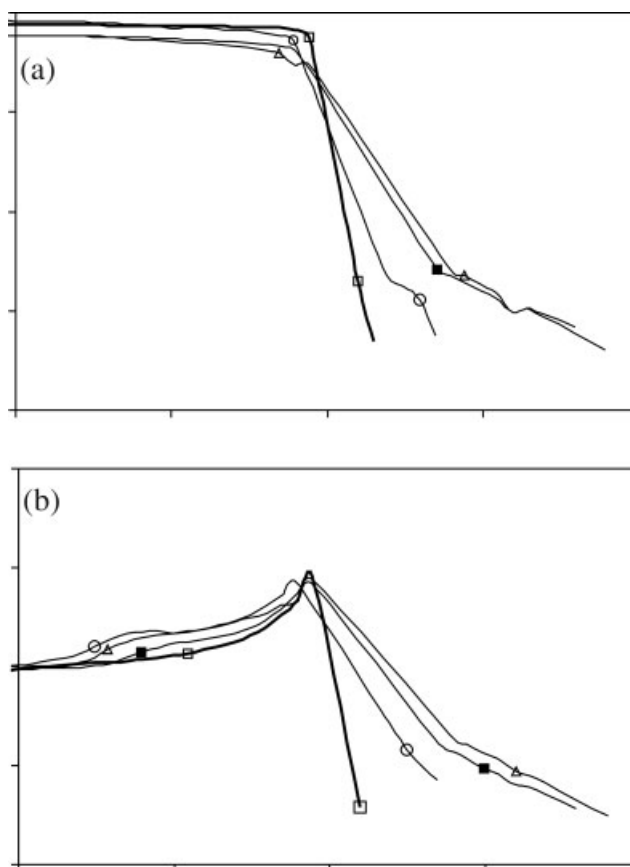
Figure 3 Storage (a) and loss (b) modulus of PPE-T(6T)$_2$/T copolymers with different amounts of T(6T)$_2$: □, 0 wt %; ○, 7 wt %; △, 9 wt %; ■, 14 wt %.

TABLE II
DSC Results for Copolymers with T6T6T Units

	T6T6T Wt %	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-T6T6T-	11	261	1	9	< 10	222	−1	39
-PPE-T-C12-T6T6T-C12-T- [10]	10	267	10	91	60	249	−11	18

[a] The crystallinity of T6T6T was calculated with the enthalpy of melting of T6T6T-dimethyl (152 J/g).[12]

temperatures as measured by DMA (Table III). The crystallization temperature for the -PPE-T-spacer-T6T6T-spacer-T- is appreciable higher than for -PPE-T6T6T-; the $T_m - T_c$ is also smaller, which means that the (-PPE-T-spacer-T6T6T-spacer-T-) copolymer crystallizes faster. The melting endotherm and crystallization exotherms for -PPE-T6T6T- were very difficult to determine well. The melting endotherm and crystallization exotherms are stronger for the (-PPE-T-spacer-T6T6T-spacer-T-) copolymer. The crystallinity of T6T6T in these copolymers was calculated from their enthalpy of melting compared with the enthalpy of melting of T6T6T-dimethyl.[12] The crystallinity of T6T6T in -PPE-T6T6T- as measured from the melting endotherm is very low (< 10%). This values correspond quite well with the crystallinities that were calculated from the storage modulus above the T_g (Table III).

The DMA results of copolymers of -PPE-T6T6T, -PPE-T(6T)$_2$-, and -PPE-T-spacer-T6T6T-spacer-T-, with an amide content of (∼ 11 wt %) are compared (Table III). The glass transition temperature of the copolymers is at 179–188°C. The T_g of the copolymer with the C12 spacer is slightly lower. With the spacer units, the shoulder in the loss modulus graph is at 100°C,[10] while for the others it is at 130°C. The spacer units decrease the T_g of the T6T6T amorphous phase. The storage modulus between T_g and T_{flow} are of the copolymers very similar, with for the copolymer with the C12 spacer somewhat higher. The T_{flow} is sharp for -PPE-T6T6T- and the copolymer with the C12 spacer, while for the -PPE-T(6T)$_2$- is this transition broader.

The copolymer with the C12 spacer has higher modulus and thus a higher crystallinity at some cost

of the T_g. The -PPE-T6T6T and -PPE-T(6T)$_n$- copolymers are remarkable comparable except for the sharpness of the T_{flow} transition. The increased amide segment distribution in these series had mainly an effect on the sharpness of the melting transition.

CONCLUSIONS

High-molecular-weight copolymers can be obtained from PPE-2OH and either T6T6T-diphenyl or 6T6 + DPT. The phenolic terephthalate ester is apparently sufficient reactive for making these block copolymers. The amide concentration could be lowered by replacing some of the amide units by DPT. The synthesis with 6T6 + DPT is simpler, as not first the T6T6T-diphenyl has to be made. The polymerization with the low melting 6T6 can even be carried out without a solvent, this as the reactants 6T6 and DPT are not high melting materials. With T6T6T units, the segments are monodisperse, while with the -T(6T)$_2$- segment, they are expected to have a broader distribution. The copolymers have a high T_g and a high melting temperature. With -T(6T)$_2$- segments, the melting transition is less sharp. The T_gs are somewhat lower that that of pure PPE (PPO-803). The flow temperatures increase from 220°C without T6T6T to 255–265°C with 911 wt % -T6T6T- or -T(6T)$_2$-. The crystallinity of the amide segments in the studied copolymers is not so high, however (∼ 20%). Also, the $T_m - T_c$ is not so low, suggesting that the crystallization rate is not very fast. A part of the non crystalline T6T6T is present in the PPE phase and a part as an amorphous PA phase with a glass transition temperature of 130°C. The crystallinity in the copoly-

TABLE III
DMA Properties of Copolymers

	PPE (g/mol)	T6T6T (wt %)	η_{inh} (dL/g)	T_g (°C)	G′ (at T_g + 40°C) (MPa)	T_{flow} (°C)	T_g/T_{flow} (−)	Calc. cryst. (%)[a]
-PPE-T6T6T-	3500	11	0.34	183	1.6	254	0.87	10
-PPE-T(6T)$_2$-	3500	11	0.42	188	2.0	264[b]	0.86	20
-PPE-T-C12-T6T6T-C12-T- [10]	3100	10	0.56	179	6	266	0.84	70

[a] Estimated crystallinity from the storage modulus at T_g + 40°C [eq. (3)].
[b] Flow temperature is not well defined because there is not a sharp decrease in modulus.

mers can probably be improved by optimizing the molecular weight and the processing conditions.

The properties of the -PPE-T6T6T- and -PPE-T(6T)$_2$- copolymers are fairly comparable and also with those of the copolymer with spacer units, -PPE-T-spacer-T6T6T-spacer-T-. However, the crystallinities and the crystallization rates were higher with the -PPE-T-spacer-T6T6T-spacer-T-copolymer.

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