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Copolymers of poly(2,6-dimethyl-1,4-phenylene ether) and ester units

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Abstract

Copolymers of telechelic poly(2,6-dimethyl-1,4-phenylene ether) segments with terephthalic methyl ester endgroups (PPE-2T, 3700 g/mol) and different diols were made via a polycondensation reaction. The terephthalic endgroups of PPE-2T are stable during this reaction. The T_g of these polyether–ester copolymers decreases with increasing diol length and diol flexibility. The T_g can be set between 100 and 200 °C by changing the type of diol. However at increasing diol length the T_g becomes broader and the test bars are less transparent because the extent of phase separation increases with increasing diol length. Only polymers with a diol length up to C12 are homogeneous. Phase separation is probably enhanced by the bimodal molecular weight distribution of PPE-2T. Phase separation can be suppressed by using shorter PPE-2T segments with a short diol. It is even better to use fractionated, monomodal PPE-2T. Copolymerisation is much more effective in decreasing the T_g of PPE and therefore its processability than blending with polystyrene. It is expected that the processability of these copolymers is much better than that of PPE.

Keywords: Poly(2,6-dimethyl-1,4-phenylene ether); Copolymer; Polycondensation

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1. Introduction

Poly(2,6-dimethyl-1,4-phenylene ether) (PPE) [1–3] or PPO is a linear amorphous polymer with a very high 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, due to its high glass transition temperature, very high processing temperatures are required, which can lead to degradation. Only PPE with a molecular weight between 10,000 and 30,000 g/mol is just processable. By lowering the T_g, the processing temperature can be lowered and degradation free processing becomes possible. To lower the T_g, PPE is usually blended with polystyrene, as PPE and PS are fully miscible. However, possibilities for lowering the T_g of PPE by blending with other polymers than PS are limited due to the low miscibility with PPE [1–3].

Next to blending, also copolymerisation might change the glass transition temperature and improve the processability of PPE. Block copolymers (diblock or triblock) that contain PPE are described mainly in patent literature [3, 5–21] and are sometimes used as compatibiliser in blends of PPE and a second polymer. For segmented or multi-block copolymers bifunctional PPE segments (PPE-2OH) [22] with a phenolic endgroup at both chain ends are needed. These can be prepared by different methods, starting from monomers (copolymerisation) [23–28], from low molecular weight PPE–OH (coupling) [9,23] or from high molecular weight PPE (redistribution) [22,29–32].

Redistribution or depolymerisation of high molecular weight PPE with tetramethyl bisphenol A is a simple and fast way to make short bifunctional PPE telechelics [22]. The reaction is catalysed by tetramethyl diphenoquinone (TMDPQ). PPE-2OH segments having a bimodal molecular weight distribution with a number average molecular weight of 1500–4000 g/mol and a functionality of 1.6–1.9 can be produced in this way [22]. The phenolic endgroups of PPE-2OH are transferred into terephthalic methyl ester groups by reaction with methyl chlorocarbonyl benzoate (MCCB) [22, 33,34]. This PPE segment with two methyl ester functionalities is called PPE-2T (in which *T* stands for the terephthalic endgroup, Fig. 1). The composition of the PPE-2OH and PPE-2T is described in detail in Ref. [22,32].

Copolymers of PPE-2T and different diols can be made by polycondensation (Fig. 1). The expectation is that the

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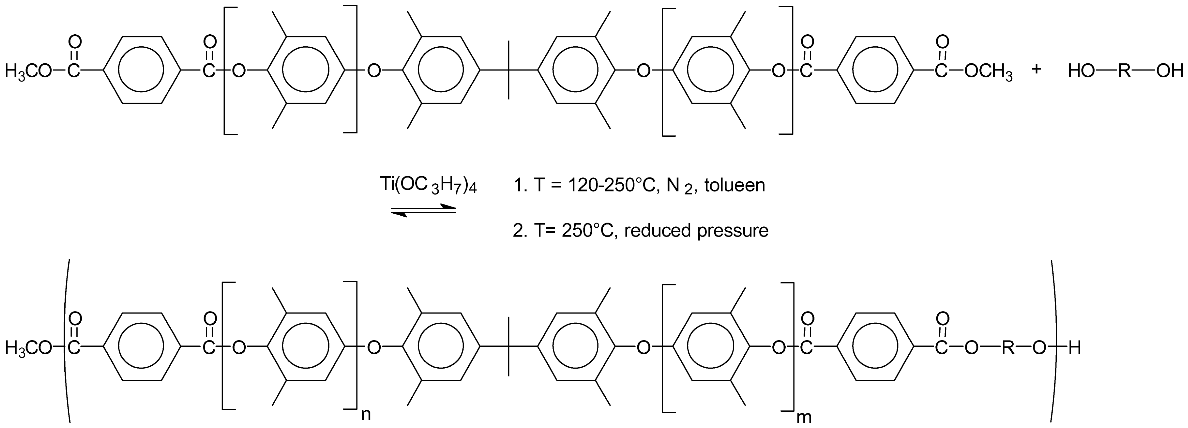

Fig. 1. Synthesis of a PPE-2T/diol copolymer from PPE-2T and a diol.

low molecular weight PPE-2T segments and the diols will mix and the polymers will have one glass transition temperature. This T_g will then be lower than that of pure PPE, depending on the flexibility and length of the diol used. It is envisaged that this will lead to improved processability. However, the diol should not be too long and incompatible with the PPE segment, as this will result in partial phase separation giving a broad T_g, or more than one T_g.

In this article alternating polyether–ester copolymers based on PPE-2T and different diols are studied. First, a copolymer based on PPE-2T of ~3700 g/mol and C36-diol will be discussed using GPC, ^{1}H NMR and DMA. Then four different polymer series based on PPE-2T in which the structure and length of the PPE and ester segments are varied will be analysed using DMA. The effect of composition on glass transition and flow temperature will be discussed. The results are used to study the phase separation in relation with the segment length.

2. Experimental

2.1. Materials

Dimethyl terephthalate (DMT), 1,2-ethanediol, 1,6-hexanediol, 1,12-dodecanediol (C12) and toluene were purchased from Merck. Tetraisopropyl orthotitanate ($Ti(i\text{-}OC_3H_7)_4$), obtained from Merck, was diluted in anhydrous *m*-xylene (0.05 M), obtained from Fluka. C36-dimerised fatty diol was obtained from Uniquema, Gouda (The Netherlands). Di-ethoxylated bisphenol A (Dianol220®) was obtained from Akzo Nobel (The Netherlands). Poly(2,6-dimethyl-1,4-phenylene ether) (PPO-803®, 11,000 g/mol) was obtained from GE Plasctics (The Netherlands). Poly(tetramethylene oxide) (PTMO, $M =$ 650, 1000, 1400, 2000 and 2900 g/mol) was provided by DuPont. $PTMO_{1000}$, for example, is PTMO of 1000 g/mol. All chemicals were used as received. Diphenyl terephthalate (DPT) was synthesised from terephthaloyl chloride and phenol [35]. Bimodal PPE-2OH (~3500 g/mol) was made by redistribution [22,32]. Bimodal PPE-2T was made in a two-step or a one-pot reaction. Monomodal PPE-2T with a narrow molecular weight distribution that was obtained after fractionation was used as well. The average molecular weight of the PPE-2T segments was between 1600 and 3700 g/mol and the segments had a functionality of 1.6–1.9 (NMR) (number of methyl ester endgroups per chain).

2.2. Synthesis of PPE-2T/diol copolymers

The PPE-2T/diol copolymers were synthesised via an ester type polycondensation reaction using PPE-2T and different diols. The preparation of a copolymer of PPE-2T (~3700 g/mol, functionality = 1.79, 480 μmol OCH_3/g (NMR)) [22] and C36-diol is given as an example.

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, 4.8 mmol OCH_3), C36-diol (1.3 g, 2.4 mmol), 10 ml toluene and catalyst solution (0.3 ml of 0.05 M $Ti(i\text{-}OC_3H_7)_4$ in *m*-xylene). This mixture was first heated in an oil bath to 120 °C under nitrogen flow. After 30 min the temperature was increased in steps: 30 min at 180 °C, 30 min at 220 °C and 60 min at 250 °C. The pressure was then reduced slightly ($P < 20$ mbar) for 30 min and then further reduced ($P < 1$ mbar) for 30 min. 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.

2.3. NMR

^{1}H NMR spectra were recorded on a Bruker spectrometer at 300 MHz at 25 °C. Deuterated chloroform ($CDCl_3$) was used as a solvent.

2.4. Viscometry

The inherent viscosity of the polymers was determined with a capillary Ubbelohde type 0C at 25 °C, using a polymer solution with a concentration of 0.1 g/dl in chloroform.

2.5. GPC

GPC measurements were carried out with polymer solutions in chloroform (5 mg/ml), filtrated via 0.45 μm Schleicher and Schuell filters. The molecular weight was determined using GPC with a Waters model 510 pump, differential refractometer model 411, viscotek H502 viscometer and Waters columns HR4 + HR2 + HR0.5 and a 500 Å guard column in series. A flow rate of 1.5 ml/min was used with chloroform as a solvent at 25 °C. Calibration was performed with nine monodisperse polystyrene standards (range 827–1450 g/mol).

2.6. DMA

Samples for the DMA test (70 × 9 × 2 mm) 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. This maximum was 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 flow temperature (T_{flow}) was determined as the temperature where the storage modulus G' reached 1 MPa. Two measures were used to get some indication of the extent of phase separation. The broadness of the T_g was defined as the temperature range over which the modulus as measured by DMA drops from 100 to 10 MPa. The drop in the storage modulus G' between -100 °C and 10 °C below the T_g was determined as well.

3. Results and discussion

3.1. Introduction

Copolymers of PPE-2T and different diols were made in a polycondensation reaction with a maximum temperature of 250 °C. A little toluene was added after putting all the reactants in the reactor to make sure that all the reactants mix well and are able to melt on increasing temperature. A clear solution is formed in toluene. After 30 min, when the temperature is raised to 180 °C, toluene starts to evaporate. Above 220 °C the reaction is in the melt. The melt is clear and the viscosity of this melt increases with reaction time.

The average degree of polymerisation that can be obtained starting with a PPE-2T segment with an average molecular weight of 3500 g/mol and an average functionality of 1.7 with a stoichiometric amount of diol can be calculated with Eq. (1), using Eq. (2) to calculate f_{avg} (with $N_A = N_B$) [36].

$$\bar{X}_n = \frac{2}{2 - pf_{avg}} \tag{1}$$

$$f_{avg} = \frac{\sum N_i f_i}{\sum N_i} = \frac{N_A f_A + N_{A'} f_{A'} + N_B f_B}{N_A + N_{A'} + N_B} \tag{2}$$

With

N_A = number of molecules PPE with functionality $f_A = 2$.
$N_{A'}$ = number of molecules PPE with functionality $f_{A'} = 1$.
N_B = number of molecules diol with $f_B = 2$ (with $N_B = N_A + N_{A'}/2$)

The f_{avg} using PPE-2T with a functionality of 1.7 and a stoichiometric amount of diol is 1.8. With $p = 1$ a maximum average degree of polymerisation of 10 can be obtained. With an average segment length (PPE, diol) of ~2000 g/mol, this corresponds to a molecular weight of 20,000 g/mol. This is high compared to the industrial PPE (11,000 g/mol) that was used for redistribution.

Different series of alternating polyether–ester copolymers based on PPE-2T and different diols were studied. First, a copolymer based on bimodal PPE-2T of ~3700 g/mol and C36-diol will be discussed. With GPC the molecular weight distribution of the copolymer was compared with that of PPO-803® and PPE-2T. A ^{1}H NMR study was done to show the extent of transesterification of the phenyl ester side of the terephthalic endgroups of PPE-2T during the polymerisation reaction. The thermal-dynamical behaviour was studied by DMA.

Then the properties of three different PPE/diol copolymer series will be discussed:

1. Bimodal PPE-2T and different diols.
2. Fractionated monomodal PPE-2T and different diols.
3. PPE-2T of different lengths with C36-diol.

The effect of composition on glass transition temperature, flow temperature and phase separation was studied by DMA.

3.2. PPE-2T/C36-diol copolymer

An alternating polyether–ester copolymer based on PPE-2T and C36-diol (-T-PPE-T-C36-)$_n$ was made. The average molecular weight of the PPE-2T segment used was 3700 g/mol and the segment has around 1.8 methyl ester endgroups per chain [22]. The structure of C36-diol is given in Fig. 2.

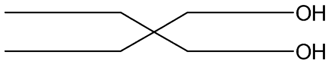

Fig. 2. Structure of C36-diol dimerised fatty diol.

3.2.1. GPC

With GPC the molecular weight distribution of PPE-2T/C36 was measured. The data are compared with that of the PPE-2T segment that was used as a starting material for copolymerisation and the commercial PPO-803® (Fig. 3).

PPO-803® shows a molecular weight distribution with $M_n = 11,000$ g/mol and $M_w/M_n = 2.0$. PPE-2T shows a bimodal molecular weight distribution with a high molecular weight fraction at the position of the peak of PPO-803® and a low molecular weight fraction with a narrower peak. The high molecular weight fraction forms about 24% of the area and the low molecular weight fraction 76% of the total area [22]. The PPE-2T/C36-diol copolymer has a broad molecular weight distribution ($M_w/M_n = 3.1$). The average molecular weight of the copolymer (14,000 g/mol) is higher than the average molecular weight of PPO-803® (11,000 g/mol).

The molecular weight of the copolymer was also studied by inherent viscosity determination in diluted chloroform solution. The inherent viscosity of the copolymer was 0.44 dl/g. The commercial PPO-803® had an inherent viscosity of 0.37 dl/g and the PPE-2T segment 0.19 dl/g (Table 1).

The phenyl ester side of a terephthalic ester generally has a higher reactivity than the methyl ester side [37]. The high molecular weight of the copolymer that is made from PPE-2T and C36-diol suggests that transesterification of the terephthalic endgroups of PPE-2T is mainly at the methyl ester side and not at the phenyl ester side. The reason for this is probably the steric hindrance of the 2,6-dimethyl groups at the phenyl unit that is linked to the terephthalic endgroup.

3.2.2. NMR

A ^{1}H NMR study was done to determine the stability of the terephthalic endgroups of PPE-2T during the polymerisation reaction. The transesterification of the phenyl ester side of the terephthalic endgroup is an undesirable side reaction. This reaction will yield a phenolic endgroup, which has a low reactivity. The presence of the phenolic endgroup should be visible in the NMR spectrum. The ^{1}H NMR spectra of PPE-2OH, PPE-2T and a PPE-2T/C36 copolymer are given in Fig. 4.

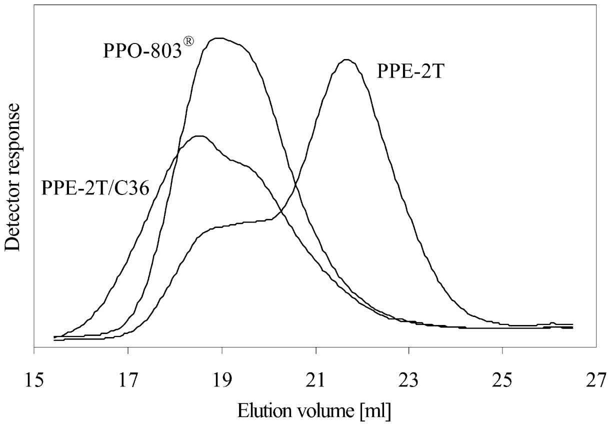

Fig. 3. GPC data for PPE-2T/C36 copolymer compared to PPE-2T and PPO-803®.

The peak at 6.36 ppm is for the aromatic H of the phenolic PPE 'head' endgroup. The bifunctional PPE-2OH shows a large peak at 6.36 ppm. After modification of the phenolic endgroups of PPE-2OH with methyl chlorocarbonyl benzoate (MCCB) to PPE-2T, this peak has disappeared completely. Also the TMBPA endgroups are transferred completely into terephthalic methyl ester endgroups by reaction with MCCB as the peaks at 6.84 and 6.94 ppm are absent in PPE-2T. Copolymerisation of PPE-2T with C36-diol results in the formation of a very small amount of new phenolic endgroups as a result of transesterification of the phenyl ester side of the terephthalic endgroup with the diol. The transesterification of the phenyl ester side of the terephthalic endgroups in PPE-2T is less than 5%.

The phenolic endgroups are hardly reactive in this type of polycondensation reaction. The new average degree of polymerisation that can be obtained in this situation can be calculated with Eq. (1), using Eq. (3) to calculate the f_{avg} for the case that the B groups (diol) are in excess [36].

$$f_{avg} = \frac{2(N_A f_A + N_{A'} f_{A'})}{N_A + N_{A'} + N_B} \quad (3)$$

When 5% of the functional methyl ester endgroups is transformed into a non-reactive phenolic endgroup, the methyl ester functionality of PPE-2T decreases from 1.7 to 1.6. The f_{avg} using PPE-2T with an original functionality of 1.7 and a stoichiometric amount of diol after 5% transesterification is 1.74. With $p = 1$ a maximum average degree of polymerisation of 8 instead of 10 can be obtained. This value is still sufficient to obtain high enough molecular weight. The maximum average molecular weight of the product that can be obtained is 16,000 g/mol. In most cases there is less transesterification and the functionality of the starting material is higher, so high molecular weight copolymers can be obtained easily.

3.2.3. DMA

The PPE-2T/C36 copolymer was injection moulded into test bars. These bars are slightly transparent. The bars were used to measure the dynamic-mechanical behaviour by DMA. In Fig. 5 the DMA results of the PPE-2T/C36 copolymer can be compared with that of PPO-803®.

The commercial PPO-803® has a high and constant modulus up to the glass transition temperature at 200 °C. For the T_g the temperature at which the loss modulus G'' has its maximum is taken. This temperature is 0–10 °C lower than the actual T_g of the polymer, because the DMA apparatus is unable to measure around the T_g because of the high damping. The T_g of PPO-803® is sharp. The flow

Table 1
Properties of the PPE-2T/diol copolymers based on bimodal PPE-2T or PPE-2OH

	PPE [wt%]	η_{inh} [dl/g]	T_g [°C]	T_g broadness [°C]	T_{flow} [°C]
Starting materials					
PPO-803®	100	0.37	200	8	222
PPE-2OH[a]	–	0.18	182[b]	–	–
PPE-2T[c]	–	0.19	173[b]	–	–
Copolymers					
PPE-2T/C2	92	0.33	190	9	217
PPE-2T/C6	91	0.31	185	8	210
PPE-2T/C12	88	0.33	170	8	195
PPE-2T/C36	83	0.44	150	13	185
PPE-2T/PTMO$_{650}$	82	0.40	140	18	175
PPE-2T/PTMO$_{1000}$	77	0.48	115	18	161
PPE-2T/PTMO$_{1400}$	69	0.66	80	20	145
PPE-2T/PTMO$_{2000}$	66	0.51	50	21	113
PPE-2T/PTMO$_{2900}$	57	0.66	−40	36	100
PPE-2OH/DPT	96	0.33	195	8	220
PPE-2T/Dianol220®	87	0.41	185	9	211

[a] Bimodal, ~3500 g/mol [22].
[b] Measured by DSC instead of DMA.
[c] Made by two-step synthesis, bimodal, ~3700 g/mol [22].

temperature, defined as the temperature where the modulus reaches 1 MPa, is 222 °C.

The copolymer of PPE-2T and C36-diol with an average PPE-2T molecular weight of 3700 g/mol consists of 83% PPE and 17% ester segments (-T-C36-T-). The PPE-2T/diol has a high and constant modulus up to its T_g as well. However, the modulus starts to drop a little above 50 °C. This is a result of the broader T_g of the copolymer compared to PPO-803® and can be seen as a broader peak in the loss modulus G''. The T_g of PPE-2T/C36 is 150 °C, which is 50 °C lower than the T_g of PPO-803®. The flow temperature is 185 °C.

3.3. Series 1. Bimodal PPE-2T with diols

In series 1, alternating polyether–ester copolymers of bimodal PPE-2T of constant length (~3700 g/mol) and different diols were synthesised. The length and type of diol were varied to change the T_g of the PPE-2T/diol copolymer. Next to different aliphatic diols (C2–C36) also

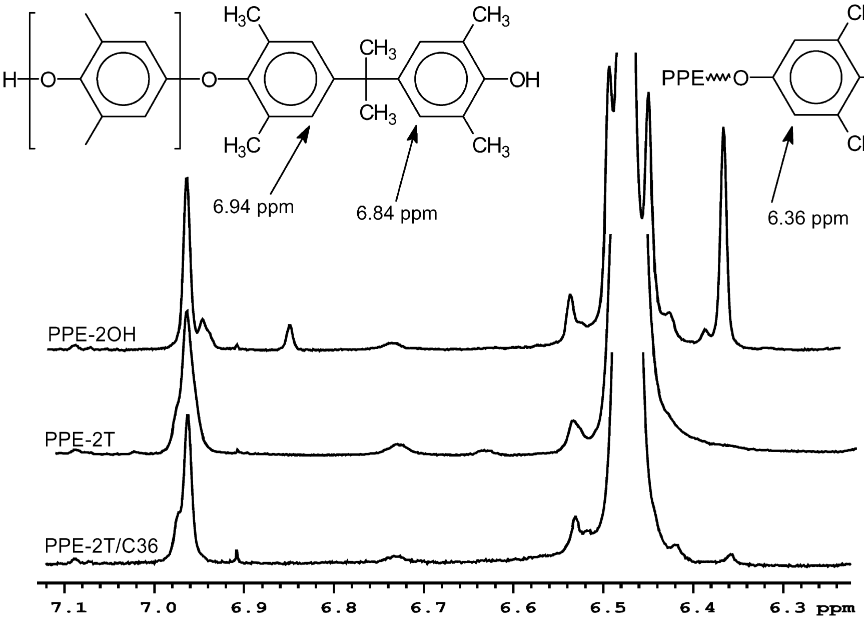

Fig. 4. ^{1}H NMR spectra of PPE-2OH, PPE-2T and PPE-2T/C36.

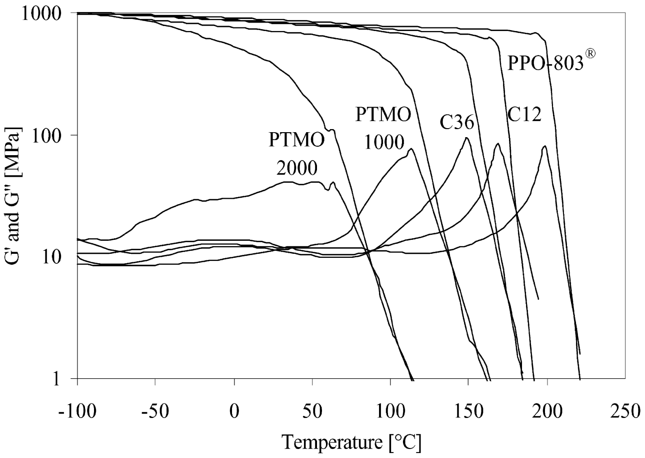

Fig. 5. Storage and loss modulus of several PPE-2T/diol copolymers based on bimodal PPE-2T (3700 g/mol) compared to the commercial PPO-803® starting material for redistribution; the type of diol used in each copolymer is given in the figure.

poly(tetramethylene oxide) or PTMO of different lengths (650–2900 g/mol) and Dianol220® (bisphenol A with hydroxyethyl endgroups, Fig. 7) were used. A copolymer of PPE-2OH (~3500 g/mol) and diphenyl terephthalate was studied as well. The synthesis was the same as described for the PPE-2T/C36 copolymer. First the copolymers with C12 and longer and than those with C12 and shorter as extender will be discussed.

All polymers had high molecular weights (>10,000 g/mol) as was measured by GPC. For other diols than C36-diol a comparable molecular weight distribution was obtained. With the longer diols the molecular weight of the copolymer was a little higher than with the shorter diols which can be expected when the molecular weight of the repeating units increases. The inherent viscosity, a measure for the molecular weight, increases with increasing diol length as well. The results for the PPE-2T/diol polymers of series 1 are given in Table 1.

3.3.1. Long diols

In Fig. 5 the DMA results for several PPE-2T/diol copolymers based on long flexible, aliphatic diols (C12, C36 and PTMO) are compared with that of PPO-803®.

By copolymerising PPE-2T segments with dodecanediol (C12), a PPE polymer with a lower, but still sharp T_g is obtained. The modulus of PPE-2T/C12 is high up to the T_g at 170 °C. The T_g and the T_{flow} are decreased by about 30 °C compared to the commercial PPO-803®. The broadness of the T_g is the same as that of PPO-803®. The test bars of this polymer are transparent. Apparently this copolymer is homogeneous. The ester segment based on dodecanediol (-T-C12-T-) is too short to phase separate.

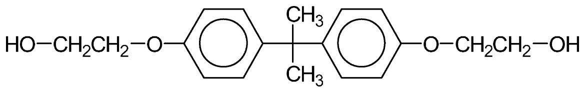

Fig. 7. Structure of Dianol220®.

When C36-diol is used in the copolymer the T_g is decreased by 50 °C and the T_g is a little broader than for the commercial PPO-803®. The modulus with C36-diol is less high and constant up to the T_g as compared to the PPE-2T/C12 copolymer. However, the test bars of this polymer are only slightly transparent. Therefore, it can be concluded that this copolymer is nearly homogeneous. The high molecular weight PPE fraction that is present next to the PPE-2T/C36 copolymer will probably phase separate partially from the copolymer on a microscale.

With $PTMO_{1000}$ the T_g is broadened further compared to C36-diol, but as the loss modulus start to increase above 50 °C a separate PTMO phase is not present. Pure PTMO/DMT has a T_g of −65 °C [38]. The T_g becomes very broad with $PTMO_{2000}$ segments. Already at −70 °C the G'' starts to increase, which indicates the presence of an almost pure T-PTMO-T phase. Furthermore, PPE/PTMO mixed phases of different concentrations are present as a result of partial phase separation between PPE and PTMO. Test bars with PTMO as a diol are not transparent.

3.3.2. Short diols

When a copolymer with a high T_g close to that of PPO-803® is desired there are three approaches. The first approach is to use very short aliphatic diols. The second method is to couple PPE-2OH segments directly with diphenyl terephthalate (DPT). And a third approach is to use less flexible diols.

In Fig. 6 the storage modulus as a function of temperature for copolymers of PPE-2T and hexanediol (C6) or ethanediol (C2) is given. In this figure the result for a copolymer of PPE-2OH and DPT is given as well. This polymer was made with doubled reaction time. In this way high enough molecular weight is obtained (0.33 dl/g), although the reactivity of the sterically hindered OH endgroups of PPE-2OH with the phenyl ester endgroups of DPT is low. The results are compared with that of PPO-803® and the PPE-2T/C12 copolymer.

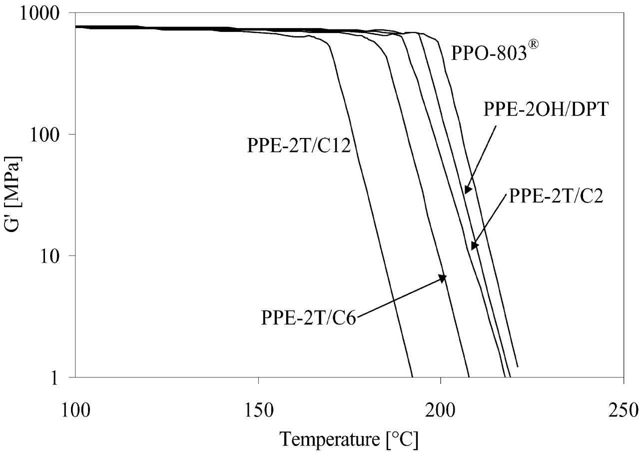

Fig. 6. Storage modulus of the PPE-2T/diol copolymers using short diols and PPE-2OH/DPT compared to the commercial PPO-803® starting material for redistribution.

The T_g and T_{flow} of the PPE-2T/diol copolymer increase when the diol length is decreased. With very short diols, such as hexanediol or ethanediol the effect of the flexible diol is small and the T_g is close to that of PPO-803®. With short diols sublimation of the diol can occur during the polymerisation reaction. Therefore care has to be taken to use the right excess of diol in order to obtain high molecular weight.

The copolymer of PPE-2OH and DPT has a T_g and T_{flow} that are almost the same as that of PPO-803®. The only difference between these polymers is that in PPE-2OH/DPT terephthalic groups are incorporated. The phenyl ring is not likely to effect a decrease of 5 °C in the T_g of the copolymer. Therefore probably the two ester-bonds that are introduced for each DPT unit that is incorporated are responsible for the small drop of 5 °C in T_g compared to PPO-803®. The effect of the ester bonds on the T_g is much smaller than the effect of introducing a flexible aliphatic structure.

A third method to obtain a PPE copolymer with a T_g more close to that of PPO-803® is to use a less flexible diol, for example Dianol220®, or bisphenol A with hydroxyethyl endgroups. The structure of Dianol220® is given in Fig. 7.

The PPE-2T/Dianol220® copolymer has a T_g of 185 °C and a T_{flow} of 211 °C. The T_g and T_{flow} are comparable with that of a copolymer of PPE-2T and hexanediol. The T_g and T_{flow} with Dianol220® are higher than with an aliphatic diol of the same length (so at the same weight percentage PPE) (Table 1). This is the result of the low flexibility of the Dianol220®, compared to the other, fully aliphatic, diols that were used. Next to the four CH_2 units, probably the ether bonds and the aliphatic structure in the centre of the bisphenol contribute to the flexibility of this diol. An advantage of using this diol instead of hexanediol is that no correction for sublimation of the diol to preserve stoichiometry is necessary.

It is remarkable that the polymers that show a sharp T_g, so the polymers with a diol length up to C12, turned out to be transparent, while the materials with a somewhat broadened T_g such as PPE-2T/C36-diol are only slightly transparent and the copolymers with PTMO are not transparent at all. Probably the phase separation between the PPE-2T/diol copolymer and the high molecular weight PPE fraction in the product is responsible for this. It is expected that phase separation will occur at lower PPE content, so with increased diol length, when this high molecular weight fraction is absent.

3.4. Series 2. Fractionated PPE-2T

In this second polymer series, alternating polyether–ester copolymers of fractionated, monomodal PPE-2T of constant length (~1600 g/mol) and different diols were synthesised. The synthesis was the same as described for the PPE-2T/C36 copolymer. All polymers had high molecular weights as was measured by GPC and inherent viscosity. The results for the PPE-2T/diol polymers of series 2 are given in Table 2. In Fig. 8 the DMA results for several PPE-2T/diol copolymers based on an aliphatic diol or PTMO are given.

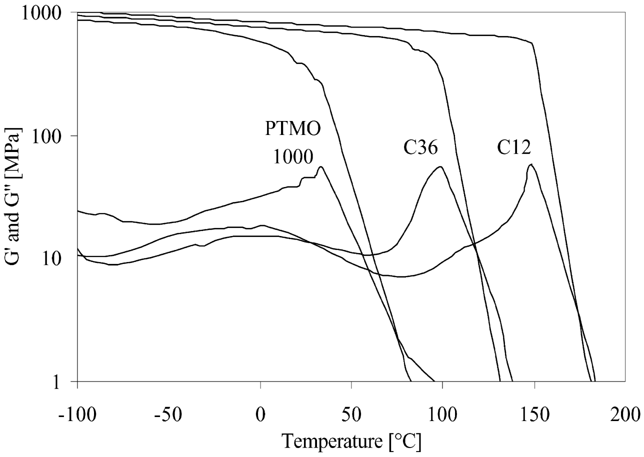

Fig. 8. Storage and loss modulus of several PPE-2T/diol copolymers based on fractionated, monomodal PPE-2T (1600 g/mol); the type of diol used in each copolymer is given.

The T_g and T_{flow} of the PPE-2T/diol copolymer decrease with increasing diol length and decreasing PPE content. Also the broadness of the T_g increases with increasing diol length. However the T_g is much less broadened than in the copolymers based on bimodal PPE-2T of series 1. Also the loss modulus is lower up to the T_g and the storage modulus remains higher up to the T_g. The broadness of the T_g will be discussed in more detail later on.

It can be concluded that there is less phase separation between PPE and -T-diol-T- phase in these copolymers compared to the polymers of series 1. This can be attributed to the absence of the high molecular weight PPE fraction that is not redistributed in bimodal PPE-2T. This high molecular weight fraction can be copolymerised only partially and will phase separate more easily because of the higher molecular weight that reduces miscibility. The copolymers of series 2 with C12 and C36 as a diol were transparent, the copolymer based on $PTMO_{1000}$ was not. Apparently the copolymer with $PTMO_{1000}$ and fractionated PPE-2T has a more phase separated morphology and is not homogeneous on a microscale.

3.5. Series 3. PPE-2T length

A third series of polyether–ester copolymers was based on PPE-2T of different lengths and C36-diol. In Table 3 and Fig. 9 the DMA results for these copolymers are given.

With decreasing length of the PPE-2T in PPE-2T/C36-diol copolymers, the T_g decreases. The T_g is hardly broadened when the C36-diol content increases. Only the copolymer with the shortest bimodal PPE-2T segment (~2000 g/mol) has a broadened T_g compared to the other three. The high molecular weight PPE fraction is probably phase separated more from the PPE-2T/C36 copolymer in this polymer, because the

Table 2
Properties of the PPE-2T/diol copolymers based on fractionated, monomodal PPE-2T

	PPE [wt%]	η_{inh} [dl/g]	T_g [°C]	T_g broadness	T_{flow} [°C]
Starting materials					
PPO-803®	100	0.37	200	8	222
PPE-2T[a]	–	0.08	140[b]	–	–
Copolymers					
PPE-2T/C12	74	0.34	150	11	182
PPE-2T/C36	63	0.37	100	13	132
PPE-2T/PTMO$_{1000}$	52	0.62	35	20	95

[a] Made by one-pot synthesis and fractionation, monomodal, ~1600 g/mol [22].
[b] Measured by DSC instead of DMA.

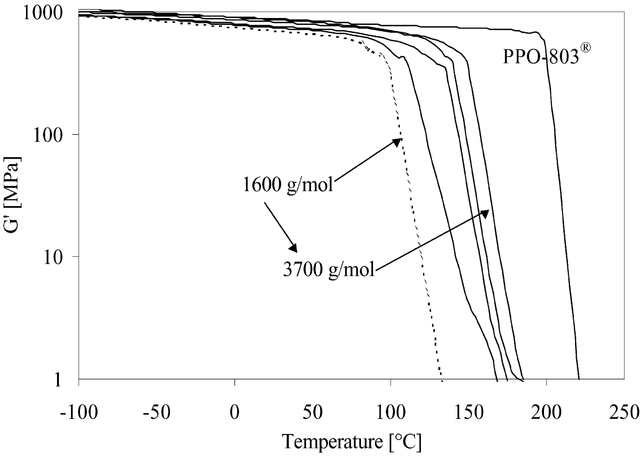

Fig. 9. Storage modulus for PPE-2T/C36-diol copolymers with PPE-2T of different lengths as indicated (1600, 2000, 2500, 3100 and 3700 g/mol); PPE-2T of 1600 g/mol (– – –) was made by partial precipitation and has a monomodal molecular weight distribution (series 2).

PPE-2T/C36 copolymer becomes less 'PPE-like' at lower molecular weight of the PPE-2T and contains relatively more high molecular weight PPE [22].

When monomodal PPE-2T that is obtained after partial precipitation is used the T_g is decreased further and remains sharp. Phase separation is less likely to occur, because this PPE-2T does not contain the high molecular weight PPE fraction that phase separates more easily. Also the transparency of this PPE-2T/C36 polymer is much better than that of the polymers based on the bimodal PPE-2T.

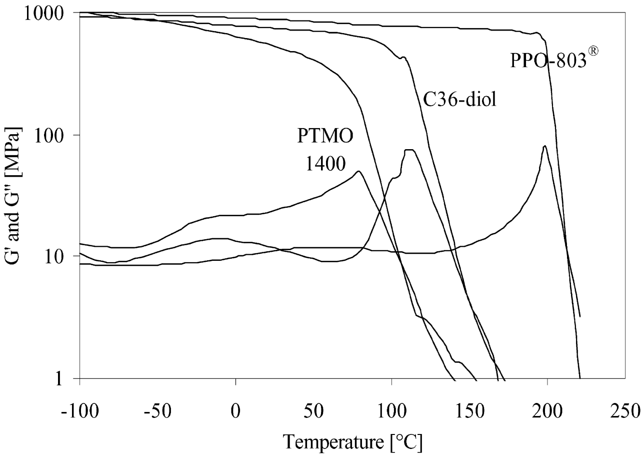

Fig. 10. Storage and loss modulus of the PPE-2T(2000 g/mol)/C36 and PPE-2T(3700 g/mol)/PTMO$_{1400}$ copolymer; both contain 69 wt% PPE.

In Fig. 10 the modulus of the PPE-2T/C36 copolymer with bimodal PPE-2T segments of 2000 g/mol is compared with that of the PPE-2T/PTMO$_{1400}$ with bimodal PPE-2T segments of 3700 g/mol. Both copolymers have a PPE content of 69 wt% (Table 1). The T_g is about 50 °C degrees lower with PTMO$_{1400}$ compared to C36-diol. This can be attributed to the larger flexibility of PTMO$_{1400}$ (T_g of T-PTMO-T is −65 °C) [38] as compared to C36-diol (T_g of T-C36-T is −35 °C) [39] in combination with increased phase separation with PTMO$_{1400}$. The copolymer with C36-diol has a higher and more constant modulus up to the T_g and the loss modulus is lower. It can be concluded that with

Table 3
Properties of the PPE-2T/C36 copolymers with PPE-2T of different lengths

PPE-2T length [g/mol]	TMBPA [gram]	PPE [wt%]	η_{inh} [dl/g]	T_g [°C]	T_g broadness	T_{flow} [°C]
3700[a]	6	83	0.44	150	13	185
3100[b]	4	79	0.55	140	13	180
2500[b]	6	75	0.41	135	14	174
2000[b]	8	69	0.50	115	18	168
1600[c]	8	63	0.37	100	13	132

[a] Made by two-step synthesis [22].
[b] Made by one-pot synthesis with different amounts of TMBPA [22].
[c] Monomdal PPE-2T, obtained after fractionation (series 2) [22].

$PTMO_{1400}$ some phase separation occurs, while with C36-diol there is hardly phase separation. Thus, decreasing the PPE-2T length is a better way to decrease the T_g of PPE than increasing the diol length.

3.6. Glass transition of polyether–esters

In Fig. 11 the T_g is given as a function of the PPE content for the copolymers of series 1–3. This figure shows that it is better to use monomodal PPE-2T segments (series 2) or shorter PPE-2T segments with a short diol (series 3) instead of using longer PPE-2T segments with a longer diol (series 1). In this way phase separation is suppressed and the T_g remains sharp and decreases gradually with decreasing PPE content. For series 3 with varying PPE length and C36-diol the T_g decreases linearly with decreasing PPE content.

From Fig. 11 it can be concluded that the effectiveness of decreasing the T_g of PPE is much higher by copolymerisation with diols to polyether–esters than by blending with polystyrene. For a polymer with a T_g of 150 °C, a 50/50 blend PPE/PS can be used. The same T_g can be obtained after copolymerisation with C36-diol in a copolymer that contains 83 wt% of PPE.

Copolymerisation using flexible aliphatic diols is much more effective than blending with polystyrene, because the T_g of a homopolymer of C36-diol and dimethyl terephthalate (DMT) ($T_g = -35$ °C) [39] is much lower than that of pure polystyrene ($T_g = 100$ °C). In Fig. 11 the calculated T_g of a theoretical PPE/C36-DMT blend as function of the PPE content, based on the Fox relationship [40], is given. This calculated line lies a little bit lower than that of the copolymer. So copolymerisation is a little less effective in lowering the T_g than a theoretical blend. The T_g of the PPE-2T/C36 polymer based on the monomodal low molecular weight fraction of PPE-2T lies on the same line as the other polymers of series 3. So using PPE-2T of narrow molecular weight distribution does not influence the value of the T_g, only its broadness (Fig. 12).

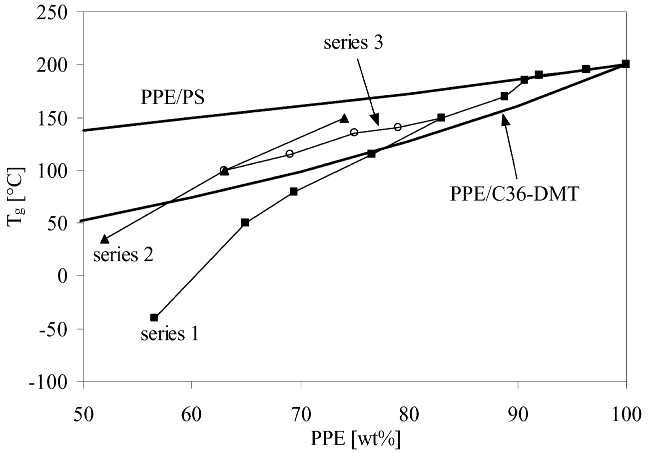

Fig. 11. T_g for PPE-2T/diol copolymers compared with the T_g of a PPE/PS blend and that of a (theoretical) blend of PPE with the copolymer of C36-diol and DMT [39] (both according to the Fox relation) [40]: (■), PPE-2T/diol (series 1); (▲), PPE-2T/C36 with fractionated PPE-2T (series 2); (○), PPE-2T/C36 (series 3).

The effect of different diols (C12, C36 and PTMO) on T_g can be seen clearly for the copolymers of series 2 that are based on fractionated, monomodal PPE-2T. The T_g of the DMT/diol copolymer decreases with decreasing diol length, thus the effectiveness of the diol after copolymerisation decreases with decreasing diol length. A homopolymer of dodecanediol and DMT with a T_g of 0 °C (series 4) is less effective than C36-diol/DMT. A homopolymer of PTMO and DMT [38] has a T_g of −65 °C and is the most effective. However, due to phase separation with long PTMO segments, this flexible segment is less preferred for copolymerisation with PPE, in particular when bimodal PPE-2T is used.

A definition for the broadness of the glass transition temperature was set. The broadness of the T_g was defined as the temperature range over which the modulus as measured by DMA drops from 100 to 10 MPa. The broadness of the T_g as a function of the PPE content for copolymers of series 1–3 is given in Fig. 12(a). Increasing broadness of the T_g

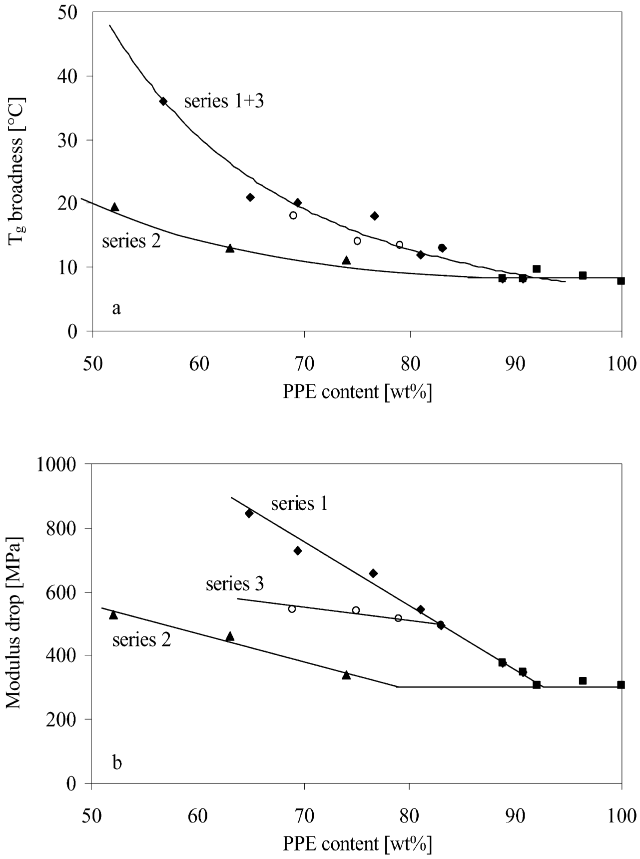

Fig. 12. Broadness of the glass transition temperature (T_g broadness $= T_{(G'=10\ \mathrm{MPa})} - T_{(G'=100\ \mathrm{MPa})}$ is used) (a) and modulus drop between −100 °C and $T_g - 10$ °C (b) with PPE content: (■), PPE-2T/diol up to C12 (series 1); (◆), PPE-2T/diol from C36 (series 1); (▲), PPE-2T/C36 with fractionated PPE-2T (series 2); (○), PPE-2T/C36 (series 3).

indicates that PPE phases with different diol concentrations are present.

Another definition was set to quantify the presence of a phase separated diol 'rich' phase. When such a second phase is present, the modulus drops before the main T_g of the PPE 'rich' phase (Fig. 10). The drop of the modulus between − 100 and 10 °C below the T_g is given as function of the PPE content in Fig. 12(b). When the modulus decreases more up to the T_g, the copolymer is more phase separated.

For the copolymers of series 1 the T_g is sharp at high PPE contents (> 88 wt%), corresponding to a copolymer of PPE-2T and dodecanediol or shorter diols. When C36-diol is used the T_g becomes broader. The T_g broadness increases more sharply for the longer diols, due to partial phase separation. Also with increasing diol length the modulus decreases more before the main T_g is reached. Probably the poor miscibility with increasing diol length is due to the presence of the high molecular weight PPE fraction in the PPE-2T starting material.

When bimodal PPE-2T with a lower molecular weight is used (series 3) the broadness of the main T_g does not change compared to copolymers of series 1. However the modulus up to the T_g is higher, which indicates that there is less phase separation when the average PPE-2T length is lower.

The copolymers that were made with the low molecular weight fraction of PPE-2T only (series 2), show a much sharper T_g than the copolymers based on bimodal PPE-2T. Even the copolymer with PTMO_{1000} as a diol has a reasonably sharp T_g. Also the copolymer with C36-diol and monomodal PPE-2T has good transparency as compared to the copolymers with C36-diol of series 3 that were only slightly transparent. So without the high molecular weight fraction in PPE-2T phase separation is suppressed and the segmented copolymers can have a sharp T_g and a higher modulus up to the T_g at much lower PPE contents.

4. Conclusions

PPE-2T/diol polyether–ester copolymers can be made via a polycondensation reaction with high molecular weights (> 10,000 g/mol). The terephthalic endgroups of PPE-2T are stable enough during the polycondensation reaction. With NMR analysis it was confirmed that transesterification of the terephthalic endgroup occurs preferably at the methyl ester side.

The T_g of the PPE-2T/diol copolymer with bimodal PPE-2T of 3700 g/mol decreases with increasing diol length and diol flexibility. The T_g can be set between 100 and 200 °C by changing the type of diol. However at increasing diol length the T_g becomes broader and the test bars are less transparent because the extent of phase separation increases with increasing diol length. Only polymers with a diol length up to C12 are homogeneous. It is expected that the presence of the high molecular weight fraction in PPE-2T is responsible for the phase separation.

An other and better way to decrease the T_g of PPE is to use shorter bimodal PPE-2T segments with a short diol. In this way the T_g can be lowered further while phase separation is suppressed. It is even better to use fractionated, monomodal PPE-2T. Copolymers with fractionated PPE-2T phase separate less compared to copolymers based on bimodal PPE-2T.

Due to the low T_g and T_{flow} the processability of this type of PPE copolymers is expected to be improved compared to commercial PPE. Copolymerisation is much more effective in decreasing the T_g of PPE and therefore its processability than blending with polystyrene.

The PPE-2T segment can be used in copolymerisation with other bifunctional segments. All types of diol or di-ester segments or telechelics can be used. Segments can be aliphatic or aromatic, for example poly(propylene oxide) or polycarbonate telechelics.

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