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Synthesis and characterisation of telechelic poly(2,6-dimethyl-1,4-phenylene ether) for copolymerisation

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Abstract

Telechelic poly(2,6-dimethyl-1,4-phenylene ether) (PPE) segments are interesting starting materials, for example for copolymerisation. A good method to make partly bifunctional PPE-2OH is by redistribution or depolymerisation of high molecular weight commercial PPE with tetramethyl bisphenol A. The product has a bimodal molecular weight distribution because only ~70–80% of high molecular weight starting material is depolymerised. The phenolic endgroups can be modified easily by a fast and complete reaction with methyl chlorocarbonyl benzoate. The product after endgroup modification is called PPE-2T and has two terephthalic methyl ester endgroups and a molecular weight of 2000–4000 g/mol. The functionality of these PPE-2T products is around 1.8. The bimodal PPE-2OH and PPE-2T products can be separated in a high and low molecular weight fraction by selective precipitation. The low molecular weight fraction has a narrow molecular weight distribution with a polydispersity between 1.2 and 1.5.

Keywords: Poly(2,6-dimethyl-1,4-phenylene ether); Redistribution; Telechelic

1. Introduction

Poly(2,6-dimethyl-1,4-phenylene ether) [1–3] (PPE) or poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) is a linear amorphous polymer with a very high glass transition temperature of approximately 215 °C [4]. PPE has excellent properties such as high toughness, high dimensional stability, good flame retardation and low moisture uptake. PPE can be made by several methods. The commercial route to high molecular weight PPE is by oxidative polymerisation of 2,6-dimethylphenol (DMP) (Fig. 1) [1–3,5–7]. Alternative methods are halogen displacement polymerisation [1–3,8–11] and phase transfer catalysed polymerisation [1–3,12] of 4-bromo-2,6-dimethylphenol (BDMP).

Due to a side reaction during the oxidative polymerisation of DMP PPE contains Mannich base type endgroups (Fig. 2(a)) [13] that have a lower reactivity than normal phenolic endgroups. A second side reaction yields the coloured TMDPQ (3,3′,5,5′-tetramethyl-4,4′-diphenoquinone) that can be incorporated in the polymer chain and leads to a chain with two OH-functionalities (Fig. 2(b)). In linear polymers each polymer chain may contain at most one tetramethylbiphenyl unit derived from TMDPQ either as an endgroup or internally [14–16]. In commercial high molecular weight PPE grades over 80% of the polymer chains contain a tetramethylbiphenyl unit derived from TMDPQ or a Mannich base type endgroup [14,17].

The phenolic functionality (concentration of 3,5-dimethyl-4-hydroxyphenyl 'head' endgroups) of commercial PPE is in general lower than one, especially at high molecular weight [2,14,17]. Bifunctional poly(2,6-dimethyl-1,4-phenylene ether) segments or α,ω-bishydroxy functional PPE telechelics (PPE-2OH) of 500–5000 g/mol are interesting for use in copolymerisation to segmented copolymers or multiblock copolymers.

There are three different methods to make low molecular weight PPE-2OH segments. The first method is to make PPE-2OH from the monomers (B)DMP and 2,2′-di(4-hydroxy-3,5-dimethylphenyl)propane (tetramethyl bisphenol A, TMBPA) in a copolymerisation reaction (Fig. 3) [18–24]. However, it is difficult to control the degree of polymerisation and the polymer chain ends functionality. Alternatively coupling of two low molecular weight

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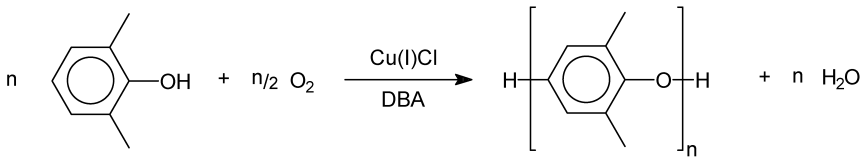

Fig. 1. Oxidative polymerisation of 2,6-dimethylphenol.

PPE-OH chains leads to telechelic PPE-2OH [15,18], however, the functionality of the coupling product is lower than two. The most elegant method to obtain PPE-2OH is by redistribution (depolymerisation).

1.1. Redistribution

Recently a good and simple method to produce short bifunctional PPE-2OH segments was described [17,25,26]. Bifunctional PPE telechelics with two phenolic endgroups can be prepared by redistribution (depolymerisation) of high molecular weight PPE with tetramethyl substituted bisphenols. The reaction without a catalyst is possible but slow. The rate of redistribution is increased by adding tetramethyldiphenoquinone (TMDPQ) as a catalyst [17,25,27,28]. Some TMDPQ is incorporated in the polymer chain during the reaction (Fig. 2(b)).

The mechanism of the redistribution reaction catalysed by TMDPQ is well-studied [15,17,25,27–32]. A requirement for the redistribution reaction is that both of the reacting species have at least one phenolic 'head' endgroup. It was found that endgroups such as the 2,6-dimethylphenoxy 'tail' endgroups, Mannich type endgroups and tetramethylbiphenyl endgroups derived from TMDPQ are degradation resistant and do not react in the redistribution reaction [28]. As a result the redistribution product of commercial PPE will consist of two fractions; a low molecular weight depolymerised fraction and a high molecular weight fraction that has not reacted. Also, some chains will be depolymerised only partially (up to the TMBPA or TMDPQ unit in the chain). Due to rearrangement reactions the product hardly contains 2,6-dimethylphenoxy 'tail' endgroups.

An alternative depolymerisation route by phase transfer catalysed depolymerisation of PPE is described by Percec et al. [32,33] and shows the same effects when working with commercial PPE.

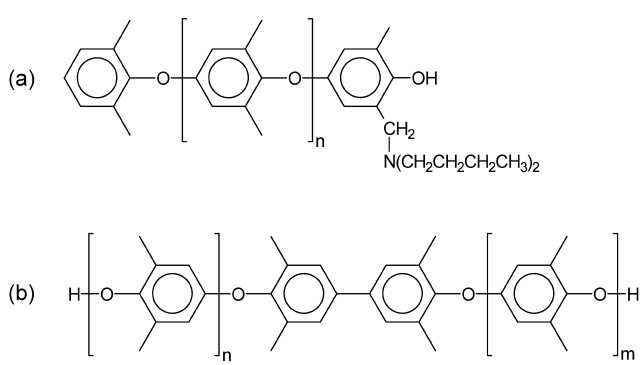

Fig. 2. Impurities in PPE: (a) Mannich base endgroup, (b) TMDPQ incorporation.

1.2. Endgroup modification

A disadvantage of the telechelic PPE-2OH segments in a reaction is the low reactivity of the phenolic endgroup [34]. Possible modification routes are based on etherification or esterification reactions [34–38]. Modification by ether linkage is preferred, because the phenolic esters are less stable [37]. However, with shielded aromatic esters like these PPE-esters with 2,6-dimethyl substitution this effect might not be so strong. Etherification reactions seem commercially less interesting.

In theory esterification of phenolic endgroups can be performed using acid chlorides, acid anhydrides, phenyl esters and methyl esters. However, the reactivity decreases strongly in this order. In practice only reactions where functionalisation is obtained with aromatic acid chlorides or anhydrides are fast and complete and yield stable products [14,39–42]. In this study the phenolic endgroups are modified using the half ester half acid chloride methyl chlorocarbonyl benzoate (MCCB) (Fig. 4). When PPE-2OH is used as a starting material, this reaction results in PPE with terephthalic methyl ester groups on both ends of the chain. This PPE segment with two methyl ester functionalities is called PPE-2T (in which T stands for the terephthalic endgroup). It is expected that next to the phenolic 'head' units also tetramethyl bisphenol A and tetramethylbiphenyl endgroups will be functionalised by the acid chloride. The Mannich base type endgroups have a lower reactivity and will react only partially with the acid chloride.

In this article, the synthesis and characterisation of PPE-2OH and PPE-2T will be described. Also a method to separate the bimodal redistribution product into two monomodal fractions will be presented. The products were analysed using titration, ^{1}H NMR, GPC, viscometry and DSC.

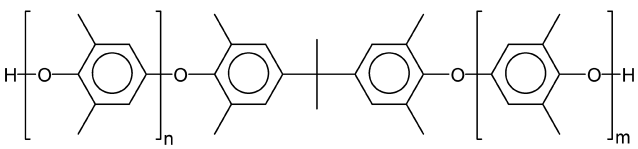

Fig. 3. PPE-2OH (n or m can be 0) by copolymerisation of DMP and TMBPA.

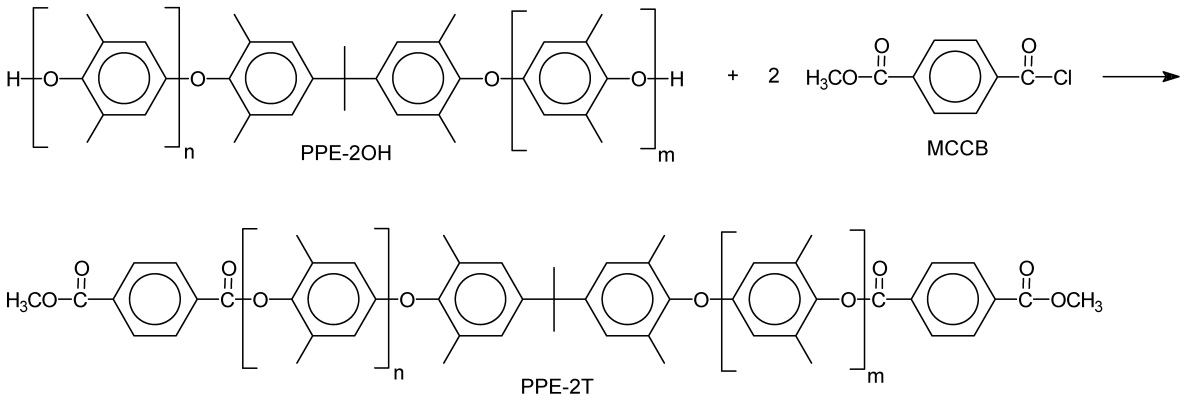

Fig. 4. Molecular structure of PPE-2T that is obtained after reacting PPE-2OH with methyl chlorocarbonyl benzoate (MCCB).

2. Experimental

2.1. Materials

Dimethyl terephthalate (DMT), triethylamine, toluene and methanol were purchased from Merck. 4,4′-Isopropylidenebis(2,6-dimethylphenol) (tetramethyl bisphenol A, TMBPA) was purchased from Aldrich. Methyl-(4-chlorocarbonyl) benzoate (MCCB) was obtained from Dalian (No.2 Organic Chemical Works, P.R.C.O.). Poly(2,6-dimethyl-1,4-phenylene ether) (PPO-803®) used in the redistribution reaction and 3,3′,5,5′-tetramethyl-1,4-diphenoquinone (tetramethyl diphenoquinone, TMDPQ) were obtained from GE Plastics (Bergen op Zoom, The Netherlands). PPO-803® has a number average molecular weight of 11.000 g/mol. All chemicals were used as received.

2.2. PPE-2OH

PPO-803®,40 g, was dissolved in 400 ml toluene at 60 °C in air. Subsequently tetramethyl bisphenol A (TMBPA) (4.0 g, 14 mmol) dissolved in 20 ml methanol was added. The reaction was started by the addition of tetramethyl diphenoquinone (TMDPQ) (0.40 g, 1.7 mmol). After 3 h the reaction mixture was added to a 10-fold excess of methanol to precipitate the product. The precipitated polymer was collected by filtration, washed with methanol and dried in a vacuum oven at 50 °C.

2.3. PPE-2T (two-step)

Redistributed PPE-2OH, 10 g, (5.1 mmol OH) was dissolved in 100 ml toluene at 70 °C under nitrogen flow. Then a 1.5 excess of methyl chlorocarbonyl benzoate (MCCB) (1.5 g, 7.6 mmol) was added. After 30 min a 1.5 excess (to MCCB) of triethylamine (1.2 g, 11 mmol) was slowly added dropwise. After 3 h the reaction mixture was added to a 10-fold excess of methanol to precipitate the product. The precipitated polymer was collected by filtration, washed with methanol and dried in a vacuum oven at 50 °C.

2.4. PPE-2T (one-pot)

The synthesis of PPE-2T was simplified by performing the redistribution reaction with TMBPA and the endgroup modification reaction with MCCB in one pot without precipitation between both steps. PPO-803®, 40 g, was dissolved in 400 ml toluene at 60 °C in air. Subsequently TMBPA (4.0 g, 14 mmol) was added. The reaction was started by the addition of TMDPQ (0.40 g, 1.7 mmol). After 2 h reaction time, the temperature was raised to 70 °C and set under nitrogen flow. Then 1.5 excess to the total OH concentration of PPE, TMBPA and TMDPQ (10 g, 50 mmol) of MCCB was added. After 30 min 1.5 excess (to MCCB) of triethylamine (7.6 g, 75 mmol) was slowly added dropwise. After 3 h the reaction mixture was added to a 10-fold excess of methanol to precipitate the product. The precipitated polymer was collected by filtration, washed with methanol and dried in a vacuum oven at 50 °C.

2.5. Fractionated PPE-2OH and PPE-2T

The receipt for the synthesis of PPE-2OH or PPE-2T in 400 ml toluene is followed up to precipitation step. After the reaction, 200 ml (PPE-2OH) or 175 ml (PPE-2T) of methanol was added to the reaction mixture to precipitate the high molecular weight fraction selectively. The high molecular weight product was collected by filtration, washed with methanol and dried in a vacuum oven at 50 °C. The filtrate was then added to a 10-fold excess of methanol to precipitate the low molecular weight fraction. The low molecular weight product was collected by filtration, washed with methanol and dried in a vacuum oven at 50 °C.

2.6. NMR

^{1}H NMR spectra were recorded on a Bruker spectrometer at 300 MHz. $CDCl_3$ was used as a solvent.

2.7. 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.

2.8. 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, a differential refractometer model 411, a 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 9 monodisperse polystyrene standards (range 827–1450 g/mol).

2.9. OH concentration

The concentration of phenolic endgroups (3,5-dimethyl-4-hydroxyphenyl 'head' endgroups, tetramethyl bisphenol A endgroups and tetramethylbiphenyl endgroups) was determined by titration using a Metrohm titroprocessor type EA636 with Ross glass electrodes. PPE samples (400 mg) were dissolved in pyridine and tetrabutyl ammonium hydroxide in isopropanol/methanol (0.1 M) was used as a titrant.

2.10. DSC

DSC spectra were recorded on a Perkin–Elmer DSC7 apparatus, equipped with a PE7700 computer and TAS-7 software. Dried samples of 3–7 mg PPE-2OH or PPE-2T 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 50 °C and reheated to 300 °C. The glass transition temperature (T_g) was determined in the second heating scan.

3. Results and discussion

3.1. PPE-2OH

PPE-2OH is made by redistribution of PPO-803® with TMBPA and with TMDPQ as a catalyst. All products are white and the yield is 66–94%, depending on the amount of TMBPA used. In Table 1 the properties of the products after redistribution of 40 g PPO-803® with 4–10 g (10–25 wt%) TMBPA are given.

Typical GPC curves of the products obtained after redistribution with TMBPA and the starting material PPO-803® are given in Fig. 5. PPO-803® has a molecular weight distribution with $M_n = 11.000$ g/mol and $M_w/M_n = 2.0$. PPE-2OH shows a bimodal molecular weight distribution with a major peak at about 2,000 and a shoulder at 11.000 g/mol molecular weight and this suggests incomplete depolymerisation.

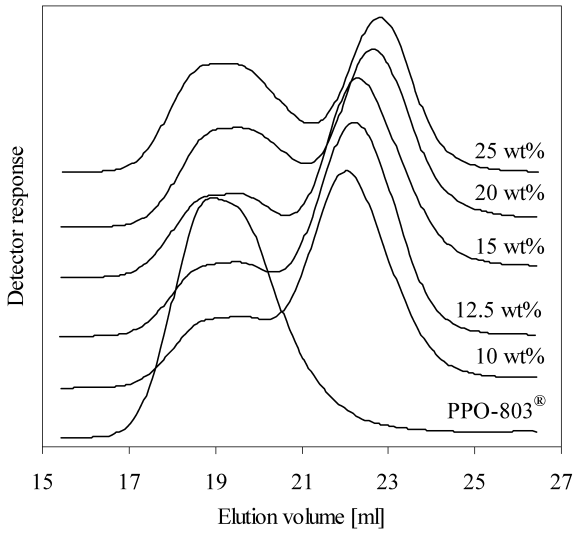

Fig. 5. GPC molecular weight distribution of the PPE-2OH products made with different amounts of TMBPA after precipitation compared to PPO-803®.

The hydroxyl end concentration of PPO-803® as measured by titration was 75 μmol OH/gram and this corresponds to a 'head' endgroup functionality of ~0.82 or around 82% of the chains contain a phenolic 'head' endgroup and the other 18% has no such endgroup. Based on these data, a maximum of only 82% of the chains can participate in the redistribution reaction [15,28,30–32]. Therefore, it is not possible to obtain a product that is completely depolymerised after redistribution and PPE-2OH shows a bimodal molecular weight distribution. The molecular weight of this high molecular weight fraction is comparable with that of the commercial PPO-803® starting material for redistribution (11.000 g/mol). The high molecular weight fraction forms about 23% of the area and the low molecular weight fraction 77% of the total area. These results correspond quite well with the expectation that a maximum of 82% of PPO-803® chains have a phenolic endgroup and can be redistributed.

The GPC-graphs of PPE-2OH (Fig. 5) show a bimodal molecular weight distribution whereby the peak of the high molecular weight fraction that has not reacted is at the same position as the peak for PPO-803®. The peak of the low molecular weight fraction is shifted towards lower values when the amount of TMBPA used increases, due to more extensive redistribution. However, the molecular weight of the precipitated product does not decrease likewise (Table 1). Also the amount of low molecular weight fraction decreases from 77 to 50%. This can be explained by the fact that the lowest molecular weight chains are lost during the precipitation step because they are soluble in the 10:1

Table 1
Molecular weight and functionality by different methods of PPE-2OH made by redistribution of PPO-803® with different amounts of TMBPA

	TMBPA (wt%)	Yield (%)	NMR			Titration			GPC		
			F^a (-)	$M_n{}^a$ (g/mol)	[OH]^a (μmol/g)	[OH] (μmol/g)	F^a (-)	$M_n{}^a$ (g/mol)	M_n (g/mol)	M_w/M_n (-)	High M^b (%)
1	10	94	1.74	3500	503	508	1.79	3500	3250	2.7	23
2	12.5	90	1.72	3250	528	564	1.84	3250	3150	3.0	27
3	15	85	1.75	3150	554	574	1.84	3200	2850	3.3	30
4	20	74	1.84	3750	490	488	1.78	3650	2500	3.6	42
5	25	66	1.71	3400	507	510	1.79	3500	3250	4.0	50
6[c]	10	92	1.80	4150	432	450	1.74	3850	3650	3.0	31
7[d]	12.5	91	1.65	3400	487	537	1.82	3400	3250	3.3	32

[a] For calculation methods see [43].
[b] The area of the high molecular weight fraction is given.
[c] TMBPA was added without methanol.
[d] A reaction time of 1 h was used instead of 3 h.

methanol/toluene mixture that is used for precipitation. Chains with a molecular weight up to 800 g/mol are soluble in methanol [21,32]. In a 10:1 methanol/toluene mixture, chains with a little higher molecular weight will be soluble as well. Thus the precipitation procedure seems to have a strong effect on the composition and yield.

The redistribution products have a complicated composition and detailed analysis of these are given elsewhere [43]. The aromatic part of the ^{1}H NMR spectrum (Fig. 6) was used to calculate the molecular weight of the redistribution product [43]. In Fig. 7 the peak assignments for different types of chains in the product are given.

The average functionality, molecular weight and concentration of phenolic endgroups of different bimodal PPE-2OH products as calculated from the NMR spectra [43] are given in Table 1. The molecular weight was also calculated from the concentration of phenolic endgroups (peak d′, f and f′) as measured by titration (Table 1) [43].

Within the error ranges of 5–10% the molecular weight distributions as calculated from the different measuring methods are in reasonable agreement, although some data show larger deviation. In particular the [OH] and M_n from NMR and titration correspond quite well. The functionality that is calculated from the titratable OH endgroup concentration has somewhat higher values in general than that calculated from NMR measurements. The GPC data are less reliable, because the program is not well suitable for the calculation of the molecular weight of a bimodal product. It is concluded that the NMR data for average molecular weight of the bimodal product are the most accurate because here the least assumptions were used. The [OH] concentration as measured by titration can be used best to calculate

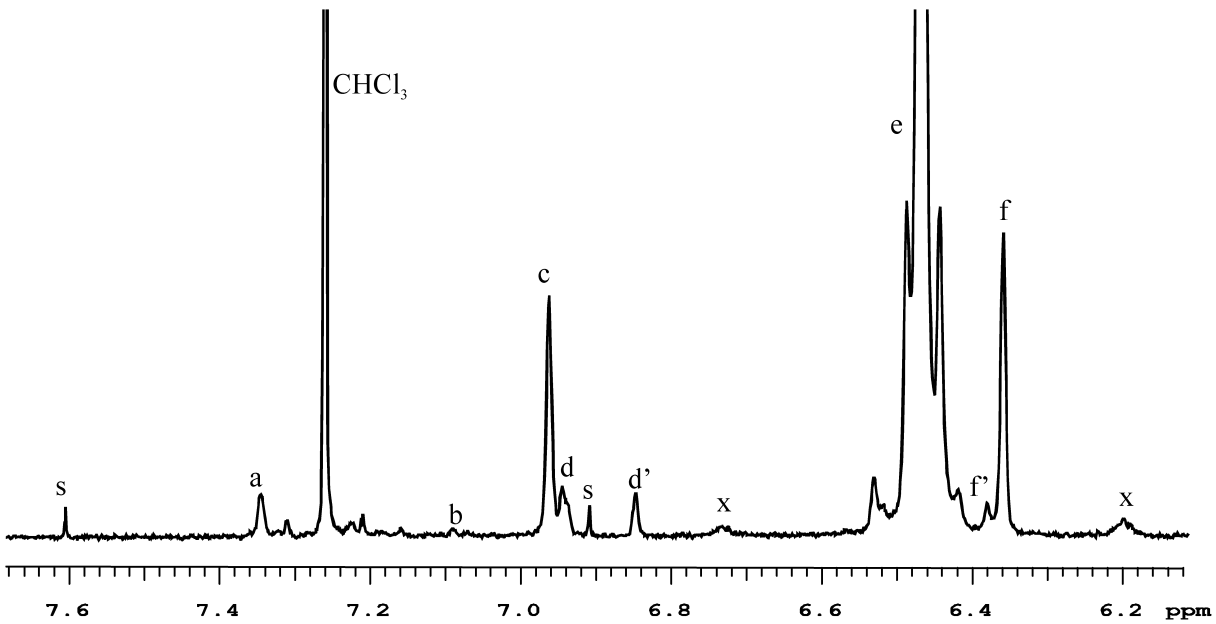

Fig. 6. Aromatic region of the ^{1}H NMR spectrum of PPE-2OH, made by redistribution of PPO-803® with 15 wt% TMBPA (s = spinning side bands $CHCl_3$ and x = C^{13} satellites peak e).

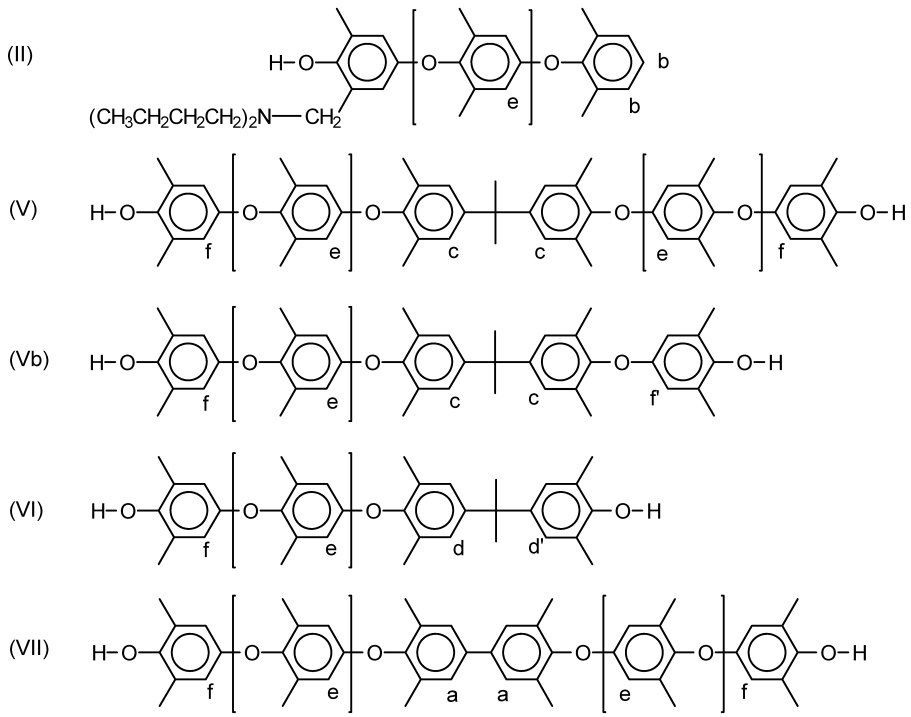

Fig. 7. Peak assignments from the NMR spectrum given in Fig. 6 for different chains in the product PPE-2OH, made by redistribution of PPO-803®.

quantities when the PPE segments are used in a further reaction, such as endgroup modification.

When the redistribution reaction is performed in toluene only (product 6), the molecular weight of the product is higher than when it is performed in a 20/1 mixture of toluene/methanol (product 1) as is shown in Table 1. Apparently the redistribution reaction is a little faster and more complete when it is performed in a reaction mixture of 20:1 toluene/methanol [26]. Probably the phenolic endgroups are better accessible in this solvent/non-solvent mixture.

The reaction time has little influence on the composition of the product. When a reaction time of 1 h is used instead of 3 h (product 7 vs. 2), the product had a little higher average molecular weight, lower functionality and larger high molecular fraction. Apparently the reaction is not fully completed after 1 h and the equilibrium is not yet established. A reaction time of 16 h was studied as well, however, no difference in the composition with the 3 h product was measured. Other variables that were tested include a higher amount of TMDPQ and adding the TMDPQ in three portions spread over the reaction time. These variations had no effect on the molecular weight distribution of the product.

3.2. PPE-2T

The phenolic endgroups of PPE-2OH were modified by reaction with methyl chlorocarbonyl benzoate (MCCB) to obtain PPE-2T (Fig. 4). The reaction of the phenolic endgroups with the acid chloride is a fast and complete reaction. Next to the phenolic 'head' endgroups, also the tetramethyl bisphenol A and a part of the Mannich base type endgroups of PPE-2OH will be functionalised by reaction with MCCB. So next to the low molecular weight fraction of PPE-2OH, also some chains of the high molecular weight fraction that is not depolymerised can be functionalised. The products are white and the yield of the endgroup modification reaction is over 95% (Table 2).

After endgroup modification, the molecular weight of the PPE chains is increased compared to the PPE-2OH starting material, as MCCB is incorporated (Fig. 8 and Table 2). The position of the high molecular weight PPE fraction is unchanged after reaction with MCCB, while the depolymerised low molecular weight PPE-2OH fraction is shifted

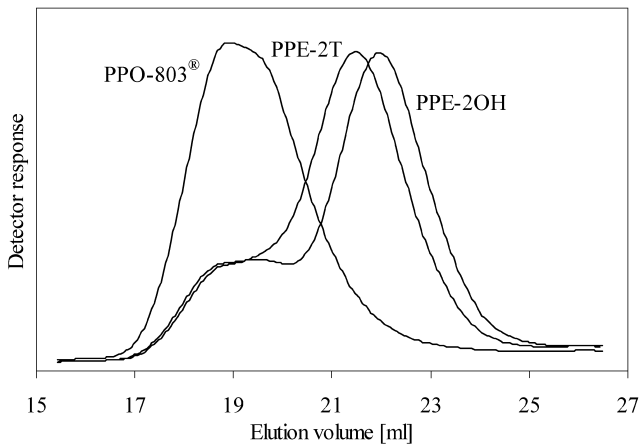

Fig. 8. GPC molecular weight distribution of PPE-2OH-1 (10 wt% TMBPA) and PPE-2T-1 made out of this PPE-2OH.

Table 2
Molecular weight and functionality by different methods of PPE-2T made by the two-step and one-pot reaction using different amounts of TMBPA

	Reaction type	TMBPA (wt%)	Yield (%)	NMR			GPC		
				M_n[a] (g/mol)	F[a] (-)	$[OCH_3]$[a] (μmol/g)	M_n (g/mol)	M_w/M_n (-)	High M[b] (%)
1	Two-step	10	98 (92)[a]	3900	1.76	454	4500	2.2	17
2	Two-step	15	97 (83)[c]	3700	1.79	481	4300	2.4	24
3	One-pot	10	95	3100	1.79	573	3150	3.1	27
4	One-pot	15	91	2500	1.84	733	2800	3.2	31
5	One-pot	20	87	2000	1.73	875	2450	3.6	33

[a] For calculation methods see [43].
[b] The area of the high molecular weight fraction is given.
[c] The yield of the second step (endgroup modification) is given first; between parenthesis the yield of the combined reaction is given.

to the left -to higher molecular weight- after reaction with MCCB.

With NMR it was shown that the peaks of the phenolic endgroup (f, f′ at 6.36, 6.38 ppm) of PPE-2OH have disappeared completely after reaction with MCCB to PPE-2T (Fig. 9). Also the TMBPA endgroups (d, 6.84 ppm and d′, 6.94 ppm) have reacted fully with MCCB. So the endgroup modification reaction is complete and the segments preserve their high functionality. There are two new doublets at 8.18 and 8.29 ppm of the reacted MCCB and a singlet at 4.00 ppm, origination from the new methyl ester endgroups. The integral of the new endgroup peaks is approximately the same as that of the phenolic OH and TMBPA endgroups of PPE-2OH together.

The ^{1}H NMR spectrum and calculation of molecular weight are discussed in detail in [43]. The peak of the TMDPQ unit at 7.34 ppm is not effected by endgroup modification reaction. Thus TMDPQ can be found mainly in the PPE chain, instead of as an endgroup. PPE-2T that is made by the two-step reaction contains about the same amount of TMDPQ groups per DMP unit as PPE-2OH. Next to the peak of the Mannich base type endgroups at 0.88 ppm there is a new triplet at 0.75 ppm. So a part of the Mannich base type endgroups has probably reacted with MCCB, resulting in this shift of a part of the triplet.

The synthesis of PPE-2T was simplified by combining the redistribution and endgroup modification reaction. In this one-pot reaction the redistribution is directly followed by the endgroup modification step with MCCB. In this case the redistribution reaction is performed in toluene solution without methanol, because methanol can react with the acid chloride instead of a phenolic endgroup which is not wanted. The advantage of this one-pot reaction is in the first place that only one precipitation step is necessary. Also the yield can be higher because part of the low molecular weight PPE-2OH chains that are soluble in 10:1 methanol/toluene are insoluble after reaction with MCCB. And as

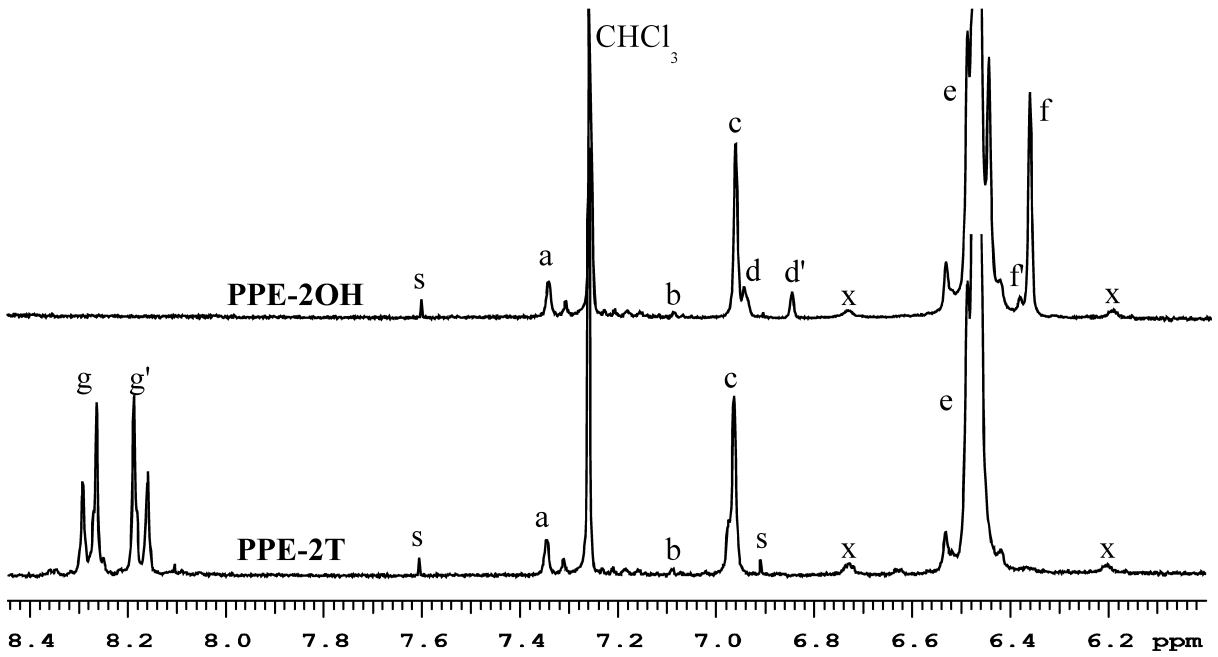

Fig. 9. ^{1}H NMR spectrum of PPE-2OH (10 wt% TMBPA) and PPE-2T made with this PPE-2OH.

a result of this, the average molecular weight of PPE-2T that can be obtained with the one-pot reaction is lower than that of PPE-2T in the two-step reaction when the same amount of TMBPA is used (Table 2).

The yield of the endgroup modification reaction, which is the second step in the two-step reaction, is very high. However, the combined yield over the two steps is lower than that of the one-pot reaction. The lowest molecular weight that can be obtained by the two-step method is 3700 g/mol. It is not well possible to obtain PPE-2T with a lower average molecular weight by this two-step method, because PPE-2OH with a lower average M_n cannot be made (see Section 3.1). In the two-step as well as one-pot reaction the yield decreases with increasing amount of TMBPA used. It seems that PPE-2T is less soluble in the methanol/toluene mixture than PPE-2OH as the yield is higher at high TMBPA content. As a result the average molecular weight that can be obtained with high TMBPA contents is lower in the one-pot reaction.

3.3. Narrow molecular weight PPE-2OH and PPE-2T

The major disadvantage of using PPO-803® in the redistribution reaction is that products with a bimodal molecular weight distribution and functionality lower than two are obtained, which is not desirable when PPE-2OH or PPE-2T will be used in a copolymerisation reaction. The low functionality will prevent the synthesis of copolymers with a high molecular weight. The presence of high molecular weight PPE chains might give rise to phase separation in a copolymer. Therefore, it would be nice to have a well-defined PPE-2OH or PPE-2T segment with a narrow molecular weight distribution that does not contain a high molecular weight fraction.

A way to obtain PPE-2OH or PPE-2T with a narrow molecular weight distribution and functionality near 2.0 after redistribution of PPO-803® was developed. This was done by fractionation (precipitation in two steps). In Table 3 the properties of some PPE-2OH and PPE-2T products that were obtained after partial precipitation with different amounts of methanol to precipitate the high molecular weight fraction are given. Details on the calculation of the molecular weight from NMR and endgroup concentration are given in [43]. In Fig. 10 GPC-results of PPE-2T before and after fractionation with different amounts of methanol are given.

The low and the high molecular weight fraction of PPE-2T can be separated if just enough methanol is used (Fig. 10(a)). When too much methanol is added (Fig. 10(b)), a part of the low molecular weight fraction is precipitated together with PPE-2T-high. In this case the yield of PPE-2T-low decreases and the molecular weight distribution becomes more narrow (Table 3). When too little methanol is added, the high molecular weight fraction is not completely separated and the PPE-2T-low product will still have a bimodal molecular weight distribution. It can be concluded that in a one-pot reaction to PPE-2T in 400 ml toluene, 175 ml methanol is just enough to precipitate the high molecular weight PPE-2T fraction selectively.

PPE-2OH was fractionated as well. When 200 ml of methanol is added at the end of the reaction the high molecular weight fraction precipitates selectively. With 800 ml methanol for precipitation of PPE-2OH-high, a PPE-2OH-low fraction with a very narrow molecular weight distribution of $M_w/M_n = 1.14$ can be obtained (Table 3). However, at the same time the yield becomes very low and most of the redistributed product will be part of PPE-2OH-high fraction. Therefore, using too much methanol is not

Table 3
Molecular weight and functionality by different methods of PPE-2OH and PPE-2T after fractionation (all were made with 8 g TMBPA and 40 g TMBPA in 400 ml toluene)

	MeOH (ml)	Fraction	Yield (%)	NMR			Titration		GPC	
				F[a] (-)	M_n[a] (g/mol)	[OX][a,b] (μmol/g)	[OH][a] (μmol/g)	M_n[a,c] (g/mol)	M_n (g/mol)	M_w/M_n (-)
PPE-2OH										
8	200	Low	27	1.70	2150	797	790	2150	1900	1.5
		High	35	–	–	–	–	–	12000	1.9
9	300	Low	15	1.70	2100	794	789	2150	1600	1.6
		High	40	–	–	–	–	–	8500	2.5
10	800	Low	9	1.86	1800	1018	990	1900	1400	1.14
		High	61	–	–	–	–	–	4900	3.3
PPE-2T										
6	175	Low	55	1.74	1600	1088	–	–	2050	1.3
		High	28	–	–	–	–	–	10500	2.0
7	200	Low	36	1.87	1550	1189	–	–	1700	1.2
		High	38	–	–	–	–	–	6500	2.8

[a] For calculation methods see [43].
[b] For PPE-2OH (8–10) the OH endgroup concentration and for PPE-2T (6,7) the OCH_3 endgroup concentration is given.
[c] M_n was calculated from [OH] by titration by using the functionality as calculated by NMR.

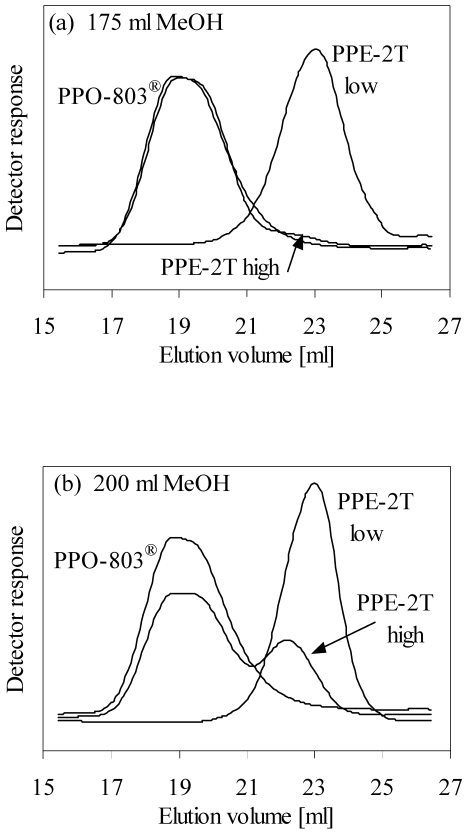

Fig. 10. GPC molecular weight distribution of PPE-2T products made by redistribution in 400 ml toluene and obtained by partial precipitation with: (a), 175 ml methanol; (b) 200 ml methanol.

desirable. For PPE-2OH the phenolic concentration as measured by titration corresponds nicely with that calculated from the NMR spectrum (Table 3).

As expected, the functionalities of the fractionated PPE-2OH-low and PPE-2T-low are little higher than that of bimodal PPE-2OH and PPE-2T (Tables 1 and 2). Theoretically, a functionality of 2.0 can never be obtained, due to the presence of non-reactive endgroups. PPE-2OH-high and PPE-2T-high fractions that are obtained after precipitation with 200 or 175 ml methanol hardly contain phenolic or methyl ester functional groups.

3.4. Inherent viscosity and T_g

Next to the number average molecular weight of the different PPE-2OH and PPE-2T as given in Tables 1–3, also the inherent viscosity and T_g were determined ([43]). The inherent viscosity was measured with a diluted polymer solution (0.1 dl/g in $CHCl_3$, at 25 °C). The inherent viscosity of the bimodal products and PPO-803® increases with decreasing number average molecular weight. The high molecular weight fraction has a much stronger effect on inherent viscosity than the low molecular weight fraction and as a result the inherent viscosity of a bimodal product with a certain average molecular weight is higher.

The glass transition temperature decreases with decreasing molecular weight. There are different equations to predict this dependence; the most commonly used being that of Fox and Flory [44] (Eq. (1))

$$T_g = T_{g,\infty} - \frac{K}{M_n} \quad (1)$$

T_g, glass transition temperature of a polymer with M_n (in K); $T_{g,\infty}$, the T_g of a polymer of infinite chain length (PPE: $T_{g,\infty} = 490$ K) [45]; K, constant related to the volume of chain ends (PPE: $K = 12.73 \times 10^4$ g K/mol) [45].

The T_g as measured by DSC is plotted as a function of $1/M_n$ for PPE-2OH and PPE-2T in Fig. 11. There does not seem to be a difference between bimodal or monomodal PPE-2T as was seen for the effect of molecular weight on inherent viscosity. The T_g of PPE-2T is approximately 10 degrees lower than the T_g of PPE-2OH. The same was found for PPE-2OH modified with *p*-chloromethylstyrene to PPE-2VB [21]. The difference in T_g between PPE-2OH and PPE-2VB was 10 °C. This was ascribed to the difference in hydrogen bonding of the phenolic chain ends [21]. Such a difference in hydrogen bonding of the chain ends could account for the difference between PPE-2OH and PPE-2T as well. It could also be that the introduction of terephthalic methyl ester endgroups makes the chain less stiff, resulting in a lower T_g.

The calculated T_g dependence on molecular weight according to Fox and Flory is given in Fig. 11 as well. In this approximation the effect of the product consisting of two fractions of high and low molecular weight with higher and lower T_g is not taken into account. As a result the T_g dependence on M_n will be non-linear as can be calculated using the Fox relationship [46]. When the T_g of PPE-2OH is compared with that of PPE according to Eq. (1), we see a

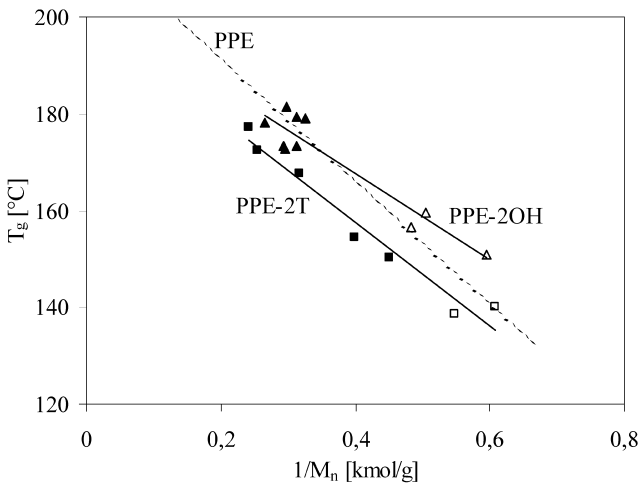

Fig. 11. T_g as a function of the inverse value of M_n (NMR): (▲), bimodal PPE-2OH; (△), fractionated PPE-2OH; (■), bimodal PPE-2T; (□) fractionated PPE-2T. Also given in this figure is the T_g as function of $1/M_n$ according to Fox and Flory [44] for PPE (- - -).

good agreement for the higher molecular weights (above 2500 g/mol). It could be that at lower molecular masses the 'excess free volumes' of the chain ends are overlapping (K smaller) [47]. As a result the polymer chains are more stiff than predicted with Eq. (1) and the glass transition temperature is higher.

4. Conclusions

Redistribution or depolymerisation of high molecular weight commercial PPE with tetramethyl bisphenolA is a good method to make partly bifunctional PPE-2OH. The product has a bimodal molecular weight distribution because only 70–80% of the chains of the commercial PPO-803® has at least one reactive endgroup that is needed to start the depolymerisation reaction. The average molecular weight of the product decreases with increasing amount of TMBPA used. However, when too much TMBPA is added, the molecular weight of the precipitated product increases because the molecular weight of the redistributed fraction in the product becomes too low and is soluble in 10:1 toluene/methanol solvent mixture that is used for precipitation.

The phenolic endgroups can be modified easily by a fast and complete reaction with methyl chlorocarbonyl benzoate. The product after endgroup modification is called PPE-2T and has terephthalic methyl ester endgroups instead of OH endgroups and a molecular weight of 3700–3900 g/mol. PPE-2T has a higher molecular weight than PPE-2OH. When PPE-2T is made in a one-pot reaction segments with a lower average molecular weight of 2000–3000 g/mol can be obtained. The functionality of all PPE-2T products is around 1.8.

The bimodal PPE-2OH and PPE-2T products can be separated in a high and low molecular weight fraction by selective precipitation of the high molecular weight fraction in ~2:1 toluene/methanol. The low molecular weight fraction has a narrow molecular weight distribution with a polydispersity between 1.2 and 1.5. The functionality of the low molecular weight fraction after partial precipitation is 1.7–1.9. The high molecular weight fraction contains hardly functional endgroups.

The inherent viscosity and the T_g decrease with the molecular weight. The T_g of the PPE-2T segments is about 10 °C lower than that of PPE-2OH.

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