

Synthesis of polyether-based block copolymers based on poly(propylene oxide) and terephthalates

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Abstract

Poly(propylene oxide) (PPO) is a low reactive telechelic polyether and the synthesis of high molecular weight poly(propylene oxide)-based block copolymers was studied. The poly(propylene oxide) used was end capped with 20 wt % ethylene oxide and had a molecular weight of 2300 g/mol (ultra-low monol PEO-*b*-PPO-*b*-PEO). The type of terephthalic acid based precursors was varied: terephthalic acid, dimethyl terephthalate, diphenyl terephthalate, di(trifluoro ethyl) terephthalate, di(*p*-nitrophenyl) terephthalate) and terephthalic acid chloride. High molecular weight poly(propylene oxide) based segmented block copolymers were obtained with diphenyl terephthalate (inherent viscosity: 1.6 dl/g).

The synthesis of polyether(ester–amide)s comprising PPO and isophthalamide-based segments was also studied by varying the polymerization temperature and time. High molecular weight poly(propylene oxide) block copolymers could be obtained if the reaction was carried out for 2 h at 250 °C under vacuum. Higher temperatures (280 °C) and longer times result in lower inherent viscosities, probably due to degradation of the polyether.

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1. Introduction

Segmented block copolymers based on poly(propylene oxide) (PPO) are known to exhibit excellent low-temperature flexibility [1]. Moreover, PPO is readily available as a telechelic polyether and has found extensive use in for instance segmented polyurethanes, like polyether(urethane–urea) that are commonly applied as elastic materials for foams. PPO-based block copolymers are therefore commercially interesting materials.

However, in the synthesis of segmented polyester and polyamides block copolymers these conventional PPO's are not often used as they contain secondary hydroxyl end groups, which have low reactivity, and also because these PPO's have poor difunctionality [2]. The use of new catalyst

systems has led to PPO's with very low concentrations of mono-functional polyether (ultra-low monol PPO's). This resulted in telechelic PPO's with functionalities of 1.99 [2]. However, the 'ultra-low monol' PPO's still contain a large amount of the low reactive secondary hydroxyl groups making it difficult to synthesize high molecular weight segmented polyether(ester) and polyether(ester–amide) block copolymers. The reactivity was further improved by end capping the 'ultra-low monol' PPO with ethylene oxide (EO). This PEO-*b*-PPO-*b*-PEO contains a small amount of 10–12 mol% secondary hydroxyl groups [3]. The use of these PEO-*b*-PPO-*b*-PEO in the synthesis of segmented polyurethanes has resulted in an improvement of properties [2,4]. High molecular weight poly(butylene terephthalate) based polyether(ester)s have been made starting from telechelic PEO-*b*-PPO-*b*-PEO (molecular weight 6000 g/mol), dimethyl terephthalate and with the help of a chain branching agent [5].

Segmented polyether(esters) are commonly synthesized via alcoholysis of dimethyl terephthalate [5–10], often

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assisted by catalysts like titanium alkoxides [6,7]. When titanium compounds are used to catalyze the alcoholysis of esters, the reaction is assumed to follow a concerted mechanism (Fig. 1) [7]. In this mechanism the formation of the intermediate is probably the rate-determining step. This intermediate can be stabilized when R is a phenyl group instead of a methyl group. Diphenyl terephthalate is therefore expected to give a higher reaction rate than dimethyl terephthalate. Removal of the condensate (ROH) during the reaction, by applying a vacuum, increases the molecular weight of the final block copolymer.

Terephthalates other than dimethyl terephthalate, e.g. diphenyl terephthalate, have been used to synthesize high molecular weight polyesters, polyamides and also segmented PEEs [7,8,11–16].

The ‘ultra-low monol’ PEO-*b*-PPO-*b*-PEO is an interesting new starting material for polyether(ester–amide)s (PEEA) and PEE’s. As still little is known about the synthesis of these block copolymers with this PPO, the reaction of PEO-*b*-PPO-*b*-PEO with different terephthalic acid based precursors is studied at first. The terephthalic acid based precursors used in this paper differ in reactive end groups. Later, with the knowledge gained about the synthesis of PEO-*b*-PPO-*b*-PEO based copolymers, the more complex melt synthesis of PEEA block copolymers (Fig. 2) is studied. In future papers the structure–properties relationships of the synthesized PEEA’s will be studied.

2. Experimental

2.1. Materials

Terephthalic acid, dimethyl terephthalate (DMT), diphenyl isophthalate (DPI), tetra-isopropyl *ortho*titanate (0.05 M Ti(*i*-OC₃H₇)₄ solution in *m*-xylene), phenol, 1,1,2,2-tetrachloroethane, tetrahydrofuran (THF), 4-nitrophenol, 2,2,2-trifluoroethanol, terephthaloyl dichloride (TPC), trifluoro

acetic acid and *N*-methyl-2-pyrrolidone (NMP) were purchased from Aldrich. *m*-Xylylene diamine was a gift from Mitsubishi Gas Chemical Company (Japan). Irganox 1330 was obtained from CIBA. All chemicals were used as received. Poly(propylene oxide) end capped with 20 wt % EO with a *M_n* of 2300 g/mol (PEO-*b*-PPO-*b*-PEO) was a gift from Bayer AG (Acclaim Polyol PPO-2220 N). Before use, the polyol was dried in vacuum at 80 °C overnight.

2.2. Synthesis of terephthalic diesters

A 500 ml flask was charged with 200 g of either phenol, 4-nitrophenol, or 2,2,2-trifluoroethanol and heated to 80 °C (or with 4-nitrophenol to 120 °C). The reaction flask was equipped with a nitrogen inlet, condenser, magnetic stirrer and an outlet to lead the HCl through a NaOH solution in water. Terephthaloyl dichloride was added under nitrogen flow (the molar ratio of alcohol to TPC was 2.2:1). The reaction mixture was stirred for 2 h at 95 °C (120 °C with 4-nitrophenol), after which the ester was precipitated in water. The excess of the hydroxy- compound was subsequently removed by washing (three ×) with hot ethanol (70 °C). The terephthalic diesters were dried in vacuum at 70 °C overnight before use. ¹H NMR indicate a purity >98%.

2.3. Synthesis of polyether(ester) copolymers

A reactor of 250 ml was charged with 10 g (4.4 mmol) of PEO-*b*-PPO-*b*-PEO and an equimolar amount of terephthalic diester, 100 ml NMP and 1 wt % Irganox 1330 (based on PPO) under nitrogen flow. The reactor (a stainless steel cylindrical flange flask type cmd 075) was equipped with nitrogen inlet, condenser and a stirring device with magnetic coupling (the magnetic coupled stirring device was important to obtain high vacuum conditions). The reaction mixture was stirred under N₂-flow and heated to a temperature of 120 °C and kept at 120 °C for 2 h. Hereafter, the temperature was increased to 150 °C and a catalyst

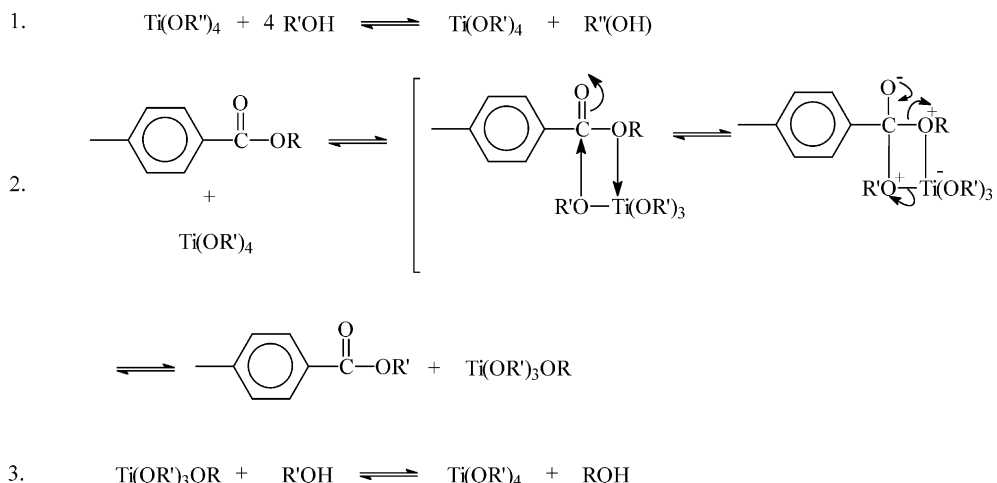


Fig. 1. Mechanism of alcoholysis reaction catalyzed by titanium compounds [7].

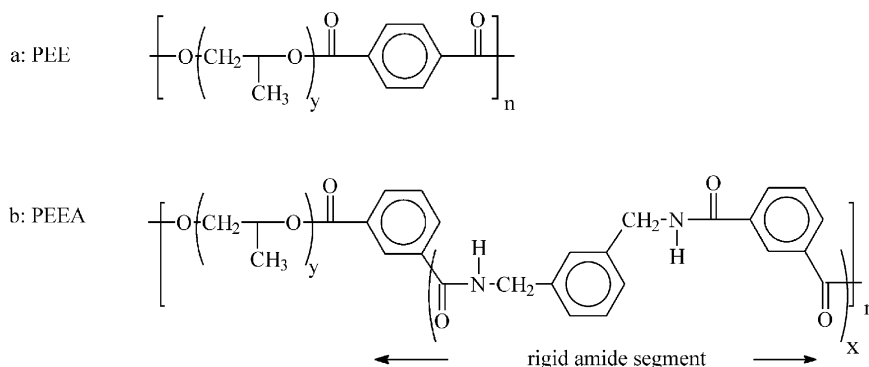


Fig. 2. Structure of PPO-based polyether(ester) copolymers (PEE) and polyether(ester–amide) block copolymers (PEEA) with x as the rigid amide segment length.

(2 ml, 0.05 M $\text{Ti}(\text{OC}_3\text{H}_7)_4$ in *m*-xylene) was added. Subsequently, the temperature increased to 250 °C over a period of 1 h. At 250 °C low vacuum (10–1 mbar) was applied for 1 h and finally high vacuum (0.1–0.08 mbar) for 2 h, after which the product was cooled to room temperature whilst maintaining a vacuum. The polymers were dried overnight in vacuum at 70 °C before use.

2.4. Synthesis of polyether(ester–amide)s with random amide segments

An example of a polymerization is given for a PEEA, whereby the amide segment has an average length of $x=3$ (Fig. 2). A stainless steel cylindrical flange flask type cmd 075 equipped with a magnetic coupled stirrer was charged with PEO-*b*-PPO-*b*-PEO (20.0 g, 8.69 mmol), *m*-xylylene diamine (3.54 g, 26.0 mmol), DPI (11.1 g, 35.0 mmol), 100 ml NMP and 1 wt % Irganox 1330 (based on PPO) under nitrogen flow. The reaction mixture was heated to a temperature of 120 °C under stirring and N_2 -flow and kept for 2 h at 120 °C. The temperature was increased to 150 °C and catalyst (2.0 ml, 0.05 M $\text{Ti}(\text{OC}_3\text{H}_7)_4$ in *m*-xylene) was added to the reaction mixture. Hereafter, the temperature was increased in 1 h to 250 °C. At 250 °C low vacuum (10–1 mbar) was applied for 1 h and finally high vacuum (0.1–0.08 mbar) for 2 h, after which the product was cooled to room temperature whilst maintaining a vacuum.

2.5. Viscometry

Inherent viscosities of polymer samples at a concentration of 0.1 g/dl in phenol/1,1,2,2-tetrachloroethane (1:1 molar mixture) were measured at 25 °C using a capillary Ubbelohde 1B viscometer.

2.6. ^1H NMR

^1H NMR spectra of a polyether(ester–amide) was recorded on a Bruker AC 300 spectrometer at 300.1 MHz. Deuterated trifluoro acetic acid (TFA-*d*) was used as the solvent.

2.7. GPC

GPC experiments on polyether(ester–amides) samples were conducted with a Waters GPC apparatus equipped with a Waters 515 HPLC pump, differential refractometer model 411, a series of Waters Styragel H columns and a Viscotek H502 viscometer. The polyether(ester–amide)s were dissolved in THF (5.0 mg/ml). Elution was performed at 25 °C at a flow rate of 1.5 ml/min using THF as the eluent. The universal calibration method was used to determine the number and weight average molecular weight (respectively, M_n and M_w) and the molecular weight distribution (M_w/M_n) using a series of polystyrene standards with narrow molecular weight distribution (in the range of 1.04).

3. Results and discussion

The synthesis of block copolymers based on poly(propylene oxide) with ultra-low monol moieties and a number average molecular weight of 2300 g/mol and 20 wt % of ethylene oxide (i.e. PEO-*b*-PPO-*b*-PEO) is studied. First, the type of leaving group on the terephthalic acid based precursor is evaluated. Later the synthesis of the more complex polyether(ester–amide)s (PEEA) is studied.

3.1. Type of reactive end group of the terephthalic acid based precursors

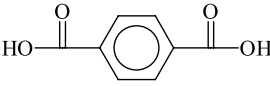
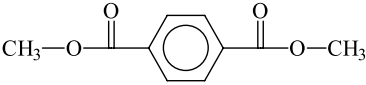
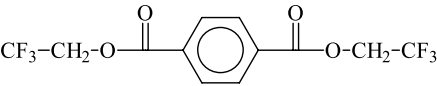
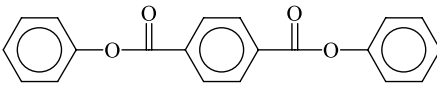
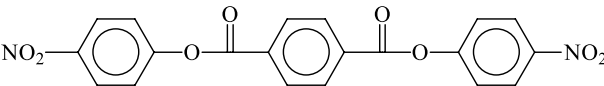
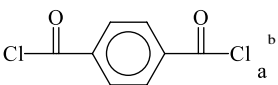
The polymerization is studied of PEO-*b*-PPO-*b*-PEO with terephthalic acid, terephthalic acid based esters and acid chlorides (Table 1). Reaction conditions for the synthesis of these PEE copolymers were chosen as such that these conditions could be applied to the synthesis of PEEA block copolymers.

During polymerization, the reaction mixture appeared to be homogeneous. On cooling the PEE copolymers were viscous and transparent liquids, as expected [11].

With terephthalic acid, as the terephthalic acid based precursor, the viscosity of the resulting PEE copolymer was very low. It is known that direct polymerization of

Table 1

Inherent viscosities of polyether(ester) copolymers synthesized using PPO-2300 and terephthalic acid, terephthalic acid based esters, or acid chlorides (boiling NMP, $\text{Ti}(\text{OC}_3\text{H}_7)_4$, 2 h transesterification, 2 h polycondensation (pressure ≤ 0.1 mbar))

Terephthalic acid based monomer:	η_{inh} (dl/g)
	0.3
	0.7
	1.3
	1.6
	0.1 ^a
	0.1 ^a

^a Degradation.

^b No catalyst was used.

polyethers with terephthalic acid is not well possible due to the acidity of the terephthalic acid and possibly even complexation of the terephthalic with the catalyst tetra-isopropyl *orthotitanate* [11,18]. The complex formed precipitates from the reaction mixture thereby preventing any further reaction.

With dimethyl terephthalate (DMT) reasonably high molecular weight block copolymers are obtained [5]. In this polymerization removal of the condensate methanol is easy because of the low boiling point of methanol.

With trifluoro ethanol based terephthalic ester precursor a high molecular weight PEE was obtained. This terephthalate has an end group that might be able to stabilize the reaction intermediate (Fig. 1), which may eventually result in a high molecular weight block copolymer. Moreover, the condensation product trifluoro ethanol has a relatively low boiling point, which allows an easy removal of the condensate shifting the equilibrium in favor of the block copolymer product.

Diphenyl terephthalate (DPT) has a high melting temperature and the corresponding condensation product phenol has a high boiling point. The use of this terephthalic ester precursor has resulted in PEE copolymers with the highest molecular weight obtained in the series studied (inherent viscosity of 1.6 dl/g), probably due to the ability of the phenolic group to stabilize the intermediate (Fig. 1). Stripping of the highly boiling phenol condensate at 250 °C under vacuum seems to go without any problem.

With the *p*-nitro phenol terephthalate the obtained

inherent viscosity was low and the reaction mixture colored black during polymerization. *p*-Nitro phenol is known to yield high molecular weight polyesters, however, the condensate *p*-nitro phenol is more acidic than phenol [11]. Probably, degradation of poly(propylene oxide) due to the acidic nature of *p*-nitro phenol resulted in a low viscosity of the final product.

The reaction product obtained from the reaction of PEO-*b*-PPO-*b*-PEO with terephthaloyl dichloride (TCl) was also black and had a very low inherent viscosity. HCl, the condensate, is known to cause degradation of the polyether [11].

From the studied terephthalic acid based precursors, it has been found that diphenyl terephthalate gives the highest viscosity. Diphenyl terephthalate and probably also diphenyl isophthalate are therefore suitable terephthalates to obtain high molecular weights block copolymers based on 'ultra low monol' PEO-*b*-PPO-*b*-PEO. If instead a PEO-*b*-PPO-*b*-PEO without being an 'ultra low monol' (obtained from Shell, Caradol 56-10, M_n 2000 g/mol) is used in the copolymerization with DPT, a copolymer was obtained with a inherent viscosity of only 0.62 dl/g.

3.2. Synthesis of PEEA block copolymers

In the synthesis of polyether(ester–amide), diphenyl isophthalate (DPI) was used to avoid crystallization because it may hinder the synthesis of high molecular weight block copolymers. The PEEA block copolymers were synthesized

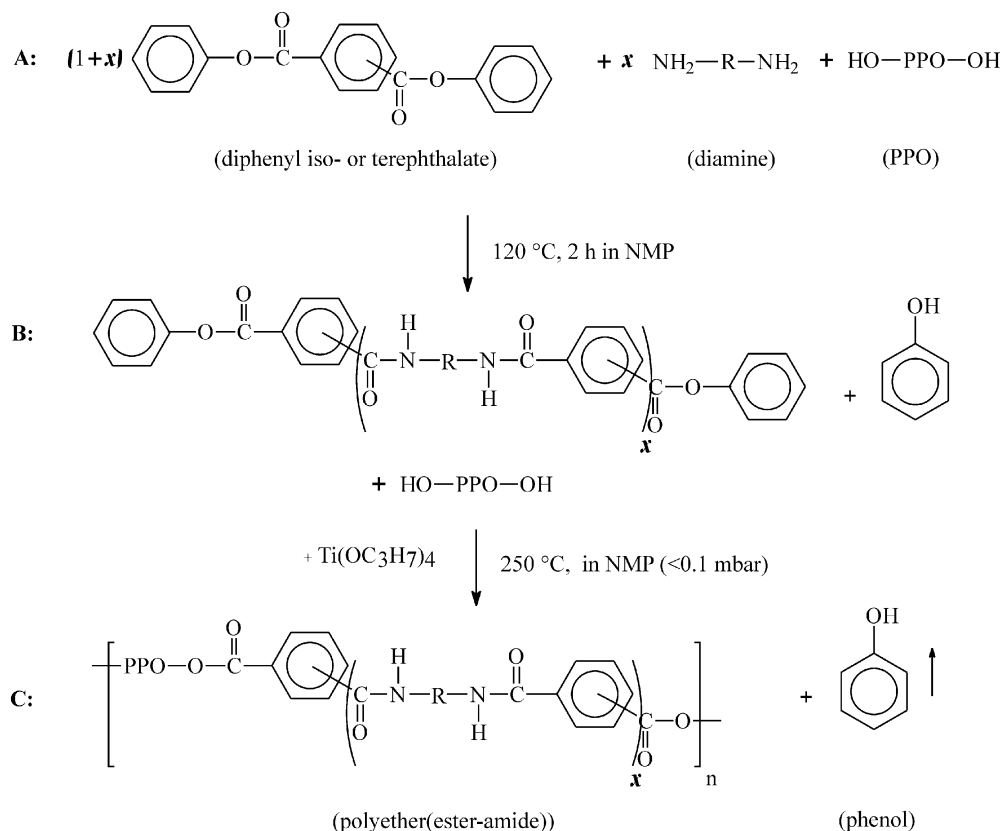


Fig. 3. Reaction scheme for the synthesis of PEEA's containing PPO segments and amide segments of length x . Step (A–B), Synthesis of bis(ester-oligo amide) by aminolysis of ester groups; Step (B–C), Polymerisation by alcoholysis of the ester groups by hydroxyl groups of PPO, part of this step is at high vacuum (the post-condensation)

in a one-pot process. The reaction, however, is expected to occur in steps: first the amide segments are formed at 120 °C (step A–B) after which the transesterification step follows (step B–C) (Fig. 3).

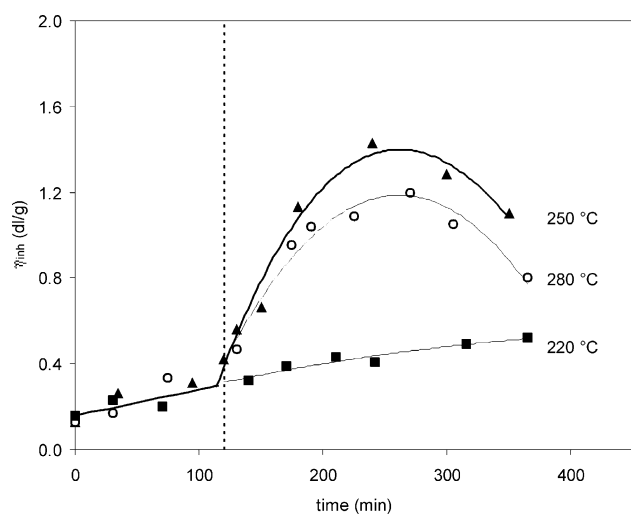


Fig. 4. The inherent viscosity of PEEA's as function of polymerisation time and polymerisation temperature (amide segment length $x=3$, PPO-2300). ■, 220 °C; ▲, 250 °C; ○, 280 °C. The first 2 h of polymerisation is at 250 °C in NMP-solution. (Dashed line is the time at which vacuum is applied, i.e. start of melt polymerisation (≤ 0.1 mbar)).

The reaction is started with NMP as a solvent, to ensure that the formed amide segments remained dissolved at 120 °C. The solvent is stripped slowly when the reaction mixture was slowly heated to 250 °C and the rest during the 2 h reaction at 250 °C under vacuum. The last part of the block copolymer synthesis occurred therefore in the melt. The influence of the melt-polymerization temperature and time on the inherent viscosity of the PEEA is studied (Fig. 4).

During melt-polymerization at 220 °C under vacuum, the inherent viscosity of the PEEA increases only slowly with time. At 250 °C, the inherent viscosities increases fast but dropped after 2 h under these conditions. This decrease at longer times is expected to be due to degradation of the PEO-*b*-PPO-*b*-PEO. A melt-polymerization step at 280 °C did increase the inherent viscosity in the first 2 h, but not as much as for the polymerization at 250 °C. The lower viscosities obtained at 280 °C are probably due to stronger degradation at the higher temperature used. A one-pot polymerization starting at 120 °C in solution and ending with a melt-polymerization under high vacuum for 2 h at 250 °C yielded high molecular weight PEEA block copolymers.

It is known that at 120 °C, the reaction of diamines with diphenyl isophthalate goes well [8]. The diamine used in this paper is *m*-xylylene diamine, which is of interest for the

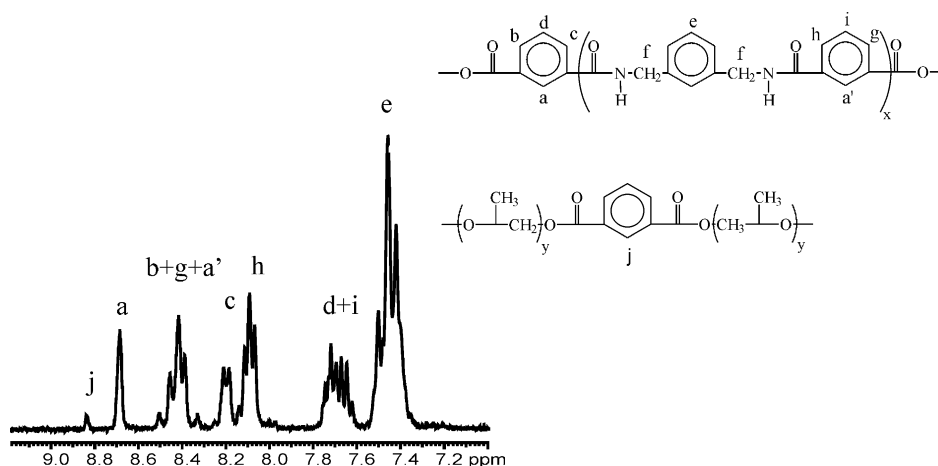


Fig. 5. ^1H -NMR spectrum (7.0–9.0 ppm) and segment structures of a poly(ether(ester–amide)) with expected amide segment length $x=3$ and PEO-*b*-PPO-*b*-PEO.

study of the structure–property relationships of PEEA block copolymers. We have assumed that at 120 °C the reaction of diphenyl isophthalate with the diamine is much faster than the un-catalyzed reaction of diphenyl isophthalate with the PEO-*b*-PPO-*b*-PEO. In this way, a small amount of isophthalate was lost in extending the PPO to PPO-*I*-PPO (wherein *I* is the incorporated isophthalate unit). To verify this a ^1H NMR spectrum of a synthesized PEEA based on PEO-*b*-PPO-*b*-PEO and poly(*m*-xylylene isophthalate) segments is shown (Fig. 5). The peaks, in the aromatic region, a, b, c and d refer to the different aromatic protons of the isophthalic end group of the amide segments and peaks e and f refer to the protons of the incorporated *m*-xylylene group. Peak j is assigned to the protons of the isophthalic group incorporated in between two polyether chains. The intensity of this peak is small and thus a small amount of DPI is lost in the extension of the polyether. Most of the diamine appears to be used in the reaction with diamine.

During the synthesis of segmented block copolymers from dimethyl terephthalate (DMT) and a polyether, some

of the DMT is lost from the reaction mixture by sublimation [7,11,12]. An excess of DMT is therefore necessary to keep a stoichiometric balance necessary to obtain high molecular weight block copolymers. With the use of other diesters, like diphenyl phthalates, sublimation might also affect the stoichiometric balance limiting the synthesis of high molecular weight PEEA's. The inherent viscosity of PEEA's as function of the stoichiometric balance of the feed was therefore studied, i.e. the ratio DPI to diamine plus PPO (Fig. 6).

The stoichiometric balance is described as the molar excess of DPI relative to the number of moles of diamine and PPO. A value of 0 is equivalent to stoichiometric balance and negative values represent an excess diamine relative to DPI.

At stoichiometric balance, i.e. $r = \text{DPI}/(\text{diamine} + \text{PPO}) = 1$, the highest inherent viscosity of the PEEA was obtained. This suggests that with diphenyl phthalates hardly any sublimation has occurred during polymerization. A similar behavior is expected when the isomer DPT is used. After all, DPT has even a higher melting temperature than DPI (200 °C vs. 137 °C [17]).

3.3. Inherent viscosity vs molecular weight of PEEA's

The PEEA's with random amide segments (amide segment length $x=3$), based on DPI and *m*-xylylene diamine, and PEO-*b*-PPO-*b*-PEO were found to be soluble in THF. The number and weight average molecular weights (respectively, M_n and M_w), the molecular weight distribution (MWD) measured by GPC and the inherent viscosity (η_{inh}) of these PEEA's are given in Table 2. Inherent viscosities of 1 or higher relate to relatively high molecular weight segmented block copolymers: $M_n = 19.4\text{--}36.7 \times 10^3$ g/mol. The use of diphenyl terephthalate and isophthalate and optimized polymerization conditions makes it possible to obtain PPO-based PEE's and PEEA's with a relatively high molecular weight. Although the molecular

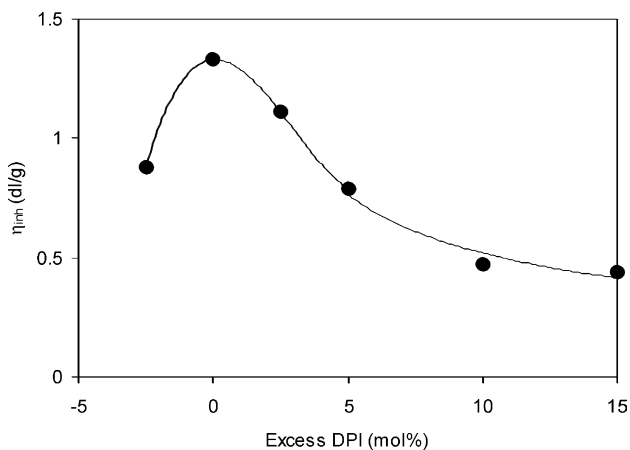


Fig. 6. The inherent viscosity of PEEA's as function of the excess of DPI in the feed. Polymerisation for 2 h at 250 °C under vacuum (0 refers to stoichiometric balance, negative values represent excess diamine).

Table 2

The results of viscometry and GPC experiments of synthesized PEEA block copolymers of different molecular weights, with amide segments based on diphenyl isophthalate (DPI) and *m*-xylylene diamine ($x=3$) and PEO-*b*-PPO-*b*-PEO

Polymer No:	η_{inh}^a (dl/g)	M_n^b ($\times 10^3$ g/mol)	M_w^b ($\times 10^3$ g/mol)	M_w/M_n^b
1	0.65	9.1	20.0	2.2
2	0.86	13.5	23.0	1.7
3	1.0	19.4	34.9	1.8
4	1.3	31.4	56.5	1.8
5	1.6	36.7	87.7	2.4

^a Viscometry (0.1 g/dl in 1:1 phenol/tetrachloroethane).

^b MWD by GPC, universal calibration with PS standards.

weights are high the number average degree of polymerization (DP_n) with a repeat block length of 2900 is low (± 10). Still, such a low number average degree of polymerization is quite common for PEE's and PEEA's segmented block copolymers. The molecular weight distributions are close to 2, which is also common for polymers made by polycondensation [18].

From the data in Table 2 a linear relation between the logarithm of the inherent viscosity and the logarithm of M_n is obtained (Eq. (1)):

$$\log(\eta_{inh}) = 0.61 \log(M_n) - 2.58 \quad (R^2 = 0.98) \quad (1)$$

4. Conclusions

The attainable molecular weight of block copolymers based on 'ultra low monol' PEO-*b*-PPO-*b*-PEO with a molecular weight of 2300 g/mol and terephthalic acid based precursors depends on the end group of the latter and on degradation of the polyether in acidic media. In the melt-polymerization of PEE the highest inherent viscosities were obtained with diphenyl terephthalate.

The synthesis of polyether(ester-amide)s (PEEA) was studied in a one-pot process with PEO-*b*-PPO-*b*-PEO, *m*-xylylene diamine and diphenyl isophthalate. The reaction was started at 120 °C in NMP-solution and ended in a melt-polymerization at high temperatures and high vacuum. High molecular weight PEEA segmented block copolymers could be obtained with a melt-polymerization for 2 h at 250 °C. At higher polymerization temperatures and/or longer reaction times, degradation seemed to take place. The PEEA's have inherent viscosities up to 1.6 dl/g as measured by viscometry. This is equivalent to a number average molecular weight of 37.000 g/mol (M_n) as measured by GPC (universal calibration). The molecular weight distribution (M_w/M_n) was close to 2, which is normal for the type of polymerization used [18].

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