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Scale-up of the synthesis of ureidopyrimidinone functionalized telechelic poly(ethylenebutylene)

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Abstract

The scale-up of the synthesis of high purity hydrogen-bonded supramolecular polymers is described. The synthesis involves functionalization of telechelic hydroxy-terminated poly(ethylenebutylene) with 2-ureido-4[1H]-pyrimidinone quadruple hydrogen-bonding groups via dibutyltindilaurate catalyzed urethane formation. A procedure with optimized reaction conditions was developed and applied on a 10 dm^3 mini plant scale. The hydrogen-bonded supramolecular polymer was isolated in a yield of 86% (803 g) and the 2-ureido-4[1H]-pyrimidinone functionalization of the end product was accurately determined with ^{19}F NMR to be 99.8% of the available hydroxy end groups in the telechelic hydroxy terminated poly(ethylenebutylene). Tensile tests showed that the product of the optimized large scale synthesis has better mechanical properties than the product of the unoptimized synthesis reported earlier.
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Keywords: Supramolecular polymers; Synthesis; Scale-up

1. Introduction

Supramolecular polymers form a new class of polymers where the reversibility of the non-covalent bonds between the monomers gives rise to interesting material properties [1,2]. We have developed supramolecular polymers based on quadruple hydrogen bonds as non-covalent interactions, because of their directionality and relative strength of hydrogen bonds (Fig. 1). The 'monomers' in these supramolecular polymers are bi-functional molecules, formed by connecting two strongly dimerizing quadruple hydrogen bonding 2-ureido-4[1H]-pyrimidinone groups with a linker [3,4].

By using telechelic polymers as linkers, high molecular weight polymers can be formed with a relatively small amount of hydrogen-bonding ureidopyrimidinone groups. [5,6] The functionalization of Kraton L2203, a hydroxy telechelic poly(ethylenebutylene) ($PEB(OH)_2$) on a 50 g scale (Scheme 1) has been reported earlier by us and involves the urethane formation between synthon **1** and the hydroxy end groups of $PEB(OH)_2$ with dibutyltindilaurate (DBTL) as a catalyst [6].

The functionalized telechelic polymer forms long linear polymeric chains, which combine mechanical properties of conventional linear macromolecules and the low melt viscosity of organic compounds [5,6]. The degree of polymerization (DP) of these hydrogen-bonded supramolecular polymers depends on the height of the association constant and the amount of chain-stopper (mono-functional molecules) present. Calculations show that due to the high association constant of the ureidopyrimidinone group (6×10^7 l/mol in chloroform at room temperature) the DP is not limited by the dissociation of the ureidopyrimidinone units, but rather by the presence of mono-functional impurities. Even incorporation of as little as 1 mol% of chain-stopper, which is often already there due to impurities in the starting material, lowers the degree of polymerization to 200 [3]. The molecular weight of a hydrogen-bonded supramolecular polymer is a calculated-equilibrium molecular weight (vide infra), which cannot be determined directly and is therefore a 'virtual' molecular weight. The mechanical properties of (hydrogen-bonded supramolecular) polymers are among other factors determined by their (virtual) molecular weight. Therefore, it is important that

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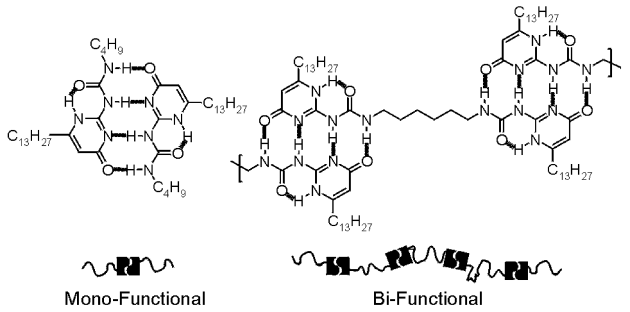


Fig. 1. A dimer of mono-functional ureidopyrimidinone (*left*) and a polymer of bi-functional ureidopyrimidinone groups linked via a hexamethylene spacer (right).

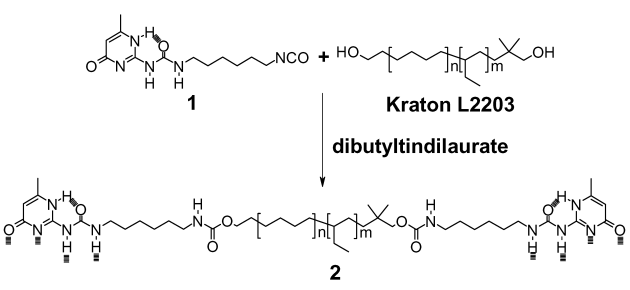
the amount of mono-functional compound in the end product is reduced as much as possible.

These supramolecular polymers are now beyond the idea of a scientific curiosity and can enter into technology, provided very pure polymers can be made at large scale. Thus, the twofold objective of this research was to produce ureidopyrimidinone telechelic PEB oligomers of high purity and furthermore to develop an optimized procedure to scale-up the functionalization from laboratory scale (50 g) to 10 dm^3 miniplant scale. Finally, the suitability of ^{19}F NMR spectroscopy and tensile testing as methods to establish the quality of the final product were investigated.

2. Experimental section

2.1. Instrumentation

^1H NMR, ^{19}F NMR, and ^{13}C NMR spectra were recorded on a Bruker AM-400 NMR spectrometer. Chemical shifts in ^1H NMR are in ppm downfield from TMS. ^{19}F NMR was measured with at = 9.999 s, np = 90,000, sw = 4500.5 Hz and d1 = 4.000 s. Chemical shifts in ^{19}F NMR are in ppm with $HFA{\cdot}H_2O = -82.47$ ppm as reference peak. Quantitative ^{13}C NMR was measured using inverse-gated decoupling with a relaxation time of 30 s. 2D HETCOR NMR was recorded on a Varian Inova 500 at a frequency of 499.8 and 125.7 Hz for, respectively, ^1H NMR and ^{13}C NMR. Elemental analyses were carried out using a Perkin Elmer 2400 series II CHNS/O Analyzer. Infrared (IR) spectra were recorded on a Perkin Elmer Spectrum One FT-IR spectrometer with a Universal ATR Sampling Accessory. Melting points were determined on a Büchi melting point B-540 apparatus. Electrospray ionization mass spectrometry (ESI-MS) was carried out on a PE-Sciex API 300 LC/MS/MS System mass spectrometer with a mass range of 3000. Gel permeation chromatography (GPC) was performed with a sampling rate of 2 Hz on a Shimadzu FCV-10AL VP with SCL-10A System Controller, LC-10AD VP Liquid Chromatograph, DGU-14A Degasser, SIL-10A Auto injector, and SPD-10AV UV–Vis Detector. Ureidopyrimidinone functionalization of $PEB(OH)_2$ on 10 dm^3 scale was done in a 10 dm^3 Belatec LRA-10e batch reactor, equipped with a six-bladed 'pitched blade' stirrer, glass reflux cooler, temperature sensor, pressure sensor and a Belatec BLT-9/TK-5 thermostat. Reaction calorimetry was performed with a Mettler Toledo RC1*e* reaction calorimeter equipped with a 2-dm^3 HP60 stainless steel high-pressure reactor with a pitched-blade impeller. Centrifugation was done in two Heraeus Megafuge 1.0 centrifuges containing 4 × 200 ml centrifuge tubes each.



Scheme 1. Synthesis of ureidopyrimidinone functionalized PEB **2**.

2.2. Chemicals

2-amino-4-hydroxy-6-methylpyrimidine, 1,6-hexanediisocyanate and dibutyltindilaurate were obtained from Acros, Fluka, and Aldrich, respectively. Toluene AR was obtained from Biosolve. All chemicals were used without further purification.

2.3. Synthesis of 2(6-isocyanatohexylaminocarbonylamino)-6-methyl-4[1H]pyrimidinone (*1*)

A solution of 2-amino-4-hydroxy-6-methylpyrimidine (111.59 g, 0.892 mol) in 1,6-hexanediisocyanate (1050.0 g, 6.24 mol) and pyridine (70 ml, 0.906 mol) was heated at 100 °C for 16 h under a nitrogen atmosphere. Three hundred millilitres pentane was added and the resulting precipitate was filtered and washed with acetone. The white powder was dried at 50 °C under reduced pressure and stored water free. The excess of 1,6-hexanediisocyanate was recovered by distillation. The product was obtained in a yield of 98.5% (257.81 g, 0.879 mol). Mp. 215 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 13.1 (s, 1H, CH_3-C-NH), 11.9 (s, 1H, $CH_2-NH-(C=O)-NH$), 10.2 (s, 1H, $CH_2-NH-(C=O)-NH$), 5.8 (s, 1H, $CH=C-CH_3$), 3.3 (m, 4H, $NH-(C=O)-NH-CH_2 + CH_2-NCO$), 2.2 (s, 3H, $CH_3-C=CH$), 1.6 (m, 4H, $N-CH_2-CH_2$), 1.4 (m, 4H, $CH_2-CH_2-CH_2-CH_2-CH_2$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.8, 156.3, 154.4, 148.1, 121.6, 106.4, 42.6, 39.5, 30.9, 29.1, 26.0, 25.9, 18.7 ppm. Anal. Calcd for $C_{13}H_{19}N_5O_3$: C, 53.23; H, 6.53; N, 23.88. Found: C, 53.37; H, 6.27; N, 23.77.

2.4. Large scale synthesis of ureidopyrimidinone functionalized PEB **2**

A solution of 800 g (0.228 mol) $PEB(OH)_2$ in 8.4 l toluene was heated to 60 °C in a 10 dm^3 Belatec reactor while stirring at 300 rpm. 134.3 g (0.457 mol) **1** and 1.44 g (2.28 mmol, 1.0 mol%) dibutyltindilaurate were added and the suspension was heated to reflux temperature (113 °C). At regular intervals (starting at 84 min) a sample was taken to determine the conversion with ^1H NMR. For every sample the reaction mixture was cooled to 105 °C and afterwards reheated to reflux temperature. After 2.5 h the reaction mixture was cooled to 105 °C and 28.15 g (96,0 mmol) **1** was added followed by reheating of the reaction mixture to reflux temperature. Again after 5.5 h, the reaction mixture was cooled to 105 °C and 13.4 g (11.3 mmol) **1** was added followed by reheating the reaction mixture to reflux temperature. The reaction was ended after 6.5 h by cooling the reaction mixture to room temperature, after which the reaction vessel was emptied. The reaction mixture was centrifuged for 40 min at 4300 rpm and decanted off. The residue was extracted with toluene and centrifuged for 40 min at 4300 rpm and decanted off. The toluene was evaporated and the product was obtained in yield of 86%.

2.4.1. Ureidopyrimidinone functionalized PEB **2**

^1H NMR (500 MHz, $CDCl_3$): δ 13.1 (s, 2H, CH_3-C-NH), 11.9 (s, 2H, $CH_2-NH-(C=O)-NH$), 10.1 (s, 2H, $CH_2-NH-(C=O)-NH$), 5.8 (s, 2H, $CH=C-CH_3$), 4.9 + 4.6 (s, 2H, $NH-(C=O)-O$), 4.1 (m, 2H, $CH_2-CH_2-O(C=O)-NH$), 3.8 (m, 2H, $C(CH_3)_2-CH_2-O(C=O)NH$), 3.3 (m, 4H, $CH_2-NH-(C=O)-NH$), 3.2 (m, 4H, $CH_2-NH(C=O)-O$), 2.2 (s, 6H, $CH_3-C=CH$), 1.6–1.1 (m, 372H, $CH_2-CH_2-CH_2$), 0.8 (m, 182H, CH_2-CH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 173.36, 157.21, 157.01, 156.80, 154.94, 148.47, 106.93, 73.04, 63.59, 39.31, 39.09, 38.59, 38.09, 36.32, 33.65, 33.45, 30.88, 30.43, 29.98, 29.59, 27.00, 26.82, 26.66, 26.49, 26.34, 26.26, 26.10, 24.44, 19.17, 11.11, 10.87, 10.59 ppm.

2.4.2. $PEB(OH)_2$

^1H NMR (500 MHz, $CDCl_3$): δ 3.7 (m, 2H, CH_2-CH_2OH), 3.3 (s, 2H, $C(CH_3)_2-CH_2OH$), 1.3–1.1 (m, 364H, $CH_2-CH_2-CH_2$), 0.8 (t, 96H, CH_2-CH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 39.10, 38.58, 38.10, 33.66, 33.46, 30.89, 30.44, 29.98, 27.00, 26.83, 26.66, 26.36, 26.27, 26.11, 24.07, 24.2, 11.11, 10.93, 10.88 ppm.

2.5. Hexafluoroacetone solution in chloroform

A 10% solution of hexafluoroacetone (HFA) in chloroform was obtained by adding 18.1 mmol $HFA{\cdot}1.5H_2O$ (Aldrich) drop wise to concentrated (95%) H_2SO_4 of 135 °C in an argon atmosphere. The gas that evolved was bubbled through 10 ml of stirred, ice-cooled $CDCl_3$, which had been pre-dried over active alumina. The solution contained a mixture of free HFA and the water adduct of HFA ($(CF_3)_2CO{\cdot}H_2O$), due the presence of traces of water. ^{19}F NMR (376.5 MHz, $CDCl_3$): δ −75.05 (s, $(CF_3)_2CO$) and δ −82.47 (s, $(CF_3)_2CO{\cdot}H_2O$) ppm.

2.6. ^{19}F NMR on HFA adducts of hydroxy groups

A ^{19}F NMR sample of the HFA adduct of the hydroxy groups of $PEB(OH)_2$ and ureidopyrimidinone functionalized PEB **2** was made by adding 0.9 ml HFA solution in $CDCl_3$ to a solution of 0.020 mmol $PEB(OH)_2$ or 0.050 mmol ureidopyrimidinone functionalized PEB **2** in 1 ml of $CDCl_3$, pre-dried over active alumina. 0.020 mmol 4-*tert*-butylcyclohexanol (Janssen Chimica) was added as internal standard.

2.7. Trimethylsilylized (hydrophobic) petri dishes

Glass petri dishes were cleaned with concentrated H_2SO_4 with 30% H_2O_2, rinsed with demineralized water and dried at 120 °C. A solution of 10 mmol 1,1,1,3,3,3-hexamethyldisilazane and 5 mmol trimethylsilylchoride in 40 ml toluene was added and the petri dishes were left 24 h under a nitrogen atmosphere. The petri dishes were rinsed with successively toluene, acetone and demineralized water, dried and stored in a water free atmosphere.

2.8. Tensile testing

Stress–strain measurements were performed on a Wick Z010 Universal Tensile Tester at an elongation rate of 1 mm/min and a preload of 0.1N. Films of the polymers were obtained by solution casting from toluene in a hydrophobic petri dish. From these films tensile bars were punched with a test section of 18 mm length (between the clamp region) and a cross section of 2.5 mm^2.

3. Results and discussion

3.1. Preparation of the starting materials

For scale-up and optimization it is important to know the quality and composition of the starting materials, because of possible side reactions, by-products and the stoichiometry of the reaction. The starting materials for this reaction are synthon **1**, and the telechelic $PEB(OH)_2$.

Synthon **1** was synthesized on a 250 g scale by coupling of hexamethylenediisocyanate to methylisocytosine, which are both commercially available. Methylisocytosine was mixed with a sevenfold excess of the diisocyanate, which acts as the solvent for the reaction. Pyridine (1 equiv.) was added as a catalyst and to solubilize the isocytosine. The product precipitated from the reaction mixture and was obtained in 98.5% yield as a white powder after filtration.

The excess of hexanediisocyanate was recovered by vacuum distillation.

Telechelic polymer $PEB(OH)_2$ (Scheme 1) is a hydrogenated random copolymer of 1, 2- and 1, 4-polymerized 1, 4-butadiene units with a molecular weight of 3500 g/mol (determined by ^1H NMR and GPC) and a polydispersity (PDI) of 1.17 [7,8]. ^1H, ^{13}C, signals of the end groups were assigned using 2D Heteronuclear correlated (HETCOR) NMR measurements. The two different end groups of $PEB(OH)_2$ give different signals in ^1H NMR; the CH_2 next to the primary alcohol resonates at 3.7 ppm and the CH_2 of the *neo*-alkyl next to the alcohol resonates at 3.3 ppm. From the integration of these signals it was concluded that 8% of the polymers lack the primary alcohol end group, which gives a total hydroxy functionalization of 96% (1.92 mol hydroxy groups per mol $PEB(OH)_2$).

3.2. Optimization experiments

In the original procedure for chain extension of $PEB(OH)_2$ 70 mmol (20.5 g; 2.43 equiv.) of **1** was added to a solution of 15 mmol (52.5 g) $PEB(OH)_2$ in 500 ml of dry chloroform [6]. After addition of two drops of dibutyltindilaurate the resulting solution was stirred at 60 °C for 16 h. The reaction mixture was filtered and purified by column chromatography over silica.

This procedure was taken as the starting point for the optimization of a number of parameters towards the scale-up of the chain extension to 10 dm^3 miniplant scale. Several parameters like the amount of catalyst, work-up procedure and reaction time were selected to be optimized for scale-up.

3.2.1. Type of solvent, reaction time, and reaction temperature

As more environmental friendly alternatives to chloroform, isopropylether, THF, and toluene were tested as solvents at their respective reflux temperatures (Table 1). The conversion was monitored by disappearance of the neo-alkyl alcohol end groups of $PEB(OH)_2$ in the ^1H NMR spectrum. In toluene the reaction was complete after 1.5 h at reflux temperature (110 °C). After the same amount of time the conversion in the other solvents (isopropylether and THF) was very low or no reaction was observed at all, probably due to deactivation of the catalyst by solvent coordination.

Table 1
Reaction times and yields for different solvents

Solvent	Reaction time (h)	Conversion (%)
Chloroform	16	90
Isopropylether	>24	No reaction
THF	>24	<30
Toluene	1.5	>95

3.2.2. Amounts of the starting materials

The concentration of $PEB(OH)_2$ that can be used in the reaction is limited by the viscosity of the reaction mixture at full conversion, due to the formation of the supramolecular polymer **2**. A concentration of 100 g $PEB(OH)_2$/1 dm^3 toluene resulted in a practical reaction mixture.

An excess of synthon **1** is needed for complete functionalization of $PEB(OH)_2$, in order to compensate for losses due to reaction with atmospheric water and subsequent formation of urea **3** (Fig. 2).

Because it is difficult to estimate how much of **3** is formed during the reaction, it was decided to use 2.00 equiv. at the beginning of the reaction and to determine the additional amount of synthon needed to complete the reaction with ^1H NMR after 1.5 h.

3.2.3. The amount of catalyst

The influence of the amount of catalyst was studied using 0.6, 1 and 40 mol% of DBTL in toluene. There was no difference in reaction rate between 1 and 40 mol%; after 1.5 h the conversion was over 95% for both amounts of catalyst. With 0.6% of DBTL, the reaction rate was significantly lower resulting in a reaction time of 4 h before 95% of conversion was obtained.

3.2.4. Work-up procedure

In the initial stage of the reaction, the reaction mixture is a suspension due to the moderate solubility of synthon **1** in toluene. The suspension gradually dissolves, because synthon **1** reacts with $PEB(OH)_2$, but after 30 min the reaction mixture becomes gradually more turbid and more viscous due to gel formation. The gelator is believed to be urea **3** (Fig. 2); it is well known [9] that urea derivatives may aggregate at very low concentrations to form gels. After the reaction centrifugation was used in order to remove this gel. From IR-spectroscopy it was concluded that after centrifugation no synthon **1** with an isocyanate band at $\nu = 2268\ cm^{-1}$ was present anymore. The small amount of catalyst, which remains in the product phase, was not removed.

3.3. Reaction calorimetric measurement (RC1)

A well-known risk in large-scale synthesis is a 'runaway' due to poor heat transfer in a highly exothermic reaction. Therefore a 1 dm^3 reaction calorimetric measurement (RC1) was performed (Fig. 3).

The heat of reaction was calculated to be 72.0 kJ/mol

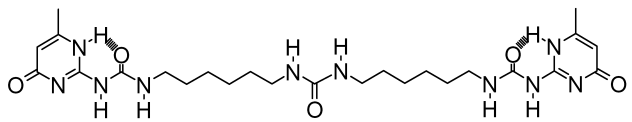


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Fig. 2. Bi-functional ureidopyrimidinone **3**.

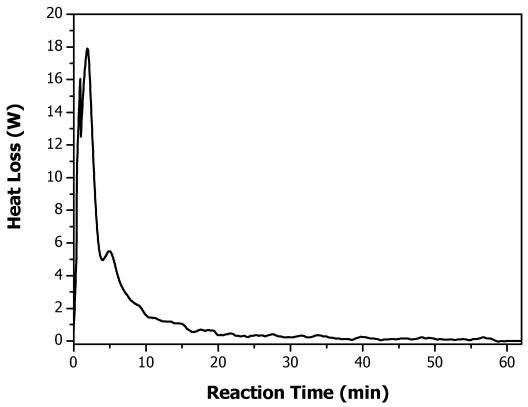

Fig. 3. RC1 heat loss measurement of the synthesis of ureidopyrimidinone functionalized PEB **2**.

OH-groups. This is an average of the two different hydroxy groups of $PEB(OH)_2$. The two peaks in the RC1 heat loss measurement can be explained by the difference in reactivity of the primary and the *neo*-alkyl hydroxy groups of $PEB(OH)_2$, which was also observed with ^1H NMR. Since 0.23 mol $PEB(OH)_2$ is being functionalized in the large scale 10 dm^3 synthesis, the total produced heat of reaction is estimated at 31.5 kJ. As the heat capacity of toluene at 25 °C is 157.3 kJ/mol, the instantaneous adiabatic temperature rise is 2.7 °C. The cooling capacity of the 10 dm^3 reactor is more than sufficient to accommodate this.

3.4. Large-scale synthesis

From the optimization experiments a procedure for large-scale synthesis was developed and subsequently applied.

$PEB(OH)_2$ (0.228 mol, 800 g) was dissolved in 2 l toluene and loaded into the 10 dm^3 reactor, stirred with a six-bladed 'pitched blade stirrer' at 300 rpm. Additionally 6 l of toluene were added and the reaction mixture was heated to 60 °C. Synthon **1** (0.457 mol, 2.0 equiv., 134.3 g) and dibutyltindilaurate, (1.44 g, 1.0 mol%) were added at 60 °C and the reaction mixture was heated at reflux temperature (110 °C) for 1.5 h. After 1.5 h the conversion was determined with ^1H NMR and was found to be lower than expected, 82.0% instead of 95%. After 2.5 h, another 0.47 equiv. of synthon **1** (28.15 g; 96.0 mmol) was added.

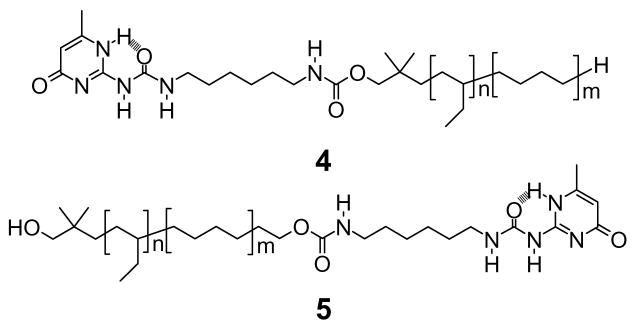

Fig. 4. Mono-functional compounds **4** and **5**, which act as chain-stopper molecules in the product.

After 5.5 h the conversion was 98.8% and the calculated additional amount of synthon **1** (approximately 13.4 g, 0.2 equiv.) needed to drive the reaction to completion was added. Heating was continued for another hour, when the conversion was complete, as judged with ^1H NMR. The mixture was cooled down and the reaction vessel was emptied. For the work-up the reaction mixture was centrifuged for 40 min at 4300 rpm and the clear solution of ureidopyrimidinone functionalized PEB **2** in toluene was decanted off. The remaining gel was extracted with 2 l toluene and centrifuged again. The total yield was 803 g (86%) of product **2**. The remaining material (165 g after drying) contains gelator **3** (37 g) and 128 g of product **2**, which could not be separated from **3** due to gelation.

3.5. Product purity

An important factor in the end-quality of product **2** is the amount of mono-functional chain-stopper in the end product, because this determines the DP of supramolecular polymer **2**. Two chain stopper molecules **4** and **5** (Fig. 4) can be found in the product.

Mono-functional chain stopper **4** is derived from mono-functional PEB(OH) that constitutes 8% of the starting material as determined by ^1H NMR (the conversion to **4** is presumed to be 100%). Chain stopper **5** is present if the conversion of the *neo*-alkyl hydroxy end groups is incomplete.

^1H NMR and ^{13}C NMR do not allow the quantitative determination of very small amounts of **5** in the product, because of severe peak overlap and insufficient sensitivities, respectively. An alternative method for the determination of OH end groups in polymers has been described in literature where hexafluoroacetone (HFA) was used [10,11]. The strength of this method lies in the high sensitivity of ^{19}F NMR, the high ^{19}F chemical shift dispersion, the absence of fluorine in polymer, and the fact that the proton of the hydroxy group is replaced by six fluorine atoms. As an internal standard a mixture of the *cis*

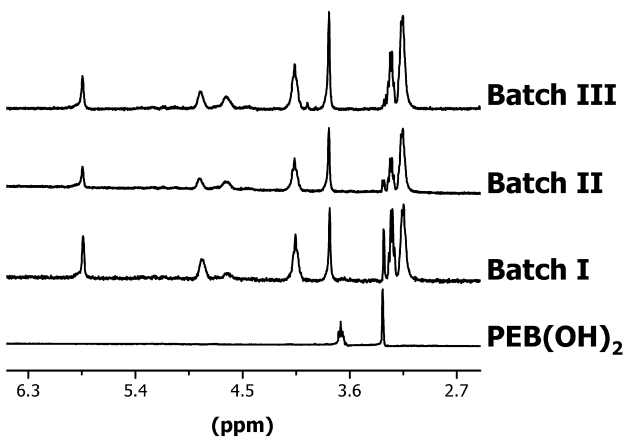

Fig. 5. ^1H NMR spectra (2.5–6.5 ppm) of $PEB(OH)_2$, Batch I–III in $CDCl_3$ at 298 K.

Table 2
Results of ^{19}F NMR analysis on ureidopyrimidinone functionalized PEB **2** synthesized in three different batches

Batch	Fraction *neo*-alkyl OH	Total OH conversion (%)	Total fraction end groups	DP[a]	Virtual Mn (g/mol)
I	0.208	89.2	0.288	7	28,500
II	0.142	92.6	0.222	9	36,750
III	0.004	99.8	0.084	24	98,000

[a] According to Eq. (2).

and *trans*-4-*tert*-butylcyclohexanol (TBCH) was used. TBCH has chemical shifts at −80.68 and −80.78 ppm compared to the HFA-adducts of PEB(OH)$_2$: *neo*-alkyl OH two singlets at −79.59 and −79.62 ppm and primary OH multiple singlets at −79.66 to −79.73 ppm. This method was applied to the 10 dm^3 material (batch III), the product of the RC1 measurements (batch II) and the product earlier obtained by synthesis on lab-scale (batch I) [6]. The materials from batch II and batch I were chosen as comparison, because from the resonance at 3.3 ppm in the ^{1}H NMR spectrum (Fig. 5) it is clear that at least 10% of *neo*-alkyl alcohol groups are still present in both materials.

The fraction unreacted *neo*-alkyl alcohol groups was calculated as follows:

$$x = \frac{I_{\text{(Func.) Kraton}}}{I_{\text{Internal standard}}} \times \frac{m_{\text{Internal standard}}}{m_{\text{(Func.) Kraton}}} \times \frac{\bar{M}_{n\text{(Func.) Kraton unit}}}{M_{\text{Internal standard}}} \quad (1)$$

where x = fraction unreacted *neo*-alkyl hydroxy groups. I = integral of the peaks in ^{19}F NMR, m = weighed in mass, and M molecular weight.

As shown in Table 2 the material from batch III contains 0.4% of unreacted *neo*-alkyl alcohol end groups, while the materials from batch II and I contain, respectively, 14.2 and 20.8%. Taking into account the 8% of stopper **4** present, the material from batch III contains 8.4% of chain-stopper, the batch II material 22.2% and batch I material 28.8%. When the association of the end groups is sufficiently strong, the DP is determined by the amount of chain-stopper and can be calculated as follows [3]:

$$\text{DP} = \frac{2}{\text{fraction chain-stopper}} \quad (2)$$

Therefore the calculated degrees of polymerization of functionalized PEB **2** for batches I, II and III are 7, 9, and 24, respectively.

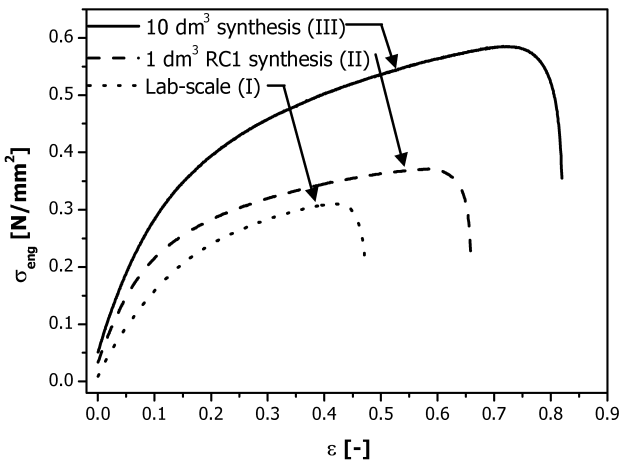

Fig. 6. Stress–strain curves of ureidopyrimidinone functionalized PEB **2** with different hydroxy group functionalization at 1 mm/min.

3.6. Mechanical properties

Tensile tests were performed on material from batches I, II and, III in order to compare the mechanical properties of these three materials with different virtual molecular weights (Table 2). Films of the material from batches I, II, and, III were cast from toluene and yielded transparent and flexible films. For the tensile tests flat tensile bars were punched out of these non-oriented films. The samples were tested at a speed of 1 mm/min and stretched until fracture. The Young's (E)-modulus was determined by the slope of the stress–strain plot (Fig. 6) at small strains. The E-modulus, the Ultimate Tensile Strength (σ_{UTS}) and the strain at break (ϵ_{br}) are given in Table 3.

The results of the tensile tests show that the material from batch III with higher conversion has a higher E-modulus of 3.3 MPa and a σ_{UTS} of 0.57 MPa compared to batches I and II with E-moduli of 2.2 and 2.6 MPa and σ_{UTS} of 0.31 and 0.35, respectively. Thus, the mechanical properties of the material from batch III are improved compared to the material synthesized at smaller scale (batches I and II). This increase of the E-modulus and ultimate tensile strength with the increase of the (virtual) molecular weight has been observed for covalent polymers before by Jérôme [12,13] and described theoretically for covalent polymers by Drozdov [14].

4. Conclusions

A procedure has been developed for the functionalization of PEB(OH)$_2$ with hydrogen-bonding groups after optimization of reaction conditions. The reaction performed on a 10 dm^3 mini plant scale yielded 803 g (86%) of functionalized PEB **2**. The reaction time at the 10 dm^3 (6.5 h) was longer than the planned 1.5 h. Apparently more of the synthon **1** was converted to urea **3**, than in the lab scale experiments.

The ureidopyrimidinone functionalization of the end

Table 3
Results of the tensile tests on bulk samples of batches I–III at 1 mm/min (averages of 7, 7, and 10 tests, respectively)

Batch	DP	Virtual Mn (g/mol)	Young's-modulus E (MPa)	Strain at break ϵ_{br}	Ultimate tensile strength σ_{UTS} (N/mm^2)
I	7	28,500	2.2	0.43	0.31
II	9	36,750	2.6	0.57	0.35
III	24	98,000	3.3	0.75	0.57

product **2** was accurately determined with ^{19}F NMR. The degree of functionalization of the available hydroxy end groups in the material from batch III is high (99.8%) compared to the small scale batches I and II (89.2 and 92.6%, respectively), which results in a high degree of polymerization — DP = 24. In order to increase the DP further a hydroxy terminated polymer is needed, with a higher hydroxy functionalization than PEB(OH)$_2$. From the tensile tests it is clear that the increased virtual molecular weight of the material from batch III compared to the batch I and II materials improve the mechanical properties.

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