Rapid and controlled synthesis of hydrophobic polyethers by monomer activation*

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Abstract: A series of polyethers was prepared by monomer-activated anionic polymerization. The combination of an ammonium salt with triisobutylaluminum allowed the polymerization of epoxides containing various aliphatic side chains (1,2-butene oxide (BO), 1,2-hexene oxide (HO), and 1,2-octadecene oxide (ODO)) or a fluorinated group (3,3,3-trifluoro-1,2-epoxypropane (TFEP)). Polymers of molar masses up to 35 000 g/mol with relatively narrow molar mass distribution could be synthesized. Polymer structures were analyzed by ^{13}C NMR, and the thermal behavior was studied by differential scanning calorimetry (DSC). The evolution of hydrophobicity was investigated according to the length and composition of the side chain. Using a long aliphatic side-chain epoxide (C16) imparted crystallinity to the resulting atactic polymer.

Keywords: hydrophobicity; monomer activation; polyether; poly(alkylene oxide); ring-opening polymerization.

INTRODUCTION

Epoxides and glycidyl ethers represent interesting monomers due to a large diversity of corresponding polyethers which can be potentially obtained. This allows preparation of polymers in which glass transition temperature, hydrophilicity or hydrophobicity, lower critical solubility temperature, and reactivity for post-polymerization can be tuned.

Polymerization mechanisms can be anionic [1–3], cationic [4–6], or coordinative [7–10]. However, their synthesis is often disturbed by the occurrence of side reactions, such as transfer to monomer, and prevents achievement of high-molar-mass polyethers with a good control of the polymerization [11]. These side reactions have mainly limited the study of polyethers synthesis to the polymerization of ethylene oxide and propylene oxide. They are especially used as amphiphilic block copolymers with usually a hydrophilic block of poly(ethylene oxide) (PEO) and a hydrophobic one of poly(propylene oxide) (PPO). This kind of polymer finds applications in surfactant or gelling additives, for example [12]. However, PPO does not display a very strong hydrophobic behavior. Indeed, it is soluble in water at low temperature (~4 °C). To improve this behavior and therefore the difference with the hydrophilic part in copolymers, epoxides containing hydrophobic substituents can be polymerized [13–21]. For aliphatic substituents such as 1,2-butene oxide (BO) or 1,2-hexene oxide (HO), the main results have been obtained using crown ethers [15,22,23]. As the hydrogen in α-position of the epox-

ide function is less reactive with an aliphatic chain than for propylene oxide, polymerization of those epoxides is carried out with fewer side reactions, and higher molar masses can be achieved. A major limitation concerns the rate of polymerization as days are needed. For epoxides containing fluorinated side chains, their main applications are oligomers in fluid for electronics [24]. Synthesis is currently based mainly on anionic polymerization limited to very low molar masses [25,26] or in a copolymer with propylene oxide using a coordinated mechanism [27]. However, with higher molar masses, other applications may be investigated as, for example, surface treatment. Only a recent initiating system based on the combination of phosphonium salt and trialkylaluminum allows the synthesis of fluorinated polyethers with molar masses up to 20 000 g/mol and narrow dispersity ($I_p < 2$) [28,29]. This initiating system is very similar to the one we developed previously for other epoxides. It was based on the association of alkali metal alkoxides [30] or ammonium salts [31–37] with trialkylaluminum and used for the high-speed synthesis of several polyethers with high molar masses. In this paper, we report the use of this system for the polymerization of epoxides bearing various alkyl or fluorinated groups and their characterization in terms of thermal and hydrophobic properties.

EXPERIMENTAL

Materials

Toluene (98 %, J.T. Baker) and hexafluorobenzene (99 %, Aldrich) were purified with polystyryllithium seeds. They were distilled under reduced pressure and then stored in graduated glass tubes under reduced pressure. BO (or 1,2-epoxybutane, 99 %, Aldrich), HO (or 1,2-epoxyhexane, 97 % Aldrich), and 3,3,3-trifluoro-1,2-epoxypropane (TFEP) (Tech, Apollo) were purified over CaH_2, distilled under reduced pressure, and stored for 15 min in a glass flask equipped with poly(tetrafluoroethylene) (PTFE) stopcocks in the presence of i-Bu$_3$Al to remove traces of impurities. They were finally distilled under reduced pressure and stored under reduced pressure at 20 °C in graduated glass tubes until use. ODO (or 1,2-epoxyoctadecane, 90 %, ABCR) was washed three times with dry toluene. Toluene was evaporated under reduced pressure. Tetraoctylammonium bromide (NOct$_4$Br) (98 %, Aldrich) was dissolved in dried toluene and stored in graduated glass tubes fitted with PTFE stopcocks. Triisobutylaluminum (1 mol/L in toluene, Aldrich) was used without further purification.

Procedures

All polymerizations were performed at 20 °C under argon in a glass reactor equipped with a magnetic stirrer and fitted with PTFE stopcocks. As an example, a polymerization reactor was flamed under reduced pressure and cooled prior to introduction of toluene (10 mL) and BO (1 mL, 11.5 mmol) through connected glass tubes. Then, a toluene solution of NOct$_4$Br (0.12 mL, 0.0276 mmol, C = 0.22 mol/L) followed by i-Bu$_3$Al solution in toluene (0.07 mL, C = 1 mol/L) were added via a syringe under argon. Polymerization was allowed to proceed for 5 h at 20 °C and then stopped by addition of ethanol. The yield (100 %) was determined gravimetrically after complete drying of the polymer under reduced pressure at 50 °C. $\overline{Mn}$ size exclusion chromatography (SEC) = 30 200 g/mol, $\overline{D}$ = 1.42. ^{1}H NMR of PBO: –O–CH$_2$(1)–CH(2)[CH$_2$(3)–CH$_3$(4)]: 1, 2, 3.2–3.75 ppm; 3, multiplet 1.4–1.7 ppm; 4, triplet at 0.9 ppm.

Polymerization of HO, following the same procedure, was carried out with HO (1 mL, 8.3 mmol), toluene (7 mL), NOct$_4$Br solution in toluene (0.12 mL, 0.0276 mmol, C = 0.22 mol/L) and i-Bu$_3$Al solution in toluene (0.07 mL, C = 1 mol/L) for 6 h at 20 °C. Yield = 100 %, $\overline{Mn}$ (SEC) = 35 000 g/mol, $\overline{D}$ = 1.25. ^{1}H NMR of PHO: –O–CH$_2$(1)–CH(2)[CH$_2$(3)–CH$_2$(4)–CH$_2$(5)–CH$_3$(6)]: 1, 2, 3.2–3.75 ppm; 3, 4, 5, 1.2–1.6 ppm; 6, triplet at 0.87 ppm.

Polymerization of ODO was carried out with ODO (1 g, 3.7 mmol), toluene (2.4 mL), NOct$_4$Br solution in toluene (0.88 mL, 0.19 mmol, C = 0.22 mol/L), and i-Bu$_3$Al solution in toluene (0.39 mL,

C = 1 mol/L) for 4 h at 20 °C. Yield = 100 %, $\overline{Mn}$ (SEC) = 5 700 g/mol, $\bar{D}$ = 1.13. ^{1}H NMR of poly(octadecene oxide) (PODO): –O–CH$_2$(1)–CH(2)[(CH$_2$)$_{15}$(3)–CH$_3$(4)]: 1, 2, 3.2–3.75 ppm; 3, 1.2–1.6 ppm; 4, triplet at 0.87 ppm. ^{13}C NMR of PODO: –O–CH$_2$(1)–CH(2)[(CH$_2$)$_{15}$(3)–CH$_3$(4)]: 1, doublet at 72 and 73 ppm; 2 triplet at 79.7 ppm; 3, singulet at 29.9 ppm; 4, singulet at 14.1 ppm.

Polymerization of TFEP was carried out with TFEP (1 g, 8.9 mmol), toluene (2.4 mL), NOct$_4$Br solution in toluene (0.31 mL, 0.069 mmol, C = 0.22 mol/L) and *i*-Bu$_3$Al solution in toluene (0.21 mL, C = 1 mol/L) for 2.5 h at 20 °C. Yield = 100 %, $\overline{Mn}$ (SEC) = 11 000 g/mol, $\bar{D}$ = 1.43. ^{1}H NMR of poly(trifluoro-1,2-epoxypropane) (PTFEP): –O–CH$_2$(1)–CH(2)CF$_3$: 1, 2, 3.2–3.75 ppm. ^{13}C NMR of PTFEP: –O–CH$_2$(1)–CH(2)CF$_3$(3): 1, multiplet 70–72 ppm; 2 triplet at 78.7 ppm; 3, quadruplet at 127.8, 124.9, 122.1, 119.4 ppm.

Analysis

Polymer molar masses were determined by size exclusion chromatography (SEC) using tetrahydrofuran (THF) as eluent. Measurements were performed on a PL GPC50 integrated system with RI and UV detectors and three TSK columns: G4000HXL (particles of 5 μm, pore size of 200 Å, and exclusion limit of 400 000 Da), G3000HXL (particles of 5 μm, pore size of 75 Å, and exclusion limit of 60 000 Da), G2000HXL (particles of 5 μm, pore size of 20 Å, and exclusion limit of 10 000 Da) at an elution rate of 1 mL/min. Polystyrenes were used as standards.

^{1}H and ^{13}C (400 MHz) NMR measurements were perfomed on a Brüker Avance 400 spectrometer at room temperature.

Optical images were obtained using an Axioskop 40 Zeiss microscope equipped with a numeric camera (Canon Powershot A640). The spherulite morphology was observed in thin films prepared between microscope coverslips by cooling slowly from the melt state to the ambient temperature.

Calorimetric measurements were carried out using a differential scanning calorimeter (TA Instruments DSC Q100) and were scanned typically twice from –150 to 200 °C at heating and cooling rates of 10 °C/min.

Contact angles with chosen liquids were determined using a Krüss DSA100 (Germany) contact angle measuring system at room temperature. A liquid droplet of 2 μL was placed on the films. A charge-coupled device camera was used to capture images of droplets for the determination of contact angles.

RESULTS AND DISCUSSION

Efficiency of initiating system composed of NOct$_4$Br/*i*-Bu$_3$Al (1/>1) on the polymerization of BO, HO, and ODO (Scheme 1) was first investigated.
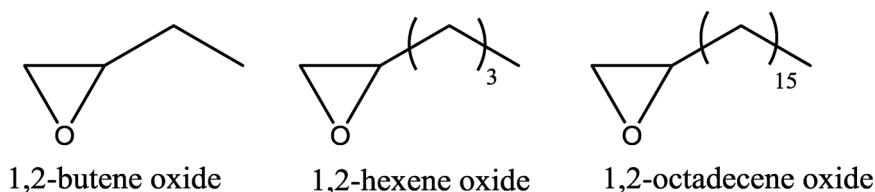
Scheme 1 Structures of the alkylene oxides used.

Syntheses of poly(alkylene oxide)s were carried out in toluene at 20 °C. Poly(butene oxide) (PBO) and poly(hexene oxide) (PHO) with molar masses up to 30 000 g/mol were synthesized in quantitative yield after a few hours (Table 1). It was necessary to increase the proportion of triisobutyl-aluminum from 1.5 to 2.5 in order to achieve such molar masses whilst retaining short polymerization times. At this higher level, some broadening of the dispersity was also observed and attributed to competing transfer to the Lewis acid as described elsewhere [31,35]. ODO could also be polymerized with the same system and in similar conditions. This monomer appears much less reactive than other alkylene oxides as more i-Bu$_3$Al was needed ([Al]/[NOct$_4$Br] = 4) to obtain 13 000 g/mol and non-quantitative yield.

**Table 1** Polymerization of BO, HO, and ODO using NOct$_4$Br/i-Bu$_3$Al (1/>1) (toluene, 20 °C, [M] = 1 mol/L).

Run	Monomer	[i-Bu$_3$Al]/ [NOct$_4$Br]	Time (h)	Conversion[a] (%)	$\overline{Mn}$ th[b] (g/mol)	$\overline{Mn}$ exp[c] (g/mol)	$\bar{D}$[c]
1	BO	1.5	4	100	15 000	13 300	1.19
2	BO	2.5	5	100	30 000	30 200	1.42
3	HO	1.5	15	90	11 000	17 000	1.08
4	HO	2	6	100	10 000	14 000	1.10
5	HO	2.5	6	100	30 000	35 000	1.25
6	ODO	2	4	100	5 000	5 700	1.13
7	ODO	4	22	71	14 000	13 000	1.18

[a]Determined gravimetrically.
[b]$\overline{Mn}$ th = [M]/[NOct$_4$Br] × M$_M$ × conversion.
[c]Determined by SEC in THF using a calibration with PS standards.

A similar initiating system has been used for the polymerization of an epoxide containing a fluorinated substituent, TFEP (Scheme 2).
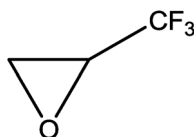
Scheme 2 Structure of the fluorinated epoxide (TFEP) polymerized by NOct$_4$Br/i-Bu$_3$Al.

Synthesis of poly(trifluoro-1,2-epoxypropane) (PTFEP) was successfully achieved in toluene with molar masses up to 11 000 g/mol. Increase of i-Bu$_3$Al amount, up to 3 or 5 equiv as compared to the initiator, was needed to get full conversion in short time (5 h). This amount leads to an increase of dispersity. It can be explained by precipitation phenomenon observed in the medium for an expected molar mass of 14 000 g/mol (run 3). Heterogeneity of the polymerization in toluene, due to precipitation of fluorinated products, leads to a loss of control. A fluorinated solvent was used as it is known to be efficient for such compounds [28]. Some limitation in solubility was still observed with this solvent, but syntheses of polyethers with molar masses up to 18 000 g/mol were successfully achieved with a low dispersity (run 5, Table 2). After 24 h and for a ratio [Al]/[NOct$_4$Br] = 1.5 conversion was not complete.

Table 2 Polymerization results of TFEP using NOct$_4$Br/*i*-Bu$_3$Al (1/>1) initiating system (toluene, 20 °C).

Run	Solvent	[*i*-Bu$_3$Al]/ [NOct$_4$Br]	[M] (mol/L)	Time (h)	Conversion (%)	$\overline{Mn}$ th[a] (g/mol)	$\overline{Mn}$ exp[b] (g/mol)	$\overline{D}$[b]
1	Toluene	1.5	3	24	93	9 300	5 700	1.09
2	Toluene	3	3	2.5	100	10 000	8 700	1.16
3	Toluene	5	3	5	100	14 400	11 000	1.43
4	C$_6$F$_6$	1.5	1.9	26	100	2 000	1 600	1.10
5	C$_6$F$_6$	1.5	3	24	58	17 400	18 000	1.06

[a]Determined gravimetrically.
[b]$\overline{Mn}$ th = [M]/[NOct$_4$Br] × M$_M$ × conversion.
[c]Determined by SEC in THF using a calibration with PS standards.

Regioregularity and stereospecificity were investigated by ^{13}C NMR analysis. The spectrum of poly(octadecene oxide) (PODO) (Fig. 1) shows that the observed methylene and methine signals of the polyether backbone are composed with one signal each in agreement with exclusive head-to-tail (HT) linkage. In addition, the absence of side peaks related to H-H or T-T junctions is indicative of an anionic coordinated-type mechanism involving attack of nucleophilic active species onto the less substituted carbon of the alkylene oxide. Multiplicity of the signal corresponding to the methine of PODO main chain (peak #2) is related to polymer tacticity. The presence of signals corresponding to *mm*, *rr*, and *mr/rm* triads [38] reveals that PODO obtained is atactic.
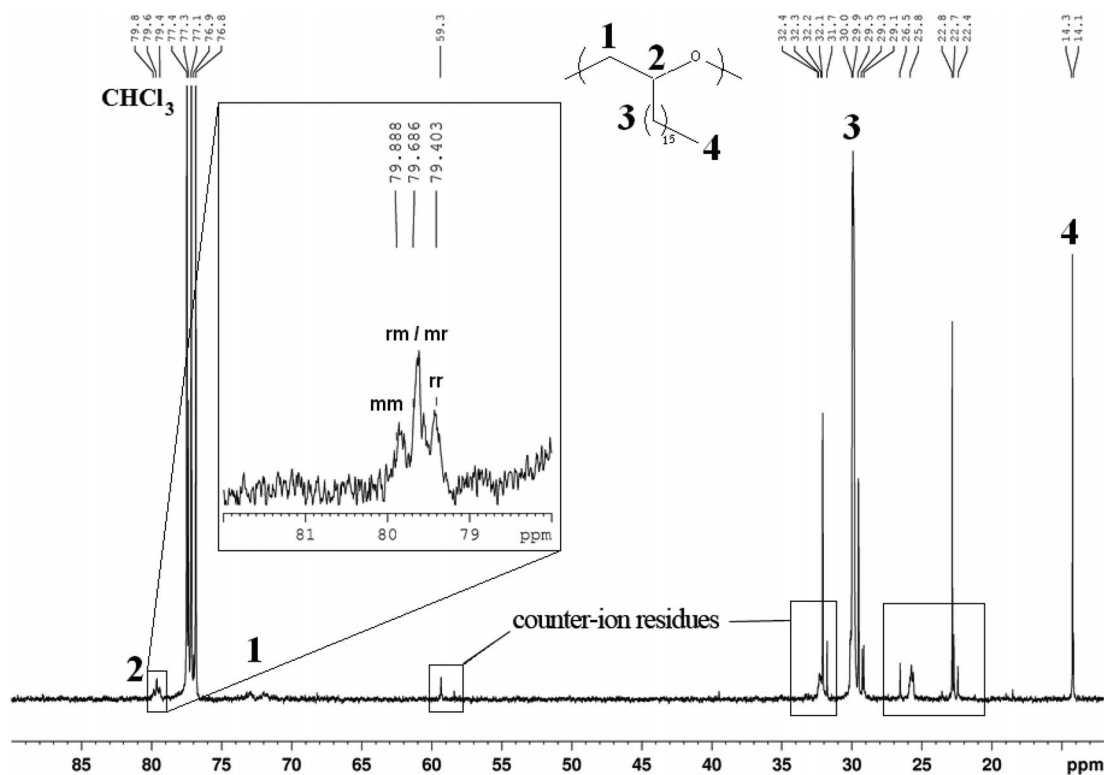
Fig. 1 ^{13}C NMR spectrum of PODO synthesized by NOct$_4$Br/*i*-Bu$_3$Al system (1/2) in toluene ($\overline{Mn}$ = 5 700 g/mol, $\overline{D}$ = 1.13; run 6, Table 1).

A similar analysis was carried out on PTFEP, and similar results were obtained. Signals corresponding to the methylene group of the main chain were divided into isotactic and syndiotactic diads. Four peaks of the methylene carbon in the main chain were assigned to *mm*, *mr* (or *rm*), *rm* (or *mr*), and *rr* triads from lower magnetic field to higher [29], in agreement with formation of an atactic structure.

Thermal characterization of different polyethers with aliphatic side chains was carried out by DSC, Fig. 2.
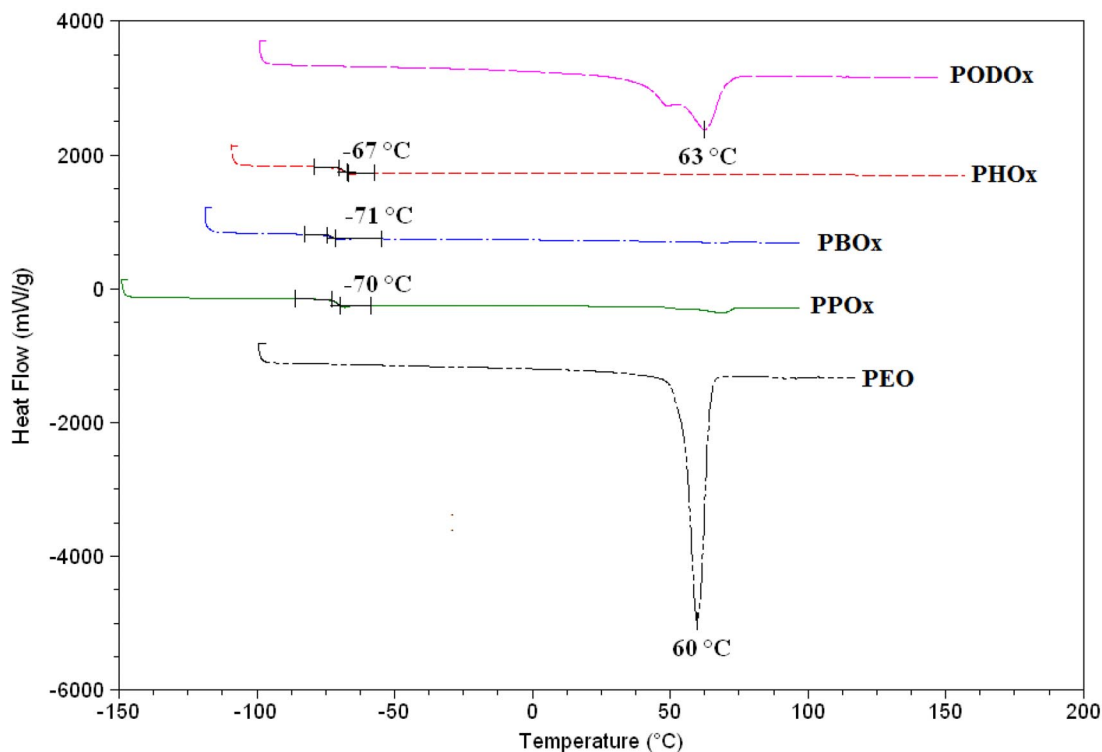

Fig. 2 DSC analysis of PEO ($\overline{Mn}$ = 5000 g/mol, $\overline{D}$ = 1.23), PPO ($\overline{Mn}$ = 10700 g/mol, $\overline{D}$ = 1.17), PBO ($\overline{Mn}$ = 13300 g/mol, $\overline{D}$ = 1.19; run 1, Table 1), PHO ($\overline{Mn}$ = 35000 g/mol, $\overline{D}$ = 1.25; run 5, Table 1), and PODO ($\overline{Mn}$ = 5700 g/mol, $\overline{D}$ = 1.13; run 7, Table 1) synthesized by NOct$_4$Br/*i*-Bu$_3$Al (1/>1) system in toluene.

The glass-transition temperature (T_g) is directed by the presence or not of an aliphatic side chain. Indeed, for PEO, T_g is known to be around –56 °C (not visible here), and it is decreased to –70 °C for PPO. PBO and PHO T_g values are in the same range and not dependent on the length of the side chain. The T_g of PODO was not observed by this technique or by dynamic mechanical analysis carried out between –120 and 30 °C.

PEO and PODO are crystalline polymers with a near melting temperature around 60 °C, where the other polyethers are amorphous. One can assume that aliphatic side chains are long enough to crystallize despite the atactic structure [19]. The crystalline structure of PODO was confirmed by optical microscopy under polarized light where a spherulitic structure was exhibited.

A similar DSC analysis was carried out on the fluorinated polyether PTFEP. T_g was observed at –31 °C and a melting transition around 78 °C. The presence of a fluorinated side chain increases rigidity of the structure and T_g value compared to the hydrogenated one, PPO. A crystallization was observed by optical microscopy with polarized light, Fig. 3. The spherulites observed exhibit both Maltese cross and concentric extinction bands with a periodic distance around 1.5–2 μm. These extinc-

Fig. 3 Optical microscopy image of a PTFEP ($\overline{Mn}$ = 8 700 g/mol, $\overline{D}$ = 1.16, run 2, Table 2).

tion rings indicate a regular axial twisting of lamellar ribbons probably due to the rigidity of the chains given by fluorine atoms.

Hydrophobic behavior of each polyether was investigated by contact angle measurements with appropriate liquids. Polymer films were prepared by spin-coating from THF solutions of polyethers. At first, water contact angle measurement was carried out on those films (Fig. 4).

Fig. 4 Water contact angle measurements of various polyether films.

As expected, the length of the aliphatic side chain has a direct impact on the hydrophobicity of the polymer. PEO is well known to be hydrophilic, whereas PPO is hydrophobic. However, these differences are not highly accentuated, since an aliphatic side chain of at least four carbons is necessary to observe truly hydrophobic surface behavior. It is most prominently displayed by PODO, with a water contact angle at 104°. The Owens–Wendt–Rabel–Kaelble method [39,40] was used to calculate surface

energies (γ) of polyethers (Table 3). The polar component (γ_s^p), for instance, showed a strong decrease down to 0.1 mN·m^{-1} and a surface energy equal to 26.9 mN·m^{-1}. The use of a short-fluorinated side-chain polyether is also shown to strongly increase the hydrophobic character of the polymer. PTFEP displays a water contact angle of 96º and $\gamma = 24.6$ mN·m^{-1}, which is very close to the one calculated for the longest aliphatic side-chain polyether.

Table 3 Static contact angle values and surface energy and its components for various polyethers.

Polymer	Mn (g/mol)	Water	Ethylene glycol	Diiodomethane	γ_s^p	γ_s^d (mN·m^{-1})	γ_s
PEO	5 000	14.3 ± 5.9	45.0 ± 1.6	26.8 ± 2.8	32.3	30.4	62.7
PPO	10 000	42.1 ± 0.7	19.3 ± 1.2	19.2 ± 1.5	19.2	39.8	59.0
PBO	10 000	66.8 ± 1.0	36.3 ± 0.6	27.0 ± 0.9	7.4	41.0	48.4
PHO	35 000	79.0 ± 2.0	47.0 ± 2.9	34.2 ± 1.2	3.4	39.3	42.7
PODO	10 000	104.0 ± 2.7	79.3 ± 0.8	59.7 ± 1.5	0.1	26.8	26.9
PTFEP	18 000	94.8 ± 4.9	70.4 ± 1.6	70.1 ± 8.0	2.4	22.2	24.6

CONCLUSION

Synthesis of various polyethers containing aliphatic side chains of different lengths, up to 16 carbons, or fluorinated side chain, with molar masses up to 35 000 g/mol and narrow molar mass distributions was achieved by anionic ring-opening polymerization and monomer activation. The reaction was conducted in the presence of triisobutylaluminum in hydro- (or fluoro-) carbons in relatively short times. The effect of the length of aliphatic side chain on crystallinity and hydrophobicity was studied and shown to display in particular a high hydrophobicity for a 16-carbon atom side chain. The use of TFEP as monomer led to the synthesis of a crystalline and hydrophobic polymer as well.

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