The Thermo Responsive Behavior of Glycol Functionalized Ring Opening Metathesis Polymers

THOMAS BAUER, CHRISTIAN SLUGOVC

Institute for Chemistry and Technology of Materials (ICTM), Graz University of Technology, Stremayrgasse 16, A-8010 Graz, Austria

Received 6 December 2009; accepted 15 February 2010
DOI: 10.1002/pola.23977
Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Herein a further step towards self-assembly of polymers exhibiting a lower critical solution temperature (LCST) effect is presented. Ring opening metathesis polymerization has been chosen as polymerization method because of its high functional group tolerance, the reliability and the capability to synthesize different polymer architectures such as self-assembling block copolymers, which currently gain much attention in nanotechnology, electronics, and biomedical applications. In a first step, the polymerization behavior of oligo(ethylene glycol) monoalkyl ether [HO—$(CH_2CH_2—O)_n$—R, n = 2, 3 and 5–9, R = *Et* or Me] substituted norbornene derivatives with [(H_2IMes)(py)Cl_2Ru(3-phenyl-indenylid-1-ene)] (H_2IMes = N,*N*-bis(mesityl) 4,5-dihydroimidazol-2-yl, py = pyridine) was assessed. While monomers bearing short oligo(ethylene glycol)monoalkyl ether groups (n = 2 or 3) allowed for controlled polymerization, the monomers featuring long oligo(ethylene glycol) monoalkyl ether groups could not be polymerized in a controlled manner. Only polymers prepared from *endo,exo*-bicyclo [2.2.1]hept-5-ene-2,3-dicarboxylic acid, bis[2-[2-(2-ethoxyethoxy)ethoxy]ethyl] ester (2) showed satisfactory water solubility and a LCST of about 25 °C. This temperature is largely independent from the molecular weight and the macromolecular architecture of the polymers as it was revealed from determination of the LCST of a series of statistic and block copolymers incorporating less-polar comonomers. The molecular weight affects the complete transition value (ΔT), which is rising with increasing degree of polymerization. ΔT values smaller than 1 °C can be obtained with statistic copolymers of 2 with less polar monomers like *endo,exo*-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acid dimethyl ester. © 2010 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 48: 2098–2108, 2010

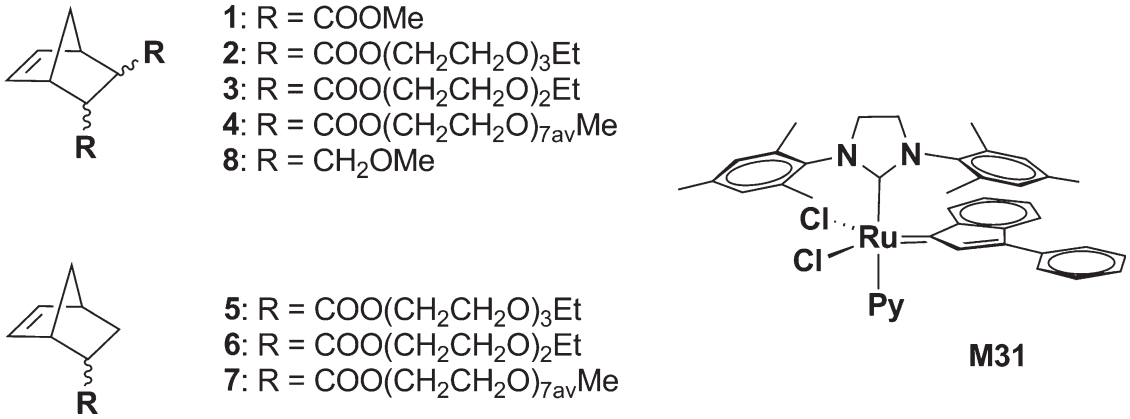
KEYWORDS: block copolymers; lower critical solution temperature; ROMP; self-assembly

INTRODUCTION In the last several years, the demand for new and well defined water soluble polymers has gained more and more interests because of their broad variety of applications in fields like bioseparation, gene- or protein-therapy, diagnostics, implants, sensor applications, or controlled release of bioactive agents.[1–3] Drug release can be achieved by diffusion of simple micelles,[4] by using pH-sensitive micelles,[5,6] or by breaking disulfide cross-links.[7,8] Another promising approach is to make use of phase separation driven by increasing temperature,[9–11] which is a feature of, among other polymers, poly(ethylene oxide) (PEO)[12] and polymers bearing oligo(ethylene oxide) groups in the side chain.[13] The temperature dependent phase separation, which is characterized by the lower critical solution temperature (LCST), is enthalpy-driven. Below the LCST ether-water hydrogen bonds are formed because of the very favorable ΔG^{EX} ($\Delta G^{EX} = G$(solution) − [G(solvent) + G(ideal gas solute)], consistent with the solubility of PEO in water. By increasing the temperature above the LCST the ether-water interactions become unfavorable compared with water-water hydrogen bonding. The entropy augments by the break-up of ether-water hydrogen bonds is more efficient then the enthalpic effects going along with the break-up of the aforementioned bonding.[14,15]

To encapsulate a desired drug in an amphiphilic polymer and to obtain a new and well defined polymers, living polymerization[16] such as atom transfer radical polymerization (ATRP),[17,18] reversible addition fragmentation transfer[19,20] anionic polymerization,[21] cationic polymerization,[22,23] and ring opening metathesis polymerization (ROMP),[24–26] are the methods of choice. Narrow molecular weight distributions and the possibility to make block copolymers[27] paved the way for applications in nanomedicine[28,29] and also in optoelectronic applications and catalysis.[30]

Herein the synthesis and characterization of a series of polynorbornenes bearing different oligoglycol side chains is described with the aim to describe their ability to show a LCST in water. ROMP was chosen as polymerization method. ROMP became a very versatile and powerful tool in the last decade because of its living nature, high functional group tolerance, and narrow distribution of polymer weights.[31]

Correspondence to: C. Slugovc (E-mail: slugovc@tugraz.at)



SCHEME 1 Investigated monomers and the used initiator.

Furthermore, it is already very well studied for obtaining complex polymer structures.[32–37]

RESULTS AND DISCUSSION

Monomer Synthesis

To investigate ROM polymers on their LCST behavior, prerequisites on the one hand in terms of sufficient solubility of the polymers in water and on the other hand in organic solvent, for example, dichloromethane, which is indispensable for the polymerization process, with standard initiators must be fulfilled.[38,39] Oligo(ethylene glycol) esters of norbornenes were anticipated to execute both requirements based on literature reports on ATRP of corresponding acrylate derivatives.[40–44] However, research on ROMP as the polymerization method and using properly functionalized norbornenes is still in its infancy.[45–47]

Disubstituted norbornene derivatives (cf. Scheme 1) were synthesized via esterification of commercially available *endo,exo*-5-norbornene-2,3-dicarbonyl chloride (1 eq) with different types of ethylene glycol monoethyl ethers [tri(ethylene glycol)monoethyl ether, di(ethylene glycol)monoethyl ether, and an oligo(ethylene glycol)monomethyl ether with an average molecular weight of 350 g mol^{-1}, purchased from Sigma Aldrich, CAS Nr. 9004-74-4] (2.2 eq) by nucleophilic catalysis with 4-dimethylaminopyridine and pyridine as the base was prepared according to literature.[48,49] Purification was done by column chromatography, using silica gel as stationary phase. A mixture of cyclohexane and ethyl acetate was used for **2** (ratio = 1:5, R_f = 0.6) and **3** (ratio = 1:2, R_f = 0.5), whereas a dichloromethane/methanol mixture of 30:1 was used for **4** (R_f = 0.2-0.7). The solvent was removed under reduced pressure and the oily product was dried under vacuum. Characterization was done by ^{1}H- and $^{13}C\{^1H\}$-NMR spectroscopy as well as IR-spectroscopy and matrix assisted laser desorption ionisation time of flight mass spectroscopy (MALDI TOF MS) (cf. experimental part). MALDI data for **4** show a mass distribution from 650 to 1000 *m/z* with a maximum at 849.4460. This is in accordance with the calculated product of 14 glycol groups [$C_{33}H_{72}O_{18}$·Na]. Furthermore also the norbornene derivatives with 10 (673 *m/z*), 11 (717 *m/z*), 12 (761 *m/z*), 13 (805 *m/z*), 15 (893 *m/z*), 16 (938 *m/z*) and 17 (982 *m/z*) ethylene glycol units are found.

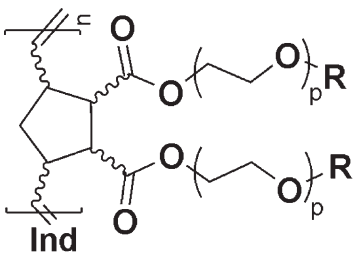
Different kinds of monosubstituted norbornene derivatives (cf. Scheme 1) were synthesized in a two step reaction.[45] First, norbornene acyl chloride was prepared via [4 + 2] cycloaddition.[50] Freshly distilled cyclopentadiene (2 eq) was dissolved in dry CH_2Cl_2. Then acryloyl chloride (1 eq) was added drop wise. After three hours, the desired monomers were synthesized via esterification of the not isolated intermediate with the corresponding ethylene glycol monoether derivatives (1.5 eq). In these cases, triethylamine (2.5 eq) was used as the base. Characterization of the obtained products were again done by ^{1}H- and $^{13}C\{^1H\}$- NMR spectroscopy and IR-spectroscopy (cf. experimental part). In case of **7**, MALDI TOF MS revealed a mass distribution from 439 to 703 *m/z* with a maximum at 571 *m/z*, representing the corresponding monomer with 9 ethylene glycol units.

Polymer Synthesis

Homopolymers

All synthesized glycol functionalized norbornene derivatives (**2–7**) were polymerized via ROMP, using [(H_2IMes)(py)Cl_2Ru(3-phenylindenylid-1-ene)] (H_2IMes = N,*N*-bis(mesityl) 4,5-dihydroimidazol-2-yl, py = pyridine) (**M31**) (cf. Scheme 2) as the initiator.[51] To achieve well-defined polymers with a narrow molecular weight distribution, reaction conditions and monitoring were done according to literature.[38] Polymerizations of **2–7** using a monomer to initiator ratio of 100:1, 200:1, and 300:1 were performed (Scheme 2). The polymerization time necessary for complete conversion, checked by TLC, varied from 2 to 4 h depending on the desired polymer length. The series of **poly4** and **poly7** behaved differently and are discussed below. In some cases, poor or moderate yield were obtained, which is because of product loss during diligent purification of the polymers by repeated precipitation (cf. experimental part).

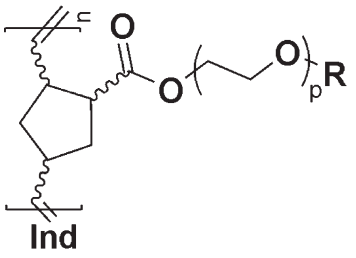
Characterization of the obtained polymers was done by ^{1}H-NMR spectroscopy. Exemplarily, the ^{1}H-NMR spectrum for **poly2-100** is discussed. The broad signal from 5.59 to 5.10 ppm represents the double bond situated in the backbone of



poly2-100: n = 100, p = 3, R = Et
poly2-200: n = 200, p = 3, R = Et
poly2-300: n = 300, p = 3, R = Et

poly3-100: n = 100, p = 2, R = Et
poly3-200: n = 100, p = 2, R = Et
poly3-300: n = 100, p = 2, R = Et

poly4-100: n = 100, p = 7av, R = Me
poly4-200: n = 200, p = 7av, R = Me
poly4-300: n = 300, p = 7av, R = Me



poly5-100: n = 100, p = 3, R = Et
poly5-200: n = 200, p = 3, R = Et
poly5-300: n = 300, p = 3, R = Et

poly6-100: n = 100, p = 2, R = Et
poly6-200: n = 100, p = 2, R = Et
poly6-300: n = 100, p = 2, R = Et

poly7-100: n = 100, p = 7av, R = Me
poly7-200: n = 200, p = 7av, R = Me
poly7-300: n = 300, p = 7av, R = Me

SCHEME 2 Synthesized homopolymers and their labeling.

the polymer. Distinctive cyclopentane signals are located from 3.37 to 2.61 ($cp^{1,2,3,5}$) and from 1.82 to 1.35 (cp^{4}) ppm. The typical signals of the oligoglycol moiety are located from 4.36 to 4.01 ($COOCH_2$), from 3.86 to 3.41 ppm (OCH_2) and between 1.25 and 1.15 (OCH_2CH_3) ppm.

Number molecular weight (M_n) and polydispersity index (PDI) were determined relative to poly(styrene) standards by gel permeation chromatography (GPC) in Tetrahydrofuran (THF). Results are presented in Table 1 and Figure 1. In case of the series of **poly2**, **poly3**, **poly5**, and **poly6** a linear increase of the number molecular weights with decreasing initiator amount was observed. The solid lines in Figure 1 represent the linear fit of the relation of the number average molecular weight and the monomer feed. The nice fit is a strong evidence for controlled living polymerization of these monomers under the employed reaction conditions. It is important to note that PDIs of these polymers are higher than expected for *endo-exo* disubstituted norbornene derivatives.[25,38,52]

The difunctionalized norbornene derivative **4** gave polymers with a number average molecular weight of about 40 kg mol^{-1} independent from the used monomer to initiator ratio. Comparing this value with published results on oligo-ethylene glycol functionalized polymers, with more than 3 repeating units, it became clear, that this is the highest molecular weight ever reported for such polymers.[47] Presumably, polymerization is hampered at a certain degree by the steric conditions imposed by the polymer chain attached to the initiator. This is corroborated by the fact that polymerizations of **4** and **7** did not reach completion, even after prolonged reaction times of 24 h. In case of the series **poly7**, a broadening of the molecular weight distribution was noted. Presumably, back-biting occurred.

Finally, the water solubility of the polymers was investigated. Only **poly2**, **poly4**, and **poly7** exhibited water solubility of about 5–15 g/L. The solubility decreases with increasing polymer length. **Poly2-100** was already dissolved at 20 °C after 30 min, whereas **poly2-300** had to be stirred for 24 h at 20 °C. The other polymers were not water soluble, that is, solubility was less than 0.1 g/L.

As conclusion from the results presented above, **2** is the best suited monomer within the investigated monomers. Polymers prepared from **2** are water soluble and **2** allows the preparation of block copolymers, which is not in the case for monomers **4** and **7**. Consequently, some copolymers, namely statistic and block copolymers of **2** with nonwater soluble monomers, were prepared and results are reported in the forthcoming section.

Copolymers

Two types of statistic polymers were synthesized using two different nonpolar monomers, namely **1** and **8** (Scheme 1). A solution of the initiator (**M31**) was added to a mixture of monomer **2** as the polar part and either **1** or **8** as the nonpolar part. The polymerization was finished typically after 3 h.

Characterization was done by ^{1}H-NMR spectroscopy and GPC measurement. Exemplarily, the ^{1}H-NMR spectrum of **poly8-2stat** is discussed. The broad signal from 5.61 to 5.08 ppm

TABLE 1 GPC Characterization of the Synthesized Homopolymers

Sample	[*M*]:[*I*]	Yield [%]	M_n [g mol^{-1}]	$M_{n\ calc.}$ [g mol^{-1}]	PDI
poly2-100	100:1	34	36,100	50,300	1.2
poly2-200	200:1	61	73,200	106,000	1.3
poly2-300	300:1	50	107,000	159,000	1.4
poly3-100	100:1	86	37,000	41,400	1.1
poly3-200	200:1	81	65,500	82,800	1.2
poly3-300	300:1	58	104,000	124,200	1.3
poly4-100	100:1	70	47,200	85,000	1.3
poly4-200	200:1	53	45,400	170,000	1.3
poly4-300	300:1	51	36,000	255,000	1.3
poly5-100	100:1	83	35,400	29,700	1.1
poly5-200	200:1	78	67,400	59,400	1.2
poly5-300	300:1	84	102,000	89,100	1.3
poly6-100	100:1	75	30,200	25,400	1.2
poly6-200	200:1	81	60,100	50,800	1.2
poly6-300	300:1	73	92,200	76,200	1.3
poly7-100	100:1	59	21,500	47,000	1.3
poly7-200	200:1	65	25,400	94,000	1.6
poly7-300	300:1	60	40,900	141,000	1.5

represents the double bond of the backbone. Distinctive glycol signals are located between 4.35 and 4.00 ($COOCH_2$), 3.41 and 2.82 (CH_2CH_3) and a triplet from 1.26 to 1.13 (OCH_2CH_3) ppm, whereas the typical ether peaks are from 3.41 to 2.82 (CH_2OCH_3) and between 2.81 and 2.46 (OCH_3) ppm. All integrals are in good agreement with the applied monomer ratios. The characteristic cyclopentane peaks are located from 3.41 to 2.82 ($cp^{1,2,3,5}$) and from 2.44 to 1.55 (cp^4) ppm. The ratio of polar to nonpolar repeating units was determined by integration of appropriate signals in the ^{1}H-NMR spectra. In Table 2, the GPC data for **poly1-2stat** and **poly8-2stat** are compiled. In both cases statistical copolymers with narrow molecular weight distributions and similar hydrodynamic volumes were obtained.

Finally, a series of block copolymers were synthesized using monomers **2** (polar), **1** and **8** (nonpolar), and varying the block lengths (Scheme 3). The glycol functionalized norbornene derivative 2 was dissolved in dry CH_2Cl_2 and then the initiator (**M31**) was added. After consumption of the monomer, the nonpolar monomer (either **1** or **8**) was added. After complete polymerization, the reaction was stopped with an excess of ethyl vinyl ether, and the product was purified by precipitation in cold *n*-pentane. Block copolymers were characterized by ^{1}H-NMR spectroscopy, GPC measurements, and dynamic light scattering (DLS). NMR spectra are given in the experimental part. The ratio of polar to nonpolar repeating units in the corresponding polymer segment was determined by integration of appropriate signals in the ^{1}H-NMR spectra. The results are listed in Table 2. GPC data revealed narrow molecular weight distributions, similar to the statistic polymer samples. All block copolymers form aggregates in water as determined by DLS measurements. Aggregate sizes are in the range of 9 to 78 nm and vary with polymer and/or segment length and with the nature of the monomer.

LCST Effect

To characterize the LCST effect, a differential turbidity measurement cell (DTM) (cf. experimental part) was used and the polymers were measured in aqueous solution with a concentration of 5 mg mL^{-1}. Only the polymers derived from 2 exhibited a LCST effect. **Poly4** and **poly7** did not show a LCST effect up to 95 °C. This might be best explained by increased water solubility of those two polymers bearing the longer oligoglycol side-chains attached to the polymer backbone.

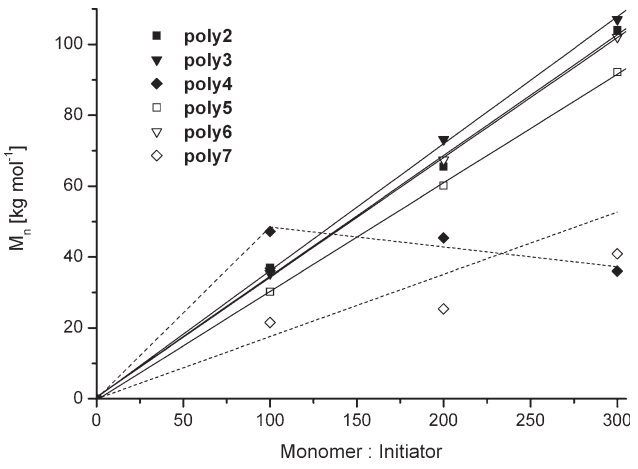


FIGURE 1 M_n and PDI versus monomer to initiator ratio of the synthesized homopolymers.

TABLE 2 Characterization Data for the Copolymers

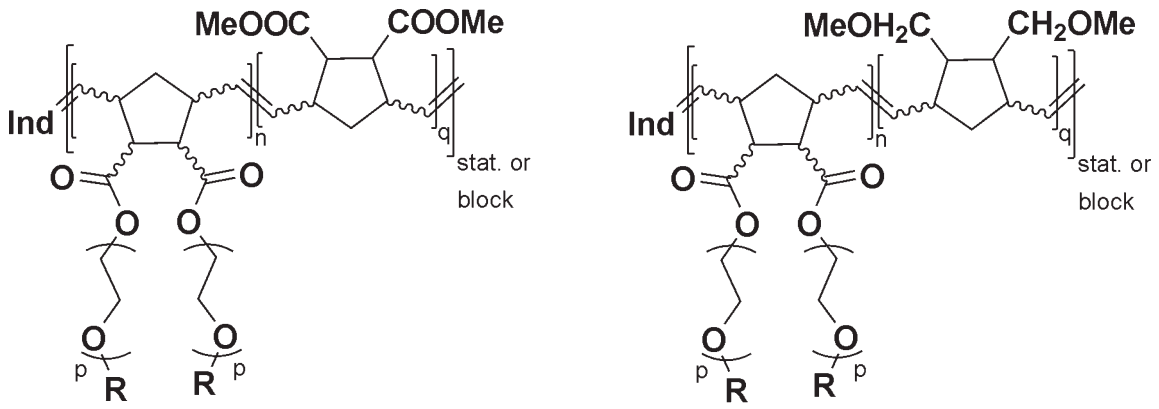
Polymer	Polar:Nonpolar[a]	Polar:Nonpolar[b]	M_n [g mol^{-1}]	$M_{n\ calc.}$ [g mol^{-1}]	PDI	Yield [%]	d [nm] (PDI_{DLS})
poly1-2stat	90:30	2.7:1	36,100	51,500	1.1	55	–
poly8-2stat	85:40	2.0:1	30,000	50,000	1.1	54	–
poly1$_{10}$-2$_{90}$	90:10	2.8:1	32,000	47,300	1.1	62	9 (0.290)
poly1$_{30}$-2$_{90}$	90:30	3.2:1	39,600	51,500	1.1	71	22 (0.080)
poly1$_{60}$-2$_{120}$	120:60	1.6:1	32,100	72,900	1.2	54	38 (0.210)
poly1$_{60}$-2$_{210}$	210:60	2.8:1	50,700	118,000	1.2	65	78 (0.271)
poly2$_{90}$-8$_{30}$	90:30	2.3:1	30,500	50,700	1.1	68	33 (0.111)

[a] Equivalents of the corresponding monomers used in the preparation.
[b] Ratio from integration of the ^{1}H-NMR spectra ± 10%.

Figure 2(a) shows the heating and cooling cycle for **poly2-200**. It is obvious that hysteresis is very small, resulting in a very steady and reversible system. The phase transition occurs at 26.1 ± 0.5 °C. Lowering or increasing the degree of polymerization hardly affects the transition temperature [Fig. 2(b)], but affects the complete transition value (ΔT). ΔT is rising with increasing degree of polymerization (e.g., **poly2-100**: ΔT = 3.0 °C, **poly2-300**: ΔT = 9.0 °C), compare Table 3, entries 1–3. This is in accordance with observations of Schild and Tirrell for poly(*N*-isopropylacrylamide).[53] Although 3 °C is a notable small ΔT value, it can be further improved by copolymerization as revealed by the temperature dependent turbidity measurement of **poly1-2stat** and **poly8-2stat**.

Complete transition is already reached in a temperature range of only 0.7 °C (**poly1-2stat**) or 0.9 °C (**poly8-2stat**), respectively, (cf. Fig. 3 and Table 3, entries 4 and 5). These values can compete with typical ΔT values of modified polyoxazolines[54,55] and are even lower as those described for glycol modified[41] and pyrrolidine containing methacrylates.[56] A similar observation was made with the block copolymers with low-degree of polymerization. ΔT values from 1.3 to 0.5 °C were observed. However, as it was already described for the homopolymer series the ΔT value increases with increasing polymer length (Table 2, entry 8). Remarkably, the LCST is almost the same for all polymers and copolymers, and block copolymer aggregates under investigation, which means that the LCST depends only on the water-oligoglycol interactions and not influenced by incorporation of a less polar comonomer. This is in accordance with the study of Smith and Bedrov[14] on the LCST of poly(ethylene oxide) in water with studies of the LCST of poly(*N*-isopropylacrylamide) by Chung et al.[57]

In case of **poly1$_{10}$-2$_{90}$** and **poly2$_{90}$-8$_{30}$**, the LCST was not only studied by transmission measurements but also with temperature dependent DLS. LCST and ΔT are concurring in both measurements. Additionally, DLS gives an impression of the aggregation of the small polymer aggregates (9 and 33



poly1-2stat: n = 90, q = 30

block copolymers:
poly1$_{10}$-2$_{90}$: n = 90, q = 10
poly1$_{30}$-2$_{90}$: n = 90, q = 30
poly1$_{60}$-2$_{120}$: n = 120, q = 60
poly1$_{60}$-2$_{210}$: n = 210, q = 60

poly8-2stat: n = 85, q = 40

block copolymers:
poly2$_{90}$-8$_{30}$: n = 90, q = 30

SCHEME 3 Synthesized statistic and block copolymers.

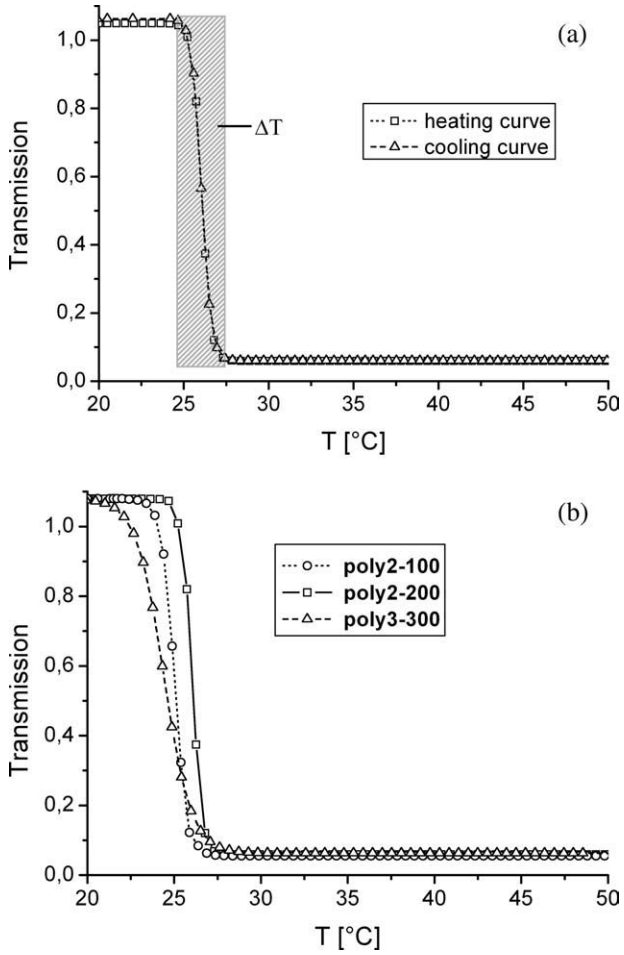


FIGURE 2 (a) DTM of **poly2-200** dotted line represents the heating run; dashed line represents the cooling run and (b) DTM of **poly2** with different degrees of polymerization.

nm, respectively) above the LCST to objects of about 3–5 μm in diameter (cf. Figs. 4 and 5).

CONCLUSIONS

Evaluation of a series of mono- and disubstituted norbornene derivatives bearing oligo(ethylene glycol)monoalkyl ether groups revealed *endo,exo*-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acid, bis[2-[2-(2-ethoxyethoxy)ethoxy]ethyl] ester (**2**) as the preferred monomer for the preparation of water soluble, temperature responsive polymers with ROMP. Polymers of **2** can be prepared in a controlled manner and combine satisfactory water solubility with the occurrence of a LCST. The LCST of these polymers is about 25 °C and is largely independent from the corresponding degree of polymerization. The molecular weight affects the complete transition value (ΔT), which is rising with increasing degree of polymerization. ΔT values smaller than 1 °C can be obtained with statistic copolymers of **2** with less polar monomers like *endo,exo*-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acid dimethyl ester (**1**). Amphiphilic block copolymers of **2** and **1** (or **8**) formed nanoscale aggregates in water, which show a very similar LCST as the homopolymers of **2**. All findings suggest that ROM polymers made of **2** provide a sharp LCST at about 25 °C, which is hardly affected by incorporation of other monomers. These features show great promise for envisaged applications of thermo-responsive polymers. Currently, the possibility to tune the LCST to higher temperatures and particularly to 37 °C is under investigation in our laboratories.

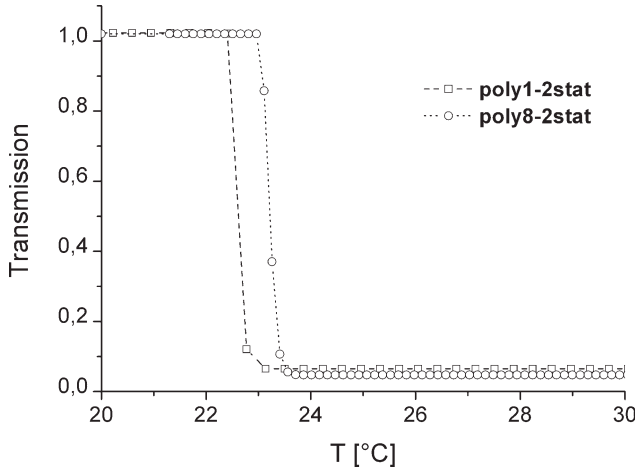


FIGURE 3 DTM of **poly1-2stat** and **poly8-2stat**.

TABLE 3 LCST of the Polymers

Entry	Polymer	Polar:Nonpolar	LCST [°C ± 0.5]	ΔT [°C]
1	**poly2-100**	–	25.3	3.0
2	**poly2-200**	–	26.1	3.4
3	**poly2-300**	–	24.2	9.0
4	**poly1-2stat**	90:30	23.1	0.7
5	**poly8-2stat**	85:40	23.7	0.9
6	**poly1$_{10}$-2$_{90}$**	90:10	23.7	0.9
7	**poly1$_{30}$-2$_{90}$**	90:30	22.4	1.3
8	**poly1$_{60}$-2$_{210}$**	210:60	24.1	5.6
9	**poly2$_{90}$-8$_{30}$**	90:30	23.5	0.5

The LCST was determined by the loss of 50% of the complete transmission.

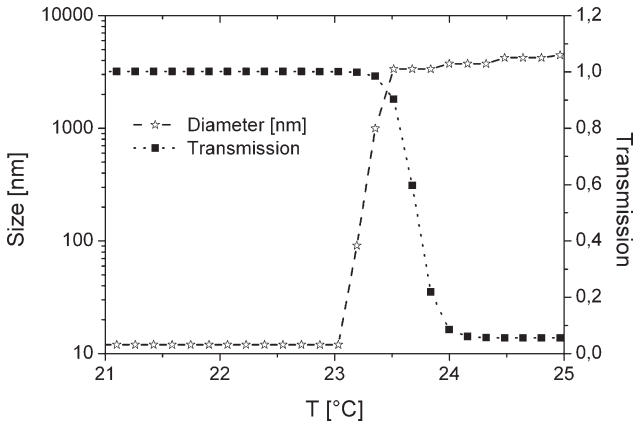


FIGURE 4 Transmission and average size distribution by volume of **poly1$_{10}$-2$_{90}$**.

EXPERIMENTAL

Methods

If not otherwise explicitly mentioned, then all reactions were carried out under inert atmosphere (Ar) using standard Schlenk techniques. Solvents were purified, dried, and degassed according to standard literature.[58] Furthermore all chemicals, if not noted otherwise, were obtained from commercial sources (Aldrich, Fluka or Lanchester) and used without further purification. *Endo,exo*-Bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acid dimethyl ester (**1**) was provided by Orgentis Chemicals GmbH and further purified by distillation.[59] *Endo,exo*-Bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acid dimethyl ester (**8**) was prepared according to literature.[60,61] The pyridine initiator $RuCl_2$(pyridine)(H_2IMes)(Ind) (**M31**) was prepared according to literature.[51] NMR spectroscopy was performed on a VARIAN INOVA 500 MHz spectrometer. ^{1}H spectra were recorded at 499.764 MHz, whereas ^{13}C{^{1}H} spectra were recorded at 125.665 MHz. Deuterated solvents were obtained from Cambridge Isotope Laboratories, and the remaining peaks were referenced according to literature.[62] Peak shapes are indicated as follows: s (singlet), d (doublet), dd (doublet of doublets), t (triplet), q (quadruplet), m (multiplet), b (broad), and bs (broad singlet). The relaxation time of the polymer ^{1}H-NMR spectra was set to 5s to guarantee complete relaxation. FT-IR spectra were recorded with a Perkin-Elmer Spectrum One and a DTGS-detector. Samples were measured on NaCl-plates (diameter 20 mm, width 2 mm) as thin films. Intensities at different wave numbers (cm^{-1}) were characterized as w (weak), m (medium), and s (strong). GPC measurements for obtaining both number average M_n and PDI were performed in THF using following settings: Merck Hitachi L6000 pump, separation columns of polymer standards service, 8 × 300 mm STV 5 μm grad size (10^6 Å, 10^4 Å, and 10^3 Å), refractive index detector from Wyatt Technology, and model Optolab DSP interferometric refractometer. Calibration was done with polystyrene standards purchased from polymer standard services. Particle sizes were determined with a Malven Instruments ZetaSizer NanoZS provided with a 633 nm laser. If not otherwise mentioned, then the polymers were measured against a polystyrene latex standard at 20 °C, sample concentration was 5 mg mL^{-1} and equilibration time was 24 h. Identification of the cloud point was done with a DTM cell (cf. Fig. 6).

In a heat- and cool able copper pipe a test tube with an aqueous polymer solution was placed. Two drill holes in an arrangement of 180° were made next to the bottom. In the first one, a light source (white light emitting diode, 3.6 V, 20 mA, 1000 mcd) and in the second one a photo diode (BPW 34, 500-10,000 nm, 0.62 AW^{-1}) for sensing the differential transmission was placed. On the shell of the copper pipe, a heating element (heating cable 50W, using a PTFE isolation, Horst GmbH, Lorsch, Germany), for linear heating, was placed, using a KS 40 controller (Prozeß- und Maschinen-Automation GmbH, Kassel, Germany). Furthermore, the temperatures down to 14 °C were achieved by cooling coils, which is placed on the outside of the copper pipe. The typical heating up- and cooling down curve is shown in Figure 6.

Monomer Synthesis

Endo,Exo-*Bicyclo[2.2.1]Hept-5-Ene-2,3-Dicarboxylic Acid, Bis[2-[2-(2-Ethoxyethoxy)Ethoxy]Ethyl] Ester (2)*

Monomer **2** was prepared according to literature.[25] The crude product was purified by column chromatography (silica; Cy:EE = 1:5). Yield: 9020 mg (80%) colorless oil.

IR and NMR data were in accordance with the reference. MALDI MS (m/z): [C25H42O$_{10}$·Na] 525.2657 (calcd 525.2676).

Endo,Exo-*Bicyclo[2.2.1]Hept-5-Ene-2,3-Dicarboxylic Acid, Bis[2-(2-Ethoxyethoxy)Ethyl] Ester (3)*

Compound **3** was prepared according to **2**, using *endo,exo*-5-norbornene-2,3-dicarbonyl chloride (0.75 mL, 4.56 mmol, 1 eq), di(ethylene glycol)monoethyl ether (1.37 mL, 10.0 mmol, 2.2 eq), 4-dimethylaminopyridine (DMAP; 0.0278 g, 0.23 mmol, 0.05 eq), and pyridine (0.93 mL, 11.4 mmol, 2.5 eq) in 10 mL dry CH_2Cl_2 as starting materials. Purification

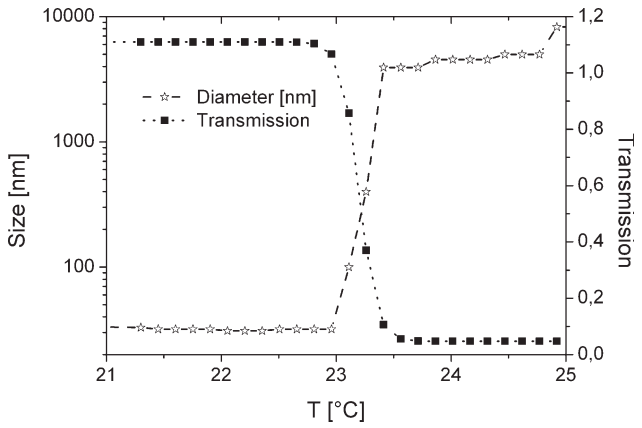


FIGURE 5 Transmission and average size distribution by volume of **poly2$_{90}$-8$_{30}$**.

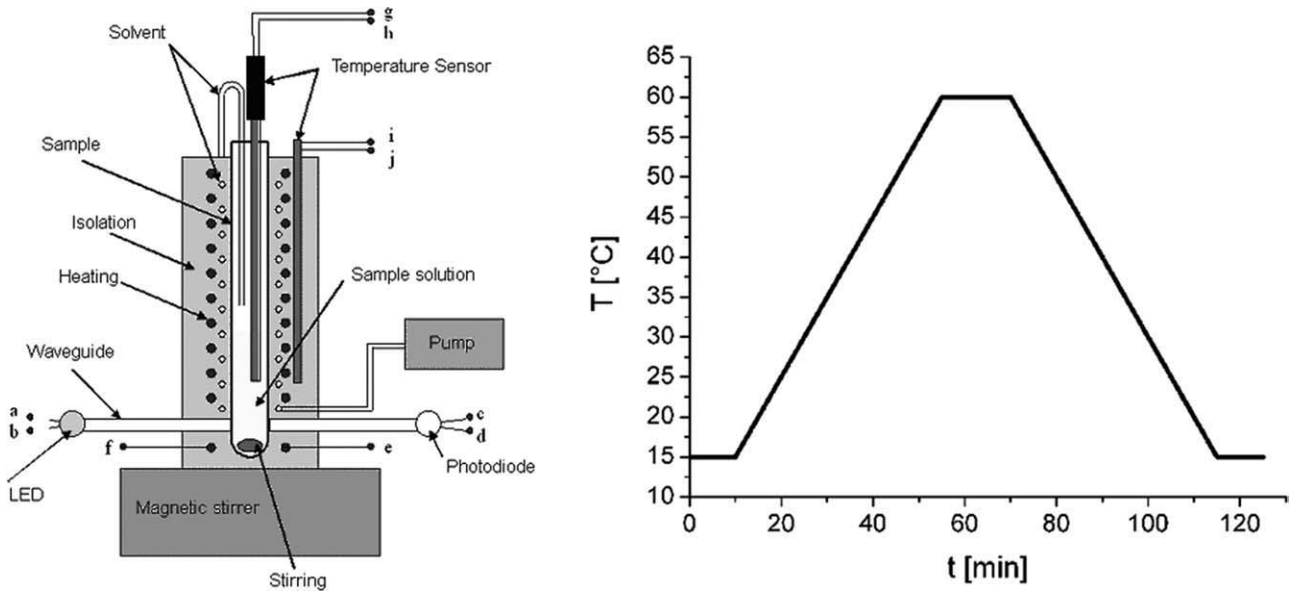


FIGURE 6 Schematic assembly and temperature program of the DTM cell.

was done by column chromatography (silica, Cy:EE = 1:2). Yield: 1360 mg (72%) colorless oil.

^{1}H-NMR (δ, 20 °C, $CDCl_3$, 500 MHz): 6.26 (m, 1H, nb^5), 6.08 (m, 1H, nb^6), 4.33–4.10 (m, 4H, $COOCH_2$), 3.71–3.56 (m, 16H, OCH_2), 3.53 (q, 4H, CH_2CH_3), 3.43 (t, 1H, nb^3), 3.28 (bs, 1H, nb^4), 3.14 (bs, 1H, nb^1), 2.73 (dd, 1H, nb^2), 1.61, 1.44 (2x d, 2H, nb^{7a,b}), 1.21 (t, 6H, CH_3). ^{13}C-NMR (δ, 20°C, $CDCl_3$, 125 MHz): 174.3, 173.2 (2C, C=O), 137.5 (1C, nb^5), 135.1 (1C, nb^6), 70.6, 69.8, 69.1 (6C, OCH_2), 66.7 (2C, CH_2CH_3), 63.9, 63.6 (2C, $COOCH_2$), 47.9 (1C, nb^3), 47.7 (1C, nb^1), 47.2 (1C, nb^7), 47.1 (1C, nb^2), 45.8 (1C, nb^4), 15.1 (2C, CH_3). MALDI MS (m/z): [C21H34O$_8$·Na] 437.2181 (calcd 437.2151).

Endo,Exo-*Bicyclo[2.2.1]Hept-5-Ene-2,3-Dicarboxylic Acid, Bis[Oligo(Ethylenglycol)Methyl] Ester (4)*

Compound **4** was prepared analogously to **3**, using *endo,exo*-5-norbornene-2,3-dicarbonyl chloride (0.75 mL, 4.56 mmol, 1 eq), oligo(ethylene glycol)monomethyl ether (3.18 mL, 10.0 mmol, 2.2 eq, av. 350 g mol^{-1}, purchased from Sigma Aldrich, CAS Nr. 9004-74-4), 4-dimethylaminopyridine (DMAP; 0.0285 g, 0.23 mmol, 0.05 eq), and pyridine (0.93 mL, 11.4 mmol, 2.5 eq) as starting materials. The reaction was monitored by TLC (CH_2Cl_2:MeOH = 30:1; detection: UV/VIS, 2% $KMnO_4$ solution, R_f value: 0.2–0.7). Purification was done by column chromatography (CH_2Cl_2:MeOH = 30:1) sampling R_f: 0.2–0.7. Yield: 2360 mg (61%) colorless oil.

^{1}H-NMR (δ, 20 °C, $CDCl_3$, 500 MHz): 6.27 (m, 1H, nb^5), 6.07 (m, 1H, nb^6), 4.25–4.11 (m, 4H, $COOCH_2$), 3.72–3.61 (m, 52H, OCH_2), 3.54 (m, 4H, CH_2OCH_3), 3.42 (t, 1H, nb^3), 3.37 (q, 6H, OCH_3), 3.28 (bs, 1H, nb^4), 3.14 (bs, 1H, nb^1), 2.72 (dd, 1H, nb^2), 1.60, 1.43 (2x d, 2H, nb^{7a,b}). ^{13}C-NMR (δ, 20°C, $CDCl_3$, 125 MHz): 174.3, 173.1 (2C, C=O), 137.6 (1C, nb^5), 135.1 (1C, nb^6), 71.9, 70.6–70.5, 69.1 (28C, CH_2), 63.9, 63.6 (2C, $COOCH_2$), 59.0 (2C, OCH_3), 47.9 (1C, nb^3), 47.7 (1C, nb^1), 47.2 (1C, nb^7), 47.1 (1C, nb^2), 45.8 (1C, nb^4). MALDI MS (m/z): maximum: [$C_{33}H_{72}O_{18}$·Na] 849.4446 (calcd 849.4460).

Bicyclo[2.2.1]Hept-5-Ene-2-Carboxylic Acid, [2-[2-(2-Ethoxyethoxy)Ethoxy]Ethyl] Ester (Mixture of the Endo- *and* Exo-*Form) (5)*

Modifying a procedure by Carlise et al.,[45] cyclopentadiene (1.25 mL, 15.1 mmol, 2 eq) was diluted with 15 mL dry CH_2Cl_2. Then, acryloyl chloride (0.62 mL, 7.56 mmol, 1 eq) was added dropwise. The clear reaction mixture was stirred for 3 h at room temperature. Afterwards, tri(ethylene glycol) monoethyl ether (1.6 mL, 9.08 mmol, 1.2 eq) was added. Then, the reaction mixture was cooled with an ice bath and triethylamine (2.7 mL, 19.4 mmol, 2.5 eq) was added dropwise. After 30 min of stirring, the ice bath was removed and the reaction mixture was stirred for further 18 h at room temperature. The reaction was monitored by TLC (Cy:EE = 1:2; detection: UV/VIS, 2% $KMnO_4$ solution, R_f: 0.5). The reaction was quenched with 15 mL H_2O and stirred for additional 30 min. The organic layer was extracted with a saturated $NaHCO_3$ solution (4 × 250 mL) and with 2% HCl (4 × 200 mL). The organic layer was dried over Na_2SO_4 and the solvent was removed under reduced pressure. Purification was done by column chromatography (silica gel, Cy/EE = 1:2). Yield: 1400 mg (62%) colorless oil. It is a mixture of 27% *exo*- and 73% *endo*-derivative.

^{1}H-NMR (δ, 20 °C, $CDCl_3$, 500 MHz): 6.18 (m, 1H, nb^5), 5.93 (m, 1H, nb^6), 4.23–4.15 (m, 2H, $COOCH_2$), 3.71–3.56 (m, 10H, OCH_2), 3.52 (q, 2H, OCH_2CH_3), 3.22 (bs, 1H, nb^1), 2.97 (m, 1H, nb^2), 2.90 (bs, 1H, nb^4), 1.89 (m, 1H, nb^{3a}), 1.41, 1.26 (2x d, 3H, nb^{7a,7b,3b}), 1.20 (t, 3H, CH_3). ^{13}C-NMR (δ, 20°C, $CDCl_3$, 125 MHz): 174.7 (1C, C=O), 137.7 (1C, nb^5), 132.3 (1C, nb^6), 70.6, 69.8, 69.2 (3C, OCH_2), 66.6 (1C, CH_2CH_3), 63.3(1C, $COOCH_2$), 49.6 (1C, nb^7), 45.7 (1C, nb^1), 43.2 (1C, nb^2), 42.5 (1C, nb^4), 29.2 (1C, nb^3), 15.1 (1C, CH_3). MALDI MS (m/z): [C16H26O$_5$·Na] 321.1692 (calcd 321.1678).

Bicyclo[2.2.1]Hept-5-Ene-2-Carboxylic Acid, [2-(2-Ethoxyethoxy)Ethyl] Ester (Mixture of the Endo- *and* Exo-*Form) (6)*

Compound **6** was prepared according to **5**, using cyclopentadien (1.25 mL, 15.1 mmol, 2 eq), acryloyl chloride (0.62 mL, 7.56 mmol, 1 eq), di(ethylene glycol)monoethyl ether (1.25 mL, 9.19 mmol, 1.2 eq) and triethylamine (2.7 mL, 19.4 mmol, 2.5 eq) as reactants. Purification was done by column chromatography (silica gel, Cy/EE = 2:1). Yield: 1150 mg (60%) colorless oil. It is a mixture of 23% *exo*- and 77% *endo*-derivative.

^{1}H-NMR (δ, 20 °C, $CDCl_3$, 500 MHz): 6.17 (m, 1H, nb^5), 5.93 (m, 1H, nb^6), 4.25–4.17 (2H, $COOCH_2$), 3.70–3.56 (m, 6H, OCH_2), 3.52 (m, 2H, OCH_2H_3), 3.21 (bs, 1H, nb^1), 2.96 (m, 1H, nb^2), 2.89 (bs, 1H, nb^4), 1.89 (m, 1H, nb^{3a}), 1.41, 1.26 (2x d, 3H, $nb^{7a,7b,3b}$), 1.20 (t, 3H, CH_3). ^{13}C-NMR (δ, 20°C, $CDCl_3$, 125 MHz): 174.7 (1C, C=O), 137.7 (1C, nb^5), 132.3 (1C, nb^6), 70.6, 69.8, 69.2, 66.6, 63.3 (5C, CH_2), 49.6 (1C, nb^7), 45.7 (1C, nb^1), 43.2 (1C, nb^2), 42.5 (4C, nb^4), 29.2 (1C, nb^3), 15.1 (2C, CH_3). MALDI MS (*m*/*z*): [C14H22O$_4$·Na] 277.1432 (calcd 277.1416).

Bicyclo[2.2.1]Hept-5-Ene-2-Carboxylic Acid, [(Oligoglycol)Ethyl] Ester (Mixture of the Endo- *and* Exo-*Form) (7)*

7 was prepared analogously to **5**, using cyclopentadien (1.25 mL, 15.1 mmol, 2 eq), acryloyl chloride (0.62 mL, 7.56 mmol, 1 eq), oligo(ethylene glycol)monomethyl ether (2.9 mL, 9.17 mmol, 1.2 eq, av. 350 g mol^{-1}, purchased from Sigma Aldrich, CAS Nr. 9004-74-4) and triethylamine (2.7 mL, 19.4 mmol, 2.5 eq) as educts. Purification was done by column chromatography (silica gel, CH_2Cl_2/MeOH = 30:1). Yield: 163 mg (56%) colorless oil. It is a mixture of 19% *exo*- and 81% *endo*-derivatives.

^{1}H-NMR (δ, 20 °C, $CDCl_3$, 500 MHz): 6.18 (m, 1H, nb^5), 5.93 (m, 1H, nb^6), 4.27–4.08 (2H, $COOCH_2$), 3.73–3.59 (m, 26H, OCH_2), 3.54 (m, 2H, CH_2OCH_3), 3.37 (s, 3H, CH_3), 3.21 (bs, 1H, nb^1), 2.97 (m, 1H, nb^2), 2.90 (bs, 1H, nb^4), 1.90 (m, 1H, nb^{3a}), 1.44-1.22 (m, 3H, $nb^{7a,7b,3b}$). ^{13}C-NMR (δ, 20°C, $CDCl_3$, 125 MHz): 174.7 (1C, C=O), 137.7 (1C, nb^5), 132.4 (1C, nb^6), 71.8, (1C,$COOCH_2$), 70.7–70.4, 69.2, 63.3, 60.4 (12C, CH_2), 59.0 (1C, CH_3), 49.6 (1C, nb^7), 45.7 (1C, nb^1), 43.2 (1C, nb^2), 42.5 (4C, nb^4), 29.2 (1C, nb^3). MALDI MS (*m*/*z*): maximum: [C23H40O$_9$·Na] 483.2570 (calcd 483.550).

Preparation of Homopolymers

Monomers **2–7** were polymerized by using **M31** as initiator and varying the ratio of monomer to initiator from 1:100 to 1:300. Exemplarily, the polymerization procedure with monomer 2 is given.

To a solution of **2** (220.0 mg, 0.44 mmol, 100 eq) in dry CH_2Cl_2 (5 mL), a solution of the initiator **M31** (3.13 mg, 0.0043 mmol, 1 eq) in dry CH_2Cl_2 (1 mL) was added. After consumption of the monomer, monitored by TLC (Cy:EE = 1:5; detection: UV/VIS, 2% $KMnO_4$ solution, R_f: 0.0), the reaction was terminated with ethylvinyl ether (100 μL, excess) and stirred for 15 min at room temperature. The polymer was purified by repeated precipitation of CH_2Cl_2 solutions (1 mL) of the polymer into cold *n*-pentane (80 mL). Yield: 150 mg (81%) brownish, gluey solid.

Spectral characterizations for the synthesized homopolymers of monomer to initiator ratios of 100 to 1 are given; data for 200 and 300 monomer units were identical. IR spectra only vary in their intensities.

Poly2-100: ^{1}H-NMR: (δ, 20 °C, $CDCl_3$, 500 MHz): 5.59–5.10 (bt, 2H, CH=CH), 4.36–4.01 (m, 4H, $COOCH_2$), 3.86–3.41 (m, 20H, OCH_2), 3.37-2.61 (m, 4H, CH_2CH_3, 4H, $cp^{1,2,3,5}$), 1.82–1.35 (m, 2H, cp^4) 1.25–1.15 (m, 6H, OCH_2CH_3). FT-IR (film on CaF_2, cm^{-1}): 2921–2864 (m), 1732 (s, $\nu_{C=O}$), 1645 (m), 1465 (w), 1362 (w), 1352 (w), 1264 (w), 1177 (w), 1099 (s).

Poly3-100: ^{1}H-NMR: (δ, 20 °C, $CDCl_3$, 500 MHz): 5.60–5.12 (bt, 2H, CH=CH), 4.37–4.02 (m, 4H, $COOCH_2$), 3.72–3.45 (m, 12H, OCH_2), 3.33–2.63 (m, 4H, CH_2CH_3, 4H, $cp^{1,2,3,5}$), 1.77–1.30 (m, 2H, cp^4) 1.26–1.09 (m, 6H, OCH_2CH_3).

Poly4-100: ^{1}H-NMR: (δ, 20 °C, $CDCl_3$, 500 MHz): 5.62–5.09 (m, 2H, CH=CH), 4.38–3.99 (m, 4H, $COOCH_2$), 3.85–3.44, (m, 52H, OCH_2) 3.45–2.83 (m, 6H, CH_3, 4H, $cp^{1,2,3,5}$), 2.33–1.13 (m, 2H, cp^4).

Poly5-100: ^{1}H-NMR: (δ, 20 °C, $CDCl_3$, 500 MHz): 5.60–5.12 (bt, 2H, CH=CH), 4.37–4.02 (m, 2H, $COOCH_2$), 3.72–3.45 (m, 10H, OCH_2), 3.33–2.63 (m, 2H, CH_2CH_3, 3H, $cp^{1,2,4}$), 2.09–1.30 (m, 2H, cp^3, m, 2H, cp^5) 1.26–1.09 (m, 3H, OCH_2CH_3).

Poly6-100: ^{1}H-NMR: (δ, 20 °C, $CDCl_3$, 500 MHz): 5.47–5.11 (m, 2H, CH=CH), 4.34–3.98 (m, 2H, $COOCH_2$), 3.72–3.44, (m, 6H, OCH_2) 3.21-2.36 (m, 2H, CH_2CH_3, 3H, $cp^{1,2,4}$), 2.10–1.27 (m, 2H, cp^3, m, 2H, cp^5), 1.23-1.15 (m, 3H, OCH_2CH_3).

Poly7-100: ^{1}H-NMR: (δ, 20 °C, $CDCl_3$, 500 MHz): 5.58–5.11 (m, 2H, CH=CH), 4.35–3.98 (m, 2H, $COOCH_2$), 3.88–3.36, (m, 26H, OCH_2) 3.34–2.38 (m, 3H, CH_3, 3H, $cp^{1,2,4}$), 1.98–1.28 (m, 2H, cp^3, m, 2H, cp^5).

Preparation of Statistic Copolymers

Poly1-2stat: To a solution of monomer **2** (186.7 mg, 0.37 mmol, 90 eq) and monomer **1** (24.5 mg, 0.12 mmol, 30 eq) in dry CH_2Cl_2 (5 mL), a solution of the initiator **M31** (2.9 mg, 0.0039 mmol, 1 eq) in dry CH_2Cl_2 (1 mL) was added. After consumption of the monomers, monitored by TLC (Cy:EE = 1:5; detection: UV/VIS, 2% $KMnO_4$ solution, R_f: 0.0) the reaction was terminated with ethylvinyl ether (100 μL, excess) and stirred for 15 min at room temperature. The polymer was purified by repeated precipitation of CH_2Cl_2 solutions (1 mL) of the polymer into cold *n*-pentane (80 mL). Yield: 110 mg (55%) brown, gluey polymer.

^{1}H-NMR (δ, 20 °C, $CDCl_3$, 500 MHz): 5.60–5.09 (m, 2H, CH=CH), 4.35–4.04 (m, 3H, $COOCH_2$) 3.80–3.46 (m, 18H, OCH_2, 1.5H $COOCH_3$), 3.38–2.65 (m, 4H, $cp^{1,\ 2,\ 3,\ 5}$), 2.15–1.35 (m, 2H, cp^4), 1.27–1.12 (m, 4.5H, OCH_2CH_3).

Poly8-2stat was prepared according to **poly1-2stat**, using monomer **2** (180.7 mg, 0.36 mmol, 90 eq), monomer **8** (30.3 mg, 0.16 mmol, 30 eq) in dry CH_2Cl_2 (5 mL) and a solution

of the initiator **M31** (3.2 mg, 0.0043 mmol, 1 eq) in dry CH_2Cl_2 (1 mL) as starting materials. Yield: 97 mg (54%) brown, gluey polymer.

^{1}H-NMR: (δ, 20 °C, $CDCl_3$, 500 MHz): 5.61–5.08 (m, 2H, CH=CH), 4.35–4.00 (m, 3H, $COOCH_2$), 3.76–3.44, (m, 15H, OCH_2) 3.41–2.82 (m, 3H, CH_2CH_3, 1H CH_2OCH_3, 4H, cp^{1,2,3,5}), 2.81–2.46 (m, 1.5H, OCH_3), 2.44–1.55 (m, 2H, cp^4, 0.5H cp^{1,2}), 1.26–1.13 (m, 4.5H, OCH_2CH_3). ^{13}C-NMR (δ, 20°C, $CDCl_3$, 125 MHz): 174.4–172.1 (2C, C=O), 134.9–127.6 (2C, CH=CH), 75.4–73.4, 71.1–70.6, 70.0, 69.3–69.0, 66.8, 64.3–63.5 (12C, OCH_2), 59.2–58.7 (0.5C, OCH_3), 54.2–51.3, 50.8–47.6, 46.2–43.5, 42.4–38.3 (5C, cp$^{1-5}$), 15.4 (21.5C, OCH_2CH_3). FT-IR (film on CaF_2, cm^{-1}): 2976-2867 (m), 1731 (s, $\nu_{C=O}$), 1638 (m), 1452 (w), 1380 (w), 1354 (w), 1261 (w), 1181 (w), 1105 (s).

Preparation of Block Copolymers

Poly1$_{10}$-2$_{90}$: To a solution of monomer **2** (198.8 mg, 0.39 mmol, 90 eq) in dry CH_2Cl_2 (5 mL), a solution of the initiator **M31** (3.2 mg, 0.0043 mmol, 1 eq) in dry CH_2Cl_2 (1 mL) was added. After consumption of the monomer, monitored by TLC (Cy:EE = 1:5; detection: UV/VIS, 2% $KMnO_4$ solution, R_f: 0.0), monomer **1** (9.2 mg, 0.044 mmol, 10 eq) was added directly in the solution. After finished polymerization, monitored by TLC (Cy/EE = 5:1, R_f: 0.0) the reaction was terminated with ethylvinyl ether (100 μL, excess) and stirred for 15 min at room temperature. The polymer was purified by repeated precipitation of CH_2Cl_2 solutions (1 mL) of the polymer into cold *n*-pentane (80 mL). Yield: 136 mg (62%) brown, gluey polymer.

^{1}H-NMR (δ, 20 °C, $CDCl_3$, 500 MHz): 5.63–5.08 (m, 2H, CH=CH), 4.34–3.98 (m, 3H, $COOCH_2$) 3.76–3.44 (m, 18H, OCH_2, 1.5H $COOCH_3$), 3.38–2.83 (m, 4H, cp^{1,2,3,5}), 2.23–1.33 (m, 2H, cp^4), 1.26–1.09 (m, 4.5H, CH_3). FT-IR (film on CaF_2, cm^{-1}): 2967–2869 (m), 1732 (s, $\nu_{C=O}$), 1645 (m), 1444 (w), 1382 (w), 1357 (w), 1259 (w), 1177 (w), 1110 (s).

Poly2$_{90}$-8$_{30}$ was prepared according to **poly1$_{10}$-2$_{90}$**, using monomer **2** (179.4 mg, 0.36 mmol, 90 eq), a solution of the initiator **M31** (3.2 mg, 0.0043 mmol, 1 eq) in dry CH_2Cl_2 (1 mL) and monomer 8 (22.8 mg, 0.13 mmol, 30 eq) as reactants. Yield: 139 mg (68%) brown, gluey polymer.

^{1}H-NMR: (δ, 20 °C, $CDCl_3$, 500 MHz): 5.60–5.08 (m, 2H, CH=CH), 4.36–4.00 (m, 3H, $COOCH_2$), 3.73–3.41, (m, 15H, OCH_2) 3.41–2.82 (m, 3H, OCH_2CH_3, 1H CH_2OCH_3, 4H, cp^{1,2,3,5}), 2.81–2.44 (m, 1.5H, OCH_3), 2.65–1.57 (m, 2H, cp^4, 0.5H cp^{1,2}), 1.23–1.09 (m, 4.5H, OCH_2CH_3).

Financial support by the Austrian Science Fund (FWF) in the range of the Austrian Nano Initiative (RPC 0700 - ISOTEC - RP 0715 DEVFAB) is gratefully acknowledged. Wolfgang Reinberger is thanked for the provision of the differential turbidity measurement cell and also for his help creating the setup and the software modification. Robert Saf and Karin Bartl are acknowledged for MALDI-TOF MS measurements.

REFERENCES AND NOTES

1 Langer, R.; Tirell, D. A. Nature 2004, 428, 487–492.

2 Klok, H.-A. J Polym Sci Part A: Polym Chem 2005, 43, 1–17.

3 Qiu, L. Y.; Bae, Y. H. Pharm Res 2006, 23, 1–30.

4 Lavasanifar, A.; Samuel, J.; Kwon, G. S. Adv Drug Delivery Rev 2002, 54, 169–190.

5 Han, K. S.; Na, K.; Bae, Y. H. Colloids Surf A 2003, 214, 49–59.

6 Lee, E. S.; Shin, H. J.; Na, K.; Bae, Y. H. J Control Release 2003, 90, 363–374.

7 Kakizawa, Y.; Harada, A.; Kataoka, K. J Am Chem Soc 1999, 121, 11247–11248.

8 Kakizawa, Y.; Harada, A.; Kataoka, K. Biomacromolecules 2001, 2, 491–497.

9 Kohori, F.; Sakai, K.; Aoyagi, T.; Yokoyama, M.; Sakurai, Y.; Okano, T. J Control Release 1998, 55, 87–98.

10 Chung, J. E.; Yokoyama, M.; Yamato, M.; Aoyagi, T.; Sakurai, Y.; Okano, T. J Control Release 1999, 62, 115–127.

11 Kohori, F.; Yokoyama, M.; Sakai, K.; Okano, T. J Control Release 2002, 78, 155–163.

12 Harris, J. M.; Zalipsky, S. Poly(ethylene glycol) Chemistry and Biological Applications. A Chemical Society: Washington, DC. 1997.

13 Lutz, J.-F. J Polym Sci Part A: Polym Chem 2008, 46, 3459–3470.

14 Smith, G. D.; Bedrov, D. J Phys Chem B 2003, 107, 3095–3097.

15 Wang, X.; Qiu, X.; Wu, C. Macromolecules 1998, 31, 2972–2976.

16 Szwarc, M. Nature 1956, 178, 1168–1169.

17 Wang, J. S.; Matyjaszewski, K. Macromolecules 1995, 28, 7901–7910.

18 Kontani, Y.; Kato, M.; Kamigaito, M.; Sawamoto, M. Macromolecules 1996, 29, 6979–6982.

19 Chiefari, J.; Chong, Y. K.; Ercole, F.; Krstina, J.; Jeffery, J.; Le, T. P. T.; Mayadunne, R. T. A.; Meijs, G. F.; Moad, C. L.; Moad, G.; Rizzardo, E.; Thang, S. H. Macromolecules 1998, 199, 923–934.

20 Chong, Y. K.; Le, T. P. T.; Moad, G.; Rizzardo, E.; Thang, S. H. Macromolecules 1999, 32, 2071–2074.

21 Webster, O. W.; Hertler, W. R.; Sogah, D. Y.; Farnham, W. B.; Rajanbabu, T. V. J Am Chem Soc 1983, 105, 5706–5708.

22 Dreyfuss, M. P.; Dreyfuss P. Polymer 1965, 6, 93–95.

23 Higashimura, T.; Mitsuhashi, M.; Sawamoto, M. Macromolecules 1979, 12, 178–182.

24 Buchmeiser, M. R. Chem Rev 2000, 100, 1565–1604.

25 Sandholzer, M.; Fritz, G.; Slugovc, C. J Polym Sci Part A: Polym Chem 2008, 46, 401–413.

26 Stubenrauch, K.; Moitzi, C.; Fritz, G.; Glatter, O.; Trimmel, G.; Stelzer, F. Macromolecules 2006, 39, 5865–5874.

27 Riess, G. Prog Polym Sci 2003, 28, 1107–1170.

28 Amphiphilic Block Copolymers: Self Assembly and Applications; Alexandridis, P.; Lindemann, B., Eds.; Elsevier: Amsterdam, 2000, pp 347.

29 Kwon, G. S.; Okano, T. Adv Drug Delivery Rev 1996, 21, 107–116.

30 Schmid, G. Cluster and Colloids. From Theory to Application; Wiley: New York, 1994.

31 Choi, T.-L.; Grubbs, R. H. Angew Chem 2003, 115, 1785–1788.

32 Bertin, P. A.; Gibbs, J. M.; Shen, C. K.-F.; Thaxton, C. S.; Russin, W. A.; Mirkin, C. A.; Nguyen, S. T. J Am Chem Soc 2006, 128, 4168–4169.

33 Chen, B.; Metera, K.; Sleiman, H. F. Macromolecules 2005, 38, 1084–1090.

34 Bullock, S. E.; Kofinas, P. Macromolecules 2004, 37, 1783–1786.

35 Sandholzer, M.; Schuster, M.; Varga, F.; Liska, R.; Slugovc, C. J Polym Sci Part A: Polym Chem 2008, 46, 3648–3660.

36 Sandholzer, M.; Bichler, S.; Stelzer, F.; Slugovc, C. J Polym Sci Part A: Polym Chem 2008, 46, 2402–2412.

37 Niedermair, F.; Sandholzer, M.; Kremser, G.; Slugovc, C. Organometallics 2009, 28, 2888–2896.

38 Slugovc, C.; Demel, S.; Riegler, S.; Hobisch, J.; Stelzer, F. Macromol Rapid Commun 2004, 25, 475–480.

39 Handbook of Metathesis; Grubbs, R.H. Ed.; Wiley- VCH: Weinheim, Germany, 2003.

40 Tao, L.; Mantovani, G.; Lecolley, F.; Haddleton, D. M. J Am Chem Soc 2004, 126, 13220–13221.

41 Lutz, J.- F.; Hoth, A. Macromolecules 2006, 39, 893–896.

42 Wang, X.- S.; Lascelles, S. F.; Jackson, R. A.; Armes, S. P. Chem Commun 1999, 18, 1817–1818.

43 Wang, X.- S.; Armes, S. P. Macromolecules 2000, 33, 6640–6647.

44 Lutz, J.- F.; Wechenhan, K.; Akdemir, Ö.; Hoth, A. Macromolecules 2007, 40, 2503–2508.

45 Carlise, J. R.; Kriegel, R. M.; Rees, W. S, Jr.; Weck, M. J Org Chem 2005, 70, 5550–5560.

46 Alfred, S. F.; Al-Badri, Z.; Madkour, A. E.; Lienkamp, K.; Tew, G. N. J Polym Sci Part A: Polym Chem 2008, 46, 2640–2648.

47 Cheng, G.; Hua, F.; Melnichenko, Y. B.; Hong, K.; Mays, J.W.; Hammouda, B.; Wignall, G. D. Macromolecules 2008, 41, 4824–4827.

48 Kattnig, E.; Albert, M. Org Lett 2004, 6, 945–948.

49 Spivey, A. C.; Arseniyadis, S. Angew Chem 2004, 116, 5552–5557.

50 Diels, O.; Alder, K. Synthesen in der hydroaromatischen Reihe, Liebigs Annalen der Chemie 1928, 460, 98–122.

51 Burtscher, D.; Lexer, C.; Mereiter, K.; Winde, R.; Karch, R.; Slugovc C. J Polym Sci Part A: Polym Chem 2008, 46, 4630–4635.

52 Slugovc, C.; Demel, S.; Riegler, S.; Hobisch, J.; Stelzer, F. J Mol Catal A 2004, 213, 107–113.

53 Schild, G. H.; Tirrell, D. A. J Phys Chem 1990, 94, 4352–4356.

54 Park, J.-S.; Kataoka, K. Macromolecules 2006, 39, 6622–6630.

55 Park, J.-S.; Kataoka, K. Macromolecules 2007, 40, 3599–3609.

56 Iskander, G. M.; Baker, L. E.; Wiley, D. E.; Davis, T. P. Polymer 1998, 39, 4165–4169.

57 Chung, E. J.; Yokoyama, M.; Okano, T. J Controlled Release 2000, 65, 93–103.

58 Perrin, D. D.; Armarego, W. L. F. In Purification of Laboratory Chemicals, 3rd ed.; Pergamon: New York, 1988.

59 Haller, H. L. J Ind Eng Chem 1947, 39, 467–473.

60 O'Dell, R.; McConville, D. H.; Hofmeister, G. E.; Schrock, R. R. J Am Chem Soc 1994, 116, 3414–3423.

61 Demel, S.; Schoefberger, W.; Slugovc, C.; Stelzer, F. J Mol Catal A 2003, 200, 11–19.

62 Gottlieb H. E.; Kotlyar A.; Nudelman A. J Org Chem 1997, 62, 7512–7515.