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Potential of amphiphilic NLO polymers

Polymers bearing chromophores of the push-pull type are potentially useful non-linear optical (NLO) materials, but the necessary non-centrosymmetric alignment of the NLO chromophores imposes severe problems[1-3]. A particularly useful strategy is the use of the Langmuir-Blodgett (LB) technique, requiring the use of amphiphilic compounds[2-4]. Unfortunately, the synthesis of such polymers is troubled by the poor compatibility of most NLO chromophores with standard polymerization reactions, in particular when bearing nitro moieties.
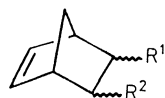
Stimulated by the recent progress of the ring-opening metathesis polymerization (ROMP)[5-8], we wanted to explore its potential for the polymerization of amphiphilic monomers bearing NLO chromophores. Some simple catalysts such as $RuCl_3$ exhibit a remarkable insensitivity against protic and aerobic polymerization conditions[8], as would be desirable for amphiphilic, and thus often hygroscopic, monomers.
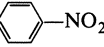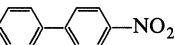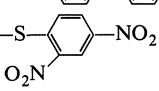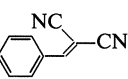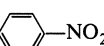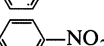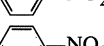
Norbornene monomers were chosen for our studies due to their high reactivity in ROMP, and due to their facile functionalization. Monomers were varied with respect to mono- versus disubstitution of the norbornene core, to stereoisomerism (*exo, endo, trans*), to use of long-chain derivatives, and to chromophores incorporated (Tab. 1). These variations were aimed to investigate their influence on the polymerizability, as well as on the amphiphilic behavior.

Ring-opening metathesis polymerization (ROMP)

Reaction conditions and polymer yield are listed in Tab. 2. The well-known polymers of norbornene carboxylic acid **1** and norbornene dicarboxylic acid diethylester **7** were only prepared to verify the activity of the catalyst system. Although the catalyst always proved to be active for these two reference monomers, within the non-functionalized amphiphilic compounds only the long-chain ester of the norbornene carboxylic acid **2** was polymerized readily, whereas the long-chain esters **8–14** of norbornene

Tab. 1. Norbornene monomers synthesized and investigated

Monomer	R^1	R^2	Isomer (%)
1	—COOH	H	*exo*(10)/*endo*(90)
2	—COO—$(CH_2)_{15}$—CH_3	H	*exo*(15)/*endo*(85)
3	—COO—$(CH_2)_{11}$—O—⟨benzene⟩—NO_2	H	*endo*(100)
4	—COO—$(CH_2)_{11}$—O—⟨benzene⟩—⟨benzene⟩—NO_2	H	*exo*(50)/*endo*(50)
5	—COO—$(CH_2)_{11}$—S—⟨benzene, O_2N⟩—NO_2	H	*exo*(45)/*endo*(55)
6	—COO—$(CH_2)_{11}$—O—⟨benzene⟩—C(NC)=CN... (1,1-dicyanoethylene)	H	*exo*(15)/*endo*(85)
7	—COO—C_2H_5	R^1	*trans*(100)
8	—COO—$(CH_2)_{15}$—CH_3	—COOH	*endo*(100)
9	—COO—$(CH_2)_{15}$—CH_3	—COOH	*exo*(90)/*endo*(10)
10	—COO—$(CH_2)_{15}$—CH_3	R^1	*endo*(100)
11	—COO—$(CH_2)_{15}$—CH_3	R^1	*exo*(80)/*endo*(20)
12	—COO—$(CH_2)_{11}$—O—⟨benzene⟩—NO_2	—COOH	*endo*(100)
13	—COO—$(CH_2)_{11}$—O—⟨benzene⟩—NO_2	R^1	*endo*(100)
14	—COO—$(CH_2)_{11}$—O—⟨benzene⟩—NO_2	R^1	*trans*(100)

dicarboxylic acid did not react. This is not only true for the *endo*-isomers which are known to be difficult to polymerize[5], but as well for the preferentially *exo*-isomers, which usually represent useful monomers. Obviously, the long-chain alcohols impede the polymerization by the $RuCl_3$-based catalyst system. These findings suggest steric effects, as the aliphatic chains would not directly interfere with the metathesis reaction.

However, the $RuCl_3$-based catalyst system proved to be rather insensitive to the incorporation of the push-pull dyes: the norbornene esters **3** and **4** bearing NLO chromophores with ether groups as donor, and nitro groups as acceptor can successfully be polymerized. Considering the difficulties encountered usually in the polymerization of nitro-group containing monomers, this result is remarkable[9]. Only when strong ligands such as sulfur or the 1,1-dicyanoethylene moiety were incorporated into the chromophores as in the monomers **5** and **6**, polymerization failed with the simple initiator system studied.

Tab. 2. Polymerization conditions and yields

Monomer	Amount in g	Solvent	Reaction time in d	Yield in g	Time for crosslinking	$T_g/°C$
1	0,5	C_2H_5OH [a]	1	0,05	8 h	
2	1,0	C_2H_5OH [a]	2	0,57	— [d]	(8) [e]
3	2,5	C_2H_5OH [a]	4	1,1	2 months	7
4	1,0	C_2H_5OH [a]	1	0,27 [c]	24 h	44 (83) [e]
5	1,0	C_2H_5OH [a]	6	0		
6	1,0	toluene	2	0		
7	3,0	C_2H_5OH [a]	2	1,1	12 h	
8	0,5	C_2H_5OH [a]	2	0		
9	1,0	C_2H_5OH [a]	21	0		
10	a) 0,5	C_2H_5OH [a]	2	0		
	b) 0,5	THF [b]	2	0		
11	0,5	C_2H_5OH [a]	2	0		
12	1,0	C_2H_5OH [a]	2	0		
13	1,0	C_2H_5OH [a]	2	0		
14	1,0	C_2H_5OH [a]	2	0		

[a] Solvent: ethanol/water (vol ratio: 10/1).
[b] Ethanol was evaporated after catalyst preparation, and replaced by 10 mL of the given solvent.
[c] Crosslinking upon prolonged reaction time.
[d] No crosslinking observed after 1 year storage.
[e] Melting point.

Properties of the polymers

The polymers P-2 and P-4 are brittle solids, but the polymer P-3 is a rubber-like material. Thermogravimetry shows polymer decomposition starting above 270 °C. Differential scanning calorimetry shows the semicrystalline character of the polymers P-2 and P-4, with broad melting points at 8 °C and 83 °C, respectively. Whereas P-4 exhibits an additional glass transition at 44 °C, no glass transition could be found for P-2. In case of P-3, only a glass transition is observed at 7 °C.

All polymers are soluble in tetrahydrofuran (THF) or chloroform, but insoluble in methanol and ethanol. However, the polymers tend to crosslink on storage in air. In case of P-4, partial crosslinking is already observed under prolonged polymerization conditions (see Tab. 2). Polymer P-2 proved to be exceptional, exhibiting excellent long-time stability against curing (>12 months). The reasons are not clear.

Characteristically in the ¹H NMR spectra of the polymers, the norbornene olefin signals between 6 and 6,5 ppm are replaced by new broad signals centered around 5,3 ppm due to the protons of the linear olefines formed. This is exemplified for monomer 4 and its polymer P-4 in Fig. 1.

The molecular weights of the polymers obtained were estimated by gel-permeation chromatography (GPC) using polystyrene standards. The polymers exhibit broad molecular-weight distributions, as often observed for polymers obtained by ROMP, with a number-average molecular weight $(\overline{M}_n)$ of ca. 10^4 and a weight-average molecular weight $(\overline{M}_w)$ of ca. 10^5.
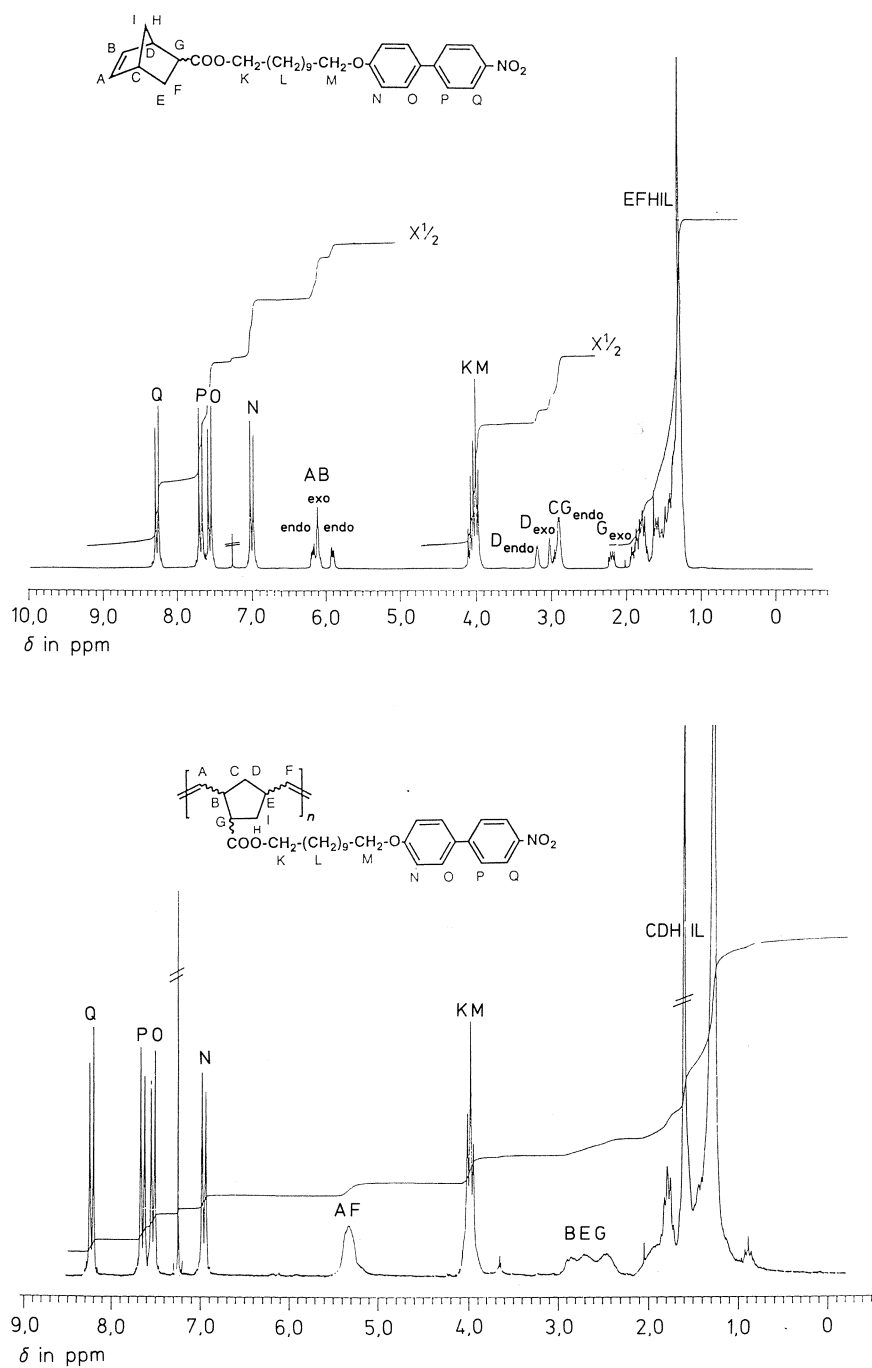
Fig. 1. ^{1}H NMR spectra (200 MHz) of monomer **4** and polymer **P-4** in CDCl$_3$

Monolayer properties

Due to the presence of both the polar ester groups which can act as hydrophilic "head groups", and the hydrophobic moieties, the norbornene monomers can be classified as amphiphiles. Hence, their ability to form insoluble monolayers at the air-water interface[10] was studied.

The spreading behavior of the non-functionalized, long-chain norbornene derivatives 2 and 8−11 is illustrated in Fig. 2. The surface-pressure area diagrams demonstrate the formation of well-defined monolayers, despite the bulky norbornene group present. The rather large collapse areas of ca. 0,4 nm²/molecule and of ca. 0,6 nm²/molecule for single- and double-chain monomers, respectively, suggest that the norbornene moiety acts as an additional hydrophobic chain.
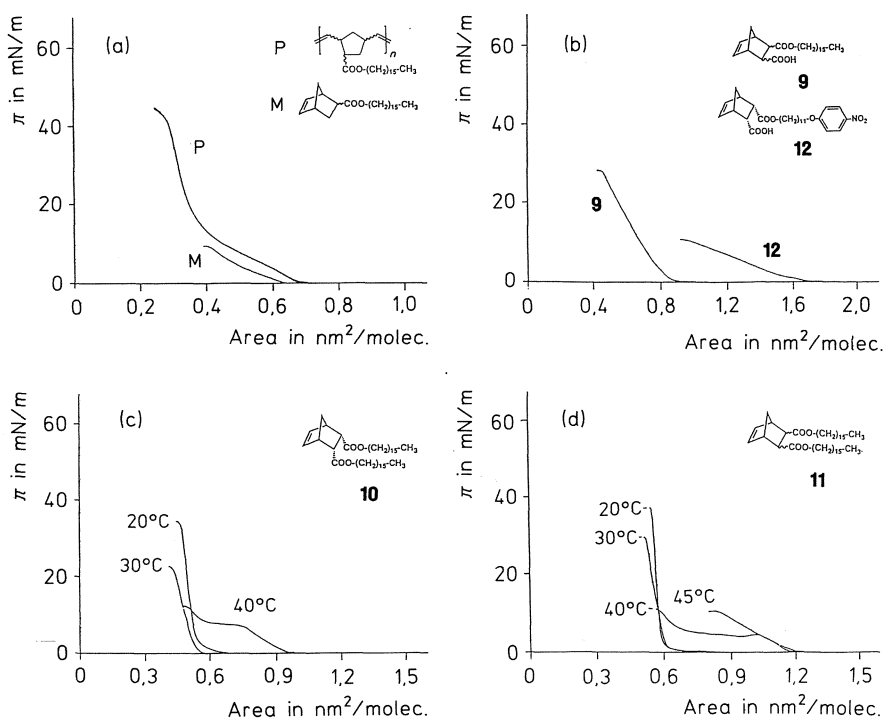
Fig. 2. Surface pressure — area diagrams of norbornene monomers and polymers, on pure aqueous subphase: (a) monomer 2 and polymer P-2, Temp. = 20 °C, (b) halfesters 9 and 12, Temp. = 20 °C, (c) diester 10 (*endo*), (d) diester 11 (*exo*)

Looking in more detail, the hexadecylester of norbornene carboxylic acid 2 exhibits only an expanded phase with low collapse pressure (Fig. 2a), pointing to an hindered packing of the hexadecyl chains. Upon incorporation of an additional hydrophilic

group to the norbornene core, such as the carboxyl group in the monoesters **8** and **9**, expanded phases are formed exclusively, too, but with much higher collapse pressures of ca. 30 mN/m (Fig. 2b): Whereas the increased hydrophilic-hydrophobic balance is not able to improve the poor packing of the hydrophobic chains, it clearly improves the stability of the monolayer. Interestingly, only small differences are observed between the *exo-* and the *endo-*isomer **8** and **9**.

In contrast, the diesters **10** and **11** exhibit condensed phases up to 30 °C, and coexisting expanded and condensed phases at 40 °C (Fig. 2c and d). Such condensed phases are the prerequisite for the production of high-quality Langmuir-Blodgett films of low-molecular-weight compounds[10]. The collapse areas of ca. 0,6 nm²/molecule are still rather large for double-chain amphiphiles, suggesting that the norbornene moiety acts as an additional hydrophobic chain. Nevertheless, efficient chain packing is achieved allowing for condensed phases. Collapse areas and pressures of the *exo-* and the *endo-*isomer are comparable, but the *exo-*isomer **11** shows a slightly higher phase transition temperature, thus pointing to an improved packing of the hydrophobic chains (Fig. 2c and d).

As shown in Fig. 2a, not only monomer **2**, but polymer **P-2** as well forms defined monolayers. The collapse area is ca. 0,26 nm²/alkyl chain, and the collapse pressure is ca. 40 mN/m. The strongly improved collapse pressure and the reduced collapse area compared to its monomer **2** are attributed to the ring opening of the bulky norbornene moiety, which facilitates a dense packing of the hexadecyl chains. Thus, norbornene polymers are suitable materials for the production of oriented, ultrathin films.

In contrast to the simple long-chain derivatives, the norbornenes functionalized with the chromophores spread poorly. Nitrophenyl ethers **3**, **13** and **14**, nitrobiphenyl ether **4** and thioether **5** do not form monolayers at all. Dicyanoethylene **6** forms barely monolayers below 10 °C, with a marginal collapse pressure of 5 mN/m, and an extensive collapse area of about 1 nm²/molecule. Presumably, the chromophores incorporated at the end of the hydrophobic chain act as additional weakly hydrophilic groups, thus competing with the ester moiety. Thus lacking a preferred orientation at the air-water interface, monolayer formation is prevented. In agreement, the polymers **P-3** and **P-4** do neither form well-defined monolayers in spreading experiments.

To overcome this problem, additional hydrophilic groups could be incorporated into functionalized norbornene monomers and polymers, as done for **8** and **9**. Indeed, the halfester **12** is capable of monolayer formation. But still, monolayers are formed only below 20 °C, exhibiting a low collapse pressure of ca. 10 mN/m and a high collapse area of ca. 1 nm²/molecule. Therefore, more efficient head groups than the carboxyl moiety, or improved amphiphile geometries will be needed for a successful monolayer and LB-multilayer work with such functionalized norbornenes.

Experimental part

Methods

NMR spectra were recorded with a Bruker AC200 (200 MHz) spectrometer. Thermogravimetry was performed using an analyzer TG85 (Setaram) under nitrogen, differential scanning calorimetry (DSC) was performed using a Perkin-Elmer DSC2, applying a heating rate of 20 °C/min.

Gel-permeation chromatography (GPC) was performed on a HPLC system (Waters, columns: PL-Gel, standard: polystyrene, eluent: $CHCl_3$). Monolayer behaviour was investigated with a computer controlled film balance[11], on a pure aqueous subphase. Spreading solutions were prepared in $CHCl_3$. Water was purified by a Milli-Q purification system (resistance 18 MΩ).

Materials

RuCl$_3$ · xH$_2$O (Aldrich) was used as received. Monomers **1**[12] and **7**[13] were prepared according to the literature. The other monomers were synthesized by standard esterification procedures[14, 15], starting from **1** or its *exo/endo*-isomer mixture[12], *endo*-5-norbornene-2,3-dicarboxylic anhydride (Fluka) or its *exo*-isomer[13], or from 5-norbornene-*trans*-2,3-dicarboxyl chloride (Aldrich). Functional alcohols were prepared by alkylation of the phenols with 11-bromo-undecanol[16]. The thioether in **5** was obtained from the nucleophilic substitution of 4-fluoro-1,3-dinitrobenzene with 11-thioundecanol[17]. All monomers were purified by flash-chromatography on silicagel.

Analytical data

2 (M_r = 362,33, 15% *exo*, 85% *endo*): n_D^{25} = 1,4668;
C$_{24}$H$_{42}$O$_2$ Calc.   C 79,46   H 11,67
                    Found   C 79,36   H 11,66
^{1}H NMR (200 MHz, CDCl$_3$): δ = 0,87 (t; 3 H), 1,1–1,7 (m; 31 H), 1,8–2,0 (m; 1 H), 2,15–2,25 (m; 0,15 H, *exo*), 2,8–2,95 (m; 1,85 H, *endo*), 3,0 (m; 0,15 H, *exo*), 3,2 (m; 0,85 H, *endo*), 3,9–4,15 (m; 2 H), 5,9–6,18 (m; 2 H).

3 (M_r = 429,26; *endo*): m.p.: 43 °C;
C$_{25}$H$_{35}$NO$_5$ Calc.   C 69,99   H 8,21   N 3,26
                    Found   C 69,79   H 8,19   N 3,27
^{1}H NMR (200 MHz, CDCl$_3$): δ = 1,2–1,95 (m; 22 H), 2,8–3,0 (m; 2 H), 3,18 (m; 1 H), 3,9–4,1 (m; 4 H), 5,9–6,15 (m; 2 H), 6,9 (d; 2 H), 8,18 (d; 2 H).

4 (M_r = 505,29, 50% *exo*, 50% *endo*): m.p.: 57 °C;
C$_{31}$H$_{39}$NO$_5$ Calc.   C 73,62   H 7,78   N 2,77
                    Found   C 73,73   H 7,76   N 2,75
^{1}H NMR (200 MHz, CDCl$_3$): δ = 1,2–1,95 (m; 22 H), 2,15–2,25 (m; 0,5 H, *exo*), 2,83–3,03 (m; 1 H), 3,2 (m; 0,5 H, *endo*), 3,93–4,13 (m; 4 H), 5,91–6,18 (m; 2 H), 7,0 (d; 2 H), 7,55 (d; 2 H), 7,67 (d; 2 H), 8,24 (d; 2 H).

5 (M_r = 460,28, 45% *exo*, 55% *endo*): m.p.: 54 °C;
C$_{25}$H$_{34}$N$_2$O$_6$S   Calc   C 61,20   H 6,99   N 5,71   S 6,52
                    Found   C 61,26   H 6,99   N 5,83   S 6,16
^{1}H NMR (200 MHz, CDCl$_3$): δ = 1,2–1,9 (m; 22 H), 2,15–2,25 (m; 0,45 H, *exo*), 2,85–3,1 (m; 4 H), 3,2 (m; 0,55 H, *endo*), 3,9–4,1 (m; 2 H), 5,9–6,15 (m; 2 H), 7,55 (d; 1 H), 8,35 (m; 1 H), 9,1 (m; 1 H).

6 (M_r = 460,28, 15% *exo*, 85% *endo*): m.p.: 58 °C;
C$_{29}$H$_{36}$N$_2$O$_3$ Calc.   C 75,61   H 7,88   N 6,08
                    Found   C 74,82   H 7,68   N 5,88
^{1}H NMR (200 MHz, CDCl$_3$): δ = 1,2–2,0 (m; 22 H), 2,15–2,25 (m; 0,15 H, *exo*), 2,85–3,15 (m; 2 H), 3,2 (m; 0,85 H, *endo*), 3,9–4,2 (m; 4 H), 5,9–6,2 (m; 2 H), 7,0 (d; 2 H), 7,65 (s; 1 H), 7,9 (d; 2 H).

8 (M_r = 406,32; *endo*): m.p.: 64 °C (lit. 63–64 °C [18]);

$C_{25}H_{42}O_4$ Calc.   C 73,83   H 10,41

                    Found   C 73,98   H 10,47

^{1}H NMR (200 MHz, CDCl$_3$): δ = 0,85 (t; 3 H), 1,1–1,7 (m; 30 H), 3,15 (m; 2 H), 3,3 (m; 2 H), 3,8–4,1 (m; 2 H), 6,15–6,3 (m; 2 H).

9 (M_r = 406,32, 90% *exo*, 10% *endo*): m.p.: 57 °C;

$C_{25}H_{42}O_4$ Calc.   C 73,83   H 10,41

                    Found   C 74,01   H 10,50

^{1}H NMR (200 MHz, CDCl$_3$): 0,87 (t; 3 H), 1,15–1,7 (m; 29,1 H), 2,1 (m; 0,9 H, *exo*), 2,6 (m; 1,8 H, *exo*), 3,1 (m; 1,8 H, *exo*), 3,15 (m; 0,2 H, *endo*), 3,3 (m; 0,2 H, *endo*), 3,9–4,1 (m; 2 H), 6,3 (s; broad, 2 H).

10 (M_r = 630,57, *endo*): m.p.: 54 °C (lit. 54 °C [18]);

$C_{32}H_{74}O_4$ Calc.   C 78,02   H 11,83

                    Found   C 78,13   H 11,78

^{1}H NMR (200 MHz, CDCl$_3$): δ = 0,85 (t; 6 H), 1,1–1,6 (m; 58 H), 3,1 (m; 2 H), 3,25 (m; 2 H), 3,8–4,1 (m; 4 H), 6,2 (m; 2 H).

11 (M_r = 630,57, 80% *exo*, 20% *endo*): m.p.: 61 °C;

$C_{32}H_{74}O_4$ Calc.   C 78,02   H 11,83

                    Found   C 78,21   H 11,83

^{1}H NMR (200 MHz, CDCl$_3$): δ = 0,85 (t; 6 H), 1,1–1,7 (m; 57,2 H), 2,1 (m; 0,8 H, *exo*), 2,6 (m; 1,6 H, *exo*), 3,05 (m; 1,6 H, *exo*), 3,14 (m; 0,4 H, *endo*), 3,25 (m; 0,4 H, *endo*), 3,9–4,1 (m; 4 H), 6,1–6,3 (m; 2 H).

12 (M_r = 473,25, *endo*): m.p.: 75–76 °C;

$C_{26}H_{35}NO_7$ Calc.   C 65,93   H 7,45   N 2,96

                    Found   C 65,95   H 7,55   N 3,01

^{1}H NMR (200 MHz, CDCl$_3$): δ = 1,1–1,9 (m; 20 H), 3,15 (m; 2 H), 3,25 (m; 2 H), 3,8–4,1 (m; 4 H), 6,1–6,3 (m; 2 H), 6,9 (m; 2 H), 8,15 (m; 2 H).

13 (M_r = 764,34, *endo*): m.p.: 54 °C;

$C_{43}H_{60}N_2O_{10}$ Calc.   C 67,50   H 7,91   N 3,66

                    Found   C 67,31   H 7,99   N 3,66

^{1}H NMR (200 MHz, CDCl$_3$): δ = 1,2–1,9 (m; 38 H), 3,1 (m; 2 H), 3,25 (m; 2 H), 3,8–4,1 (m; 8 H), 6,2 (d; 2 H), 6,9 (m; 4 H), 8,15 (m; 4 H).

14 (M_r = 764,43, *trans*): m.p.: 49 °C;

$C_{43}H_{60}N_2O_{10}$ Calc.   C 67,50   H 7,91   N 3,66

                    Found   C 67,00   H 7,96   N 3,81

^{1}H NMR (200 MHz, CDCl$_3$) δ = 1,2–1,9 (m; 38 H), 2,64 (d; 1 H), 3,05 (s; 1 H), 3,22 (s; 1 H), 3,35 (t; 1 H), 3,9–4,1 (m; 8 H), 6,01 (m; 1 H), 6,15 (m; 1 H), 6,9 (d; 4 H), 8,15 (m; 4 H).

General polymerization procedure [19, 20]

The active catalyst was prepared by refluxing 30 mg of commercial RuCl$_3$ hydrate in 5 mL of 90% ethanol for 2–3 h. When polymerizations were performed in toluene or tetrahydrofuran, ethanol was evaporated and replaced by the respective solvent. After purging with argon, the monomer was added and polymerized while refluxing the mixture. The polymer formed precipitated from the reaction mixture. Polymerization proceeded under air as well, but argon was used to minimize the formation of insoluble, presumably crosslinked material. The polymer was filtered, and twice dissolved in CHCl$_3$ and reprecipitated in methanol.

Conclusions

Ring-opening metathesis polymerization (ROMP) enables the synthesis of functionalized, amphiphilic polymers. This includes monomers bearing nitro moieties. Working with the simple $RuCl_3$-based catalyst system, only monosubstituted amphiphilic derivatives of norbornene monocarboxylic acid seem to be suitable, but not disubstituted ones. Both norbornene monomers and polymers are capable of monolayer formation, if properly substituted. Despite the bulky rings involved, tightly packed monolayers can be formed which are the prerequisite for the production of high-quality Langmuir-Blodgett films.

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