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Ring-closing olefin metathesis in the aqueous phase of amphiphilic conetworks consisting of fluorophilic and hydrophilic compartments

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ABSTRACT

A Grubbs–Hoveyda-Type metathesis catalyst bearing a tris(perfluoroalkyl)silyl tag was immobilized in the fluorophilic phase of amphiphilic conetworks (APCNs). This catalytic system was applied to ring-closing metathesis (RCM) reactions in aqueous media. Different substrates were evaluated and with 10 mol% of catalyst at 60 °C good conversions were observed. Reuse of the catalytic system was possible, but resulted generally in lower conversions.

1. Introduction

With the development of Ru-carbenoid based catalysts by Grubbs and coworkers [1] and Hoveyda and coworkers [2], olefin metathesis has found a broad spectrum of applications and has proven to be an efficient method for the formation of new carbon–carbon bonds. Among the different applications, the ring-closing metathesis (RCM) of 1,ω-dienes has emerged as a useful method for the synthesis of carbocycles and heterocycles and is usually carried out in organic solvents. For the RCM-reactions in aqueous media, the stability of the catalysts has turned out to be a critical issue. Grubbs has reported the first metathesis reaction in water mediated by a water-soluble Ru-catalyst [3]. The water solubility issue has also been addressed by immobilization of catalyst in a polymer matrix [4] or by covalent attachment of catalyst to water-soluble polymers [5].

As an alternative, we describe RCM-reactions in water mediated by amphiphilic conetworks using a Ru-catalyst modified with perfluoroalkyl tags thereby transfering fluorophilic properties to the catalyst.

Amphiphilic polymer conetworks (APCNs) [6,7] are polymer conetworks containing two different phases, i.e. a hydrophilic and a fluorophilic phase. Although they are covalently bound to each other, the two polymeric constituents are essentially immiscible and lead to a bicontinuous nanophase separated polymer network. The morphology of the networks was examined with AFM [8]. The hydrophilic PHEA forms a sponge-like structure with a domain size of 15–30 nm. The perfluoropolyether appears as roundish coalescent domains of 10–20 nm in diameter embedded in the hydrophilic phase. An increasing PFPE content in the conetworks results in an increasing coalescence of the hydrophobic PFPE domains. The morphology of the networks with a PFPE content of 70 wt% is cocontinuous.

They respond in a predictable manner to the medium with which they come into contact. Fig. 1 helps to illustrate the characteristics of APCNs.

In the center of Fig. 1, an amphiphilic system in dry state is depicted. In this state, the two phases occupying approximately the same volume. In an amphiphilic solvent, the two phases swell to approximately the same size (a). The lower two cartoons represent the APCN coming into contact with a hydrophilic or a fluorophilic solvent, respectively. In the hydrophilic solvent only the hydrophilic phase is swollen, while the fluorophilic phase collapses (b). Conversely, in a fluorophilic solvent, the fluorophilic phase swells and the hydrophilic phase collapses (c). This phase rearrangement is a dynamic and reversible process [6,9]. These unique features led to several applications like soft contact lenses [10] or as carriers for biocatalysts in organic solvents [11]. In our

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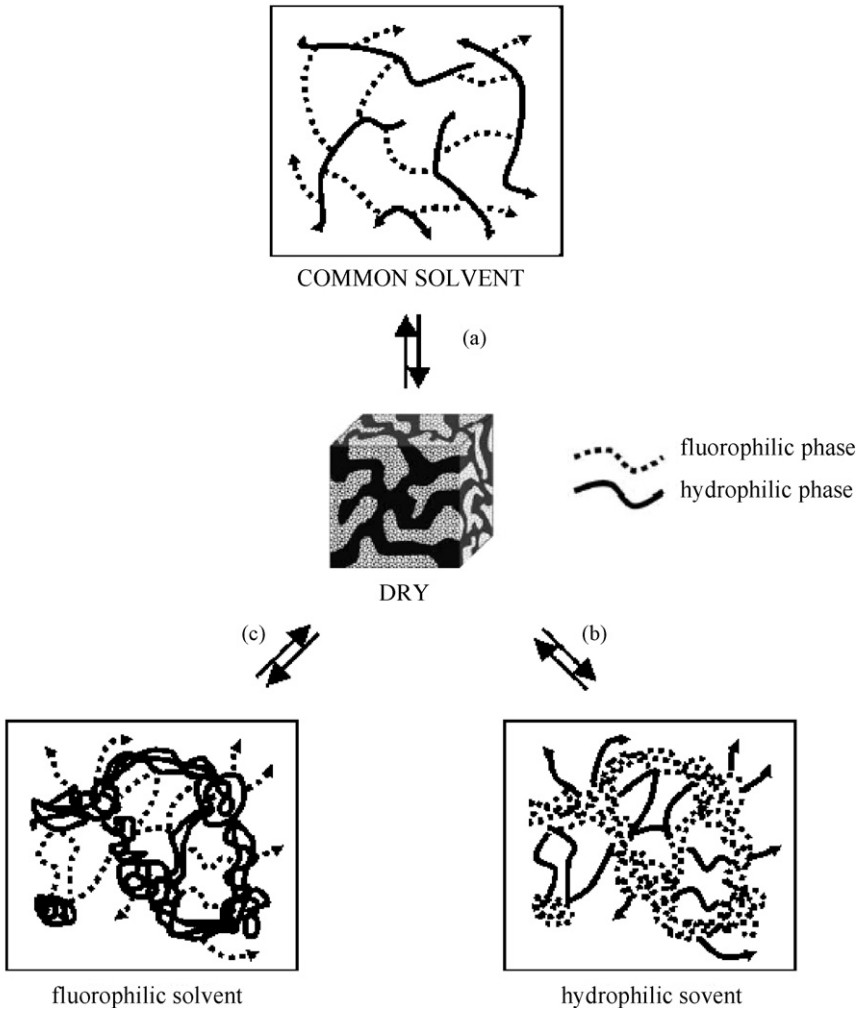


Fig. 1. Characteristics of APCNs.

amphiphilic conetworks, the fluorophilic phase consisted of perfluoropolyether (PFPE), whereas the hydrophilic phase was represented by poly-(2-hydroxyethylacrylate) (PHEA) [12].

As catalyst for the RCM-reactions in amphiphilic systems we have chosen the perfluoro-tagged Hoveyda-Type catalyst **3**. Its utility in RCM-reactions had been demonstrated by us after its noncovalent attachment to fluorous silica gel [13]. The advantage of this system is twofold: (a) noncovalent attachment allows for easy removal of the catalyst by filtration and (b) it obviates the need for perfluorinated solvents, which are expensive and environmentally persistent [14–16].

Central to the concept of reactions with fluorophilic/hydrophilic APCNs is that in ethereal solvents (such as TBME or Et_2O), the fluorophilic phase swells and allows the dissolved perfluoro-tagged catalyst to enter the network (Fig. 2).

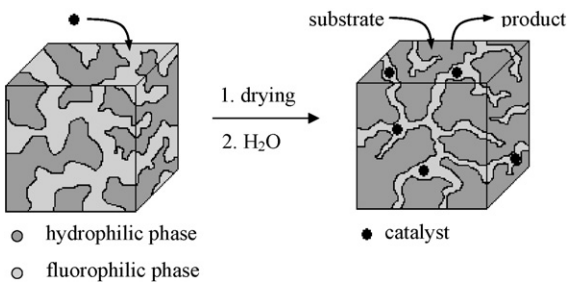


Fig. 2. Concept of reactions with amphiphilic systems.

Upon drying, the fluorophilic phase shrinks and encapsulates the catalyst. In a hydrophilic solvent, i.e. water, the hydrophilic phase swells and allows the water-soluble substrates to enter into the network and thereby coming into contact with the trapped catalyst *via* the large interface between the two phases [11].

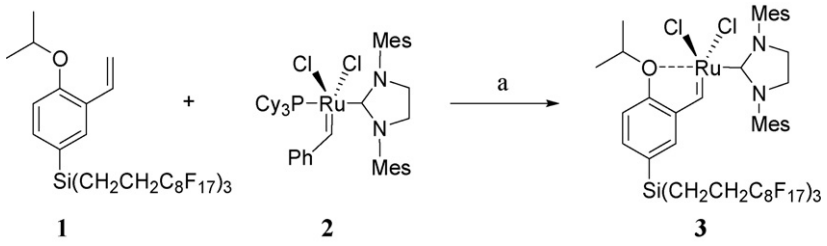
The nanophase separated amphiphilic conetworks were synthesized as previously reported [8].

2. Results and discussion

According to Scheme 1, the perfluoro-tagged ligand **1** was transformed into the perfluoro-tagged catalyst **3** by reacting it with Grubbs catalyst **2** (second generation). The desired product was obtained in pure form as a green solid after purification by column chromatography.

The synthesis of the perfluoro-tagged ligand **1** was achieved in 4 steps starting from 4-bromophenol according to our published procedure [17].

First, we examined the activity of the perfluoro-tagged catalyst **3** in comparison with the Hoveyda-Type catalyst (second generation). Raines and coworkers described the activity and the utilization of the Hoveyda-Type catalyst (second generation) in acetone/H_2O and DME/H_2O solvent mixtures [18]. They monitored



Scheme 1. Synthesis of the perfluoro-tagged catalyst **3**. (a) CuCl, CH_2Cl_2/BTF, reflux, 4 h, 50%.

the RCM-reaction of *N*-tosyl diallylamine **4** to evaluate the rate of the reaction and the lifetime of the catalytically active species.

The tests were standardized by using 2.5 mol% of catalyst, *N*-tosyl diallylamine **4** as substrate in an acetone/H_2O 4:1 or in a DME/H_2O 4:1 mixture. Fig. 3 shows the results obtained from these experiments.

Direct comparison of the curves in Fig. 3 indicates that the Hoveyda catalyst is more active than the perfluoro-tagged catalyst **3**. Compared to DME/H_2O, acetone/H_2O turned out to be the more suitable solvent for this kind of RCM-reactions. However, after a reaction time of 5 h with either catalyst in either solvent mixture nearly identical conversions were achieved. In accordance with data published by Raines, the majority of the RCM occurred within 90 min.

Next, the activity of the catalysts with diethyl 2,2-diallylmalonate **6** as substrate was investigated (Fig. 4), because our aim was to use finally derivatives of malonates as substrates for the RCM-reactions in amphiphilic systems.

Compared to *N*-tosyl diallylamine **4** as substrate, both catalysts, the Hoveyda-Type catalyst (second generation) and the perfluoro-tagged catalyst **3** revealed a decreased activity. As demonstrated before, acetone/H_2O mixtures appear to be more effective for this RCM-reaction than DME/H_2O combinations. Whereas the conversions with *N*-tosyl diallylamine **4** were nearly identical after 5 h, here a noticable variation was observed. These results were used to outline the reaction conditions for the first RCM-reactions with amphiphilic systems. However, before these reactions were carried out, the perfluoro-tagged catalyst **3** had to be immobilized in the amphiphilic system. The loading of the catalyst was determined by UV/vis-spectroscopy (see Section 4 for details). For the first two sets of RCM-reactions (Tables 1 and 2) the loading of the catalyst was 10 mol%. Two APCNs with a different weight content of the fluorophilic phase were used. One amphiphilic system consisted of 50 wt%, the other of 70 wt% of perfluoropolyether (PFPE). The first RCM-reactions in APCNs were carried out with a substrate concentration of 0.01 M, 10 mol% catalyst loading at rt. for 2 h. The results are summarized in Table 1.

In contrast to the reaction in the absence of amphiphilic systems, poor conversions (14–25%) were obtained, both in acetone/H_2O and DME/H_2O for either composition (i.e. 50/50 or 30/70) of the amphiphilic systems (entries 1–4). Because of the low

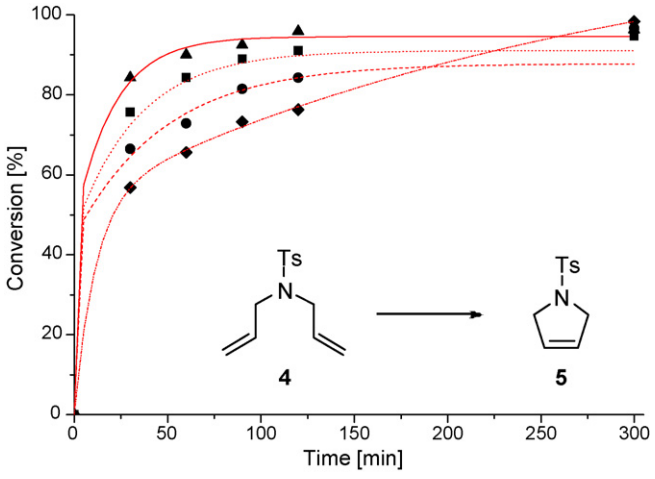


Fig. 3. Kinetics of RCM of *N*-tosyl diallylamine **4** (0.05 M) in acetone/H_2O and DME/H_2O: Hoveyda-catalyst in acetone/H_2O (▲), Hoveyda-catalyst in DME/H_2O (■), perfluoro-tagged catalyst **3** in acetone/H_2O (●), perfluoro-tagged-catalyst in DME/H_2O (◆).

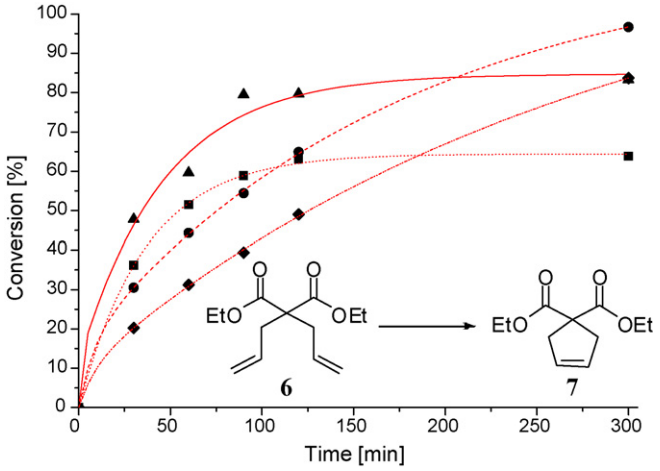


Fig. 4. Kinetics of RCM of diethyl 2,2-diallylmalonate **6** (0.05 M) in acetone/H_2O and DME/H_2O: Hoveyda-catalyst in acetone/H_2O (▲), Hoveyda-catalyst in DME/H_2O (■), perfluoro-tagged catalyst **3** in acetone/H_2O (●), perfluoro-tagged-catalyst in DME/H_2O (◆).

Table 1
Results obtained in RCM-reactions in APCNs with diethyl 2,2-diallylmalonate **6** in different solvents at rt.

Entry	Solvent	APCN	Conversion[a]	
		Composition	1. run	2. run
1	Acetone/H_2O[b]	30/70	18%	4%
2	Acetone/H_2O[b]	50/50	14%	6%
3	DME/H_2O[b]	30/70	16%	6%
4	DME/H_2O[b]	50/50	25%	8%
5	H_2O	30/70	69%	49%
6	H_2O	50/50	60%	46%
7	Acetone	30/70	63%	27%
8	Acetone	50/50	52%	13%
9	DME	30/70	38%	15%
10	DME	50/50	44%	4%

[a] Determined by HPLC.
[b] 2:1 mixture of the two solvents.

Table 2
Results obtained in RCM-reactions with diethyl 2,2-diallylmalonate **6** in different solvents at 60 °C applying 10 mol% of catalyst

Entry	Solvent	APCN	Conversion[a]	
		Composition	1. run	2. run
1	H_2O[b]	30/70	90%	80%
2	H_2O[b]	50/50	60%	40%
3	Acetone[c]	30/70	80%	7%
4	Acetone[c]	50/50	85%	12%
5	DME[c]	30/70	74%	18%
6	DME[c]	50/50	78%	5%
7	Acetone/H_2O[d]	30/70	6%	4%
8	Acetone/H_2O[d]	50/50	18%	4%
9	DME/H_2O[d]	30/70	4%	3%
10	DME/H_2O[d]	50/50	10%	5%

[a] Conversion determined by HPLC.
[b] 0.002 M.
[c] 0.01 M.
[d] 2:1 mixture of the two solvents, 0.01 M.

conversions, these experiments RCM-reactions were repeated in H_2O, acetone and DME as pure solvent systems. In each case we achieved better conversions than in the mixture of the solvents (entries 5–10) with the highest conversion obtained in water. To investigate the potential for recycling of the catalytic system, the amphiphilic systems were washed with TBME after use, dried and reused in a subsequent RCM-reaction (2. run). Compared to the first use, poor conversions were obtained in all cases except in water where the decrease was moderate.

To examine the influence of the reaction temperature, we carried out RCM-reactions with diethyl 2,2-diallylmalonate **6** as substrate at 60 °C (Table 2).

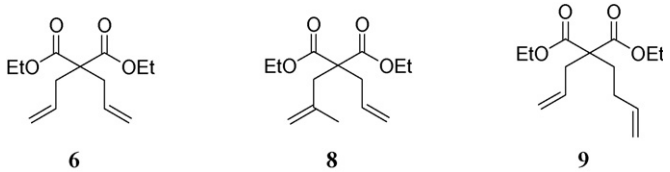
RCM-reactions at elevated temperature in H_2O, acetone and DME as pure solvents led to higher conversions (entries 1–6). With the two solvent mixtures only moderate conversions were obtained (entries 7–10). The reuse of the recycled amphiphilic systems led to comparable results: a strong decrease of conversions in acetone and DME, good conversions in H_2O.

Because of the promising results in Tables 1 and 2, subsequent RCM-reactions with amphiphilic systems were carried out in H_2O at 60 °C using the 3 substrates (**6**, **8**, and **9**) shown in Fig. 5. A decreased loading of 5 mol% catalyst was investigated at the same time.

Table 3 summarizes the results obtained from RCM-reactions with catalyst **3** with the 3 substrates **6**, **8** and **9**.

After a reaction time of 2 h, high conversions were achieved for all substrates with 10 and 5 mol% catalyst loading. Reuse of the amphiphilic systems with 10 mol% of the catalyst loading led to good conversions with the only exception in entry 6. No clearcut results for the use of APCNs consisting of 50% fluorophilic phase against the 30/70 system were obtained.

Recycling of the amphiphilic systems with 5 mol% of the catalyst led in all cases to only moderate conversions. Also a prolongation of the reaction time from 2 to 4 h did not result in higher conversions (entries 4, 7, and 8). The lower conversions in the recycling experiments are probably due to decomposition of



6 8 9

Fig. 5. Diene substrates for RCM-reactions.

Table 3
Results obtained in RCM-reactions with different substrates in H_2O at 60 °C

Entry	Starting material	mol% Catalyst	APCN	Conversion[a]	
			Composition	1. run	2. run
1	**6**	10[b]	30/70	90%	80%
2		10[b]	50/50	60%	40%
3		5[c]	30/70	73%	29%
4		5[c]	50/50	83%	26–33% 2 → 4 h
5	**8**	10[c]	30/70	100%	72%
6		10[b]	50/50	83%	17%
7		5[c]	30/70	85%	13–14% 2 → 4 h
8		5[c]	50/50	81%	19–22% 2 → 4 h
9	**9**	10[c]	30/70	92%	72%
10		10[c]	50/50	100%	52%
11		5[c]	30/70	78%	35%
12		5[c]	50/50	84%	72%

[a] Determined by HPLC.
[b] 0.002 M solution of the starting material.
[c] 0.01 M solution of the starting material.

the catalyst in aqueous media which is in accordance with data published by Raines and coworkers [18].

3. Conclusion

It was demonstrated that it is possible to carry out RCM-reactions in water using a perfluoroalkyl-tagged Hoveyda-Type catalyst immobilized in the fluorophilic compartment of an amphiphilic system consisting of fluorophilic and hydrophilic entities. Good conversions were achieved at 60 °C using 10 and 5 mol% loading of the immobilized catalyst. The reuse of the catalytic system resulted generally in lower conversions.

4. Experimental

4.1. General remarks

UV/vis: *Lambda 35* system from PerkinElmer. HPLC: *Agilent-1100* system with binary pump, sample charger, column oven and diode array detector. IR: *Paragon 1000* system from PerkinElmer. NMR: *Am 400* from Brucker and *Mercury 300* from Varian. MS: *Finnigan MAT312* system or *Finnigan MAT8200* system. CHN: *elementar varion EL* system from Elementar Analysesysteme GmbH.

4.1.1. General procedure for the immobilization of the perfluoro-tagged catalyst 3 in the amphiphilic systems

The unloaded amphiphilic systems were placed in a solution of the perfluoro-tagged catalyst **3** in TBME (1 mM) and were first shaken at rt. for 2 h. Then they were heated to 40 °C (oil bath) to remove the solvent.

For the determination of the loading of the catalyst, these amphiphilic systems were measured by UV/vis-spectroscopy. The loaded amphiphilic systems were placed on the cuvette which was placed directly in the beam of the spectrometer. The absorption of the catalyst was measured. The concentration of the catalyst could be determined from the Lambert–Beer-law:

$$c = \frac{A}{\varepsilon \cdot d}.$$

A, absorption; ε, coefficient of absorption; d, thickness of the cuvette.

4.1.2. General procedure for activity experiments

The ruthenium complex (2.5 mol%) was dissolved in acetone or DME. Deionized water was added to this solution, followed by *N*-tosyl diallylamine **4** or diethyl 2,2-diallylmalonate **6** (0.05 M in a 4:1 mixture of the solvents). After 30, 60, 90 and 120 min, 1.5 mL of the reaction mixture were taken out, ethylvinylether (0.5 mL) was added and the solution was concentrated under reduced pressure. After 5 h, ethylvinylether (1.0 mL) was given to the remaining solution and also concentrated under reduced pressure. The conversion was determined by the ratio of the integrals of the methylene-groups.

4.1.3. General procedure for the ring-closing metathesis in amphiphilic systems

The starting material (0.002 M for **6** and 0.01 M for **8** and **9**) was dissolved in the corresponding solvent and the loaded amphiphilic system was added. The reaction mixture was shaken for 2 h at 60 °C (oil bath). After cooling to rt. the amphiphilic systems were taken out and the solution was measured by HPLC to determine the conversion.

The recycled amphiphilic systems were washed with TBME, dried and were reused again under the same conditions.

*4.1.4. [1,3-Bis(2,4,6-trimethylphenyl)imidazolidin-2-ylidene]dichloro{2-(isopropoxy-κO)-5-[tris(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl)silyl]benzylidene-κC}ruthenium **3***

Grubbs-Complex **2** (0.19 g, 0.23 mmol, 1.5 equiv.) was dissolved under Ar in anhydrous CH_2Cl_2 (10 mL). Then, **1** (0.23 g, 0.15 mmol) dissolved in BTF (5 mL) and CuCl (0.02 g, 0.21 mmol, 1.4 equiv.) were added, and the mixture was heated for 4 h at 60 °C (oil bath). After cooling to rt., the mixture was filtered over silica gel and the filtrate was purified by column chromatography (eluent: cyclohexane → cyclohexane/CH_2Cl_2 1:1) to obtain the perfluoro-tagged catalyst **3** as a green solid (0.15 g, yield: 50%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.07–1.10 (6H, m ($C_8F_{17}CH_2CH_2)_3Si$), 1.28 (6H, d, J = 6.1 Hz, Me_2CH), 1.97–2.07 (6H, m ($C_8F_{17}CH_2CH_2)_3Si$), 2.38–2.47 (18H, m, Mes-CH_3), 4.07 (4H, s, NCH_2CH_2N), 4.93 (1H, septett, J = 6.0 Hz, Me_2CH), 6.89 (1H, d, J = 8.3 Hz, arom. H), 7.00 (1H, d, J = 1.2 Hz, arom. H), 7.06 (4H, s, Mes-$H_{arom.}$), 7.53 (1H, dd, J = 8.2 Hz, 1.2 Hz, arom. H), 16.54 (1H, s, Ru=CHAr).

^{13}C NMR (400 MHz, $CDCl_3$): δ = 1.6, 20.9, 21.2, 25.3, 25.5, 25.7, 75.9, 114.0, 118.1, 124.1, 128.5, 129.5, 134.7, 139.1, 145.3, 154.4, 210.4.

MS-posESI; *m*/*z* (%): 2000 (28), 1999 (83), 1998 (100), 1997 (63), 1996 (85), 1995 (79), 1994 (86), 1993 (57), 1992 (42), 1991 (20), 1990 (21), 1989 (14), 1988 (12), 1986 (8), 1985 (8), 1981 (5), 1980 (11), 1979 (13), 1978 (17), 1977 (26), 1976 (22), 1975 (15), 1974 (11), 1972 (8), 1971 (7), 1966 (9), 1965 (22), 1964 (19), 1963 (45), 1962 (59), 1961 (39), 1960 (45), 1959 (32), 1958 (22), 1957 (20), 1956 (19), 1955 (6), 1952 (6), 1941 (5), 1923 (7), 1922 (6), 1921 (5), 1918 (6), 1899 (6), 1896 (5), 1883 (11), 1882 (11), 1881 (20), 1880 (12), 1879 (10), 1878 (8), 1777 (5), 1729 (8), 1659 (5), 1447 (11), 1004 (48), 1003 (78), 1002 (85), 1001 (19), 1000 (8), 983 (8), 982 (7), 981 (8), 980 (8), 964 (17), 963 (30), 962 (82), 961 (56), 960 (35), 959 (34), 958 (13), 957 (9), 956 (8), 953 (5), 943 (9), 942 (31) 941 (83), 940 (32), 939 (8), 938 (9), 912 (6), 557 (6), 524 (7), 523 (20), 522 (6), 521 (30), 520 (24), 519 (14), 518 (16), 515 (8), 513 (6), 489 (11), 488 (10), 486 (13), 485 (7), 484 (13), 483 (9), 482 (6), 481 (7), 449 (14), 448 (31), 447 (20), 446 (43), 445 (33), 444 (26), 443 (20), 442 (10), 441 (10), 440 (15), 439 (6), 438 (7), 435 (8), 432 (7), 425 (6), 424 (10), 423 (19), 422 (15), 421 (13), 420 (16), 419 (14), 411 (6), 409 (8), 407 (15), 406 (9), 405 (20), 404 (13), 403 (10), 402 (6),391 (6), 307 (12), 303 (6), 301 (9), 299 (6), 294 (6), 275 (6).

*4.1.5. Diethyl 2,2-diallylmalonate **6***

NaH (11.8 g of a 60% suspension in mineral oil, 296 mmol, 15.0 equiv.) was suspended in anhydrous THF (40 mL) and cooled to 0 °C. Then diethylmalonate (3.16 g, 3.00 mL, 19.8 mmol) was added dropwise. After warming to rt., allylbromide (4.86 g, 3.40 mL, 40.2 mmol, 2.1 equiv.) was added over 30 min and the reaction mixture was heated to reflux for 30 min. The reaction mixture was cooled to 0 °C and HCl (2N, 50 mL) was added. The aqueous phase was extracted with Et_2O (2 × 50 mL), dried over $MgSO_4$, filtered and concentrated under reduced pressure. The title compound, a colourless oil, was obtained after Kugelrohr distillation (65 °C, 7.1 × 10^{-2} mbar) (3.35 g, yield: 70%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.24 (6H, t, J = 7.1 Hz, $MeCH_2$), 2.63 (4H, dt, J = 7.4 Hz, 1.2 Hz, CH_2-CH=CH_2), 4.18 (4H, q, J = 7.1 Hz, $MeCH_2$), 5.08–5.14 (4H, m, CH=CH_2), 5.66 (2H, ddt, J = 16.5 Hz, 10.6 Hz, 7.4 Hz, CH=CH_2).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 14.1, 36.8, 57.3, 61.2, 119.1, 132.4, 170.8.

GC/MS-CI(NH_3); *m*/*z* (%): 259.1 (5), 258 (33) [$(M-NH_4)^+$], 242 (14), 241 (100) [$(M-H)^+$].

IR (Film): ν = 3464, 3080, 2982, 2936, 1733, 1642, 1465, 1445, 1418, 1390, 1367, 1324, 1286, 1257, 1217, 1196, 1144, 1097, 1037, 994, 921, 858, 806 cm^{-1}.

Anal. Cald for $C_{13}H_{20}O_4$: C, 64.98; H, 8.39. Found: C, 65.28; H, 8.59.

*4.1.6. Diethyl 2-allyl-2-(2-methylallyl)malonate **8***

NaH (0.17 g of a 60% suspension in mineral oil, 4.20 mmol, 3.0 equiv.) was suspended in anhydrous THF (20 mL) and a solution of diethyl 2-(2-methylallyl)malonate (0.30 g, 1.40 mmol) in anhydrous THF (5 mL) was added. After 30 min at rt., allylbromide (0.51 g, 0.36 mL, 4.20 mmol, 3.0 equiv.) was added dropwise. After stirring for 24 h at rt., H_2O was added and the aqueous phase was extracted with Et_2O (3 × 50 mL), dried over $MgSO_4$ and concentrated under reduced pressure. The crude product was purified by column chromatography (d = 5 cm, h = 3.5 cm, CH:EE 10:1) to give the title compound as a colourless oil (0.34 g, yield: 95%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.25 (6H, t, J = 7.1 Hz, $MeCH_2$), 1.67 (3H, m_c, CH_2-C(CH_3)=CH_2), 2.67 (2H, ddt, J = 7.3 Hz, 1.2 Hz, 1.2 Hz, CH_2-CH=CH_2), 2.70 [2H, m_c, CH_2-C(CH_3)=CH_2), 4.12–4.23 (4H, m, $MeCH_2$), 4.76 (1H, m_c, CH_2-C(CH_3)=CH_2], 4.87 (1H, m_c, CH_2-C(CH_3)=CH_2), 5.06–5.12 (2H, m, CH=CH_2), 5.69 (1H, ddt, J = 16.6 Hz, 10.5 Hz, 7.3 Hz, CH=CH_2).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 14.0, 23.2, 36.8, 40.1, 57.0, 61.2, 115.7, 118.9, 132.7, 140.6, 171.2.

GC/MS-CI(NH_3); *m*/*z* (%): 272 (6) [$(M-NH_4)^+$], 256 (15), 255 (100) [$(M-H)^+$].

IR (Film): ν = 3464, 3079, 2983, 2939, 1733, 1643, 1446, 1367, 1325, 1292, 1278, 1244, 1210, 1187, 1141, 1096, 1064, 1036, 898, 867, 774 cm^{-1}.

Anal. Cald for $C_{14}H_{22}O_4$: C, 66.12; H, 8.72. Found: C, 65.91; H, 8.63.

*4.1.7. Diethyl 2-allyl-2-(but-3-enyl)malonate **9***

NaH (0.55 g of a 60% suspension in mineral oil, 13.8 mmol, 2.9 equiv.) was suspended in anhydrous THF (40 mL) and diethyl 2-(but-3-enyl)malonate (1.00 g, 4.70 mmol), dissolved in anhydrous THF (5 mL), was added dropwise. After stirring for 30 min at rt., allylbromide (1.67 g, 1.18 mL, 13.8 mmol, 2.9 equiv.) was added. After 24 h at rt., H_2O (50 mL) was added and the aqueous phase was extracted with Et_2O (3 × 60 mL). After drying over $MgSO_4$ and concentration under reduced pressure, the title compound was obtained as a colourless oil (1.07 g, yield: 90%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.25 (6H, t, J = 7.1 Hz, $MeCH_2$), 1.97 (4H, m_c, CH_2-CH=CH_2 and CH_2-CH_2), 2.66 (2H, dt, J = 7.4 Hz, 1.2 Hz, CH_2-CH_2), 4.18 (4H, q, J = 7.1 Hz, $MeCH_2$), 5.00 (2H, m_c, CH_2-CH_2-CH=CH_2), 5.07–5.14 (2H, m, CH_2-CH=CH_2), 5.65 (1H, ddt, J = 17.2 Hz, 9.9 Hz, 7.3 Hz, CH_2-CH_2-CH=CH_2), 5.73–5.84 (1H, m, CH_2-CH=CH_2).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 14.2, 29.4, 30.1, 37.1, 57.2, 61.2, 115.1, 118.9, 132.5, 137.7, 171.2.

GC/MS-CI(NH_3); m/z (%): 272 (22) [$(M-NH_4)^+$], 256 (15), 255 (100) [$(M-H)^+$], 209 (6), 200 (10).

IR (Film): ν = 3449, 3080, 2981, 2960, 2928, 2856, 1733, 1642, 1448, 1367, 1271, 1242, 1211, 1142, 1096, 1036, 997, 916, 860, 774 cm^{-1}.

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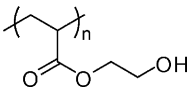
[12] Poly-(2-hydroxyethylacrylate) (PHEA):



perfluoropolyether (PFPE): $-(CF_2CF_2O)_n-(CF_2O)_m-$.
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