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Monomeric and polymeric amphiphiles with oligofunctional carboxylic headgroups

1. Synthesis of amphiphiles with different numbers of ester and acidogroups

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Dedicated to Professor Hinrich Seidel on the occasion of his 60th birthday

Summary

Monomeric amphiphiles with oligofunctional carboxylic headgroups have been synthesized. The molecules were provided with allylic endgroups which enabled the preparation of side-chain polymers by a platinum-catalyzed addition to Si-H containing poly(siloxanes)s. DSC and polarizing microscopy indicate no mesomorphic behavior in the case of monomers while the polymers exhibit smectic lc phases.

Introduction

Since Lord Rayleigh first reported on monomolecular films on a water surface about 100 years ago there has been a considerable interest in organized mono- and multilayers. Their potential applications for surface modification, nonlinear optics, microelectronics and chemical or biolological sensing devices have increased the research activity in the last few years /1-3/. Besides the investigation of classical monolayer forming molecules like long chain fatty acids /4/, many new amphiphiles with cationic, anionic or nonionic headgroups and a variety of specially designed hydrophobic tails have been synthesized and their film building properties have been studied /5,6/. A great problem which restricts the practical utility of the mono- and multilayers is the poor longterm stability since the molecules in a monolayer are in general held together largely by van der Waals forces. Therefore several approaches have been made to enhance the stability of the monolayer structure e.g. by incorporation of functional groups providing greater intermolecular interactions. The introduction of a polymerizable group offers another possibility of stabilization by creating covalent bondings between the molecules in a monolayer by a polymerization. Two different routes can be used for amphiphilic monomers: the polymerization after monolayer or multilayer building with the danger of disturbing the order in the film during the polymerization /7,8/ or the spreading of a preformed amphiphilic polymer on the water surface /9,10/, where difficulties from thermodynamic reasons can arise by forcing a three-dimensional polymer coil into a two-dimensional order at the air-water interface.
Although numerous investigations have been made in the recent years, the various interactions that lead to the formation of stable monolayers on the water surface are not completely enlightened. In order to obtain more informations about the influence of variations in a molecule on its film-building properties, we have prepared amphiphilic substances with different numbers of carboxylic ester and acido groups. The molecules were provided with allylic endgroups, so polymers with amphiphilic side chains could be made by the addition

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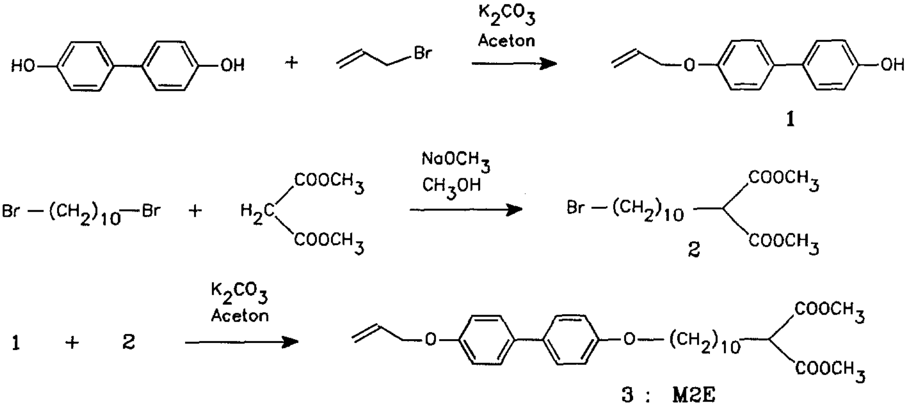
to Si-H containing siloxanes. The siloxan backbone was chosen because of the good stability and the high flexibility which facilitates the ordering of the polymer molecules on the water surface.

Results

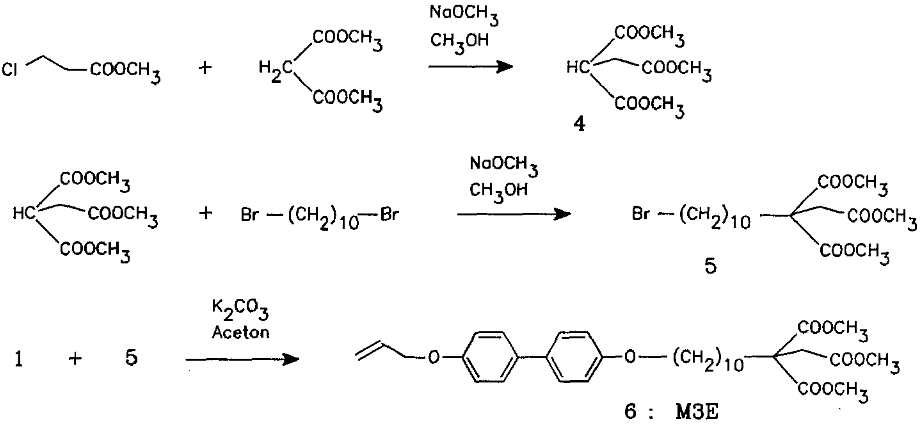
The monomers with 2 - 4 ester groups were synthesized according to scheme 1.

Scheme 1:

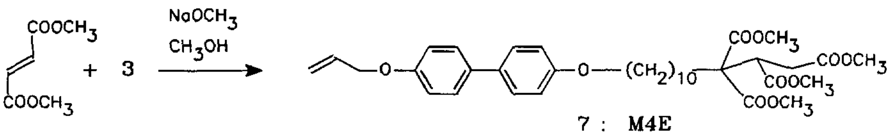
M2E:



M3E:



M4E:



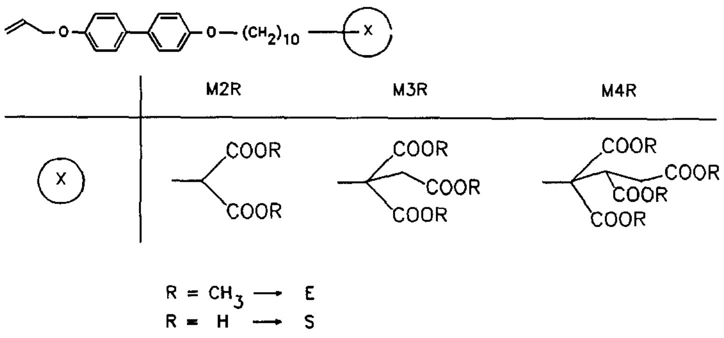
The hydrophobic unit is identical for all monomers, consisting of an allyl group that allows the addition to a siloxan-backbone, a biphenyl unit which is known from liquid crystals as a good mesogen enhancing the ordering tendency, and a flexible decylene spacer decoupling the hydrophilic headgroup from the rigid part of the molecule.

The amphiphilic diester **M2E** was synthesized via alkylation of dimethylmalonat with dibromodecan followed by the reaction of the 10-bromodecyl-dimethylmalonat with 4-allyloxy-4'-hydroxybiphenyl. The introduction of an additional ester group by a preceeding alkylation of dimethylmalonat with methyl-(2-chloro)acetate led to the amphiphilic triester **M3E**. This route, however, was not suitable for the preparation of **M4E**, since the alkylation of a tetraester, obtained by the reaction of dimethylfumarat with dimethylmalonat, gave only poor yields presumably caused by sterical hindrance. Hence the fumaric ester was added in the last step to **M2E** yielding the desired amphiphilic tetraester **M4E**. The number of ester groups was confirmed by analyzing the integral of the peaks at 3,6 to 3,8 ppm in the ^{1}H-NMR spectrum.

Saponification of the esters **M2E** - **M4E** under basic conditions yielded the corresponding acids **M2S**, **M3S** and **M4S**. The ^{1}H-NMR spectra of the acids do not show any signal at 3,6 - 3,8 ppm thus confirming complete hydrolysis.

Table 1 gives a summary of the synthesized monomers.

Table 1: Monomeric amphiphiles

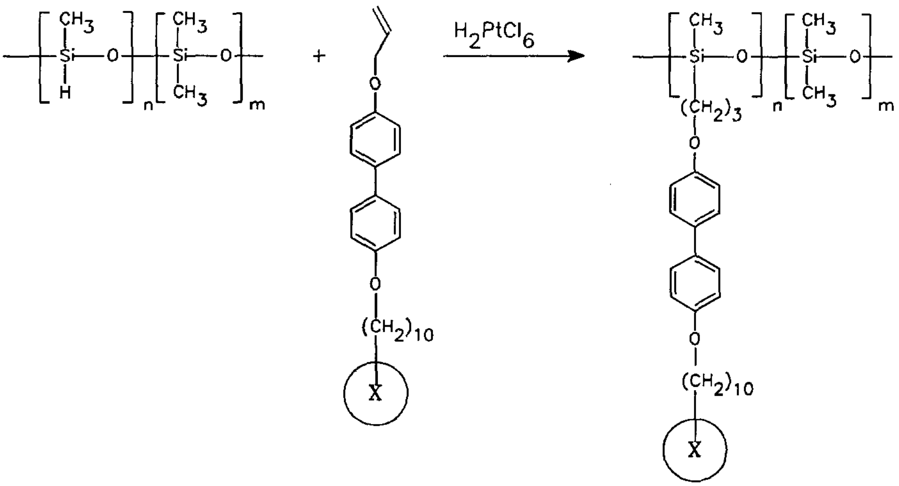


Polymers with a highly flexible backbone and amphiphilic side chains were obtained by a platinum-catalyzed addition of the corresponding monomers to poly(hydrogen methylsiloxan) (scheme 2) yielding **Si2E**, **Si3E** and **Si4E**. Additionally, copolymers with Si-H-contents of 45% and 18% were prepared by equilibration of poly(HMS) and octamethylcyclotetrasiloxane in order to study the effect of dilution of amphiphilic sidechains. The hydrosilylation reaction of these copolymers with **M2E** yielded **Co50Si2E** and **Co20Si2E**.

The catalyst solution H_2PtCl_6 in isopropanol was freshly prepared each time prior to use, nevertheless the polymers were lightly coloured from traces of finely dispersed platinum-metal, an effect that has been already described by GRAY and coworkers /11/, who observed that the intensity of colour depends on the age of catalyst solution. All polymers were easily soluble in THF or chloroform, so crosslinking can be excluded. The GPC traces of all polymers exhibit unimodale distributions and reasonable molecular weights, a further indice for the regular nature of the hydrosilylation reaction.

The synthesis of polymeric acids could not be achieved because the addition of the free acids analogous to the esters would lead to side reactions due to the hydridic character of the Si-H bonds. Hydrolysis of the polymeric methylesters under basic or acid conditions as well as nucleophilic cleavage of the methylesters led to a degradation of the polymer backbone. Attempts to introduce other protecting groups, e.g. the preparation of trimethylsilylesters, were not successful. The densitiy of carboxylic groups prevents the complete reaction with the protecting agens and the separation of reacted and unreacted acid groups, who partly are present in the same molecule, is not possible. Therefore our investigations were restricted to the polymeric esters.

Scheme 2:



	n	m	X
Si2E	1	-	2E
Si3E	1	-	3E
Si4E	1	-	4E
Co50Si2E	0,45	0,55	2E
Co20Si2E	0,18	0,82	2E

Table 2: Thermal transitions of monomers and polymers, determined by DSC and polarizing microscopy

	T_g (°C)	T_1 (°C)	T_2 (°C)	T_i (°C)
MBr	-	76[1)]	-	98
M1E	-	-	-	116
M2E	-	70[2)]	-	98
M3E	-	-	-	93
M4E	-	-	-	85
Si2E	-48	84	115	133
Si3E	-29	87	-	122
Si4E	-14	75	-	109
Co50Si2E	-47	77	-	80

T_g = glass transition temperature; T_i = transition to isotropic state
1) only in the cooling curve; 2) small peak, no lc transition

Differential scanning calorimetry (DSC) and polarizing microscopy were used to get first informations about ordering tendency and phase transitions. The acids undergo decarboxylation when they are heated over their melting point and therefore only the esters were investigated.

Table 2 summarizes the phase behaviour of monomers and polymers. Surprisingly for the monomers **M2E** - **M4E** no phase transition to a lc phase was observed, though related molecules with the biphenyl moiety as mesogen show smectic liquid crystal structures /12/. The small peak at 70°C in the DSC curve of **M2E** is presumably caused by a transition between two crystalline phases. In order to get more informations about the influence of the headgroup, the monoester **M1E** and **MBr**, representing the hydrophobic part of the amphiphiles with X = Br, were prepared. While **MBr** shows a lc transition to a smectic phase, **M1E** as well as the other monomeric esters does not exhibit a liquid crystalline structure. Propably interactions of the polar estergroups restrict the mobility of the flexible tails which is known to be necessary for lc behaviour.

All polymers display several thermal transitions. At low temperature, they exhibit a glass transition. For **Si2E** two transitons at T_1 and T_2 are observed before the melting point is reached, while the other polymers present only the transition at T_1. Above T_1 all polymers display a smectic mesophase. The siloxane backbone may facilitate the formation of lc phases due to its flexibility. The increase in number of estergroups leads to a rise in T_g

caused by polar interactions, while the melting points for monomers as well as for polymers is lowered due to sterical hindrances in the arrangement of side chains.
The balance between rigid and flexible parts in a molecule including the polymer backbone is expected to have influence on the arrangement at the water surface too, but the more important fact will be the balance of hydrophobic and hydrophilic components. So even if no lc behaviour is observed, the formation of well-ordered monolayers at the air-water interface is possible.

Experimental

4-Allyloxy-4'-hydroxybiphenyl **1**:
1 was synthesized according to a procedure given by FINKELMANN et al. /13/. Pure product was obtained by recrystallization from methanol with a small amount of hydrochloric acid.
Yield: 39% mp: 168-169°C
^{1}*H-NMR* (CH_3OD, δ ppm): 8,5-8,0 (s, broad, 1H, O$\underline{H}$); 7,6-6,8 (m, 8H, aromatic);
6,3-5,9 (m, 1H, C=C$\underline{H}$-C-O); 5,6-5,1 (m, 2H, C$\underline{H}_2$=C-C-O); 4,6 (m, 2H, C=C-C$\underline{H}_2$-O)

10-Bromodecyl-dimethylmalonate **2**:
2,3 g (0,1 mol) sodium were dissolved in 50 ml absolute methanol. To the hot solution 13,2 ml dimethylmalonate (0,09 mol) and 30 g (0,1 mol) dibromodecane were added successively, and the mixture was heated under reflux for 16 h. Methanol was distilled off, the residue was poured into 150 ml of ice water and the aqueous phase was extracted three times with diethylether. The combined ether extracts were dried over sodium sulfate and the ether was removed on a rotovapor. A colourless oil was obtained after purification of the crude product by column chromatography with a mixture of ethyl acetate/cyclohexane (1:5) as eluent.
Yield: 48% (GC: 99,2%)
^{1}*H-NMR* ($CDCl_3$, δ ppm): 3,7 (s, 3H, -COOC$\underline{H}_3$); 3,4 (t, 2H, -C$\underline{H}_2$-Br); 3,35 (t, 1H, -C$\underline{H}$(COOR)$_2$);
2,1-1,7 (m, broad, 4H, -C$\underline{H}_2$-CH$_2$-Br, -C$\underline{H}_2$-CH(COOR)$_2$); 1,5-1,2 (s, broad, 14 H, -C$\underline{H}_2$-)

1,1,2-(Tricarbomethoxy)ethane **4**:
4 was synthesized from dimethylmalonate and methyl(2-chloro)acetate according to the preparation of **2**. The crude product was distilled in vacuo at 90°C / 31 mbar.
Yield: 48% (GC: 96%)
^{1}*H-NMR* ($CDCl_3$, δ ppm): 3,8 (t, 1H, -C$\underline{H}$(COOR)$_2$-); 3,75 (s, 6H, -(COOC$\underline{H}_3$)$_2$);
3,65 (s, 3H, -COOC$\underline{H}_3$); 2,9 (d, 2H, -C$\underline{H}_2$-COOR)

2-(10-Bromodecyl)-1,1,2-(tricarbomethoxy)ethane **5**:
5 was synthesized by the alkylation of **4** with dibromodecane according to the preparation of **2**. This time, the Na-methanolate solution was added to the mixture of **4** and dibromodecane. The crude product was purified by column chromatography with ethyl acetate/cyclohexane (1:5) yielding a colourless, viscous oil.
Yield: 35% (GC: 98,5%)
^{1}*H-NMR* ($CDCl_3$, δ ppm): 3,75, 3,6 (2 s, 6+3 H, -COOC$\underline{H}_3$); 3,4 (t, 2H, -C$\underline{H}_2$-Br);
2,9 (s, 2H, -C$\underline{H}_2$-COOR); 2,1-1,2 (14 H, -C$\underline{H}_2$-)

Monomers **M1E** through **M3E** were prepared via Claisen etherification of **1** with the corresponding ω-bromo-compounds (methyl-(11-bromo)undecanoate, **2** or **5**), as described below:
A mixture of 8 g (35 mmol) of **1**, 4,8 g (35 mmol) potassium carbonate, 40 mmol of ω-bromo-compound and a small amount of potassium iodide in 200 ml of absolute acetone was refluxed for 72 h. The solvent was removed on a rotavapor, the residue was poured into 200 ml of ice water and the aqueous phase was extracted with chloroform. The combined organic extracts were washed with 5% aqueous solution of sodium bicarbonate and water, dried over anhydrous sodium sulfate, filtered and the solvent was evaporated. The product was purified by column chromatography with ethyl acetate/cyclohexane (1:4) as eluent, followed by recrystallization from cyclohexane.

M1E: *4-Allyloxy-4'-(10-carbomethoxy-decyloxy)biphenyl*:
Yield: 56% mp: 116°C
^{1}H-NMR ($CDCl_3$, δ ppm): 7,6-6,9 (2 m, 8 H, aromatic); 6,3-5,9 (m, 1H, $C{=}C\underline{H}$-C-O);
5,6-5,2 (m, 2H, $C\underline{H}_2{=}C$-C-O); 4,6 (m, 2H, $C{=}C$-$C\underline{H}_2$-O); 4,0 (t, 2H, -$C\underline{H}_2$-O);
3,7 (s, 3H, $COOC\underline{H}_3$); 2,3 (t, 2H, -$C\underline{H}_2$-COOR); 1,8-1,2 (16H, -$C\underline{H}_2$-)

M2E 3:
4-Allyloxy-4'-(11,11-biscarbomethoxyundecyloxy)biphenyl:
Yield: 68% mp: 98°C
^{1}H-NMR ($CDCl_3$, δ ppm): ≥ 3,9 ppm (see **M1E**); 3,7 (6H, $COOC\underline{H}_3$); 3,35 (1H, -$C\underline{H}(COOR)_2$);
2,1-1,2 (18H,-$C\underline{H}_2$-)

M3E 6:
4-Allyloxy-4'-(11,11,12-triscarbomethoxydodecyloxy)biphenyl:
Yield: 76% mp: 93°C
^{1}H-NMR ($CDCl_3$, δ ppm): ≥ 3,9 ppm (see **M1E**); 3,75-3,65 (9H,$COOC\underline{H}_3$); 2,9 (2H, -$C\underline{H}_2$-COOR);
2,1-1,2 (18H, -$C\underline{H}_2$-)

M4E 7:
4-Allyloxy-4'-(11,11,12,13-tetrakiscarbomethoxytridecyloxy)biphenyl:
7 was synthesized from **2** and dimethylfumarate according to the procedure described for the preparation of **5**. The crude product was purified by column chromatography with ethyl acetate/cyclohexane (1:3) as eluent.
Yield: 65% mp: 85°C
^{1}H-NMR ($CDCl_3$, δ ppm): (≥ 3,9 ppm see **M1E**); 3,8-3,5 (13 H,-$COOC\underline{H}_3$, -$C\underline{H}$(COOR)-);
2,8 (2H, -$C\underline{H}_2$-COOR); 2,1-1,2 (18H, -$C\underline{H}_2$-)

The monomeric acids **M2S** through **M4S** were obtained by basic saponification of the corresponding esters with an excess of KOH in ethanol/H_2O. An example is given below:
A mixture of the ester and a 1,5-fold molar excess of KOH for each carboxylic group in ethanol/H_2O (5:1) were heated under reflux for 48 h. During the hydrolysis the monomer dissolves as its potassium salt is formed. The reaction mixture was extracted with diethylether for separating nonhydrolyzed parts, then the mixture was acidified with dilute hydrochloric acid, until the pH remains at 2. The free carboxylic acids were filtered off, washed with water and recrystallized two times from ethyl acetate/cyclohexane (1:1).

M2S: Yield: 78% **M3S**: Yield: 65% **M4S**: Yield: 69%
The *^{1}H-NMR* Spectra of the monomeric acids correspond to the ester spectra, but the signal at 3,6-3,8 ppm is absent.

Si-H-containing copolymers:
The equilibration of appropriate amounts of octamethylcyclotetrasiloxane, poly(HMS) and hexamethyldisiloxane with trifluoroacetic acid was carried out as described in the literature /14/. The Si-H content was estimated by ^{1}H-NMR spectroscopy.

Side chain polymers:
The polymers **Si2E** through **Si4E**, **Co50Si2E** and **Co20Si2E** were prepared by a hydrosilylation reaction of the corresponding allyl-terminated monomer (10 mol% excess related to Si-H bonds) in toluene at 80°C with H_2PtCl_6 $6H_2O$ in isopropanol as catalyst /14/. The reaction was monitored by IR spectroscopy where the disappearence of the Si-H absorption band at 2175 cm^{-1} indicated complete conversion. The polymers except **Co20Si2E** were precipitated several times (6-8 times) from chloroform in methanol or petroleum ether, until no monomer could be detected by thin layer chromatography. **Co20Si2E** is a very viscous oil that could not be precipitated. Therefore this polymer was purified by preparative gel permeation chromatography with THF as eluent.
Yields: 60 - 75%
^{1}H-NMR ($CDCl_3$, δ ppm): 0,1-0,3 (-Si-C$\underline{H}_3$); 0,4-0,9(-Si-C$\underline{H}_2$-R); with exception of the allyl group all the other peaks correspond to the monomer spectra with the typical broadening of polymer peaks.

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