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**ORIENTED SUPRAMOLECULAR SYSTEMS -
POLYMERIC MONOLAYERS AND MULTILAYERS FROM PREPOLYMERIZED
AMPHIPHILES**

A. Laschewsky, H. Ringsdorf^{*)}, J. Schneider

Summary

Oriented polymeric membranes were originally prepared by polymerization or polycondensation of preoriented monomers. The introduction of hydrophilic spacer groups into the polymeric amphiphiles allowed the formation of highly ordered systems (monolayers, liposomes, multilayers) from prepolymerized amphiphiles: due to the partial decoupling of the different mobilities and orientation tendencies of the polymer chain and the amphiphilic side groups, these polymers are able to self-organize. In monolayer experiments the high order of these membranes could be demonstrated by their surface pressure area-diagrams. In addition the combination of order and mobility of these spacer groups containing polymeric amphiphiles allowed the formation of Langmuir-Blodgett-multilayers with a high layer correlation. Thus, disturbances in highly oriented layers can be avoided normally taking place during the polymerization reaction (e.g. contractions) or oriented monomeric layers.

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1. Self-Organization and the Formation of Supramolecular Systems

Order and mobility are two basic principles of mother nature. The two extremes are realized in the perfect order of crystals missing mobility and in the high mobility of liquids and gases missing the order. Both properties are combined in liquid crystalline phases based on the self-organization of structure anisotropic molecules. Their importance became more and more visible during the last years: in Material Science they are a basis of new materials, in Life Science they are responsible for many structure associated functions of biological systems. The main contribution of Polymer Science to thermotropic and lyotropic liquid crystals as well as to biomembrane models consists in the fact that macromolecules can stabilize organized systems and at the same time retain mobility. Polymer Science in between Life Science and Material Science?

Mesogenic units, detergents and lipids are formanisotropic molecules, showing a tendency to self-organize. Thus - as mentioned above - they are able to form organized structures like thermotropic liquid crystals, micelles and lyotropic liquid crystals, monolayers and liposomes. The functionalization of these organized units leads to synthetic supramolecular systems. They combine order and mobility and their function is based on their organization.

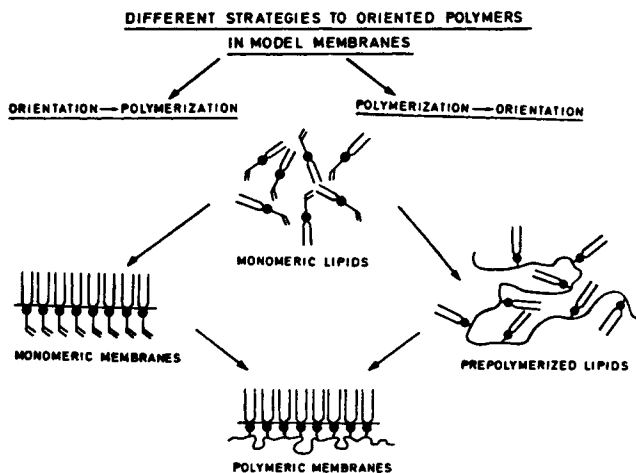
2. Strategies to Oriented Polymers in Model Membranes

Currently, there is great interest in liposomes, monolayers, bilayer membranes (BLM) and Langmuir-Blodgett multilayers as biomembrane models and furthermore because of their manifold potential applicability¹⁻⁶⁾. In general, these types of aggregates show poor stability in comparison with biomem-

branes. This lack of stability can be overcome by the polymerization of reactive groups within the amphiphiles^{2,3)}. In most cases, however, the resulting polymer chains interfere with the motion of the oriented side groups. Thus, a decrease or even the loss of the fluid phases of the membranes usually occurs^{2,3)}. More drastically, the reduced mobility, which is due to the polymer backbone, hinders the efficient self-organization of prepolymerized lipids.

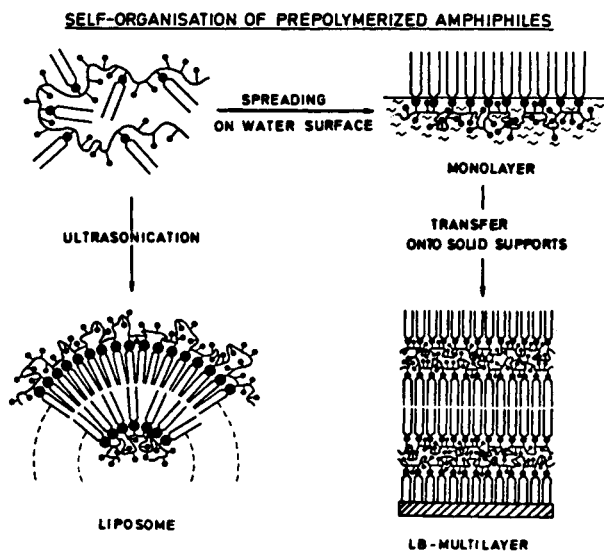
To overcome this problem and to retain the fluidity, which is a fundamental property of biological membranes, the incorporation of hydrophilic spacer groups into polymerizable lipids has recently been realized⁷⁾. Due to the decoupling of the motion of the polymer main chain and the bilayer via a side group spacer, these polymers directly form model membranes from prepolymerized lipids. Highly ordered monolayers from polymeric lipids were obtained and could be transferred onto solid supports to build up polymeric LB-multilayers⁷⁾.

The two different strategies to oriented polymers in model membranes are summarized in the following scheme.



Polymeric amphiphiles with three types of spacers were obtained. The polymerization of lipids with hydrophilic spacer groups between the amphiphilic parts and the polymerizable units (spacer lipids)⁷⁾ leads to homopolymers with side group spacers. The copolymerization of conventional monomeric lipids with hydrophilic comonomers results in copolymers with main chain spacers only. The copolymerization of monomeric spacer lipids and hydrophilic comonomers leads to polymers containing both main chain spacers as well as side group spacers (combined spacers).

The self-organization of copolymers from monomeric lipids and hydrophilic comonomers is outlined in the following scheme.

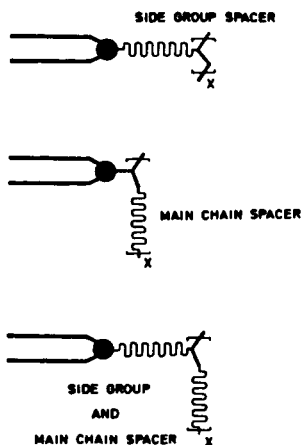


The application of prepolymerized spacer lipids has the advantage that side reactions and structural changes of the membranes induced by the polymerization reaction of oriented monomeric layers following the other route are avoided.

Up to now, the spacer concept has mainly been used for rather complicated lipids with hydrophilic spacer groups between the polymer chain and the amphiphilic side groups. In this contribution it will be demonstrated that this spacer model can be expanded by using copolymers prepared from easily accessible unsaturated amphiphiles and hydrophilic comonomers forming a main chain spacer. A similar concept has successfully been realized in liquid crystalline side group polymers where spacers can be placed either in the side groups⁸⁾ or in the polymer backbone⁹⁾. It has also been shown that the introduction of flexible comonomer units did not prevent the formation of LC-phase of copolymers⁹⁾.

The different possibilities for spacer groups containing amphiphilic polymers to decouple the motions of the polymer main chains from the membrane forming side groups are summarized in the following scheme.

SPACER GROUPS IN POLYMERIC AMPHIPHILES



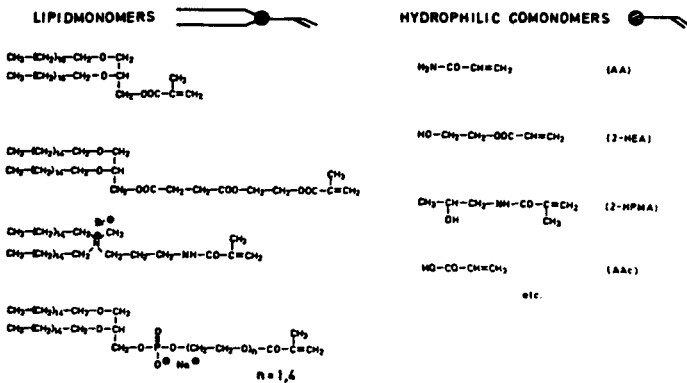
The spreading of amphiphilic copolymers containing hydrophilic spacer groups on water surfaces should lead to monolayers. Their orientation is not disturbed by the polymer chain whereas the isotherms are strongly effected by the length of the spacer group. In addition, the combination of order and mobility within the monolayers of these polymers might lead to LB-multilayers with perfectly packed bilayers and a high layer correlation.

First attempts to use polymers for the self-organization in monolayers, multilayers and liposomes have already been described in literature^{7,10-13}).

3. Possibilities to Introduce Hydrophilic Spacer Groups into Amphiphilic Polymers

The monomeric lipids and hydrophilic comonomers used for the preparation of amphiphilic homopolymers and copolymers containing hydrophilic spacer groups are summarized in the following chart.

HOMOPOLYMERS AND COPOLYMERS PREPARED FROM:



4. Influence of Hydrophilic Spacer groups on the Spreading Behavior of Polymeric Amphiphiles

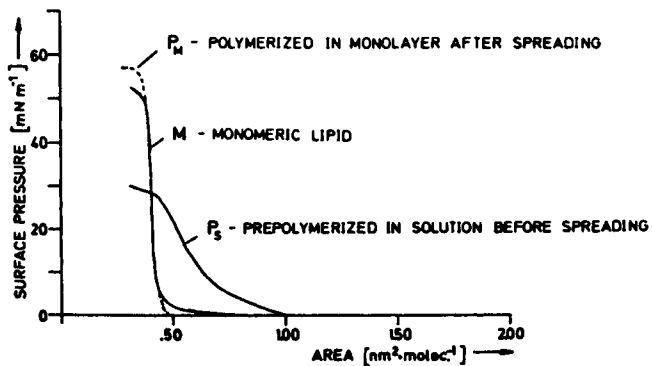
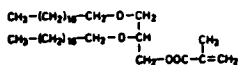
Spreading Behavior of Monomeric and Polymeric Lipids without Spacers:

As shown in chapter 2, there are two strategies to obtain polymeric membranes. Although the spreading of prepolymerized lipids is much easier to perform experimentally, the resulting monolayers are less defined than polymeric monolayers obtained by the other method, namely the polymerization of oriented monomers. An efficient self-organization of the amphiphilic side groups is hindered by the polymer backbone.

These problems are demonstrated by comparing the polymeric monolayers prepared from prepolymerized lipids (P_S) and from oriented monomeric lipids (M) followed by polymerization (P_M).

SPREADING BEHAVIOUR OF MONOMERIC AND POLYMERIC LIPIDS WITHOUT SPACERS

POLYMERIZABLE LIPID WITHOUT SPACER



The "classical" way, i.e. the UV polymerization of monomeric monolayers¹⁵⁾ of the glycerolipid without spacer leads to polymeric monolayers (P_M). The tight chain packing in the solid analogue phase is preserved after polymerization, whereas the collapse pressure is even slightly increased compared to the monomer (M). If the prepolymerized lipid (P_S) is spread, much less defined monolayers are formed: there is no hint on a defined condensed phase. The slope of the curve is less steep and the collapse pressure is strongly reduced. This indicates a poor self-organization of the prepolymerized homopolymer. The direct attachment of the amphiphilic side groups to the polymeric backbone obviously reduces the capability of self-organization. The remarkable difference in the spreading behavior of the prepolymerized lipid (P_S) and the lipid polymerized in the monolayer (P_M) demonstrates the importance of the spacer concept: a separation of the amphiphilic side groups and the polymer backbone via flexible spacers is necessary.

Spreading Behavior of Homopolymers with Side Group Spacers (Type A):

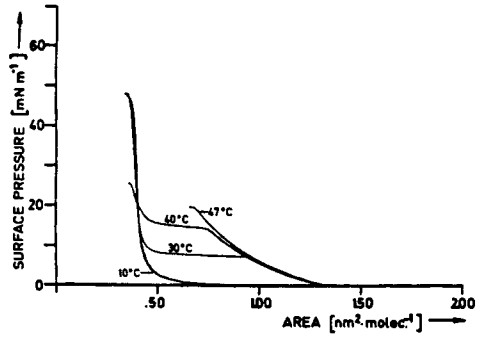
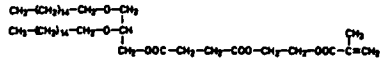
The influence of spacer groups on the spreading behavior of prepolymerized systems can be demonstrated by the following figures.

The monomeric glycerolipid with an ester spacer group shows a temperature dependent spreading behavior with a coexistence of fluid and solid analogue phases.

If this monomer is prepolymerized in solution the polymer can be used for spreading experiments leading to the following surface pressure - area diagram of the prepolymerized homopolymer.

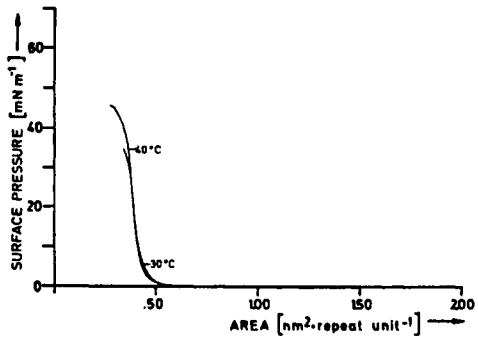
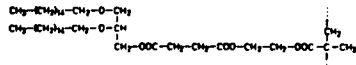
SURFACE PRESSURE-AREA DIAGRAM OF A MONOMER

POLYMERIZABLE LIPID WITH A SHORT SIDE GROUP SPACER



SURFACE PRESSURE-AREA DIAGRAM OF A HOMOPOLYMER

LIPID WITH A SHORT SIDE GROUP SPACER



The isotherms of the prepolymerized homopolymer exhibits a solid analogue phase with a collapse area of ca. 0.4 nm^2 per repeat unit, indicating a tight packing of the alkyl chains, directly comparable to the packing behavior of the monomer. Thus even the incorporation of a short side group spacer allows an efficient self-organization of prepolymerized amphiphiles. In contrast to the isotherms of the monomer, only a solid analogue phase is observed. An increased mobility leading to a liquid analogue phase but retaining the solid analogue packing can be accomplished by increasing the spacer length of either type⁷⁾. This is demonstrated in the following chapter.

Spreading Behavior of Copolymers Combining Main Chain Spacers and Side Group Spacers (Type C):

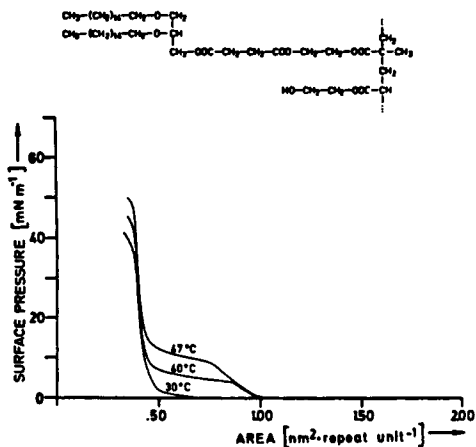
In addition to the use of side group spacers, the efficient decoupling of polymer backbone and amphiphilic side groups is also achieved by the incorporation of flexible main chain spacers. This is possible e.g. by copolymerization of polymerizable spacer lipids with hydrophilic comonomers according to the examples given in chapter 3. The spreading behavior of copolymers with side group and main chain spacers is demonstrated in the following figures.

In the case of the copolymer with a 1:1 lipid/comonomer ratio a solid analogue phase with tightly packed alkyl chains and a high collapse pressure is observed as well as in the case of the monomer and the homopolymer described in the figures above. In contrast to the homopolymer bearing only a short side group spacer, the additional main chain spacer leads to a coexisting fluid phase as shown for the monomer. Even the temperature dependence of the isotherms of the monomer and the 1:1 copolymer are comparable.

SURFACE PRESSURE-AREA DIAGRAM OF A COPOLYMER

LIPID WITH A SHORT SIDE GROUP SPACER AND A HYDROPHILIC COMONOMER

RATIO: LIPID / COMONOMER 1:1



The formation of fluid phases of the copolymers is favoured with an increasing content of hydrophilic comonomers (increasing spacer length) as demonstrated for the copolymer with a 1:5 lipid/comonomer ratio.

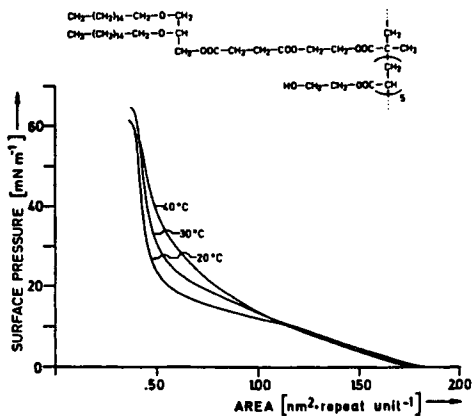
The fluid phase is enlarged from $1.05 \text{ nm}^2/\text{repeat unit}$ of the 1:1 copolymer at 40°C to $1.80 \text{ nm}^2/\text{repeat unit}$ of the 1:5 copolymer. This is due to the increased mobility of the monolayers caused by the increased spacer length.

For the discussed system with combined spacers the influence of the hydrophilic comonomer units as main spacers is once more summarized in the following figure.

SURFACE PRESSURE-AREA DIAGRAM OF A COPOLYMER

LIPID WITH A SHORT SIDE GROUP SPACER AND A HYDROPHILIC COMONOMER

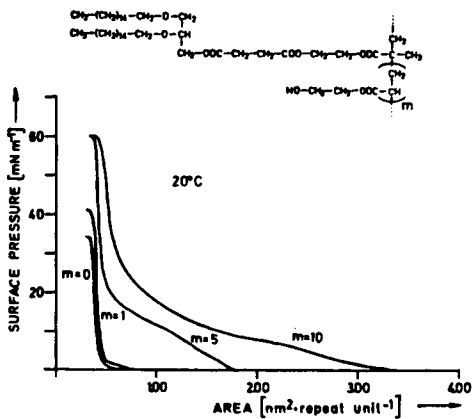
RATIO: LIPID / COMONOMER 1:5



SURFACE PRESSURE-AREA DIAGRAMS OF POLYMERS

INFLUENCE OF THE LENGTH OF THE MAIN CHAIN SPACER

ON THE SPREADING BEHAVIOR



At 20°C the isotherm of the 1:1 copolymer is directly comparable to the isotherm of the homopolymer, but additionally showing a slightly increased collapse pressure. The isotherms of the 1:5 and the 1:10 copolymers show large liquid analogue phases retaining the solid analogue phase. These monolayers even have higher collapse pressures than those of the homopolymer and the 1:1 copolymer.

5. Formation of Multilayers from Prepolymerized Amphiphiles

LB-Multilayers show a great potential for various applications^{1,5,6,16}). A sufficient stability of the multilayers is a basic requirement which can in general be achieved by covalent linkage of the amphiphiles, i.e. by polymerization¹⁷⁻¹⁹).

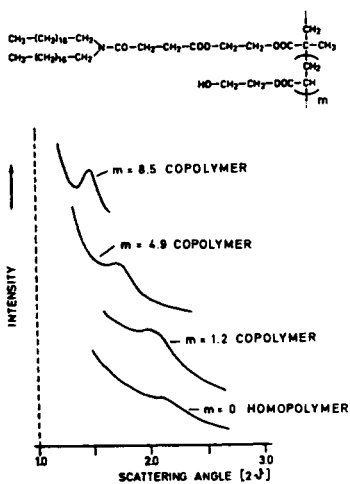
However, the classical route to polymeric multilayers, which is the transfer of monomeric layers and a subsequent polymerization in the multilayers¹⁷), gives rise to structural changes which can damage the layer structure and cause defects^{7,20-22}).

First attempts to use prepolymerized amphiphiles to avoid these problems have already been published. Polymeric amphiphiles with side group spacers have been used⁷). In addition the spreading behavior and multilayer formation of alternating copolymers based on hydrophobized maleic anhydride derivatives were described^{10,23,24}).

Based on the positive results of the monolayer experiments of prepolymerized lipids with combined spacers, the question arose if they can be used to prepare LB-multilayers and to investigate the influence of the spacer length on the structure of the multilayers. First experiments will be described here and the results are summarized in the following figures.

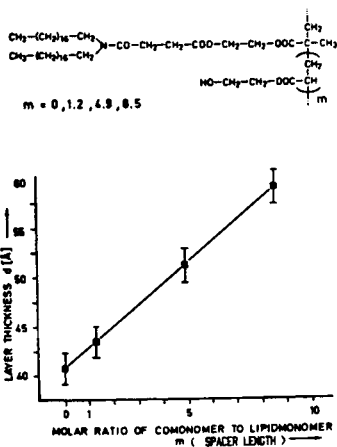
It could be shown that it was possible to build up polymeric Langmuir-Blodgett multilayers from the copolymers described in chapter 3. By small angle x-ray scattering investigations (SAXS) of LB-multilayers from amphiphilic copolymers with different lengths of the main chain spacer scattering reflexes were found for all the compounds.

SMALL ANGLE X-RAY SCATTERING OF POLYMERIC LB-MULTILAYERS



SPACINGS OF LANGMUIR-BLODGETT MULTILAYERS FROM PREPOLYMERIZED AMPHIPHILES

IN DEPENDENCE OF THE LENGTH OF THE
MAIN CHAIN SPACER

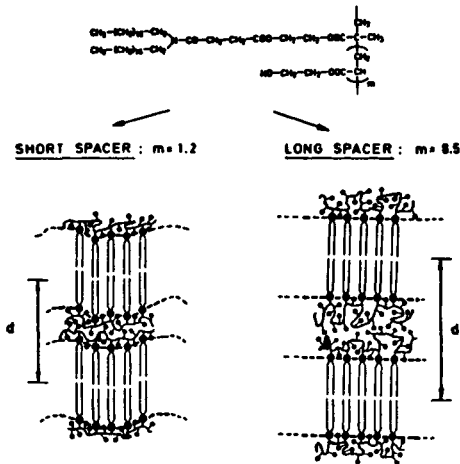


The introduction of the hydrophilic comonomers (main chain spacer) causes two effects. The first effect is the shifting of the reflexes to smaller scattering angles with increasing comonomer content, showing an increase in layer thickness of the multilayers. If the layer thickness (spacings) of the polymeric bilayers is plotted against the comonomer content a linear relationship is found.

The second effect caused by the increasing comonomer content, corresponding to a higher flexibility within the layers is the enhanced scattering intensity which indicates that the quality of the layer correlation increases. This is once more demonstrated schematically in the last figure.

MULTILAYERS FROM PREPOLYMERIZED AMPHIPHILES

LAYER THICKNESS (d) AND LAYER CORRELATION (—) ARE INCREASED WITH THE LENGTH OF THE MAIN CHAIN SPACER



It was not to be expected that with increasing comonomer content that means with an increasing polymer load between the oriented bilayers their packing order increases, too. This points to an increased mobility within the LB-multilayers of main chain spacer containing copolymers.

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