Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Polymerization of Substituted Butadienes at the Gas-Water Interface

H. Ringsdorf[a]; H. Schupp[a]
[a] Institute of Organic Chemistry, University of Mainz, Mainz, West-Germany

To cite this Article Ringsdorf, H. and Schupp, H.(1981) 'Polymerization of Substituted Butadienes at the Gas-Water Interface', Journal of Macromolecular Science, Part A, 15: 5, 1015 — 1026

To link to this Article: DOI: 10.1080/00222338108056780

URL: http://dx.doi.org/10.1080/00222338108056780

J. MACROMOL. SCI.-CHEM., A15(5), pp. 1015-1026 (1981)

Polymerization of Substituted Butadienes at the Gas-Water Interface

H. Ringsdorf, H. Schupp, Institute of Organic Chemistry,
University of Mainz, 6500 Mainz, West-Germany

ABSTRACT

In order to investigate the polymerization behaviour of long-chain amphiphilic compounds in dependence of their orientation, 1,4-disubstituted butadienes of the type:

$$CH_3\text{-}(CH_2)_{12}\text{-}CH{=}CH\text{-}CH{=}CH\text{-}X \qquad X = \text{-}COOH,\ \text{-}CHO,\ \text{-}CH_2OH$$

have been synthesized and investigated in a monolayer at the gas-water interface. The orientation of the compounds has been studied by means of a Langmuir film balance. The alcohol exhibits an orientation similar to that of saturated compounds. The orientation of the aldehyde and the acid differ from the expected behaviour because of the enhanced hydrophilicity of the headgroup due to the conjugation of the carbonyl group to the diene unit. Attempts to polymerize the substances radically have been made in melt, in solution, in the crystalline state and in monolayers. A polymer was only obtained in the case of monolayer polymerization. This fact can be explained with the necessity of a defined orientation of the monomers before the polymerization. The polyreaction was followed by the contraction of the film. The kinetics of the polymerization show a different reactivity for the alcohol and the carbonyl compounds. The resulting polymer is assumed to have a poly-1,4-trans backbone.

INTRODUCTION

Up to now there have been numerous studies to influence a polyreaction by orienting amphiphilic molecules in a monolayer (1-4), which offers the unique possibility to orient and vary the packing of molecules without a suppression of the mobility (5). Whereas the former attempts were concerning with systems, the polymerizable unit of which is located in the hydrophilic headgroup (e.g. Octadecylmethacrylate (2,3), Vinylstearate (1) etc.), substances with a polymerizable group within the aliphatic chain were investigated more recently. The most intensive studies have been made with the Diacetylene carbonic acids (4). The solid-state polymerization of Diacetylenes has long been studied (5), and the orientation of the molecules within the crystal has then been substituted by a similar orientation in the monolayer or multilayer, respectively.

Therefore the question arose to prove the model considerations for polymerization behaviour by a system which is unable to polymerize neither in the crystalline state nor in solution. As model compounds, 1,4-disubstituted butadienes of the type:

$$CH_3\text{-}(CH_2)_{12}\text{-}CH{=}CH\text{-}CH{=}CH\text{-}X \qquad X = \begin{array}{l} -COOH \\ -CHO \\ -CH_2OH \end{array}$$

1a-c

have been synthesized and investigated in a monolayer.

EXPERIMENTAL

Octadecadienal (1b) was prepared according to the method of E.L. Pippen and M. Nonaka (9): 1-Methoxybut-1-en-3-yne, 41.9 g (0.51 mole), dissolved in 280 ml of tetrahydrofuran was added dropwise with stirring to a Grignard reagent prepared from 11.7 g (0.48 mole) of magnesium and 52.48 g (0.48 mole) of ethyl bromide in 300 ml of tetrahydrofuran while the mixture was maintained at about 40°C. After an additional hour of stirring at room temperature, the reaction flask was cooled and there was added over a period of 30 min a solution of 84.95 g (0.4 mole) of tetradecanal dissolved in 150 ml of tetrahydrofuran. After 2 hours of stirring at room temperature, the mixture was heated to reflux. 30 min later, the flask was cooled and the mixture was treated with 18.4 ml of ethanol. Twenty minutes later solid sodium aluminium hydride, 20 g (0.5 mole), was added in small portions over a period of 30 min. The mixture was stirred for 2 hours and permitted to stand overnight. It was then treated successively with ethyl acetate (20 ml), water (90 ml), and 4 N sulfuric acid (450 ml). The organic layer was separated and the aqueous layer was extracted with ether. The combined organic layers were washed with 10% sodium carbonate solution, 3 times with water and dried over sodium sulfate. The solvent was distilled under reduced pressure and the resulting solid was recrystallized several times from hexane. Yield: 48.5 g (46%) of a white solid with melting point of 33 °C.

Elemental analysis:			
	calc:	C: 81.75%	H: 12.20%
	found:	C: 81.54%	H: 12.34%

Octadecadienoic acid (1a): A solution of 8.16 g (0.05 mole) of silver nitrate in 100 ml of water was treated with a solution of 2.2 g (0.08 mole) sodium hydroxide in 20 ml of water. The precipitated silver oxide was washed with water and suspended in a solution of 10.4 g (0.26 mole) of sodium hydroxide in 150 ml of water. To this suspension 13.2 g (0.05 mole) of Octadecadienal in

40 ml ethanol was added over a period of 20 min at a temperature of 50-60 °C. The mixture was stirred for 3 hours and permitted to stand overnight. Then the mixture was acidified with hydrochloric acid and extracted several times with ether. From the ether extract the salt of the acid was removed by extraction with concentrated sodium carbonate solution; the water extract was reacidified and extracted with ether. The ether layer was dired over sodium sulfate and the solvent was allowed to evaporate. The resulting crystals were recrystallized from hexane. Yield: 4 g (29%), MP: 71 °C.

Elemental analysis: calc: C: 77.09% H: 11.50%
found: C: 77.24% H: 11.54%

Octadecadienol (1c): A solution of 10 g (0.04 mole) of Octadecadienal in 50 ml of ether was added dropwise to a suspension of 0.86 g (0.02 mole) of lithium aluminium hydride in 50 ml of ether. After 3 hours of stirring, the mixture was cooled and the remained hydride was destroyed by addition of ethyl acetate. The mixture was washed with water, the ether layer was separated and dried over sodium sulfate. After evaporation of the solvent, a white solid was obtained. Recrystallization from hexane yielded the pure product in 67% yield (7.2 g). MP: 58 °C.

Elemental analysis: calc: C: 81.13% H: 12.86%
found: C: 81.14% H: 13.04%

Monolayers were spread from chloroform solutions all having a concentration of approximately 1 mg/ml. The films were spread on a Lauda film balance, surface pressure and area were automatically recorded. Polymerization was carried out via UV-irradiation (254 nm) with an energy of 5 mW/cm^2 at the water surface. The enclosed film balance was purged with nitrogen 1 hour to and during polymerization. The water substrate was ion exchanged and then double distilled in an all-glass-apparatus.

The polymerization attempts in solution were carried out under nitrogen in sealed ampoules with 1 mole % azobisisobutyronitrile in benzene for 24 hours at 60 °C.

Irradiation experiments were made with an 200 W UV-lamp in a quartz ampoule for 8 hours. No change could be detected by TLC and IR-spectroscopy.

RESULTS AND DISCUSSION

The orientation of the molecules at the gas-water interface was studied by recording the pressure-area diagrams:

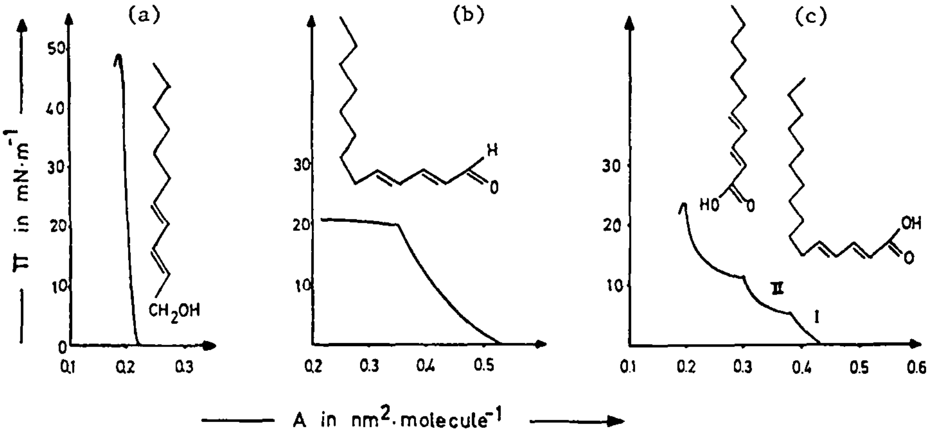


FIGURE 1a-c: Surface pressure-area diagrams at 20 °C of Octacecadienol (a), Octadecadienal (b) and Octadecadienoic acid (c)

The alcohol shows the same pressure-area diagram which was known from saturated compounds: The strong chain-chain interaction leads to a condensed film with an occupied area of about 0.20 nm^2/molecule, which is near to the closest packing of aliphatic chains, thus indicating a high degree of orientation and a dense packing.

The aldehyde forms an expanded film. The occupied area at the collapse point (0.35 nm^2/molecule) leads to the assumption that the whole diene group acts as a part of the headgroup and lies flat on the water surface. This orientation is caused by the conjugation of the diene unit to the carbonyl group, which polarizes the whole headgroup. At further compression of the film collapse occurs without forming a condensed phase.

In the case of the acid three phases can be seen depending on the temperature. The occupied area at the first transition point shows again, that the whole diene group lies flat on the water surface. When compressing the film the molecules are forced into an upright position and exhibit the normal expanded phase, as it is known from the saturated compound. Further compression leads to a condensed film.

Each of these three compounds was investigated with regard to their ability to undergo radical polymerization. The result is shown in table 1.

A polymer can only be obtained in monolayer polymerization. We assume the following reasons:

A polyreaction requires an orientation of the monomers before polymerization. Therefore a reaction in solution or melt is impossible. A polyreaction in the crystalline state, however, does not take place, because the diene units are not in the required close distance from each

TABLE 1

Polymerization Attempts of Disubstituted Butadienes

STATE	INITIATION	POLYM.
solution	AIBN	-
solution	UV	-
melt	UV	-
crystal	UV	-
monolayer	UV	+

other and the mobility of the molecules is too much suppressed.

The polymerization can be followed by measuring the contraction of the film versus the polymerization time. In the next figures the pressure-area diagrams of the monomeric and polymeric compounds and the area change versus time are shown.

Although in the case of the alcohol the change of the area per molecule is not very big, it can easily be measured. The reaction is finished after about 20 min. The resulting area is 0.23 nm^2/monomer unit, which corresponds to a close packing of the molecules. The reaction takes place without a change in the orientation of the molecules during the polyreaction.

The aldehyde has been polymerized at 15 °C at a constant pressure of 7 mN/m and 15 mN/m. In each case the same polymer was obtained. Two results of this reaction are remarkable:

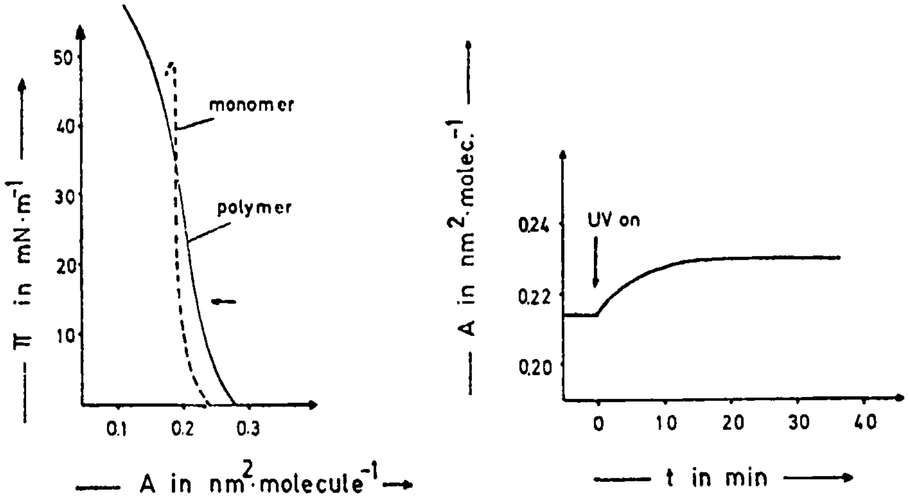


FIGURE 2: Pressure-area diagram and film contraction of Octadecadienol

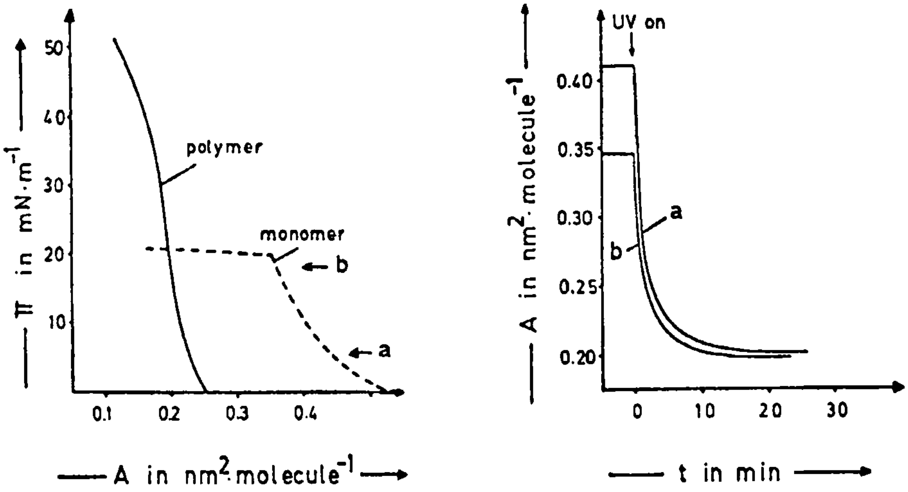


FIGURE 3: Pressure-area diagram and film contraction of Octadecadienal

1. The unexpected high polymerization rate; the contraction starts within a few seconds after switching on the UV-lamp and is finished after about 5 min.

2. The contraction curve of the films shows, that the resulting polymer has a very dense packing in spite of the comparably great occupied area of the monomer.

This can be explained by following assumptions:
The monomeric molecules in the monolayer and especially the headgroup which lies flat on the water, are oriented. This allows the very fast reaction. The polymerization rate is higher than in the case of the alcohol. This is caused, as mentioned before, by the conjugation of the carbonyl group to the diene units, which activates the diene moiety. During the reaction this conjugation is lost; only the aldehyde group can act as a headgroup, the occupied area of which is considerably lower; the molecules are therefore forced to stand up during the polyreaction, and the resultin polymer is closely packed.

The investigation of the acid was more complicated than in the case of the alcohol and the aldehyde, because the acid exhibits a condensed and two expanded phases. Therefore the polymerization has been carried out at different temperatures and in all three phases. Polymerization in the condensed phase leads to a polymer with an occupied area of about 0.23 nm^2/monomer unit. The same polymer is obtained by polymerization in the normal expanded phase, for which we proposed an erected position of the monomer molecules. Polymerization in the second expanded phase leads to a polymer with a less dense packing of the molecules, which confirms our assumption of an orientation with the diene group lying

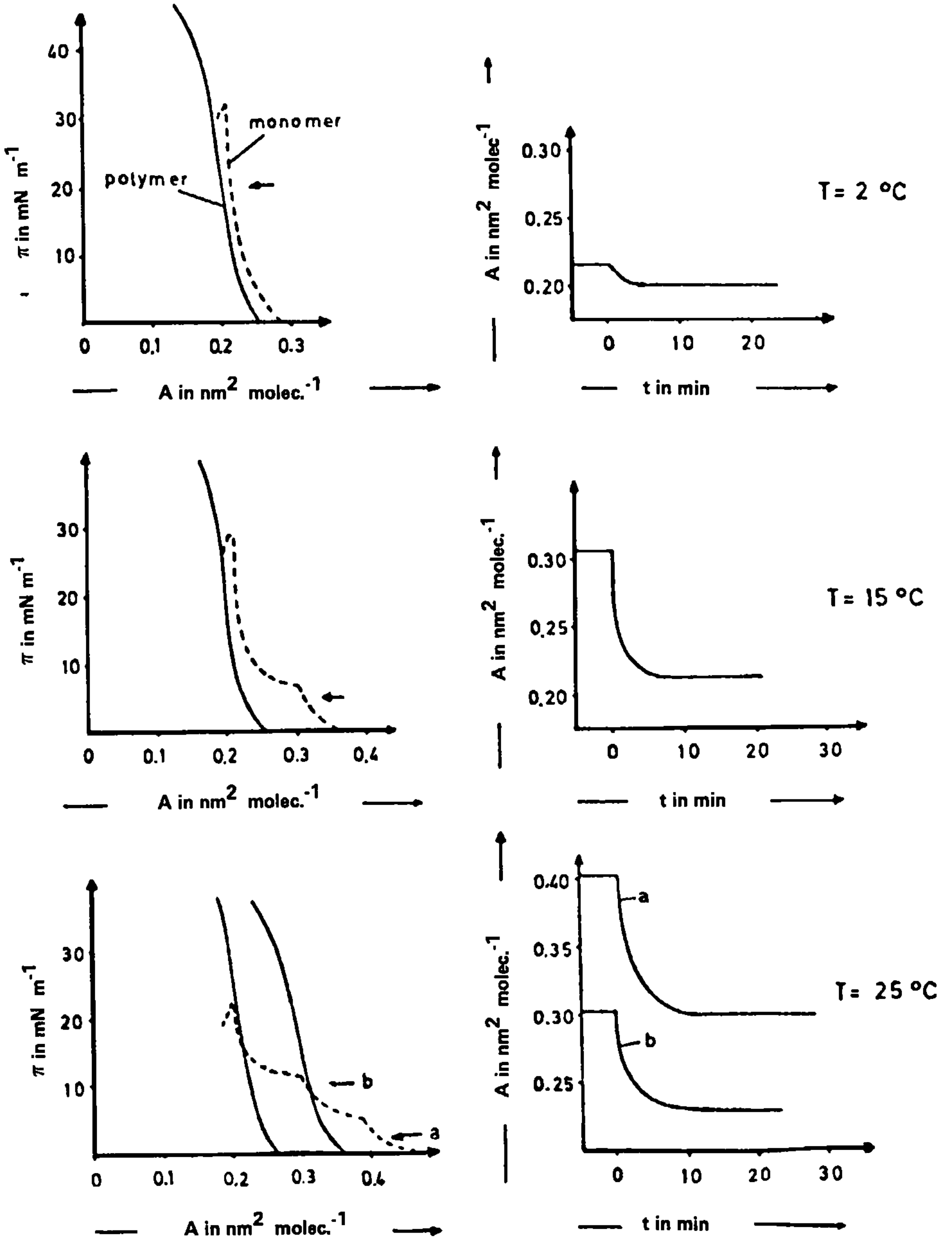
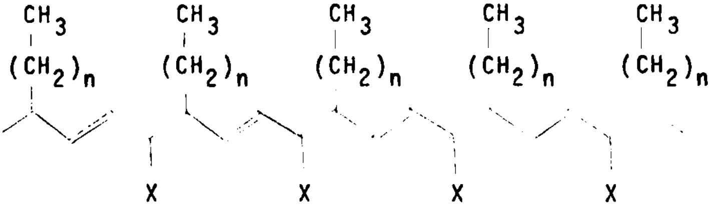


FIGURE 4: Pressure-area diagrams and film contraction of Octadecadienoic acid

flat on the water surface. In each case the polyreaction starts within seconds after switching on the UV-lamp and is finished after about 5 min.

The structure of the resulting polymer is not yet fully established. IR-measurements together with theoretical considerations leads to the assumption, that the polymer has a 1,4-trans backbone:



The possible use of the monolayer polymers as synthetical membranes is already discussed elsewhere (4). In contrast to the Diacetylenes which form a rigid film due to the conjugated backbone, the polydienes are much more flexible and a better approach to biological membrane properties should be possible.

REFERENCES

1. S.A. Letts, T. Fort Jr., J.B. Lando, J. Coll. Interface Sci., 56, 64 (1976)
2. R. Ackermann, O. Inacker, H. Ringsdorf, Kolloid-Z. u.Z. Polym. 249, 1118 (1971)
3. M. Hatada, M. Nishii, J. Polym. Sci. 15, 927 (1977)
4. D. Day, H. Ringsdorf, J. Polym. Sci. Polym. Lett. 16, 205 (1978)
5. G. Wegner, Makromol. Chem. 154, 35 (1972)

6. G.L. Gaines, Insoluble Monolayers at Liquid-Gas Interfaces, Interscience Publishers New York, 1966, p.184

7. G.C. Nutting, W.D. Harkins, J. Am. Chem. Soc. 61, 2040 (1939)

8. G.L. Gaines, Insoluble Monolayers at Liquid-Gas Interfaces, Interscience Publishers New York, 1966, p.162

9. E.L. Pippen, M. Nonaka, J. Org. Chem. 23, 1580 (1958)