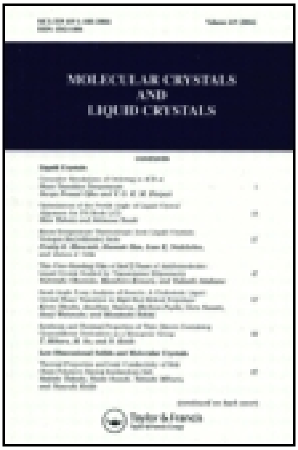

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Some Soluble Polydiacetylenes Derived from 10, 12-Docosadiyn-1, 22-Diol

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SOME SOLUBLE POLYDIACETYLENES DERIVED FROM 10,12-DOCOSADIYN-1,22-DIOL

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Abstract Synthesis and physical properties of some new soluble polydiacetylenes obtained by solid state polymerization of derivatives of 10,12-Docosadiyn-1,22-diol(1) are described.

$$HO-(CH_2)_9-C\equiv C-C\equiv C-(CH_2)_9-OH$$

1

INTRODUCTION

The polymers obtained by solid state polymerization of conjugated diynes[1] are in most cases insoluble and non-fusible with only some few exceptions[2-3].

Recently, we synthesized several polymers derived from (1)[4] which can be investigated by usual methods of polymer analysis such as viscometry, light scattering, osmometry and GPC.

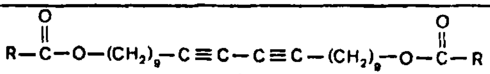
Furthermore, film forming by casting of solutions or molding from melt and fiber spinning from solutions are possible with these polymers.

SYNTHESIS OF MONOMERS

Following the method of Khan[5] 10-undecen-1-01 was brominated and subsequently dehydrobrominated by sodium amide in liquid ammonia to give 10-undecyn-1-01 (yield: 77%; m.p. 5°C).

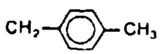
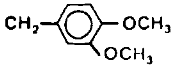
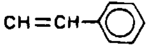
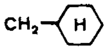
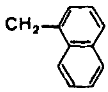
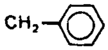
Oxidative coupling[6] gave (1) (yield: 61%; m.p. 80°C). This diol was then esterified with several aliphatic and aromatic acids, using 1,1'-carbonyldiimidazole as condensation agent.[7] In this manner we obtained the esters 2a-2i in 50-95% yields. We also obtained the monoesters

TABLE 1 Structure and melting points of the diyne monomers.



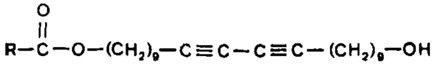
$R{-}C({=}O){-}O{-}(CH_2)_9{-}C{\equiv}C{-}C{\equiv}C{-}(CH_2)_9{-}O{-}C({=}O){-}R$

2

	R	m.p./°C		R	m.p./°C
a	CH_3	36 a)	f		47/51 b)
b	CH_2Cl	41	g		47 a)
c	$CH(CH_3)_2$	24 a)	h		48/52 b)
d		15 a)	i		32 a)
e		36 a)			

a) determined by DTA

b) Compounds 2f and 2h crystallize in two modifications with two different melting points. The modification of 2f with m.p. 47°C forms a blue polymer; 2f with m.p. 51°C polymerizes red. 2h melting at 48°C is polymerizable in the solid state while the other modification (melting at 52°C) does not polymerize.



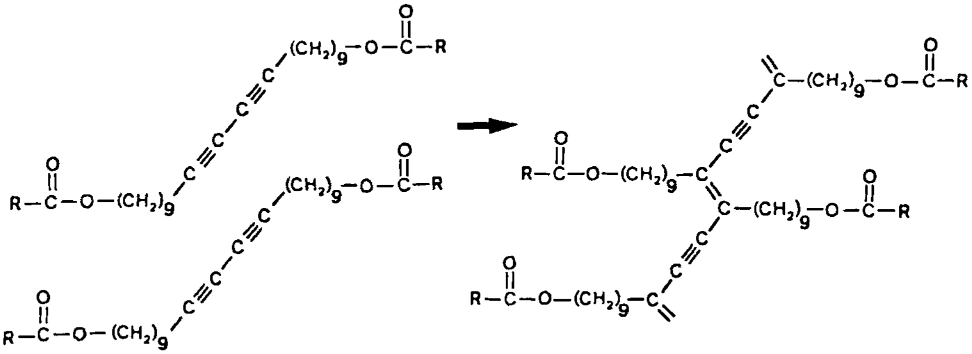
$$R-\overset{\overset{\displaystyle O}{\|}}{C}-O-(CH_2)_9-C\equiv C-C\equiv C-(CH_2)_9-OH$$

3

with R=benzyl(3a); 3,4-dimethoxybenzyl(3g); 1-naphthylmethyl (3i) as by-products.

SYNTHESIS AND PROPERTIES OF POLYMERS

The symmetrical diesters described here polymerize in the solid state by a 1,4-addition reaction.[1]



Polymerization was carried out either by UV- or γ -irradiation. In the former case, crystals of the monomers were triturated, suspended in water, stirred and irradiated with the unfiltered light of a high pressure mercury-vapour lamp at 4°C under nitrogen atmosphere. In the latter case, polyethylene tubes containing large monomer crystals were exposed to γ -irradiation.

During polymerization the colourless monomers turn blue within few seconds, with the exception of 2g which turns red.

Unreacted monomer was removed by extraction with acetone at room temperature. Polymer conversion (ranging from 10-40%) was determined by weighing the residue.

The polymers dissolve at room temperature in chloroform, dichloromethane, 1,2-dichloroethane, THF, and toluene to give yellow solutions. They also dissolve in DMF and DMSO, however only at elevated temperatures; cooling of these yellow solutions (2% w/w) result in the formation of red gels. Red self-supporting films were obtained on evaporating the chloroform solutions.

The absorption spectra of the chloroform solutions show a broad band with a maximum at 47o-475 nm (Table 2).

According to Patel et al[8] the band around 47o nm can result from an average conjugation length of 6-7 repeating units. Solutions of these polymers are very viscous; the Staudinger indices are above 500 $ml \cdot g^{-1}$ (Table 2).

The number-average molecular weights in chloroform (determined by membrane osmometry) range from 200 000 to 300 000 $g \cdot mol^{-1}$

Weight-average molecular weights were determined by light scattering at $\lambda = 578$ nm. The values range from 800 000 to 1 300 000 $g \cdot mol^{-1}$.

This relatively large polydispersity is also evident from gelpermeation chromatography.

In spite of their high viscosities, the polymer solutions permit ^{13}C-NMR measurements. The signals suggest an alternating ene-yne structure

TABLE 2 Characteristics of the synthesized polydiacetylenes

	λ_{max}/nm	ε_{max}/ $(l \cdot mol^{-1} \cdot cm^{-1})$	$[\eta]/(ml \cdot g^{-1})$	$\bar{M}_n$	$\bar{P}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$	$\sqrt{\bar{r}^2}$/Å
Poly (2c)	470	17300	1150	240000	510	800000	3.33	1100
Poly (2e)	473	18000	970	340000	600	1340000	3.94	1310
Poly (2i)	475	17300	520	320000	480	1200000	3.75	1260

for the polymer back-bone (Table 3)[9]. DTA- or DSC-measurements of the monomer-free polymers show two endothermic peaks, which are completely reversible (Figure 1).

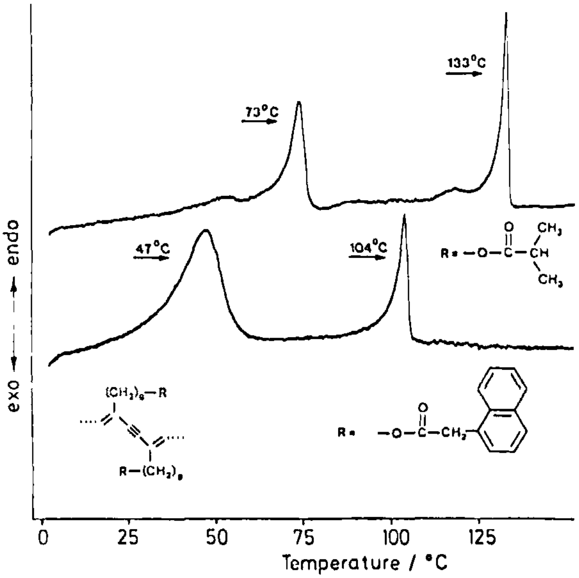
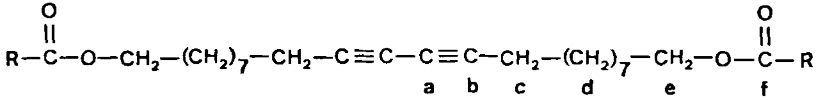


FIGURE 1. DSC-curves of poly(2c) and poly (2i); heating rate: 10°/min.

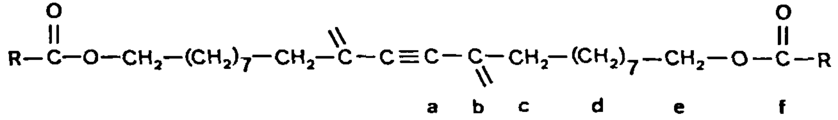
Polarization-microscopic investigations show that the polymer melt behaves anisotropic over the whole melting range. The endothermic peak at higher temperatures corresponds to a thermochromic transformation from red to yellow.

An exothermic peak for this thermochromic transformation can be observed on slight undercooling of the polymer melt. For the first transformation, the peak can be seen by undercooling by about 20°C.

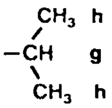
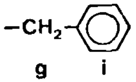
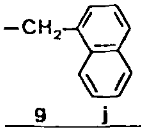
TABLE 3 ^{13}C-NMR chemical shifts of the monomeric and polymeric diacetylenes (in ppm) in $CDCl_3$



$R-\overset{O}{\overset{\|}{C}}-O-CH_2-(CH_2)_7-CH_2-C\equiv \underset{a}{C}-\underset{b}{C}\equiv C-\underset{c}{CH_2}-\underset{d}{(CH_2)_7}-\underset{e}{CH_2}-O-\underset{f}{\overset{O}{\overset{\|}{C}}}-R$ Monomer (M)



$R-\overset{O}{\overset{\|}{C}}-O-CH_2-(CH_2)_7-CH_2-\overset{\backslash\backslash}{C}-C\equiv \underset{a}{C}-\underset{b}{\underset{\backslash\backslash}{C}}-\underset{c}{CH_2}-\underset{d}{(CH_2)_7}-\underset{e}{CH_2}-O-\underset{f}{\overset{O}{\overset{\|}{C}}}-R$ Polymer (P)

R		a	b	c	d	e	f	g	h	i	j
	2c	65.3	77.4	19.1	29.2-25.8	64.3	177.2	34.o	18.9	-	-
	Poly (2c)	99.5	129.5	35.5	29.6-25.9	64.3	177.1	34.o	19.o		
	2e	65.3	77.4	19.1	29.o-25.7	64.9	171.5	41.4	-	134.2-126.9	-
	Poly (2e)	99.6	129.2	35.5	29.6-29.5	64.9	171.5	41.4	-	134.2-127.o	-
	2i	65.8	77.5	19.2	29.2-25.7	65.o	171.5	39.3	-	-	133.8-125.4
	Poly (2i)	99.7	129 5	35 6	29.6-25.8	64.9	171.5	39.2	-	-	133.8-123.8

Temperature dependent wide-angle X-ray measurements show a diffraction maximum for the side-chain methylene groups at $2\theta=21^{o}$, indicating a lattice distance of about 4.2 Å. At a temperature above the first melting peak, the diffraction maximum is shifted to a lower value of 2θ indicating a larger lattice distance. This observation leads to the conclusion that the first endothermic peak corresponds to a melting of the side chains, while the second is due to the melting of the polymer backbone. It is possible to stretch films or fibers of these polymers at a temperature between these two endothermic peaks. X-ray fiber patterns show that these stretched fibers are highly oriented. From the analysis of the fiber patterns, a structure given in Figure 2 can be suggested.

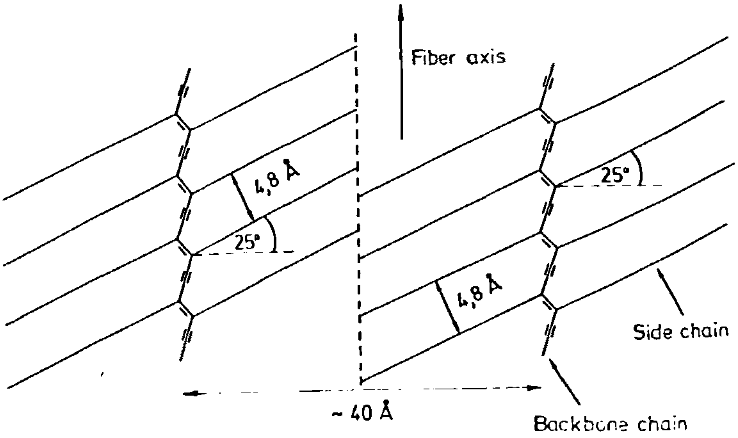


FIGURE 2. Proposed structure of the long side chain polydiacetylenes, indicating packing of macromolecules in the oriented fiber.

MONOESTER BEHAVIOUR AT THE AIR-WATER-INTERFACE

Ringsdorf and Day[10] were able to obtain crystalline arrays of diacetylene fatty acids by spreading the monomers on water and compressing the films formed. These films could be polymerized by UV-light.

Due to their long-chain structure the monoesters 3 are able to form monolayers, too. The esters 3g (m.p. 39°C) and 3i (two modifications, m.p. 40 and 44°C) show an expanded phase at 20°C and both expanded and condensed phase at 5°C in the area-pressure-isotherms. The ester 3e (m.p. 43°C) forms a condensed phase between room temperature and 1°C, which completely disappears at 34°C (Figure 3).

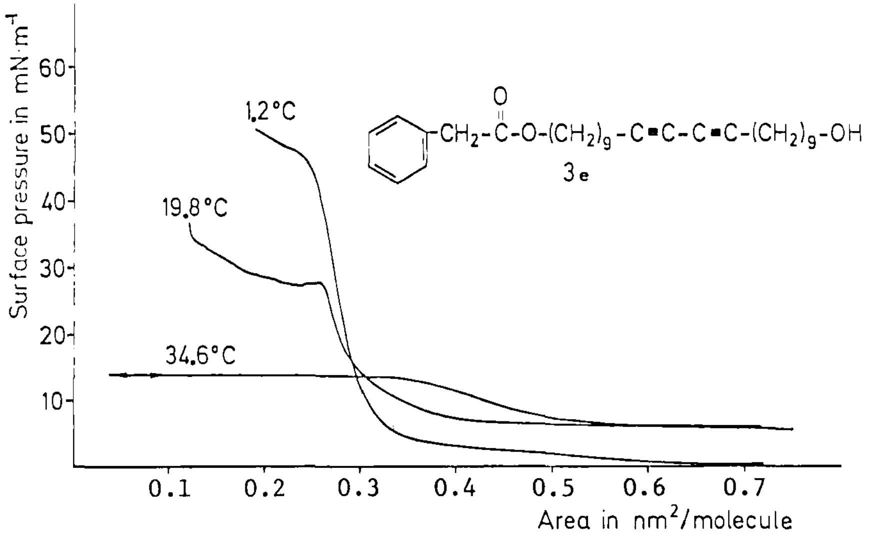


FIGURE 3. Area-pressure isotherms of 3e on water.

The films of 3g and 3i, held under a constant surface pressure of 10 $mN \cdot m^{-1}$ at 5°C (condensed phase) are polymerized on irradiation with UV-light. The irradiation causes no remarkable change of the film-covered area. After compressing the film completely, a blue, insoluble polymer is obtained. Irradiation of 3e under the same conditions results in a rapid decrease of the required area from 0.29 to 0.265 nm^2/molecule within five minutes. The resulting polymer is red and is insoluble. In contrast to 3g and 3i (m.p. 44°C), the ester 3e is not polymerizable with UV-light in the solid state.

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