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Diacetylenic Liquid Crystalline Polymers II: Derivatives of 10,12-Docosadiyne-1,22-Dioic Acid

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Polymers of 10,12-docosadiyne-1,22-dioic acid with different mesogenic groups have been prepared. The mesogenic groups were diphenyl (Polymer I); *p*-diphenylazoxy (Polymer II); 2,2'-dimethyldiphenylazoxy (Polymer III); 2-methyldiphenylazomethine (Polymer IV) and α -methylstilbene (Polymer V).

All polymers crystallized extensively at room temperature, but only polymers I and V have displayed an enantiotropic smectic mesophase. The X-ray diffractograms were consistent with a smectic H mesophase for both polymers. Polymers I and V differed also from polymers II–IV by enhanced reactivity of the diacetylenic moiety. A model for chain packing consistent with the X-ray diffraction pattern of the crystalline and the smectic phase is proposed.

Keywords: diacetylenic polyesters, synthesis of, liquid crystalline order

INTRODUCTION

Diacetylenic compounds with various substituent groups have been the object of intensive study.^{1,2}

Diacetylenic main-chain polyesters have also been synthesized and the reactivity of the conjugated triple bond incorporated into the polymeric chain was studied.^{3,4,5,6} Very little information is available on mesomorphic properties of diacetylenic monomers and polymers. This is surprising in view of the possibility of topochemical and

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topotactic effects which could be expected from mesomorphic order locked into such polymers by mesophase polymerization.

We have previously reported on liquid crystalline properties of Flexible-Rigid-Flexible diesters,⁷ polyesters and copolyesters⁸ of diphenyldiacetylene as well as Rigid-Flexible-Rigid-Flexible-Rigid diesters⁹ of 10,12-docosadiyne-1,22-dioic acid with different mesogenic groups.

We found that the diesters of diphenyldiacetylene have shown nematic mesophases for $n = 1-7$, (n , number of methylene units in the flexible moiety) and were stable to heat and radiation. The polymers and copolymers exhibited very high isotropic transition temperatures above the stability range of diacetylenic groups. Liquid crystalline mesophases were observed by polarizing microscopy by rapidly elevating the temperature of the sample.⁸

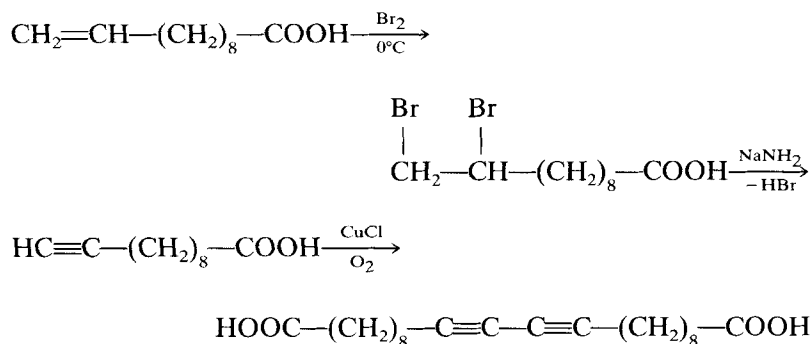
The mesogenic properties of the diesters of 10,12-docosadiyne-1,22-dioic acid were determined by the type of the mesogenic units.⁹

In this paper, we report the synthesis and characterization of polyesters in which the diacetylenic unit is in the flexible portion of the repeating unit.

EXPERIMENTAL

The polymers studied are given in Table I together with corresponding data on elemental analysis.

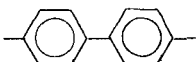
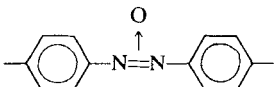
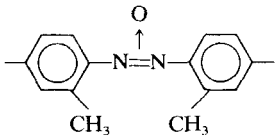
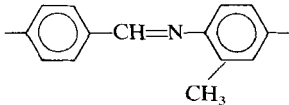
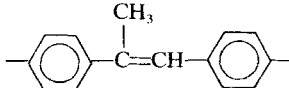
All reagents were purchased from Aldrich Chemical Company. 10,12-Docosadiyne-1,22-dioic acid has been prepared from 10-undecenoic acid.^{10,11} The preparation is schematically illustrated below:



Elemental analysis; calculated: C = 72.89, H = 9.45; found: C = 73.27, H = 9.50; M.p. = 111–112°C.

TABLE I
Elemental analysis of the diacetylenic polymers

$$\left[-O-RO-\overset{\overset{O}{\parallel}}{C}-(CH_2)_8-C\equiv C-C\equiv C-(CH_2)_8-\overset{\overset{O}{\parallel}}{C}- \right]_n$$

Polymer	R	Theory			Found		
		C	H	N	C	H	N
I		79.64	7.88	—	79.49	7.88	—
II		73.34	7.26	5.03	72.63	7.30	4.84
III		73.93	7.60	4.79	73.87	7.59	4.81
IV		78.09	7.83	2.53	77.44	8.38	2.57
V		80.40	8.02	—	79.15	7.73	—

^{13}C and ^1H NMR spectra were consistent with the structure (^{13}C NMR diacetylene 77.95; 65.33 ppm).

Since diacetylenic diacid is very sensitive to light, it was kept under dark during storage and during treatment with oxalyl chloride.

The acid chloride of 10,12-docosadiyne-1,22-dioic acid was obtained by stirring the acid with excess oxalyl chloride for four hours. The excess oxalyl chloride was then removed at room temperature under vacuum and the mixture stirred for four more hours under vacuum to remove the last traces of the oxalyl chloride.

4,4'-Dihydroxybiphenyl was recrystallized from ethanol-water. 4,4'-Dihydroxyazoxybenzene has been prepared from *p*-nitrosophenol by reductive coupling.^{12,13} 4,4'-Dihydroxy(2,2'-dimethyl)-azoxybenzene was prepared from *m*-cresol and 4-hydroxy-2-methylaniline.^{12,13} 4,4'-

Dihydroxy(2-methyl)benzanilide was prepared from *p*-hydroxybenzaldehyde and 4-hydroxy-2-methylaniline.¹⁴ 4,4'-Dihydroxymethylstilbene was prepared from phenol and chloroacetone.¹⁵

Except for polymer II, the polyesters were prepared by interfacial polymerization according to the following procedures: 90 ml of water and 135 ml of 1,2-dichloroethane and 0.003 moles of benzyltriethyl ammonium chloride were placed into an explosion proof blender. While stirring at low speed, a mixture of 0.015 moles of the diol in 0.03 moles (60 ml of 0.5 N) of sodium hydroxide was added. The blender speed was increased to full speed and 0.015 moles of the diacid chloride in 90 ml of dry, freshly distilled 1,2-dichloroethane was added as fast as possible. The blender was covered tightly and the vigorous stirring was continued for an additional 4–5 minutes. The mixture was precipitated from ethanol.

Polymer I–IV was dissolved in chloroform and reprecipitated in ethanol.

Polymer V was only partially soluble in chloroform. It was extracted with chloroform to separate the insoluble (probably crosslinked) polymer. The chloroform solution was precipitated into ethanol.

Polymer II was prepared by solution polymerization according to the following procedure: 0.006 moles of diol in 50 ml of dry, freshly distilled 1,2-dichloroethane containing 5 ml pyridine (10%) were added to a flask having 0.006 moles of the diacid chloride chilled with dry ice/acetone mixture. After the addition of the diol, the flask was closed with a ground glass stopper and wrapped with parafilm to protect the contents from moisture. The mixture was stirred for 12 hours at room temperature. The contents of the flask were poured into 1000 ml of ethanol. The precipitate was dissolved in chloroform and reprecipitated twice. The product was washed with lukewarm water to remove the pyridinium chloride and dried in vacuo at room temperature overnight.

Standard characterization of polymers included ¹H and ¹³C NMR, IR and elemental analysis (Table I).

The transition characteristics and the textures of the polymers were studied by using a Leitz Ortholux polarizing microscope equipped with a hot-stage and a Mettler FP-52 temperature programmer. The thermal properties were investigated by means of a Perkin Elmer 2C differential scanning calorimeter with a heating rate of 20°C/min.

Reduced viscosity was obtained for a concentration of 0.5 g/dl. of polymer in tetrachloroethane at 30°C.

X-ray diffractograms were obtained with a Warhus flat plate camera mounted on a Norelco generator, using Ni-filtered CuK alpha radia-

tion of wavelength 1.54\AA with a sample to film distance 5 cm (WAXS) and 17 cm (SAXS).

RESULTS AND DISCUSSION

The properties of the prepared polymers are given in Table II. In certain cases the transition enthalpies could not be determined due to the overlap of neighboring peaks and therefore have not been included in Table II.

The polymers are all crystalline at room temperature (Table III).

They are soluble in chloroform at room temperature.

The ^{13}C and ^1H NMR spectra were consistent with corresponding polymer structures.

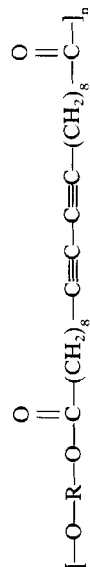
The DSC thermogram of polymer I gave two heating and cooling peaks (Table II, Figure 1). Under the microscope, the polymer I has shown a very viscous birefringent melt below the isotropization peak.

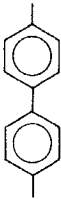
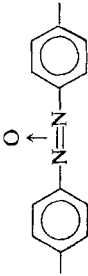
The X-ray diffractogram of polymer I at a temperature below the isotropization peak has shown a pattern typical of a smectic H (an intense and a weak outer ring, and an intense small angle ring) (Table III, Figure 2). The spacings indicate that the packing of chains is not hexagonal. The inner ring spacing, 24.9\AA , is considerably shorter than the extended repeat unit length. Thus, presumably the chain axes are tilted relative to the smectic planes. Assuming that the wide angle spacings in the crystalline state are due to packing in the plane normal to the chain axes, this packing is consistent with the model shown in Figure 3. This model gives calculated spacings of 4.8, 4.2, 3.9, 3.7 and 3.0\AA . It is interesting to note the similarity between this packing and that normal to chains for polyethylene.

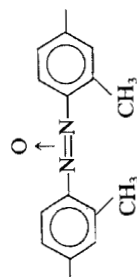
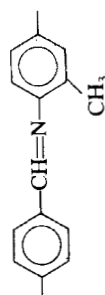
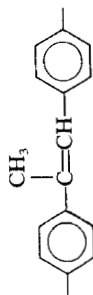
In the smectic state, the wide angle spacings are consistent with lateral chain packing not very different from the crystalline state, with the angle γ close to 90° and $a = 8.95\text{\AA}$ and $b = 4.77\text{\AA}$. The decreased spacing of the inner ring would indicate a greater tilt between the smectic planes and the chain axis, while the packing between chains expands along the a axis.

The polymer I was very sensitive to daylight and ultraviolet radiation like its model compound.⁹ It changes from colorless to blue in the daylight and dark blue on exposure to u.v. radiation. The irradiated blue polymer was partially soluble in chloroform leaving an insoluble yellow gel suggesting crosslinking. The blue polymer was also thermochromic and reversibly changed its color to red on heating. This phenomenon was observed for other solid-state polymerized

TABLE II
The properties of the diacetylenic polymers



Polymer	R	Viscosity ^a 30°η _{Red}	Transition Temp. °C ^b		ΔH ^b Kcal/m.r.u.	
			Heating	Cooling	Heating	Cooling
I		0.41	C ₁ 122Sm Sm161I	Sm84C ₁ 1144Sm	1.38 3.27	1.41 3.41
II		0.11	C ₁ 71C ₅ C ₂ 132C ₃ C ₃ 160I	— — 1135C ₃	— — —	— — —

III		0.99	C ₁ 100I	I71C ₁	3.89	3.58
IV		0.45	$\left. \begin{matrix} C_1 84C_2 \\ C_2 101I \end{matrix} \right\}$	$\overline{I78C_2}$	$\left\{ \begin{matrix} 3.82 \\ \end{matrix} \right\}$	$\overline{3.80}$
V		0.34	$\left. \begin{matrix} C_1 64C_3 \\ C_2 117C_3 \\ C_3 122Sm \\ Sm 134I \end{matrix} \right\}$	$\begin{matrix} C_2 78C_1 \\ C_3 90C_2 \\ Sm 104C_3 \\ I 117Sm \end{matrix}$	$\begin{matrix} - \\ - \\ - \\ - \end{matrix}$	$\begin{matrix} - \\ - \\ - \\ - \end{matrix}$

^a0.5 g/dl in tetrachloroethane.^bSecond heating and cooling (20°C/min.)^cFirst heating.

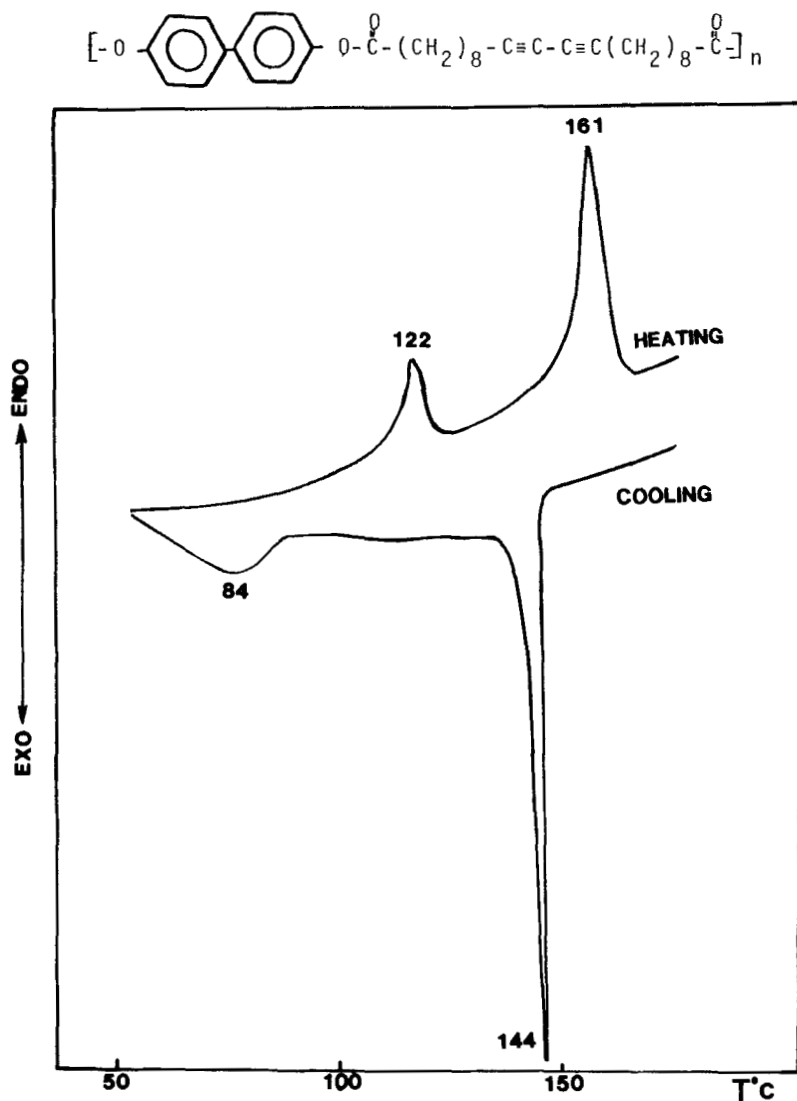


FIGURE 1 DSC scan of Polymer I (heating and cooling rate 20°C/min.).

diacetylenic compounds and explained in terms of backbone configuration changes.¹⁶

There was no evidence for thermal solid-state reactivity. The sample did not show any decrease of the isotropization enthalpy after annealing in a DSC pan below the isotropization peak under the nitrogen atmosphere.

TABLE III
X-ray spacings of the diacetylenic polymers

Polymer	Room temperature	d Spacings in Å
I	$3.1 \pm 0.05(w)$, $3.6 \pm 0.05(s)$ $3.9 \pm 0.05(s)$, $4.2 \pm 0.05(s)$ $4.8 \pm 0.05(w)$, $14.7 \pm 0.5(m)$ $29.2 \pm 0.5(s)$	$140^\circ\text{C} = 4.2 \pm 0.05(s)$, $4.8 \pm 0.05(w)$ $24.9 \pm 0.5(s)$
II	$3.7 \pm 0.05(m)$, $3.9 \pm 0.05(m)$ $4.8 \pm 0.05(s)$, $5.5 \pm 0.05(w)$ $6.0 \pm 0.05(w)$, $10.7 \pm 0.5(s)$	$140^\circ\text{C} = 4.0 \pm 0.05(s)$, $4.4 \pm 0.05(s)$ $8.3 \pm 0.05(m)$, $9.9 \pm 0.5(w)$ $14.1 \pm 0.5(w)$
III	$4.1 \pm 0.05(s)$, $4.5 \pm 0.05(s)$ $4.9 \pm 0.05(s)$, $6.1 \pm 0.05(m)$ $19.6 \pm 0.5(s)$	$75^\circ\text{C} = 4.0 \pm 0.05(s)$, $4.3 \pm 0.05(s)$ $4.6 \pm 0.05(s)$, $5.7 \pm 0.05(m)$ $19.3 \pm 0.5(s)$
IV	$3.5 \pm 0.05(m)$, $3.7 \pm 0.05(m)$ $4.1 \pm 0.05(m)$, $4.5 \pm 0.05(s)$ $5.1 \pm 0.05(m)$, $8.0 \pm 0.05(vw)$ $10.5 \pm 0.5(m)$, $24.0 \pm 0.5(m)$	$99^\circ\text{C} = 3.6 \pm 0.05(s)$, $3.9 \pm 0.05(s)$ $4.2 \pm 0.05(m)$, $4.6 \pm 0.05(s)$ $5.2 \pm 0.05(m)$, $5.7 \pm 0.05(w)$ $10.6 \pm 0.5(s)$, $23.5 \pm 0.5(s)$
V	$3.7 \pm 0.05(w)$, $3.9 \pm 0.05(w)$ $4.3 \pm 0.05(s, \text{broad})$ $4.7 \pm 0.05(m)$, $26.5 \pm 0.5(m)$	$123^\circ\text{C} = 4.2 \pm 0.05(s)$, $4.7 \pm 0.05(w)$ $24.4 \pm 0.5(m)$

s, strong; m, medium; w, weak; vw, very weak

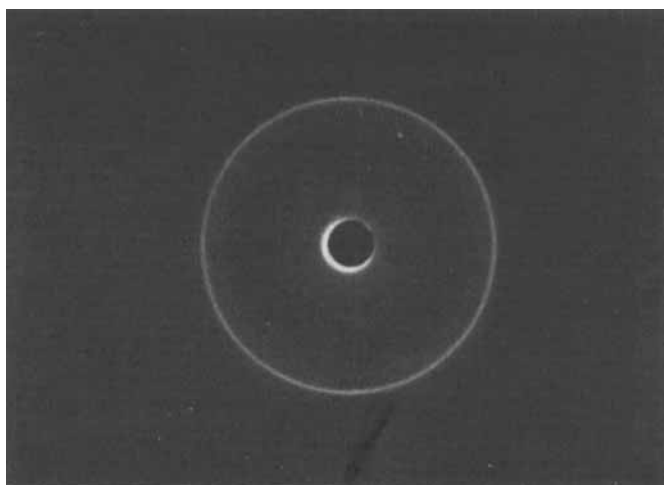


FIGURE 2 X-ray diffractogram of Polymer I taken at 140°C , wide angle.

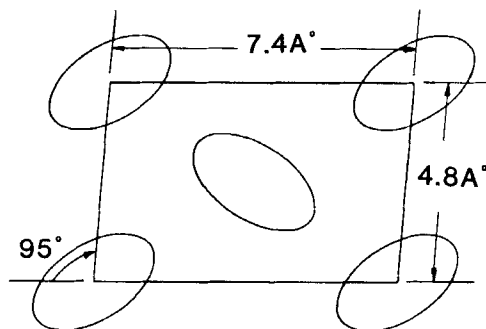


FIGURE 3 Suggested lateral packing of Polymer I chains in the crystalline state.

Polymer II was prepared by solution polymerization. Viscosity measurement indicated a low molecular mass (Table II).

The X-ray diffractograms of Polymer II at 140°C gave multiple sharp peaks indicating crystallinity and no evidence of mesophase formation.

The thermograms revealed a change in pattern on multiple heating to the isotropization temperature (170°C) and subsequent coolings. It may well be that at the high isotropization temperature of 160–170°C the polymer becomes unstable. Polarizing microscopy did not reveal any textures characteristic of nematic or smectic mesophases.

Broadening of the mesogen by methyl substitution (Polymer III) produced a sharp drop in the melting point, a difference of 60°C (Table II). The polymer gave on cycling one reproducible single peak which according to X-ray data (Table III) was characteristic of a crystal to isotropic transition. The microscopic observation confirmed the direct passage from crystalline to the isotropic phase of polymer III.

Similarly, the polymer IV did not show any mesophase under microscope. The DSC thermogram gave multiple peaks on heating (Table II). The absence of mesophase was confirmed by X-ray data characteristic of extensive crystallinity (Table III).

The thermogram of polymer V displayed multiple peaks on heating and cooling (Figure 4, Table II). It has shown a viscous flow under the microscope below the isotropization peak indicating a mesophase.

The X-ray pattern at 123°C gave an intense and a weak outer ring and an intense small angle ring similar to polymer I (Table III), possibly indicating similar packing.

In contrast to polymer I and V, polymers II–IV did not show any color change in daylight and under the ultraviolet radiation, sug-

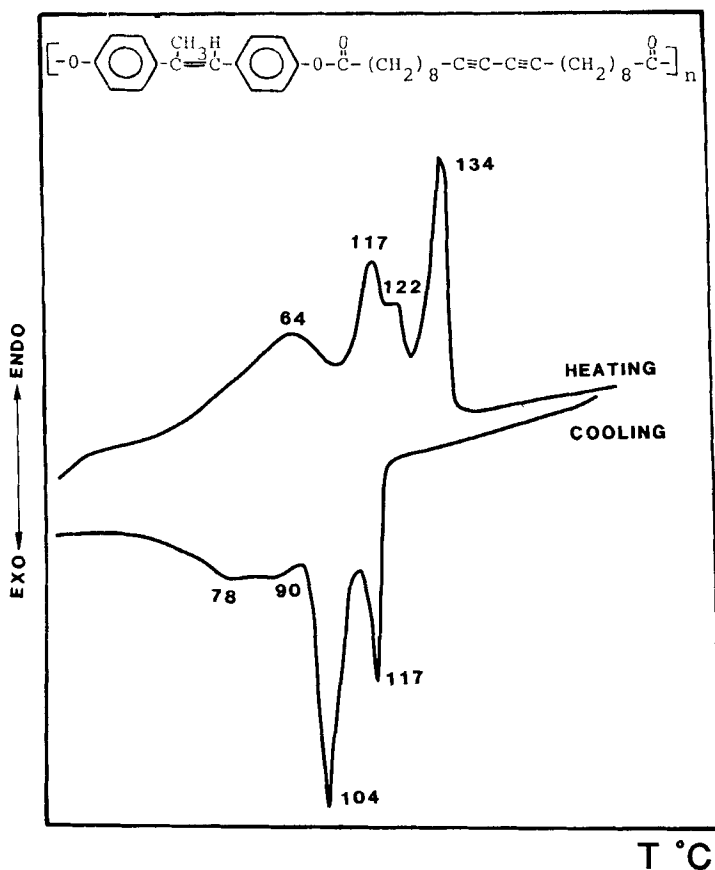


FIGURE 4 DSC scan of Polymer V (heating and cooling rate 20°C/min.).

gesting that these polymers did not meet the packing requirements for the reactivity of the diacetylenic groups.

Polymers exposed to X-ray at room temperature remained soluble. When exposed to X-rays at higher temperature, the polymers changed color and became partially insoluble.

In conclusion, out of the five diacetylenic polyesters synthesized only two, polyester I (biphenyl-mesogene) and V (α -methylstilbene mesogene) showed an enantiotropic mesophase. Both mesophases were characterized as smectic by X-ray diffraction and appeared of similar nature. The X-ray diffractograms were consistent with a smectic H mesophase.

The reactivity of the diacetylenic moiety in polyesters I and V appears to be significantly higher than for the polyesters II–IV which could be attributed to the favorable packing of chains. A model for chain packing consistent with the X-ray diffraction pattern is proposed.

Acknowledgment

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