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Lead(II)alkadiynoates. A novel class of liquid-crystalline precursors to poly(diacetylenes)

G. S. Attard[a]; Y. D. West[a]
[a] Department of Chemistry, The University, Southampton, England

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Lead(II)alkadiynoates

A novel class of liquid-crystalline precursors to poly(diacetylenes)

by G. S. ATTARD and Y. D. WEST
Department of Chemistry, The University, Southampton SO9 5NH, England

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Lead(II) salts of aliphatic diacetylenic carboxylic acids are found to form highly ordered smectic phases which thermodynamic data indicate are similar to those reported for the saturated lead(II)alkanoates. At room temperature the materials exist as glassy mesophases which can be readily polymerized by U.V. radiation to yield highly coloured poly(diacetylenes).

1. Introduction

Since the pioneering of Wegner in the early seventies on the solid state topochemical polymerization of diacetylene derivatives [1], there has been considerable research on both the fundamental properties of poly(diacetylene) systems and on their application in technologies based on non-linear optical effects [2]. The technological interest stems from the extensive conjugation of the polydiacetylenic backbones which results in large third order optical hyperpolarizabilities and picosecond non-linear optical responses [3].

Extensive studies of the polymerization of a large number of diacetylene derivatives in the solid state have enabled the formulation of empirical structural and geometrical criteria which must be satisfied if materials with high degrees of polymerization are to be achieved [4]. Recent reports indicate that mesogenic diacetylene derivatives can also be thermally polymerized in the liquid-crystalline phase [5–8]. These observations are of considerable technological importance because the fluidity of many of the liquid-crystalline phases, coupled with their response to electric or magnetic fields could be exploited to obtain bulk polymers of high optical quality through polymerization of mesophases which are macroscopically aligned [7]. It is therefore desirable for both fundamental and technological reasons to extend our knowledge of the relationship between mesophase structure, molecular structure, and polymerization processes in liquid-crystalline phases.

In this paper we describe the synthesis, thermal properties, and response to U.V. radiation, of a novel class of mesogenic diacetylenic monomers, namely the lead(II) salts of alkadiynoic acids:

$$(CH_3(CH_2)_m\text{–}C{\equiv}C\text{–}C{\equiv}C\text{–}(CH_2)_nCOO^-)_2Pb^{2+}. \qquad (A)$$

Previous observations [9, 10] have shown that the lead(II) salts of straight chain carboxylic acids exhibit thermotropic mesomorphism at relatively low temperatures (80°C to 160°C). Soaps of homologues lower than tridecanoic acid show two mesophases [9]. The first mesophase which occurs on cooling the isotropic melt has been identified as a smectic A phase, while the second mesophase, which occurs at lower temperatures, was not assigned, but from thermodynamic and X-ray diffraction data

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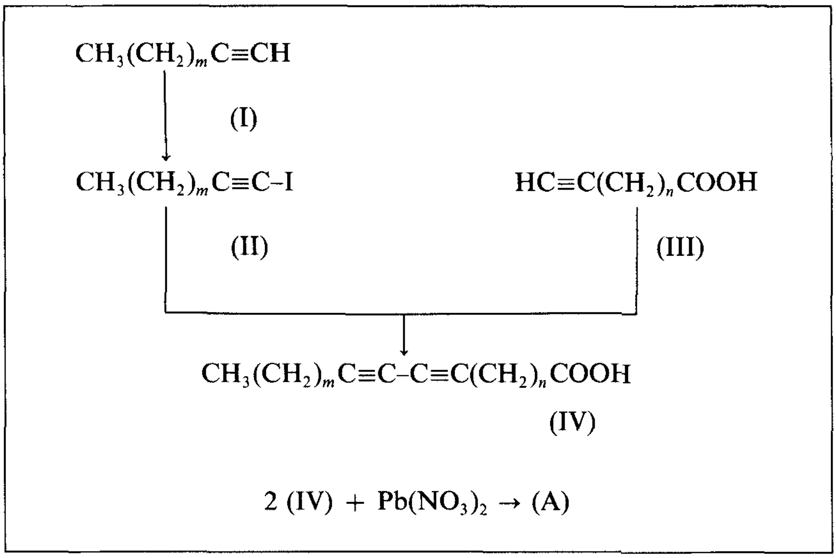
appears to be a highly ordered smectic, e.g. a S_E phase [10] or possibly a crystal modification. For homologues higher than tridecanoate salts only the more highly ordered phase is formed [9].

It was anticipated that lead(II) salts of alkadiynoic acids would exhibit a similar behaviour to that found in the analogous alkanoate salts. Although similar diacetylenic carboxylate salts of divalent metal ions have been reported as components of polymerizable Langmuir–Blodgett films [11, 12], to our knowledge there have been no reports of the thermotropic properties of the bulk phases. In accord with our expectations, the lead(II)alkadiynoates were found to exhibit smectic mesomorphism over a wide temperature range. They also appear to form glassy mesophases at lower temperatures. Consequently the smectic structures could be observed at room temperature. All of the materials which we have synthesized could be polymerized by low intensity U.V. radiation, although the ease of polymerization seems to depend on the separation between the diacetylenic unit and the polar carboxylate centre.

2. Experimental

2.1. *Synthesis*

The lead(II)alkadiynoates were synthesized according to the scheme:



2.1.1. *Synthesis of 1-iodalkynes* [*13*]

The general method for the synthesis of the 1-iodoalkynes is illustrated for the case of 1-iodooctyne (structure I, $m = 5$). 4·56 g (0·19 mol) magnesium turnings were placed in a three-necked round bottom flask equipped with magnetic stirring bar, reflux condenser, calcium chloride guard tube, and a dropping funnel. The magnesium was covered with 40 ml sodium-dried diethylether and a few crystals of iodine were added to start the reaction. Whilst stirring vigorously 19·05 g (0·17 mol) bromoethane in sodium-dried ether was added dropwise. An exothermic reaction with progressive dissolution of the magnesium was observed. Following completion of bromoethane addition, the reaction mixture was refluxed for 15 minutes, then allowed to cool to room temperature. A solution of 22·2 ml (16·5 g; 0·15 mol) 1-octyne in 35 ml sodium-dried ether was added dropwise to the reaction mixture. Following complete addition of the 1-octyne the mixture was refluxed for 30 min and 40·25 g (0·16 mol) iodine crystals were dropped, in small portions, into the reaction mixture through the condenser. The contents of the flask were poured into 200 ml water and acidified with acetic acid. The ether layer was collected and washed with 2 × 50 ml portions of 10 per cent aqueous sodium thiosulphate, and with 3 × 50 ml portions of aqueous sodium bicarbonate. The organic layer was dried over anhydrous sodium sulphate, filtered, and the solvent removed on a rotary evaporator to yield a brown oil which was distilled under vacuum in a short path distillation apparatus. The first fraction, consisting of unreacted 1-octyne, was discarded. The 1-iodooctyne was obtained as a colourless liquid, b.p. 120°C at 5 mm Hg. The yield was 27·2 g (77 per cent). [I.R. characterization: $2195\,\mathrm{cm}^{-1}$ (m) = –C≡C– stretch; no –C≡C–H stretch at $3315\,\mathrm{cm}^{-1}$].

2.1.2. *Coupling of 1-iodoalkynes with alkynoic acids* [*12*]

The Cadiot–Chodkiewicz coupling of the 1-iodoalkynes with alkynoic acids is illustrated by the coupling of 1-iodododecyne and 4-pentynoic acid (structures II and III with $m = 9$ and $n = 2$ respectively). 0·98 g (0·10 mol) of 4-pentynoic acid, placed in a three necked flask equipped with a magnetic stirring bar, reflux condenser, and dropping funnel, was neutralized with 7·5 ml of 10 per cent aqueous KOH. The flask was cooled in ice/water and 0·05 g (7×10^{-4} mol) hydroxylamine hydrochloride, and 0·25 g ($2{\cdot}5 \times 10^{-4}$ mol) copper(I)chloride in 2·6 ml (2 g; 0·044 mol) 70 per cent aqueous ethylamine solution were added successively. 1-iodododecyne (2·92 g; 0·01 mol) in 5 ml methanol was added dropwise to the cold solution which was stirred vigorously. Stirring was continued for a further 10 min and the reaction mixture was poured into 50 ml of 2 M H_2SO_4. The organic layer was extracted with diethylether, dried over anhydrous sodium sulphate, and the solvent removed on a rotary evaporator to yield a viscous dark brown oil. The oil was treated with hot 40–60 petroleum ether and the solution filtered while hot. The filtrate was cooled in ice and the resulting light-sensitive, white crystals collected and dried in a vacuum oven to afford 0·65 g (25 per cent) of pure heptadeca-4,6-diynoic acid (structure IV: $m = 9$, $n = 2$); mp 80–80·5°C. (I.R. characterization: $1695\,\mathrm{cm}^{-1}$ (s) = C=O stretch; $2190\,\mathrm{cm}^{-1}$ (vw) and $2200\,\mathrm{cm}^{-1}$ (vw) = –C≡C– stretch; no –C≡C–H stretch at $3315\,\mathrm{cm}^{-1}$.)

2.1.3. *Synthesis of lead*(*II*)*alkadiynoates*

The general synthesis of the unsaturated lead(II) carboxylates is illustrated for lead(II)heptadeca-4,6-diynoate (structure A with $m = 9$ and $n = 2$) which we denote as $[10,2]C_{17}Pb$, where the numbers in square brackets denote the number of carbons in the chains attached to the diacetylene unit, excluding the carboxyl carbon: the first number corresponds to the methyl terminated chain while the second number corresponds to the carboxyl terminated chain. The subscript shows the total number of carbon atoms in the chain.

Heptadeca-4,6-diynoic acid (0·254 g; 0·001 mol) was dissolved in 30 ml of hot 95 per cent ethanol. Potassium hydroxide (0·06 g; 0·001 mol; BDH Ltd. ANALAR grade) was dissolved in a minimum amount of ethanol. This solution was added to the heptadeca-4,6-diynoic acid solution. Lead(II)nitrate (0·166 g; 5×10^{-5} mol; Aldrich 99·9999 per cent pure) dissolved in the minimum quantity of distilled water was added with vigorous stirring. The reaction mixture was allowed to cool to room temperature, and the resulting precipitate filtered, washed with distilled water, absolute ethanol, and acetone. The white solid was dissolved in hot benzene and filtered while hot to remove the basic carboxylate. The benzene solution was cooled in ice to yield a crop of white crystals which were recrystallized twice from benzene. The yield of $[10,2]C_{17}Pb$ was 0·409 g (59 per cent). [I.R. characterization: $1520\,\mathrm{cm}^{-1}$ (s) = C=O stretch. Elemental analysis: expected = C (55·92 per cent), H (6·91 per cent), Pb (28·4 per cent); found = C (55·84 per cent), H (6·86 per cent), Pb (28·3 per cent)].

2.2. *Characterization*

The thermodynamics of the order–disorder transitions in the materials synthesized were investigated by means of a Perkin–Elmer DSC-2 differential scanning calorimeter. Polarized light microscopy studies, which were used to determine the transition temperatures and to investigate the optical textures of the mesophases, were conducted on an Olympus BHP polarizing microscope equipped with a Linkam THM600 hot stage. The sample temperature was controlled by a Linkam TMS90 temperature control system. Heating/cooling rates of $0{\cdot}2\,\mathrm{K\,min}^{-1}$ were used to ensure sample equilibration and to allow the optical textures of the mesophases to develop.

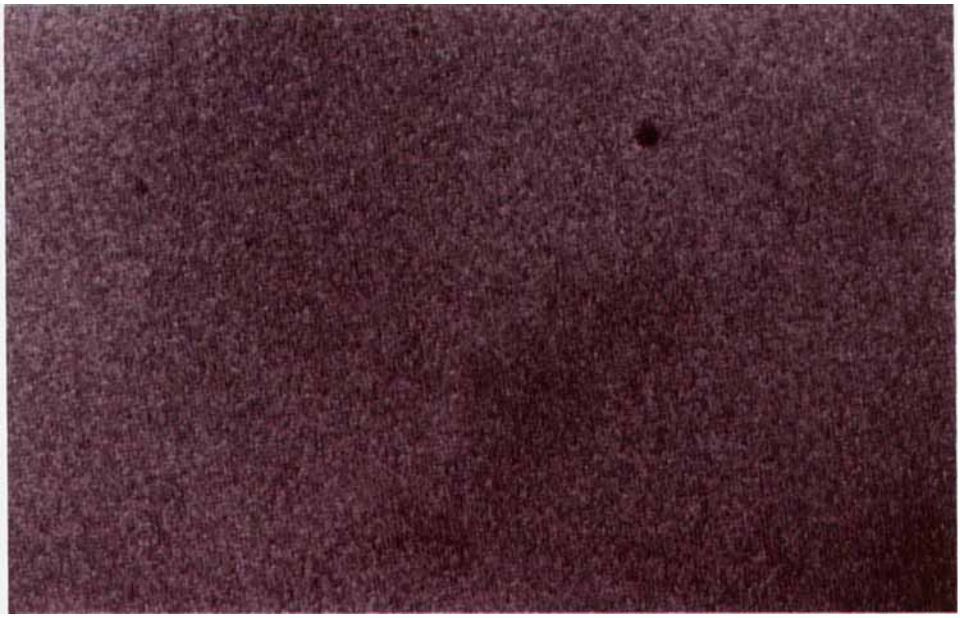
Reproducible values for the transition temperatures could not be obtained if traces of water/ethanol were present in the compounds. Accordingly all samples used in these studies were placed in a vacuum oven at 50°C for 36 hours prior to the physical investigations. Although repeated measurements on the same sample did not reveal decomposition or appreciable thermal-induced polymerization at temperatues below 403 K, it was found that at temperatures greater than ~415 K an increasing coloration, indicative of polymerization, occurred.

The response of the lead(II) salts to U.V. radiation was investigated qualitatively by exposing films of the materials supported on glass slides to 254 nm radiation from a hand-held U.V. lamp (Ultra-Violet Products, model UVGL58).

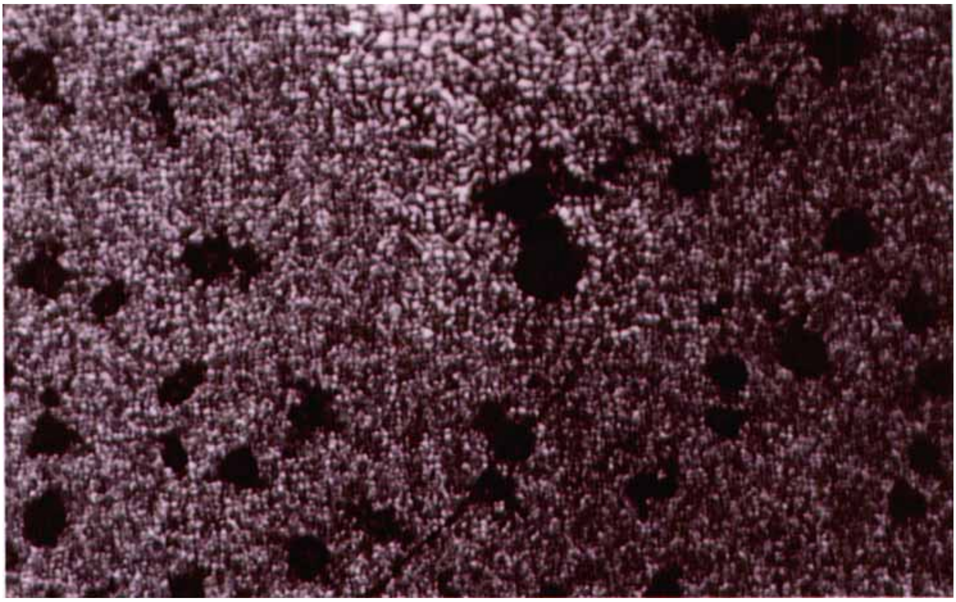
3. Results and discussion

The optical studies showed that most of the mesophases had ill-defined sandy textures even after prolonged annealing (30 hours) as illustrated in figure 1(*a*) for compound $[8,2]C_{15}Pb$. Careful, high magnification (× 500) observations in the neighbourhood of the transition showed that the mesophase separated from the isotropic phase as small weakly birefringent batonents, suggesting that the mesophase is a smectic phase. The only clearly resolved texture was obtained for the mesophase of compound $[10,8]C_{23}Pb$, which, as can be seen in the figure (*b*), has a spherulitic mosaic texture. On shearing the sample by displacing the coverslip some deformation of the textures could be observed for all the compounds. Even at temperatures close to the transition only slight deformation of the textures could be induced. More vigorous shearing resulted in the appearance of irregular cracks within the material similar to those observed on shearing gels. On cooling to temperatures below ~333 K no deformation of the samples could be observed when they were subjected to shear.

In this glassy state the materials are very brittle. The DSC traces for all our compounds show a small but definite shift in the baseline starting at ~340 K and ending at ~315 K, indicating the onset of a second order phase transition. Due to the small baseline change and the width of the process it was not possible to pinpoint the glass transition temperatures with any accuracy. We believe that glass phase



(*a*)



(*b*)

Figure 1. Optical textures of lead(II)alkdiynoates. (*a*) Compound $[8,2]C_{15}Pb$ (structure A; $m = 7$, $n = 2$) at 367 K, (*b*) compound $[10,8]C_{23}Pb$ (structure A; $m = 9$, $n = 8$) at 351 K.

formation in these materials is a consequence of their relatively high molecular weights, although we do not exclude the possibility that the glassy phase may result from suppression of crystallization by impurities.

The transition temperatures of the lead(II) salts determined from optical microscopy are listed in the table. Because of the weak birefringence of the samples at the transition accurate location of the transition temperatures was difficult. Consequently all the temperatures quoted have an associated error of ± 0·2 K, and it is possible that a biphasic region is present within this range. No significant hysteresis in the transition temperatures was detected at the heating/cooling rates employed in our studies. These clearing temperatures are comparable with those of the lead(II)alkanoates, and as with the saturated lead soaps, the members of both the $[x,2]C_nPb$ and $[x,8]C_nPb$ series show an increase in the transition temperature with increasing n. The transition enthalpies and entropies are higher than is the case for most thermotropic liquid crystals but are comparable with those reported for lead(II)alkanoates obtained from carboxylic acids higher than tridecanoic acid (C_{13}). Both the transition enthalpies and entropies increase with increasing x in the two series shown in the table. The large entropy discontinuities at the transition further support the view that the mesophases are highly ordered smectic phases.

Thermal properties of lead(II)alkadiynoates (cf. structure A).

Compound	m	n	T_c/K	$\Delta H/kJ\,mol^{-1}$	$\Delta S/R$
$[6,2]C_{13}Pb$	5	2	373·5	28·2	9·0
$[8,2]C_{15}Pb$	7	2	377·0	30·6	10·1
$[10,2]C_{17}Pb$	9	2	387·2	57·1	18·4
$[6,8]C_{19}Pb$	5	8	354·8	29·9	10·8
$[8,8]C_{21}Pb$	7	8	355·7	39·8	14·2
$[10,8]C_{23}Pb$	9	9	360·2	66·9	22·8

Although neither the extent to which the lead(II) carboxylate moiety is ionized in the absence of polar or protic solvents, nor the stereochemistry of the carboxylate groups about the metal ion are known, the mechanism which is responsible for the formation of mesophases in these materials appears to be analogous to the solvent-driven aggregation that results in the lyotropic mesomorphism of amphiphilic molecules. In this model the principal driving force towards mesophase formation is the segregation of the polar and apolar regions to form lamellar mesophases with varying degrees of intralamellar and interlamellar spatial ordering. Such a segregation generally results from the melting of the aliphatic chains in the molecules. However this may not always be the case as indicated by the X-ray diffraction studies of the highly ordered phases of the lead(II)alkanoates which suggest that the chains could exist in an amorphous frozen state. This contrasts with the case of conventional thermotropic liquid crystals where the drive towards mesophase formation results from the anisotropic interaction of highly anisometric rigid groups.

The presence of the diacetylene unit in an aliphatic chain could alter the melting behaviour, and consequently the mesomorphism, of a divalent metal soap in two ways. Unlike the case for the C–C bonds in methylene chains, the $CH_2{-}C{\equiv}$ bond exhibits virtually free rotation. An acetylene or diacetylene unit located in a straight chain aliphatic hydrocarbon would therefore effectively increase the conformational entropy of the molecule compared with the homologous fully saturated hydrocarbon.

Although the conformational distribution of each chain would be peaked at the *all-trans* conformation the two chains are no longer constrained to be *trans* with respect to one another. The diacetylenic metal carboxylates could therefore exhibit highly ordered smectic phases through the enhanced, though localized, fluidity of the aliphatic chains resulting from the decoupling of the two methylene segments by the diacetylene unit. Another way in which the diacetylene unit may affect the transitional behaviour in our compounds is through anisotropic interactions with the diacetylene units of neighbouring molecules. Because of the anisometry of the diacetylene unit it is expected that these interactions will tend to induce alignment of the diacetylene units in the same way that the anisotropic interactions of conventional mesogens lead to the formation of liquid-crystalline phases. The tendency for the diacetylene units to align will result in a decrease in the conformational entropy of the methylene chain which links the diacetylene group to the polar core since the conformational distribution of this chain will be strongly peaked at the *all-trans* conformation. On the basis of this argument it would be expected that the clearing temperatures for the compounds with two methylene groups in the linking chain should be higher than the clearing temperatures for the compounds with eight methylene units in the linking chain. Comparison of the transitional data for compounds $[x,2]C_nPb$ and $[x,8]C_{n'}Pb$ shows this to be the case in spite of the fact that $n' > n$. This contrasts with the case for the saturated lead(II) carboxylates in which the clearing temperature increases as a function of n, the total number of carbon atoms in the aliphatic chain. If the anisotropic interactions of the diacetylene units are sufficiently strong it may be possible that the terminal alkyl chains melt at a lower temperature than the methylene chains linking the diacetylene group to the polar core. This behaviour would also be expected to enhance the formation of highly ordered lamellar phases.

It is interesting to note that lead(II) *trans*-9-octadecenoate, $[8,7]C_{18}Pb$ in our notation but with an alkene unit rather than a diacetylene unit in the chain, does not appear to form a liquid-crystalline phase, melting from the crystal to the isotropic at 372·5 K with an enthalpy of transition of 113·2 kJ mol^{-1} and with $\Delta S/R$ of 36·6 [14]. By contrast, lead(II) octadecanoate, $C_{18}Pb$ has an unassigned smectic phase which melts to an isotropic liquid at 387·2 K with a $\Delta H = 56{\cdot}9$ kJ mol^{-1} and $\Delta S/R = 17{\cdot}7$. It would appear therefore that the presence of the *trans*-alkene link suppresses the formation of a mesophase. In terms of the arguments presented here this may be rationalised by noting that the *trans*-alkene unit effectively lowers the conformational entropy of the whole aliphatic chain. Because of its small anisometry compared with the diacetylene unit, the strength of its anisotropic interactions with other alkene groups will be comparable with the interaction strengths of saturated C–C bonds. Therefore no additional stabilization of the mesophase is present, favouring instead a lamellar crystal which melts directly to an isotropic phase when the whole alkyl chain melts.

Our qualitative studies of the polymerizability of the diacetylenic salts reflect the conformational statistics of the alkyl chains outlined here. Although all of the monomers exhibit some response to UV radiation, a marked difference was observed between the photoproducts of the $[x,2]C_nPb$ series and those of the $[x,8]C_{n'}Pb$ series. In the former materials polymerization was virtually instantaneous yielding deep blue polymers with a metallic sheen, while in the latter series the polymers were orange to red in colour and only developed following exposure of at least three minutes. These colour differences may indicate that the $[x,2]C_nPb$ materials produce polymers with higher degrees of polymerization than the $[x,8]C_{n'}Pb$ series, or, alternatively, that polymers from the latter series have structures with a large number of *cis* double bonds.

Further studies on the structures and optical properties of the polymerized mesophases prepared from the lead(II)alkadiynoates are currently in progress and will be reported elsewhere.

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