Growth, polymerization and oxidation characteristics of PA–PDA single crystals

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The growth, polymerization and oxidation characteristics of PA–PDA (polyacetylene–polydiacetylene) crystals are described. Simultaneous crystallization and polymerization of $(HC\equiv C(CH_2)_8-C\equiv C)_2$ from a solution in 1,11-dodecadiyne was found to be the best means for obtaining fully polymerized PA–PDA crystals. The electrical conductivity of PA–PDA decreased by approximately two orders of magnitude upon exposure to air over the period of a year. The oxidation characteristics of the polyacetylene chain in PA–PDA were essentially similar to that of *trans*-polyacetylene by itself. However, oxygen probably remained as a dopant in these crystals for a long time before chemically bonding to the backbones.

(Keywords: polymerization; polyacetylene; polydiacetylene; conductivity)

INTRODUCTION

Conjugated polymers such as polyacetylene, polydiacetylene, etc. have generated a great deal of research interest recently[1-3]. Over the past few years, extensive attention has been paid to polyacetylene as a prototype conducting polymer[1]. As an ideally one-dimensional single crystalline system, polydiacetylene has received continued attention from the standpoints of both solid state physics as well as chemistry[2]. More recently, another unique polymeric system has been reported which combines both polyacetylene and polydiacetylene within the same framework and yet preserving the single crystalline regularity[4]. From a detailed X-ray structure analysis, it has been shown that in this polyacetylene–polydiacetylene system (PA–PDA) the two polymer backbones run parallel and coplanar with each other, having eight methylene units as the spacer group (see *Figure 1*). The general physical and electronic properties of this material lie somewhere in between that of polyacetylene and polydiacetylene. The crystal size of PA–PDA is much smaller than that of a typical polydiacetylene. The intrinsic electrical conductivity and stability, on the other hand, is higher than pristine all-*trans* polyacetylene. Thus, PA–PDA is a unique composite of two principal conjugated polymers, possessing a variety of interesting properties that include high electrical conductivity, excellent order and large optical anisotropy, etc.

The crystal structure of PA–PDA was described in an earlier paper[4]. In this article, the growth, polymerization and the oxidation characteristics of PA–PDA will be discussed with *FT*i.r. and optical absorption data.

SYNTHESIS

The monomer of PA–PDA, $(HC\equiv C-(CH_2)_8-C\equiv C)_2$ was prepared by an oxidative coupling of 1,11-dodecadiyne using a copper–pyridine catalyst (Glaser coupling scheme)[5]. The details of the reaction for obtaining long chains containing diyne segments was reported earlier[6]. For this specific case under consideration, a critical ratio of the coupling agents and reaction time was decided via a trial and error approach so that the dimerization of 1,11-dodecadiyne was maximized. Approximately 0.050 mol or 1,11-dodecadiyne was coupled using approximately 0.7 g of cupric acetate and 34 ml of pyridine in 34 ml of methanol as the solvent for a reaction time of approximately 20–25 min at $\simeq 45°C$. The final product was a clean solution containing approximately 75% of $(HC\equiv C-(CH_2)_8-C\equiv C)_2$, 22% of 1,11-dodecadiyne and 3% of the trimer of 1,11-dodecadiyne. This composition was determined by h.p.l.c. with precalibration. The solution sample was subsequently used for the growth and polymerization of PA–PDA crystals.

Simultaneous crystallization and polymerization

A part of the solution obtained from the above synthesis was deposited as a thin layer on a clean glass substrate at a higher temperature ($\simeq 70°C$) and left for crystallization under room light at room temperature. Over the period of a few weeks spherulitic growth of partially polymerized PA–PDA having a reddish yellow colour was observed. The material was swollen because of the presence of liquid 1,11-dodecadiyne which was acting as a solvent. Complete polymerization was subsequently effected by Co^{60} γ-radiation which led to a blue–black spherulitic material. The conductivity of this material was measured using a four point probe on a pressed powder sample after extraction of the residual 1,11-dodecadiyne with chloroform. As reported in an earlier paper, the conductivity was in the range of $10^{-3}-10^{-2}$ ohm^{-1} cm^{-1} at room temperature[4].

In order to obtain single crystals of PA–PDA, a portion of the solution in an enclosed glass container was left
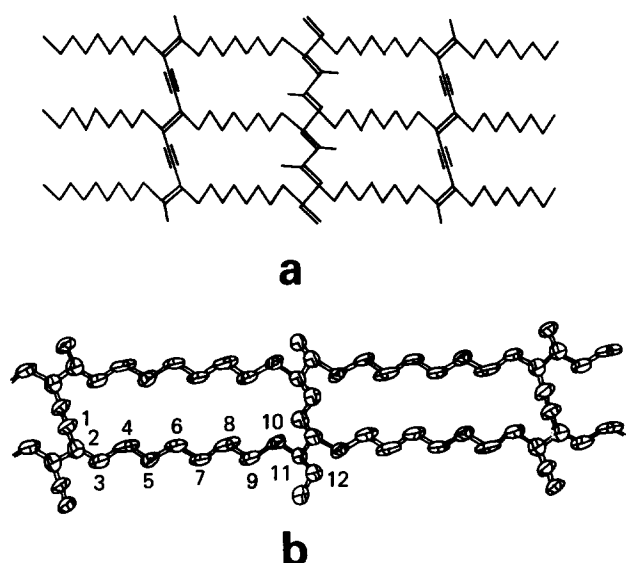
Figure 1 (a) The ac section of PA–PDA (schematic). (b) The *ac* section of PA–PDA (after ref. 4). 1,2: carbon atoms of the polydiacetylene backbone; 11,12: carbon atoms of the polyacetylene backbone; 3–10: methylene carbons

under Co^{60} γ-radiation at ambient temperature. Over the period of a few weeks, partially polymerized red coloured small single crystals of PA–PDA were observed to grow on the walls of the glass container. These crystals within the solution were subsequently annealed at approximately 35°C which resulted in a slight increase in the overall size of the crystals. Complete polymerization of these crystals leading to a blue–black colour was achieved by a prolonged exposure (approximately 50 Mrad) to γ-radiation.

Unlike the polymerization of a typical diacetylene, that takes place in the solid state, in steps of a solid solution, PA–PDA was simultaneously grown and polymerized from a liquid phase[2,7]. Earlier in the literature, such crystal growth during polymerization was reported for many other systems which include polyoxymethylene from formaldehyde, poly-*p*-xylylene from paraxylylene, etc.[8] The subject of simultaneous polymerization and crystallization was initiated by Staudinger and subsequently elaborated with many examples by Wunderlich[9]. Various initiators which include heat, radiation and specific cationic catalysts have been utilized for various monomers to initiate the simultaneous growth and polymerization[9b]. For PA–PDA, the concentrated solution of the monomer in 1,11-dodecadiyne and γ-radiation as the initiator were found to be appropriate and effective.

The results of some of the recent experiments performed in our laboratory and elsewhere show that both the functional groups in $(HC{\equiv}C-(CH_2)_8-C{\equiv}C{-})_2$, namely the acetylene and the diacetylene, do not undergo complete polymerization if the polymerization is attempted in the solid state[10a]. Only the diacetylene functionalities react and the acetylenic functional groups remain predominantly unreacted. Similar low level of reactivity of acetylenes in the solid state was noticed for other substituted monoacetylenes as well[10b]. In the light of these results, it is concluded that the simultaneous crystallization and polymerization provides the most favourable conditions for acetylenes to react and form fully polymerized PA–PDA crystals.

Optical absorption

The single crystals of PA–PDA were too small (approximately $1.5 \times 0.5 \times 0.05\,mm^3$) to be used for optical absorption measurements. Polarized optical microscopy showed that the single crystals possess a large optical anisotropy typical of polydiacetylenes (*Figure 2*). Therefore, in the transmission mode, the crystals look opaque for polarization parallel to the chain axis and transparent for polarization perpendicular to the chain direction. The optical absorption spectrum of PA–PDA was recorded using a KBr pellet of powdered sample and is shown in *Figure 3*. As *Figure 3* shows, the onset of absorption was below 1 eV with a distinct shoulder at approximately 2.3 eV. The shoulder was presumably due to the polydiacetylene backbone and the absorption coefficient was approximately $10^5\,cm^{-1}$. The onset of the absorption was below 1 eV unlike a typical polydiacetylene or pristine polyacetylene[11]. Such low onset could be attributed to the strong interchain coupling between the interlayer polyacetylene and polydiacetylene chains in PA–PDA, having an interchain distance of approximately 3.6 [12]. Alternatively, the low energy absorption could be explained as a result of partial oxygen doping[13].
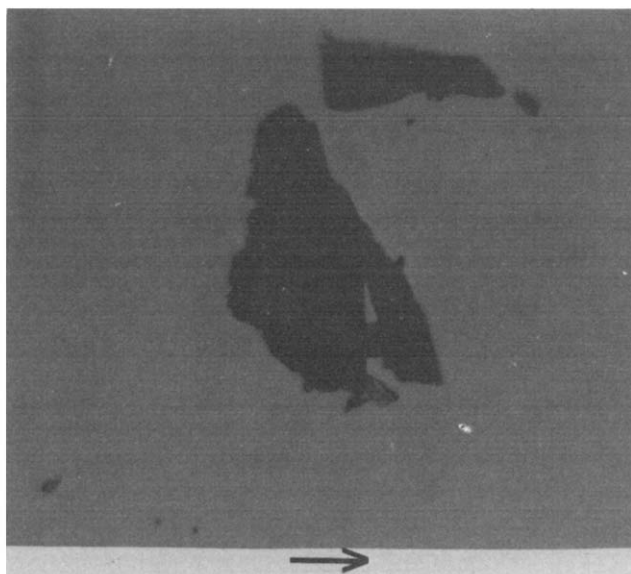

Figure 2 Transmission optical micrograph of PA–PDA single crystals. The polarization direction is indicated by the arrow. The crystal for which the polarization is parallel to the chain axis looks opaque
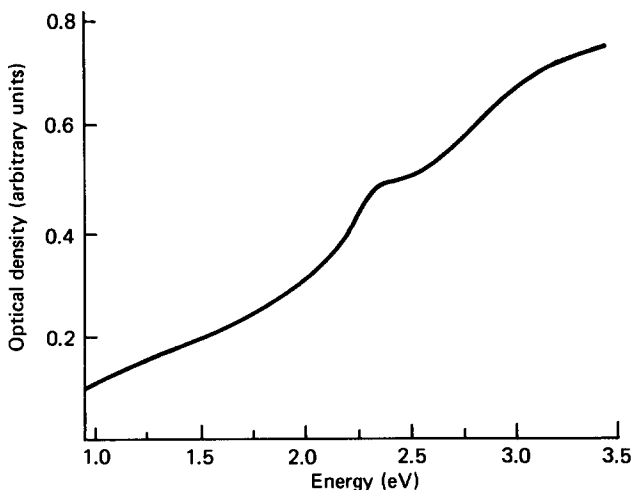

Figure 3 Optical absorption spectrum of PA–PDA

Oxidation characteristics

The oxidation characteristics of PA–PDA were studied using FTi.r. spectroscopy for different times of exposure of the material to air. The FTi.r. spectrum of pristine PA–PDA is shown in *Figure 4* and compared with all-*trans* polyacetylene prepared by Shirakawa[14]. The peak at $1018\,cm^{-1}$ was due to the out of plane deformation of hydrogen of –C=CH in PA. The C=C stretching mode of R–C=C–H in the PA backbone of PA–PDA appears at $1625\,cm^{-1}$. The C=C stretching mode in the polydiacetylene backbone of PA–PDA probably has a weak contribution to this peak as well.

Upon oxidation, new peaks and a broad background appear in the region between 1000 and $1800\,cm^{-1}$. The corresponding spectrum is shown in *Figure 5* with a comparison to an oxidized polyacetylene film[15]. The spectrum in *Figure 5* was recorded after a year of exposure of the material to air. The conductivity decreased by more than an order of magnitude in this time period. Most of the new peaks in the FTi.r. spectrum have been assigned by comparing with the oxidized *trans*-polyacetylene[15]. The bands at 1640 and $1730\,cm^{-1}$ were due to mono and diketone vibrations, respectively. The two peaks around $1465\,cm^{-1}$ were due to $-CH_2-$ deformation modes. As anticipated, the relative intensity of the =CH out of plane deformation band at $1018\,cm^{-1}$ decreased as oxygen reacted with the backbone. The band at $1190\,cm^{-1}$ was most likely due to C–O stretching vibration of the alcohol that was formed upon oxidation[15].

Figure 6 shows the FTi.r. spectrum of oxidized PA–PDA between 2600 and $3800\,cm^{-1}$. The C–H stretching of the PA backbone appeared at $3018\,cm^{-1}$ and the $-CH_2-$ stretching modes appeared at 2855 and $2926\,cm^{-1}$ as expected.

The peak at $3400\,cm^{-1}$ was assigned to the –OH vibration of the alcohol that resulted from oxidation. However, it is important to note that the same band with comparable intensity appeared in the case of supposedly pristine PA–PDA as well. Since there was no signature of
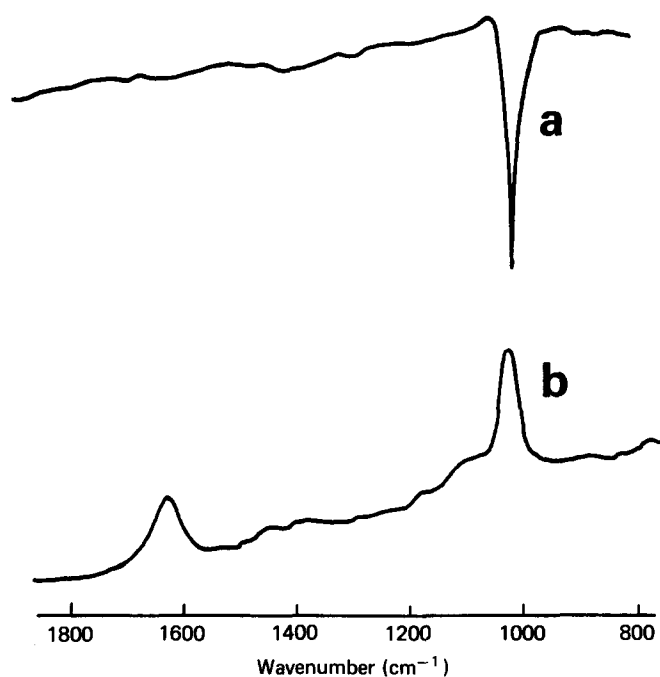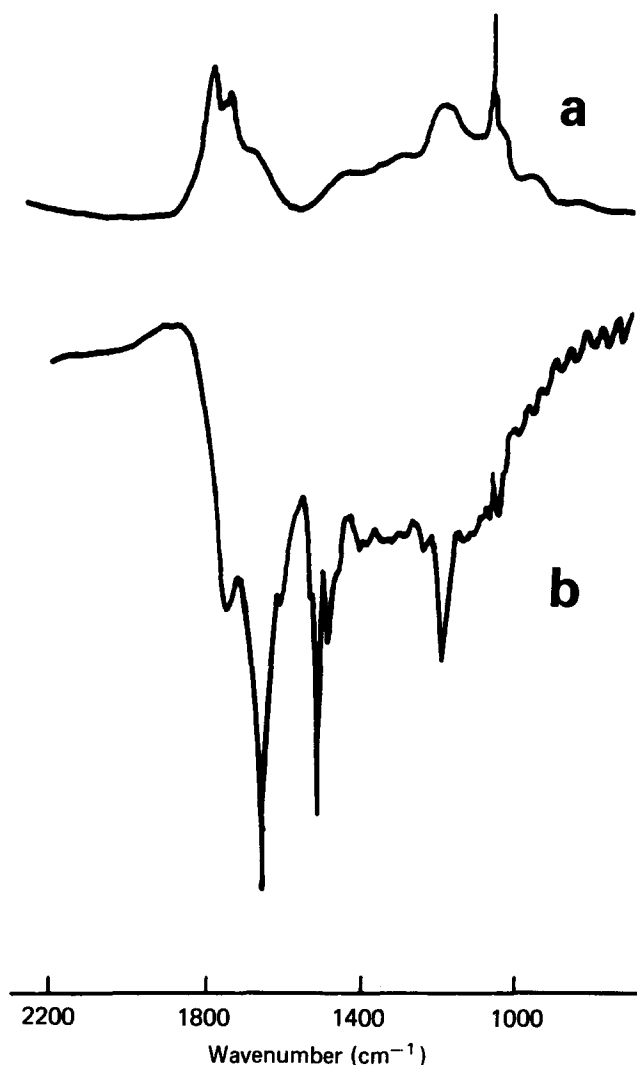
Figure 5 (a) FTi.r. absorption spectrum of oxidized polyacetylene (after ref. 15) $1000–2200\,cm^{-1}$. (b) FTi.r. transmission spectrum of oxidized PA–PDA
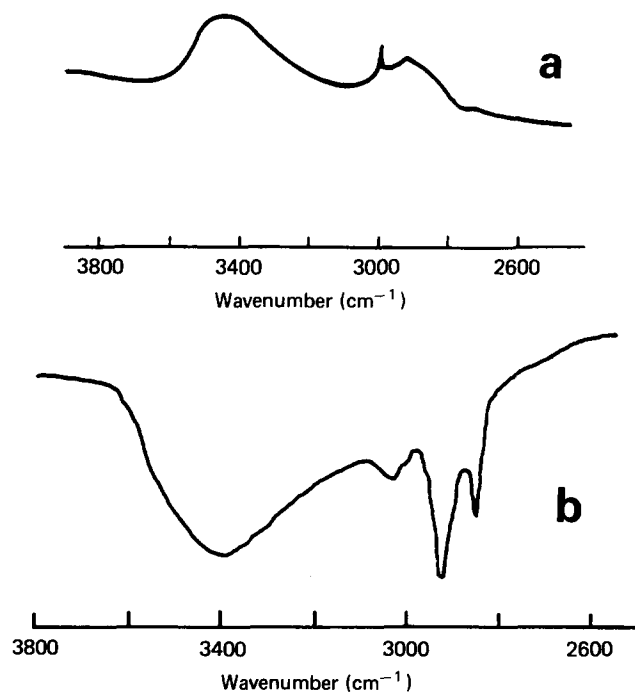
Figure 4 (a) FTi.r. transmission spectrum of pristine *trans*-polyacetylene (after ref. 14). (b) FTi.r. absorption spectrum of pristine PA–PDA

Figure 6 (a) FTi.r. spectrum of oxidized polyacetylene (after ref. 15) $2600–3800\,cm^{-1}$. (b) FTi.r. transmission spectrum of oxidized PA–PDA

chemical reaction (e.g. ketone formation) of oxygen at that stage, one may conjecture that oxygen was residing in the lattice as a dopant. Thus, the apparently pristine PA–PDA could be actually doped (not chemically bonded) with oxygen. The higher stability of PA–PDA could have resulted from a symmetrical placement of the oxygen counterions in the interplanar spacings of the crystals. In addition, as stated earlier, the possible interchain coupling between the interplanar polyacetylene and polydiacetylene chains in the PA–PDA could, alternatively, be the origin of the observed absorption at $3400\,cm^{-1}$ ($\simeq 0.4\,eV$)[12a]. Other possible interpretations of the same absorption are also reported[12b].

SUMMARY

The growth, polymerization and oxidation characteristics of PA–PDA crystals have been described. Simultaneous crystallization and polymerization was apparently the only means for forming the two polymer backbones to completion. The oxidation characteristics of the polyacetylene chain in PA–PDA were essentially identical to that of *trans*-polyacetylene by itself. However, oxygen probably remained as a dopant within the interplanar spacings in the crystals of PA–PDA, for long before chemically reacting with the backbones. Consequently, in air, PA–PDA was found to be more stable than polyacetylene. As discussed in an earlier paper, the higher stability of PA–PDA may also arise from the coulomb coupling of the interplanar polyacetylene and polydiacetylene chains[12]. The onset of optical absorption of PA–PDA was below 1 eV, unlike pristine polyacetylene or polydiacetylene. Finally, one may note that the method described provides the first example of fully ordered polyacetylene chains.

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