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Polymerisation and characterisation of nitrile-terminated diacetylene materials

R P Grasso, J B Lando
Department of Macromolecular Science, Case Western Reserve University, Cleveland, Ohio 44106, USA

ABSTRACT. A family of nitrile-terminated diacetylene materials were synthesised. Samples were prepared in various forms and polymerisation was performed photochemically and thermally. The resulting materials exhibited low molecular weights and were obtained in low yields. Although the diacetylene group had oligomerised, no evidence was found in support of $-C\equiv N$-chain formation. Thermochromism was exhibited by the irradiated 8-nitrile sample and a molecular interpretation of this chromic transition was discussed. Diffraction data implied that strong intermolecular interactions were present between adjacent nitrile groups in the low temperature phase. It is suggested that stresses are built up during polymerisation which cause the low degree of polymerisation and yield.

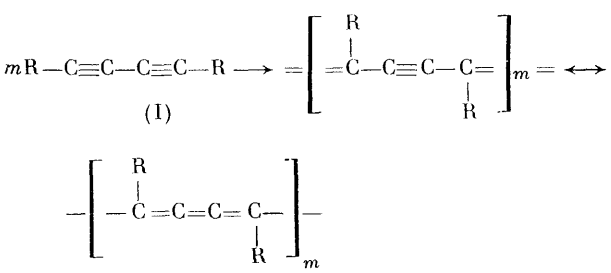
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I. Introduction

The polymerisation of diacetylenes has attracted a great deal of interest which was initially due to the unique nature of this solid state polymerisation reaction.[1–5] Initiation can be carried out simply by exposing crystals of the diacetylene monomer to high energy radiation (UV, gamma, X-ray) or by annealing the crystals at temperatures below their melting points. The resulting polymers are highly crystalline since there is relatively little movement of the molecules during polymerisation. As a result, fully extended conjugated backbones are formed which give rise to their deeply coloured appearance.



In recent years, polydiacetylenes have been reported to exhibit unique properties in fields such as non-linear optics, ferromagnetism, thermochromism/solvatochromism and electrical conductivity.[6–11] The polymerisation of acetylenes has also been the focus of much interest recently. Most of this interest has been a result of the relatively high electrical conductivity of this organic material when oxidised or reduced.[12–14]

Our previous work has concentrated on the polymers of a family of diacetylene materials of the form: $HC\equiv C(CH_2)_nC\equiv C-C\equiv \equiv(CH_2)_nC\equiv CH$. The polymers obtained from this class of diacetylene monomers are interesting not only from the viewpoint of polymer physics and crystallography, but, in addition, they have been observed to exhibit several properties unique for the crystalline solid state such as electrical and optical conductivity.[15–17]

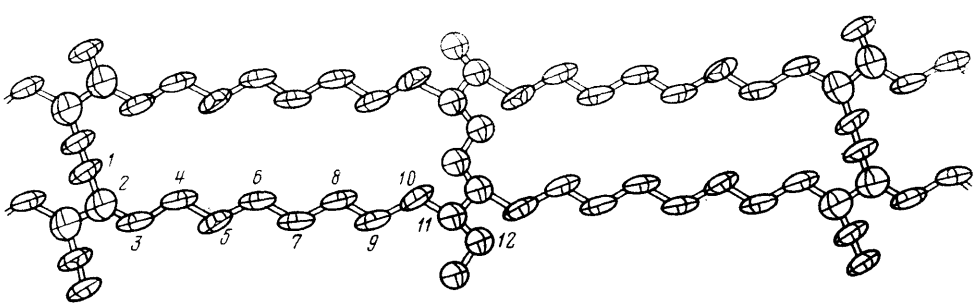
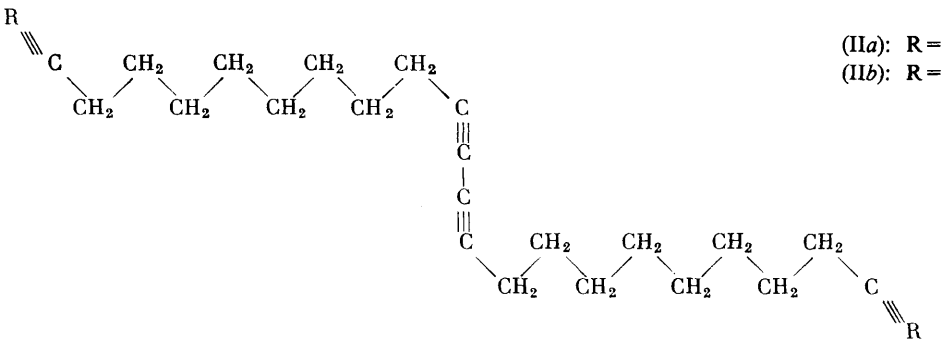


Figure 1. The *ac* section of the polymerised 1,11-dodecadiyne dimer. *1,2*, carbons in the PDA backbone; *11,12*, carbons in the PA backbone; *3–10*, methylene carbons.



(II*a*): R = CH,
(II*b*): R = N.

Figure 2. Nitrile terminated analogue of the 1,11-dodecadiyne dimer.

In addition to possessing a polydiacetylene backbone, the crystalline polymerised dimer of 1,11 dodecadiyne (II*a*) has been shown to have its adjacent acetylene groups polymerised in a head-to-head fashion. The resulting structure is composed of sheets of two dimensional networks of polyacetylene (PA) and polydiacetylene (PDA) backbones interconnected by eight methylene groups (Fig. 1).[18] Adjacent sheets are shifted one-half of a unit cell dimension along the "*a*" direction relative to one another. This results in a three-dimensional structure where polyacetylene chains are "sandwiched" between two polydiacetylene chains and *vice versa*. One possible explanation of its high room temperature conductivity of ca. 10^{-3} Ω^{-1} cm^{-1} utilised partial charge calculations in addition to π-electron overlap to propose a "self-doping" mechanism between sheets.[16]

One problem that persisted in working with this family of symmetric dimers (II*a*) is a result of the fact that they are aliphatic and contain no polar functional groups. Therefore, they are difficult to crystallise prior to solid state polymerisation. Due to this difficulty, a multistep synthetic route was developed with the intention that chemically pure species crystallise easier than the oligomeric mixtures which had been obtained previously using a controlled condensation reaction.[17] While the crystallisability of this diacetylene product was slightly increased, large macroscopic single crystals could not be obtained for other measurements.

We are presently considering a system analogous to the acetylene terminated dimers where the end groups have been replaced by nitrile groups (Fig. 2, II*b*). The added polarity of this functional group compared to substituted acetylene should aid the attempt to obtain large crystals of this polymerisable monomer. As an analogue to the acetylene terminated dimer, we can expect the diacetylene linkage to polymerise by the previously mentioned 1,4-addition reaction since the chemical distinction between the two materials is far removed from the diacetylene group.

The cyano group has been polymerised by cationic, anionic, radical and coordination catalysts.[19–23] Recent interest in these polymers has also focussed on their use as potential electrically conductive materials. However, the measured conductivities from various nitrile polymers were not as high as were anticipated ($10^{-8}-10^{-6}$ Ω^{-1} cm^{-1}). This is at least partially a result of the low crystallinity of the samples which is caused by the extra degrees of freedom allowed by the polymerisation conditions (solution or bulk liquid).

The radiation chemistry of the nitrile group has also been studied and is comparable to the acetylene group in that the main reaction is addition to the triple bond. The majority of work in this area has been performed on acetonitrile in both the solid and liquid phases. Although the degree of polymerisation is lower in nitrile compounds than in the acetylene compounds, the main product is a solid polymer. Ultraviolet and infrared spectroscopies are consistent with a conjugated $-C=N-$ chain.[24,25]

Perhaps the most interesting example of nitrile polymerisation is the one which occurs as polyacrylonitrile (PAN) is heated to 250–350 °C. The reaction of these nitrile groups in PAN and its copolymers was originally studied in order to understand the thermal discolouration of these polymers. The resulting material is sometimes referred to as "black Orlon" and typically exhibits 5–10 consecutively reacted nitrile groups.[26]

The colouration process has been studied using a variety of characterisation techniques. Thermal analysis has shown that an exothermic reaction occurs at about 250–350 °C.[27,28] Simultaneous gravimetric analysis indicates that a 10% loss in weight occurs at 270 °C, while spectral analysis of the products evolved showed that HCN and NH_3 are the major constituents. Hydrogen is suggested to be evolved at higher temperatures (450–700 °C). A series of papers by Coleman, et al.[29–31] utilises the advantages of FTIR spectroscopy to monitor the thermally induced reaction. It was found that the intensity of the nitrile absorbance steadily decreased as a function of degradation time. During the same period, numerous bands appeared which could be assigned to functional groups consistent with the proposed mechanism discussed in Ref. 21.

The conductivity of vacuum pyrolysed PAN has been studied by Lerner.[32] Using FTIR as a probe, it was reported that the pyrolysed PAN did not absorb iodine until the length of the cyclised segments exceeded a threshold value of 18 units. When the cyclicity exceeded this value, iodine could be absorbed by the polymer at room temperature to the extent of almost two iodine atoms per cyclised ring. The highest conductivity obtained was 10^{-2} Ω^{-1} cm^{-1}. Variable temperature studies yielded an activation energy of 0.59 eV and the room temperature mobility was calculated to be on the order of 10^{-5} cm^2/V sec. This is of the same order of magnitude as the mobilities of other polymeric conductors such as lightly doped polyacetylene.[33,34] Conduction in the iodine-doped pyrolysed PAN was suggested to be due to a hopping mechanism.

It was therefore decided to investigate the polymerisation and properties of the diacetylene-nitrile materials. This decision was made on the basis of the polarity and the polymerisability of the nitrile group, the electrical properties of the resulting nitrile polymers and the assumption of non-interaction between the nitrile and diacetylene groups. Since these materials are not commercially available, a synthetic route was devised to obtain the diacetylene nitrile analogues.

II. Experimental

In order to perform a more complete study, it was desired to obtain all members of the diacetylene-nitrile family with the number of methylene groups varying between 0 and 8. Materials with fewer than 2 methylene groups had to be prepared differently due to their reactivity. The synthetic pathways used here are illustrated in Fig. 3. Further synthetic details can be found elsewhere.[35] The convention used for nomenclature here and throughout takes the form of "*n*-nitrile dimer", where "*n*" represents the number of methylene groups present between the diacetylene and nitrile groups.

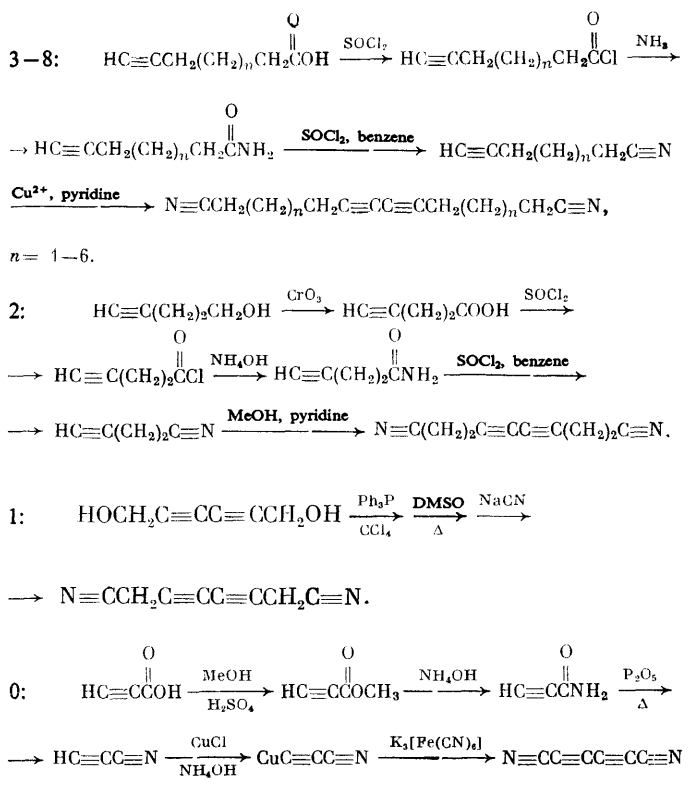


Figure 3. Synthetic pathways used in the preparation of the 0-through 8-nitrile diacetylene materials.

3-Through 8-nitrile synthesis:

A sample of acetylenic acid was reacted to form its amide using the method of Bishop.[36] The dehydrolysis of the amide to form the nitrile was accomplished using the method described by Krynitsky and Carhart.[37] Yields were typically on the order of 80%. The acetylenic nitrile was oxidatively coupled using a modified Glaser reaction[38] to give the desired product. All products were purified using column chromatography.

2-Nitrile synthesis:

The oxidation of 4-pentyn-1-ol to form 4-pentynoic acid was performed following the method of Heilbron, et al.[39] The acid could then be converted to the desired product as described above.

1-Nitrile synthesis:

The diacetylenic diol, 2,4-hexadiyn-1,6-diol, could be directly converted to the desired nitrile compound using the procedure described by Brett, et al.[40] to replace the hydroxyl groups with nitriles.

0-Nitrile synthesis:

Cyanoacetylene could not be obtained through commercial sources and was therefore prepared using the method of Moureu and Bongrand.[41] The coupling of the cyanoacetylene was accomplished using a cuprous derivative intermediate as described by Brockman.[42]

III. Polymerisation of nitrile diacetylenes

Sample preparation. Numerous experiments were performed on all of the synthesised nitrile materials in an attempt to polymerise both the diacetylene and nitrile functional groups. Three methods were employed to prepare samples for the solid state polymerisation experiments. The samples thus prepared were in the form of macroscopic crystals, thin microscopic polycrystalline films and thick microscopic polycrystalline films.

Chromic studies were performed on a Perkin-Elmer Lambda Nine UV/Visible/NIR spectrometer. The thermal characterisation was carried out using a Perkin-Elmer DSC-7 differential scanning calorimeter equipped with a workstation. X-Ray diffraction was measured using a Philips Diffractometer (Model APD 3520) with nickel filtered CuK_α radiation.

Ultraviolet polymerisation. Ultraviolet (UV) irradiation was performed at an intensity of 1600 μW/cm^2 at a wavelength of 254 nm. Ultra High Purity (UHP) argon was used as a purge gas in order to provide an inert atmosphere during irradiation. Samples were intentionally kept thin in order to minimise the surface absorption of UV light by the coloured reaction products. Exposure times of 5, 10, 20 and 45 minutes were used.

Gamma polymerisation. Gamma irradiation was carried out using a Gammacell 220 ^{60}Co source. The intensity of the source at the sample position has been calculated to be 48.2 krad/hour. The samples were flushed with UHP argon and sealed in glass containers before placing them into the source. The sample temperature could be controlled either internally or externally.

Thermal polymerisation. Polymerisation attempts at elevated temperatures were performed using a vacuum oven. Before heating, the oven was repeatedly purged with UHP argon and evacuated. Temperatures of 225, 250 and 300 °C and treatment times of 5, 15, and 30 hours were utilised.

IV. Results and discussion

The 0-nitrile dimer was found to be unstable during the course of these experiments and, therefore, no meaningful data could be obtained regarding its polymerisability.

It is known from numerous studies on other compounds that both polydiacetylenes and poly(nitriles) are highly coloured due to the conjugation present in the polymer backbone. It was, therefore, immediately noted that the absence of a coloured product from the various treatments in the case of the 1-, 2-, 3- and 4-nitrile materials probably inferred that no polymerisation had occurred. In addition, the physical appearance of the original diacetylene compounds and their experimental products were identical. This conclusion was substantiated by the infrared spectra of the monomer and irradiated samples which were identical throughout the scanned region ($3600-450$ cm^{-1}). A possible explanation for this observation will be discussed later.

A synopsis of the polymerisation attempts on the remaining crystalline diacetylene-nitrile materials (with $n > 4$) and the general results are listed in Table 1. Overall, the various methods employed were unsuccessful in producing a material with fully polymerised diacetylene and nitrile groups.

Table 1. Synopsis of polymerisation attempts and the general observations.

Treatment	Appearance	Physical characterisation	Spectroscopy
UV	blue → orange (R.T.)	melts, soluble	No C=N–
Gamma	blue → orange (R.T.)	melts, soluble	No C=N–
UV/gamma	blue → orange (R.T.)	melts, soluble	No C=N–
Heat	melts/evaporates	—	—
UV/gamma/heat	blue → orange → black	insoluble, not crystalline	No C≡N, –C=N–
n-Butyllithium	viscous yellow liquid	insoluble in benzene	No C≡N

The ultraviolet treatment of the crystalline nitrile dimers at subambient temperatures resulted in materials which are blue in reflected light. When these products were allowed to warm to room temperature, they underwent a transition from blue to reddish-orange in colour. In addition, the crystal habit was destroyed and the resulting material exhibited an appearance which could best be described as severely fragmented, pieces of orange film which precipitated from the crystallisation solution or the bulk melted dimer depending on which sample preparation was used. The coloured product was isolated in low yield (2–3%) and was found to be soluble in a variety of common solvents (e.g. acetone, methylene chloride, carbon tetrachloride and tetrahydrofuran). Infrared samples were prepared by solution casting a film onto a KBr plate. The resulting spectra gave no indication of polymerisation through the C≡N bond. This was determined by the intensity ratio of the C≡N stretching band (2240 cm^{-1}) relative to that of the aliphatic C–H stretching bands which remained constant throughout the radiation treatment. In addition, no absorbances which could be attributed to a poly(nitrile) chain were found (e.g. conjugated –C=N– bonds at 1570 cm^{-1}, C=N linkages at 1640–1610 cm^{-1} or C–N bonds at 1220 and 1145 cm^{-1}).[28,43]

Since the coloured product was soluble in tetrahydrofuran (THF), gel permeation chromatography could easily be used to follow the conversion of the diacetylene-nitrile dimers. The elution volume/molecular weight relationship was calibrated with monodisperse polystyrene standards using THF as a solvent. The maximum extent of polymerisation was not large. Using the 8-nitrile dimer as an example, the approximate maximum degree of polymerisation was calculated to be ca. 12 assuming that the calibration of the GPC data is valid in this low molecular weight range.

The results of experiments performed using gamma radiation for initiation were very similar in many respects. A blue sample at subambient temperatures transformed into the orange form after warming to room temperature. Infrared spectroscopy suggested that the C≡N groups did not appreciably react using this technique. Solubility and maximum molecular weight data were also in agreement with UV results. It was interesting to note that the yield of coloured product, although low in all cases, was approximately equal for the UV and gamma treatments in samples prepared in similar manners. That is Yield (crystals, UV) ≈ Yield (crystals, gamma) or Yield (thin film, UV) ≈ Yield (thin film, gamma). However, the yields using thin films were larger than those using thick films or crystals. Since the major difference between these samples lies in the surface area/volume ratio, which is largest for these thin samples, it would appear to be a surface related phenomenon. Certainly, it cannot be related to a surface absorption effect since the penetrating power of gamma radiation is much higher in this case than UV. But the observation does appear to be related to the relative surface area and this will be discussed later in more detail.

Several other solid state polymerisation techniques were utilised in an attempt to polymerise the nitrile group and increase the molecular weight and yields. A combination of UV treatment followed by gamma irradiation at low temperature was not found to be statistically different from either of the two separate treatments. Although expected, heat treatment of the nitrile dimers under vacuum similar to that used in the cyclisation of polyacrylonitrile resulted in the material melting and finally evaporating. A combination of UV irradiation followed by gamma irradiation, which was then followed by heat treatment, gave rise to a black-coloured product. X-Ray diffraction suggested that the material was not crystalline. Since the product was not soluble, infrared samples were prepared using a KBr pellet. Analysis of the spectra gave no indication that –C=N– bonds formed even though the C≡N band at 2240 cm^{-1} was absent. The presence of broad bands centred around 1636 cm^{-1} suggested that a dehydrocyanation reaction[26] may have occurred to form C=C linkages. Crosslinking may then randomly occur through these groups by the radical species which can form at elevated temperatures.

1. Thermochromism

The ability of a material to exhibit a shift in the UV/visible absorbance maximum with a change in temperature is referred to as thermochromism. A large number of polydiacetylenes have been shown to exhibit these effects. Initially, these chromic changes in polydiacetylenes were thought to be a manifestation of an electronic transition along the polymer backbone.[44] This can be visualised as a change in the bonding arrangement from the acetylenic to the butatrienic mesomer. More recently, experimental evidence suggests that the chromic transition in crystallisable samples is brought about conformationally by a transition which causes a decrease in the effective conjugation length of the polydiacetylene backbone.[45–47] This reduction in conjugation can be induced in the polydiacetylene backbone by either a crystal–crystal transformation[48] or by disordering the flexible side groups, if present.[49] It should be noted that the order–disorder transition can be caused not only by thermally randomising the side groups, but also by other methods which increase the entropy or disorder of these groups. An example of this can be found in situations where the polydiacetylene chains are soluble. When the solvating power of the solvent is reduced in these cases by the addition of a miscible non-solvent, intramolecular forces predominate over the intermolecular (solvating) ones and the conformation of the extended polydiacetylene backbone is regained. With the increase in effective conjugation length, a bathochromic (red) shift is observed in the visible absorbance maximum. This reversible, solvent-induced change of conformation in polydiacetylenes is commonly referred to as the coil-to-rod transition,[50] which emphasises the nature of the polydiacetylene chain in solution. The ease of reversibility of this transition has been attributed to the presence of functional groups which are capable of intrachain interactions (e.g. urethanes, esters, etc.). Although a sizable amount of work was performed in this area, a controversy still exists as to whether the chromic transition is a result of an isolated chain event[51–54] or an aggregation event.[55,56]

Polydiacetylenes have also been observed to undergo irreversible chromic transitions.[57] A number of these irreversible changes can occur during polymerisation. It is well established that the solid state polymerisation of diacetylenes requires a simultaneous rotation and translation of the diacetylene rod.[58] The movement of this set of atoms in each of the reacted monomeric units leads to the production of large stresses within the crystalline material for some diacetylene compounds. At some point, these stresses are relieved in the form of a crystallographic phase change and/or an order–disorder transition.[47] Disorder in the side groups can induce a conformational change in the polydiacetylene backbone as discussed above. This has the effect of reducing the coordinated conjugation length and a chromic shift is observed.

In the present study, the family of diacetylene-nitrile materials which could be polymerised all exhibited similar thermochromic characteristics. Since most of the data could easily be obtained using the 8-nitrile dimer, those data will be discussed throughout this section. Generalisation to the other materials may be implied except where noted.

As was mentioned previously, the nitrile materials which polymerised at subambient temperatures in the solid state all exhibited a blue colour in reflected light. When allowed to warm to room temperature, the result was a breakup of the crystal habit and the material became reddish-orange in colour. This product was isolated and a film was solution-cast onto a clean quartz plate. A UV/Visible spectrum of the resulting reddish-orange 8-nitrile material exhibited its lowest energy optical transition at 528 nm (18 900 cm^{-1}).

Since the blue phase is stable only at subambient temperatures, an isothermal spectrum could not be obtained for it, due to the lack of a sample cooling device. However, several qualitative spectra were obtained on the blue phase using quick scans over a short range. A piece-by-piece comparison of the spectra, which were cumulatively taken over the range of 300 nm to 700 nm, indicated that the lowest energy optical transition for the blue phase occurs at about 628 nm (15 900 cm^{-1}). These values are in good agreement with those reported for most polydiacetylene crystals or films which exhibit the chromic transition.[59–62]

Numerous recent studies have shown that the optical transition is accompanied by a loss of planarity in the polymer backbone.[45,59,63] A variety of experimental techniques have been used in these studies. For example, infrared spectroscopy has been used to monitor the disruption of hydrogen bonding in the side groups and the formation of "free" N–H in the polydiacetylene, poly-3BCMU (R = $(CH_2)_3OCONHCH_2COOC_4H_9$). Furthermore, ^{13}C NMR chemical shift and relaxation time data has been used to explain the post-transition changes as resulting from a decrease in the delocalisation of π-electrons and thus a decrease in the conjugation length.[63]

Studies performed on an optical microscope equipped with a hot stage in conjunction with DSC measurements have shown that the blue-red transition temperature correlates with the melting temperature of the original dimer. It appears that the melted dimer may act as a solvent for the polymer side groups. As will be discussed later, a large amount of stress is incurred on polymerisation. Once this stress is relieved by disordering the side chains, which in turn decreases the conjugation length of the polydiacetylene backbone, the order present in the original unpolymerised material cannot be recovered. As a result of the unrecoverable conjugation length, the transition from red back to blue does not occur.

It should be noted that another chromic transition, from reddish-orange to yellow, can be observed in these materials. This has been accomplished both in the solid state (thermochromism) and in solution (solvatochromism). Furthermore, it appears to be reversible unlike the previously discussed transition. A similar transition has been observed in other polydiacetylenes such as poly-3BCMU, poly-4BCMU and the polymerised dimers of α,ω-alkadiynes.[59,62,64,65] It had been suggested that the low temperature transition (blue–red) was due to the melting of the side groups whereas the high temperature transition (red–yellow) was a result of the polydiacetylene backbone becoming disordered.[61]

2. Structure work

In an attempt to understand at the molecular level why the yields and molecular weights of the products were so low, X-ray structure analyses of the unpolymerised dimer, the blue phase of the polymer in solid solution with the monomer and the reddish-orange phase of the polymer were sought for the 8-nitrile material.

Both the unpolymerised dimer and the partially polymerised blue phase undergo a transition if allowed to warm to room temperature. Various attempts at subambient-temperature single crystal work were unsuccessful, therefore, polycrystalline diffractometer data at subambient temperatures was taken instead. The reddish-orange phase was obtained from the blue phase by allowing the sample to warm to room temperature. This polymeric phase transition was accompanied by the melting of the dimer which constituted the

larger fraction of the sample. Note that all the samples include a rather large percentage of unpolymerised dimer. The results are shown in Fig. 4. All three spectra were taken on approximately equal amounts of material and the scales for each run are identical.

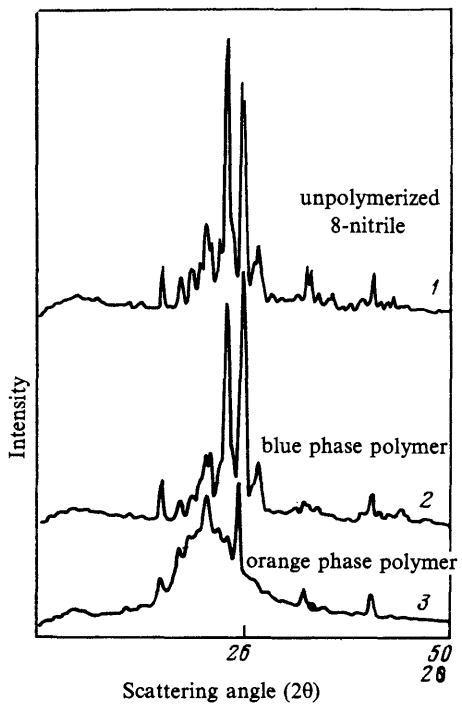


Figure 4. X-Ray diffractograms illustrating the crystallographic changes which accompany the polymerisation and the blue to reddish-orange transition in the 8-nitrile material.

A number of crystalline peaks can be observed in the top two diffractograms. Upon closer examination, it can be noted that peak positions and intensities are nearly identical for the unpolymerised dimer and the blue phase. There is a slight shifting of some of the peaks in the polymerised sample to larger scattering angles suggesting some contraction in the unit cell upon exposure to radiation. This would be expected in the solid state polymerisation of unsaturated compounds. In comparison to the other two diffractograms, the orange sample displayed a broad amorphous peak with some fine structure still present. The amorphous contribution is largely due to the melted dimer which is present in the sample. The observed crystalline peaks are located approximately at the same scattering angle as those seen in the blue phase. Some shifting to larger *d*-spacings is noted and can be attributed to a release of structural constraints which will be discussed later.

d-Spacings of the unreacted 8-nitrile dimer were measured and a unit cell which fits the data was determined by the method of least squares (see Table 2).

X-Ray density calculations performed on the unit cell indicated that there were two molecules per unit cell. A ball and stick model of the molecule was constructed using standard bond lengths, bond angles and dihedral angles. One molecule was placed at each corner of the unit cell and was centred at the midpoint of the diacetylene rod. The other molecule could be placed at (0, ½, ½), (½, ½, 0) or (½,½,½) in fractional coordinates. There are not enough data at the present time to determine which position is correct. The dimensions of the unit cell imply that there is some interdigitation of the nitrile groups on adjacent molecules. This interdigitation could be in either the *c* direction or the *b* direction (see Fig. 5).

Table 2. Unit cell data for the 8-nitrile material.

a=26.03 Å,	α=90.0°	
b=8.10 Å,	β=92.8°	Volume = 1122.4 Å^3
c=5.33 Å,	γ=90.0°.	Density = 0.960 g/cm^3

Considering the former case, the strong polar interactions of the adjacent nitrile groups obviously stabilise this structure. In addition, the intermolecular distance and orientation of the diacetylene rods in the polymerisation direction meet the requirements for diacetylene polymerisation as described by Baughman.[58] The other possibility for interdigitation would also have the polar interactions to stabilise the structure, but in order for these groups to be positioned as shown, the angle that the diacetylene rod makes with the *c*-axis must be larger than in the previous case. A qualitative calculation of this angle (ca. 57°) suggests that the diacetylene molecule will not polymerise according to Baughman's criteria.[58] From the experimental observations on the 8-nitrile material, it can be concluded that the diacetylene group does react and therefore the former model is more probable.

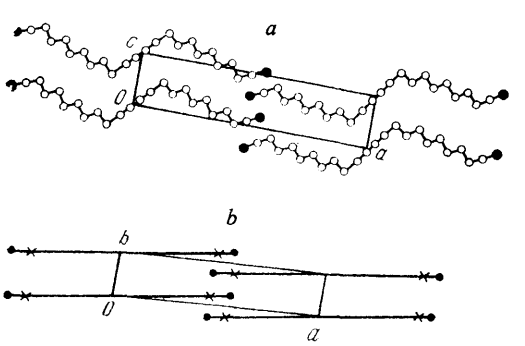


Figure 5. Projections of the 8-nitrile material illustrating nitrile interdigitation in the (*a*) *c*-direction and (*b*) *b*-direction. Hydrogens have been omitted for clarity, ● = nitrogen.

The reason as to why the diacetylene compound does not polymerise to a large degree can now be addressed. From a comparison of the crystal size and the rate of crystallisation for the

nitrile dimers and their acetylene terminated analogues, it is apparent that the polar nitrile groups interact strongly with each other. The interaction is strong enough such that one may consider the interdigitated nitriles to act as non-covalent "tie-points". Once the polymerisation of the diacetylene group is initiated, the rotation and translation which accompanies the diacetylene polymerisation is restricted at a certain point. This is a result of stresses which are built up with the addition of each molecule to the growing chain (lattice mismatch between dimer and polymer). Energetically, one may consider that the decrease in free energy associated with the polymerisation of the diacetylene group (with its required movement) is not great enough to overcome the intermolecular attraction of adjacent nitrile groups. This explains why the yield and the molecular weights of the reaction products are so low. Since the diacetylene polymerisation is considered to be topochemical, initiation occurs homogeneously throughout the crystalline lattice.[66] Thus, one would expect relatively similar yields for samples of the same mass even though the surface area may be different. The observation that this does not occur suggests that the polymerisation stress may be relieved at the crystal edges or faces by relaxation of the polymer.

The blue-to-red colour change exhibited by the polymer can be explained as a crystal–crystal transition or as an order/disorder transition. From the polymer yield calculations, the blue polymer phase can be considered to be dissolved in a crystalline matrix of dimer. As the temperature is increased, the dimer melts and can solvate the polymer side groups in the conventional sense. The disorder induced in these side groups can be covalently transmitted to the polydiacetylene backbone which is then manifested by a change in colour. However, the presence of crystalline peaks in the diffractograms of the orange phase implies that order is still present in this phase. This observation would favour the suggestion that the polymer itself undergoes a crystalline phase change once the structural constraints of the monomer are released as the monomer melts. Crystallographic phase changes which cause a chromic transformation have been observed in other polydiacetylene materials.[48,67] Finally, one must consider the possibility that a combination of these effects may account for the observed results. There are not enough data at the present time to determine which of these explanations governs the chromic transition.

At this point, some explanation must be given as to why the 8-nitrile material was chosen for most of the experimental work and discussion. Quite simply, this material exhibited the highest yields and molecular weight of all the nitrile dimers which were prepared. In consideration of the cyclisation reaction in polyacrylonitrile, it was initially believed that the nitrile groups in the irradiated 8-nitrile material would not polymerise because the long methylene chains were too flexible. As a result, adjacent nitrile groups could not be brought together into position to react. It was believed that after polymerising the diacetylene groups in nitrile dimers with fewer methylenes ($n < 8$), the nitrile group could be subsequently polymerised thermally if not photochemically. However, the number of nitrile groups per unit volume increases as the number of methylene groups decreases and the strong electrostatic interactions of the C≡N groups prevent the diacetylene polymerisation from occurring at all at a certain point.

3. Further work

Other attempts at obtaining a material which possessed both conjugated polydiacetylene and polynitrile chains were investigated. One of these involved varying the crystallisation procedure since there is a possibility that the diacetylene materials may exhibit polymorphism with one of the phases being more reactive than the others.[68,69] Crystallisations in various solvents and at different rates were performed. However, the results indicate that no different phases were achieved.

A number of procedures which may result in the simultaneous crystallisation and polymerisation of the materials were also attempted. Diacetylene materials which are analogous to those used in the present study have been reported to simultaneously crystallise and polymerise from solution upon exposure to gamma radiation.[70,71] This procedure was attempted using the nitrile materials but no polymer was observed before radiation damage took place.

Nitrile groups have been polymerised electrochemically from solution as was demonstrated by Tourillon, et al.[72] using acetonitrile. They have also been polymerised from pendant groups on polyacrylonitrile which had been deposited on the electrode.[43] It is known that polar species such as the C≡N group are oriented by an electric field and this may aid in the polymerisation process. However, the various electrochemical and chemical methods which were performed gave no evidence of the desired effect.

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