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# Novel polydiacetylenes for optical materials: beyond the conventional polydiacetylenes

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**Polydiacetylenes (PDAs) are of great interest due to their π-conjugated backbone related properties, such as linear and nonlinear optical properties. As a consequence, design and preparation of PDAs assume enormous importance today. This review deals with one aspect of PDA, that is, design and preparation of the diacetylene monomers and their polymers, PDAs having conjugated side groups. The aim of such an investigation is to produce materials which exhibit large third-order nonlinear optical susceptibilities and which consequently, can be obtained in a form to be customised for optical devices.**

## Introduction

Polydiacetylene (PDA) is obtained by solid state 1,4-addition polymerisation of diacetylene (DA) and has the general molecular formula $R{-}C{\equiv}C{-}C{\equiv}C{-}R'$.‡ The first example of the polymerisation of DA into PDA was reported by Wegner in 1969.[1] Since then, research on PDA has been sustained due to several interesting aspects of this polymerisation.[2,3] First, the polymerisation reaction is unique in the sense that single crystal monomer to single crystal polymer formation is possible. The reaction is topochemical in nature and therefore the monomer arrangement in the crystalline lattice has an important role to play, which makes it an interesting candidate for topochemical solid state polymerisation studies. Second, PDA has a quasi-one-dimensional π-conjugated backbone structure which gives it interesting electrical properties, chromic properties and optical properties. However, over time, the third-order nonlinear optical (NLO) properties of PDAs have been found to be most promising and therefore have attracted tremendous attention among researchers in this field.[4,5] The reason for enhanced NLO properties in PDAs can be identified in the basic structure of the polymer. As mentioned above, PDAs are one-dimensional systems of conjugated π-electrons, which can be highly polarisable. The polarisation depends strongly on effective π-electron delocalisation length. Moreover, the electronic origin of NLO susceptibility implies a short response time. The above factors, in combination with the ability to form single crystals or thin films in the case of some PDAs, make them promising materials from the viewpoint of fabrication and application and thus gives them an edge over conventional inorganic NLO materials.

Although PDAs have been obtained with variety of substituent groups such as aromatic, aliphatic, amphiphilic, *etc.*, this review will mainly deal with the development of novel PDAs which are designed with the primary goal of enhancing the π-conjugation length or increasing the π-conjugation density. In doing so, we will attempt to summarise our work as well as work done by other researchers.

## Solid state polymerisation

Solid state polymerisation of DA is a topochemical reaction which can be initiated photochemically (by high energy UV, X-ray or γ-ray) or thermally (by annealing) or even by applying pressure (Fig. 1). The structural uniqueness of the reaction product can be at one or more of three different levels: molecular or crystalline or morphological level. In ideal cases, for example in hexa-2,4-diynylene bis(toluene-*p*-sulfonate) (PTS), the polymer enters the polymerisation lattice as a solid state solution over the entire monomer to polymer conversion.[1] As a consequence a perfect single crystal polymer can be obtained.

Due to the low degree of disorder in the crystals, experimental techniques such as high resolution optical and magnetic spectroscopy have yielded a great deal of information about the individual reaction steps and intermediates involved

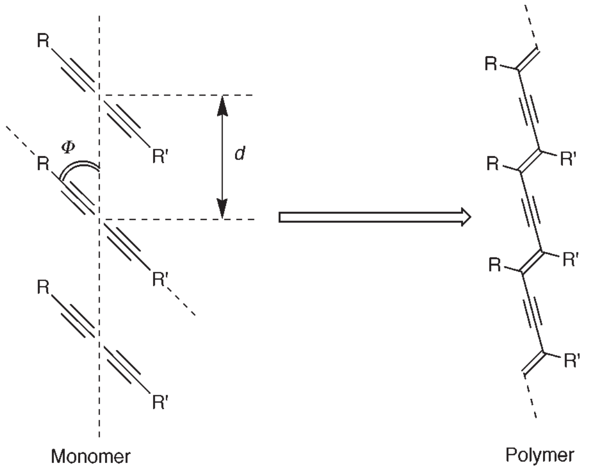

**Fig. 1** Topochemical 1,4-addition polymerisation of DA. When the monomer in the crystal has appropriate geometry, *i.e.* where the distance *d* and the angle *ϕ* are approximately 5 Å and 45°, respectively, it can be polymerised *via* topochemical 1,4-addition.

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‡For this type of compound, butadiyne is a better term than DA. However, in this review, DA has been used since the name PDA originates from the polymer of DA.

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in the polymerisation process.[6] This has led to a better understanding of the diacetylene polymerisation process in particular and topochemical polymerisation in general.

## Crystal packing requirements for DA to PDA conversion

Topochemical reaction implies that the reaction occurs with minimum movement of the monomer molecules in the crystal lattice. Several criteria must be satisfied if solid state polymerisation occurs and the resulting product retains the perfection of the initial monomer crystal. The DA monomer packing in crystal is most conveniently displayed using the monomer separation and tilt angles ($d$ and $\phi$ respectively in Fig. 1).[7] Crystal structure data for both reactive and unreactive compounds were used for comparison of reactivity. This showed that when the adjacent DA molecules in a crystal lattice are parallel stacked at a distance of about 5 Å and the angle made by the monomer with the stacking axis is about 45°, the topochemical 1,4-addition reaction was, in general possible. However, the above arrangement presupposes an extended conformation of the DA molecule. The situation is different for monomers with bulky end groups. The side groups then impede the reaction, in contrast to the situation in reactive monomers where the side group interactions bring the DA moieties into desired reactive position. On the other hand, there are DAs which, despite having unfavorable packing parameters, polymerise in the solid state. Thus, the above mentioned packing arrangement at best can be treated as the criterion which encourages solid state polymerisation of DA but is not an absolute rule.

Also, in the case of molecules with a larger number of conjugated acetylenic units, 1,4-addition reaction is not the only possible topochemical reaction. Other possibilities are 1,2-addition, 1,6-addition and so on. This means that by going beyond two conjugated acetylenic units, to monomers such as tetraynes, hexaynes, *etc.*, one can stretch the limitations of topochemical polymerisation and consequently, may increase the possibility of polymer formation.

## Effect of side groups in polymerisation reaction

Even though the electronic, optical and electrical properties of PDAs are primarily dominated by the backbone, theoretical and experimental investigations clearly suggest the marked influence of side groups on these and other properties.[8] The side groups also have a profound effect on the physical properties of the monomers as well as of the polymers, such as morphology and crystallinity. And most importantly, since the packing arrangement of a DA monomer is the determining factor for its solid state reactivity, manipulation of the side groups to promote reaction is most desired. It may be possible to choose side groups such that the corresponding polymer contains the desired properties. In this matter, computer modelling should be useful for predicting the chemical and optical properties of DAs and their polymers.[9] Such models can save time and labour in the laboratory by screening compounds which polymerise from those which do not. However, the extent of knowledge gained in the field of solid state polymerisation of DAs is not yet enough to enable us to predict the reactivity of a particular DA before it has actually been prepared. As a consequence, numerous DAs have been prepared and only a fraction of them show solid state reactivity.

The side groups also determine the lateral interactions of the polymers and monomer lattice during polymerisation. The balance of inter- and intra-state interactions is critical. The dimensional changes during polymerisation can be large. For instance, PTS (where $R = -CH_2SO_3C_6H_4CH_3$) have an overall lattice contraction of 5% on polymerisation.[10] However, the interstate interaction is strong enough to distribute the strain throughout the lattice during polymerisation. The smooth conversion to polymer is reflected by continuous changes in the physical properties of the crystals during polymerisation. On the other hand, hexa-2,4-diyn-1-ol is an example where weak interstack interaction leads to break-up of the polymer into a polycrystalline form.[11]

## Design and synthesis of monomers

Although the third order NLO properties of PDA are significantly large, further improvements of the polymer are necessary before it can become a viable candidate for NLO applications. Proper substituents for DA monomers have to be found which first help the monomers to polymerise topochemically to give regular polymers and then will help to produce PDAs with optimal qualities, such as large NLO susceptibilities and short response times. The realisation of these qualities also depends on, aside from other factors, the physical form of the polymer. Hence the factor whose improvement is aimed at, is the versatility of the polymer's physical form so that the material can exist in a most desired morphological form such as a single crystal or can form thin films.

The other vital factor for NLO proprety enhancement of PDA is to increase the effective π-conjugation length of the PDA backbone. The electronic structure of the backbone is perturbed by electron donation or withdrawal due to the substituents. Fig. 2 shows the various possibilities for achieving PDAs with enlarged NLO properties. Electronically, the side groups in PDAs can be broadly classified into two categories: (i) side groups without a π-electron system or side groups whose π-electron systems are insulated from the backbone by a saturated group acting as a spacer such as a methylene moiety and (ii) side groups whose π-electron systems are in formal conjugation with the backbone. The side groups in PDAs of the first category will be unable to modify the electronic structure and properties of the backbone through π-electron delocalisation. Nevertheless, environmental effects such as strain in the crystal and steric factors due to the side groups have been shown to affect the electronic structure of the backbone in this category of PDAs. On the other hand, π-conjugated substituents directly bound to the backbone can be expected to do fine tuning of the electronic structure of the backbone. In the latter cases, as mentioned above, properties of PDA related to extensive π-delocalisation may be affected.

Another way to achieve absorption at longer wavelength is by increasing the number of acetylene units in the backbone itself. Various substituted oligoynes such as triynes, tetraynes, pentaynes, and hexaynes are examples for this type. Once these oligoynes are polymerised, the resulting PDAs will have acetylenic side groups which are in direct conjugation with the backbone. In both of the above cases, an increased conjugation length is achieved by introduction of conjugated side groups, either aromatic or acetylenic moiety. The following subsections will review the various oligoynes prepared till now. Also, a compound with two conjugated acetylenic units, that is, DA, is introduced in brief.

### DAs

Although DAs having various side groups have been synthesised and studied by different research groups, DAs having side groups which are formally conjugated to the backbone are less investigated than those having side groups without conjugation.[12,13] This is partly due to the lack of reactivity of such DAs towards topochemical polymerisation. Use of aromatic side groups in DAs is one of the possibilities for preparation of PDAs with enhanced optical and electrical

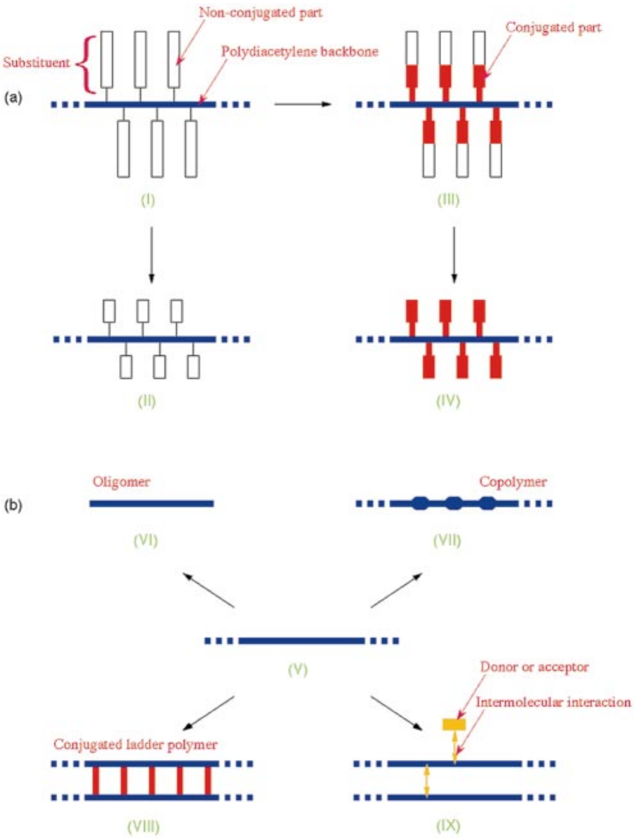
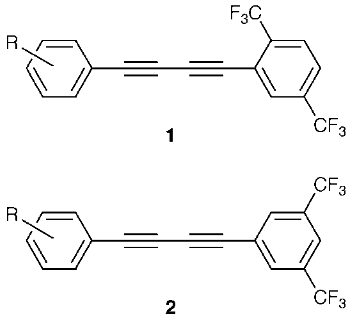


**Fig. 2** Schematic representation of various possible modifications to obtain PDA with enhanced $\chi^{(3)}$ values. (a) and (b) show modifications on the side chain and main chain, respectively: (I) PDA having no π-conjugation between polymer backbone and side chains, (II) PDA with similar conditions except that the side chain is of smaller volume, (III) PDA with π-conjugation between polymer backbone and a part of side chains, (IV) PDA with full π-conjugation between polymer backbone and side chains, (V) conventional PDA, (VI) PDA with defined main chain length, *e.g.* oligomers, (VII) copolymer-type PDA, *e.g.* alternating polymerisation of two monomers, (VIII) ladder-type PDA with π-conjugation between two polymer backbones, and (IX) PDA with electronic interaction between two polymer backbones or between polymer backbone and molecules.

properties. A symmetrically substituted DA with a simple phenyl side group is topochemically unreactive. However, when the phenyl moiety is modified with various other substituents, some of the DAs become solid state reactive.[14,15] Wegner reported several derivatives of diphenyl DAs.[16] Among them a few are solid state polymerisable.

On the other hand, comparatively more investigations have been carried out on asymmetrically substituted DAs containing aromatic side groups. Okada *et al.*[17] have prepared DAs **1a** to **1k** and **2a** to **2k** with 2,5- and 3,5-bis(trifluoromethyl)phenyl groups as one of the side groups (Fig. 3) since symmetrically substituted DAs with these bis(trifluoromethyl)phenyl groups could be polymerised.[15] However, only three out of twenty-two DAs, *i.e.* **1b**, **1c** and **2j** are solid state reactive. Highly polarisable, push–pull diacetylene derivatives **3a** to **3n** having phenyl units containing various substituents have been prepared and studied for nonlinear optics (Fig. 4).[18] These DAs do not undergo 1,4-addition reaction topochemically but show liquid crystalline behaviour upon heating. Similar studies have also been done by Milburn and coworkers (**4a** to **4d**).[19] Some of the DAs show solid state polymerisation whereas others show liquid crystalline behaviour which is smectic or nematic and polymerise in the liquid crystalline state. It seems that the polymerisation in the liquid crystalline state proceeds *via* an alternative route to that observed in the topochemical polymerisation.



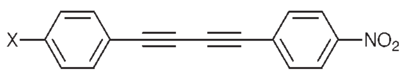
| No. | R | 1 | 2 |
|---|---|---|---|
| a | 2-$CH_3O$ | – | – |
| b | 3-$CH_3O$ | + | – |
| c | 4-$CH_3O$ | + | – |
| d | 4-$CH_3S$ | – | – |
| e | 2-$NH_2$ | – | – |
| f | 3-$NH_2$ | – | – |
| g | 4-$NH_2$ | – | – |
| h | 2-$NH_2$ | – | – |
| i | 2-$CH_3NH$ | – | – |
| j | 3-$CH_3NH$ | – | + |
| k | 4-$CH_3NH$ | – | – |

+: reactive, -: unreactive

**Fig. 3** Asymmetrical DAs having substituted phenyl moiety as the side groups and their solid state reactivity.

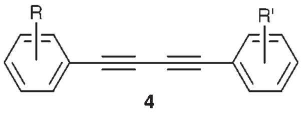
Heteroaryl groups have also been used as the side groups to prepare symmetrical DAs.[12–24] However, the only symmetrical DA in this category which polymerises in the solid state is 1,4-bis(3-quinolyl)buta-1,3-diyne (DQ).[20] This monomer has 3-quinolyl moieties as the two side groups. The polymer exhibits very long $\lambda_{max}$ (at 714 nm) which is at lower energy than those of typical PDAs with a spacer group, *i.e.* 620 nm for polyPTS, indicating that there is extensive π-conjugation in the polymer backbone. DAs with a heteroaryl moiety as one side group and the other side group as an alkyl group with or without a urethane moiety attached to it (**5a** to **5e**; **6a** to **6d**) were often found to undergo 1,4-addition polymerisation (Fig. 5).[12,21,22]

A new strategy for obtaining a PDA with extended π-conjugation has recently been reported.[23] In this case, functionality containing sulfur atoms directly bound to the main chain has been employed to prepare the DA monomers, **7a** to **7k**. This strategy was successful in producing DAs which polymerise in the solid state (Fig. 6). The PDAs obtained from these monomers exhibit absorption maxima as high as 750 nm which is longer than that of the corresponding PDA, poly(dodeca-5,7-diynylene bis(phenylcarbamate)) (polyTCDU) which has no side group π-electron contribution to the backbone.



**3**

| | X |
|---|---|
| a | $NH_2$ |
| b | $n\text{-}C_6H_{13}NH$ |
| c | $n\text{-}C_7H_{15}NH$ |
| d | $n\text{-}C_8H_{17}NH$ |
| e | $n\text{-}C_9H_{19}NH$ |
| f | $n\text{-}C_{10}H_{21}NH$ |
| g | $n\text{-}C_{11}H_{23}NH$ |
| h | $n\text{-}C_{12}H_{25}NH$ |
| i | $CH_2{=}CH(CH_2)_3NH$ |
| j | $CH_2{=}CH(CH_2)_6NH$ |
| k | $CH_3(OCH_2CH_2)_2NH$ |
| l | $CH_3CH_2(OCH_2CH_2)_2NH$ |
| m | $CH_3(OCH_2CH_2)_3NH$ |
| n | $CH_3CH_2(OCH_2CH_2)_3NH$ |



**4**

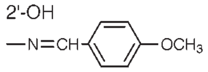
| | R | R' |
|---|---|---|
| a | $4\text{-}NO_2$ | $2'\text{-}OCH_3$ |
| b | $2\text{-}NO_2$ | $2'\text{-}OCH_3$ |
| c | $4\text{-}NO_2$ | $2'\text{-}OH$ |
| d | $2\text{-}NO_2$ |  |

**Fig. 4** Push–pull DA derivatives.

## Hexatriynes

For extending the PDA backbone conjugation and thus achieving enhancement of the $\chi^{(3)}$ values of PDA, another alternative should be to increase the number of conjugated acetylenic units in the monomers, *i.e.* oligoynes such as hexatriyne, octatetrayne, decapentayne and dodecahexayne.

There are few reports on triyne monomers and their solid state polymerisation. However, these molecules tend to be unstable and hence have not much been investigated. Kiji *et al.* have prepared octa-2,4,6-triyne-1,8-diol and its derivatives as model compounds, **8a** to **8e** (Fig. 7).[24] These monomers are colourless when freshly prepared. They are highly photosensitive in the solid state. Based on the X-ray diffraction results on lattice parameters, the mechanical properties and dichroism of the polymer crystals, it has been concluded that the polymerisation proceeds *via* 1,4-addition reaction. Only two of the triple bonds of the backbone are used to form the PDA backbone. The residual triple bond is regularly arranged in an all-*trans* position as part of the substituents. The kinetics of the thermal and photopolymerisation of these monomers are quite similar to those of the corresponding diynes. However, these monomers were found to have other crystal modifications which were photostable. This fact complicated the isolation of the reactive triynes in pure form even though various solvents were used to crystallise the monomers. A comparison of the photopolymerisation of the urethane of triyne (**8b**) and hexa-2,4-diynylene bis(*N*-phenylcarbamate) (PU), which differ only in the number of conjugated triple bonds, is interesting. At least two absorption maxima at 560 nm and 600 nm were obtained for the polymer from PU, due to exciton and its phonon side band. These absorptions disappeared with increased conversion and finally an absorption with a broad maximum at 490 nm was observed. On the other hand, upon photopolymerisation of **8b**, no absorption maximum was observed but optical density increased monotonically over the whole wavelength range starting from about 700 nm towards shorter wavelengths.

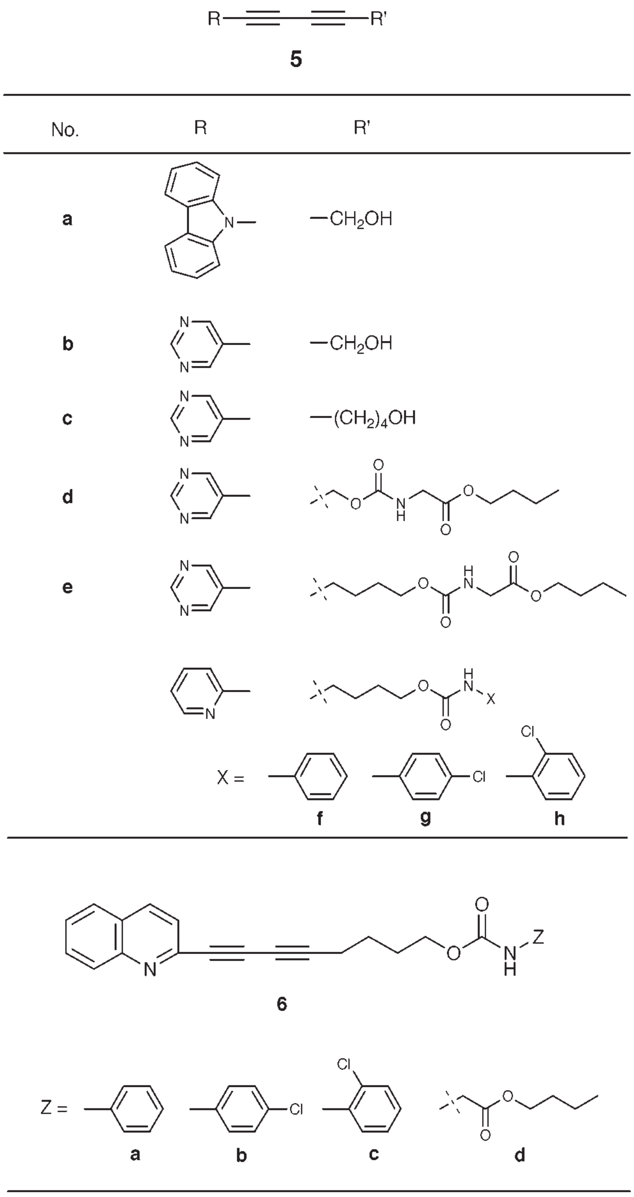
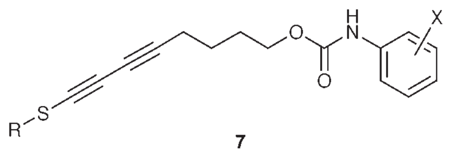


**Fig. 5** Asymmetrical DAs having a directly linked aromatic side group at one end and a methylene spacer containing group at the other end of the backbone.

Baughman and Yee have also investigated solid state polymerisation of triynes.[25] The triynes can polymerise either by 1,4-addition reaction or by 1,6-addition reaction, or by a combination of these two types of reaction. However, according to their investigations, 1,4-addition reaction rather than 1,6-addition reaction was found to occur in these triynes, thus involving two adjacent triple bonds of each monomer unit.

Our group too has designed various monomers with varying numbers of conjugated acetylenic units in the backbone.[26] We prepared nonacosa-10,12,14-triynoic acid **8f**, which is an amphiphilic triyne monomer for solid state polymerisation. The long alkyl sidegroups attached to the triyne backbone makes the monomer favourable for topochemical polymerisation. The PDA from this monomer exhibited a $\chi^{(3)}$ value which is almost comparable to that of the corresponding PDA from the butadiyne derivative. The similarity in $\chi^{(3)}$ values may be due to the fact that this PDA has only one acetylenic unit as the side group which is used in elongating the effective $\pi$-conjugation. This, in reality, emulates a PDA with directly



**7**

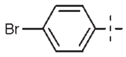
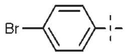
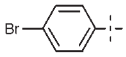
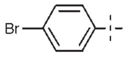
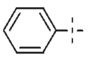
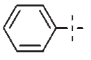
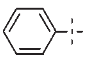
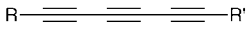
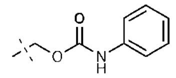
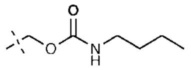
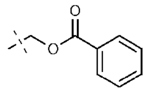
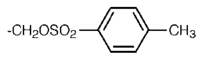
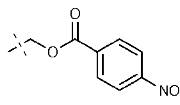
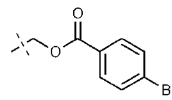
| No. | R | X |
|---|---|---|
| **a** |  | H |
| **b** |  | *o*-Cl |
| **c** |  | *m*-Cl |
| **d** |  | *p*-Cl |
| **e** |  | H |
| **f** |  | *p*-Cl |
| **g** |  | *p*-Br |
| **h** | $CH_3(CH_2)_{11}$— | H |
| **i** | $CH_3(CH_2)_{11}$— | *o*-Cl |
| **j** | $CH_3(CH_2)_{11}$— | *m*-Cl |
| **k** | $CH_3(CH_2)_{11}$— | *p*-Cl |

**Fig. 6** DAs with sulfur atom directly conjugated to the backbone.



**8**

| No. | R | R' | Reactivity |
|---|---|---|---|
| **a** | $—CH_2OH$ | R | +++ |
| **b** |  | R | +++ |
| **c** |  | R | ++ |
| **d** |  | R | + |
| **e** |  | R | ++ |
| **f** | $—(CH_2)_{13}CH_3$ | $—(CH_2)_8COOH$ | +++ |
| **g** | $—C(CH_3)_2OH$ | R | – |
| **h** |  | R | +++ |
| **i** |  | $—CH_2OH$ | + |

Reactivity level; +++: high, ++: moderate, +: less, –: unreactive

**Fig. 7** Triynes and their solid state reactivity.

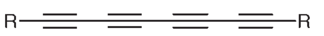
linked aromatic moiety as one side group. However on extrapolating our postulation, the enhancement of the π-conjugation should be expected for polymers from higher orders of the oligoyne series, that is tetraynes, pentaynes and hexaynes.

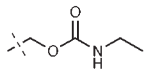
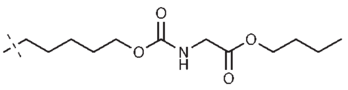
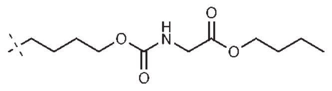
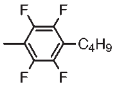
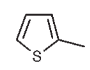
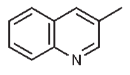
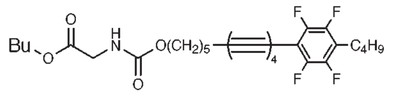
Recently, Enkelmann has reported a series of triynes **8g** to **8i** and their solid state reactivity.[27] The crystal structures of all the monomers have also been reported. Three out of four of the investigated monomers polymerise in the solid state. The possibilities of 1,4- and 1,6-addition were checked out and it was found that the reaction proceeds by a 1,4-addition reaction. However, the reactions do not provide single crystal polymers from single crystal monomers.

## Octatetraynes

In the late seventies, the first report came out on an octatetrayne compound which polymerise in the solid state.[25] This monomer is an extension of the conjugated acetylenic backbone in order to increase the overall π-conjugation of the resulting PDA. The solid state polymerisation of the needle-like crystals of the tetrayne $R–(C{\equiv}C)_4—R$ (where, $R = –CH_2OCONHC_2H_5$: 1EU-4A, Fig. 8) have been investigated. Its polymerisation yields the corresponding PDA. However, the polymerisation reaction does not preserve the three-dimensional perfection of the precursor phase. γ-Ray induced polymerisation (0.5 MGy dose from $^{60}$Co source) results in a chain aligned but otherwise amorphous polymer. There are numerous reaction possibilities for the solid state polymerisation of tetraynes. Namely, reaction can proceed by the addition of DA groups *via* 1,4- or 3,6-addition (producing a polymer backbone), by the addition of triacetylene groups *via* 1,6-addition, by addition of tetraacetylene groups *via* 1,8-addition or by a combination of two or more of these processes. Which of these reactions takes place depends upon the molecular packing of the monomer crystal. From the measured chain-repeat length (4.75 Å), polymerisation seems to occur by reaction of the DA groups of adjacent molecules. However, it could not be established whether the polymerisation occurs symmetrically (by 3,6-addition) or asymmetrically (by 1,4- or 5,8-addition).

It was surprising that not much work was done on solid state polymerisation of tetraynes. However, this is logical since, in the initial days of PDA research, the only aspect which was thought to be of significance was the polymerisation process. The emergence of the NLO properties of PDAs as a significant aspect led to the revival of research on tetraynes with renewed vigour. Nakanishi's group have been working on preparation of tetraynes and investigation of their solid state polymerisation with the aim of preparing better third-order NLO materials. Several tetrayne compounds have been prepared by this group (Fig. 8). It was found that hexatriaconta-15,17,19,21-tetrayne (14-4A) can be polymerized in the solid state to give a PDA with diacetylenic substituents.[26] By using high resolution solid state $^{13}$C NMR spectroscopy, the polymerisation was confirmed to occur in an asymmetric manner, *i.e.* 1,4-addition at the 1,4-positions of the octatetrayne moiety. The octatetrayne monomer with urethane groups as substituents, *i.e.* hexadeca-5,7,9,11-tetraynylene bis(*N*-(butoxycarbonyl)methyl)carbamate (4BCMU-4A) was also synthesised in order to confirm the generality of the polymerisation behaviour.[28] The PDA from a similar deriva-



| Name | R | Reactivity |
|---|---|---|
| 1OL-4A | $—CH_2OH$ | +++ |
| 1EU-4A |  | +++ |
| 14-4A | $—(CH_2)_{13}CH_3$ | +++ |
| 18-4A | $—(CH_2)_{17}CH_3$ | +++ |
| 5BCMU-4A |  | +++ |
| 4BCMU-4A |  | +++ |
| BTFP-4A |  | – |
| 2T-4A |  | (+) |
| 3Q-4A |  | (+) |
| 5BCMU-4A-BTFP |  | ++ |

Reactivity level; +++: high, ++: moderate, (+): only reacted by heating, –: unreactive

**Fig. 8** Tetraynes and their solid state reactivity.

tive with five methylene between acetylene and urethane groups, *i.e.* 5BCMU-4A, was found to show sharper excitonic absorption than that from 4BCMU-4A.[29] Though the reaction of the remaining DA moiety of the PDAs could be accomplished by thermal treatment, polymers with a regular structure have not been obtained.

The combined effect of acetylenic side groups as well as aromatic side groups, which may further extend the effective π-conjugation, is expected for a tetrayne monomer with a directly linked aromatic substituent as one or both of two side groups. As a monomer of this category, PDA from asymmetrically substituted octatetrayne compound, 5BCMU-4A-BTFP, was prepared where one of the side groups is a urethane derivative and the other is a directly linked aryl moiety.[30] In this PDA, the conjugation effect from the aromatic side group was not significant though regioselective polymerisation, *i.e.* 1,4-addition at the DA moiety just near the alkylurethane side group, was achieved. We also designed two tetraynes having symmetrically substituted heteroaryl moieties as the two side groups.[31] 2-Thienyl and 3-quinolyl groups were used as directly linked aromatic substituents in monomers 2T-4A and 3Q-4A, respectively. These two monomers were inactive towards UV or γ-radiation. However, they undergo solid state polymerisation when heated. The polymerisation rate was found to be directly related to the heating rate. The polymers were amorphous and insoluble in organic solvents. They did not exhibit absorption corresponding to a PDA π-conjugated structure. One of the monomers (2T-4A) could be obtained in single crystal form whose X-ray structure revealed the arrangement of the molecules in the crystal lattice. The monomer molecules are packed in parallel stacks along the *c*-axis with a perpendicular distance of 3.9 Å. The angle $\phi$ in Fig. 1 is 71°, which is not suitable for a 1,4-addition reaction. These crystallographic data suggest that a 1,2-addition reaction is the most probable route as an initial step in the polymerisation. High temperature allows intense molecular vibration in the crystalline lattice, which triggers polymerisation between the nearest unsaturated carbons of adjacent monomer molecules. The polymerisation process corroborates this fact. At higher temperature, the polymerisation was possible, most probably due to the flexibility induced in the crystal geometry. However, the final products are not simply a 1,2-addition product, since there was no evidence for acetylenic C-atoms or bonds in the final polymers. The solid state NMR studies indicate that the 1,2-addition reaction must have been followed by a cyclisation reaction to form an irregular structure having aromatic character.

## Decapentaynes

A gradual increase in the number of conjugated acetylenic units in the monomer is more desirable if one is to understand the subtle effect on the resulting conjugated polymer chains. Also, polymerisation by 1,4-addition at both DA groups in a tetrayne is not a likely reaction possibility. This is because either the reaction product would have too high an intramolecular strain energy or complete reaction would require too large a displacement. In view of the strain factor of the resulting ladder-type polymers, the preparation and polymerisation of pentaynes or higher alkynes is worthwhile because at least one acetylenic unit could survive to play a role of spacer between two PDAs in the ladder-type polymer, resulting in reduction of steric hindrance between two PDA backbones. However, monomers having odd numbers of conjugated acetylenic units are not so easy to synthesise because the simple oxidative coupling reaction of the precursor ethyne with a terminal hydrogen can be used only for obtaining an even number of acetylenic units. Naturally, there are almost no reports on pentayne monomers.

Recently Nakanishi and coworkers have prepared a pentayne monomer having symmetrical substituents,[32] *i.e.* icosa-6,8,10,12,14-pentaynylene 1,20-bis((*N*-butoxycarbonyl)-methyl)carbamate (5BCMU-5A) was prepared. This monomer can be polymerised topochemically and the polymer obtained shows absorption peaks at 718 nm and at 964 nm. Though the former absorption peak could be assigned as the excitonic band of PDA substituted by hexatriynyl groups, the latter broad absorption with smaller absorbance than the former has never been observed for PDAs except for the polymers from hexayne as described in the next section. This latter absorption in the near IR region clearly indicated that the elongation of π-conjugation system beyond the simple PDA backbone structure, *i.e.* a ladder-type polymer composed of two PDAs linked by an ethynylene group in each repeating unit, has been partially formed by using a pentayne monomer. Solid state NMR study also supports this consideration.

## Dodecahexaynes

Fig. 9 shows the dodecahexayne monomers which have so far been prepared for solid state polymerisation. Solid state polymerisation of hexayne monomers can start gradually by heating or even by just keeping them at ambient temperature, without any light or radiant ray source. Investigations on solid state polymerisation of an alkyl-substituted dodecahexayne, *i.e.* tetraconta-15,17,19,21,23,25-hexayne (14-6A)[33] using solid

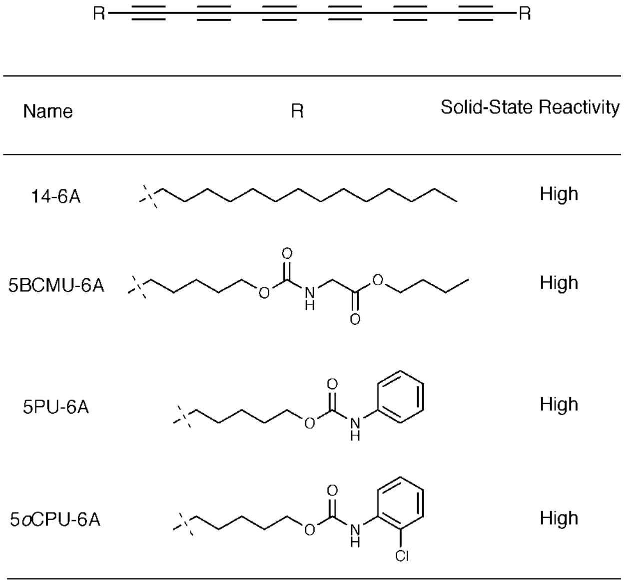
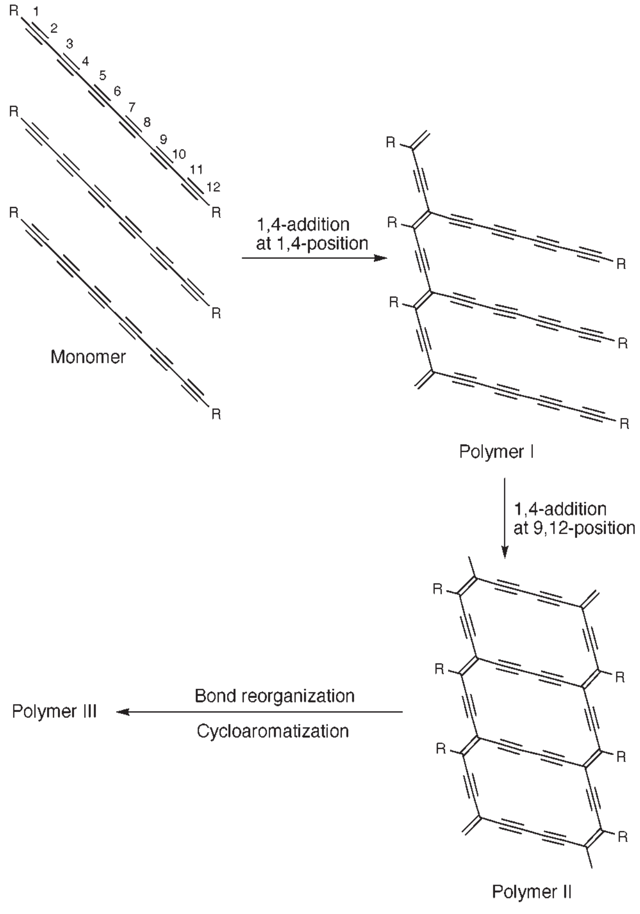


**Fig. 9** Hexaynes and their solid state reactivity.

state NMR spectroscopy revealed that in the first step of polymerisation, the monomer reacts at the 1,4-position of dodecahexayne, just the same way as in hexatriyne, octatetrayne and decapentayne, to give a PDA substituted by octatetraynyl groups (polymer I). This polymer was found to react further as summarised in Scheme 1. In the second step, polymerisation of polymer I occurs at the 9,12-position of the original dodecahexayne moiety to give a ladder-type polymer of two PDAs bonded by butadiynylene groups (polymer II). Finally, an allene structure is produced in conjugated backbone and cycloaromatisation occurs simultaneously (polymer III). One of the problems for this polymer is the deterioration of crystallinity in the course of solid state polymerisation because of its mobile alkyl group substituents. Decreased crystallinity is expected to reduce the effective $\pi$-conjugated structure of the polymer. The NLO properties of the polymer have not been determined since thin film fabrication and growth of a single crystal of 14-6A were difficult. In order to maintain the crystallinity even in the polymers and to prepare thin films to evaluate their third-order NLO properties, Nakanishi and coworkers prepared three more hexaynes, namely 5BCMU-6A, 5PU-6A and 5*o*CPU-6A.[34] In these octatetrayne derivatives having urethane groups, the polymers show higher crystallinity than those from alkyl-substituted ones because of hydrogen bonding between adjacent side chains in the urethane-substituted ones. The solid state polymerisation scheme of urethane-substituted dodecahexayne is similar to that of the alkyl-substituted one: monomer can be converted into polymer I quantitatively and polymer I partially gives ladder-type polymer II as shown in Scheme 1. Formation of the ladder-type polymers from hexayne derivatives was also confirmed by absorption in the near IR region, as in the case of pentayne. Absorption of the excitonic bands for polymer I from 14-6A and 5BCMU-6A were observed at 776 nm and 746 nm, respectively. Besides the excitonic peak, two broad peaks in near IR region were also detected: 917 nm and 1028 nm for 14-6A and 914 nm and 1016 nm for 5BCMU-6A. In the above studies, 1,4-addition polymerisation was confirmed to be the general route of solid state polymerisation for all oligoynes, from diacetylenes up to hexaynes. However, as an exception, 1,2-addition reaction has been shown to be the pathway for the polymerisation of tetraynes with directly linked quinolyl and thienyl side groups.



**Scheme 1** Solid state reaction steps for hexayne monomers.

### Bis(butadiynyl) arylenes

As mentioned above, pentayne and hexayne derivatives were found to give ladder-type polymers. *i.e.* two PDAs connected by ethynylene and butadiynylene in each repeat unit, respectively. In order to expand the monomer compounds for such ladder-type polymers, introduction of aromatic rings as $\pi$-conjugated bridging groups between two PDAs was intended. First, 1,4-bis(octadeca-1,3-diynyl)phenylene 14-4A(Ph) was synthesised and its solid state polymerisation induced by $\gamma$-ray irradiation was investigated.[35] This monomer gave a blue-coloured PDA substituted by 4-butadiynylphenyl groups below 27 °C. However, further polymerisation at the remaining DA moiety did not proceed. Above 27 °C, flipping of the central phenyl ring of the monomer in crystal was found to begin, as observed using $^2$H solid state NMR spectroscopy, and that obstructed the regular polymerisation. In order to avoid such complexity under the polymerisation conditions, urethane groups were introduced to the side groups so as to fix the monomer structure with the aid of hydrogen bonding. Accordingly, the series, *i.e.* 4BCMU-4A(Ar), containing three monomers was prepared (Fig. 10).[32] Among them 4BCMU-4A(PhF) and 4BCMU-4A(Biph) were found to undergo one-step 1,4-addition reaction to give the respective PDAs having butadiynylaryl moieties as a side chain. On the contrary, 4BCMU-4A(Ph) did not show solid state polymerisation. The molecular arrangement of 4BCMU-4A(Ph), which is affected strongly by a central phenyl moiety, did not satisfy the topochemical polymerisation conditions in contrast with the case of 14-4A(Ph) and as a consequence this monomer did not give PDA. The PDAs obtained from 4BCMU-4A(PhF) and 4BCMU-4A(Biph) exhibited $\lambda_{\max}$ at 593 nm and 646 nm, respectively, which unexpectedly is in the usual range for conventional PDAs. Although the second 1,4-addition reaction did not take place in these monomers like 14-4A(Ph), this concept is very interesting and novel for obtaining maximum

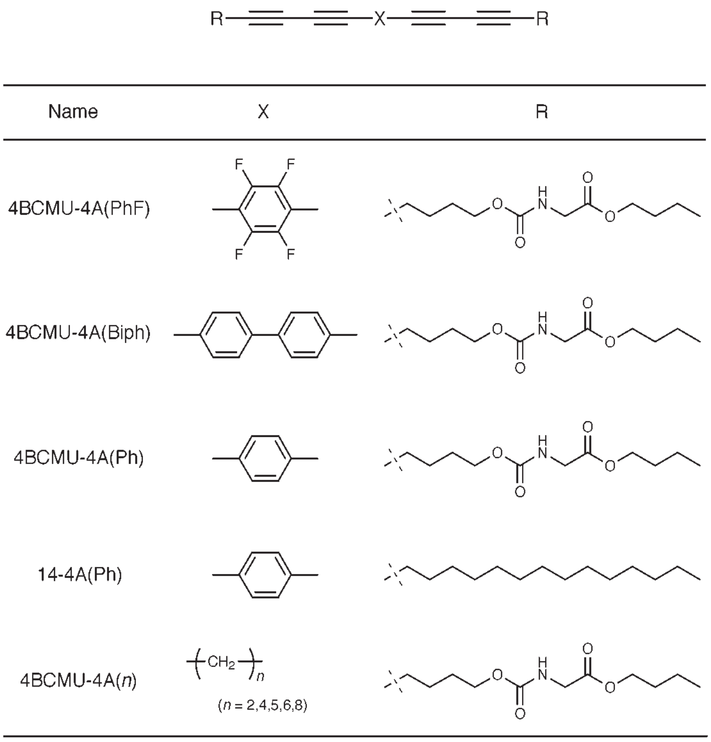


**Fig. 10** DAs with a bridging moiety for ladder-type PDAs.

π-conjugation. With suitable selection of bridging groups, it should be possible to obtain highly regular ladder-type PDAs.

### Monomers with two DAs linked by alkylene group

A problem in ladder-type polymers from pentayne and hexayne derivatives is their imperfect structure. One of the reasons seemed to be the deterioration of crystallinity in the course of solid state polymerisation. Even when urethane groups, which can form hydrogen bonds, were introduced as the side groups of monomers, the deterioration of crystallinity could not be totally prevented. In order to fine tune the structure of ladder-type PDA so as to get better material with regular structures and hence longer conjugation length due to the planar structure, monomers having two DA moieties linked by an inner alkylene substituent 4BCMU-4A(*n*), were synthesised (Fig. 10).[36] The improvement of NLO properties in this case is only due to the increase in the density of the PDA backbone, which may sum up to almost double compared to the corresponding normal PDA. When the number of inner methylene *n* is more than 4, both DA groups could be polymerised quantitatively by γ-ray irradiation to give the ladder-type polymer. Though crystallinity of the polymer from 4BCMU-4A(4) was lost during two-step polymerisation, that of the polymer from 4BCMU-4A(8) was maintained without serious deterioration. For 4BCMU-4A(2), polymerisation occurs at only one of the DA moieties to give linear PDA. In this case, the crystallinity of the polymer has already been lost at the first step of polymerisation and succeeding polymerisation in a regular manner at the remaining DA moiety seemed to be impossible. Since the polymer backbone density of polymers from 4BCMU-4A(4) and 4BCMU-4A(8) is considered to be almost twice that of the polymer from 4BCMU-4A(2), the absorbance of the excitonic band of polymers from 4BCMU-4A(4) and 4BCMU-4A(8) becomes about twice that of the polymer from 4BCMU-4A(2). Of course, the absorption maximum wavelengths of these polymers are in the usual range for conventional PDAs, because there is no π-conjugated interaction from side groups to the PDA backbone.

## Optical and nonlinear optical properties of PDAs

One of the unique aspects of DA polymerisation is the formation of deeply coloured PDAs, often with a golden metallic reflectance. The colour change of a monomer crystal upon polymerisation is spectacular, even a crystal containing about 1% polymer becoming highly absorbing. The backbone conjugation of PDA is the main factor in determining its optical properties. This becomes very clear if we compare the excitonic absorption of alkyl substituted oligoynes, for example. The excitonic absorption of PDA is known to shift to longer wavelength, when the acetylenic numbers in the monomers increase. In the oligoynes with 5BCMU-type substituent, a similar trend is observed. Fig. 11 shows a plot for absorption wavelength maximum, $\lambda_{\max}$, of the PDAs *versus* the number of acetylenic units which is contained in the corresponding monomers' backbone. It can be observed that π-conjugation increases linearly for the polymers with the increase in the number of conjugated acetylenic units in the corresponding monomers. This is exactly what we were aiming for before designing the monomers.

Similarly, when there is a directly linked aromatic substituent as the side group in PDA, the $\lambda_{\max}$ shifts to longer wavelength. A case in point is that of PDA with a 3-quinolyl moiety as the side group. The $\lambda_{\max}$ in this case is as long as 715 nm. In the case of an asymmetrical DA having a 3-quinolyl moiety too, the absorption maxima reaches as long as 710 nm.

Various forms of PDAs, such as single crystals, solutions and

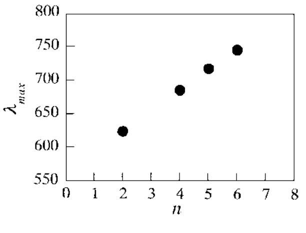


**Fig. 11** Plots for $\lambda_{\max}$ of PDAs *vs.* number of conjugated acetylenic units in the corresponding monomers.

thin films including LB films, have been used to investigate their NLO properties. The first report on PDA's NLO property was by Sauteret *et al.* in 1976, where they reported that single crystalline PDA from PTS shows a large resonant third-order NLO susceptibility, $\chi^{(3)}$ of $8.5 \times 10^{-10}$ esu at 1.89 μm obtained by third-harmonic generation (THG) method.[37] However, since most of the PDAs could only be obtained in polycrystalline form, efforts toward enhanced $\chi^{(3)}$ should be put within this constrain.

Although NLO properties for all sorts of PDAs have been investigated, here we limit the types of PDAs which are obtained from the DA having larger than two numbers of conjugated acetylenic units. Nakanishi and coworkers have reported the NLO susceptibilities of a variety of such PDAs,[38] with an attempt to shed some light on the effectiveness of directly bound aromatic substituents in increasing the third-order optical nonlinearities of PDAs. The directly bound aromatic substituents were found to be effective in increasing the third order optical nonlinearities of PDAs.

The PDA obtained from tetraynes and hexaynes are a series of promising candidates for NLO materials. Such a PDA may be able to circumvent the limitation of PDAs with directly linked aromatic groups, where the dihedral angle $\theta$ can decrease only to 43° and thus no more increase in $\chi^{(3)}$ value is possible. The $\chi^{(3)}$ values for THF of polycrystalline polymer thin films of the tetraynes, 4BCMU-4A and 5BCMU-4A are $3.3 \times 10^{-11}$ esu, and $8.0 \times 10^{-11}$ esu, respectively.[28,29] The PDA from asymmetrical tetrayne, 5BCMU-4A-BTFP exhibited a lower value than that of the symmetrical poly(5BCMU-4A). Table 1 shows the $\chi^{(3)}$ value of some PDAs with conjugated side groups.

The $\chi^{(3)}$ values for THG of the polymer from 5BCMU-6A otbained for various pumping wavelengths between 1.8 to 2.1 μm are more than one order of magnitude higher than that of the polymer from hexayne 5PU-6A and above five times larger than those of the polymer from 5*o*CPU-6A.[34] However, in the case of a polycrystalline thin film of the polymer from 5BCMU-6A, the $\chi^{(3)}$ values were from $1.4 \times 10^{-11}$ to $2.8 \times 10^{-11}$ esu. Since these values were evaluated at a shorter wavelength than the absorption maximum, they are smaller than the maximum value for polymers from tetrayne. However, a larger value is expected near the absorption maximum of the polymer from 5BCMU-6A. The difference in $\chi^{(3)}$ values among the hexayne polymers is most probably due to the quality of spin-coated films.

## Potential applications

Polymerisation of crystalline DA generates an ordered array of one-dimensional conjugated polymer chains in one direction. The increase of the extent of π-conjugation, initially confined to the DA linkage, over many polymer repeat units causes a dramatic lowering of the excitation energy which is manifested in a shift of the optical absorption into the red. For this reason PDAs appear attractive materials to be used as active elements in devices for optical information storage or photolithography.

The colour change of DA upon polymerisation either thermally or by UV or γ-radiation, can be used in temperature–dose or radiation–dose indicators. Their high sensitivity towards a wide dose range of 0.5 Gy to 500 kGy is uniquely advantageous in this aspect.

Some other potential applications of PDAs are latent fingerprint recording, as biological sensors and in drug delivery systems.[39] However, except for a few preliminary applications, these remain to be seen.

The other potential application of PDAs is based on their large and fast third-order NLO properties.[40] PDAs can be used as efficient elements for all optical switching. Also, the NLO properties of PDAs have opened attractive prospects for their application in three or four wave parametric amplifiers.

## Conclusion and future research prospects

The research into diacetylene polymerisation has not lost its vigour even though it has already encompassed almost three decades. Naturally, the research aspects are numerous and to deal with all of them in a single review is not pragmatic if the aim is to create a concept and ideas in a clear manner in general reader's mind. This review has dealt with one of the most vital aspects of PDA research and that is the molecular engineering of DA to obtain PDAs with the desired properties, specifically, in processable form and with large NLO properties. The research done to date on PDAs with conjugated side groups has revealed several criteria which will be useful for further fine tuning of the polymer. Nevertheless, PDAs need further improvements before they can become viable candidates for NLO applications. PDA films or single crystals must satisfy all the important figures of merit for ultrafast all-optical devices. Among other things, the temperature dependence of the refractive index needs to be sorted out. In this regard, progress has been made, particularly for polyPTS single crystals.[41] It has been observed that at 1.32 μm communication wavelength one can circumvent the problem of refractive index changes due to temperature by adopting certain limitations. Proper substituents for DA monomers have to be found which first will help the monomers to polymerise topochemically to give regular polymers and then will help them to reproduce PDAs with optimal qualities. In this regard, the information obtained will help future researchers to concentrate the search more narrowly and thus lessen their efforts without compromising their chances of success.

One of the most promising areas which should be looked

**Table 1** Third-order nonlinear optical susceptibility ($\chi^{(3)}$) values for PDAs with conjugated sidegroups evaluated by third-harmonic generation (THG)

| PDA | Pumping wavelength/μm | $\chi^{(3)a}$/esu | Remarks |
|---|---|---|---|
| **2j** | 1.96 | $1.0 \times 10^{-10}$ | |
| **7k** $Cd^{2+}$ salt–PIBM (1 : 1) | 1.90 | $1.1 \times 10^{-11}$ | *b* |
| 14-4A | 2.10 | $1.4 \times 10^{-11}$ | *c* |
| 4BCMU-4A | 1.86 | $8.9 \times 10^{-11}$ | |
| 5BCMU-4A | 2.10 | $2.1 \times 10^{-10}$ | |
| 5BCMU-4A-BTFP | 2.10 | $3.7 \times 10^{-11}$ | |
| 5BCMU-6A | 2.10 | $7.5 \times 10^{-11}$ | *d* |
| 5PU-6A | 2.04 | $5.1 \times 10^{-12}$ | *c* |
| 5*o*CPU-6A | 2.04 | $1.6 \times 10^{-11}$ | *c* |

[a] The maximum $\chi^{(3)}$ values among measured wavelength. Most compounds showed the maximum $\chi^{(3)}$ values just near the absorption maximum where THG is in three-photon resonance. All the $\chi^{(3)}$ values were corrected into those along the PDA main chain direction. For example, when the PDA backbone is random on the plane parallel to the substrate, the raw $\chi^{(3)}$ value is multiplied by an orientational factor of 8/3. The $\chi^{(3)}$ value of $1.0 \times 10^{-14}$ esu for fused quartz was used as the reference. [b] PDA was mixed with poly(isobutyl methacrylate) (PIBM) in LB films. [c] The thin film prepared was not perfectly uniform. [d] The maximum $\chi^{(3)}$ value is expected for longer pumping wavelength.

into, is the enhancement of π-electron density by use of ladder polymers. In this regard, the proper choice of bridging moiety should be the key for success. If such a PDA can be obtained and if it can be in processable form, say, as thin film or a good single crystal, the third-order nonlinear susceptibility of that material should be large. Another area which needs attention is the cocrystallisation and the topochemical polymerisation of DAs. Finally, it is worth mentioning that, in order to bring PDAs in the realm of everyday use, the polymer morphology and processability must be drastically improved.

## Acknowledgements

It is a great pleasure to acknowledge the important efforts of our co-workers whose names appear in the references and also those whose names do not appear due to limitations on the number of references. We have tried to include all the references by using the suffix "references therein" with some references.

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