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A novel series of quinoline containing asymmetrically substituted polydiacetylenes for third-order nonlinear optical material

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Summary

A series of novel unsymmetrical diacetylenes have been prepared which have quinolyl moiety as one of the directly linked sidegroups to the acetylenic backbone. One of the diacetylenes exists in two crystal forms, one of which is solid state reactive. The polydiacetylenes obtained from the monomers have generally long effective conjugation length as indicated by their absorption spectra. The third-order nonlinear optical susceptibility ($\chi^{(3)}$) of one of the polydiacetylenes has been evaluated and found to be in the order of 10^{-11} esu.

Introduction

Polydiacetylenes(PDAs) are conjugated polymers prepared by the solid state polymerisation of diacetylene monomers having a structural formula, R_1-C≡C-C≡C-R_2, where R_1 and R_2 refer to the substituent sidegroups(1,2,3). The reaction is unique in the sense that monomer single crystal can be transformed into polymer single crystal in some cases. Investigations covering various aspects of PDA, such as electrical properties(4), solution properties(5), optical and nonlinear optical properties(6) and mechanical properties(7) have been persued. However, nonlinear optical (NLO) properties have emerged as the most potential and important aspect and PDAs are considered as the most promising candidate for third-order NLO materials. This expectation arises from the fact that PDAs have quasi one-dimensional conjugated backbone structure, suitable for high third-order nonlinear susceptibility, $\chi^{(3)}$ value. Nevertheless, PDA needs further improvements before they can become viable candidates for NLO applications. Proper substituents for monomer diacetylenes have to be found out which, first help the monomers to polymerise topochemically to give regular polymer and then, will help to produce PDAs with optimum qualities, such as large susceptibility and short response times(8). The realisation of these qualities depends, besides other factors, on 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 as a single crystal form or can form uniform thin film.

The other vital factor for NLO property enhancement is to increase the effective conjugation length of the PDA backbone. One option is to have aromatic substitutents which are directly bound to the conjugated backbone. In this way, the electronic structure of the backbone is perturbed by electron donation or withdrawal due to the substituents. One class of diacetylenes, which we have been investigating, consists of heteroaryl moieties directly bound to the diacetylene stem(9). Here we report, a series of quinoline containing novel DAs which topochemically polymerise to give PDAs. The design of such diacetylenes have been based on the premise that the aromatic sidegroup will, in suitable

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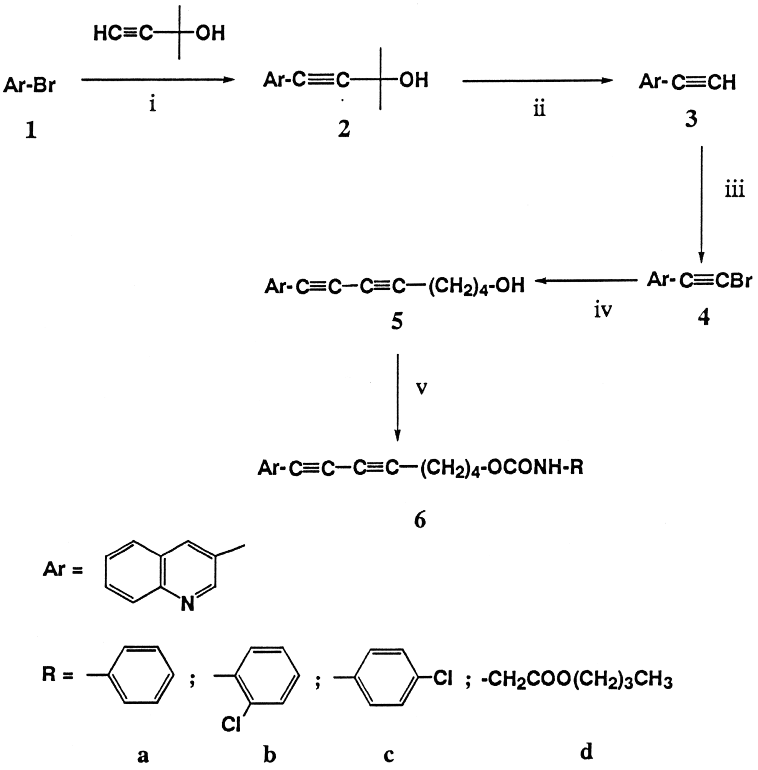

Scheme 1 Reagent and conditions : i, $[(C_6H_5)_3P]_2PdCl_2$, CuI, Et_3N; ii, KOH, C_6H_6, reflux; iii, KOBr/aqs KOH; iv, HC≡C-$(CH_2)_4$-OH, CuCl, $NH_4OH.HCl$, $EtNH_2$, MeOH, N_2-atm.; v, R-NCO, dry THF, Et_3N, dibutyltin dilaurate.

cases, help the backbone conjugation to extend further to provide longer effective conjugation length which is one of the criteria for large third-order NLO response. In addition, the π-π interaction of heteroaryl moieties of the adjacent DA molecules can be effectively used to stack them into an appropriate crystal packing for topochemical polymerisation(10). The other side group consists of a urethane moiety. This has been incorporated into the design of diacetylene to keep them properly stacked in solid state by intermolecular hydrogen bonding of urethane group.

Experimental Part

Synthesis of monomers

The monomers were prepared following the procedure as depicted in Scheme 1. The detailed procedures will be reported elsewhere. **4** was prepared from 3-bromoquinoline in three steps using previously reported procedure(11). **5** was prepared in 50% yield by cross-coupling **4** with the alcohol. The precursor compounds **5**, which are also diacetylene, does not polymerise topochemically and therefore can be stored without any protection. The monomer series **6** were prepared by reacting **5** with the appropriate aryl isocyanate or n-butyl ester of isocyanatoacetic acid in case of **5d** in presence of dibutyltin dilaurate. The m.p. of **6a**, **6b**, **6c** and **6d** are 100°C, 86°C, 146°C and 75°C respectively. All the monomers were purified by crystallisation and were characterised spectroscopically.

Solid State Polymerisation

Solid state polymerisation of the monomers were carried out using UV or γ-irradiation. Monomers **6a** and **6c**, which exists as colourless crystalline solids at r.t., could be polymerised in solid state to provide blue polymers. However, **6b**, which was crystallised from methanol as colourless needle shaped crystals, was stable at r.t. Interestingly, when **6b** was melted(at 86°C) and cooled down slowly, it crystallised under shear into a crystal form which can undergo topochemical polymerisation. **6d** was unreactive towards 1,4-addition polymerisation. Also, heat as a stimulus was not effective in inducing solid state reaction in any of the monomers.

Third harmonic Generation Measurement

Third-harmonic generation(THG) measurement for one of the polymer, **6c**, was carried out by means of Maker fringe method. The monomer, **6c**, was spin coated on a quartz plate and then polymerised by γ-radiation. The monomer was partially polymerised to PDA. 10% polymer conversion was determined by dissolving the unreacted monomer and weighing the residual polymer on the quartz plate. Since the PDA absorbs at THG wavelengths, the $\chi^{(3)}$ values obtained are for resonant region. The fundamental beam used was 1.83 - 2.10 μm pulsed (ca. 5 ns of pulse width) laser light. The power of laser light used was about 2 mJ/pulse. A fused quartz plate, whose $\chi^{(3)}$ is 1.0 X 10^{-14} esu was used as a reference sample(12). The detailed procedure for $\chi^{(3)}$ measurement can be found elsewhere(13).

Uniform Thin film of the polymer from **6a** and **6b** could not be obtainedand therefore the values could not be determined for them yet.

Results and Discussion

The monomers **6a** and **6c** upon UV or γ-irradiation, produced blue polymers which were insoluble in common organic solvents. The monomer **6b**, obtained by crystallisation

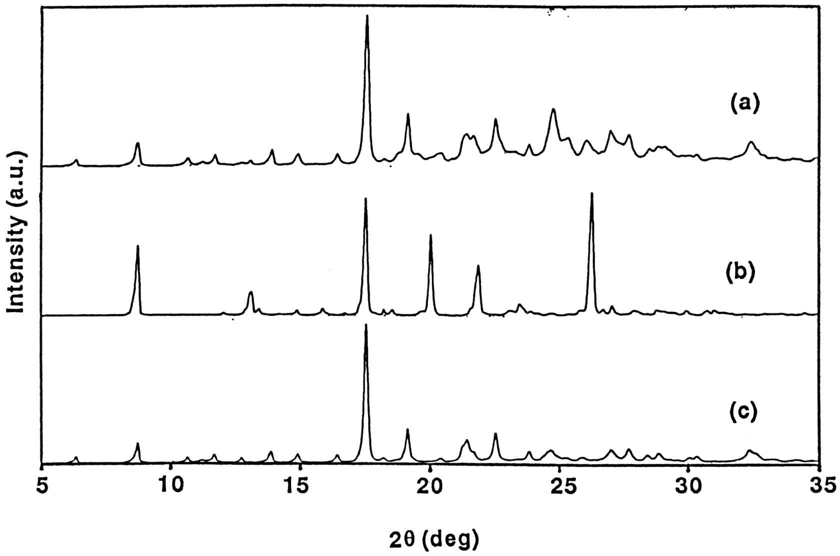

Figure 1 Powder XRD of **6b**. (a) Unreactive monomer crystals obtained by slow evaporation from methanol solution. (b) Reactive monomer crystals obtained by melt-crystallisation. (c) Partial polymer from the melt-crystallised monomer form.

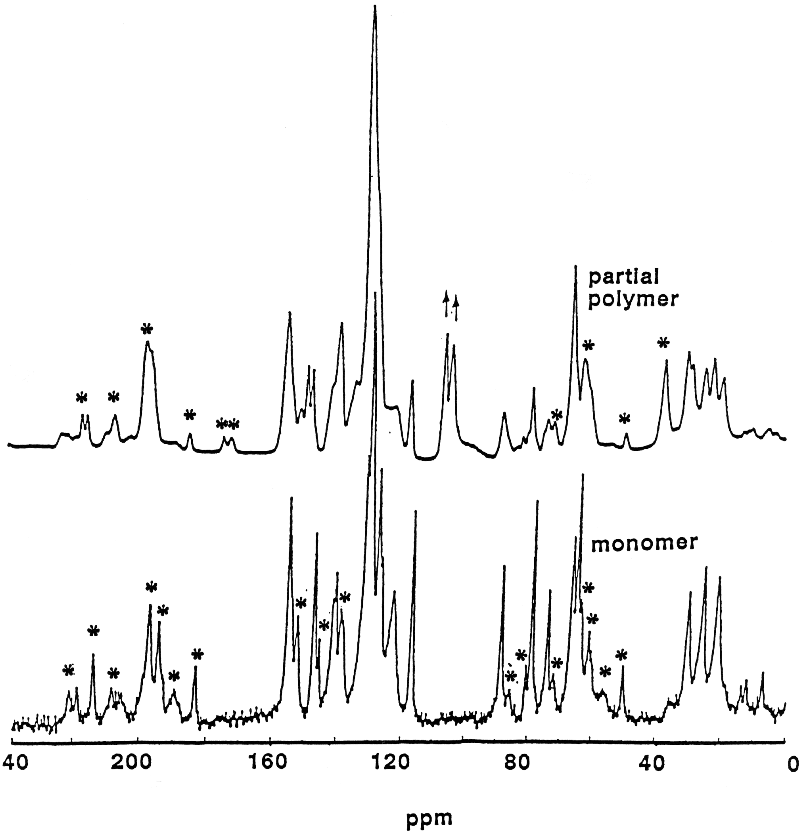

Figure 2 Solid state ^{13}C CP/MAS NMR of **6c**. The peaks with asterisk are for spinning side bands.

from methanol, was unreactive upon γ-irradiation. However, when this sample was crystallised from its melt, the sample became solid state reactive. The powder XRD patterns for the above two forms of **6b** reveal totally different crystal packing confirming the existance of two morphologies. Figure 1 shows the powder XRD scans for the monomer **6b**, its partial polymer and that of its polymer. The melt-crytallised sample, when polymerised by UV or γ-radiation, gives a blue polymer which changes to blue-green as irradiation is continued.

In order to confirm that the monomers have indeed undergone 1, 4-addition reaction to form the PDAs, we recoreded CP/MAS NMR for them. As a typical example, figure 2 shows the ^{13}C CP/MAS NMR spectra of the monomer **6c** and that of its partial polymer. The monomer shows peaks at 66, 74, 78 and 87 ppm for the four acetylenic carbon atoms of the diacetylenic goup. As the polymerisation proceeds, a pair of new peaks apear at 103 ppm and 106 ppm which can be seen in the spectrum of the partial polymer. These peaks are assigned to the acetylenic carbon atoms for the polymeric backbone of PDA. The other new peak for the alkene carbon of the polymeric backbone is expected at around 120 ppm. This position is already having peaks for the quinoline and phenyl moieties and hence the new peak must be overlapped. Similarly for **6a**, the monomer showed acetylenic carbon peaks at 65, 73, 77 and 87 ppm whereas the polymeric acetylenic carbons were observed at 103 and 105 ppm. And for **6b**, monomer's acetylenic carbon peaks were at 66, 73, 76 and 86 ppm and the polymer showed new peaks for its acetylenic carbons at 103 and 106 ppm.

The absorption spectra of all the polymers show typical excitonic absorption peak pattern for PDA having λ_{max} of 590, 715 and 660 nm. for **6a**, **6b** and **6c**, respectively. λ_{max} of 715 nm for **6b** is significantly longer than that for the other two polymers. In fact, this is one of the longest λ_{max} in this category of PDAs. Also, the absorption band for this polymer is quite sharp indicating improved ordering of the polymer chains. The change of the polymer colour from blue to blue-green indicates that the polymerisation extends for large units of monomers without any break while the sharp wavelength peak suggests that chain sizes with uniform effective conjugation lengths were obtained for the polymer. It can be observed that simply by substituting the phenyl ring with a chloro-group in the DA, the λ_{max} of PDA has greatly enhanced. Further, large red shift has been effected for **6b** against **6c** just by changing the position of the chloro-group.

In the monomer **6d**, we introduced a butoxy carbonylmethyl urethane instead of the phenyl capped urethane group. Contrary to our expectations, this monomer failed to react in the solid state. These results lead us to conclude that chloro-group on the phenyl ring of urethane side group is probably suitable for inducing planar structure of the PDA backbone which in turn produces longer effective conjugation length. Thus, by introducing quinolyl moiety as well as phenyl-capped urethane side group, one can achieve a favourable packing of the monomer molecules in crystal to react topochemically. It may be noted that 1, 4-diquinolyl-1, 3-butadiyne(DQ), a symmetric diacetylene, gives PDA with almost same λ_{max} of 710 nm (14). Therefore, it follows that only one quinolyl group is sufficient to boost the conjugation length of the polymer backbone while the use of the other quinotyl group at the other end of monomer backbone is redundent. On the other hand, the monomer to polymer conversion has been greatly improved in case of **6a**(50%), **6b**(60%) and **6c**(60%), against that of DQ (25%). Thus, monomer **6b** turns out to be providing the most promising PDA in this category of diacetylenes so far. These polymers, however, could not be dissolved in common organic solvents although they dissolved in mineral acids.

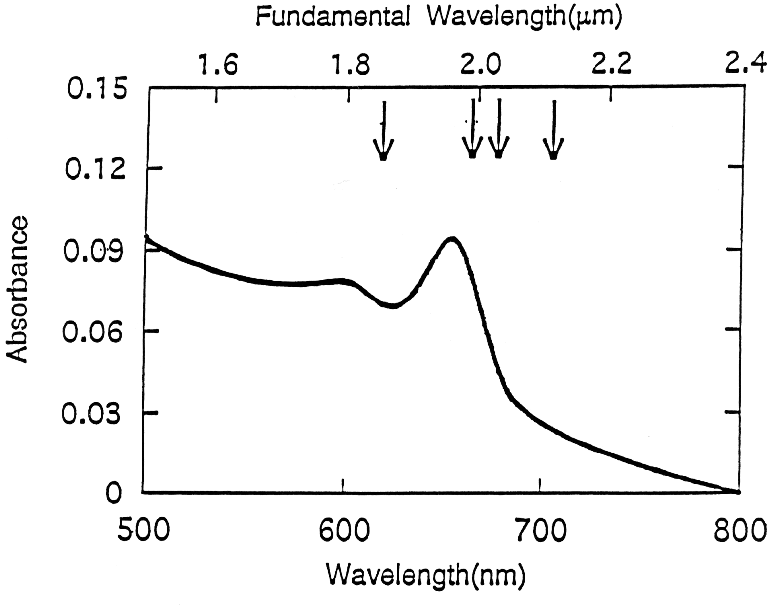

Figure 3 Absorption spectrum of polymerised film of 6c with a thickness of about 0.6 mm. The arrows indicate the fundamental wavelength. When the wavelength of arrows is read using the lower abscissa, it corresponds to the third-harmonic wavelength.

The $\chi^{(3)}$ value at 1.98 µm is 0.32 x 10^{-12} esu which is higher by two order of magnitude than the $\chi^{(3)}$ of quartz. It may be noted that if we consider 100% polymer conversion of the spin coated film of **6c**, the $\chi^{(3)}$ will be of the order of 10^{-11} esu. Further, it was found from the powder XRD analysis that the polymer crystals are deposited on the quartz plate at random, i.e. there is no regularity in the overall direction of the polymer backbone on the quartz plate. In view of this, the $\chi^{(3)}$ value of a single crystal of **6c**, in the direction of the backbone should be 5 times of the experiment value(15) which turns out to be about 1.5 x 10^{-11} esu for a fully polymerised single crystal. Figure 3 shows relationship between the absorption spectrum of PDA from **6c** and the fundamental wavelengths. The values obtained are listed in Table 1. At the pumping wavelength 1.98 µm, the $\chi^{(3)}$ value of the polymer is highest, apparantly due to the maximum resonance effect.

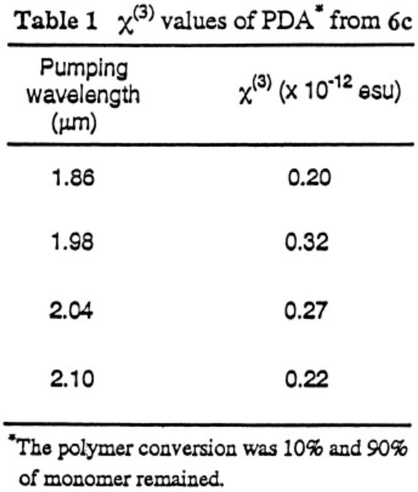

Table 1 $\chi^{(3)}$ values of PDA* from 6c

Pumping wavelength (µm)	$\chi^{(3)}$ (x 10^{-12} esu)
1.86	0.20
1.98	0.32
2.04	0.27
2.10	0.22

*The polymer conversion was 10% and 90% of monomer remained.

Although the $\chi^{(3)}$ values for the present PDA is not one of the highest among PDA family, this particular PDA has significantly large $\chi^{(3)}$ value. These preliminary results are very significant in view of the future optimisation of the structure for better third order NLO materials. Detailed studies for the PDAs prepared are in progress and will be reported subsequently.

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References

1. Wegner G (1969) Z. Naturforsch. 24: 824.
2. Bloor D, Chance RR (1984) (eds.) Poydiacetylenes, NATO ASI Series, Series E, Applied Sciences No. 102, Martinus Nijhoff, Dordrecht.
3. Okada S, Matsuda H, Nakanishi H (1996) In: Salamone JC (ed) Polymeric Materials Encyclopedia, CRC Press, Boca Raton, pp 8393.
4. Donovan KJ, Wilson EG (1981) Phil. Mag. B44: 9.
5. Lim KC, Fincher CR, Casanuovo SA, Heeger AJ (1984) Mol. Cryst. Liq. Cryst. 105: 329
6. Sauteret C, Hermann JP, Frey R, Rradere F, Ducing J, Baughman R H, Chance R R (1976) Phys. Rev. Lett. 36: 956.
7. Galiotis C, Young R J (1983) Polymer 24: 1023.
8. Carter, G M, Hryniewicz, J W, Thakur, M K, Chen Y J, Meyler S E (1986) App. Phys. Lett. 48: 998.

9. Sarkar A, Okada S, Komatsu K, Matsuda H, Nakanishi H (1996) Polym. Preprints, Jpn. 45: 1369.
10. Baughman RH (1974) J. Phys. Sci. Polym. Phys. Ed. 12: 1511.
11. (a) Ames DE, Bull D and Takundwa C (1981) Synthesis, 364; (b) Sarkar A (1993) PhD Thesis, IIT, Bombay.
12. Mito A, Hagimoto, Takahashi C (1995) Nonlinear opt. 13: 3.
13. Nakanishi H, Matsuda H, Okada S, Kato M (1990) Polym. Adv. Technol. 1: 75.
14. Talwar SS, Kamath M, Das K, Sinha UC (1990) Polym. Commun. 31: 198.
15. Kajzar F (1993) Nonlinear Opt. 5: 329.