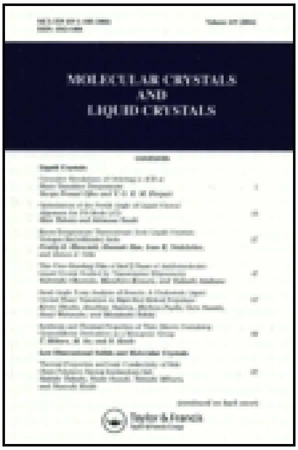

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Preparation of Asymmetrically Substituted Diacetylenes Containing Heteroaryl Sidegroups and Their Solid State Polymerisation

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Preparation of a series of asymmetrically substituted diacetylenes containing thienyl moiety or quinolyl moiety as one of the sidegroups directly bound to the diacetylene backbone and a urethane derivative as the other sidegroup were carried out and their solid state polymerisation was investigated.

Keywords: diacetylene, polydiacetylene, solid state polymerisation, third order nonlinear optical properties

INTRODUCTION

Diacetylenes(DAs) have generated a lot of interest during the last two decades due to its peculiar solid state polymerisation behaviour.[1,,2] The polydiacetylene(PDA), being a quasi one-dimentional π-conjugated system, shows nonlinear optical properties as well as chromic properties arising due to conjugated systems.[3,4,5] We have been dealing with preparation of diacetylenes with an aim to get good third order nonlinear optical materials. One class of diacetylenes, which we have been investigating, consists of aryl and heteroaryl moieties directly bound to the diacetylene backbone.[6] The design of such diacetylenes have been based on the premise that the aromatic sidegroup will, in suitable cases, help the backbone conjugation to extend further to provide longer effective conjugation length. The heteroaryl moiety, by virtue of its aromatic interactions in adjacent molecules, enhances the probability for the monomer to stack in a crystal appropriately to polymerise topochemically. The other side group consists of long alkyl chain with urethane derivative. This has been incorporated into the design of diacetylene to make it reactive in solid state as the methylene spacers attached to the backbone allows flexibility to the molecules in a crystal. The other advantage is to make the resulting polydiacetylene soluble in organic solvents. This is particularly useful as it will fecilitate thin film formation which is the alternative morphology to the much difficult single crystal formation for NLO applications. Here, we report the synthesis and solid state polymerisation of a series of diacetylenes each of which are unsymmetrically substituted with a heteroaryl moiety, namely thienyl or quinolyl, and a urethane as the two sidegroups.

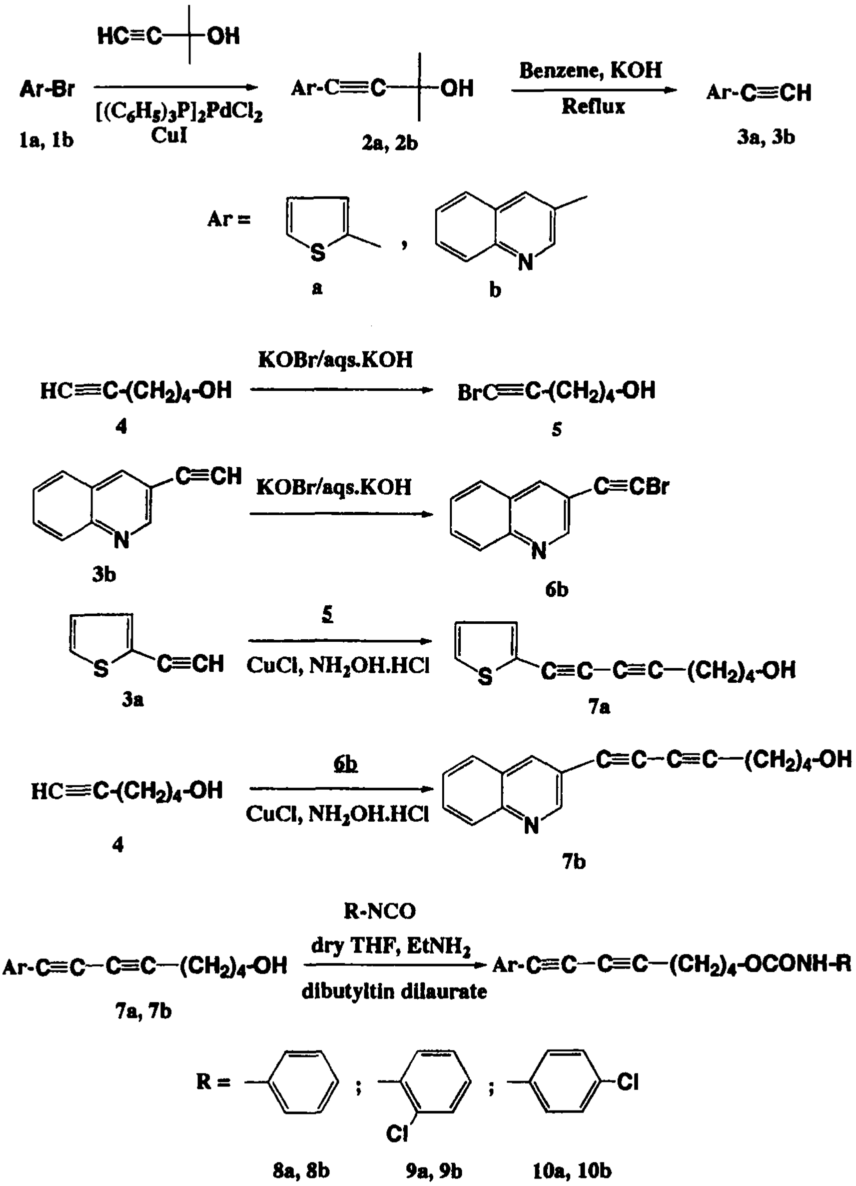
EXPERIMENTAL

The monomers were prepared according to the routes shown in Scheme 1. Synthesis of **2a**[7], **2b**[8], **3a**[7], **3b**[8], **5**[6] and **6**[9] were carried out as reported in the literature. Detailed synthetic procedure for the monomers are being reported elsewhere. All the monomers were characterised by IR and NMR spectroscopy as well as by elemental analysis.

Solid state polymerisation of the monomers were done by irradiating them with UV or γ-radiation. The polymers were characterised by IR, UV and/or solid state NMR spectroscopy. Powder XRD was used to check crystallinity for the monomers and polymers.

RESULTS AND DISCUSSION

Table 1 summarises the solid state reactivity of the synthesised diacetylenes. Half of all the diacetylenes show reactivity in solid state under UV and γ-radiation. Two interesting points can be observed. First, all of the quinolyl



SCHEME 1 Synthetic routes for various diacetylenes

diacetylenes having phenyl-capped urethane sidegroups are reactive in solid state. 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. Second, only one thienyl containing DA, **9**, shows solid state reactivity. From this result, it is not clear about the role of thiophene as far as solid state reactivity is concerned but it proves that thiophene containing DA can also form reactive monomers. Incidentally, **8a** is the first DA containing directly bound thiophene side group which shows solid state reactivity. Further, it can be observed that between **8a** and **8b**, the later which is a quinolyl DA, gives polymer with significantly longer λmax (655 nm) than thiophene containing PDA (590 nm). Other structural features being similar, the λmax of **18b** is boosted obviously due to greater contribution of directly bound quinolyl side group to the backbone; thienyl group in **8a** being less contributing. The quinolyl moiety increases the effective conjugation length of the polymer backbone either by being planar to the system or by greater π–π interaction or perhaps both.

Table 1. Solid state reactivity of the diacetylenes and optical properties of their polymers.

	solid state reactivity*			% conversion†	polymer	polymer
DA	Δ	UV	γ		λmax(nm)	colour
7a	X	X	X	---	---	---
7b	X	X	X	---	---	---
8a	X	O	O	21	590	purple
8b	X	O	O	37	655	blue
9a	X	X	X	---	---	---
9b	X	O	O	60	715	blue-green
10a	X	X	X	---	---	---
10b	X	O	O	60	660	blue

* Δ: heat; X: unreactive; O: reactive

†determined gravimetrically by extracting the monomer.

The non reactivity of **7a** and **7b** suggests that the terminal phenyl group at the urethane end of the diacetylene was responsible for appropriate crystal packing to make the monomers reactive. The phenyl groups of adjacent molecules, due to intermolecular π–π interaction, may be helping the monomers to pack in appropriate manner for solid state polymerisation to occur. However, this seems to be only one of the factors deciding the overall reactivity of the monomer. **9a** and **10a**, which are thienyl DAs with chlorophenyl-capped urethane moieties as the other side groups, do not polymerise topochemically. It may be possible that in the above cases, chloro-substitution at the phenyl group are creating sterric hindrance and are not allowing the molecules to stack properly for 1,4-addition reaction to occur. Thus it becomes apparent that in order to get reactive diacetylenes, one need to address multiple factors at the same time. The outcome of all the factors is in the form of crystal geometry and molecular arrangements inside it.

Monomer **9b** is of particular interest since it gives PDA with λmax of 715 nm which is among the longest in this category of PDAs.[10] Also, the absorption band for this polymer is quite sharp indicating improved ordering of the polymer chains(fig. 1). It may be noted that diquinolyl diacetylene(DQ), a symmetric diacetylene with quinolyl moiety at both ends of the backbone, gives PDA with almost the same λmax.[11] Therefore, it follows that only one directly bound quinolyl group is sufficient to boost the conjugation length of the polymer backbone while the use of the other quinolyl group at the other end of monomer backbone seems redundent. On the other hand, the monomer to polymer conversion has been greatly improved in case of **9b** (60%) and **10b** (60%) against that of DQ (25%). Thus, monomer **9b** turns out to be most

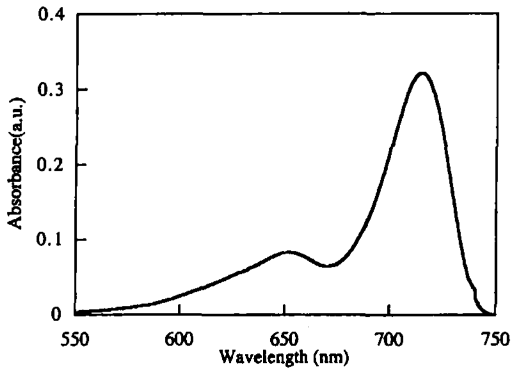


FIGURE 1 Absorption spectrum of **9b**

promising DA in this category of diacetylenes so far. The percentage conversion of other reactive DA to PDA varies from 35% to 60% (Table 1).

Powder XRD for the monomers and the polymers shows that the crystallinity is maintained while going from monomer to polymer in all the reactive DAs studied in this report. It is an improvement over DAs with long alkyl groups with urethane type moieties as both side groups which tend to give amorphous polymer even though they show high reactivity.

In conclusion, we have been able to prepare a series of diacetylenes which undergo solid state polymerisation, maintain crystallinity on polymer formation and which produce PDAs with high effective conjugation length. Thus, this investigation will contribute in our endeavor to design PDAs with optimum properties so that they can be used as NLO materials.

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