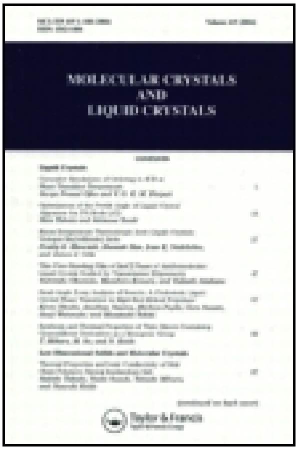

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Crystal State and Liquid Crystal State Polymerization of Unsymmetrical Diacetylenes with an Orientation-Controlling Substituent

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CRYSTAL STATE AND LIQUID CRYSTAL STATE POLYMERIZATION OF UNSYMMETRICAL DIACETYLENES WITH AN ORIENTATION-CONTROLLING SUBSTITUENT

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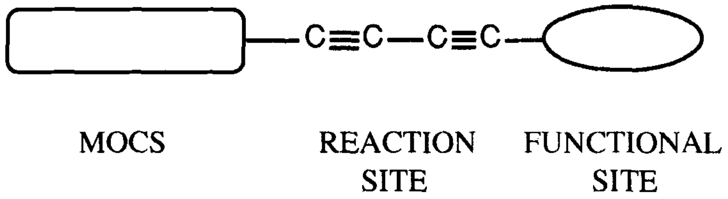
Abstract Unsymmetrically substituted diacetylenes (1-5) with a mesogenic core on one side were prepared. As a substituent on the other side was introduced para-substituted benzenesulfonyl group, which is a substituent of symmetrically substituted diacetylenes PTS and PCS. Both diacetylene monomers 1 and 2 were found to polymerize by heating in solid state with a similar reactivity, which shows a sharp contrast to a large difference in reactivity between PTS and PCS. Hydroxymethyl derivative 3 polymerized in both crystal state and liquid crystal state. Characteristic reaction behavior of 3 in a nematic phase was elucidated. Other examples of reactive unsymmetrical monomers are presented.

INTRODUCTION

Polydiacetylenes, which are obtainable from solid state polymerization of diacetylenes[1], have drawn attention from the view of their physical properties, e.g. optical nonlinearity[2], photoconductivity[3], or magnetism[4]. Reactivity of solid state polymerization, however, is strictly governed by the spatial arrangement of monomers[5].

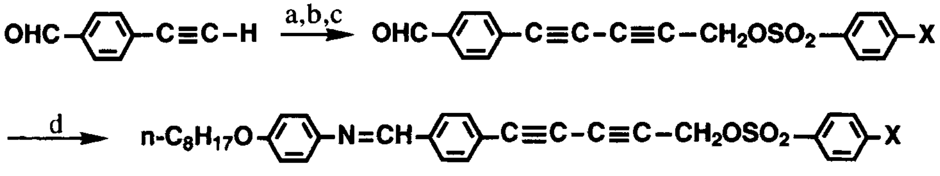
In order to reduce such a restriction on the reactivity it may be effective to introduce a substituent which can control the orientation of monomers in crystals. In this respect, we have interested in a mesogenic substituent, a benzylidene-aniline moiety with a long alkyl chain at the para position. The merit of designing such unsymmetrical diacetylenes with mesogenic orientation-controlling site (MOCS) is twofold. First, its reactivity in the crystal phase may be enhanced by the favorable alignment realized by the aid of MOCS. Second, the monomer has a potentiality to polymerize in liquid crystal phases, even if the reactivity of the monomer is poor in the crystal phase. Here we report the reactivity of newly designed monomers (1-5) with MOCS in crystal or/and liquid crystal phases.



EXPERIMENT

Unsymmetrical diacetylenes 1 or 2 (mp 101°C, 103°C, respectively) where para-methyl or para-chloro benzene-sulfonyl group is introduced on one end and MOCS on the other, were synthesized as shown in Scheme 1[6]. Thermal polymerization of 1 or 2 in the crystal phase was carried out in an electric oven at 90±2°C. The progress of the polymerization was monitored by the decrease of the intensity of $\nu_{C\equiv C}$band (2244 cm^{-1}) in FT-IR spectra.

SCHEME 1 Synthesis of umsymmetrical diacetylenes(1,2).



(a) Br-C≡C-CH_2OH, CuCl, $NH_2OH{\cdot}HCl$, $EtNH_2$aq; (b) 1N HCl,EtOH; (c) p-Me or p-Cl substituted benzenesulfonyl chloride, KOHaq,THF; (d) octyloxy-aniline, benzene

RESULTS AND DISCUSSION

Both 1 and 2 was found to polymerize smoothly after several hours of an induction period (Figure 1). The reaction behavior is characteristic to the solid state polymerization. The obtained polydiacetylenes are black and keep the shapes of monomer crystals. Absorption spectra of the polymers were measured in thin KBr disks to show an absorption end at 700 nm, which confirms the presence of a long π-conjugated chain.

The reactivity of 1 or 2 should be compared with those of 2,4-hexadiyne-1,6-diol bis(p-toluenesulfonate) (PTS) and 2,4-hexadiyne-1,6-diol bis(p-chlorobenzenesulfonate) (PCS). While PTS exhibits high reactivity of polymerization even at room temperature, PCS does not show any reactivity, although the van der Waals radius of the substituent at para-position(chloro 1.80Å, methyl 1.85Å) is approximately the same. The high reactivity of the former (PTS) is rationalized by the favorable stacking of monomers for 1,4-addition. The angle between stacking axis and the long axis of the monomer in the crystal is 45°[7] whereas the corresponding angle in PCS is as large as 67°[8]. The lack of reactivity of PCS is ascribable to the considerable deviation from the optimum condition for 1,4-addition[9]. Contrasting with the above two cases, the reactivity of

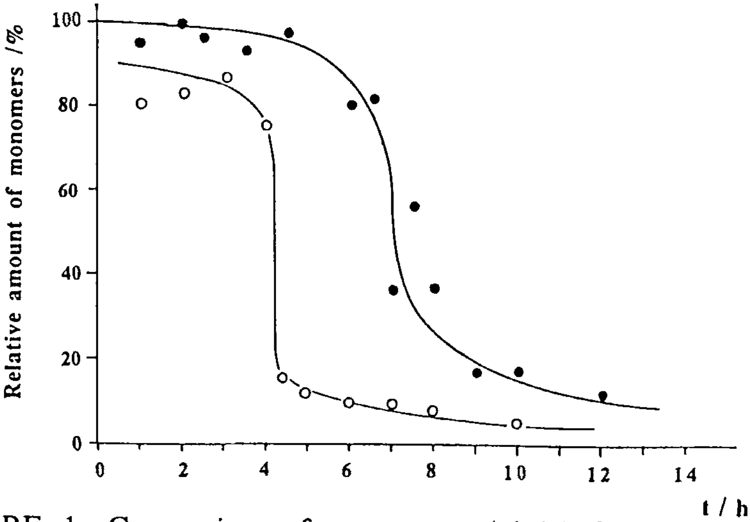


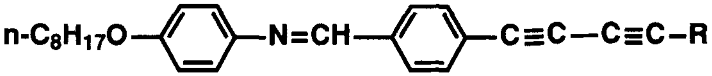
FIGURE 1 Conversion of monomers (1 (•), 2 (o)).

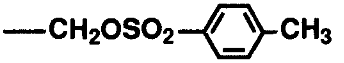
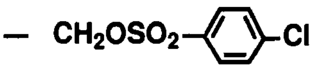
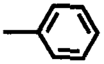
unsymmetrical monomers 1 and 2 are approximately the same. The result suggests that the arrangement of monomers is practically the same and presumably governed by MOCS.

In order to examine the validity of MOCS in the absence of benzenesulfonic group which is considered to play some role in arranging monomers in crystals, benzenesulfonic group was replaced with hydroxymethyl group or hydrogen (3,4). The diacetylene derivative 3 was confirmed to have a nematic phase above the melting point (mp 122-123°C) base on the observation of the dynamic scattering mode through a microscope under external electric fields larger than 1600 V/cm. A differential scanning calorimetric (DSC) diagram reveals that an exothermic reaction occurs at temperature higher than 130°C.

Diacetylene 3 was heated in both crystal and liquid crystal phase under a helium atmosphere at 110°C and 130°C, respectively. The decay curve at 110°C is characterized by the presence of a long induction period of ca. 50h; thereafter, the reaction proceeds smoothly giving a sigmoid trace, which is consistent with the kinetic feature of polymerization of induction period, suggesting that the favorable alignment of the monomer for 1,4-addition can be realized in the nematic phase and that the local motion of the monomer is not so restricted as in the crystal phase[10]. Another feature of the liquid-crystal polymerization is formation of oligomers at the initial stage of polymerization. The reactivity of the other unsymmetrical diacetylenes with MOCS in the nematic phase is summarized in table1.

TABLE 1 Thermal polymerization reactivity of diacetylenes with MOCS



Substituent R		Reactivity
	1	+ +
	2	+ +
—CH_2OH	3	+
—H	4	+ + +
	5	+

CONCLUSION

Although the examples are limited at present, the idea of introducing a mesogenic substituent as the orientation-controlling site (MOCS) seems effective in obtaining polydiacetylenes with various substituents. Furthermore one can carry out the polymerization in liquid crystal phases when the reactivity is poor in the crystal. The liquid-crystal phase polymerization will supply a useful method for preparing novel families of poor in the crystal. The liquid-crystal phase polymerization will supply a useful method for preparing novel families of polydiacetylenes of various interests. Preparation of unsymmetrical diacetylenes carrying donors, acceptors or stable radicals now in progress in these laboratories.

ACKNOWLEDGEMENTS

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