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Topochemical polymerization of butadiynylene dibenzamides

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SUMMARY

Series of meta- and para-substituted butadiynylene dibenzamides were synthesized, and their solid state polymerization was studied. The meta-isomers were light sensitive but not heat sensitive. The polymerizability of para-isomers depended on the type of N-substitutents. The polydiacetylenes from the para-isomers were blue, while those of the meta-isomers were light purple. Studies with molecular models and computer imaging suggested that hydrogen bonding between the topochemically polymerizable dibenzamides in the polymerization array is rather unlikely.

INTRODUCTION

There have been many studies on the polymerization of diacetylenes(DAs) since Wegner's first report in 1969[1]. However, little is known about the topochemical polymerization of aromatic DAs, probably because the polydiacetylenes(PDAs) derived from them are generally insoluble and intractable, and hence they are of limited application. Wegner[2] reported that ortho- and meta-substituted diphenyldiacetylenes are topochemically polimerizable but the para-isomers are generally inactive because their crystal packing is inadequate for solid state polymerization. It is interesting, but complicated, to study why one isomer is polymerizable while the other is not, and what factors determine the favourable crystal packing for topochemical polymerization. Recently we prepared a series of butadiynylene dibenzoic acid derivatives and found that the topochemical polymerizability of the diamides is rather complex.

PDAs are considered to be promising materials for nonlinear optical (NLO) applications[3], and those having aromatic substituents are expected to have higher nonlinear optical susceptibilities because of the more extended conjugation with aromatic rings. Furthermore, methods to make thin films of such aromatic poly-

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diacetylenes have recently become available[4,5], and it was thought to be worth studying the polymerizability of aromatic DAs in order to obtain basic data for the cross-polymerizability of DA groups in polymer matrix.

In this work, a series of meta- and para- substituted butadiynylenedibenzamides were synthesized, and their polymerization in the solid state was investigated. The results are reported in this paper.

EXPERIMENTAL

MATERIALS

Ethynylbenzoic acids were prepared by the reaction of bromomethylbenzoates with 2-methyl-3-butyn-2-ol using palladium catalysts, as reported previously[6]. They were then converted to the chlorides by the reaction with oxalyl chloride in dichloroethane, and after evaporating the solvent and excess oxalyl chloride they were reacted with different amines in dicloroethane using triethylamine as an acid acceptor. The ethynylbenzamides were then dissolved in methanol and catalytic amounts of copper(I) chloride and N,N,N',N'-tetramethylethylenediamine were added. Oxygen was bubbled into the mixture at room temperature for 20 hrs. The contents were poured into dilute hydrochloric acid, washed well with hydrochloric acid, and dried in vacuum. Recrystallization from n-propanol gave colorless crytals. The elemental analysis results and their topochemical reactivity are shown in Table 1.

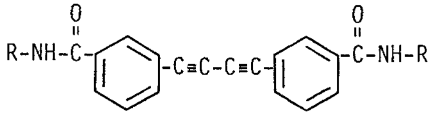
POLYMERIZATION

The topochemical polymerizability was judged by irradiating the ground DA crystals suspended in water containing a small amount of isopropanol, in a quartz tube stirred by a magnetic stirrer. A medium pressure 400 W UV lamp supplied by Ace Glass was used for irradiation. The crystals were also irradiated by an electron beam from a Van de Graff accelerator of 2 MeV (High Voltage Coorporation) with a dose rate of 12 kGy/min at 1.3 MeV.

COMPUTER IMAGING AND MOLECULAR MODELING

Taking into account the well established crystal packing requirements for topochemical polymerization [7], i.e. less than 4 Å for the distance between the two adjacent DA rods, and 45 degree for the angle between the DA rod and the stacking axis, computer imaging of the two diamides was carried out by using CERIUS software[8], followed by the MOPAC calculation[9] to optimize the geometry to search for the equilibrium distance favorable for polymerization. Molecular models by Cochranes of Oxford Ltd, were used for construction of the monomeric and polymeric DAs.

Table 1. Butadiynylene dibenzamides synthesized.



	R	Elemental analysis (%) C	H	N	mp (°C)	Reactivity*
I.	m-n-C_3H_7	77.10 (77.42)	6.80 (6.45)	7.20 (7.53)	250	deep violet
II.	m-n-C_4H_9	77.30 (78.00)	7.25 (7.00)	6.51 (7.00)	236-7	violet
III.	m-n-C_6H_{13}	78.23 (78.95)	7.35 (7.89)	6.51 (6.14)	219	purple violet
IV.	m-n-C_7H_{15}	78.84 (79.34)	8.12 (8.26)	5.30 (5.78)	210	light violet
V	p-n-C_3H_7	77.40 (77.42)	6.67 (6.45)	6.30 (7.53)	---	(no reaction)
VI.	p-n-C_6H_{13}	78.68 (78.95)	7.99 (7.89)	5.93 (6.14)	264	blue
VII.	p-C_2H_4-OH	69.87 (70.21)	5.54 (5.32)	7.32 (7.45)	---	deep blue **
VIII.	p-C_3H_6-OH	71.55 (71.29)	6.38 (5.94)	6.74 (6.93)	268	blue
IX.	p-C_6H_{12}-OH	73.38 (73.77)	7.72 (7.38)	5.69 (5.94)	233	blue
X.	p-C_6H_5	81.61 (81.82)	4.76 (4.55)	6.30 (6.36)	---	(no reaction)

* By irradiation with UV or electron beam. **Also heat sensitive(171°C)
---: no melting before decomposition.

RESULTS AND DISCUSSION

It is well known that the topochemical polymerizability of DAs depends strongly on the packing and mobility of the substituent groups attached to the triple bonds [10]. The DAs with substituents which do not interacts with each other, for example diphenylbutadiyne, do not undergo topochemical polymerization. When strongly interacting groups are directly attached to the triple bonds, the molecules become too rigid and thus no topochemical polymerization is possible[11,12]. Therefore, many of the known topochemically polymerizable DAs are the derivatives of 2,4-

hexadiyne in which the methylene groups are the separators between the diacetylenic and interacting substituent groups, acting as a mobile spacer. In the cases of DAs having aromatic substituents attached directly to the triple bonds, Wegner[2] reported that those having substituents, such as -NH_2, -NO_2, etc, at ortho- and meta-positions are topochemically active, and those at para position are inactive. The present authors have studied the polymerizability of the butadiynylene dibenzoates[13], and found that none of the meta- or para- isomers are topochemically active. The lack of hydrogen bonding in the esters may be one of the reasons why they do not form a crystal structure favourable for topochemical polymerization.

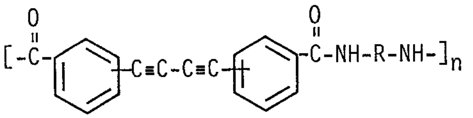
The meta-substituted benzamide crystals underwent topochemical polymerization on exposure to UV light or an electron beam, giving purple to bluish purple crystals. It was expected, considering Wegner's results[2], that the para-substituted dibenzamides might not be light sensitive, but it was found that some of them were also light sensitive, giving deep blue crystals, as shown in Table 1. As can be seen from the table, the alkyl chain length is not important for the topochemical polymerizability in the cases of meta-isomers, but is very important in the cases of the para-isomers. The short chains such as n-propyl and phenyl gave topochemically inactive DAs, while longer ones such as n-hexyl and ω-hydroxyalkyl groups, obviously gave favourable crystal packings. It should be noted that the colours of the para-dibenzamides were much deeper than those of the meta-dibenzamides, indicating that the resonance contribution of the carbonyl groups at the para position is greater.

According to Baughman[7], the favourable crystal packing of DAs for topochemical polymerization to occur, is one in which the distance between the DA rods is around 4 Å or less, with a 45 degree angle between the DA rod and the stacking axis. In order to see if this requirement was applicable to the dibenzamides, computer imaging of the molecular structures of two adjacent molecules was performed. It was found that in the case of meta-diamides, no hydrogen bonding of the amide hydrogen with the carbonyl oxygen is possible between the DA molecules in the polymerization array, if the above mentioned packing requirement is applied and the carbonyl groups and the phenyl rings are assumed to be in the same plane. A model of three adjacent molecules showed it was possible to introduce the hydrogen bonding by distorting the molecules but it was impossible in the polymer due to steric hidrance between the carbonyl oxygens and other groups, and furthermore all the phenyl rings had to be aligned almost perpendicularly to the polymer backbone due to steric hindrance of the substituted amide groups at the meta-position. This indicates that the resonance contribution of phenyl rings to the poly-DA back bone is small, and therefore the colors of these poly-DAs are less intense than those of the para-isomers. It may be concluded from the model studies that hydrogen bonding between the oxygen atom of the carbonyl group and the amide hydrogen is unlikely between the DA molecules in the same polymerization array. Therefore, hydrogen bonding, if formed, should exist between the DAs of different arrays. However the IR spectra of m-dibenzamides showed a sharp peak due to the amide hydrogen at about 3500 cm^{-1}, indicating absence of hydrogen bonding.

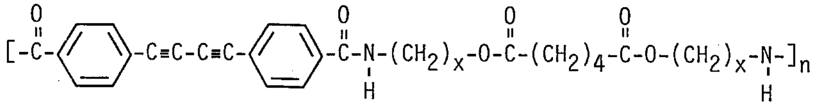
In the case of the para-isomers, the construction of the monomer crystal (R = ethyl) consisting of 3 molecules showed that it is possible to introduce hydrogen bonding between the adjacent amide groups for the monomer array if the carbonyl groups are nearly perpendicular to the phenyl rings. However, the model of the polymer structure was found to be quite favourable for hydrogen bonding. All the carbonyl groups can be placed in the same plane as the phenyl rings, and no distortion of bonds seems to exist, except that the phenyl rings are somewhat slanted with respect to the polymer chain due to the steric hidrance among themselves. It is rather difficult to imagine such a rigid structure (monomeric) being transformed into another very different rigid structure (polymeric) merely by irradiation at room temperature. It should be noted that none of these light sensitive DAs are heat sensitive; no thermal polymerization occurs below their melting points, except for **IV** which underwent topochemical polymerization when heated at 171 °C. In the cases of para-isomers also, it seems that for those which undergo topochemical polymerization, no hydrogen bonding is formed between the monomers in the same polymerization array. The crystals of DAs with phenyl and small N-substituted groups, which do not polymerize, may form crystals with hydrogen bonding between the amide groups and therefore the solid state transformation from monomer to polymer is inhibited.

The above speculation is rather contrary to the cases of 2,4-hexadiynediurethanes which are flexible DAs, in which hydrogen bonding is considered to be favourable for favourable crystal packing. Octa-3,5-diynylene-diurethanes and diesters are light sensitive and give intensely colored products by irradiation with UV light [14]. The formers can have hydrogen bonding but the latters do not. As mentioned by Wegner [15], it is extremely difficult to correlate the chemical structures of the substituents with topochemical polymerizability.

The polyamides containing these butadiynylenedibenzamides (I) have been claimed in a patent [16], but chemical and physical properties are not mentioned. In this work also, the following polyamides were prepared (II). The DA groups in



[I]



(II) x = 2,3,6.

the polymers were light sensitive, the polymers becoming blue on irradiation with UV light, but they were poorly soluble due to their rigid structures and therefore the study was discontinued. The results of this work also showed the complex nature of topochemical polymerizability of DAs, and it is concluded that hydrogen bonding is not necessary for the butadiynylene dibenzamides to be topochemically polymerizable.

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