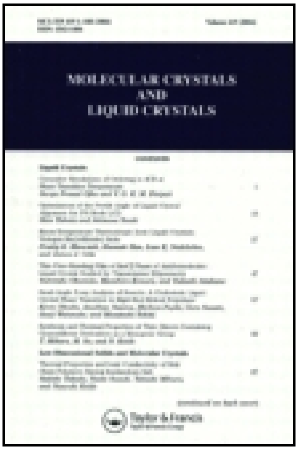

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Solid-State Polymerizability of Esters and Amides of Alkadiynedioic Acid

Hitoshi Shinbo [a], Neil Feeder [b], Shuji Okada [a], Hiro Matsuda [b], Fusae Nakanishi [b] & Hachiro Nakanishi [a]

[a] Institute for Chemical Reaction Science, Tohoku University, Sendai, 980-77, Japan

[b] National Institute of Materials and Chemical Research, 1-1 Higashi, Tsukuba, 305, Japan

To cite this article: Hitoshi Shinbo, Neil Feeder, Shuji Okada, Hiro Matsuda, Fusae Nakanishi & Hachiro Nakanishi (1998): Solid-State Polymerizability of Esters and Amides of Alkadiynedioic Acid, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 315:1, 41-46

To link to this article: http://dx.doi.org/10.1080/10587259808044308

Mol. Cryst. Liq. Cryst., 1998, Vol. 315, pp. 41–46
Reprints available directly from the publisher
Photocopying permitted by license only

Solid-State Polymerizability of Esters and Amides of Alkadiynedioic Acid

HITOSHI SHINBO[a], NEIL FEEDER[b], SHUJI OKADA[a],
HIRO MATSUDA[b], FUSAE NAKANISHI[b], and HACHIRO NAKANISHI[a]
[a]Institute for Chemical Reaction Science, Tohoku University, Sendai 980-77, Japan; [b]National Institute of Materials and Chemical Research, 1-1 Higashi, Tsukuba 305, Japan

Carboxylic-acid derivatives of butadiyne and octatetrayne including ester and amide were prepared and solid-state polymerizability was investigated. Though octatetrayne derivatives and most of carboxylic acid and amide derivatives of butadiyne can be polymerized, no esters of butadiyne show polymerizability irrespective of success in crystal growth up to centimeter order. X-ray crystallographic analysis of three esters pointed out weak intermolecular interaction in these derivatives resulting in molecular packing which is based on space filling only.

Keywords: polydiacetylene; solid-state polymerization

INTRODUCTION

For nonlinear optical (NLO) devices, one of the desired form is single crystal. Therefore, polydiacetylene (PDA), which can be uniquely obtained as single crystal by solid-state polymerization of monomer[1], is expected to be suitable for third-order NLO devices[2]. Since NLO properties are strongly affected by optical quality of the samples, quality improvement of PDA crystals is a very important subject. As the size, shape and perfection of PDA crystals are inherited from the precursor monomer crystals by virtue of topochemical polymerization, the ultimate goal seems to prepare clear monomer single crystal without any disorder at least in a certain part of it.

One of the best examples of PDA monomer for crystal growth is 2,4-hexadiynylene bis(*p*-toluenesulfonate) (PTS)[1], which gives large single crystals up to centimeter dimension by slow evaporation method with comparative ease. However, large single crystal growth is generally difficult especially for butadiyne derivatives with methylene chains, which often show high solid-state polymerizability. Thus, molecular engineering of monomer for crystal growth is worth investigating. Extending the analogy from PTS, which is ester of toluenesulfonic acid, we synthesized conjugated acetylene derivatives having ester groups of carboxylic acid in the present study. Corresponding precursors of carboxylic acid and derived amide compounds were also synthesized. Their solid-state polymerizability, crystal growth and crystal structures of three esters are reported.

EXPERIMENTAL

Synthetic routes of compounds in this study are presented in FIGURE 1. Starting from 5-hexyn-1-ol and 6-heptyn-1-ol[3], dicarboxylic acids with

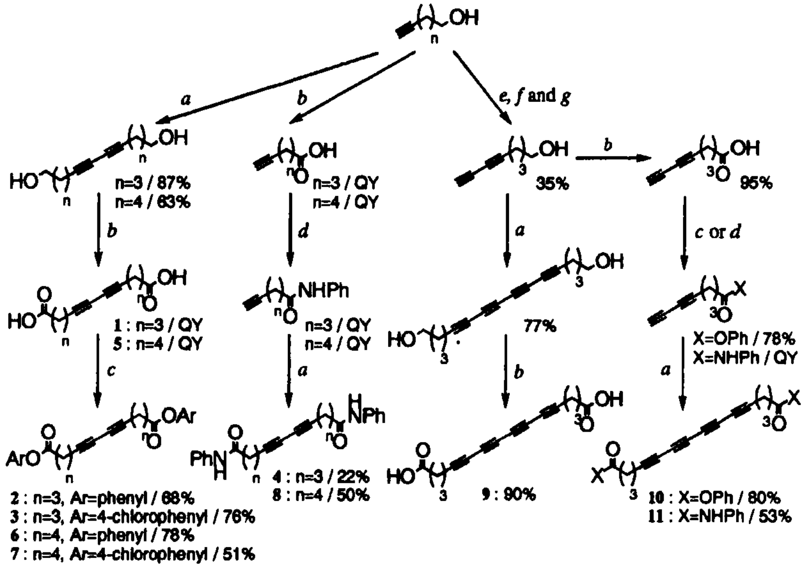

FIGURE 1 Synthetic scheme of monomers. Reagents: (a) O_2, CuCl, TMEDA; (b) CrO_3, H^+; (c) ArOH, DCC; (d) $PhNH_2$, DCC; (e) KOBr; (f) 2-methyl-3-butyn-2-ol, CuCl, 2-aminopropane; (g) KOH. QY indicates quantitative yield.

butadiyne or octatetrayne moiety (**1**[4], **5** and **9**), their diaryl esters (**2**, **3**, **6**, **7** and **10**) and their dianilides (**4**, **8** and **11**) were prepared. All the compounds were characterized by IR and NMR spectra and elemental analysis. Solid-state polymerizability was investigated by UV irradiation. Absorption maximum (λ_{max}) was measured for polymerized samples of the spin-coated films or the KBr-pellets of monomers. Single crystal growth of the monomers was performed by slow evaporation method. Typical solvents used for crystallization were acetone or ethanol for carboxylic acid, acetone or chloroform for ester and THF or DMSO for amide. X-ray crystallographic analysis was carried out using a Nonius CAD-4 system with CuK_α radiation. All calculations were performed using SHELXL-93.

RESULTS AND DISCUSSION

For all the compounds synthesized, solid-state polymerizability was examined by UV irradiation to monomer crystals. The results are summarized in TABLE I together with melting points of the compounds. Both dicarboxylic acids of butadiyne (**1** and **5**) can be polymerized. Though the polymer from **1** shows red color (λ_{max} at 540 nm), the polymer from **5** became reddish blue (λ_{max} at

TABLE I Compounds synthesized and their melting points and solid-state polymerizability

Compound	$XCO(CH_2)_n(C\equiv C)_m(CH_2)_nCOX$			Melting point* /°C	Polymerizability†
	m	n	X		
1	2	3	Hydroxy	123-125	+
2	2	3	Phenoxy	85-87	-
3	2	3	4-Chlorophenoxy	89-91	-
4	2	3	*N*-Phenylamino	ND	+
5	2	4	Hydroxy	156-158	+ (-)
6	2	4	Phenoxy	92-94	-
7	2	4	4-Chlorophenoxy	91-93	-
8	2	4	*N*-Phenylamino	182-184	-
9	4	3	Hydroxy	ND	+
10	4	3	Phenoxy	ND	+
11	4	3	*N*-Phenylamino	ND	+

*ND indicates that melting point was not determined due to polymerization.
†Examined by UV irradiation. +: Polymerizable; -: Stable.

660 nm). For compound **5**, another crystal form was found, which was non-polymerizable. Unexpectedly, all the butadiyne esters studied were obtained as photo-stable compounds. As for the amides of butadiyne, **4** gave red polymer having λ_{max} at 520 nm, while **8** could not be polymerized. Octatetrayne compounds studied so far have been generally more reactive than the corresponding butadiyne derivatives[5], and the compounds in this study are also not exceptions. The octatetrayne monomers **9**, **10** and **11** gave corresponding polymers with λ_{max} at 650 nm, 620 nm and 660 nm, respectively.

Among all monomers, only ester derivatives of butadiyne could be grown large size of single crystals by simple slow evaporation method. For example, compound **3** gave a crystal with dimension up to 11×4×1 mm^2. One of our aim to obtain large single crystals thus being accomplished, the next serious problem to tackle was lack of polymerizability for those derivatives. Therefore, crystallographic analysis of three ester compounds, i.e. **2**, **3** and **6**, was performed to get an insight into the reasons behind their lack. Crystallographic data of **2**, **3** and **6** are tabulated in TABLE II. Bond lengths and angles obtained for these three molecules are quite reasonable, compared with those of the corresponding moieties of the so-far reported compounds. FIGURE 2 displays their crystal structures. Folded molecular structure was found for **2**,

TABLE II Crystallographic data of **2**, **3** and **6**

Compound	**2**	**3**	**6**
Formula	$C_{24}H_{22}O_4$	$C_{24}H_{20}O_4Cl_2$	$C_{26}H_{26}O_4$
FW	374.43	443.32	402.48
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	$P2_1/n$	$P\bar{1}$	$P2_1/c$
a (Å)	6.235(2)	5.7194(7)	11.549(2)
b (Å)	8.955(2)	8.214(1)	7.5648(7)
c (Å)	18.193(3)	24.261(3)	12.820(2)
α (°)	-	98.128(7)	-
β (°)	92.03(2)	92.346(7)	96.795(7)
γ (°)	-	95.107(7)	-
V (Å^3)	1015.1(4)	1122.2(2)	1112.1(3)
Z	2	2	2
D_x (Mg/m^3)	1.225	1.312	1.202
Independent reflections	1973	4166	2091
R	0.0770	0.0805	0.0585

while molecules of **3** and **8** have extended structures. For **2** and **8**, each have only one molecular structure exists in their crystal lattice. However, two molecular structures in crystal lattice were detected for **3**. In spite of minor changes in these compounds, i.e. chlorine substitution at 4-position of phenyl groups from **2** to **3** and one methylene extension of alkylene group between acetylene and carbonyl groups from **2** to **8**, they show no common molecular conformation and crystal structure. This may be mainly due to lack of strong intermolecular interaction in butadiyne esters. In the carboxylic acid derivatives, long macromolecular rods are considered to be formed by

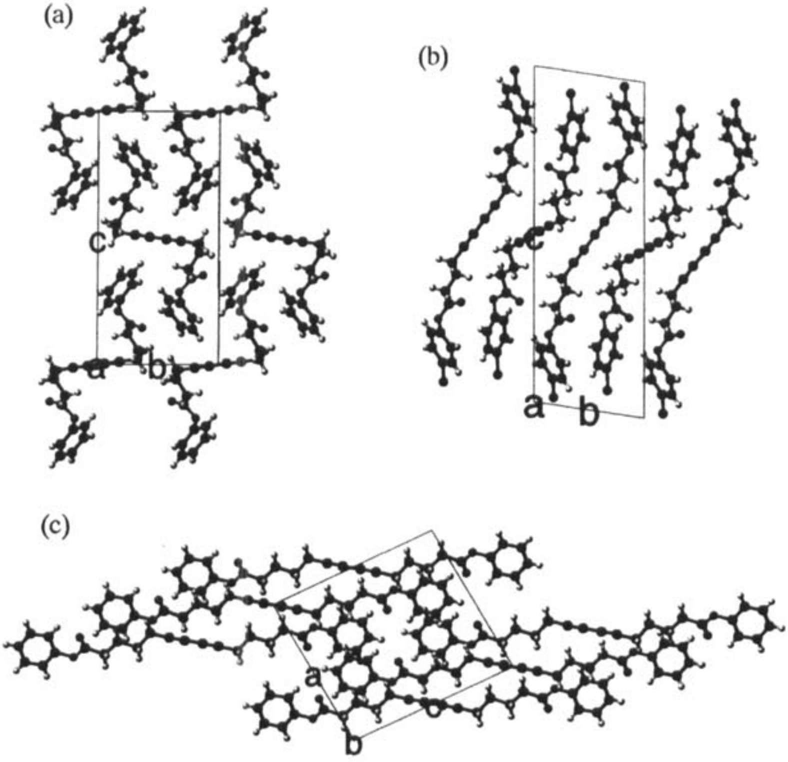

FIGURE 2 Crystal structures of butadiyne esters: (a) View along a-axis of **2**; (b) View along a-axis of **3**; (c) View along b-axis of **6**. Darkness of sphere shows kinds of atoms, and the order from light sphere to dark one is H, O, Cl and C.

intermolecular hydrogen bonding connecting carboxyl groups and these rods are piled up with van der Waals distance of the rod resulting in polymerizable stack. The similar situation also exists for butadiyne derivatives with long alkyl chains to realize polymerizable stack[5]. For amide compounds, intermolecular hydrogen bonding between amide groups is possible leading to polymerizable compounds, e.g. urethane derivatives[6]. For octatetrayne derivatives, rigid rod structure of long conjugated acetylene part seems to attract molecules to themselves resulting in enhanced polymerizability. In fact, octatetrayne ester derivative **10** can be polymerized.

In conclusion, we have synthesized carboxylic acid derivatives of butadiyne and octatetrayne. Octatetrayne derivatives and most of carboxylic acid and amide derivatives of butadiyne show solid-state polymerizability. However, all esters of butadiyne are not polymerizable in spite of success in crystal growth. From the X-ray crystallographic analysis of esters, weak intermolecular interaction seems to cause molecular packing depending on space filling only. Even in case of PTS, slight change in substituents have been reported to vanish polymerizability[6]. Further study to establish crystal engineering for butadiyne compounds, which satisfy high polymerizability along with good crystallization properties, is required.

REFERENCES

[1.] G. Wegner, *Z. Naturforsch*, **24b**, 824 (1969).

[2.] C. Sauteret, J. P. Hermann, R. Frey, F. Pradère, J. Ducuing, R. H. Baughman, and R. R. Chance, *Phys. Rev. Lett.*, **36**, 956 (1976).

[3.] S. Okada, T. Doi, A. Mito, K. Hayamizu, A. Ticktin, H. Matsuda, N. Kikuchi, A. Masaki, N. Minami, K.-H. Haas, and H. Nakanishi, *Nonlinear Opt.*, **8**, 121 (1994).

[4.] H. Nakanishi, H. Matsuda, and M. Kato, *Mater. Res. Soc. Int. Mtg. Adv. Mater.*, **1**, 291 (1989).

[5.] S. Okada, K. Hayamizu, H. Matsuda, A. Masaki, and H. Nakanishi, *Bull. Chem. Soc. Jpn.*, **64**, 857 (1991).

[6.] V. Enkelmann, in *Polydiacetylenes, Adv. Polym. Sci.*, **63**, edited by H.-J. Cantow (Springer-Verlag, Berlin, 1984), p. 91.