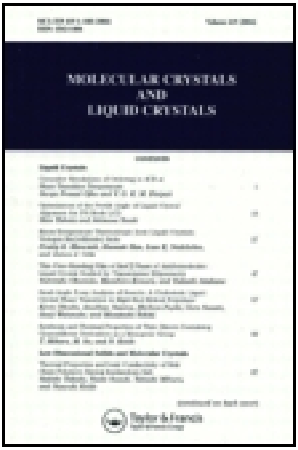

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Molecular and Crystal Engineering of Polydiacetylenes for Enlarged Nonlinear Optical Susceptibility

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MOLECULAR AND CRYSTAL ENGINEERING OF POLYDIACETYLENES FOR ENLARGED NONLINEAR OPTICAL SUSCEPTIBILITY

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Abstract Preparation of new polydiacetylenes by solid-state polymerization and their third-order nonlinear optical susceptibilities are discussed.

INTRODUCTION

Polydiacetylenes (PDAs) are the peculiar conjugated polymers which can often be obtained as large single crystals by the solid-state polymerization of diacetylene monomers. Their large third-order susceptibility $\chi^{(3)}$ was reported as early as in 1976$^{1)}$. Recently the applicability of a soluble PDA to an all-optical switching has been examined and the necessity of enlarged $\chi^{(3)}$ has been pointed out$^{2)}$. Aiming at the enlargement of susceptibility, we have been managing to synthesize new PDAs with narrower band gap, higher π-electron density, sharper excitonic absorption and so on.

PDAS WITH DIRECTLY BOUND AROMATIC SUBSTITUENTS

The first candidates of our study was the PDA with aromatic substituents directly bound to the main chain (APDA) and therefore increased munbers of π-electrons per repeating unit$^{3)}$. We obtained a lot of APDAs on the basis of crystal engineerig technique to have aromatics-substituted diacetylene monomers crystallized in a solid-state polymerizable stack (Figure 1), and demonstrated that absorption maximum and $\chi^{(3)}$ vary with the dihedral angle between main chain and aromatic substituents[4-7]: As seen from Table I[8],

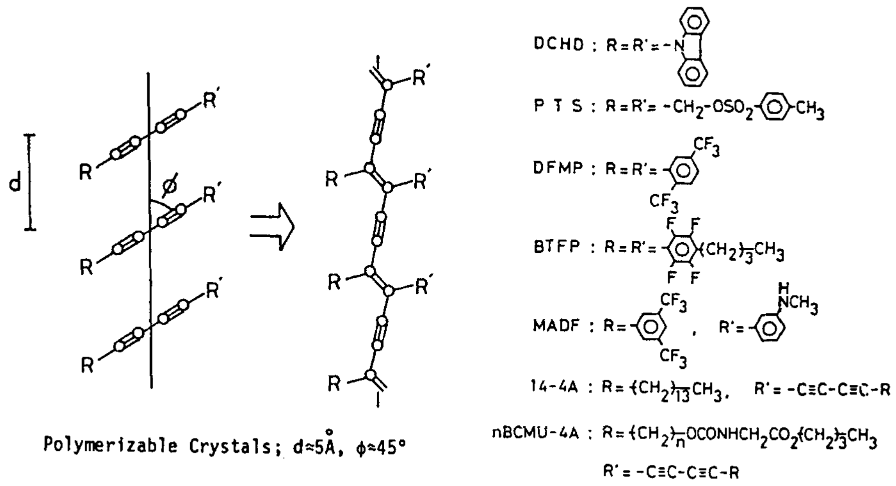

FIGURE 1 Polymerization scheme of diacetylenes and the molecular structures of representative polydiacetylenes.

TABLE I $\chi^{(3)}$ values[a] of PDAs by THG measurements.

PDA[b]	dihedral angle(°)	λ_{max}(nm)	$\chi^{(3)}(10^{-10}$esu) resonant[c]	near resonant[d]
DCHD(S)	---	650	8.0	1.7
PTS(S)	---	610	7.6	1.1
PTS(P)	---	610	1.3	0.53
DFMP(P)	67	560		1.6
BTFP(P)	58	615	7.7	2.5
MADF(P)	44 & 56	640	8.0	4.6
4BCMU-4A(P)	0	700	3.2	
5BCMU-4A(P)	0	700	4.8	

a) These $\chi^{(3)}$ values are for those along the main chain.

b) S and P in the parentheses indicate that the samples were thin film of single crystal and polycrystallites, respectively.

c) Third-hamonic wave was at the absorption maximum of excitonic band.

d) Third-harmonic wave was at 50nm longer wavelength than the excitonic absorption maximum.

poly-MADF with the smallest dihedral angle attains the almost one order of magnitude larger $X^{(3)}$ than poly-PTS at the near-resonant wavelength.

PDAS WITH DIRECTLY BOUND ACETYLENIC MOIETIES

Because of van der Waals interaction, aromatic rings of APDAs can not take coplanar conformation with respect to the main chain. The smallest dihedral angle calculated using a plausible geometry is 44°, and has been already attained by one of the phenyl rings of poly-MADF. However, if the substituent is an acetylenic moieties (AcePDA), perfect π-conjugation between the main chain and the substituent must be expected. Thus, we have synthesized tri-yne and tetra-yne monomers and found their solid-state polymerizabilities[9]. Expectedly the absorption maximum of poly-triyne shifts ca. 40nm to the longer wavelength than that of poly-diyne. The 40 nm shift was exactly the case between poly-triyne and poly-tetrayne. Structures of all these polymers have been identified to be an AcePDA in Figure 2 by solid-state NMR spectroscopy[10]. $X^{(3)}$ *values of these polymers, i.e. 4-BCMU-4A and 5-BCMU-4A in Table I* are greater than poly-PTS but less than poly-BTFP at the resonant wavelength. However, if only the π-electron moiety in volume is compared, the AcePDAs must have larger $X^{(3)}$ than poly-BTFP.

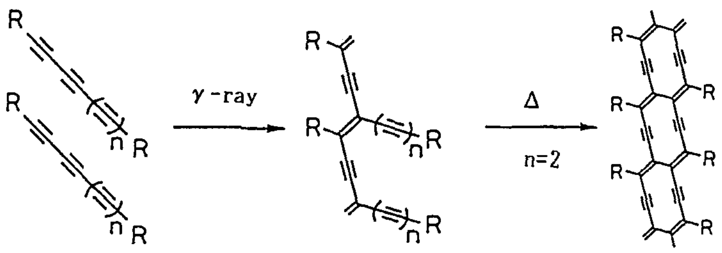

FIGURE 2 Structures of the polymers from di-(n=0), tri-(n=1), and tetra-(n=2) ynes.

DI(POLYDIACETYLENES) FROM TETRA-YNES

AcePDAs from tetra-ynes by γ-ray irradiation have another diacetylene moiety as substituent. Recently we found that the remaining diacetylene moieties can also be polymerized in the solid-state by thermal treatment. The resulting structure is estimated to be a di-polydiacetylene (DiPDA) where the two PDA chains are π-conjugated each other11). In other words, this is a new fused ring polymer of 10π-electron system. The polymers so-far prepared12) are nearly amorphous and show no excitonic absorption. Further study to obtain single crystalline polymer is in progress.

REFERENCES

1. C. Sauteret, J. P. Hermann, R. Frey, F. Pradre, J. Ducuing, R. H. Baughmann, and R. R. Chance, Phys. Rev., 36, 956 (1976).
2. W. Krug, E. Miao, M. Beranek, K. Rochford, R. Zanoni, and G. Stegeman, SPIE Proceedings, 1216, 226 (1990).
3. S. B. Clough, S. Kumar, X. F. Sun, S. Tripathy, H. Matsuda, H. Nakanishi, S. Okada, and M. Kato, in Nonlinear Optics of Organics and Semiconductors, ed. by T. Kobayashi (Springer-Verlarg, Berlin, 1989), p.149.
4. H. Nakanishi, H. Matsuda, S, Okada, and M. Kato, ibid., p.155.
5. H. Matsuda, H. Nakanishi, T. Hosomi, and M. Kato, Macromolecules, 21, 1238 (1988).
6. H. Nakanishi, H. Matsuda, S. Okada, and M. Kato, in Frontiers of Macromolecular Science, ed. by T. Saegusa, T. Higashimura, and A. Abe (Blackwell Scientific Pubs., Oxford, 1989), p.469.
7. S. Okada, M. Ohsugi, A. Masaki, H. Matsuda, S. Takaragi, and H. Nakanishi, Mol. Cryst. Liq. Cryst., 183, 81 (1990).
8. H. Nakanishi, H. Matsuda, and M. Kato, Polym. Adv. Tech., 1, 75 (1990).
9. S. Okada, H. Matsuda, H. Nakanishi, and M. Kato, Mol. Cryst. Liq. Cryst., 189, 57 (1990).
10. S. Okada, H. Matsuda, A. Masaki, H. Nakanishi, and K. Hayamizu, Bull. Chem. Soc. Jpn., 64, 857 (1991).
11. S. Okada, H. Matsuda, A. Masaki, H. Nakanishi, and K. Hayamizu, Chem. Lett., 2213 (1990).
12. S. Okada, H. Matsuda, A. Masaki, S. Minami, H. Nakanishi, K. Hayamizu, and T. Doi, to be presented at the discussion meeting of Polymer Society, Japan (1991).