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MODIFICATION OF OPTICAL PROPERTIES OF POLYDIACETYLENES FOR NON-LINEAR OPTICS

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Abstract In order to improve the third-order nonlinear optical properties of polydiacetylenes (PDAs), various types of PDAs with π-conjugation between the main chain and pendant side groups were synthesized by crystal engineering for solid-state polymerization. It was clearly seen the optical properties of PDAs could be modified by an increased of π-electrons per the repeating units.

INTRODUCTION

Polydiacetylenes (PDAs) are a unique form of conjugated polymers which can be obtained as large single crystals by solid-state polymerization[1]. They are known to have almost the largest third-order non-linear optical susceptibilities ($\chi^{(3)}$) among many conjugated polymers and fast exciton response time[2,3]. Therefore, PDAs have gained a lot of attention as a hopeful candidate for applications of non-linear optics. The results of theoretical predictions based on a simple model of polyene indicate a rapid super linear increase of second-order hyperpolarizability (γ) with increasing the conjugation length[4]. That is to say, the large $\chi^{(3)}$ values of PDAs are clearly due to the conjugated main chain. To achieve higher $\chi^{(3)}$ values needed for real applications, we surmised that PDAs with increased number of π-electrons per repeating unit through the conjugation between the main chain and the substituents might be better candidates. Such a prediction is supported by the theoretical calculation of a PDA having phenyl groups as substituents (ArPDA), where the predicted γ value is up to 60 times larger

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than that of hydrogen substituted PDA[5]. However, most of the well-known PDAs had methylene groups next to the conjugated main chain, because the crystal packing has to be d spacing of about 5 Å and inclination angle ϕ of 45 degree for solid-state polymerization[6]. Therefore, we have managed to synthesized new PDAs with narrow band gap, higher π-electron density, sharper excitonic absorption and so on. In a series of our studies on crystal engineering (crystal structure data ⇒molecular design ⇒ synthesis and polymerizability test ⇒crystal structure analysis ⇒), we have succeeded in the preparation of new PDAs with π-electron donating pools directly bound to the conjugated main chain as shown in Figure 1.

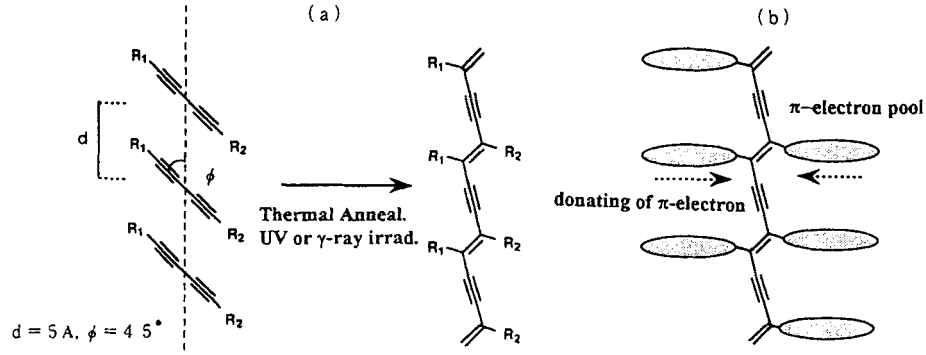

FIGURE 1 Schematic representation of (a) the solid-state polymerization of diacetylene and (b) an idea of PDA structure for enlarging the non-linear optical properties.

PDA WITH AROMATIC SUBSTITUENTS DIRECTLY BOUND TO THE MAIN CHAIN

The first candidates of our study were the PDAs with aromatic substituents directly bound to the main chain (ArPDA). Almost no empirical rules exist for the design of polymerizable crystals. However, we noticed that the characteristic molecular structure of polymerizable known-diacetylene derivatives contains a structural characteristics, i.e., bending in the methylene groups next to diacetylene moiety, hydrogen-bonding between aromatic groups, long alkyl chain with hydrophilic moiety like an amphiphilic diacetylene, and phenyl group having fluorinated substituents. Thus, in order to obtain the ArPDAs, the synthesis was carried out of unsymmetrical diacetylenes which have both an aromatic ring and another group directly bound to diacetylene moiety. For the final case K. Okuhara et. al. found the highly polymerizable diacetylenes: BTFP and DFMP[7]. We could extend the analogous MADF[8] according to the crystal engineering

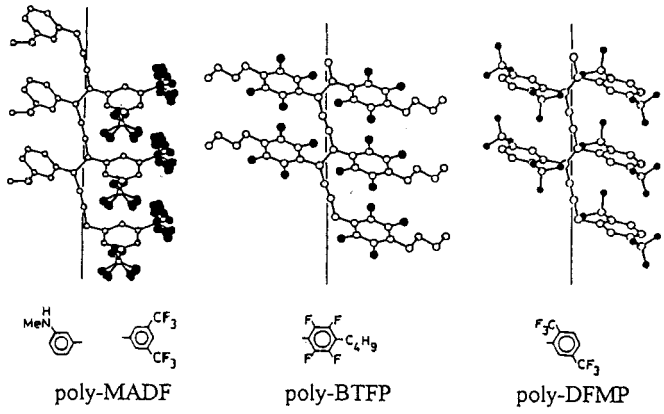

FIGURE 2 Comparison of molecular structures among ArPDAs: O C, ● F, ✪ N. In the x-ray crystallography of poly-MADF, the fluorine atoms were not perfectly fixed.

mentioned above. In Figure 2 the comparison of molecular structures of fluorinated ArPDAs are shown. The dihedral angles between the main chain and phenyl rings are 67, 58, and 44° for DFMP, BTFP, and MADF, respectively. It is clearly demonstrated that the $\chi^{(3)}$ value and the wavelength of excitonic absorption maxima (Figure 3) increase with decreasing the dihedral angle. Because of van der Waals interaction, the aromatic substituents of ArPDAs can not take coplanar conformation with respect to the main chain. The smallest dihedral angle calculated with using a plausible geometry is 44°, and has been already realized by one of the phenyl group of poly-MADF.

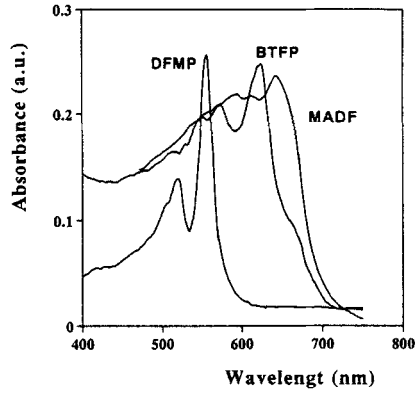

FIGURE 3 Absorption spectra of ArPDAs.

PDA WITH ACETYLENIC GROUPS DIRECTLY BOUND TO THE MAIN CHAIN

From the point of view of the π-conjugation between main chain and the side groups, the PDAs with acetylenenic groups as the substituents are expected to produce the

maximum π-orbital overlap. Thus, we have synthesized tri-ynes and tetra-ynes with long alkyl substituents and carried out their solid-state polymerization. As expected, the absorption maxima of the tri-yne and tetra-yne shift 40nm and 80nm respectively to longer wavelengths compared to the corresponding poly-diyne, respectively. There were several possibilities for the solid-state polymerization manner for such multi-acetylenic compounds, however, the structures were not determined because the crystal size was not enough for x-ray crystallography and not soluble in any usual organic solvent. Using solid-state high resolution ^{13}C-NMR spectroscopy we could obtain the useful information about the structures[9]. By using assignment of ^{13}C-NMR spectra, it has been proved that tri-yne and tetra-yne compounds are polymerized unsymetrically via 1,4-addition to give the PDAs with acetylene side groups (AcPDA) and butadiynl side groups (BPDAs), respectively[10]. In Figure 4, the sharper excitonic absorption was observed in the polymer of 5BCMU-4A compared with that of 4BCMU-4A because more effective hydrogen bond is formed between the urethane groups in adjacent side chains of 5BCMU-4A. The absorption maximum of BPDA shifted to longer wavelength of 680nm than that of ArPDAs.

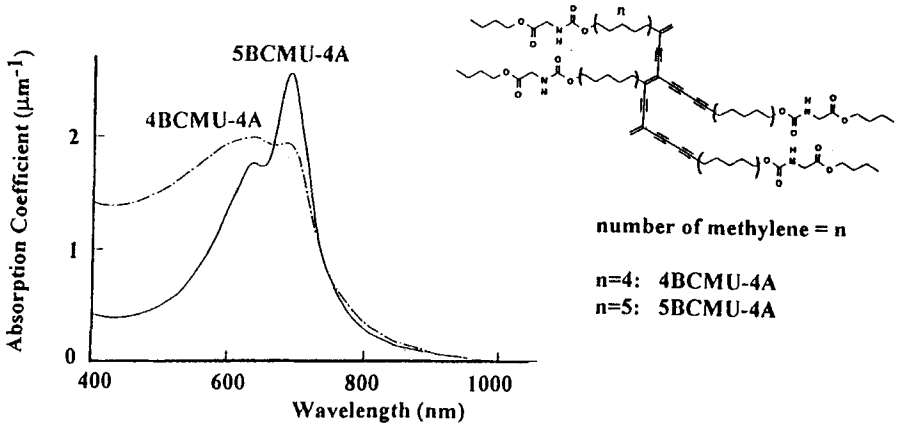

FIGURE 4 Chemical structure and absorption spectra of BPDAs.

PDA WITH HETERO ATOMS DIRECTLY BOUND TO THE MAIN CHAIN

The third candidates were PDAs with hetero atoms directly bound to the main chain. Because the ionization potential of hetero atoms is different from that of carbon atom, there is the expected large effects to modify the electronic structure of the conjugated

main chain. We could synthesized new PDAs with nitrogen or sulfur atoms directly bound to the main chain as substituents. For designing molecular structure of diacetylenes having a hetero atom directly connected to the sp carbon, it is effective that unsymmetrical diacetylenes should be crystallized to the polymerizable stack in the solid-state. We can synthesized a PDA with carbazolyl groups directly bound to the main chain(poly-CPDO) whose the band gap energy has been evaluated to be 1.6eV, suggesting π-electron donating from carbazolyl groups[11,12]. And also, PDA including sulfur atoms directly bound to the main chain has been attended to synthesize. Though a few diacetylene derivatives with sulfur atom attached to sp-carbon have been reported before, they were all oily compounds and fairly unstable in atmosphere at ambient temperature[13,14]. According to the crystal engineering above mentioned, we planned to prepare the diacetylene derivatives as monomers which had one arylthio group and one urethane functionality[15]. For a typical example, the chemical structure and the absorption spectral change in the course of γ-ray induced polymerization are shown in Figure 5. It indicates clearly that the crystal structure of monomer is favorable for solid-state polymerization proceeding by 1,4-addition. The absorption maximum was observed at the longer wavelength of 680nm than that of the conventional PDA.

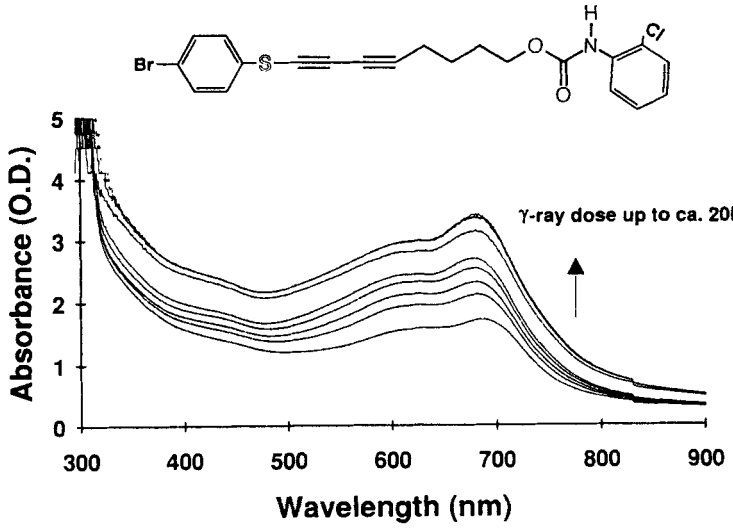

FIGURE 5 Chemical structure and absorption spectral change of diacetylenes with sulfur atom directly bound to the ethynyl group.

CONCLUSION

We have demonstrated that π-electron conjugation exists between the main chan and substituents of PDAs prepared by crystal engineering and the optical properties of not only absorption but also optical non-linearity could be modified.

REFERENCES

1. G.Wegner, Molecular Metals(Plenum Press, New York, 1979), p.209.
2. P.N.Prasad, D.J.Williams, Instroduction to Nonlinear Optical Effects in Molecules and Polymers(John Wiley & Sons, Inc., New York, 1991), p.231.
3. C.Sauteret, J.P.Hermann, R.Frey, F.Pradre, J. Ducuing, R.H.Baughman, R.R. Chance, Phys. Rev., 36, 956 (1976).
4. J.P.Herman, J.Ducuing, J. Appl. Phys., 45, 5100 (1974).
5. B.S.Clough, S.Kumar, X.F.Sun, S.Tripathy, H.Matsuda, H. Nakanishi, S.Okada, M.Kato, Nonlinear Optics of Organics and Semiconductors(Springer-Verlag, Berlin Heidelberg, 1989) p.149.
6. R.H.Baughman, J. Polym. Sci., Polym. Phys. Ed., 12, 1511 (1974)./ V.Enkelmann, Angew. Makromol. Chem., 109/110, 253 (1982).
7. K.Kodaira, K.Okuhara, Presented at the 47th annual meeting of the Chemical Society of Japan, April 1-4 (1983), Kyoto, Japan.
8. S. Okada, M. Ohsugi, A. Masaki, H. Matsuda, S. Takaragi, H. Nakanishi, Mol. Cryst. Liq. Cryst., 183, 81 (1990).
9. S.Okada, K.Hayamizu,H.Matsuda, A.Masaki, H.Nakanishi, Bull. Chem. Soc. Jpn., 64, 857 (1991).
10. S.Okada, H.Matsuda, T.Doi, K.Hayamizu, A.Masaki, N.Minami, H.Nakanishi, Organic Materials for Non-linear Optics III(The Royal Society of Chemistry, London, 1993) p.225
11. H.Matsuda, H.Nakanishi, T.Hosomi, M.Kato, Macromolecules, 21, 1238 (1988).
12. H.Matsuda, H.Nakanishi, N.Minami, M.Kato, Mol. Cryst. Liq. Cryst., 160, 241 (1988).
13. P.J.Stang, V.V.Zhdankin, J.Am. Chem. Soc., 112, 6437 (1990).
14. G.A.Kalabin, A.G.Proidakov, S.I.Radchenko, Zh. Org. Khim., 16, 512 (1980).
15. S.Shimada, H.Matsuda, A.Masaki, S.Okada, H.Nakanishi, Nonliear Optics, in press.