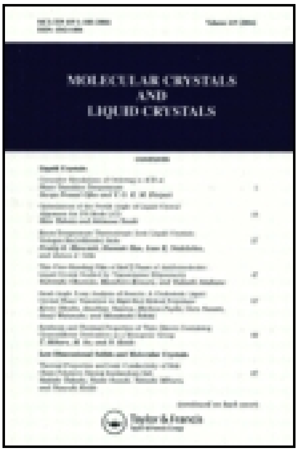

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Polydiacetylenes in Organic-Inorganic Hybrid Systems

Hiroaki Kosuge [a], Shuji Okada [a], Hideotoshi Oikawa [a] & Hachiro Nakanishi [a]

[a] Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Sendai, 980-8577, Japan

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Polydiacetylenes in Organic-Inorganic Hybrid Systems

HIROAKI KOSUGE, SHUJI OKADA, HIDETOSHI OIKAWA
and HACHIRO NAKANISHI

Institute of Multidisciplinary Research for Advanced Materials,
Tohoku University, Sendai 980-8577, Japan

Mono- and di-ammonium chloride salts with butadiyne moieties were synthesized and they were combined with cadmium chloride in thin film forms. Layered perovskite structures were confirmed for spin-coated films of bis(10,12-nonadecadiynylammonium)tetrachlorocadmate **26** and bis(10,12-heptacosadiynylammonium)tetrachlorocadmate **27** and Langmuir-Blodgett films of **27**. After UV irradiation, blue-colored polydiacetylene incorporated in the layered perovskite structure was obtained for the spin-coated films of **27**.

Keywords Polydiacetylene; Layered perovskite; Solid-state polymerization

INTRODUCTION

Polydiacetylene (PDA) is a unique π-conjugated polymer with the single-crystalline feature [1], and its optical and electronic properties have been widely investigated [2]. We have been focusing on modification of PDA in aggregation and molecular levels to enhance third-order nonlinear optical properties [3]. Our research field is also extended into PDA-inorganic hybrid systems. As the aggregates, we prepared PDA nanocrystals [4] and succeeded in their hybridization with metals, e.g., alternately deposited films of PDA nanocrystals and silver fine particles [5], silver-coated PDA nanocrystals [6] and PDA nanocrystals including silver fine particles [7].

Besides such nanocrystal approaches, PDA hybridization with inorganic materials in the molecular level was investigated in the present study. Layered perovskites are known to show interesting optical and electronic properties originated from the inorganic layered structure [8]. In their organic layers, PDA can be introduced, e.g., primary ammonium halide (R-NH_3X) with a butadiyne moiety in R and divalent metal halide (MX_2) are combined in 2:1 ratio and the resulting layered perovskite ([R-$NH_3]_2MX_4$) is polymerized in the solid state. Although such a hybrid system has already been reported [10], little has been known. In order to study the structure, polymerizability and optical properties of this hybrid system, we aimed to prepare them as thin film forms. In this article, we describe preparation of ammonium chloride possessing butadiyne moieties and their combination with cadmium chloride. Fabrication of thin films and their structures and polymerzabilities are also reported.

EXPERIMENTAL

Diammonium salts **16**-**18** and monoammonium salts **24** and **25** with butadiyne moieties were synthesized according to FIGURE 1. Cadmium chloride was combined in 1:1 molar ratio with **16**-**18**, while two equivalents of **24** and **25** were combined with cadmium chloride. Spin-coated films were prepared from 10 mM ethanol solution of **19**-**21**, **26** and **27** on glass substrates. The monolayer of **27** was prepared on pure water by spreading its 0.5 mM solution of chloroform-DMF (9:1). It was transferred on to hydrophilic quartz substrates at 30 mN/m by the Langmuir-Blodgett (LB) method. The lifting and dipping rates were 2 mm/min and 5 mm/min, respectively. In order to initiate the solid-state polymerization, a 4-W UV lamp at 254 nm was irradiated to the films. X-ray diffraction patterns were recorded using a CuK_α radiation source.

RESULTS AND DISCUSSION

The condition of solid-state polymerization of butadiyne moieties has been established that the translation distance (*d*) of two butadiyne

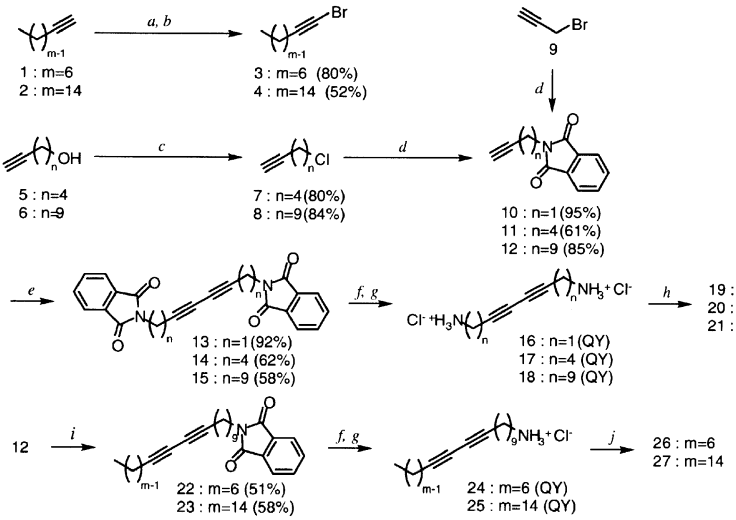

FIGURE 1 Synthetic scheme of ammonium salts with butadiyne moieties. Reagents: (a) BuLi, ether -30°C; (b) Br_2; (c)$SOCl_2$, pyridine 0°C→r.t.; (d) Potassium phthalimide, DMF (120°C for **7** and **8** and r.t. for **9**); (e) O_2, CuCl, TMEDA, THF 60°C; (f) H_2NNH_2•H_2O, THF reflux; (g) HCl; (h) $CdCl_2$ (one equivalent); (i) **3** or **4**, CuCl, *i*$PrNH_2$; (j) $CdCl_2$ (a half equivalent). Yields are shown in parenthesis and QY indicates almost quantitative yield.

moieties in an array and angle between the translation direction and the butadiyne moiety are about 5 Å and about 45°, respectively [11]. When the structure of the layered perovskite is taken into account, MX_2 should be selected from those with the M-X bond length L in octahedral structure of about 2.5 Å. Because ideal d of 5 Å is realized when the distance between the nearest two metal atoms in the inorganic layer of perovskite, i.e., the length of M-X-M, equals to 5 Å. From the three candidates of $CuCl_2$, $MnCl_2$ and $CdCl_2$, whose L values were estimated to be 2.54 Å, 2.64 Å and 2.76 Å, respectively, $CdCl_2$ was selected among them due to good film formability of its mixture with conventional alkylammonium salts.

For spin-coated films, diammonium salts **16-18** did not show either X-ray diffraction patters originated from the layered structure, i.e., a series of (00*l*) peaks, nor solid-state polymerizability. However, the spin-

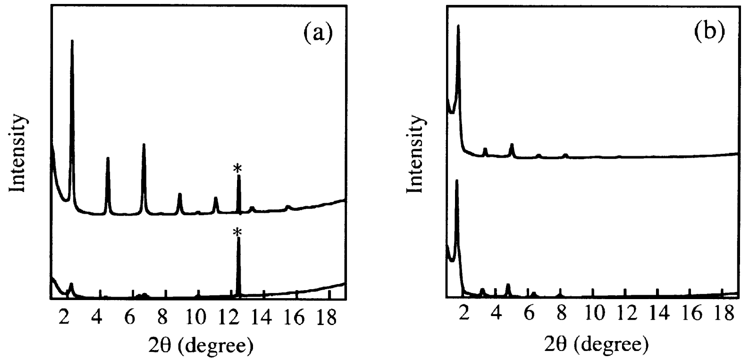

FIGURE 2 X-ray diffraction patterns of spin-coated films of **26** (a) and **27** (b). In each figure, upper and lower patterns are for before and after UV irradiation, respectively. Asterisks in (a) indicate peaks from $CdCl_2$.

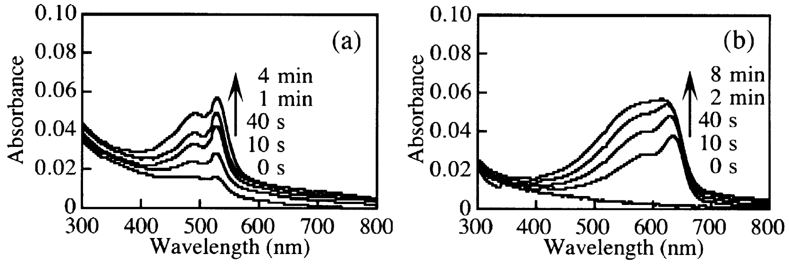

FIGURE 3 UV and visible absorption changes for the spin-coated films of **26** (a) and **27** (b) depending on UV irradiation time.

coated films of monoammonium salts **26** and **27** were found to have layered structures with spacing of 3.92 nm and 5.25 nm, respectively. After UV irradiation, the spacing of both compounds slightly increased to 3.94 nm and 5.48 nm, respectively. In the course of polymerization, the diffraction peak intensities were maintained for **27**, while those of **26** were weakened as shown in FIGURE 2. This structural difference resulted in color difference of the polymerized films. FIGURE 3 presents absorption change during solid-state polymerization. Less crystalline polymer of **26** has absorption maximum wavelength (λ_{max}) at 528 nm. On the other hand, more crystalline polymer of **26** shows longer λ_{max} at 635 nm, indicating ordered structure in the π-conjugated backbone of PDA.

Since **27** was considered to be amphiphilic, the LB method was also applied for its thin film fabrication [12]. When **25** was spread on $CdCl_2$ aqueous solution expecting to form **27** on the subphase, its Π-A isotherm only showed gas-phase behavior. However, when **27** was directly spread on pure water at 10°C, the Π-A isotherm clearly shows two condensed phases as shown in FIGURE 4 (a). The limiting surface area per molecule are 0.50 nm^2 for around 20 mN/m and 0.40 nm^2 for around 55 mN/m. The efficient deposition on the substrate could be executed under a surface pressure of 30 mN/m, although the deposition ratio was 0.6. The monolayer was transferred as Y-type films, and 11 layers of the LB film showed X-ray diffraction patterns as displayed in FIGURE 4 (b). Since the patterns at lower angles are complicated maybe due to existence of several phases, the spacing of major portion was calculated to be 6.9 nm using 2θ values at higher angles. This value is about 30% longer than that of the spin-coated film. This structural difference caused a disordered structure of the polymerized LB film after UV irradiation, which was confirmed by no X-ray diffraction peaks as shown in FIGURE 4 (c) and color change not to blue but to pale orange.

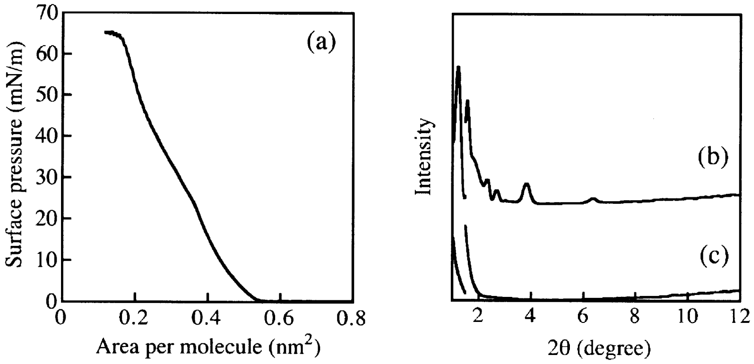

FIGURE 4 Π-A isotherm of **27** (a) and X-ray diffraction patterns of its monomer (b) and polymer (c) LB films. For (b) and (c), the intensities are divided by ten at lower angles than 1.5°.

In conclusion, we combined several ammonium chloride having butadiyne moieties with cadmium chloride and fabrication of their thin films were investigated. Blue-colored PDA incorporated in the layered perovskite structure was obtained for the spin-coated films of **27**.

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References

[1] G. Wegner, Z. Naturforsch. B: Chem. Sci., 24, 824 (1969).

[2] D. Bloor and R. R. Chance ed, Polydiacetylenes, NATO ASI Ser. E, Appl. Sci., 102, Martin Nijhoff Publishers, Dordrecht, The Netherlands (1985).

[3] S. Okada, H. Nakanishi, H. Matsuzawa, H. Katagi, T. Oshikiri, H. Kasai, A. Sarkar, H. Oikawa, R. Rangel-Rojo, T. Fukuda, and H. Matsuda, Proc. SPIE, 3796, 76 (1999); A. Sarkar, S. Okada, H. Matsuzawa, H. Matsuda, and H. Nakanishi, J. Mater. Chem., 10, 819 (2000).

[4] H. Oikawa, T. Oshikiri, H. Kasai, S. Okada, S. K. Tripathy, and H. Nakanishi, Polym. Adv. Technol., 11, 783 (2000).

[5] A. Masuhara, H. Kasai, T. Kato, S. Okada, H. Oikawa, Y. Nozue, S. K. Tripathy, and H. Nakanishi, J. Macromol. Sci.-Pure Appl. Chem. in press.

[6] H. Katagi, H. Kasai, S. Okada, H. Oikawa, H. Matsuda, H. Nakanishi, Polym. Adv. Technol., 11, 778 (2000).

[7] A. Masuhara, H. Kasai, S. Okada, H. Oikawa, M. Terauchi, M. Tanaka, H. Nakanishi, Jpn. J. Appl. Phys. in press.

[8] G. C. Papavassilious, G. A. Mousdis, and I. B. Koutselas, Adv. Mater. Opt. Electron., 9, 265 (1999); Y. Tabuchi, K. Asai, M. Rikukawa, K. Sanui, and K. Ishiguro, J. Phys. Chem. Solids, 61, 837 (2000); D. B. Mitzi, J. Chem. Soc., Dalton Trans., 2001, 1.

[9] M. Era, K. Maeda, and T. Tsutsui, Thin Solid Films, 331, 285 (1998).

[10] P. Day, R. D. Ledsham, Mol. Cryst. Liq. Cryst., 86, 163 (1982); B. Tieke, Mol. Cryst. Liq. Cryst., 93, 119 (1983).

[11] V. Enckelmann, in Polydiacetylenes, Adv. Polym. Sci., 63, ed by H.-J. Cantow, Springer-Verlag, Berlin (1984), p. 91.

[12] M. Era and S. Oka, Thin Solid Films, 376, 232 (2000).