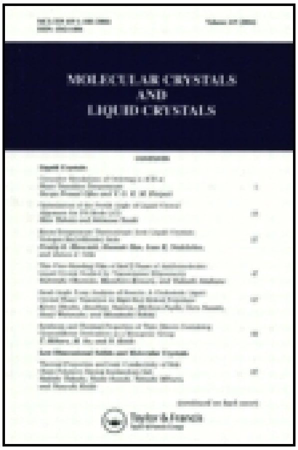

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Synthesis Of Ladder Polymers Composed of Two Polydiacetylenes Linked by Methylene Chains

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SYNTHESIS OF LADDER POLYMERS COMPOSED OF TWO POLYDIACETYLENES LINKED BY METHYLENE CHAINS

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Novel polydiacetylene (PDA) derivatives were prepared from the monomers that have two butadiyne parts linked by a methylene chain and their both ends were modified by butoxycarbonylmethyl urethane groups. Polymerization in solid state was performed by UV or γ-ray irradiation and characteristic excitonic absorption of PDA was observed at around 635 nm except for one compound (574 nm). From ^{13}C NMR spectra measured using CP/MAS and from X-ray diffraction experiment, it was clear that the spacer containing four or more methylene groups is needed to form the ladder polymer composed of two PDAs linked by methylene chains, while eight methylene groups in the spacer are necessary to preserve its polymer crystallinity.

Keywords: polydiacetylene; solid-state polymerization; ladder polymer

INTRODUCTION

Polydiacetylene (PDA)[1] has been extensively investigated as a future candidate for nonlinear optical materials because of its unique properties[2]. It has one-dimensional π-conjugated main chain which predominantly influences the third-order nonlinear optical susceptibilities ($\chi^{(3)}$). For enhancement of $\chi^{(3)}$ value, we have been synthesizing PDAs having π-conjugated substituents bound directly to π-conjugated main chain[3]. In case of dodecahexayne derivatives in which six acetylenes are conjugated, its polymerization was found to proceed in the following two steps: addition polymerization first at 1,4-positions of the dodecahexayne part to give PDA with octatetraynyl groups and then at 9,12-positions to give a ladder polymer with two PDA backbones[4]. However, it was observed that the ladder polymer could not maintain its structure for a long time due to further bond-alternation and reactions of π-conjugated ring. Although some PDA-based ladder polymers have been studied[5,6], no one shows high crystallinity.

In this study, we focused on preparation of PDA-based ladder polymers with improved crystallinity. In order to give flexibility around butadiyne moiety to be polymerized, methylene chains were selected as linking group between butadiyne moieties. If the aim is achieved, enhancement of the density of the PDA parts will be expected to increase $\chi^{(3)}$ value and the interaction between PDA chains may be investigated.

EXPERIMENTAL

Diacetylene monomers were synthesized as shown in Fig. 1. In step A, alkadiynes having acetylene group on both ends were coupled with 6-bromo-5-hexyn-1-ol in presence of Cu(I) catalyst. The reaction was carried out at ambient temperature for several hours and 4OL4A(n) derivatives were prepared. In step B, 4OL4A(n) derivatives were reacted with butyl isocyanatoacetate at 80 °C in presence of pyridine catalyst and 4BCMU4A(n) derivatives were obtained as colorless crystals. Table I shows yield of each step, melting points and the results of elemental analysis of 4BCMU4A(n). Since the crystals polymerized gradually in solid state, these were stored in solution state and were recrystallized just before starting experiments. The monomer thin films were prepared on glass plates by spin-coating method. Thin films and bulk crystals of monomers were polymerized by UV irradiation

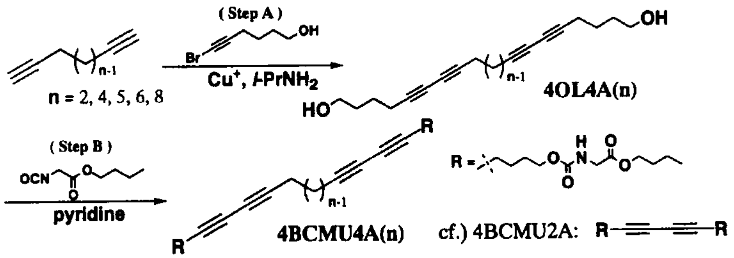

FIGURE 1 Synthetic scheme of 4BCMU4A(n) derivatives and chemical structure of 4BCMU2A.

TABLE I Yield of reactions in Fig. 1 and analytical data for 4BCMU4A(n).

n	Yield / %		M.p. / ℃	Elemental analysis Found (Calcd)
	Step A	Step B		
2	59	77	89.0-90.0	C, 65.45; H, 7.39; N, 4.84% (C, 65.73; H, 7.59; N, 4.79%)
4	40	99	91.5-92.5	C, 66.71; H, 7.80; N, 4.58% (C, 66.64; H, 7.90; N, 4.57%)
5	23	99	82.5-83.5	C, 67.11; H, 7.97; N, 4.43% (C, 67.07; H, 8.04; N, 4.47%)
6	65	84	87.0-88.0	C, 67.77; H, 8.08; N, 4.35% (C, 67.47; H, 8.18; N, 4.37%)
8	30	97	91.0-92.0	C, 68.14; H, 8.35; N, 4.10% (C, 68.23; H, 8.44; N, 4.19%)

for the measurement of visible absorption spectra and by γ-ray irradiation for high-resolution solid-state ^{13}C NMR spectroscopy and powder X-ray diffraction, respectively. As a reference compound, 4BCMU2A[7] in Fig. 1 was also synthesized. Polymer conversion was determined gravimetrically by dissolving the polymerized sample in hot toluene and weighing the insoluble part.

RESULTS AND DISCUSSION

In order to investigate solid-state polymerization behavior of the novel derivatives mentioned above, the visible absorption spectra were measured. Visible absorption spectra of 4BCMU4A(8) and 4BCMU4A(4) are shown in Fig. 2 as representative ones. After polymerization, colorless samples turned blue or red-purple. The absorption maximum wavelength (λ_{max}) of the polymers, which is originated from characteristic excitonic absorption of PDA structure, is summarized in Table II. The λ_{max} of 4BCMU4A(8) polymer shows 10 nm bathochromic shift compared with that of the typical PDA, poly(4BCMU2A). This red-shift tendency was also observed for 4BCMU4A(n) polymers with n=5 and 6. The λ_{max} of 4BCMU4A(2) polymer agrees with that of the poly(4BCMU2A). Spectral shape of these derivatives is similar to that of 4BCMU4A(8). On the other hand, 4BCMU4A(4) polymer

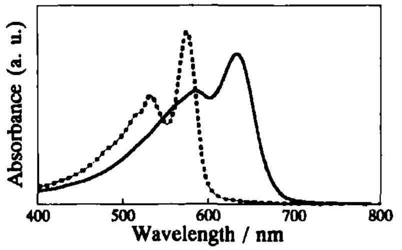

FIGURE 2 Visible absorption spectra of poly[4BCMU4A(8)] film (solid line) and poly[4BCMU4A(4)] film (dot line).

TABLE II Absorption maximum wavelength (λ_{max}) of the polymers from 4BCMU4A(n) monomers

Polymer (n=)	λ_{max} (nm)
8	634
6	637
5	634
4	574
2	625
cf. 4BCMU2A	625

shows the λ_{max} blue-shifted about 50 nm than that of poly(4BCMU2A) while the spectral shape became sharper.

The chemical structure and crystallinity of these polymers were investigated by high-resolution solid-state ^{13}C NMR spectroscopy and powder X-ray diffraction, respectively. In case of 4BCMU4A(8), it was found that both diacetylene units were polymerized by irradiation of γ-ray (0.2 kGy) and the high crystalline ladder polymer was obtained[8]. Compared with 4BCMU4A(8), the polymer conversion of 4BCMU4A(4) (59%) was lower with the same dosage of γ-ray, though upon γ-ray irradiation of 1.0 kGy dosage, 4BCMU4A(4) was polymerized quantitatively. The ^{13}C CP/MAS spectra of 4BCMU4A(4) crystals for monomer and polymer are shown in Fig. 3(a) and 3(b), respectively. In Fig. 3(b), the peak intensity at 79 ppm assigned to the monomer acetylenic carbons decreased markedly, while new peaks at 132, 101, and 39 ppm appeared. These peaks are assigned to the olefinic carbons of PDA backbone, the acetylenic carbons of PDA backbone, and the methylene carbons adjacent to olefinic carbon, respectively. This indicates that polymerization took place not only at one butadiyne part but at both butadiyne parts. Thus, it is confirmed that the ladder polymer composed of two PDAs linked by methylene chains were formed. Interestingly, quantitative polymerization of 4BCMU4A(2) needed less γ-ray irradiation than that of 4BCMU4A(4). From the ^{13}C CP/MAS spectra of 4BCMU4A(2) polymer, about half intensity of monomer acetylenic carbon peaks were observed to be remaining. X-ray diffraction patterns of 4BCMU4A(4) monomer and polymer

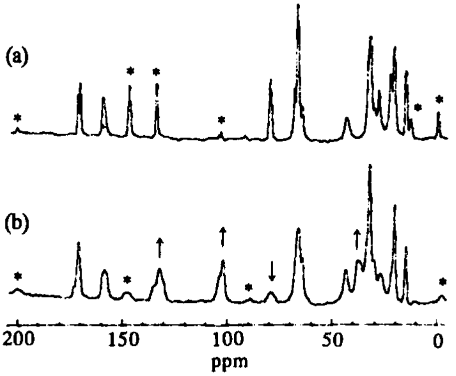

FIGURE 3 ^{13}C CP/MAS spectra of 4BCMU4A(4) monomer (a) and polymer (b). Asterisks indicate spinning side bands.

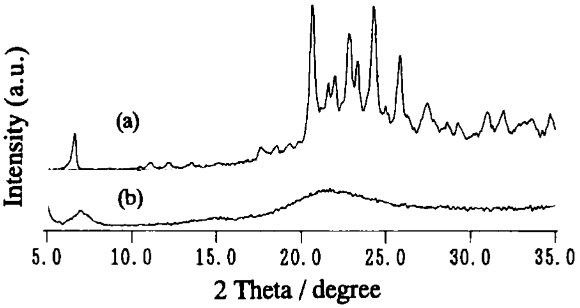

FIGURE 4 X-ray diffraction patterns of 4BCMU4A(4) monomer (a) and polymer (b), obtained using CuK_{α} radiation.

are shown in Fig. 4. The sharp peaks in monomer broadened in polymer, indicating that it was difficult to preserve its crystalline lattice during polymerization. Deterioration of crystallinity during polymerization was also observed in 4BCMU4A(2).

From these results, polymerization behavior of 4BCMU4A(n) with n=8, 4, and 2 is summarized as follows. In case of 4BCMU4A(8), long methylene spacer gives flexibility around butadiyne moieties. Thus, both moieties can be polymerized to give ladder polymer without large deterioration of crystalline lattice. Compared with 4BCMU4A(8), the methylene spacer of 4BCMU4A(4) is shorter, which causes less flexibility around butadiyne moieties resulting in restricted motion of the moiety during polymerization. Thus, much dosage of γ-ray was necessary to polymerize quantitatively and also the polymer crystallinity deteriorated. From the blue-shift of λ_{max} in the visible spectrum of 4BCMU4A(4), conjugated structure of PDA was suggested to have disorders in long range distance, whereas the sharp absorption indicates ordering in short range distance. The methylene spacer of 4BCMU4A(2) is so short that the polymerization stops at first step of polymerization. It is assumed that the conditions of solid-state polymerization to PDA are not satisfied for residual butadiyne part. Octatetrayne derivatives corresponding n=0 is the similar case, in which PDA having butadiynyl substituents are obtained by γ-ray irradiation[3]. Polymerization in 4BCMU4A(n) series is summarized in Fig. 5. It was clear that the spacer consisting of four or more methylene groups is necessary to polymerize both butadiyne moieties in monomer, and the spacer with eight methylene groups realizes preservation of crystallinity even in its polymer.

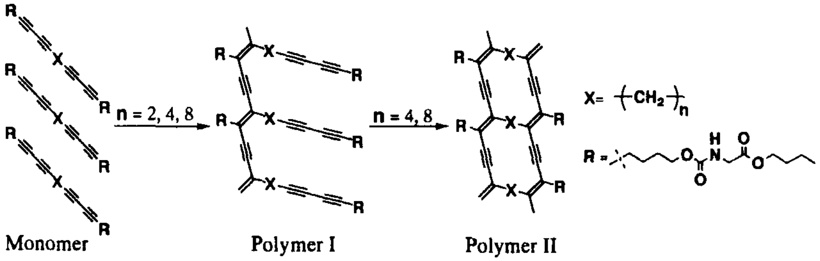

FIGURE 5 Polymerization scheme of 4BCMU4A(n) derivatives.

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. Matsuzawa, S. Okada, H. Matsuda, and H. Nakanishi, *Proc. SPIE*, **2851**, 14 (1996).

[5.] A. Banerjie, J. B. Lando, K. C. Yee, and R. H. Baughman, *J. Polym. Sci., Polym. Phys. Ed.*, **17**, 655 (1979).

[6.] F. R. Ahmed, E. G. Wilson, and G. P. Moss, *Thin Solid Films*, **187**, 141 (1990).

[7.] R. R. Chance, G. N. Patel, and J. D. Witt, *J. Chem. Phys.*, **71**, 206 (1979).

[8.] H. Matsuzawa, S. Okada, H. Matsuda, and H. Nakanishi, to be published in *Chem. Lett.*