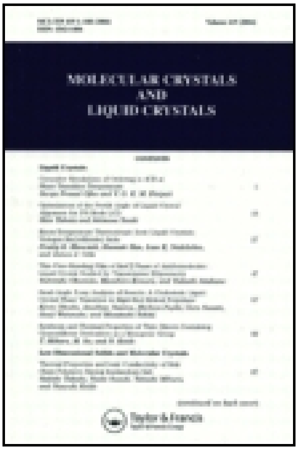

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

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

Solid-State Polymerization of Some Diacetylenic Nylon Salts

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Version of record first published: 04 Oct 2006

To cite this article: Kazuhiro Aoba, Shuji Okada, Satoru Shimada, Hiro Matsuda & Hachiro Nakanishi (1998): Solid-State Polymerization of Some Diacetylenic Nylon Salts, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 315:1, 59-64

To link to this article: http://dx.doi.org/10.1080/10587259808044311

Mol. Cryst. Liq. Cryst., 1998, Vol. 315, pp. 59–64
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From Nylon salts composed of dicarboxylic acid and diamine having butadiyne moiety in one or two of the components, two-dimensionally-crosslinked crystalline polymers were prepared by polymerization of butadiyne part to give polydiacetylene and following condensation of Nylon salt part to form amide group in solid state.

Keywords: polydiacetylene; Nylon salt; solid-state polymerization

INTRODUCTION

In order to increase mechanical strength of polymers, many studies have been performed to align extended polymer backbones with high density. Single-crystalline polydiacetylene (PDA)[1] is one of the ideal systems from the point of view of one-dimensional (1D) alignment of extended polymer chains, for which 1.7 GPa of mechanical strength and 62 GPa of modulus of elasticity along the chain direction have been reported as experimental values[2,3]. However, mechanical strength of those polymers in perpendicular direction to the polymer chain is extremely low because only weak van der Waals force bundles polymer chains in one direction. Taking a cue from the structure of the hardest material diamond, which has three-dimensional covalent bonds among carbons to form a kind of polymer single crystal, multi-dimensional crosslinking of the polymer in single crystal seems one of the best way to achieve mechanically high performance.

Since almost perfect 1D orientation of backbone has been obtained in PDA, crosslinking of the perpendicular direction to the backbone should increase mechanical properties. Though several butadiyne derivatives with crosslinkable groups such as ethynyl group at the end of the substituents were synthesized[4,5], crosslinking only occur at high temperature, at which PDA backbone is no longer ordered[6]. Thus, as an alternative crosslinking method, amide formation from Nylon salts, i.e. condensation between diammonium and dicarboxylate, was performed and two-dimensionally-crosslinked (2D) single crystals was synthesized in the previous study[6]. Vickers' hardness measured for one of 2D polymers was greater than that of pure iron in spite of its lower density. In this study, diacetylene Nylon salts, which would give 2D polymers with high density of crosslinking by shortened methylene chains, were prepared and their solid-state polymerization was investigated.

EXPERIMENTAL

Dicarboxylic acids with butadiyne moiety were prepared by Jones oxidation of corresponding alkadiynediols[6]. Diamino compounds with butadiyne moiety were synthesized in good yield as follows: 3-bromo-1-propyne or 6-chloro-1-hexyne, prepared from 5-hexyn-1-ol and thionyl chloride, was reacted with potassium phthalimide in DMF. The resulting *N*-(ω-ethynyl substituted alkyl)phthalimides were self-coupled under oxygen bubbling in THF using CuCl-TMEDA complex as a catalyst. Finally, obtained butadiynes were reacted with hydrazine monohydrate in ethanol to give 1,6-diamino-2,4-hexadiyne and 1,12-diamino-5,6-dodecadiyne. Conventional alkanedioic acids and α,ω-diaminoalkanes used were commercially available. Nylon salts shown in FIGURE 1 were prepared by mixing dicarboxylic acid and diamine solutions in which equimolar component was solved. Solvent used was ethanol or 1,2-dimethoxyethane, in which Nylon salts were precipitated. Precipitated Nylon salts were collected by suction filtration and were dried *in vacuo*. The procedure to obtain 2D polymer crystals from Nylon salts was as follows: First, PDA backbone was formed by UV or γ-ray irradiation at ambient temperature. UV irradiation was only used to examine polymerizability of salts in solid state. For the samples for structural analysis, γ-ray of about 0.9 kGy

$[\,^{-}O_2C(CH_2)_m{\equiv}{-}{\equiv}(CH_2)_mCO_2^{-}\,]\,[\,^{+}H_3N(CH_2)_nNH_3^{+}\,]$ mDA-n (m=1-3, n=3-12)

$[\,^{-}O_2C(CH_2)_xCO_2^{-}\,]\,[\,^{+}H_3N(CH_2)_y{\equiv}{-}{\equiv}(CH_2)_yNH_3^{+}\,]$ x-yDA (x=6-12, y=1,4)

$[\,^{-}O_2C(CH_2)_3{\equiv}{-}{\equiv}(CH_2)_3CO_2^{-}\,]\,[\,^{+}H_3N(CH_2)_4{\equiv}{-}{\equiv}(CH_2)_4NH_3^{+}\,]$ 3DA-4DA

FIGURE 1 Chemical structures and abbreviations of Nylon salts.

was irradiated for quantitative conversion of monomeric Nylon salts to PDA Nylon salts. Thus obtained 1D polymer crystals were heated at 130-140°C to connect by amide group in the perpendicular direction to the PDA backbone, resulting in 2D polymers. Opposite order of polymerization has already been found to give lower crystallinity than the method mentioned above. Structures of monomers and polymers were characterized by UV-visible-near IR, IR and solid-state ^{13}C NMR (CPMAS) spectra and X-ray diffractions.

RESULTS AND DISCUSSION

TABLE I summarizes polymerizability of Nylon salts by UV irradiation to give PDA. Since compounds reported in the previous study were only 8DA-n (n=4-8) and 3DA-n (n=6-8), 42 salts out of 45 in TABLE I are new compounds.

For mDA-n, precipitation of crystals did not occur in case of small numbers of m and n. Even for crystallized ones, only four salts having rather

TABLE I Crystallization and solid-state polymerizability of Nylon salts*

	mDA-n			x-yDA		
	m=1	m=2	m=3		y=1	y=4
n=3	×	×	×	x=6	●	●
n=4	×	●	×	x=7	●	○
n=5	×	×	×	x=8	○	○
n=6	●	●	●	x=9	○	○
n=7	●	●	●	x=10	○	○
n=8	●	●	●	x=11	○	○
n=9	×	●	●	x=12	○	○
n=10	●	○	○	3DA-4DA		
n=11	×	●	○			
n=12	●	●	○	○		

* ×: Not crystallized; ●: Crystallized but not polymerized by UV irradiation; ○: Crystallized and polymerized by UV irradiation.

long methylene chains, i.e. 2DA-10 and 3DA-n (n=10-12), could be polymerized, while most of 8DA-n salts studied previously are polymerizable. Polymer color was blue for 3DA-10 and red for other three, indicating that 3DA-10 has more ordered structure than others. FIGURE 2 shows ^{13}C NMR spectra of 3DA-10 monomer and its 1D and 2D polymers. Acetylenic ^{13}C peaks at 67.2 and 79.0 ppm in the monomer spectrum almost disappeared after polymerization and new peaks for acetylenic and olefinic carbons of PDA backbone appeared at 107.5 and 131.6 ppm, respectively, for 1D polymer. Since carbonyl ^{13}C peak at 183.1 ppm in the spectrum of 1D polymer shifted to 173.8 ppm in that of 2D polymer, conversion of Nylon salt part to amide group was inferred. This was also confirmed by IR spectra. Though X-ray diffraction patterns deteriorated during polymerization as shown in FIGURE 3, the broad peak around 20° in 2θ of 2D polymer corresponding to about 0.44-nm spacing suggests van der Waals interaction between 2D polymer sheets.

For x-yDA, all the salts prepared were crystallized, though only compounds with longer chains, i.e. x-1DA (x=8-12) and x-4DA (x=7-12), could be polymerized. As typical examples for y=1 and 4, ^{13}C NMR spectra of 12-1DA and 11-4DA were investigated. Monomer acetylenic ^{13}C peaks at 66.2 and 76.5 ppm for 12-1DA and those at 66.5 and 77.5 ppm for 11-4DA disappeared in spectra of 1D polymers. In the spectrum for 1D polymer of 11-4DA, ^{13}C peaks of PDA backbone was clearly observed at 106.8 ppm and 130.5 ppm. However, no peaks appeared in this region for 1D polymer of 12-1DA, as show in FIGURE 4, indicating that polymerization of 12-1DA in butadiyne part proceeds quantitatively without any stereo regularity and PDA structure is not obtained, as was observed for ω-(1,3-butadiynyl) compounds[7]. Since 12-1DA has only one methylene spacer between acetylene and salt parts, butadiyne moiety seems very flexible and polymerization may occur in varieties of manner and directions. This was also confirmed by UV-visible-near IR spectra of 1D polymers. Though characteristic excitonic bands of PDA was not observed for 12-1DA, 11-4DA showed excitonic peaks around 620 and 500 nm. 1D polymer salts from x-yDA could form amide by heating. In both 1D and 2D polymers, crystallinity was less deteriorated for 11-4DA than that of 3DA-10 and 12-1DA.

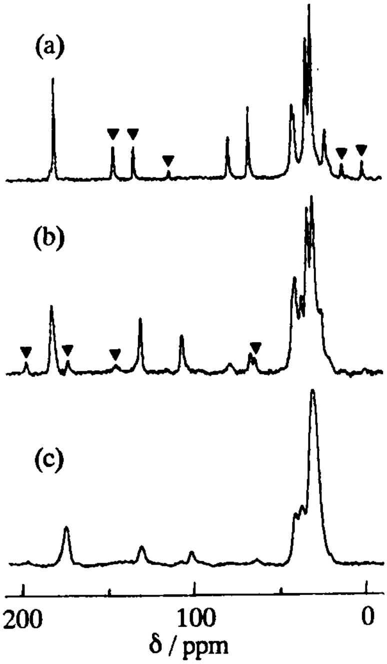

FIGURE 2 Solid-state ^{13}C NMR (CPMAS) spectra of (a) monomer, (b) 1D polymer and (c) 2D polymer for 3DA-10. Marked peaks are due to spinning sidebands.

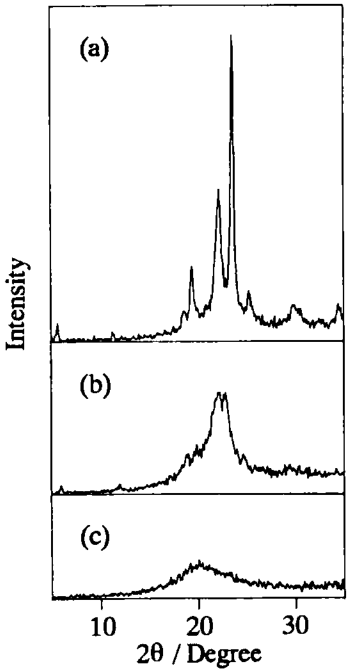

FIGURE 3 Powder X-ray diffraction patterns of (a) monomer, (b) 1D polymer and (c) 2D polymer for 3DA-10, obtained using CuK_α radiation.

Upon UV irradiation, 3DA-4DA turned into red color indicating PDA formation. In ^{13}C NMR spectra, the monomer showed four acetylenic ^{13}C peaks at 65.2, 66.2, 78.7 and 80.2 ppm. Though new peaks originating from PDA backbone carbons appeared at 102 and 133 ppm in the spectrum of 1D polymer, acetylenic carbons except for backbone still remained, as shown in FIGURE 5. From the intensity of these quaternary carbon peaks, about half of butadiyne moieties seemed to be polymerized, i.e. one of two butadiynes in dicarboxylic acid or diamine parts may have been selectively polymerized. Further γ-ray dose did not affected polymerization. Amide formation was possible.

Here, for comparison, we define the crosslinking density

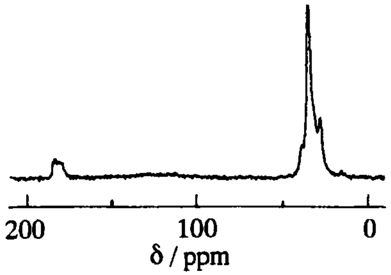

FIGURE 4 Solid-state ^{13}C NMR (CPMAS) spectra of 1D polymer from 12-1DA.

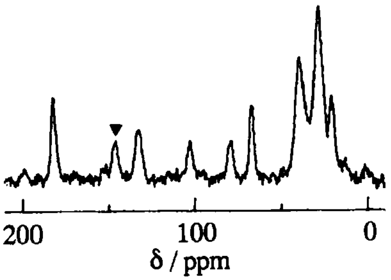

FIGURE 5 Solid-state ^{13}C NMR (CPMAS) spectra of 1D polymer from 3DA-4DA. A marked peak is due to spinning sidebands.

(D_C) of 2D polymer as a number of PDA backbone crossed in a repeating unit along polyamide chain direction divided by a number of atoms in the polyamide chain direction excluding hydrogen and carbonyl oxygen per repeating unit. The maximum D_C so far was 0.036 for 8DA-4. In the present study, we obtained larger D_C values of 0.045 and 0.043 for 2DA-10 and 7-4DA, respectively. Though D_C of 0.056 for 8-1DA is the largest, stereo regular PDA backbone has not been produced. In the case of 3DA-4DA, D_C remained at 0.038 due to only about 50% conversion of butadiyne moiety.

In conclusion, we prepared 2D polymers with higher density of crosslinking than those from 8DA-4 studied previously by shortened methylene chains from Nylon salts having diacetylene moiety.

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