

Diacetylene-Containing Polymers III. Poly(*m,m'*-butadiynylsuccindianilide) and Poly(*m,m'*-butadiynylene sebacodanilide): Novel Materials for Preparation of Transparent Polydiacetylene Containing Films

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(Received July 26, 1993)

ABSTRACT: New bis-acetylenic monomers; succin(*m*-ethynyl)dianilide and sebaco(*m*-ethynyl)dianilide were synthesized and polymerized by oxidative polycoupling to give high molecular weight semicrystalline polymers. These polymers were found to be highly light sensitive and turned blue on UV-irradiation to give transparent blue films with absorption maximum beyond 600 nm. The polymers were found to be rather stable on heating and thermal cross-linking *via* diacetylene groups took place only above 170°C.

KEY WORDS Polydiacetylene / Diacetylenes / Polyamides / Oxidative Polycoupling / 3-Ethynyl Aniline /

The incorporation of diacetylene groups in polymers either in the main or in side chain, is useful for the synthesis of new materials with high modulus or nonlinear optical properties. Especially for the latter applications, polydiacetylenes are considered to be important materials for third order nonlinear optical applications and many works have been reported.¹

Since diacetylenes generally do not form single crystals large enough for application and the Langmuir-Blodgett technique is not adequate to obtain films thick enough for practical use, processing of polydiacetylenes to films is the focus of research in this field. Nakanishi, *et al.*² reported the NLO properties of thin polydiacetylene films obtained by the deposition of sublimed diacetylenes on a quartz and subsequently polymerized by UV-irradiation. One simple method of obtaining polydiacetylene films or sheets of any desired dimension, is to prepare processable polymers

which contain diacetylenic groups and polymerize them. Such systems include the polymers containing diacetylenic groups in the side chain³ and in the main chain. The latter has been reported by some workers. Wegner⁴ reported some polyesters and polyurethanes using 2,4-hexadiyne-1,6-diol and 3,6,13,16-tetraoctadeca-8,10-diyene-1,8-diol as monomers. Keul *et al.*⁵ studied polycarbonates and polyesters containing 2,4-hexadiynyl groups. Liang and Reiser⁶ studied some diacetylene-containing block copolymers, and found that photoreactivity of the copolymers depends on monomer unit reactivity, on the width of diacetylene stacks and on the degree of phase separation in the solid films. Rubner synthesized polyurethane-diacetylene segmented copolymers.⁷ These copolymers were found to be light sensitive and transparent free standing films could be prepared. More recently Kwock *et al.*⁸ reported the synthesis of high molecular weight poly(aromatic diacetylenes) with good

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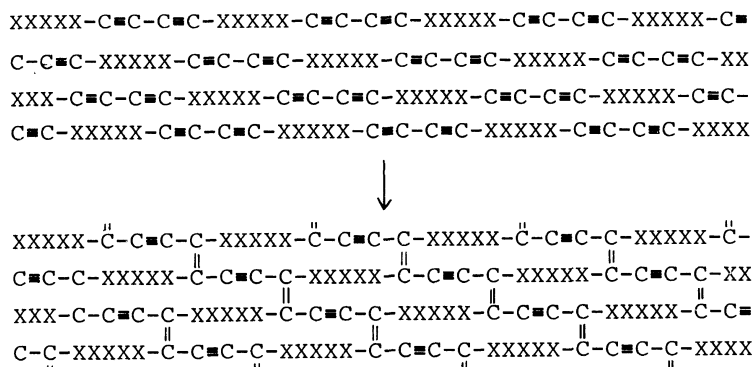


Figure 1. Model scheme of topochemical cross-polymerization of diacetylene groups.

solubility and strength.

The present authors synthesized a new aromatic diacetylene glycol; *m,m'*-butadiynyl-enedibenzyl alcohol and reported previously polyesters and polyurethanes containing this diacetylenic glycol.^{9,10} These polymers were not light sensitive and were highly crystalline. A series of new light sensitive polyesters containing 3,5-octadiynylene groups have been synthesized.¹¹ It is possible to obtain polymers in which diacetylenic groups undergo topochemical polymerization to develop a network structure of polydiacetylene, as shown in Figure 1. However, no report has been found on the formation of thin transparent films which contain aromatic diacetylenic groups.

The present authors synthesized a series of new polyamides containing *m,m'*-butadiynylene dianiline groups, and obtained transparent, flexible films which showed blue coloring on UV irradiation. The synthesis and characterization of these polyamides are reported in this paper.

EXPERIMENTAL

Materials

N-Methylpyrrolidone (N-MP) was distilled over CaH₂ in vacuum. *N,N,N',N'*-tetramethylethylenediamine (TMDA) was distilled before use. Other reagents were used as received (Aldrich).

Monomers Synthesis.

The monomers, succin(*m*-ethynyl)dianilide (5) and sebaco(*m*-ethynyl)dianilide (6) were prepared by reaction of 3-ethynylaniline (4) with succinyl chloride and with sebacyl chloride, respectively.

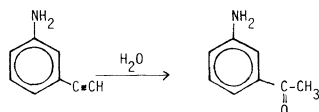
3-Ethynylaniline (5 g, 42.7 mmol) was dissolved in N-MP (15 cm³) and 20 mmol of the acyl chloride was added dropwise at 0°C after the reaction was allowed to proceed at room temperature for 30 min. The reaction mixture was poured into 200 ml of 5% aqueous potassium carbonate solution. The precipitate was filtered off and recrystallized twice from *n*-propanol in the presence of activated carbon. Yields were 73% and 78%, *T*_m = 150 and 211–212°C for monomers 5 and 6, respectively. IR (cm⁻¹) 3250 (C–H), 2120 (C≡CH) and 1640 (C=O, amide) for both compound.

Elemental Analysis. Calcd for C₂₀H₁₆N₂O₂ (compound 5): C, 75.93%; H, 5.10%; N, 8.85%. Found: C, 75.69%; H, 5.30%; N, 8.89%. Calcd for C₂₆H₂₈N₂O₂ (compound 6): C, 77.97%; H, 7.05%; N, 6.99%. Found: C, 77.65%; H, 7.30%; N, 6.90%. 3-Ethynylaniline was prepared by reducing 3-ethynylnitrobenzene (3) with SnCl₂·2H₂O. 3-Ethynylnitrobenzene (3) was prepared in two steps starting from 3-iodonitrobenzene (1) and (trimethylsilyl)acetylene using the method in literature.¹²

3-Ethynylaniline (4)

3-Ethynylnitrobenzene (3) (40 g, 0.27 mol) was dissolved in acetic acid (200 cm³) and the solution was added dropwise to a solution of SnCl₂·2H₂O (240 g, 1.1 mol) in mixture of water (200 cm³) and conc. HCl (200 cm³) keeping the temperature below 35°C. The reaction was allowed to proceed for 24 h at room temperature followed by the addition of potassium carbonate until pH = 10. The reaction mixture was extracted with benzene. After drying with MgSO₄ the solvent was removed in vacuum and the crude product a yellow oil, was used in the next step without purification. Yield 90%. IR (cm⁻¹) 3250 (C—H), 3300 (N—H), 2120 (C≡C).

The reduction of 3-ethynylnitrobenzene into 3-ethynylaniline with SnCl₂·2H₂O readily proceeds at room temperature. However, when the temperature was kept above 50–60°C the main product of the reaction was 3-aminoacetophenone (this was confirmed by its melting point and IR-spectra).



Hydration of the C≡C triple bond takes place during the reduction: When heated at 70°C under the reducing conditions 3-ethynylaniline, was completely converted to 3-aminoacetophenone within 20 min.

Polymerization

Oxidative polycondensation of bis-acetylenic monomers 5 and 6 to obtain poly(*m,m'*-butadiynilenesuccinidianilide) and poly(*m,m'*-butadiynylene sebacodanilide), respectively, was carried out as follows: 5 mmol of the monomer were dissolved in 10 cm³ of N-MP. To the solution CuCl (0.05 g) and TMDA (0.1 cm³) were added and the reaction was allowed to proceed for 24 h at 35°C under oxygen flow. The resulting viscous solution was poured into 5% aqueous solution of am-

monia and fibrous material was precipitated. It was filtered off, repeatedly washed with water and acetone and dried in vacuum for 72 h at room temperature. The yields were 99% for both polymers. Polymers 7 and 8 had η_{inh} of 0.8 and 1.2 dl g⁻¹ respectively. IR (cm⁻¹) 2250 and 2150 (C≡C—C≡C), 1640 (C=O, amide) for both polymers.

Elemental Analysis. Calcd for (C₂₀H₁₄N₂O₂)_n (polymer 7); C, 76.42%, H, 4.49%; N, 8.91%. Found: C, 75.76%; H, 4.63%; N, 8.90%. Calcd for (C₂₆H₂₆N₂O₂)_n (polymer 8); C, 78.36%; H, 6.58%; N, 7.03%. Found: C, 77.11%; H, 6.90%; N, 6.95%.

Measurements and Samples Preparation

Inherent viscosity was measured in 0.5% N-MP solution at 25°C. DSC and TGA were performed at a heating rate of 20°C min⁻¹ under nitrogen flow with Dupont 2100. IR spectra were taken as KBr disks using a Nicolet 510p FT-IR spectrometer. Polymer films, used for UV and X-ray measurements were prepared as follows: the polymers were dissolved in N-MP at 50°C and 5–8% solutions were spread onto glass or quartz slides and left at 60°C in an oven for 2 h at atmosphere pressure to give transparent and flexible films after removing the support. The solutions were unstable and the polymers precipitated after several days. UV spectra were taken using a UV-260 Shimadzu instrument. X-Ray diffractometry was performed using a Siemens D-500 diffractometer with Cu-K_α radiation of 1.540 Å. Irradiation of the films with UV light was performed with a medium pressure mercury lamp for 30 min.

RESULTS AND DISCUSSION

The synthesis of the monomers and polymers is shown in Figure 2.

The unirradiated polymer films were colorless and had no absorption bands in the visible region. A strong absorption band appeared in the long wave region on UV irradiation

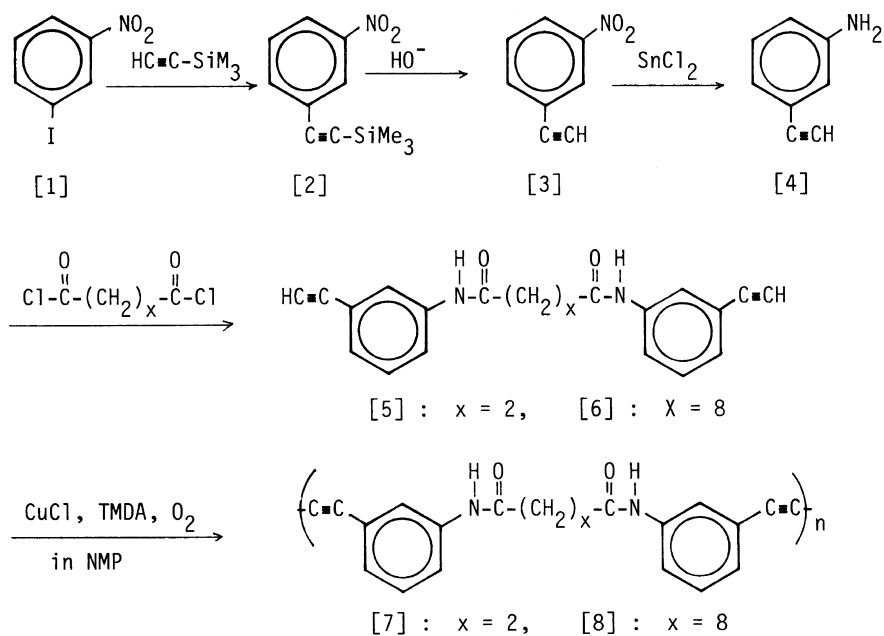


Figure 2. Reaction scheme of monomer and polymer synthesis.

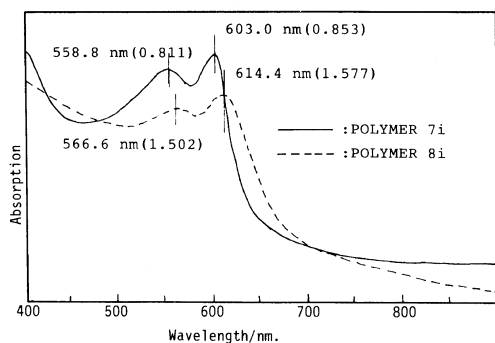


Figure 3. Visible absorption spectra of polymers **7** and **8** irradiated by UV light for 30 min at room temperature (polymers **7i** and **8i**, respectively). Values in brackets indicate optical densities.

characteristic of polydiacetylene structure and the films were deep blue. UV-visible spectra of irradiated films of the polymers **7** and **8** (polymers **7i** and **8i**, respectively) and shown in Figure 3. The long wave absorption maximum was located beyond 600 nm for both irradiated polymers indicating a high degree of conjugation. The reason for the long wave maximum location might be the poly-

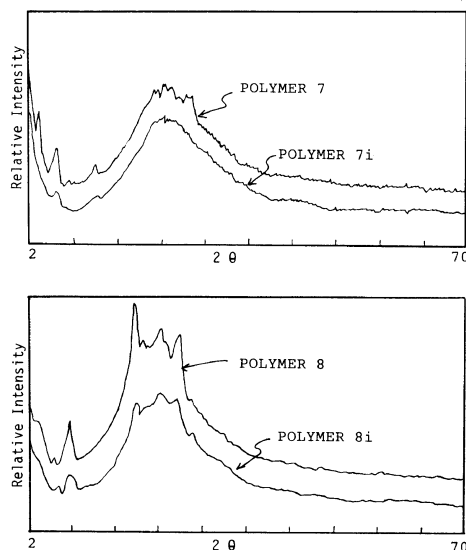


Figure 4. X-ray diffraction patterns of polymers **7**, **8**, **7i**, and **8i**.

diacetylene chain conjugation with aromatic moieties that expands the whole conjugation system. Figure 4 presents X-ray diffractograms taken for polymer films before and after ir-

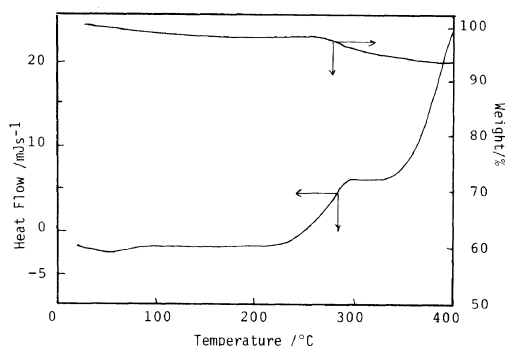


Figure 5. Thermal analysis (TGA and DSC) of polymer 7.

radiation. Polymer **8** film was more crystalline than polymer **7**. This is because polymer **8** had longer spacer chain than polymer **7** which makes crystallization easier. As shown in Figure 4 the polymer films became more amorphous during the crosspolymerization of diacetylenic groups because molecular movement during the crosslinking distorted polymer chain packing.

To study the thermal behavior of the polymers DSC and TGA were carried out. DSC and TGA of the polymer **7** are shown in Figure 5. TGA curves show that the polymers lost about 3–5% their weight below 175°C, but not below 270°C. So the initial weight loss may be attributed to evaporation of water and solvent trace because polyamides strongly kept water as well as traces of solvents used for film preparation. On the other hand DSC showed an exothermic peak starting at 250°C. Taking into account that the weight loss in this region is modest, we assigned this exotherm to thermal crosslinking of diacetylene groups.

Third order nonlinear optical susceptibility ($\chi^{(3)}$) of the polymer films was in the range of 10^{-9} – 10^{-10} esu, depending on preparation techniques using the picosecond laser consisting of a mode locked Quantel Nd: YAG laser

with frequency doubled to 532 nm.

In conclusion, we synthesized new acetylene terminated amides and polymerized them by oxidative polycoupling to give high molecular weight semicrystalline polymers. The polymers were light sensitive and turned blue on UV-irradiation to give transparent colored films. The polymers were rather stable on heating and thermal crosslinking *via* diacetylene groups took place at elevated temperature.

Acknowledgement. The authors acknowledge the financial support of CONACYT for this work under contract No 054E. Thanks are also due to Carmen Vazquez and L. Baños for their assistance in thermal analysis and X-ray diffractometry, respectively.

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