Diacetylene-Containing Polymers V. Synthesis and Characterization of High Molecular Weight Diacetylene Containing Thermoplastic Polyesters: Poly(octa-3,5-diynylene succinate), Poly(octa-3,5-diynylene adipate), and Poly(octa-3,5-diynylene sebacate)

Sergei FOMIN, Ricardo NEYRA, and Takeshi OGAWA*

*Instituto de Investigaciones en Materiales,
Universidad Nacional Autonoma de Mexico,
Apartado Postal 70-360, Coyoacan,
Mexico DF, 04510 Mexico*

(Received December 9, 1993)

ABSTRACT: New diacetylene-containing polymers: poly(octa-3,5-diynylene succinate), poly(octa-3,5-diynylene adipate, and poly(octa-3,5-diynylene sebacate) were synthesized by oxidative polycoupling of the corresponding bis-acetylenes to give high molecular weight thermoplastic film and fiber forming polymers. The polymers were thermo- and photosensitive and underwent topochemical cross-polymerization either on irradiation or heating in crystalline state to give polydiacetylene network. They can be stretched at room temperature to give strong, transparent anisotropic photosensitive materials.

KEY WORDS Polydiacetylene / Diacetylene / Polyester / Oxidative Coupling /

Polydiacetylenes have potential application in nonlinear optics because of their conjugated en-yne with great variety of substituents. However, they are materials with difficulty in processing to thin films. Diacetylenes usually do not give single crystals large enough for application, except very few examples and if they did quite often they do not undergo topochemical polymerization. The Langmuir-Blodgett technique is not so easy to obtain films thick enough for application and other techniques such as vapor phase deposition of diacetylene crystals or crystallization from the melt under pressure¹ are interesting but limited to a few particular diacetylenes. The nonlinear optical properties of polydiacetylene single crystals may be superior to those of amorphous polydiacetylenes and diacetylene-containing polymers, but the latter have a significant advantage that their processing into thin films

is simple, and therefore, the current interest is how to improve the optical quality of such films. Some of the films prepared from diacetylene-containing polymers have been proven to possess $\chi^{(3)}$ values of 10^{-9} — 10^{-10} esu.^{2,3}

There are a few studies on polymers which contain diacetylene groups in the main chains. Wegner⁴ reported early in 1970 synthesis of polyesters and polyurethanes consisting of hexa-1,3-diyn units, and they were photosensitive. However, they had low molecular weight and were useless for future study. Keul, *et al.*⁵ also reported polyesters and polycarbonates containing aliphatic diacetylene units, but no interesting properties of those polymers were found. Rubner⁶ reported qualitative studies on visible absorption spectra of polyurethanes containing 5,7-dodecadiyn units, which underwent cross-polymerization thermally or on

* To whom correspondence should be addressed.

γ -irradiation. He used poly(tetramethylene oxide), hexamethylene diisocyanate and 5,7-dodecadiyne-1,12-diol for his polyurethanes. In such systems, the concentrations of diacetylene groups are extremely low and no interesting optical properties will be found.

The present authors previously prepared polymers containing aromatic diacetylene groups. They include polyesters which contain butadiynylene dibenzyl groups⁷ and a series of new diacetylene-containing high molecular weight polyamides which consist of *m,m'*-butadiynylene dianilide units.⁸ These polyamides have η_{inh} greater than 1.0 dl g⁻¹ and can be cast into thin films which turn bluish-purple on UV-irradiation. It was also found previously⁹ that the polyesters prepared from 3-butyn-1-ol and diacid chlorides were photosensitive but the polymers had low molecular weights. By studying polymerization conditions, it was found that diacetylene-containing polyesters having extremely high molecular weight can be obtained by oxidative coupling reaction. These polymers had low melting points and could be drawn to extraordinarily strong fibers and films at room temperature. The synthesis and characterization of these polyesters are reported in this paper.

EXPERIMENTAL

Materials

1,2-Dichlorobenzene (ODCB) was distilled in vacuum. *N,N,N',N'*-tetramethylenediamine (TMDA) was distilled before use. Other reagents were used as received (Aldrich).

Monomer Synthesis

The monomers, di(butyn-3-yl) succinate (**1**), di(butyn-3-yl) adipate (**2**), and di(butyn-3-yl) sebacate (**3**) were prepared by esterification of 3-butyn-1-ol with succinyl chloride, adipoyl chloride and sebacoyl chloride respectively.

Di(butyn-3-yl) Succinate (1)

3-Butyn-1-ol (10 mmol) was dissolved in 40 ml pyridine and succinyl chloride (4.8 mmol) was added dropwise with vigorous stirring at 0–5°C. After 2 h stirring at room temperature the reaction mixture was poured into diluted cold sulfuric acid. The product was extracted with benzene and purified by column chromatography on silica gel with benzene followed by recrystallization from hexane. $T_m = 36^\circ\text{C}$, yield 67%. IR (cm⁻¹): 3280 (CC–H), 2120 (C $\equiv$ CH), and 1740 (C=O).

Di(butyn-3-yl) Adipate (2)

Compound (**2**) was prepared similarly to (**1**). The reaction mixture was poured into diluted cold sulfuric acid, the product precipitated was filtered off and recrystallized from hexane 3 times. $T_m = 42^\circ\text{C}$, yield 78%. IR (cm⁻¹): 3280 (CC–H), 2120 (C $\equiv$ CH), and 1740 (C=O).

Di(butyn-3-yl) Sebacate (3)

Compound (**3**) was prepared similarly to (**2**). $T_m = 62^\circ\text{C}$, yield 71%. IR (cm⁻¹): 3280 (CC–H), 2120 (C $\equiv$ CH), and 1740 (C=O).

Polymer Synthesis

Polymers were prepared by oxidative poly-coupling of monomers 1–3 in the presence of CuCl–TMDA complex in ODCB.

Poly(octa-3,5-diynylene succinate) (4)

2 g of di(butyn-3-yl) succinate (**1**), 0.09 g of CuCl, 1.8 ml of TMDA, and 15 ml of ODCB were heated to 75°C. Oxygen was bubbled through reaction mixture with stirring for 1 h. The green viscous solution was poured into *n*-propanol acidified with HCl and stirred for 5 h. The fibrous precipitate was filtered off, washed with water and *n*-propanol and dried in vacuum at room temperature. Yield was 97%, η_{inh} in 1,1,2,2-tetrachloroethane (TCE) at 25°C was 0.91 dl g⁻¹. IR (cm⁻¹): 2260, 2200, 2150 (C $\equiv$ C–C $\equiv$ C), 1740 (C=O).

Poly(octa-3,5-diynylene adipate) (5)

Compound (**5**) was prepared similarly to (**4**) using 2 g of di(butyn-3-yl) adipate (**2**), 0.06 g of CuCl, and 1.1 ml of TMDA. The reaction was carried out for 45 min. Yield was 99%, η_{inh}

in (TCE) at 25°C was 1.12 dl g⁻¹. IR (cm⁻¹) 2260, 2200, 2150 (C≡C–C≡C), and 1740 (C=O).

Poly(octa-3,5-diynylene sebacate) (6)

Compound (6) was prepared similarly to (5) using 2 g of di(butyn-3-yl) sebacate (3), 0.05 g of CuCl, and 0.8 ml of TMDA. Yield was 99%, η_{inh} in (TCE) at 25°C was 1.26 dl g⁻¹. IR (cm⁻¹) 2260, 2200, 2150 (C≡C–C≡C), and 1740 (C=O).

Elemental analysis data of monomers and polymers are listed in Table I. Monomer and polymer synthesis are shown in Scheme 1.

Cross-polymerization

Thermally induced cross-polymerization in the solid state and melt was carried out at 90 and 180°C, respectively under nitrogen. Irradiation-induced cross-polymerization was carried out with 500 W medium pressure mercury

lamp.

Measurements

DSC and TGA were performed at a heating rate of 20°C min⁻¹ under nitrogen flow with a du Pont 2100. IR-spectra were taken using a Nicolet 510 p FT-IR spectrometer. UV-Spectra were taken using a UV-260 Shimadzu. X-Ray diffractometry was performed using a Siemens D-500 diffractometer with Cu-K α radiation of 1.540 Å. Polymer films used for UV measurements were prepared as follows: the polymers were dissolved in CHCl₃ and the solutions were spread onto glass or quartz slides and left at room temperature for 2 h at atmosphere pressure to give semitransparent flexible films after removing the support.

RESULTS AND DISCUSSION

Polymers 4–6 were white fibrous materials. They were soluble at room temperature in chlorinated aliphatic solvents such as TCE, chloroform and methylene chloride and strong films could be cast either from solutions or the

Table I. Elemental analysis data for monomers 1–3 and polymers 4–6

Compound	Formula	Calculated in %		Found in %	
		C	H	C	H
1	C ₁₂ H ₁₄ O ₄	64.85	6.35	64.49	6.33
2	C ₁₄ H ₁₈ O ₄	67.18	7.25	67.23	7.21
3	C ₁₈ H ₂₆ O ₄	70.56	8.55	70.32	8.55
4	(C ₁₂ H ₁₂ O ₄) _n	65.45	5.49	64.98	5.51
5	(C ₁₄ H ₁₆ O ₄) _n	67.72	6.50	67.32	6.28
6	(C ₁₈ H ₂₄ O ₄) _n	71.02	7.95	70.83	7.71

Monomer synthesis

Polymer synthesis

Scheme 1.

Figure 1. X-Ray diffraction patterns of polymer 4 (1), 5 (2), and 6 (3) after melting and cooling to room temperature.

melts. The polymers were also soluble in hot aromatic hydrocarbons, ODCB, chlorobenzene and in glacial acetic acid, but slowly precipitated from the solutions when cooled to room temperature.

All polymers were highly crystalline as can be seen from the X-ray patterns in Figure 1.

Thermal Properties

DSC curves of the polymers 4–6 are shown in Figure 2. All the polymers had endotherms in the region of 100–140°C, attributed to melting. Polymers 4 and 5 had small endotherms at 110 and 123°C, respectively, before the main endotherms. No melting was observed in these regions so we could ascribe the endotherms to solidstate transitions seen often in diacetylenes.¹⁰ All the polymers had exotherms which started above 200°C due to cross-linking of diacetylene groups in liquid state accompanying by partial decomposition at temperature above 280°C. In TGA analysis of the polymers, weight loss started at 280°C and attained 35% at 400°C. In the range of 130–180°C, the polymer melts were stable enough to process the polymers into strong fibers and films.

UV-Induced Cross-Polymerization

All the polymers were photo sensitive and turned red on UV-irradiation, showing featureless absorption maximum in visible region

Figure 2. DSC curves of polymers 4 (—), 5 (---), and 6 (···) after melting and cooling to room temperature.

indicating the polydiacetylene network formation shown in Scheme 2. Such topochemical cross-polymerization is known for some polymers [4, 5, 6, 8] but not all diacetylene-containing polymers undergo this reaction.⁷ UV-Visible spectra of irradiated polymers are shown in Figure 3.

Thermally Induced Cross-Polymerization

Owing to the presence of diacetylene groups, the polymers can be cross-polymerized topochemically in the solid state on irradiation or thermally.

Thermally induced cross-polymerization in

Figure 3. UV-Visible spectra of polymers 4 (—), 5 (---), and 6 (···), irradiated with a medium pressure mercury lamp for 30 min.

Figure 4. IR-Spectra of polymer 6 before (—), after (---) thermal cross-polymerization in the solid state at 90°C for 96 h and irradiated with medium pressure mercury lamp for 30 min (···).

Scheme 2.

the solid state proceeded relatively slowly. It took several days at 90°C to attain detectable conversion of diacetylene groups as followed by IR-spectra of topochemically thermally cross-polymerized polymers. An example is shown in Fig. 4. Absorption bands characteristic of diacetylene groups at 2260, 2200, and 2150 cm⁻¹ gradually decreased in intensity while new absorption band appeared at 2230 cm⁻¹ associated with a conjugated triple bond of the polydiacetylene structure formed (Scheme 2). At the same time the polymers turned orange on heating and showed an absorption band in the visible region characteristic of polydiacetylene structure formation. All the thermally cross-polymerized polymers had broad absorption in the visible region similar to UV-cross-linked ones indicating of incompletely formed conjugated polydiacetylene network formed.

Thermal cross-linking of polymers 4–6 in the molten state was also studied. When heated at 180°C under a nitrogen atmosphere, the molten polymer solidified within several hours and became dark-brown. IR-spectra of polymer 6 before and after heating for 4 h at 180°C is shown in Figure 5. Polymers 4 and 5 had spectra similar to that of 6. As can be seen from the comparison in Figures 4 and 5, the spectra of solid-state cross-polymerized polymers and those cross-linked in the melt are identical. Absorption bands corresponding to

Figure 5. IR-Spectra of polymer 6 before (—), after (---) heating at 180°C for 4 h.

diacetylene groups at 2260, 2200, and 2150 cm⁻¹ decreased in intensity while new absorption band appeared at 2230 cm⁻¹ associated with a conjugated triple bond of polydiacetylene structure (Scheme 2). Consequently, we may conclude that thermal cross-linking of the polymers 4–6 in the melt and in the solid-state leads to a similar structure of cross-links. However, because of the nontopochemical character of cross-polymerization in the molten state, a less ordered structure will be formed as can be judged from the absence of long-length wave absorption maximum in the visible region. A recent work has shown that the 1,4-polymerization of diacetylene does not always occur exclusively within crystalline organization.¹¹

An irreversible thermochromic transition was observed for both partially UV- and thermally cross-polymerized polymers 4–6 in the solid state. This occurred for all the polymers on heating in the range of 110–120°C, accompanied by color changes from orange to light-yellow. An example of spectral changes is shown in Figure 6. The existence of a wide variety of thermochromic transitions in polydiacetylenes has been well documented on the molecular level.¹² In this case the disappearance of the long wave absorption maximum can be explained by conformational

Figure 6. UV-Visible spectra of polymer 6 irradiated with a medium pressure mercury lamp for 30 min before (—), and after heating at 115°C for 2 min (---).

Figure 7. X-Ray diffraction pattern of the oriented part of polymer 6 film (elongation 150%).

changes of the polymer chains which occur on heating when macromolecules start moving. Movement of polymer chains disrupts conjugation in the polydiacetylene network that bringing about the blue-shift of the absorption maximum.

All the polymers prepared could be stretched at room temperature up to 400%. When stretched, the translucent crystalline films turned transparent. As can be seen from Figure 7, the cold-stretched samples are highly crystalline. According to optical polarizing microscopy data, these samples are optically anisotropic, which implies one-directional crystallites orientation.

In conclusion, we synthesized a series of new high molecular weight diacetylene-containing thermoplastic polyesters by the oxidative photocoupling of aliphatic diacids 3-butynyl diesters. The polyesters were highly crystalline and photosensitive. These and the results of previous work⁸ show that the oxidative coupling reaction of terminal bisacetylenes can be successfully applied for preparation of different types of high molecular weight diacetylene containing polymers, provided that polymerization condition are suitable.

Acknowledgements. This work was supported financially by Grant IN 101793 provided by the Direction General de Asuntos de Personal Academico (DGAPA) of our University. Thanks are also due to Carmen Vazquez and L. Baños for assistance in the thermal analysis and X-ray diffractometry, respectively.

REFERENCES

1. H. Nakanishi, H. Matsuda, S. Okada, and M. Kato, *Polymers for Advanced Technologies*, **1**, 75, (1990).
2. Luping Yu, Mai Chen, and L. Dalton, *J. Polym. Sci., Polym. Chem. Ed., A*, **29**, 127 (1991).
3. T. Ogawa, "POLYMEX-93," Prepr., International Symposium on Polymers, Cancun, Mexico, November 1993, p 71.
4. G. Wegner, *Makromol. Chem.*, **134**, 219 (1970).
5. S. Kuhling, H. Keul, and H. Hocker, *Macromolecules*, **23**, 4192 (1990).
6. M. Rubner, *Macromolecules*, **19**, 2129 (1986).
7. M. Estrada, G. Burillo, and T. Ogawa, *Polymers for Advanced Technologies*, **3**, 419 (1992).
8. S. Fomine, T. Ogawa, *Polym. J.*, **26**, 95 (1994).
9. R. Neyra, C. Chavarin, and T. Ogawa, Abstracts, "Memorias de Division de Polimeros," 28th Congreso mexicana de Quimica Puro y Aplicada, Puerto Vallarta, November 1992, p 60.
10. J. Kaiser, G. Wegner, and E. Fisher, *Isr. J. Chem.*, **10**, 157 (1972).
11. M. A. Schen, K. Kotowski, and J. Cline, *Polymer*, **32**, 1821 (1991).
12. R. Chance, G. Patel, and J. Witt, *J. Chem. Phys.*, **71**, 206 (1979).