Dyes and Pigments 88 (2011) 129–134

Contents lists available at ScienceDirect

Dyes and Pigments

journal homepage: www.elsevier.com/locate/dyepig

The synthesis, characterization and third-order nonlinear optical character of poly(2,5-dipropargyloxybenzoate) containing a polar aromatic diacetylene

Sandra L. Castañon [a], Miriam F. Beristain [a], Alejandra Ortega [a], Gustavo Gómez-Sosa [a], Eduardo Muñoz [b], Ana Laura Perez-Martínez [a], Takeshi Ogawa [a,*], M. Faisal Halim [c], Francis Smith [c], Ardie Walser [c], Roger Dorsinville [c]

[a] Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México, Apartado Postal 70-360, Ciudad Universitaria, México DF 04510, Mexico
[b] Instituto de Física, Universidad Nacional Autónoma de México, Apartado Postal 20-364, Ciudad Universitaria, México DF 01000, Mexico
[c] Electrical Engineering Department, Grove School of Engineering at the City College of New York, 140th St. & Convent Avenue New York, NY 10031, USA

ARTICLE INFO

Article history:
Received 8 January 2010
Received in revised form
18 May 2010
Accepted 20 May 2010
Available online 1 June 2010

Keywords:
Polar aromatic diacetylene
Nonlinear optics
Cross-linking
Z-Scan
Free radicals

ABSTRACT

The glass transition temperature of the novel compound, poly(*2,5*-dipropargyloxybenzoate) containing a polar aromatic diacetylene was 105 °C and differential scanning calorimetry showed two exothermic peaks due to the opening of the hexa-2,4-diynylene-1,6-dioxy group and the aromatic diacetylene group. Two types of free radical were detected in the electron spin resonance spectra of the heated polymer, one formed by cross-linking of the main chain hexa-2,4-diynylene-1,6-dioxy group and another arising from the aromatic chromophore diacetylene. The third-order nonlinear optical susceptibility, $\chi^{(3)}$, of the polymer film determined using the Z-scan technique was $-4.5 \pm 1 \times 10^{-10}$ esu. When the films were irradiated by UV light at 140 °C, they formed micro-cracks due to intense cross-linking.

1. Introduction

Organic materials having nonlinear optical susceptibility have been studied intensively in recent years and several monographs on the subject are available [1]. In the case of third-order nonlinear optical (3-NLO) materials, although highly conjugated polymers such as polydiacetylenes have been considered to be important materials [2], because of their highly crystalline nature it is not easy to obtain films of satisfactory optical quality for photonic device construction. In this context, diacetylene-containing polymers may provide an option since they can readily be prepared as thin films and the polydiacetylene network can be developed in the films when heated or irradiated. The current authors have previously synthesized a series of light-sensitive polyamides containing aromatic diacetylenes that afforded purple films with 3-NLO susceptibility of 10^{-10} esu; however, the films were not quite transparent due to their polycrystalline nature [3,4]. In order to obtain films with adequate optical quality for photonic applications, amorphous polymer are required. In the case of amorphous diacetylene-containing polymers, the conjugated structures obtained are not the same as those of their light-sensitive, semi-crystalline film counterparts.

Other type of polymer that show promise for 3-NLO applications are those that contain discrete conjugated groups, as they are usually amorphous and provide films of excellent optical quality by spin coating or casting. However, there is very little work in this field. The current authors have reported previously the 3-NLO susceptibility of polymers containing fluorescein [5], tolan derivatives [6] as well as a polar azo dye [7]. The polymers were amorphous and furnished thin films of excellent optical quality by spin coating, with 3-NLO susceptibilities of the order of 10^{-10} esu. In this work a novel polymer containing an aromatic polar diacetylene was synthesized and its thermal and chemical properties, as well as its 3-NLO property using the Z-scan technique, were studied.

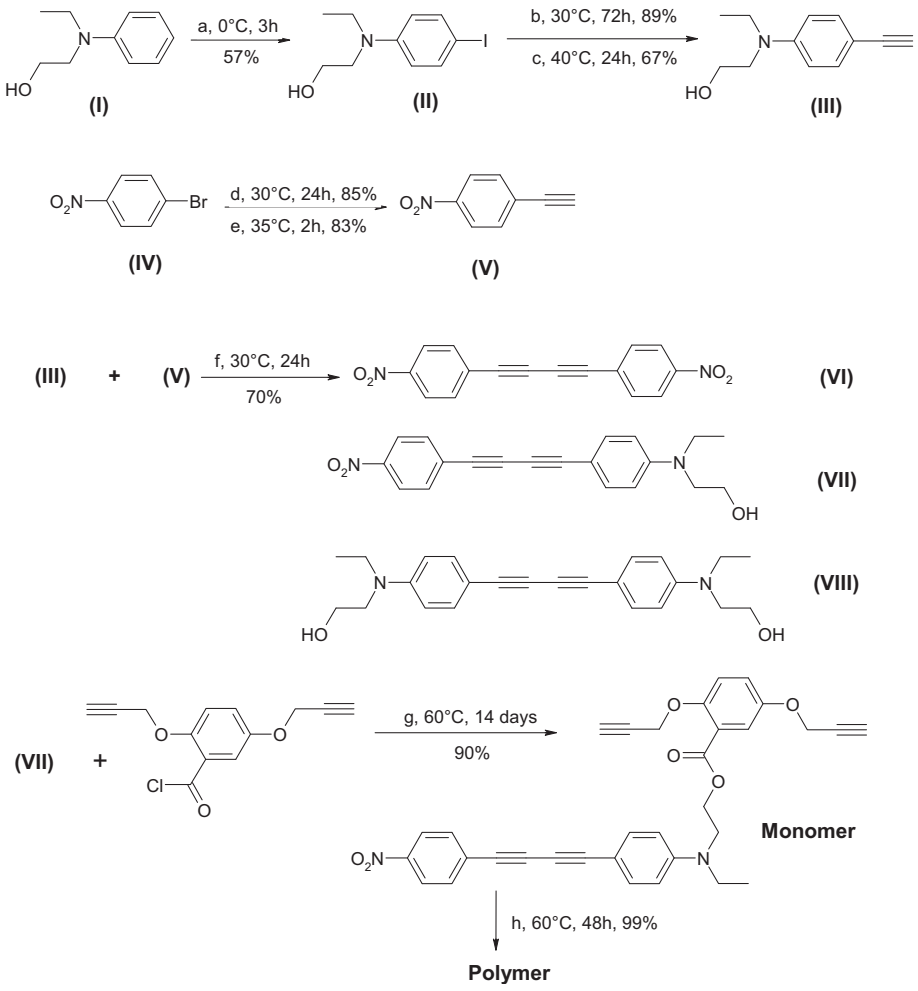
2. Experimental

2.1. Synthesis

The synthetic route to poly(4″-nitrophenylbutadiynyl-4′-*N*-ethylanilinoethyl-2,5-dipropargyloxybenzoate) is shown in Scheme 1. The iodination of ethylanilinoethanol (Aldrich) was carried out by

* Corresponding author. Tel.: +52 55 5622 4728; fax: +52 55 5616 1201.
E-mail address: ogawa@servidor.unam.mx (T. Ogawa).

0143-7208/$ – see front matter © 2010 Elsevier Ltd. All rights reserved.
doi:10.1016/j.dyepig.2010.05.012



Scheme 1. Synthetic route of poly (4″-nitrophenylbutadiynyl-4′-*N*-ethylanilinoethyl-2,5-dipropargyloxybenzoate). Reagents: a) KI, NaOCl, CH_3OH/H_2O, b) TMSA, $Pd(PPh_3)_2Cl_2$, PPh_3, CuI, THF/Triethylamine under N_2 atmosphere, c) $AgNO_3$, CH_3OH/H_2O, d) same as (b), e) NaOH, CH_3OH, f) CuCl, TMEDA, O_2, acetone, g) Triethylamine, $CH_3CH_2Cl_2$, h) CuCl, TMEDA, O_2, *N*,*N*-dimethylformamide.

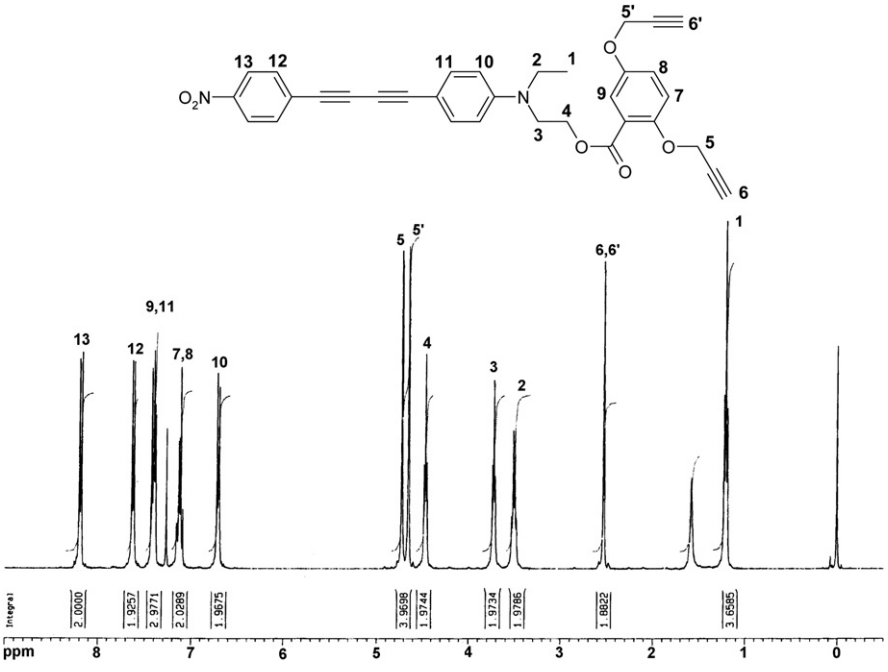


Fig. 1. ^1H NMR spectrum of the monomer in $CDCl_3$.