

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

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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.

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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.

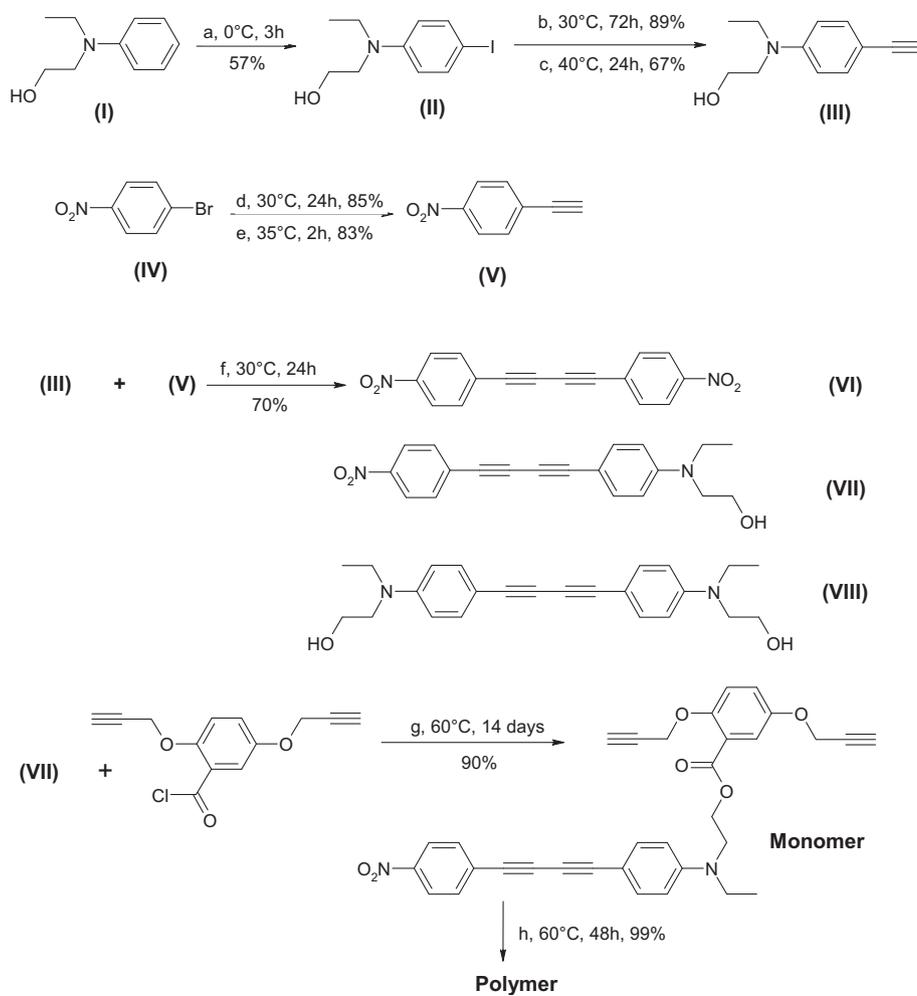
2. Experimental

2.1. Synthesis

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

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Scheme 1. Synthetic route of poly (4'-nitrophenylbutadiynyl-4'-N-ethylaniinoethyl-2,5-dipropargyloxybenzoate). Reagents: a) KI, NaOCl, CH₃OH/H₂O, b) TMSA, Pd(PPh₃)₂Cl₂, PPh₃, CuI, THF/Triethylamine under N₂ atmosphere, c) AgNO₃, CH₃OH/H₂O, d) same as (b), e) NaOH, CH₃OH, f) CuCl, TMEDA, O₂, acetone, g) Triethylamine, CH₃CH₂Cl₂, h) CuCl, TMEDA, O₂, *N,N*-dimethylformamide.

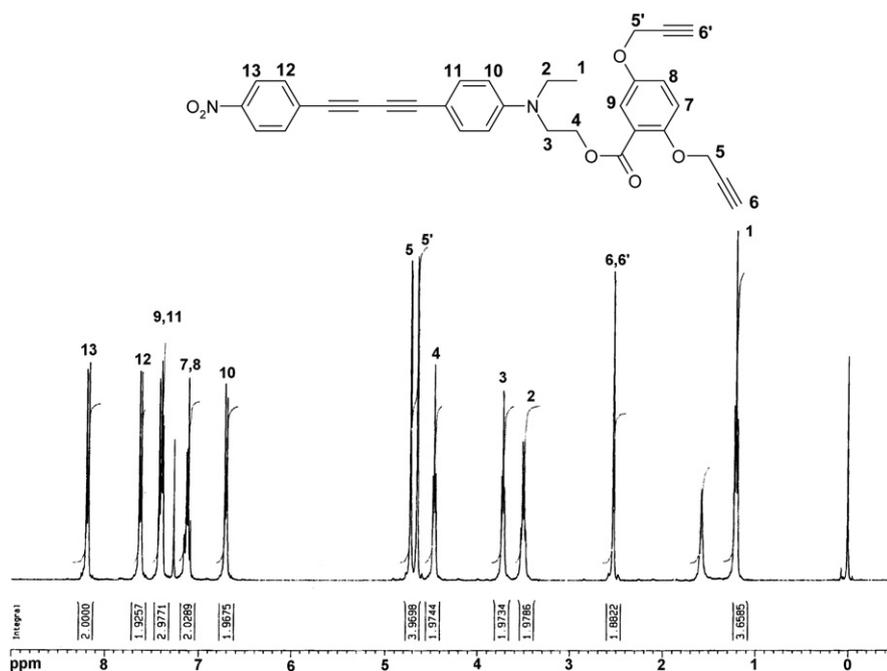


Fig. 1. ¹H NMR spectrum of the monomer in CDCl₃.

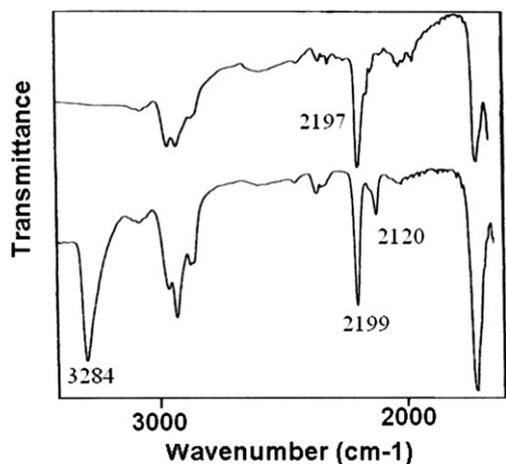
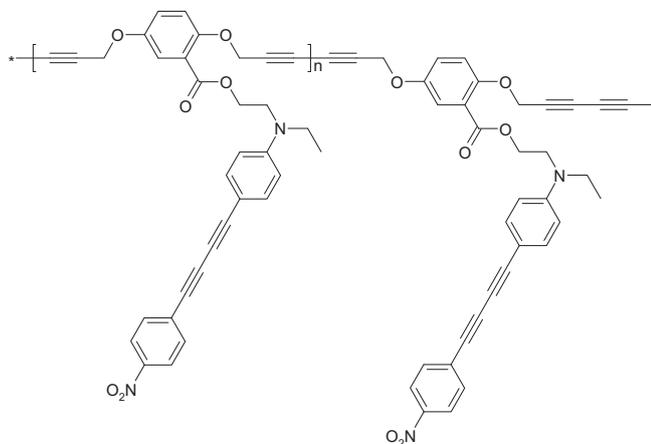


Fig. 2. FT-IR spectrum of the monomer (below) and polymer (above).

a similar method to that of Edgar and Steinmetz [8], and the iodide derivative was then reacted with trimethylsilylacetylene (TMSA) using the Sonogashira reaction to obtain *N*-ethyl-*N*-(2-hydroxyethyl)-4-ethynylaniline (III). 4-Nitroethynylbenzene (V) was prepared also using the Sonogashira reaction from 4-bromonitrobenzene and TMSA (III) and (V) (excess) were coupled by oxidative coupling in acetone using copper (I) chloride and *N,N,N',N'*-tetramethylethylenediamine (TMEDA) (VI) was insoluble and separated from the reaction system; the major product (VII) and the minor product (VIII) were separated by washing using different solvents such as acetone, chloroform, ethanol, etc. Recrystallization of (VII) from acetone gave orange crystals melting at 173 °C (DSC) with a yield of 70% (VII) was then reacted with an excess of 2,5-dipropargyloxybenzoyl chloride in dry dichloroethane using triethylamine as an acid acceptor. Finally the monomer was purified by column chromatography using silica gel column and hexane/ethyl acetate (90/10) as eluent. Yellow orange powder melted at 130 °C (DSC). Elemental analysis calculated for $C_{33}H_{26}N_2O_6$: C, 72.52%; H, 4.79%; N, 5.13%. Found: C, 72.28%; H, 4.35%; N, 5.34%.

2.2. Characterization

1H NMR were taken using Bruker Avance 400 MHz spectrometer, and FT-IR spectra were taken on KBr disk using Thermo



Scheme 2. Polymer structure.

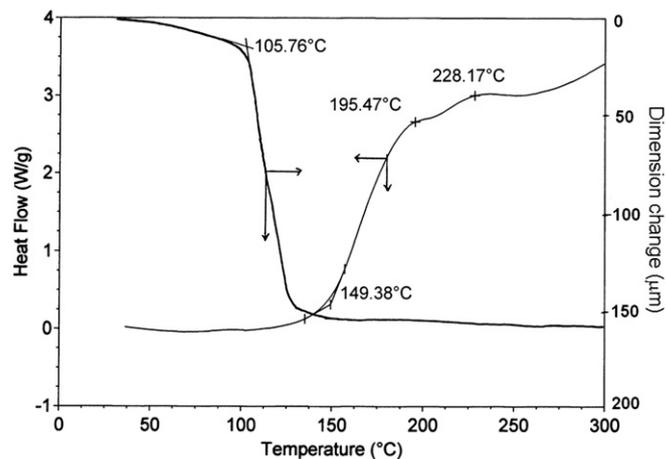


Fig. 3. DSC and TMA of polymer.

Scientific spectrophotometer model Nicolet 6700. Elemental analysis was performed at the Analytical Center of Faculty of Chemistry of our university. The molecular weight of the polymer was determined by GPC using a Waters Model 2695 ALLIANCE at 35 °C with dimethylformamide (DMF) as eluent with polymethylmethacrylate standard. The inherent viscosity was determined in DMF at 25 °C. For differential scanning calorimetry (DSC) and thermo-mechanical analysis (TMA), TA Instruments DSC 2910 and TMA 2940, were used, respectively. ESR spectra were taken using a JEOL ESR spectrometer Model RE3X. The sample was placed in a quartz tube with an inner diameter of 3 mm, supplied by Wilmad LabGlass. The tube was heated in the cavity and the spectra were taken after maintaining for 20 min at the temperature of each measurement. The number of spins (radicals) was calculated with the double numerical integration of the first derivative of the resonance curve from equation [9];

$$A = \int_{H_A}^{H_B} dH \int_{H_A}^H dH' S(H')$$

Where H_A and H_B are the initial and final parts of the resonance curve, and $S(H')$ is the value of the absorption at field H' . The NaCl:Mn²⁺ crystal calibrated by atomic absorption spectroscopy,

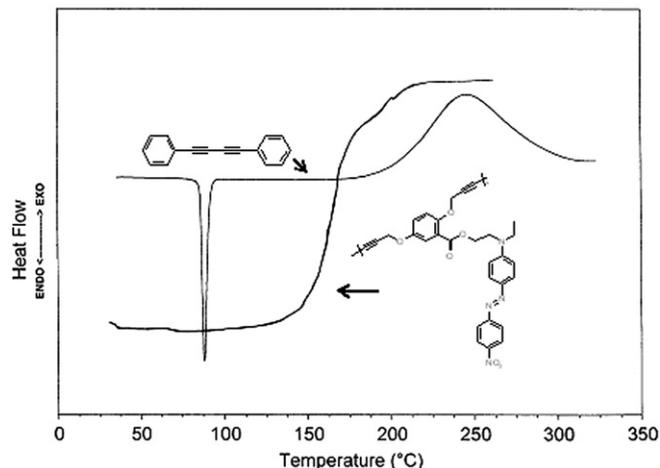


Fig. 4. DSC of diphenylbutadiyne and poly(2,5-dipropargyloxybenzoate) containing Disperse Red 1.

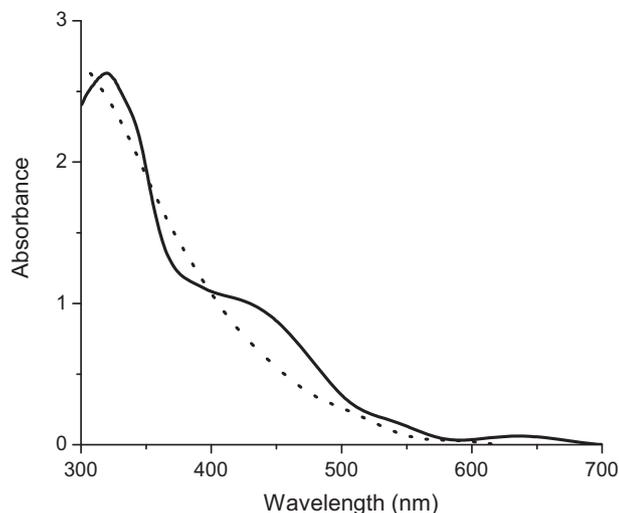


Fig. 5. UV/Vis absorption spectra of films before (solid line) and after (dotted line) heating at 120 °C with UV irradiation.

was employed for calculation of spins taking both spectra under the same conditions.

2.3. Film preparation

Polymer films were prepared by spin coating of dimethylformamide solution on a glass substrate heating at 60 °C. They were dried in a vacuum oven at 80 °C for 120 min. Films thickness was determined by a Sloan Dektak III profilometer. Films with thickness around 1 μm were prepared. UV/Vis spectra were taken using a Varian spectrophotometer Model Cary 400 Cone. The film was also heated at 140 °C in argon and irradiated by a medium pressure mercury lamp (400 W) of Aceglass Co. The refractive index and extinction coefficient of polymer were determined using a Jobin-Yvon Model Uvisel spectroscopic ellipsometer. Three separate measurements were done near the Brewster angle, i.e., from 50 to 70°, with an increment of 10° in each step. The wavelength range of these measurements was 260–830 nm, with an increment of 10 nm per step, controlled by an automatic monochromator. DeltaPsi2 software was used in order to fit ellipsometric experimental data to optical properties. A refractive index of 1.6 was determined for the film, obtained by extrapolation to 1064 nm.

2.4. The Z-scan measurement

The 3-NLO properties of the polymer films were investigated with 25 ps laser pulses, with a repetition rate of 20 Hz, from a Nd:YAG laser at wavelength 1064 nm at 0.1–1 μJ. The Z-scan setup had a lens of focal length 20 cm, and the beam radius was 35 μm. The peak power at focus was about ($I_0 \sim 0.2\text{--}2.5 \text{ GW/cm}^2$). At the excitation

wavelength used in these measurements the linear absorption of the thin films was weak and thermal effects were negligible. The known Z-scan response of a quartz plate and a 1 mm solution of CS₂ were used as references to calibrate the experimental setup. After calibration, the third-order nonlinear coefficient values of the sample could be calculated from the difference between the normalized peak and valley transmittances, following the standard Z-scan method. The difference between the normalized peak and valley transmittance ΔT_{p-v} was measured for the reference and the sample and the third-order nonlinear coefficient was calculated using: $\chi_{\text{Sample}}^{(3)} = \chi_{\text{ref}}^{(3)} ((\Delta T_{p-v} n_o)_{\text{Sample}} L_{\text{Sample}} / (\Delta T_{p-v} n_o)_{\text{ref}} L_{\text{ref}})$.

Where $L_{\text{sample/ref}}$ is the optical length of the sample/reference.

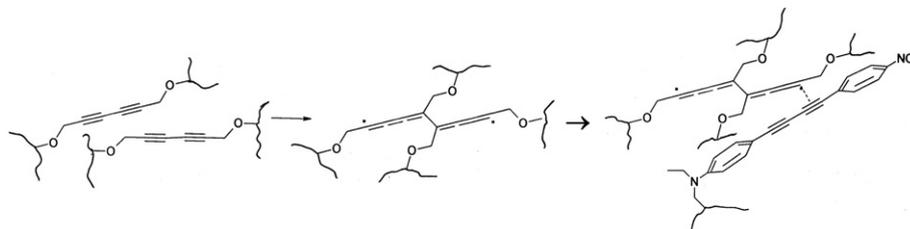
3. Results and discussion

Fig. 1 shows ¹HNMR spectra of the monomer. The peak at 2.54 ppm corresponding to the terminal acetylenic proton disappeared when polymerized indicating that the polymerization took place. The FT-IR spectra shown in Fig. 2 supports the NMR spectra, in which the peaks due to the terminal acetylene $\text{--C}\equiv\text{CH}$ at 3284 cm⁻¹ and the propargyl acetylene $\text{C}\equiv\text{C}$ at 2120 cm⁻¹ disappeared. The newly formed diacetylene (hexa-2,4-diynylene) groups in the polymer appeared in the shoulder of the peak at 2197 cm⁻¹ due to the chromophore diacetylene. The structure of the polymer is shown in Scheme 2. The inherent viscosity at 25 °C in DMF was 0.17 dl/g, and the molecular weight was found to be 8110 (Mn) and 12,560 (Mw).

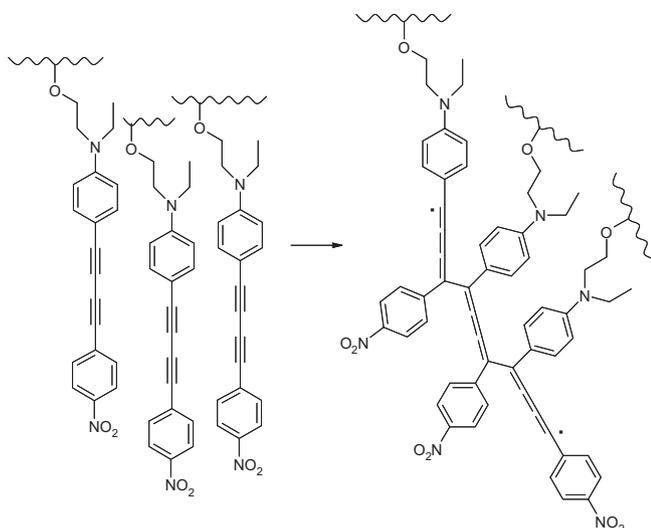
Fig. 3 shows the DSC diagram of the polymer. Its Tg was found to be around 105 °C, which was also observed by thermo-mechanical analysis (TMA) shown in Fig. 3. The exothermic peak which started at around 140 °C is due to the reaction of diacetylene groups of the polymer main chain (hexa-2,4-diynylene). This is commonly observed in most of the polymers whose main chains consist of the hexa-2,4-diynylene-1,6-dioxy group, and a highly cross-linked structure is formed when heated in the solid state at this temperature [10,11]. An example of such polymers is shown in Fig. 4, where the poly(2,5-dipropargyloxybenzoate) containing Disperse Red 1, initiates its exothermic reaction of cross-linking at around 140 °C, while an aromatic diacetylene, diphenylbutadiyne, initiates its reaction at around 180 °C. The overlapping of these two exothermal peaks gives the DSC of the polymer (Fig. 3).

Fig. 5 shows the absorption spectra of the film before (solid line) and after (dotted line) heating at 140 °C in argon with simultaneous UV irradiation. The peak of the diacetylene chromophore disappeared, and the spectrum became similar to that of oligomeric diphenylbutadiynes [12] indicating that various conjugated systems were formed as shown in Schemes 3 and 4. The film became completely insoluble in solvents.

The ESR spectra of the polymer are shown in Fig. 6, and the changes in the number of spins with temperature rise are shown in Fig. 7. The material contained radicals even at room temperature before heating. The spectra were taken several days after the polymer was prepared, and therefore the radicals were thought to



Scheme 3. Cross-linking of hexa-2,4-butadiynylene-1,6-dioxy groups and the stabilization of the resulted radicals with the chromophore diacetylene.



Scheme 4. Oligomerization of aromatic diacetylene chromophore in the polymer.

have been formed during this period. The broad signals starting at room temperature are considered to be due to the radicals formed by the reaction of the main chain hexa-2,4-diynylene groups at room temperature. The room light might have been the cause of the reaction. It is known that amorphous polymers containing aliphatic diacetylenes and hexa-2,4-diynylene-1,6-dioxy groups undergo cross-linking sometimes even at room temperature [13] as shown in Scheme 3. However, such radicals are usually not observed by ESR

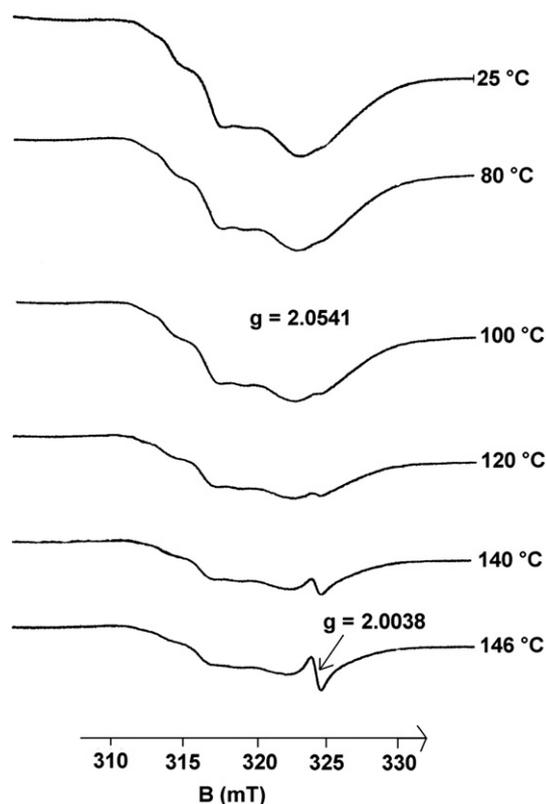


Fig. 6. Effect of heating on the ESR signals of the polymer. Magnetic central field: 320 mT, microwave power: 4 mW, microwave frequency: 9.1054 GHz, modulation amplitude: 0.2 mT, modulation frequency: 100 KHz, time constant: 0.03 s, and scan range: ± 40 mT, gain: 10.0. At each temperature the sample was kept for 20 min before measuring.

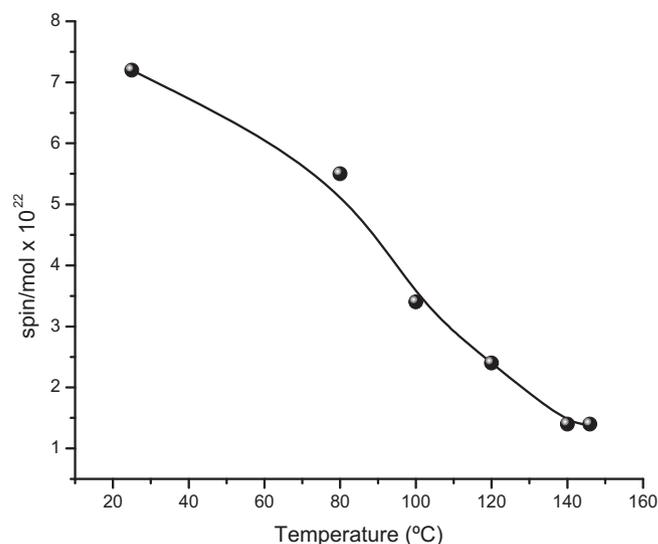


Fig. 7. Decrease in the number of spins with temperature increase observed in the ESR spectra. * based on the molecular weight of monomer.

at room temperature because they are not stable unless they are trapped and immobilized in solid. Therefore, these radicals might be trapped in the solid polymer or stabilized by the aromatic diacetylene groups in the system, and thus they can be observed by ESR spectra. The stabilization of transient radicals by aromatic diacetylenes is known for the free radical polymerization of vinyl monomers in the presence of aromatic diacetylenes. The stabilized propagating radicals show their ESR spectra at polymerization temperatures [14,15]. This means that the radicals in Scheme 3 can be stabilized by the aromatic diacetylene and detected by ESR. Note that the broad signals are those from main chain diacetylenes, and the sharp signal that appears above 100 °C is that of stable oligomeric diradicals of the aromatic diacetylene (Scheme 4). The decrease in the number of radicals with the increase in temperature is probably due to the radical recombination as can be seen in Fig. 7. These disappearing radicals are mainly the aliphatic hexadiynylene groups. The new sharp peak that appears above 100 °C is due to the radicals formed by the reaction between the aromatic diacetylenes shown in Scheme 4, and g value of 2.0038 is that of highly conjugated stable carbon radicals. The ESR signal above 140 °C, is a typical signal of stable diradicals of oligomeric aromatic diacetylenes [12,16,17]. The typical behavior of Z-scan data is shown in Fig. 8. The $\chi^{(3)}$ value of untreated film determined with 1064 nm was found to be $-4.5 \pm 1 \times 10^{-10}$ esu. That of the film irradiated with UV lamp for 30 min at 120 °C, gave a value of $-6.7 \pm 1 \times 10^{-10}$ esu. This nonlinear response was, as expected in a transparent sample, mainly real at the wavelength and intensities investigated, and they are considered to be quite high for common organic conjugated systems compared with those of highly conjugated polymers such as polydiacetylenes and polythiophenes, whose $\chi^{(3)}$ are of the order of 10^{-12} esu [18]. The $\chi^{(3)}$ value of this polymer arises from the discrete conjugated group of the polymer (chromophore diacetylene), whose concentration is high at 58% w/w. The polymer also contains substantial amounts of radicals, and this might increase $\chi^{(3)}$ value. There are some discussions on the effects of open-shell and spins-containing polymers on the 3-NLO properties, and it is said that they enhance 3-NLO properties [19–21]. However, various polymers containing discrete conjugated groups are known to possess $\chi^{(3)}$ values of an order of 10^{-10} esu [5–7]. It was expected that the films irradiated with UV light at 140 °C would have much higher 3-NLO coefficients, because of expansion of conjugation due to the

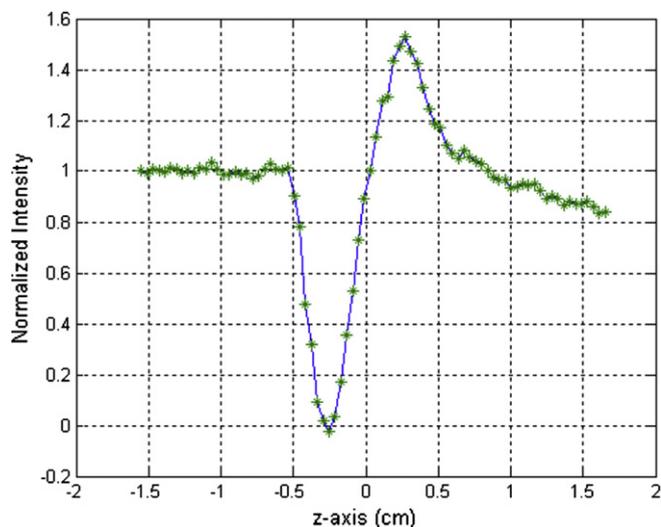


Fig. 8. Closed aperture Z-scan of the polymer heated at 120 °C with UV irradiation.

reaction of diacetylene chromophores as shown in Scheme 4. However, the 3-NLO measurement could not be carried out for the films heated at above 140 °C due to the many micro-cracks formed by the volume contraction of the film caused by the dense cross-linking of the hexa-2,4-diynylene-1,6-dioxy groups of the main chains, which was observed by an optical microscope. For further studies it is necessary to employ non-cross-linkable main chains for this chromophore in order to obtain materials with higher 3-NLO susceptibility.

4. Conclusions

A novel polymer containing polar aromatic diacetylene chromophore was synthesized in order to study its 3-NLO properties. The $\chi^{(3)}$ value of around $-4-7 \times 10^{-10}$ esu is considered to be reasonably high for a polymer containing only small conjugated molecules. The polymer cross-linked even at room temperature through the hexa-2,4-diynylene-1,6-dioxy group of the main chains. The ESR detected radicals formed by the reaction of main chain diacetylenes, are stabilized by the chromophore aromatic diacetylenes. The typical ESR signals of oligomeric diradicals of aromatic diacetylene appeared at above 100 °C.

The cross-linking of main chains via the hexa-2,4-diynylene-1,6-dioxy groups is undesirable because the polymer films shrink on heating above 140 °C causing micro-cracks. Polymers with polar diacetylene chromophores, without hexa-2,4-diynylene-1,6-dioxy groups in the main chain, are being prepared, and their 2-NLO and 3-NLO properties will be reported in future works.

Acknowledgements

This work was supported by CONACYT (Consejo Nacional de Ciencia y Tecnología) under the contract number of 49849-R. Sandra Luz Castañón thanks for her postgraduate scholarship given by CONACYT. Thanks are also due to Miguel Canseco, Salvador Lopez, and Gerardo Cedillo, for their assistance in thermal analysis, GPC and NMR spectroscopy, respectively.

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