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Diacetylene-containing polymers. XI. Synthesis and characterization of poly(hexa-2,4-diynylene-1,6-dioxydibenzoate) and poly(octa-3,5-diynylene-1,8-dicarboxylate) containing *p*-nitroaniline groups

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Summary

Two novel polymers containing *p*-nitroaniline group in the side chain and diacetylene groups in the main chain, were synthesized, and characterized. The polymers gave films of excellent optical quality by spin coating from DMF or chloroform. The one containing benzoate had a T_g of 103°C and its thermal cross-linking through the diacetylene group started at around 160°C. The one containing pentynoate had a T_g of 35°C and its cross-linking started at around 120°C. It was shown that thermosetting resins with functional groups could be obtained by using diacetylene-containing polymers. Although these two polymers have a same polar dye molecule, the second order nonlinear optical property was so different, showing that the main chains are very important for nonlinear optical property. Irradiation of UV light converted the polymer films to completely insoluble thermoset resins.

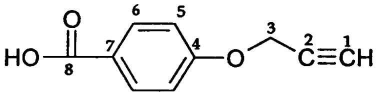
Introduction

Polymers that contain diacetylene groups in the main chains are interesting materials for obtaining novel polymeric materials. For example, halogenation with bromine or chlorine gives polymers with tetrahalogenated butadienyl groups (1), and reaction with hydrogen sulfide gives a thiophene-containing polymer (2). Some of the diacetylene groups in the main chains are light sensitive, and polydiacetylene networks can be developed in the films of such polymers (3). Some of these films develop the blue coloration of polydiacetylene networks, which have third order nonlinear optical susceptibility of an order of 10^{-10} - 10^{-11} esu (4). Another interesting application of diacetylene-containing polymers is thermosetting resins. The diacetylene groups cross-link thermally when heated at temperatures above 150°C, although this temperature varies depending on the type of diacetylene. This thermal cross-linking nature can be applied to obtain thermoset poled polymer films containing dye chromophores for second order nonlinear optical applications. The poling and cross-linking can be carried out simultaneously, and thus the relaxation of the poled chromophore may be avoided. In this work, two novel polymers containing diacetylene groups and *p*-nitroaniline group were synthesized and characterized, and their thermal behaviors were examined. The results are reported in this report.

Experimental

1). Acetylenic monomers:

4-Hydroxybenzoic acid (Aldrich) was dissolved in methanol and required amount of sodium hydroxide was added at room temperature. Then 10% excess of propargyl bromide (Aldrich) was added to the solution, and the mixture was stirred at room temperature, monitoring the reaction by thin layer chromatography. After the reaction the product was added to water, and the system was acidified with hydrochloric acid. The precipitate was filtered, washed with water, and dried in vacuum. It was recrystallized from *n*-butanol. Yield: 70%. Colorless solid with mp. 210-212°C. *IR* (cm^{-1}) KBr, 3270 (≡C-H), 3150-3100 (COO-H), 2970(CH$_2$), 2120(C≡C), 1690(C=O), 1600(C=C$_{arom}$). ^{1}H NMR: (200MHz, DMSO-d$_6$). s(ppm): 3.61 (s. 1H, H^1), 4.87 (s. 2H, H^3), 7.04(d. 2H, J=8.7Hz, H^5), 7.79 (d- 2H, J=8.7Hz, H^6), ^{13}C NMR: s (ppm) = 55.66 (C^3) , 65(C^2), 114.53 (C^5), 123.74 (C^7), 131.24 (C^6), 160.7 (C^4), 166.88(C^8). The signal of C^1 is covered with that of the solvent.



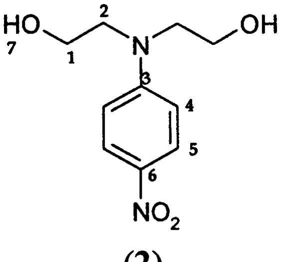
(1)

The acid thus obtained was reacted with thionyl chloride (1.3 mole equivalent to the acid) in dichloromethane at room temperature using a few drops of dimethylformamide as an accelerator to obtain 4-propargyloxybenzoyl chloride. After evaporating the solvent and the excess thionyl chloride under vacuum, a hard brown solid melting at 35°C was obtained, and this was used for the next step without further purification. *IR* (cm^{-1}), 1785 (C1-C=O).

Pentynoyl chloride was obtained by chlorination of pentynoic acid (Farchan) with thionyl chloride, and it was distilled under reduced pressure before use.

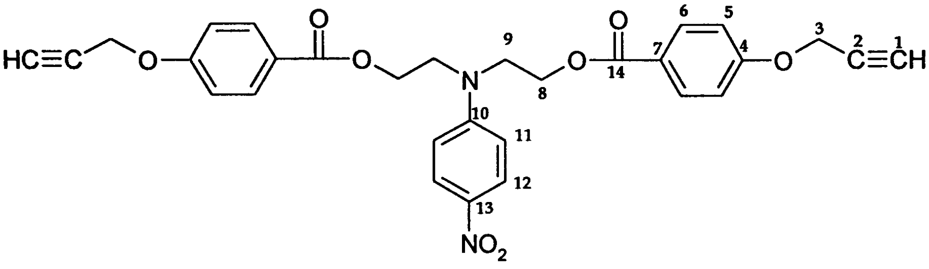
2). Synthesis of bisacetylenic monomers.

10.1 g (0.05 mole) of *p*-bromonitrobenzene were dissolved in *n*-butanol and 6.83 g (0.065 mole) of diethanolamine and 0.1 equivalent mole of copper (I) oxide and 9 g (0.065 mole) of potassium carbonate were added and the mixture was heated to reflux for 12 hours. The butanol was evaporated and N,N-bis(2-hydroxyethyl)-4-nitroaniline (**2**) was obtained. Recrystallization from water gave yellow needle crystals melting at 99-100°C with 83% yield (9.4 g). *IR* (cm^{-1}) (KBr): 3426 (O-H), 1604 (C=C$_{arom}$.), 1504 y 1336 (C-NO$_2$).*^{1}H NMR* (200MHz, DMSO-d): δ (ppm)= 2.95 (s. 1H, H^7), 4.0 (m. 2H, H^2), 4.18 (m, 2H, H^1), 6.98 (d. 1H, J=9.3Hz, H^4), 8.20 (d. 1H, J=9.3Hz, H^5). *^{13}C NMR*: δ (ppm)= 61.05 (C^2), 70.01 (C^1), 114.53 (C^4), 125.96 (C^5), 141.71 (C^6), 163.72 (C^3).



(2)

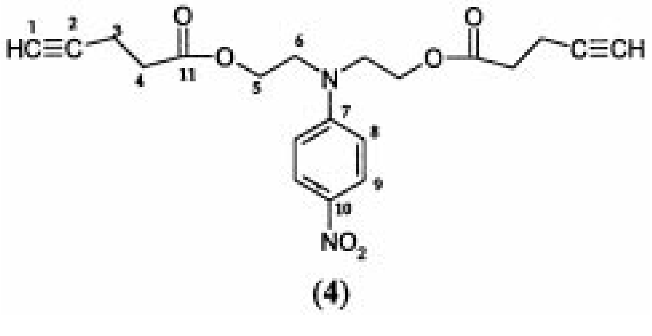
Synthesis of *N,N*-Bis[2-(*p*-propargyloxybenzoyloxyethyl)-amino]nitrobenzene (**3**). *p*-Propargyl-oxybenzoic acid (**1**) was reacted with thionyl chloride in dichloromethane at room temperature to obtain the chloride. After evaporation of the solvent and excess thionyl chloride, a brown crystalline solid was obtained. The chloride was then reacted with the N,N-diethanolnitroaniline (**2**) in dichloromethane to obtain the monomer, *N,N*-bis[2-(*p*-propargyloxybenzoyloxyethyl)amino]nitrobenzene (**3**). It was recrystallized from *n*-butanol and deep yellow sharp needle crystals with mp. of 137°C were obtained with 93% yield (overall yield: 77%). *Elemental analysis* (%): Calcd. for $C_{30}H_{26}N_2O_8$. C: 66.35, H: 4.79, N: 5.16; Found C: 66.33, H: 4.73, N: 5.41.



(3)

^1H *NMR* (δ): 3.61 (s, 1H, H^1), 4.15 (t, 2H, H^9), 4.61 (t, 2H, H^8), 4.98 (s, 2H, H^3), 7.20 (d, = 9.6Hz, 4H, H^5, H^{11}), 7.98 (d, J=9.0, 2H, H^6), 8.12 (d, J=9,6Hz, 2H, H^{12}). ^{13}C *NMR* (δ): 50.50 (C^9), 56.98(C^8), 62.95(C^3), 78.85(C^1), 79.66(C^2), 112.64(C^{11}), 115.94(C^5), 123.89(C^7), 126.92(C^{12}), 132.53(C^6), 138.07(C^{13}), 154.55(C^{10}), 165(C^4), 166.71 (C^{14}). *IR* (cm^{-1}) : 3282.63(≡C-H), 2955($-CH_2-$),2120(C≡C), 1707(-O-C=O), 1600($C=C_{arom}$).

2-2. *N,N*-Bis[2-(4-pentynoyl-oxyethyl)-amino]-nitrobenzene(**4**) was prepared by the method described below: 4 g (0.017 mole) of (**2**) were reacted with 4.53 g (0.038 mole) of 4-pentynoyl chloride in dichloromethane using 7.4 ml (0.053 mole) of triethylamine, initially cooling with an ice bath followed by heating to 40°C for 2 hours. After evaporating the solvent and triethylamine, the product was recrystallized twice from hexane to give yellow crystals melting at 62-63 with a yield of 77% (6.3 g). *Elemental Analysis:* Calcd. for $C_{20}H_{22}N_2O_6$. (%). C: 62.17, H: 5.7, N: 7.25, Found. %, C: 62.67, H: 5.66, N: 7.31. *IR* (cm^{-1}) (KBr): 3283 (≡C-H), 3113 y 3087 ($=C-H_{arom}$.), 2970 y 2927 (CH_2), 2118 (C≡C), 1731 (OC=O), 1592 ($C=C_{arom}$.), 1486 y 1400 ($C-NO_2$). ^1H *NMR* (300MHz, $CDCl_3$): δ (ppm) = 1.95 (t. 1H, H^1), 2.5 (m. 4H, H^3, H^4), 3.7 (t. 2H, H^6), 4.3 (t. 2H, H^5), 6.7 (d. 1H, J=9.3Hz, H^8), 8.1 (d. 1H, J=9.3Hz, H^9). ^{13}C *NMR*: δ (ppm) = 14.24 (C^3), 33.10 (C^4), 49.57 (C^6), 61.0 (C^5), 69.28 (C^1), 82.10 (C^2), 110.69 (C^8), 126.42 (C^9), 137.96 (C^{10}), 152.17 (C^7), 171.54 (C^{11}).



(4)

3). Polymerization.

An oxidative coupling reaction was employed for the polymerization. 2 g of the monomers were dissolved in 1 - 2 ml of *N*-methyl-2-pyrrolidone and 0.05 equivalent mole each of copper (I) chloride and of N,N,N',N'-tetramethylethylenediamine were added. Oxygen was bubbled in while stirring with a magnetic stirrer at room temperature for 4 hours. The polymers obtained were precipitated in methanol, washed well with methanol, and dried in vacuum. They were purified by reprecipitation from a chloroform/methanol system. The yields of polymerization were over 95% in both cases. The rest was probably oligomeric product which did not precipitate in methanol, and a small amount of polymer stuck to the polymerization flask which could not removed completely

4). Characterization.

Elemental analysis was performed by Desert Analytics, Tucson, Arizona. Differential Scanning Calorimetry (DSC) was carried out using a TA Instrument calorimeter Model 910. Gel permeation chromatography (GPC) of the polymers was performed using a variant GPC system consisting of a pump (Varian 9002), column (TSK gel type G4000H8) with detector (Varian RI-4) and an integrator (Varian 4400). NMR spectra were taken using a Varian 300MHz (^{1}H) and 75 MHz(^{13}C) and FT-IR spectra were taken using a Nicolet 510p spectrophotometer.

Results and Discussion

The ^{1}H NMR spectra of polymers from (**3**) and (**4**), hereafter called polymer **3** and **4**, respectively, are shown in Figs. 1 and 2, respectively. The numbers shown on the peaks correspond to those of the formula of monomers 3 and 4. The peaks of the terminal acetylenic protons at 3.61 and 1.95 ppm of monomer 3 and 4 respectively, are no longer present in the spectra of polymers. FT-IR spectra also show that the peaks due to the terminal acetylenic hydrogen at 3282 cm^{-1} totally disappeared, and the acetylene at 2120 cm^{-1} changed shape and position after the polymerization (Figs. 3 and 4). The polymers

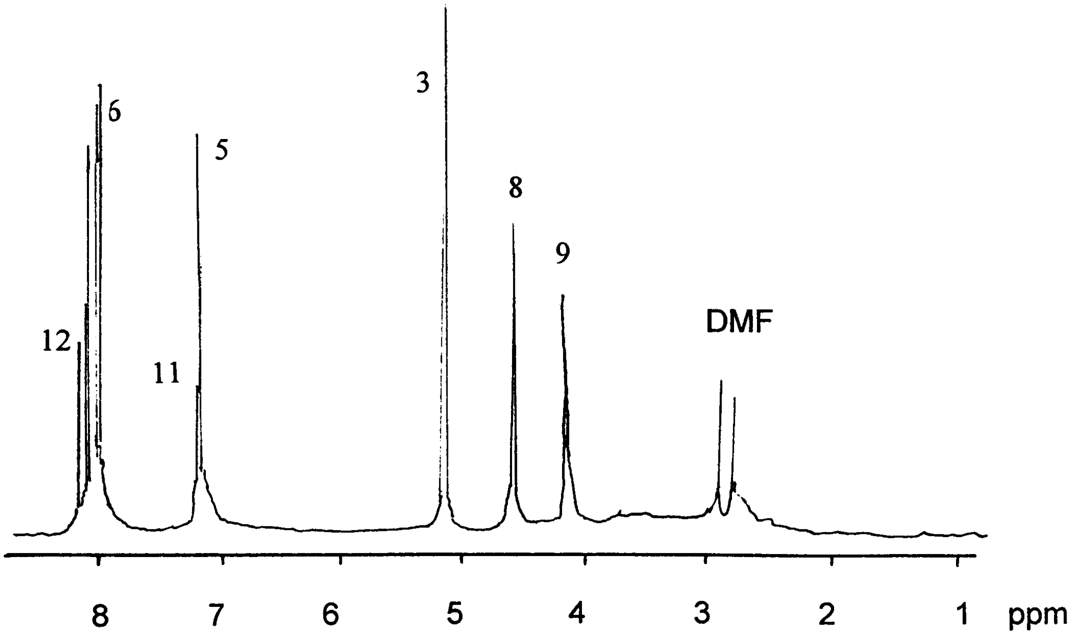


Fig. 1. ^{1}H NMR Spectra of Polymer **3** (in DMF-*d*).

gave films with excellent optical quality on spin coating. The molecular weight determined by GPC in chloroform were found to be very low being only 1000 - 1500, and the results do not seem to be reasonable, probably because this type of polymer has quite a different structure from the standard polystyrene. The inherent viscosity was measured in

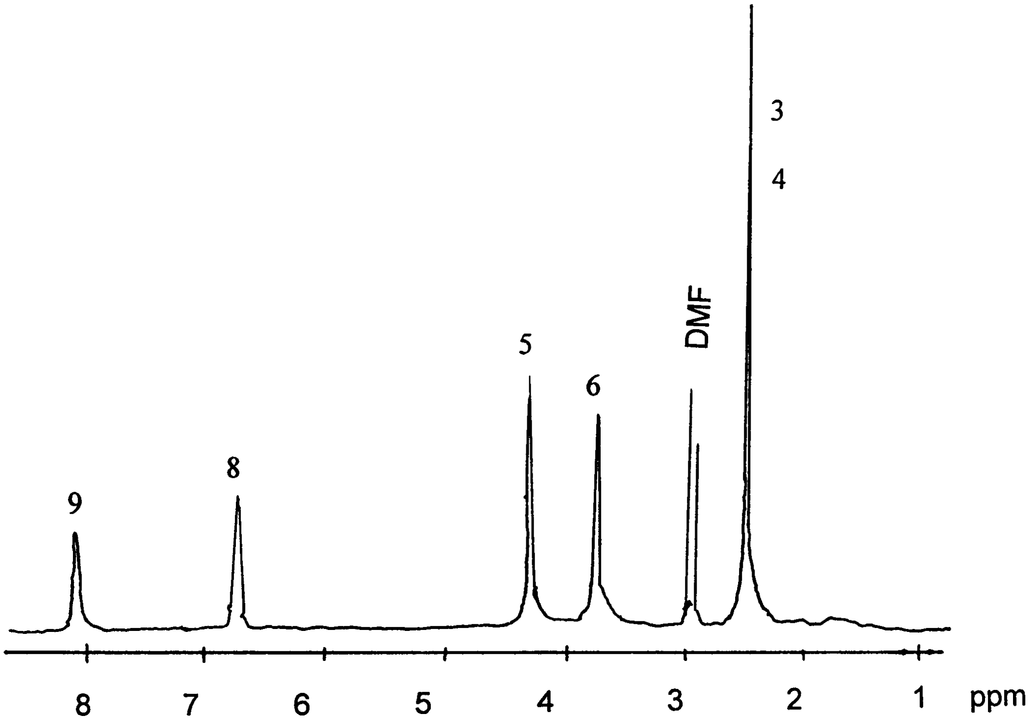


Fig. 2. ^{1}H NMR Spectra of Polymer **4** (in DMF-*d*).

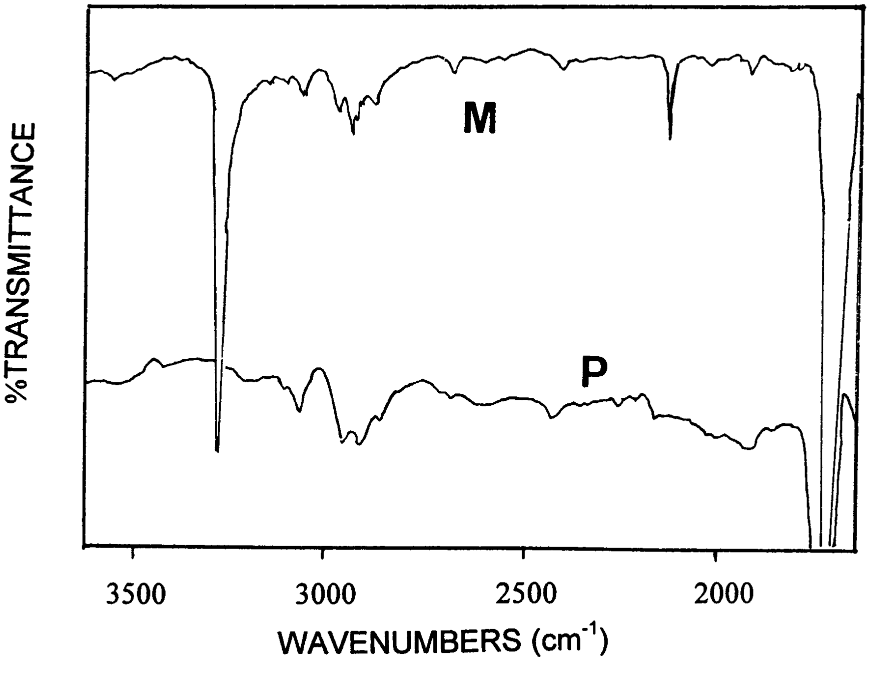


Fig. 3. IR Spectra of Monomer **3** (**M**) and Polymer **3** (**P**). KBr disk.

dimethylformamide at 25°C, and the polymer **3** was found to have an inherent viscosity of 0.85 dl/g. This value suggests that the polymer has a medium molecular weight. The UV/visible absorption spectrum of these polymers is shown in Fig. 5. The spectra of both polymers were identical showing the absorption of *p*-nitrodiethanol aniline group and had the absorption maxima at 394 nm. Fig. 6 shows the DSC curves of polymers **3** and **4**. Polymer 3 had a glass transition temperature, T_g, at 103°C. Polymer 4 had a T_g of 35°C, which was determined by the relationship between SHG and temperature under poling.

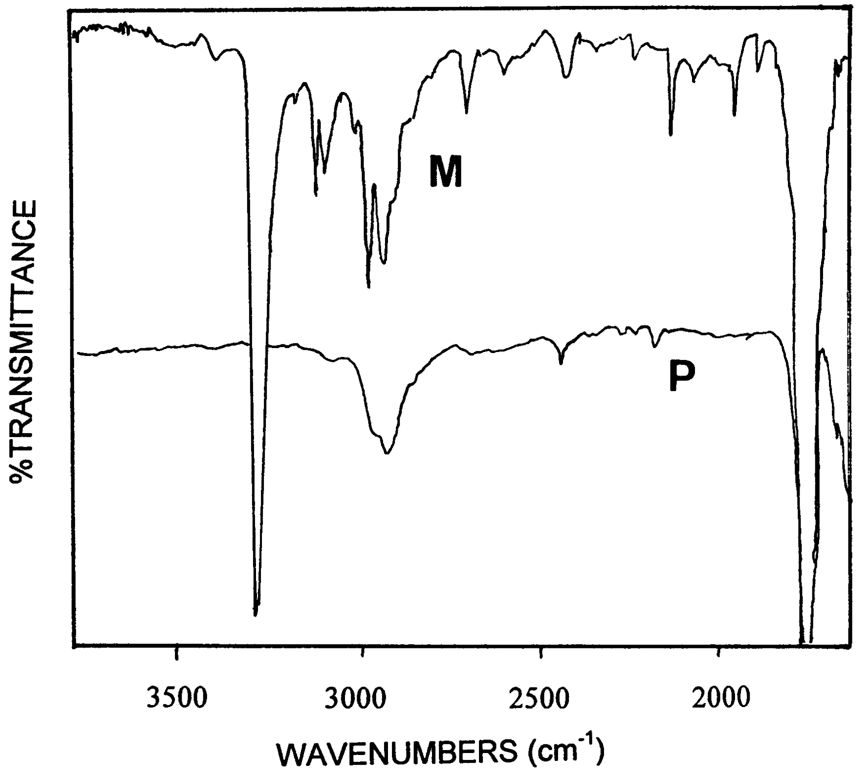


Fig. 4. IR Spectra of Monomer 4 (M) and Polymer 4 (P). KBr disk.

Polymer **3** started cross-linking at temperature around 160°C and polymer 4 at 120°C. The latter temperature is ideal for cross-linking during poling. However, polymer **4** seems to be not suitable for application in photonics because of its low T_g. It is desirable to bring T_g and the thermal cross-linking temperature to be as close as possible, in order to obtain second order nonlinear optical films. There are some previous publications on vinyl polymers containing a *p*-nitroaniline group. Miyata and coworkers have synthesized polystyrene (5) and poly (methyl methacrylate) (6) and studied their second order nonlinear optical properties. However, the vinyl polymers have an important technical disadvantage in poling, because the polymer chains consist of carbon-carbon linkages whose rotation will be much more difficult than that of polymer chains containing flexible ether and ester linkages. The orientation of chromophores by poling will cause some distortion of the polymer main chains, and the force to release this distortion may accelerate the relaxation of orientated chromophores. Or it may be simply said that the poling efficiency in vinyl polymers is low.

The second order nonlinear optical property of spin-coated films of these polymers was determined using a Q-switched Nd/YAG laser (1064nm, 8n, 10Hz) at room temperature. It was found that the polymer **3** had a NLO coefficient of d_{33} PmV while polymer **4** showed no SHG response at all. It is thought that the later has a T_g too low to maintain the orientation of dye molecules.

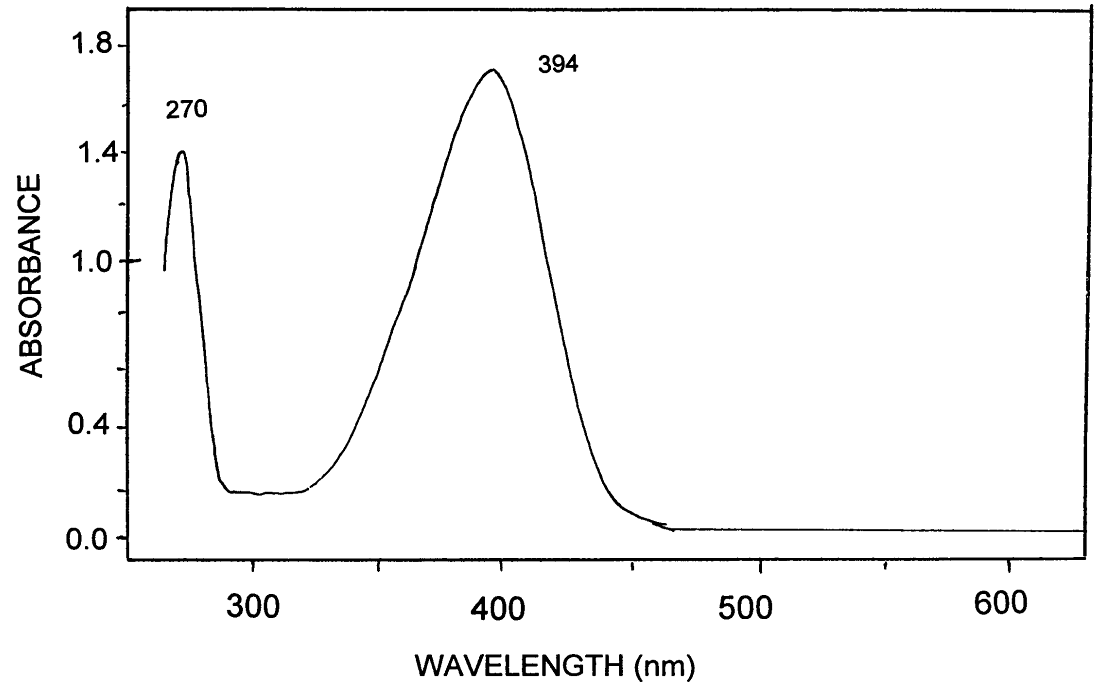


Fig. 5. Visible Absorption Spectrum of Polymer **3**.
In DMF solution (4×10^{-5} g/ml). Cell length : 1 cm.

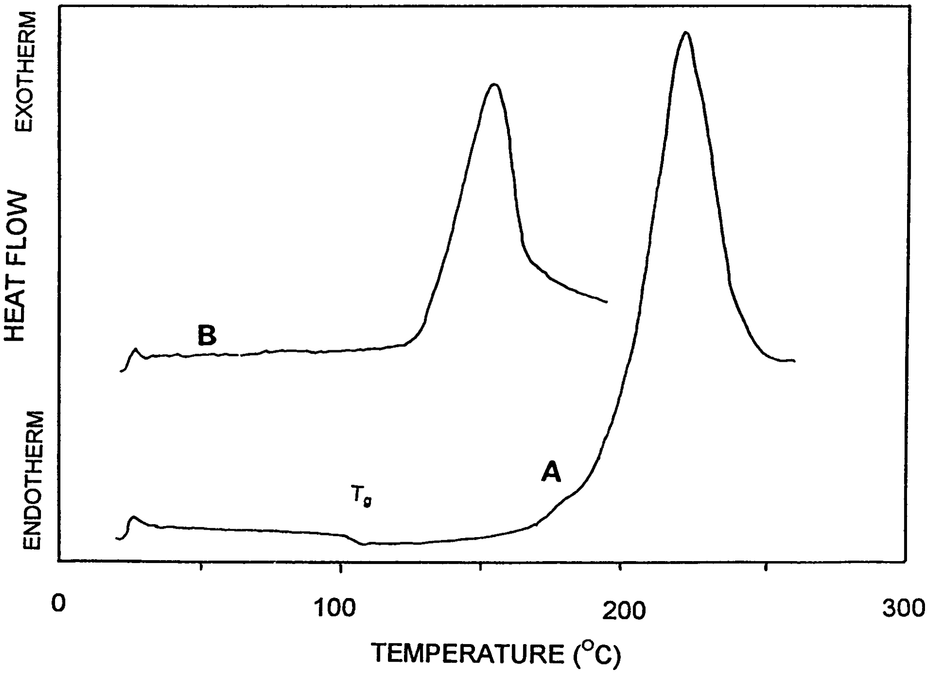


Fig. 6. DSC Curves of Polymers 3 (A) and 4(B).
Heating rate 10°C/min. under N_2

The spin-coated films of polymers **3** and **4** were irradiated with a 400W medium pressure mercury lamp at 120°C. The irradiated films were no longer soluble in the solvent indicating that cross-linking took place. This property is very useful to avoid relaxation of the orieatation of dye molecules.

In conclusion, it was shown that novel thermoset resins having various functional groups can be synthesized by the method described in this paper.

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