

NOTE

New Polymeric Material for Nonlinear Optic Prepared from Chloromethylstyrene

INTRODUCTION

In the last few years there has been increasing interest in nonlinear, optical materials; organic materials bearing electron donor and acceptor groups, separated by conjugated nuclei, have been dispersed in glassy polymers or liquid crystalline,¹⁻³ but the best method for preparing a copolymer seems to be one in which the active nonlinear species is linked to the backbone of the macromolecule. Some products have recently been synthesized chiefly with methacrylic or acrylic skeletons⁴⁻⁸; the nonlinear species are often an aminonitrostilbene or a nitroazostilbene group. The use of a spacer (aliphatic chain with an hetero atom, nitrogen or sulfur) between the dye and the polymeric backbone has been also proposed.^{9,10} As all these syntheses require lengthy procedures, modification reactions of polymers with reactive dyes have been tried; iodomethylated polystyrene, for example, prepared through a nucleophilic substitution of chloromethylated polystyrene, reacts with the "red-one dye" and gives a moderate yield of modified product.¹¹ Another functionalized polystyrene, poly 4-hydroxystyrene, whose synthesis is relatively long, has also been modified^{12,13} with 4-(4-nitrophenylazo) (N-ethyl) (2-hydroxy-ethyl) aniline.

This study reports on the two-step synthesis of a new material as a nonlinear optical material, from a commercial product, chloromethylstyrene (1) (meta, para: 60/40), and its copolymerization with styrene.

EXPERIMENTAL

Chloromethylstyrene (1) or Vinylbenzylchloride (Dow Chemical Corp.) has been purified by vacuum distillation (50–55°C/0.5 mm Hg); 4-hydroxybenzaldehyde, 4 nitrophenyl-acetic acid, 4-methyl-2,6 bis (terbutyl) phenol are commercially available and used without further purifications. The products of the syntheses have been characterized by means of ¹H-NMR spectra (Bruker at 300 MHz) (deuterated chloroform was used as solvent) and by UV spectra (Hitachi 1100 apparatus).

The glass transition temperature and melting point have been recorded with a D.S.C. 101 Setaram. The molecular masses of copolymers have been measured with a

Knauer apparatus by using 10³–10⁵ Å columns and polystyrene standards.

Microanalyses were performed at the Service Central d'Analyse CNRS Vernaison (France).

Preparation of 4-Vinylbenzyloxybenzaldehyde (2)

This aldehyde has been prepared using a previously described procedure¹⁴⁻¹⁵ (mp ≅ 40°C).

Preparation of 4[Vinylbenzyloxy]-4'nitrostilbene (3)

A 250 ml, three-necked, round-bottomed flask (fitted with a magnetic stirrer and reflux condenser) was charged with 4 nitrophenylacetic acid (16.6 g; 0.092 mol) and piperidine (7.4 g; 0.092 mol) and was heated for 1 h between 80°C and 90°C. Aldehyde 2 (22 g; 0.092 mol) and 4-Methyl-2,6 bis (terbutyl) phenol (0.2 g; 0.0009 mol) were added; the mixture was then heated at 120–130°C for 4 h, the water being distilled during the reaction. Then, the mixture was dissolved in 100 mL of chloroform and washed with 3 × 20 mL of NaOH 1 N. The solution was dried with anhydrous sodium sulfate and the chloroform was removed under vacuum. Dye 3 has been purified after dissolution in chloroform and precipitation with pentane. Microanalysis of 3 is in good agreement with the attempted structure.

¹H-NMR δ: 5.2 (s, 2H, —CH₂—O) 5.4 and 5.8 (2d, —CH=CH₂) 6.85 (m, 3H, CH=CH and CH=CH₂) 7.1 – 8.2 (m, 12H, aromatic protons). U.V. Spectrum: Two peaks are observed at λ_{max} = 253 nm (ε = 30,400), due to the vinylbenzyl group and λ = 380 nm due to the nitrostilbene moiety (ε = 20,300). The overall yield from vinylbenzylchloride is close to 70%.

Preparation of Copolymer (4)

Poly[Styrene co 4(Vinylbenzyloxy)-4'Nitrostilbene]. The dye 3 (1 g; 0.0028 mol) was dissolved in 10 mL of chlorobenzene and was mixed with styrene (2.6 g; 0.025 mol) and 36 mg of azobis isobutyronitrile (A.I.B.N.) as initiator (1% in weight). The mixture was placed in a glass tube, sealed under nitrogen, and heated at 75°C for 20 h. Copolymer

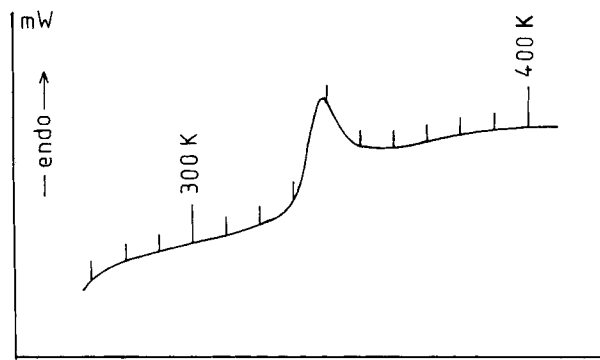


Figure 1 Glass transition temperature of copolymer 4.

4 was obtained by precipitation of the cold solution in methanol and was purified by dissolving in chloroform and precipitation by methanol. The yield is close to 40% and the molecular masses are $M_n = 18,000$ and $M_w = 39,000$. The measured glass transition temperature is 62°C (Fig. 1). Microanalysis of copolymer 4 shows that 18% of monomer 3 has been incorporated in copolymer 4.

RESULTS AND DISCUSSION

Syntheses of dyes with spacers for nonlinear optics generally require several steps. By using chloromethylstyrene as a starting monomer, we have built a polymeric chain with a benzyloxy group as a spacer linked to a nitrostilbene structure, in two-steps only and with a correct yield. This dye is, in fact, a mixture of meta and para isomers, because commercial chloromethylstyrene is also a mixture of meta and para isomers, whose separation is long and has poor yields.¹⁶ The melting point of the dye has been measured by means of a D.S.C. apparatus. Two endothermic peaks, badly separated, have been observed: the first at about

146°C and the second at about 156°C (Fig. 2). After three recrystallizations of the dye in chloroform, these two phenomena were well separated. The first peak, the intensity of which decreases after each recrystallization, remains at the same temperature of 146°C . This may be an invariant equilibrium, such as an eutectic, in a binary system. The intensity and temperature of the second peak increases after the recrystallizations and 182°C can be the melting point of pure para isomer. Several works about substituted styrenes, synthesized from commercial chloromethylstyrene, have assigned the highest melting point to the para isomer.^{17,18} Another method of preparation of dye 3 was investigated; chloromethylstyrene is a very reactive monomer in a great number of nucleophilic substitutions.¹⁹ The 4 hydroxy 4' nitrostilbene was synthesized according to a previously described procedure, that is, through the condensation of 4 hydroxy benzaldehyde with 4 nitrophenylacetic acid and piperidine as a catalyst.²⁰ Nucleophilic substitution of chlorine atoms in chloromethylstyrene by 4,4'-hydroxy nitrostilbene, in conditions similar to those used for 4 hydroxy-benzaldehyde, has failed. The copolymerization of dye 3 with styrene was carried out in a solvent because styrene cannot dissolve the comonomer. The solvent chosen was the chlorobenzene, which can easily dissolve the dye 3. The yield of copolymerization was relatively low (40%), but under the same experimental conditions, with chlorobenzene as a solvent, the polymerization of styrene gave a low yield due to the transfer reaction with the solvent.²¹ The incorporation of dye 3 in this copolymer (18%, according to the elemental analysis) did not decrease the filmability compared with polystyrene.²² The copolymer 4 has been dissolved in chloroform (1 g in 50 mL) and thin films are prepared by means of the spin-coating method. The thickness of these isotropic films is about 1 micron and the refractive index is about 1.651. The optical losses are of few dB/cm. The studies of electrooptical properties are in progress.

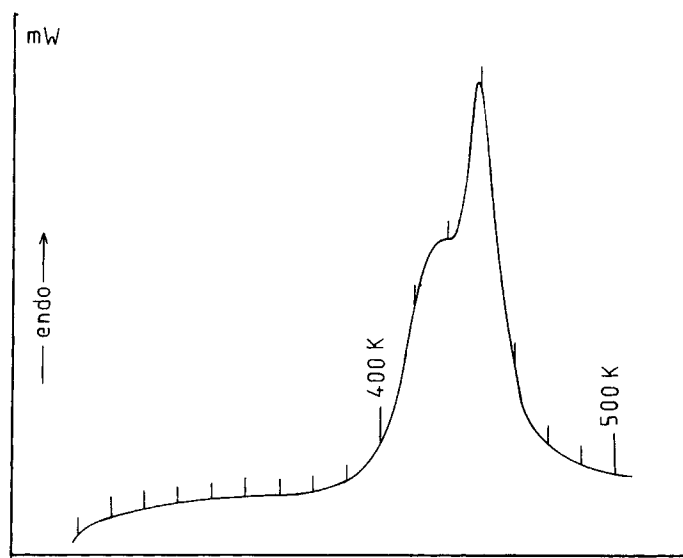
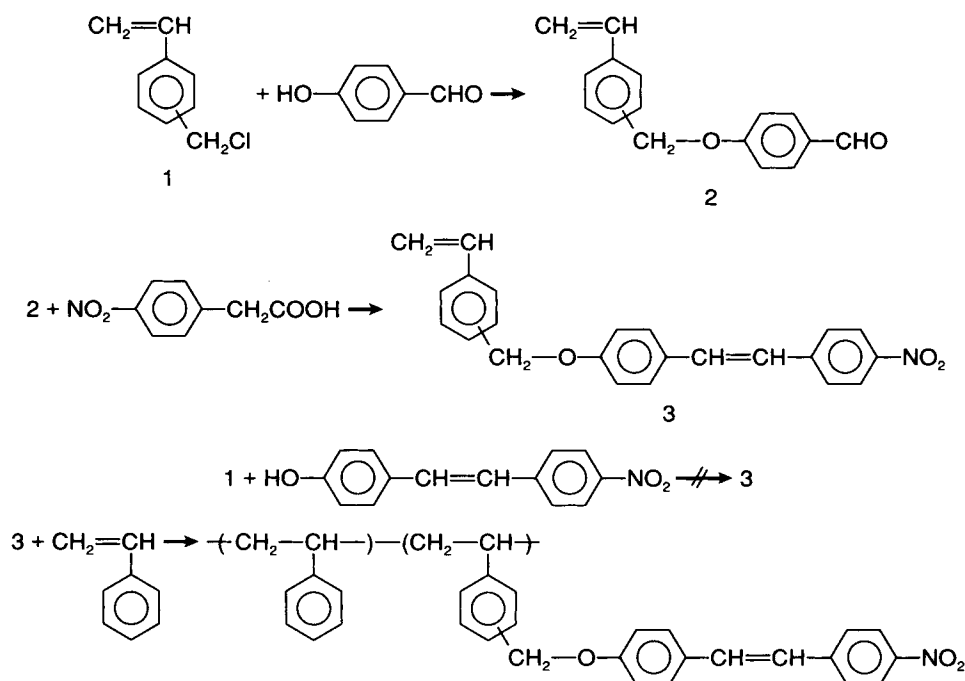


Figure 2 Melting point of monomer 3.



Scheme 1

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