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Synthesis and characterization of poly(ethyl vinyl ether) containing the NLO-phore 4′-oxy-4-nitrostilbene in the side chain

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Summary

4′-(2-Vinyloxyethoxy)-4-nitrostilbene 2 was prepared by the reaction of 4′-hydroxy-4-nitrostilbene 1 with 2-iodoethyl vinyl ether. Monomer 2 was polymerized with cationic initiators to obtain a poly(ethyl vinyl ether) with the NLO-phore 4′-oxy-4-nitrostilbene in the side chain. The resulting polymer 3 was soluble in common solvents such as chloroform and DMSO. The inherent viscosities of polymer 3 were in the range of 0.25–0.30 dL/g in chloroform. Polymer 3 showed a good thermal stability in TGA thermogram. Solution-cast films were cloudy and brittle with a T_g of 63°C.

Introduction

Functional polymers of nonlinear optical (NLO) activity have long been the subject of curiosity and have caused recent interest (1-5). It is well known that organic and polymeric materials with highly dipolar electronic systems exhibit NLO properties. Compared to other organic and inorganic substances, NLO polymers offer many advantages such as high nonlinear optical activity, light weight, chemical resistance, and good processability. A potentially NLO polymer must contain a highly polarizable π-electronic systems and these polymers have to be mechanically very strong. There are tremendous challenges in designing and synthesis of polymers of large NLO effects. Various polymers with the NLO-phores in the side chain such as poly(meth)acrylates (6-12) and polystyrene (13) were reported. Polyesters (14-18), polyurethanes (19), polyamides (20-21), and poly(phenyleneethynylenes) (22) containing the chromophoric main chain were also prepared. Dix and his coworkers (23) prepared poly(ethyl vinyl ethers) partly grafted with pendant 4′-amino-4-nitroazobenzene by the reaction of poly(2-chloroethyl vinyl ether) with azo-dyes. However, examples of polyalkyl vinyl ethers with the chromophoric side chain prepared directly by the polymerization of monomeric alkyl vinyl ethers are not shown in the literature. Recently we have prepared (24) clean poly(ethyl vinyl ethers) containing the NLO-phores p-oxybenzylidenemalononitrile and p-oxybenzylidenecyanoacetate in the side chain by cationic polymerization of the corresponding monomers.

This work is now extended with the synthesis and characterization of another poly(ethyl vinyl ether) containing the NLO-phore 4′-oxy-4-nitrostilbene in the side chain. The present report describes the synthesis and cationic polymerization of 4′-(2-vinyloxyethoxy)-4-nitrostilbene 2, as the initial phase of the NLO work.

Experimental

Materials

The reagent grade chemicals were purified by distillation or recrystallization before use. 2-Chloroethyl vinyl ether (Aldrich) was used as received. Sodium iodide was dried for 4h at 100°C under vacuum. Acetone was purified by drying with anhydrous potassium carbonate, followed by distillation under reduced pressure. p-Hydroxybenzaldehyde was recrystallized from water and dried under vacuum. Piperidine was dried with calcium hydride and fractionally distilled. Dichloromethane washed with concentrated sulfuric acid and then with water, dried with anhydrous calcium chloride, refluxed with calcium hydride, and distilled under nitrogen before use. Toluene was washed with cold concentrated sulfuric acid and then with water, aqueous 5% sodium bicarbonate, again with water, dried with anhydrous calcium sulfate, refluxed with phosphorus pentoxide, and distilled. Boron trifluoride etherate was treated with a small amount of diethyl ether and distilled under reduced pressure.

Measurements

IR spectra were taken on a Hitachi Model 260-30 infrared spectrophotometer. Proton-NMR spectra were obtained on a Varian EM 360L NMR spectrometer (60 MHz). UV-VIS spectra were obtained on a Kontron UVikon 860 spectrophotometer. Elemental analyses were performed using a Perkin-Elmer 2400 CHN elemental analyzer. The glass transition temperatures (T_g) were measured on a DuPont 910 differential scanning calorimeter in a nitrogen atmosphere. DuPont 951 thermogravimetric analyzer with a heating rate of 10°C/min up to 700°C was used for the thermal degradation study of polymers under nitrogen. Melting points were measured in Buchi 530 melting point apparatus and are corrected. Viscosity values were obtained by using a Cannon-Fenske viscometer.

Preparation of 2-Iodoethyl Vinyl Ether

Anhydrous sodium iodide (45 g, 0.30 mol) was dissolved in 320 mL of dry acetone contained in a 500 mL round-bottom flask fitted with a reflux condenser protected by a calcium chloride tube, and heated on a heating mantle for 1 h with stirring. 2-Chloroethyl vinyl ether (25.0 g, 0.23 mol) was added to the mixture, and refluxed for an additional 25 h with stirring to complete the reaction. The resulting solution was cooled to room temperature and filtered with suction. The sodium chloride on the filter was washed with 55 mL of acetone anf the filtrate was concentrated by distillation of about 260 mL of the solvent. The residue was poured into 260 mL of water contained in a separate funnel, which was shaken. The lower layer was washed successively with 55 mL of 10% sodium bisulfite solution, 55 mL of 5% sodium bicarbonate, and 30 mL of water. It was dried with anhydrous magnesium sulfate(1.8 g) and fractionated under reduced pressure to give 32.8 g (72% yield) of **1**. Bp: 50-52°C (20 mmHg). Proton-NMR ($CDCl_3$) δ 6.22-6.57 (q, 1H), 3.50-4.37 (m, 4H), 2.82-3.47 (t, 2H). IR (neat) 3105, 3034, 2960, 2922, 2845 (C-H), 1635, 1612 (C=C) cm^{-1}.

Preparation of 4′-Hydroxy-4-nitrostilbene 1

Compound **1** was prepared by a known method (25) from 4-hydroxybenzaldehyde and p-nitrophenylacetic acid, and recrystallized from 80% aqueous ethanol. Mp: 205-206°C [lit (25): 204°C]. Proton-NMR (acetone-d_6) δ 8.02-8.38 (2H, d), 7.13-7.93 (6H, m), 6.67-7.06 (2H, d). IR (neat) 3420 (O-H), 1624, 1583 (C=C) cm^{-1}.

Preparation of 4′-(2-Vinyloxyethoxy)-4-nitrostilbene 2

4′-Hydroxy-4-nitrostilbene (2.99 g, 0.012 mol), anhydrous potassium carbonate (2.22 g, 0.016 mol), and 2-iodoethyl vinyl ether (3.16 g, 0.016 mol) were dissolved in 60 mL of dry acetone under nitrogen. The mixture was refluxed in an oil bath kept at 60°C for 40 h under nitrogen. The resulting solution was cooled to room temperature, filtered, and the inorganic salts were washed with 80 mL of acetone. Rotary evaporation of acetone gave crude product, which was washed with water completely to remove the residue salts. Thus obtained product was recrystallized from acetone yielded 2.68 g (72% yield) of pure yellow crystals 2. Mp: 136-137°C. Proton-NMR (acetone-d_6) δ 8.01-8.34 (2H, d), 7.23-7.93 (6H, m), 6.87-7.14 (2H, m), 6.33-6.74 (1H, q), 3.83-4.43 (6H, m). IR (KBr) 3072, 3010, 2945 (C-H), 1624, 1605, 1593, 1572 (C=C) cm^{-1}. UV-Vis ($CHCl_3$) 375 nm (ϵ= 33,650). Anal. Calcd for $C_{18}H_{17}NO_4$: C, 69.44; H, 5.50; N, 4.50. Found: C, 69.53; H, 5.45; N, 4.43.

Cationic Polymerization of 4′-(2-Vinyloxyethoxy)-4-nitrostilbene 2

A representative cationic polymerization procedure was as follows: A solution of 2 (0.62 g, 2.0 mmol) in dichloromethane (5.0 mL) was placed in a rubber septum stopper capped glass ampule under nitrogen. The resulting solution was flushed with nitrogen for 20 min. The ampule was then placed in an ethanol-acetone bath kept at -30°c under nitrogen, and 0.0023 mL (0.020 mmol) of boron trifluoride etherate was added to the solution. After 10 h the ampule was taken out and the polymerization mixture was poured into 500 mL of methanol. The precipitated polymer was collected and reprecipitated from DMSO into methanol to give 0.55 g (88% yield) of polymer 3; η_{inh} = 0.28 dL/g (c 0.5 g/dL in chloroform at 25°C). Proton-NMR (DMSO-d_6) δ 7.83-8.34 (2H, m), 7.05-7.93 (6H, m), 6.53-7.23 (2H, m), 3.17-4.31 (5H, m), 0.84-1.93 (2H, m). IR (KBr) 3071, 3010, 2924, 2858 (C-H), 1625, 1605, 1590, 1575 (C=C) cm^{-1}. UV-Vis ($CHCl_3$) 374 nn. Anal. Calcd for $(C_{18}H_{17}NO_4)_n$: C, 69.44; H, 5.50; N, 4.50. Found: C, 69.55; H, 5.56; N, 4.58.

Results and Discussion

Synthesis of monomer 2

4′-Hydroxy-4-nitrostilbene was synthesized by the condensation of 4-hydroxybenzaldehyde with p-nitrophenylacetic acid according to a literature procedure (25), and recrystallized from 80% aqueous ethanol. 2-Iodoethyl vinyl ether was prepared by the well known halogen exchange reaction (26) from 2-chloroethyl vinyl ether and sodium iodide, and reacted with 4′-hydroxy-4-nitrostilbene to yield 4′-(2-vinyloxyethoxy)-4-nitrostilbene 2 (27). The chemical structure of the compounds was confirmed by proton-NMR, IR, UV-Vis spectra, and elemental analyses. Spectral data indicated that stilbene compound 2 was isolated as the trans-isomer. Compound 2 showed a strong uv absorption band around 375 nm in chloroform.

Cationic Polymerization of monomer 2

4′-(2-Vinyloxyethoxy)-4-nitrostilbene 2 was polymerized in solution at -30 °C with boron trifluoride etherate as cationic initiator to obtain the polymers 3. The polymerization results are summarized in Table 1.

Monomer 2 was quite reactive toward cationic initiator and polymerized readily at low temperature. The internal double bond in stilbene moiety did not participate in the vinyl polymerization. The chemical structure of the polymers were confirmed by proton-NMR, IR, UV-Vis spectra, and elemental analyses.

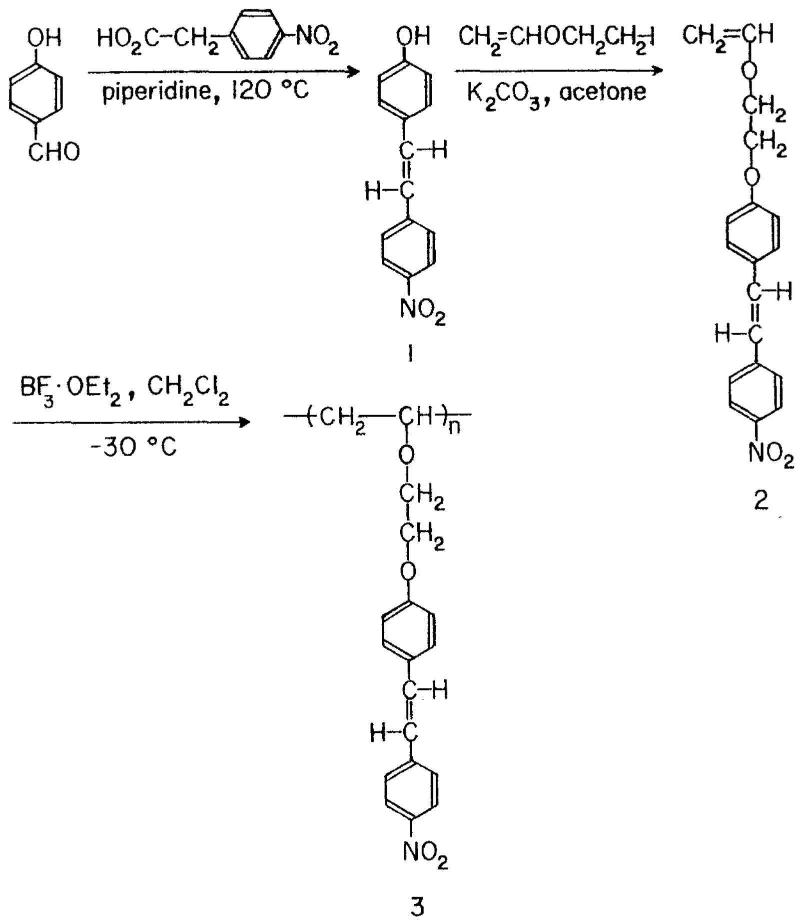

Table 1. Cationic polymerization of 2[a] under various conditions.

Monomer	Solvent	Monomer/Solvent (mol/1 L)	Initiator to Monomer (mol%)	Temp (°C)	Time (h)	Yield (%)	η_{inh}[b] (dL/g)
2	CH_2Cl_2	0.40	1.0	-30	10	88	0.28
2	CH_2Cl_2	0.57	0.9	-30	24	90	0.30
2	$C_6H_5CH_3$	0.67	1.0	-60	10	86	0.25
2	$C_6H_5CH_3$	0.80	0.9	-30	16	92	0.29

[a] 2 = 4′-(2-Vinyloxyethoxy)-4-nitrostilbene.

[b] Inherent viscosity of polymer: Concentration of 0.5 g/dL in chloroform at 25°C.

Polymer **3** in chloroform showed a strong uv absorption band around 374 nm due to the chromophore 4′-oxy-4-nitrostibene in the side chain. In most cases, conversions were quite high, but the molecular weights were rather low as indicated by the inherent viscosities.

The polymer **3** was soluble in common solvents such as chloroform, dichloromethane and DMSO, but was not soluble in methanol and diethyl ether. The inherent viscosities of polymer **3** were in the range of 0.25-0.30 dL/g indicating moderate molecular weights. The thermal behavior of the polymers were investigated by thermogravimetric analysis (TGA) and differential scanning calorimeter (DSC) to determine the thermal degradation patterns and glass transition temperature (T_g). The results are summarized in Table 2. TGA thermogram showed a double phase degradation patterns in TGA thermogram, probably due to the presence of two bezene rings in the pendant group. Polymer **3** showed a good thermal stability and was not decomposed below 300°C as shown in Table 2, which is acceptable for NLO device application. The glass transition temperature (T_g) of the polymer was 63°C. These T_g values are higher than those for poly(ethyl vinyl ether) (-43°C), probably due to the presence of polar pendant group. Solution-cast films were brittle, which could be due to the rather low molecular weight and/or high concentration of dipole moment.

Table 2. Thermal properties of polymer **3**.

Polymer	T_g[a], °C	Degradation temp, °C[b]			Residue[b] at 700°C, %
		5%-loss	20%-loss	40%-loss	
3	63	305	333	505	5.5

[a] Determined from DSC curves measured on a DuPont 910 differential scanning calorimeter with a heating rate of 10°C/min under nitrogen atmosphere.

[b] Determined from TGA curves measured on a DuPont 951 thermogravimetric analyzer with a heating rate of 10°C/min under nitrogen atmosphere.

In conclusion, we prepared a clean poly(ethyl vinyl ether) **3** containing the NLO phore 4′-oxy-4-nitrostilbene in the side chain by the cationic polymerization of the corresponding vinyl monomer **2**. The resulting substituted poly(ethyl vinyl ether) **3** was soluble in chloroform, dichloromethane and DMSO, but was not soluble in methanol and diethyl ether. Polymer **3** showed a good thermal stability, which is acceptable for NLO device application. Films cast from the polymer solution were cloudy and brittle, showing T_g value of 63°C. Copolymerization with other monomers and measurements of NLO activity are in progress, and the results will be reported later.

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