

A novel side chain liquid crystalline polyester for nonlinear optics

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Received: 2 May 1997/Revised version: 24 June 1997/Accepted: 27 June 1997

Summary

A nematic liquid crystalline polymalonate has been synthesized by melt polycondensation of a nonlinear optical (NLO) monomer and a liquid crystalline (LC) monomer. The polymer was characterized by VPO, FTIR, DSC, WAXD, UV-visible spectroscopy and polarized optical microscopy. The LC temperature interval was found between 398 K and 420 K by DSC. Some interactions originated from the attachment of the side groups to the polymer backbone were detected by UV-vis spectroscopy.

Introduction

Interest is growing and much work has been done in research on organic materials aimed at developing new NLO materials for potential applications in the areas of telecommunications, optical computing and imaging. So far, many organic compounds which possess NLO properties have been found, in fact, all noncentrosymmetric organic systems which have donor- π conjugation-acceptor molecular structure possess to a certain extent NLO susceptibilities. However much work is focusing on polymers attached with disperse red 1 (DR1), disperse red 19 (DR19) and the similar chromophores, for their large second order hyperpolarizabilities and ease to synthesize.

In order to obtain larger and long-term stable NLO properties, the key points are trying to make the maximum orientation of NLO molecules and to stabilize the orientational alignment as far as possible, that is to try one's best to retard or prevent the reorientation of the field-induced noncentrosymmetric alignment. It is common knowledge that a LC system possesses a high degree of orientated order. If NLO molecules are combined with a LC system, or in other words, if NLO molecules are induced to orient in a LC medium, it must be advantageous to the orientation of NLO molecules and to the stabilization of the molecular orientated alignment. Meredith et. al. (1) obtained considerably larger SHG (100 fold) than could be obtained with the same quantity doped into the amorphous poly(methyl methacrylate) by doping 2% 4-(dimethylamino)-4'-nitrostilbene (DANS) into a LC copolymer. If LC units and NLO units are covalently attached to a polymer backbone simultaneously, that would result in a system with a high degree of locked-in order below the glass transition temperature, and thus combines the favorable properties of both liquid crystals and polymer glasses. Ringsdorf et. al. (2) reported nematic and smectic copolyacrylates with the dye concentration of 2.0%, aligned

by magnetic field poling, quite high order parameters had been achieved. Koide et. al. (3) had reported the thermal and NLO properties of liquid crystalline copolyacrylates and copolymethacrylates.

In this investigation, we choose biphenylene as the LC unit, DR19 as the NLO unit, and the two parts are attached to a polymer backbone as side chains. Moreover a methoxy group was introduced to the biphenyl unit, the possible charge transfer interaction between the methoxy and the nitro group may interlock the movement of the two kinds of side group, thus the orientation of the two parts maybe connected each other. Therefore, if LC units are in the mesophase state at a proper temperature, let the NLO units (also the LC units) orient in a poling field, then the sample is cooled down to room temperature (below T_g) with the field on, the orientational alignment will be frozen in the sample.

In this study, the synthesis and characterization of a new liquid crystalline polymalonate was reported. The polymalonate is, to our knowledge, the first "alternate" liquid crystalline polymalonate with NLO units. The polarization of the sample film and the measurement of the second nonlinear optical susceptibilities is currently in progress.

Experimental

Materials

Bis(hydroxyethyl) aniline was purchased from Aldrich Chemical Co. and was used as received. p-Nitroaniline, 4,4'-dihydroxybiphenyl (or biphenol) and dimethyl sulfate were purchased from Shanghai Chemical Co. and were used as received. Diethyl malonate and 1,4-dibromobutane were purified by vacuum distillation, diethyl malonate at 76 °C/6 mmHg and 1,4-dibromobutane at 60 °C/5 mmHg were used.

Measurements

IR spectra were recorded on a Nicolet 5DX Fourier Transform infrared spectrophotometer. The number average molecular weight \bar{M}_n was measured by a KNAUER Vapor Pressure Osmometer. ^1H NMR spectra were obtained on a JNM-PMX 60 spectrometer using TMS as an internal standard. UV-Vis spectra were recorded on a Shimadzo UV 240. Elemental analyses were performed by the Perkin-Elmer 240C. Polymer inherent viscosities were measured at 25 °C in a chloroform solution by using an Ubbelohde viscometer. Thermal analyses were carried out on a Perkin-Elmer DSC-2C interfaced with a Model 3600 data station, a heating rate of 10 K/min under a 20 ml/min flow of nitrogen as the purge gas was used on samples of 10 ± 2 mg. Optical textures were observed with a Leitz polarizing optical microscope equipped with a Leitz-350 hot stage and a camera. The polymer sample was placed between two glass slides and heated to the isotropic melt, and the slides were then sheared to produce a thin layer of melted polymer. The sample was then cooled at 3 K/min and observed, meanwhile photographed at proper temperatures. Wide angle X-ray diffraction (WAXD) patterns were obtained using monochromatic $\text{Cu K}\alpha$ radiation ($\lambda=1.5418 \text{ \AA}$). Data were collected for 20 min, and background scans of equivalent duration were subtracted to remove background scatter. The two-dimensional data were then azimuthally averaged to generate intensity vs 2θ scans.

Synthesis

4-(Dihydroxyethylamino)-4'-nitroazobenzene (DR19)

14.0 g (0.101 mol) p-Nitroaniline was dissolved in 50% sulfuric acid solution (50 ml) and diazotized with sodium nitrite 7.0 g (0.101 mol) in 15 ml water at 0~5 °C. The mixture was filtered and the filtrate was then added dropwise to bis(hydroxyethyl) aniline (18.5 g, 0.102 mol) in dilute sulfuric acid solution (40 ml) at 0~5 °C. The mixture was stirred for 1 hr, and saturated sodium acetate solution was added to neutralize the mixture, then the mixture was stirred for another 0.5 hr. The deep red precipitate was collected and washed several times with water, then recrystallization from ethanol twice resulted in a yield of 75% (25.1 g), m.p. 210 °C (DSC, second heating). ANAL: Calcd C: 58.17%, H: 5.49%, N: 16.96%; Found C: 57.81%, H: 5.22%, N: 16.44%.

IR(KBr, cm⁻¹): 3276(s, ν_{OH}), 2924, 2875(m, ν_{CH2}), 1511, 1335(vs, ν_{NO2}).

4-methoxy-4'-hydroxybiphenyl

50.0 g (0.269 mol) biphenol was dissolved in 250 ml sodium hydroxide solution (dissolved NaOH 25.0 g), the mixture was filtered into a 500 ml three-necked flask equipped with an addition funnel and a mechanical stirrer. And 25.5 ml (0.27 mol) of dimethyl sulfate was added dropwise over 0.5 hr, the reaction mixture was stirred for another 2 hr and then filtered. The light green filter cake was washed in 300 ml of 10% NaOH aqueous solution, the dispersion solution was heated to 80 °C and then cooled to room temperature. After filtration again, the filter cake was stirred into 1.8 liter of water, and the mixture was heated to boiling. The boiling solution was filtered and the filtrate was acidified by 20 % hydrochloride solution at 70 °C. Then after cooling to room temperature the precipitate formed was collected and washed several times with water, recrystallization from ethanol twice resulted in a yield of 62% (33.4 g), m.p. 181~182 °C. ANAL: Calcd C: 77.98%, H: 6.04%; Found C: 78.10%, H: 5.95%.

IR(KBr, cm⁻¹): 3423(s, ν_{OH}), 2959, 2833(s, ν_{CH3}), 1461(m, δ_{CH3}).

4-(4-bromobutoxy)-4'-methoxybiphenyl

The synthesis of 4-(4-bromobutoxy)-4'-methoxybiphenyl was referred to literature (4) and carried out as follows: To sodium hydride (0.75 g, 0.031 mol) in 100 ml anhydrous DMF, 4-methoxy-4'-hydroxybiphenyl (4.0 g, 0.020 mol) was added and the reaction system was stirred for 15 min. Then ten times excess of 1,4-dibromobutane (45.0 g, 0.21 mol) was added and the reaction mixture was stirred for 20 hr under nitrogen at room temperature 15 °C. After the solvent and excess 1,4-dibromobutane were removed by evaporation under vacuum, 500 ml chloroform and 200 ml of 2% aqueous sodium hydroxide were mixed with the system in a separating funnel. The organic layer was collected and dried over anhydrous magnesium sulfate. After filtration and evaporation of the solvent, the residue was recrystallized from ethanol at least twice obtained white product 4.7 g, yield 70%. m.p. 125~126 °C. ANAL: Calcd C: 60.91%, H: 5.71%; Found: C: 60.69%, H: 5.83%.

¹H NMR(CDCl₃, ppm): δ 1.80~2.32 (m, 4H, -CH₂-), 3.48 (t, 2H, -CH₂Br), 3.83 (s, 3H, -OCH₃), 4.00 (t, 2H, -CH₂O-), 6.90~7.55 (m, 8H, biphenyl).

Diethyl 4-(4-methoxy-4'-biphenoxyl) butylmalonate (B1)

To a flame-dried 100 ml 3-necked flask equipped with a mechanical stirrer, an addition funnel, a reflux condenser with a drying tube, was added 115 mg (5.0 mmol) sodium particles, 35 ml absolute ethanol was added dropwise, then 0.4 g KI wasn't added until sodium was disappeared. The mixture was stirred and heated to reflux for 10 min., and 800 mg (5.0 mmol) diethyl malonate was added dropwise, the mixture was then refluxed for another 5 min. 1.6 g (4.77 mmol) 4-(4-bromobutoxy)-4'-methoxybiphenyl was added, and the reaction system was refluxed for 6 hr. After evaporation of ethanol, the yellow residue was obtained. The residue was dissolved and extracted with water/chloroform system, the combined organic material was washed with water and dried over anhydrous sodium sulfate. The chloroform was evaporated and crude product was obtained. Recrystallization from ethanol twice obtained white product 1.2 g, yield 61%, m.p. 72 °C (DSC, clear point). ANAL: Calcd C: 69.54%, H: 7.30%; Found C: 70.11%, H: 7.50%.

¹H NMR (CDCl₃, ppm): δ 1.28 (t, 6H, -CH₃), 1.71~2.08 (m, 6H, -CH₂-), 3.28 (t, 1H, -CH=), 3.85 (s, 3H, -OCH₃), 4.05~4.45 (m, 6H, -OCH₂-), 6.91~7.58 (m, 8H, biphenyl).

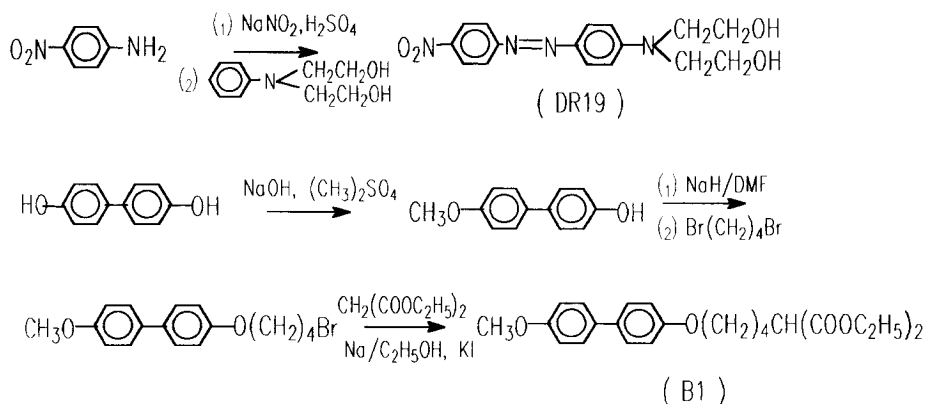
Polymerization

Refer to literature (5), the melt polycondensation was carried out as follows: the mesogenic malonate B1 and the NLO diol DR19 (mol ratio 1:1) were mixed in the two-neck reaction tube. To the melted mixture, 2 drops of a catalyst solution which was composed of tetraisopropyl orthotitanate and diethylene glycol dimethyl ether (vol 1:9) were added under nitrogen, the reaction temperature was maintained 175 °C for 2 hours. After the addition of another 2 drops of the catalyst solution, With a slow nitrogen flow to stir the melt, the reaction mixture was heated to 185 °C, then evacuated and reduced the pressure to 20 mmHg within 3 hr, followed by reducing the pressure to 10 mmHg and raising the temperature to 200 °C within 2 hr. Finally the polycondensation was completed under high vacuum (3 mmHg) and in the optimum temperature 205-210 °C for 2 hr. After completion of the reaction, the cooled product mixture was dissolved in chloroform and filtered, then reprecipitated with acetone. Purification by dissolution in CHCl₃ and reprecipitation with acetone for at least twice resulted in a brown solid product, abbreviated as a code B1-DR19, yield 30%. ANAL: Calcd for (C₃₆H₃₆N₄O₈)_n: C: 66.25%, H: 5.56%, N: 8.58%; Found C: 66.76%, H: 5.57%, N: 8.73%.

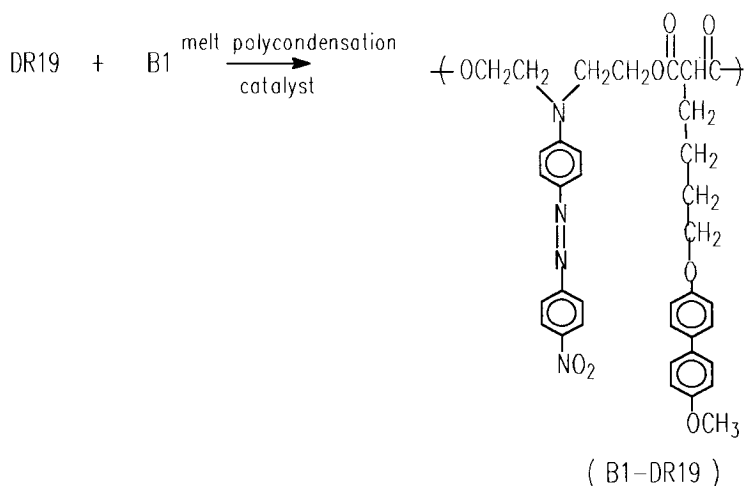
Results and discussion

Synthesis

As shown in Scheme 1, the key step of the synthesis is the monomer B1. Reck et al. (6) reported the synthesis of 6-(4'-methoxybiphenyloxy)-hexylmalonate. In their procedure, the diethyl malonate was first reacted with 1,6- dibromobutane, then reacted with 4-methoxy-4'-hydroxybiphenyl through a Claisen type etherification. Because the two carbon-bromine bonds of α,ω-dibromoalkyl are of the same reaction activity in the first step, the reaction condition must be controlled strictly and the product yield was low. The yield of the second step reaction had reported only 17%. According to our reaction procedure, the yields of both steps were all more than 60% and the reaction conditions were moderate.



Scheme 1 the synthesis of monomers



Scheme 2 Synthesis of liquid crystalline alternate polymalonate

Since the two monomers are all rigid rod-like molecules, the melt polycondensation method was employed, as shown in Scheme 2. The key point here is the controlling of the reaction temperature. Heating step by step was necessary, and the final reaction temperature should not be too low or too high. Otherwise, high molecular weight product can't be achieved or pyrolysis even carbonization will occur.

Infrared Spectroscopy

The principal IR bands (in cm^{-1}) of polymer B1-DR19 and their relative strength are: 2938(s), 2868(m), 2833(m), 1462(m), 1736(vs), 1602(vs), 1500(vs), 1518(vs), 1335(vs), 1237(vs), 1138(vs), 1103(s), 857(s), 822(vs). 1736 cm^{-1} is the typical band for malonate carbonyl C=O stretching, 1518, 1335 cm^{-1} peaks correspond to the asymmetric and symmetric stretching vibration of nitro group respectively. And the strong peak at 822 cm^{-1} reveals the existence of lots of para-substituted benzene rings. Hence from the IR spectra, the polymer structure is consistent with what we have designed.

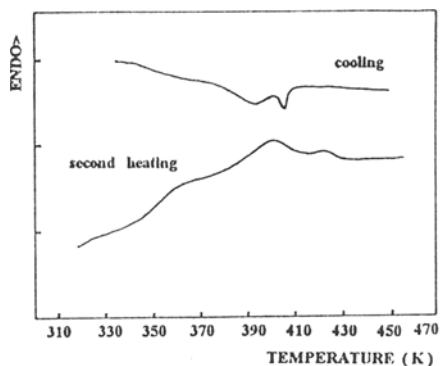


Fig.1 DSC curves of polymer B1-DR19

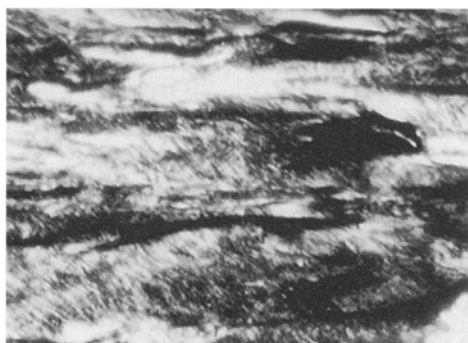


Fig.2 Optical texture of B1-DR19 at 401 K

Thermal analysis

DSC curves of polymer B1-DR19 are shown in Fig 1. The thermal properties and some other basic physical properties are summarized in Table 1. These curves are typical for liquid crystalline DSC curves, some slight super-cooling was found when cooled from the melt. The liquid crystalline temperature interval is 398–420 K from the second heating cycle, and 392–404 K from the cooling curve. The glass transition temperature is 353 K from the heating curve, and that isn't very obvious from the cooling curve.

Table 1. Thermal data and basic properties of B1-DR19

Sample	T_g (K)	T_m (K)	T_i (K)	$[\eta]$ (dl/g) ^a	\bar{M}_n ^b
B1-DR19	353	398(392 ^c)	420(404 ^c)	0.56	5560

a. measured from 0.5g/dl chloroform solution.

b. measured by VPO.

c. data from the cooling curve.

Optical texture analysis

Fig 2 shows polarized optical microphotograph of the polymer B1-DR19 at 401 K, which shows a thread texture. The texture disappeared above 426 K.

Phase behavior in WAXD measurements

Fig 3 represents the powder WAXD pattern of the polymer B1-DR19 quenched from 403 K in the liquid nitrogen, where from 0° to 40° there is only a big broad peak which centered at 20.1°. Therefore combined with the optical texture character, the polymer B1-DR19 is considered a nematic liquid crystalline.

UV-Vis spectroscopy

Fig 4 shows the UV-Vis spectra of both monomers and the polymer. From curves 1, 2 and 4, according to the Beer's Law $A = \epsilon/C$, we calculated that the concentration of B1 unit and of DR19 unit in polymer B1-DR19 is about equal, that is $C_{[B1 \text{ unit}]} \approx C_{[DR19 \text{ unit}]}$. And from the absorption spectra, we found the absorption band near 450 nm which resulted from the chromophore units shifted hypsochromically from 468 nm (DR19

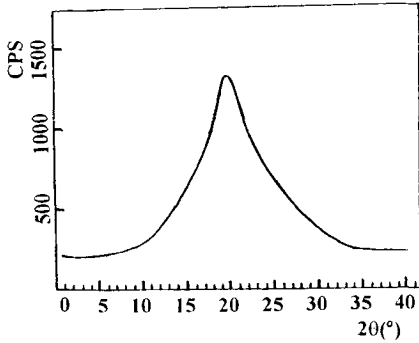


Fig.3 Powder WAXD pattern

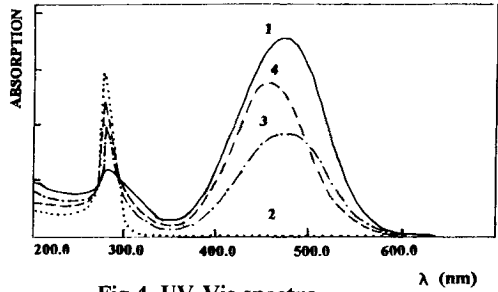


Fig.4 UV-Vis spectra

- 1(—) monomer DR19, 2(····) monomer B1,
 3(- - -) monomer mixture 1/2B1+1/2DR19,
 4(- · - ·) polymer B1-DR19.

monomer and the monomer mixture) to 442 nm (polymer B1-DR19), this presumably due to some interactions caused by attachment of the chromophores to the polymer backbone, maybe the possible charge transfer interactions between the two different side groups operate. This kind of hypsochromic shift was also reported in the copolymer of 4'-amino-4-nitroazobenzene by Robello (7).

Conclusion

A new polymalonate with both a LC unit and a NLO unit pendent in the side group has been synthesized successfully. This polymer is a nematic LC in a proper temperature interval, and the absorption bands of the chromophore units in the UV-Vis spectra shift hypsochromically obviously.

References

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