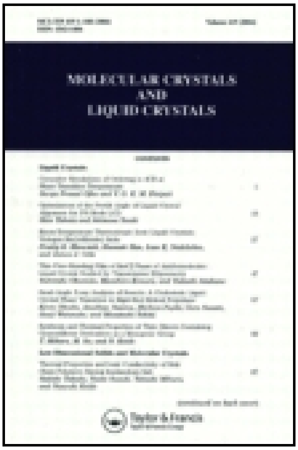

Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics

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Side Chain Polymalonate Liquid Crystals for Nonlinear Optics

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SIDE CHAIN POLYMALONATE LIQUID CRYSTALS FOR NONLINEAR OPTICS

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Abstract Three series of malonate side chain liquid crystalline polymers designed for use in nonlinear optics have been synthesized and their thermal behavior examined. All nine polymers are enantiotropic mesogens. Thermal annealing in the mesophase can increase the mesophase-isotropic temperature presumably by continued polymerization during annealing. The pyridine compounds, compared to the analogous benzene compounds, have greater mesomorphic thermal stability and show a greater tendency for smectic phases.

INTRODUCTION

Ultrafast modulation of a light signal in an intelligent manner represents the goal of state-of-the-art photonics research and development with optical computing and high speed telecommunications among attractive technologies for such devices.[1] Researchers are turning to organic nonlinear optical (nlo) materials as the medium of choice for interaction with an optical field to produce the modulation effect.

In the dipolar approximation the polarization of a molecule in an electric field can be expressed by a power series as shown below.

$$P = \alpha \cdot E + \beta \cdot E \cdot E + \gamma \cdot E \cdot E \cdot E + \dots$$

E is the strength of the electric component of the electromagnetic field; alpha is the linear polarizability; beta, the quadratic hyperpolarizability; gamma, the cubic hyperpolarizability, etc. Upon scaling from the microscopic level to the macroscopic, i.e., a crystal, the appropriate expression becomes

$$P = P_o + \chi^1 \cdot E + \chi^2 \cdot E \cdot E + \chi^3 \cdot E \cdot E \cdot E + \ldots$$

Where Po is the spontaneous polarization; χ^1, χ^2 and χ^3 are the macroscopic counterparts to α, β, and γ, respectively. The odd order chi's are not symmetry dependent and are non-vanishing for all materials. Even order chi's are symmetry dependent and are zero for centrosymmetric media. A challenge therefore is to modify an otherwise centrosymmetric system having a large beta to render it capable of exhibiting second harmonic generation. In previous papers we[2,3] and, separately, others[4,5] have described some of the advantages of liquid crystalline polymers in this regard. One of the key aspects of our work is the use of chirality[2,3] to produce a formally noncentrosymmetric medium. Electric field poling to obtain dipolar alignment can be used in conjunction with chirality or on achiral materials.

This paper describes polymerization details and characterization of the resulting polymers in which the pendant aromatic moiety of a side chain liquid crystalline polymer serves as both the mesogenic group and as the nonlinear optical species. In order to conveniently incorporate the nitroaromatic moiety into a polymer, a polycondensation route first described by Reck and Ringsdorf[6] was employed. Structures for these polymers are given on the next page.

EXPERIMENTAL

IR spectra were recorded on a Perkin-Elmer 567 spectrophotometer or a Nicolet 5 DX Fourier Transform infrared spectrophotometer. Proton NMR spectra were obtained on a Varian EM 360 A 60 MHz spectrometer using tetramethylsilane (TMS) as an internal reference. UV-Vis spectra for these materials have been reported previously[2] and will not be repeated here. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tennessee. Polymer inherent viscosities were measured in a chloroform solution by using a Blue M Magni Whirl constant temperature (25°C) water bath and an Ubbelohde viscometer (Ace Glass, size 0.6mm). Mesophase characterization was determined microscopically using a Reichert Thermovar microscope while samples were heated in a Mettler FP52 microfurnace

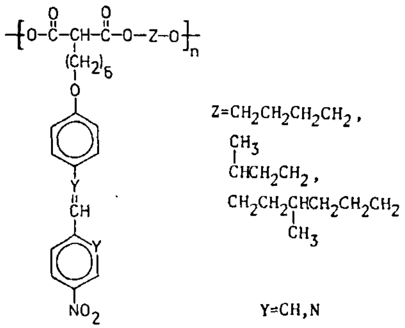


FIGURE 1. Polymalonate Mesogens.

attached to a Mettler FP5 control unit. Mesophases were identified based upon their optical textures. Differential scanning calorimetric data was obtained using a Du Pont 9900 Thermal Analysis System with a model 910 DSC cell. A nitrogen atmosphere was employed and a twenty degree per minute scan rate was used. Synthesis of the malonate monomers and their liquid crystalline properties will be the subject of a separate paper. The only diol used which was not commercially available is described below.

R(+)-3-Methyl-1,6-hexanediol

A literature procedure was adapted for this preparation.[7] A solution of lithium aluminum hydride (6.0g, 0.158mol) in dry ether (240ml) was placed in a one-liter three-necked round bottom flask; equipped with a reflux condenser, a dropping funnel, and a mechanical stirrer. The reaction flask was protected from moisture until completion of the reaction by attaching calcium chloride tubes to the openings. Through the dropping funnel, a solution of R(+)-3-methyladipic acid (10.14g, 0.063mol) in dry ether (100ml) was added while stirring at a rate so as to produce gentle reflux. One hour after the addition had been completed, and with constant stirring, water (30ml) was added cautiously to decompose excess lithium aluminum hydride. Then 10% (v/v) sulfuric acid (200ml) was added slowly, whereupon a clear solution resulted. The contents of the flask were transferred to a separatory funnel and the ether layer separated. The aqueous layer was extracted with ether (2 x 50ml). The combined ether extracts were washed with 10% sodium hydroxide solution (140ml) to remove the unreacted acid. The ether layer was dried over anhydrous magnesium sulfate. After filtration, the ether was evaporated and the residual oil was vacuum distilled at 140-150°C (bath temperature)/2 torr. The yield of the colorless diol was 2.65g (32%).

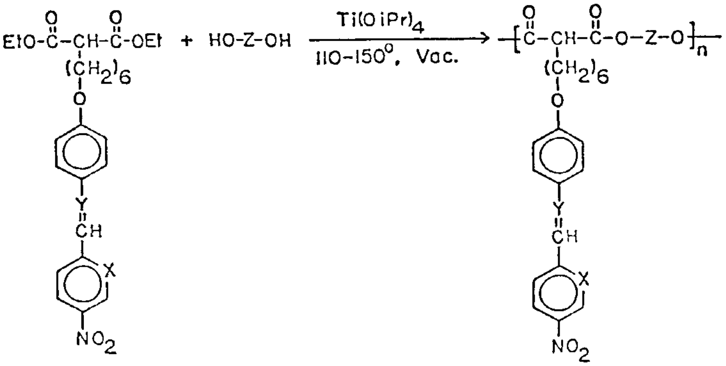
FTIR (neat): cm^{-1} 3628-3017(bd), 2964, 2944, 2864, 1456, 1377,1058, 1018.

^{1}H-NMR ($CDCl_3$): δ 0.78-1.08 (d,3H), 1.08-1.80 (m,7H), 3.13-3.80 (m,6H).

Elemental analysis for $C_7H_{16}O_2$
Calc. % C 63.60, H 12.12
Found % C 63.25, H 12.02

Polymerizations

All the nine polymers (1-9) were prepared by the same polymerization technique. Only the general procedure will be described here: The appropriate malonate monomer (4mmol) and the appropriate diol (4.8mmol of 1,4-butanediol, 4.8mmol of S(+)-1,3-butanediol, or 4mmol of R(+)-3-methyl-1,6-hexanediol) were weighed in a 25ml round bottom flask which was then fitted with a 2-neck tube. One of the necks was stoppered with a rubber septum and secured with copper wire. Through the septum a long 18-gauge stainless steel needle was inserted for nitrogen supply. The second neck of the tube was used for applying vacuum. The flask was immersed in an oil bath and the reaction mixture was heated to melting (110-120°C) while blowing dry nitrogen through the needle. Then the needle was immersed in the melt and one drop of titanium (IV) isopropoxide was injected through the septum. The reaction was carried out at atmospheric pressure for 18-22 hours, at the initial temperature setting, while using a slow nitrogen flow to stir the melt. Subsequently, low vacuum (20 torr) was applied for 8-9 hours and the temperature was raised 5-10°C. Finally, high vacuum (2 torr) was used and the temperature was raised 5-10°C at a time until the optimum temperature (130-150°C), keeping the reaction at each temperature setting for a few hours. After completion of the reaction, the cooled product mixture was dissolved in chloroform (25ml) and filtered. The polymers were reprecipitated with a nonsolvent such as methanol or diethyl ether. Dissolutions in chloroform and reprecipitations were repeated until no monomers or oligomers could be detected by TLC on alumina (50% ethyl acetate + 50% hexane). The polymers were dried in a vacuum dessicator. Yields varied from 15-70% (low yields for polymers with 1,3-butanediol).



(1) X = CH, Y = CH, Z = $-CH_2CH_2CH_2CH_2-$
(2) X = CH, Y = CH, Z = $-CH_2CH_2CH(CH_3)-$
(3) X = CH, Y = CH, Z = $-CH_2CH_2CH(CH_3)CH_2CH_2CH_2-$
(4) X = CH, Y = N, Z = $-CH_2CH_2CH_2CH_2-$
(5) X = CH, Y = N, Z = $-CH_2CH_2CH(CH_3)-$
(6) X = CH, Y = N, Z = $-CH_2CH_2CH(CH_3)CH_2CH_2CH_2-$
(7) X = N, Y = N, Z = $-CH_2CH_2CH_2CH_2-$
(8) X = N, Y = N, Z = $-CH_2CH_2CH(CH_3)-$
(9) X = N, Y = N, Z = $-CH_2CH_2CH(CH_3)CH_2CH_2CH_2-$

FIGURE 2. Polymerization Scheme for Polymers (1-9).

For DSC studies samples were, on the first run, heated just above the isotropic temperature, then cooled to -50°C using liquid nitrogen, and rerun. All values, DSC peak maxima, quoted reflect second runs. The mesophase formed from the isotropic phase upon cooling was held isothermally for extended periods until the development of a characteristic, identifiable optical texture. The isotropization temperatures quoted reflect the highest temperature of the mesophase-isotropic transition (disappearance of mesophase) observed under a polarizing microscope.

Polymer 1

IR (KBr): cm^{-1} 2958, 2880, 1735, 1595, 1516, 1480, 1400, 1348, 1260, 1184, 1116, 850.

^{1}H-NMR ($CDCl_3$): δ 1.05-2.22 (m,15H), 3.33 (t,1H), 3.75-4.48 (m,6H), 6.63-7.75 (m,8H), 8.13 (d,2H, J=17Hz).

Elemental analysis for $C_{27}H_{31}NO_7$
Calc. % C 67.34, H 6.49, N 2.91
Found % C 67.48, H 6.54, N 3.14
η_{inh} 0.11 dl/g

Polymer 2

IR (KBr): cm^{-1} 2910, 2870, 2810, 1710, 1680, 1545, 1470, 1430, 1300, 1075, 810.

^{1}H-NMR ($CDCl_3$): δ 1.05-2.20 (m,15H), 3.33 (t, 1H), 3.75-4.40 (m,5H), 6.68-7.72 (m,8H), 8.17 (d,2H, J=17Hz).

Elemental analysis for $C_{27}H_{31}NO_7$
Calc. % C 67.34, H 6.49, N 2.91
Found % C 67.14, H 6.43, N 2.85
η_{inh} 0.12 dl/g

Polymer 3

IR (KBr): cm^{-1} 2915, 2875, 1735, 1562, 1485, 1440, 1315, 848, 816.

^{1}H-NMR ($CDCl_3$): δ 0.80-2.17 (m,20H), 3.33 (t,1H), 3.80-4.38 (m,6H), 6.70-7.67 (m,8H), 8.15 (d,2H, J=17Hz).

Elemental analysis for $C_{30}H_{37}NO_7$
Calc. % C 68.81, H 7.12, N 2.67
Found % C 68.54, H 7.05, N 2.86
η_{inh} 0.27 dl/g

Polymer 4

IR (KBr): cm^{-1} 2895, 2810, 1715, 1700, 1596, 1574, 1550, 1490, 1442, 1315, 1215, 1140, 830.

^{1}H-NMR ($CDCl_3$): δ 1.13-2.20 (m,14H), 3.38 (t, 1H), 3.63-4.47 (m,6H), 6.77-7.47 (m,4H), 7.87- 8.47 (m,4H), 8.57 (s,1H).

Elemental analysis for $C_{26}H_{30}N_2O_7$
Calc. % C 64.72, H 6.26, N 5.80
Found % C 63.91, H 6.47, N 5.63
η_{inh} 0.14 dl/g

Polymer 5

IR (KBr): cm^{-1} 2894, 2805, 1730, 1712, 1702, 1595, 1570, 1550, 1490, 1320, 1220, 1080, 830.

^1H-NMR ($CDCl_3$): δ 1.03-2.13 (m,15H), 3.32 (t,1H), 3.73-4.40 (m,5H), 6.73-7.40 (m,4H), 7.80-8.40 (m,4H), 8.50 (s,1H).

Elemental analysis for $C_{26}H_{30}N_2O_7$
Calc. % C 64.72, H 6.26, N 5.80
Found % C 64.23, H 6.80, N 5.58
η_{inh} 0.067 dl/g

Polymer 6

FTIR (neat): cm^{-1} 2930, 2864, 1728, 1623, 1600, 1578, 1519, 1503, 1469, 1343, 1246, 1161, 855.

^1H-NMR ($CDCl_3$): δ 0.68-2.17 (m,20H), 3.33 (t,1H), 3.75-4.38 (m,6H), 6.72-7.40 (m,4H), 7.85-8.38 (m,4H), 8.53 (s,1H).

Elemental analysis for $C_{29}H_{36}N_2O_7$
Calc. % C 66.39, H 6.92, N 5.34
Found % C 65.91, H 6.83, N 5.14
η_{inh} 0.17 dl/g

Polymer 7

IR (KBr): cm^{-1} 2960, 2880, 1730, 1630, 1610, 1572, 1516, 1478, 1400, 1355, 1265, 1175, 1116, 1025, 842.

^1H-NMR ($CDCl_3$): δ 1.20-2.50 (m,14H), 3.35 (t,1H), 3.85-4.30 (m,6H), 6.77-7.83 (m,4H), 8.23-8.73 (m,3H), 9.45 (s,1H).

Elemental analysis for $C_{25}H_{29}N_3O_7$
Calc. % C 62.10, H 6.05, N 8.69
Found % C 63.55, H 6.24, N 9.58
η_{inh} 0.06 dl/g

Polymer 8

Because of limited quantity of this material only DSC, optical microscopy, and UV-Vis data could be obtained.

Polymer 9

IR (KBr): cm^{-1} 2940, 2880, 1730, 1570, 1510, 1470, 1355, 1025, 840.

^1H-NMR ($CDCl_3$): δ 0.78-2.17 (m,20H), 3.33 (t,1H), 3.78-4.38 (m,6H), 6.75-7.52 (m,4H), 8.22-8.75 (m,3H), 9.47 (s,1H).

Elemental analysis for $C_{28}H_{35}N_3O_7$
Calc. % C 63.99, H 6.71, N 7.99
Found % C 64.15, H 6.63, N 7.68
η_{inh} 0.112 dl/g

RESULTS AND DISCUSSION

All nine of these polymers are enantiotropic mesogens. In contrast to vinyl liquid crystalline side chain polymers which have a simple thermal behavior[8], these polyesters can exhibit complex solid state thermal transitions. Presumably, the polymalonate main chain contributes to the polymer thermal properties. Our preliminary report on these polyesters[2] noted this complexity, but did not detail the thermal behavior of these materials. Table I presents the results of DSC and optical microscopy on these polymers.

TABLE I Thermal Data for Polymalonates

Polymer	DSC Endotherms (Maxima)	Fluidity Temp.	Mesophase-Isotropic Temperature		
			Initial[a]	2nd Heating[b]	3rd Heating[c]
1	40, 54, 87, 109	91	106.5	121.8	N 122.8 I
2	39, 94 baseline shift, 60	65	88.5	91.8	S_A* 92.6 I
3	23, 43, 65	49	71.5	72.8	N* 73.3 I
4	32, 70 baseline shift, 20	32	62.0	81.6	N 85.9 I
5	48 baseline shift, 5	5[d]	52.9	53.8	N* 53.8 I
6	30 baseline shift, 10	10[d]	33.5	35.5	N* 35.9 I
7	43, 86	92	131.2	141.0	S_A 142.2 I
8	42 baseline shift, 70	45	71.4	72.4	S_A* 74.2 I
9	28, 70 baseline shift, 11	40	68.0	71.9	S_A* 73.2 I

All temperatures in degrees Celsius

a) First heating after initial sample preparation.
b) After two hours at annealing temperature.[e]
c) After four hours at annealing temperature.[e]
d) Glass transition temperature taken from DSC
e) Annealing temperature approximately ten degrees below initial isotropization temperature.

Endothermic maxima from DSC measurements, fluidity temperatures (first visible flow under stress), and the effect of annealing on the isotropization temperature (optically determined) are given. DSC values were taken from second, or subsequent, heating cycles. A clearly defined glass transition was evident only for two polymers, 5 and 6. Baseline shifts were seen for several other polymers but were not unambiguously identifiable as glass transitions. As can be seen from the table, there is only a rough correlation between fluidity temperatures and DSC thermal events. Figure 3 shows DSCs for polymers two and five. Polymer 2, top, has a complex first thermal cycle which becomes much simpler on the second heating. Polymer 5, bottom, shows only a simple glass transition followed by a clearing transition upon further heating on its second

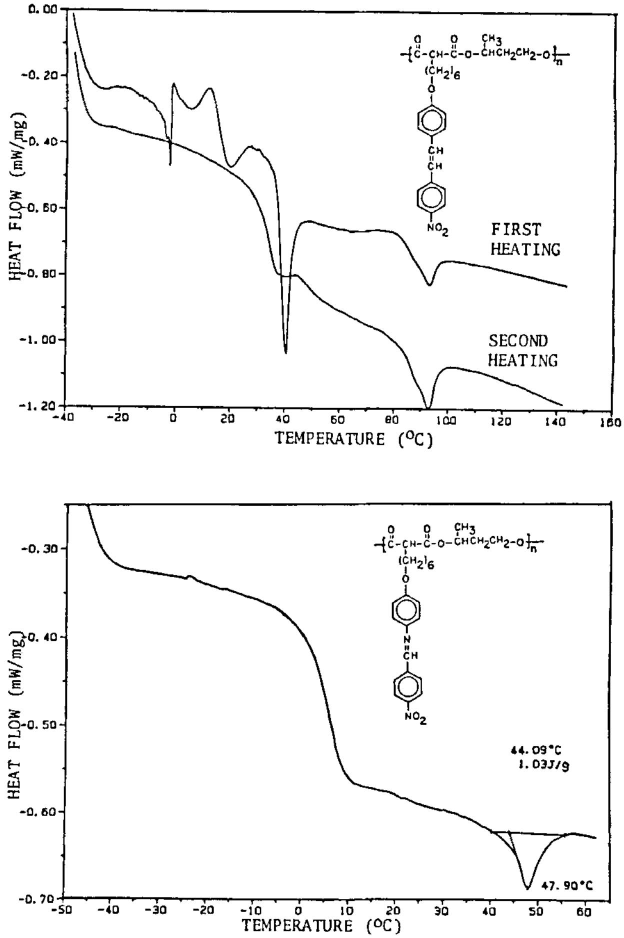


FIGURE 3. DSC Curves for Polymers 2 and 5

heating cycle. For all nine polymers the second and subsequent heating cycles are considerably less complex than the first heating curve.

These polyesters are prepared by a transesterification reaction which can continue after the nominal polymerization reaction is stopped. It is clear that the mesophase-isotropic temperature increases with increasing annealing time at elevated temperatures. We attribute this increase in isotropization temperature (seen to at least some extent in all samples) to an increase in polymer molecular weight during annealing.

From data in Table I it is seen that both chain branching and chain lengthening in the diol component lead in general to lower mesophase thermal stability. Of particular interest is the pronounced tendency for the pyridine imines to form smectic A phases; much more so than the analogous benzene imines. The strong lateral dipole of the pyridine ring is thought responsible for the smectogenic behavior of these polymers. All these polyesters can be mechanically stressed to give a transparent film between glass surfaces. Measurements of their nonlinear optical properties are currently in progress.

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