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Synthesis and Characterisation of Liquid Crystalline Polymers for Nonlinear Optical Applications

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A series of side chain liquid crystalline polymers based on a polystyrene backbone has been synthesized and characterized for non-linear optical applications.

Keywords: liquid crystal polymers, non-linear, optical, polystyrene

INTRODUCTION

Organic molecules, polymers and liquid crystalline polymers have generated considerable interest[1,2] as potential materials for nonlinear optical applications. The advantages of organic materials include increased speed of nonlinear response, whereas polymers also offer improved physical and mechanical properties for ease of fabrication. Side chain liquid crystalline polymers combine the above advantages with a potential for enhanced alignment on poling and a resultant more efficient response.

A molecular engineering approach was adopted to design polymers which would be both liquid crystalline and exhibit a large molecular second order hyperpolarisability. This involves separating the polymer into 3 separate units namely the backbone, spacer group and pendent chromophore.

The backbone confers polymeric properties to the material and can be chemically modified to improve such properties as glass transition (T_g) and optical transparency. A high glass transition (>100°C above ambient) is essential to reduce the thermal relaxation of the induced non-centrosymmetric structure obtained from electric field poling of thin films. Use of a stiff backbone can increase both T_g and the smectic character of the pendent groups. A low dielectric constant can result in improved optical properties.

The spacer group length regulates the decoupling of the pendent chromophore from the backbone and can also act as a plasticising agent lowering T_g. A long spacer group allows the chromophores to be relatively independent of the backbone

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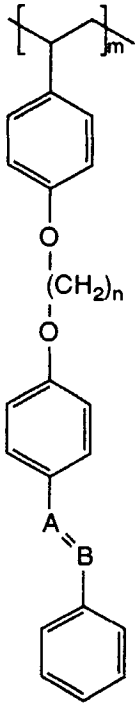
and hence the phase transitions resemble that of the side chain low molar mass analogue. However, as the chromophore becomes more detached from the backbone, the glass transition is lowered. A short spacer length results in less organizational freedom and hence the chromophore phase transitions are influenced more by the backbone.

The chromophore group dictates both the nonlinear efficiency and liquid crystallinity. Molecular characteristics such as rigidity, rod-like shape, permanent dipole moment and a high level of polarizability increase both nonlinearity and enhance liquid crystalline stability. In addition it has been shown[1,2] that a conjugated π-electron donor-acceptor system along the molecular axis, greatly increases the second order nonlinear efficiency. The chromophore group also has an effect on the polymer solubility and other physical properties.

With these criteria in mind, it was decided initially to synthesise a series of polymers with the following general structure. As is shown, the backbone chosen was polystyrene. This fulfils the criteria described earlier of good optical transparency, low dielectric constant[3] and generation of a relatively high glass transition. The polystyrene system also has good film forming properties and is chemically stable.

Polymer structure

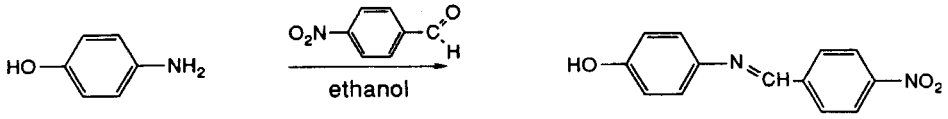


Polymer	n	A	B
P(1)	6	CH	CH
P(2)	6	N	CH
P(3)	6	N	N
P(4)	8	CH	CH
P(5)	8	N	CH
P(6)	8	N	N
P(7)	10	CH	CH
P(8)	10	N	CH
P(9)	10	N	N
P(10)	3	N	N

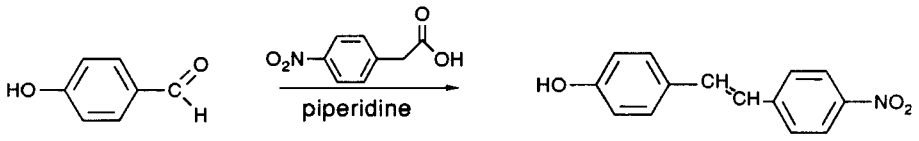
The spacer group was a methylene unit chain of varying length.

The chromophore chosen had an alkoxy donor group, a nitro acceptor group and two conjugated aromatic rings linked by either an azo, stilbene or imine group. This system was chosen as it has a λ max of around 380 nm and should exhibit little optical or nonlinear dispersion in the visible and near infrared frequency range.

Due mainly to the oxidising and chain transfer nature of the nitro group, the propagation of free radicals in inhibited; therefore vinyl monomer units proved difficult to polymerise by a radical route. Instead a grafting technique was applied to functionalise poly-4-hydroxystyrene with an alkyl bromo chromophore containing unit. This is outlined in the following reaction schemes.



SCHEME 1



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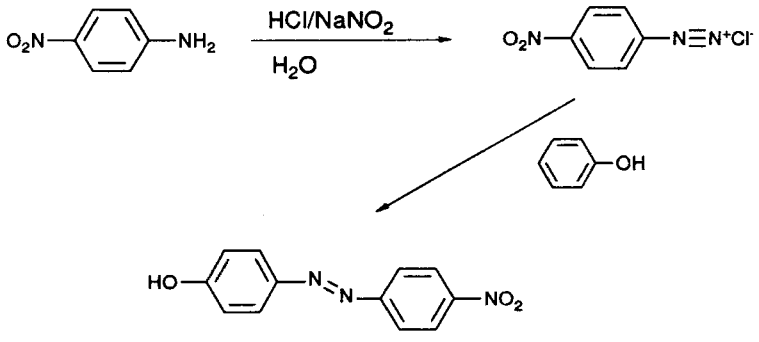

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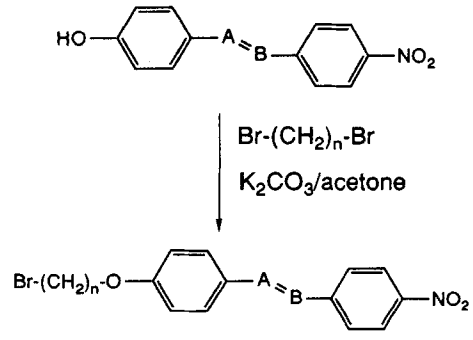

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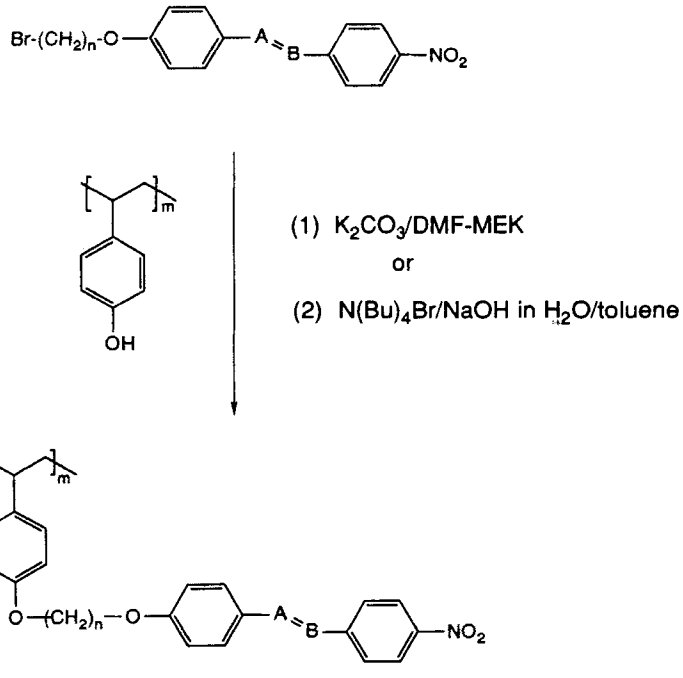
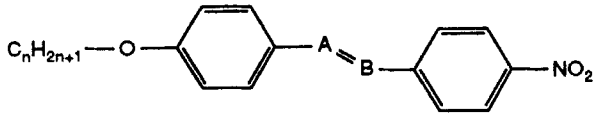


SCHEME 5

Low molar mass analogues of the side chain pendent groups were also synthesised and a comparison with their counterparts made.

Low Molar Mass Analogue



EXPERIMENTAL

N-(4-Nitrobenzylidene)-4'-hydroxyaniline (1)

4-Aminophenol (65.0 g, 0.896 mol) and 4-nitrobenzaldehyde (90.0 g, 0.896 mol) were dissolved in ethanol (400 ml) and heated under reflux for 2 h. The resultant solution was cooled, the precipitated product filtered and recrystallised from toluene. Yield 126.0 g, 67% m.p 175°C.

4-Hydroxy-4'-nitrostilbene (2)

4-Nitrophenylacetic acid (9.05 g, 52.1 mmol) was heated with 4-hydroxybenzaldehyde (12.0 g, 52.1 mmol) and 2.5 ml piperidine for two h at 140°C. TLC analysis showed several distinct products had been formed. The target material was isolated by silica gel chromatography using dichloromethane as both solvent and eluant, followed by recrystallisation from ethanol. Yield 3.9 g 19% mp 205°C.

4-(4'-Hydroxyphenylazo)nitrobenzene (3)

4-Nitroaniline (20.0 g, 0.145 mol) was added to a stirred solution of conc HCl (50 ml) and H_2O (50 ml). The temperature was maintained at below 10°C using an ice/salt bath. To this, a solution of $NaNO_2$ (10.0 g, 0.145 mol) in H_2O (30 ml) was added and the solution kept cold by the additions of portions of crushed ice. The reaction was monitored by potassium iodide-starch paper. A solution of phenol (13.6 g, 0.145 mol) and NaOH (28 g) in H_2O (100 ml) was cooled in ice and slowly added to the diazonium salt with stirring. The reaction was immediate and the resultant solution was acidified with conc HCl. The organic product formed was filtered, dried then recrystallised from methanol to yield dark red crystals. Yield 23.0 g 65% mp 218°C.

N-(4-Nitrobenzylidene)-4'-(6-bromohexyloxy)aniline

The phenolic imine (1) (40.0 g, 0.165 mol) and excess of K_2CO_3 were stirred in acetone and the purple potassium salt of the phenol was formed. To this, α,ω-dibromohexane (421 g, 1.65 mol) was added and the mixture was heated under reflux overnight. The reaction mixture was filtered to remove any inorganic solids and the solvent evaporated. Most of the excess of α,ω-dibromohexane was then recovered by vaccuum distillation whilst the resultant product was added to cyclohexane (400 ml). Yellow crystals formed which were recrystallised from ethanol. Yield 55.7 g 83% mp 96°C.

Preparation of polymer P(1) by phase catalysis[4]

To a solution of poly-4-hydroxystyrene (0.92 g, 7.66 mmol) and 4-(6-bromohexyloxy)-4'-nitrostilbene (prepared as above) (3.5 g, 8.94 mmol) in toluene was added NaOH (0.22 g, 8.63 mmol) and tetra-n-butylammonium bromide (0.123 g, 5.46 mmol) in H_2O. The reaction was carried out under reflux for 2 days, cooled to room temperature and poured into chloroform. This was then washed with water, dried over $MgSO_4$ and the solvent evaporated under reduced pressure to leave a

glassy solid. The unreacted chromophore was washed from the polymer overnight in a soxhlet extractor with methanol as the solvent. Purification was then carried out by repeated reprecipitation from a filtered (10 μm millipore) solution in THF into methanol. Yield 1.06 g, 32%.

Preparation of polymer P(2)

Poly-4-hydroxystyrene (0.92 g, 7.66 mmol) and the bromoimine (4) (3.5 g, 8.94 mmol) were dissolved in MEK and to this solution was added excess of K_2CO_3 (10 g). The resultant mixture was heated under reflux then cooled, hot filtered and the solvent evaporated under reduced pressure. Purification was carried out as above. Yield 1.53 g, 46%.

The polymer was supplied with a molecular weight of 30,000. Functionalisation was checked by ^{1}HNMR and chemical analysis, and in all cases was found to be around 100%. GPC analysis of the final polymer was unhelpful as the sample could not be calibrated with a known standard.

TABLE

Polymer	T_g°C	Phase	T_{cl} °C	ΔH_{cl} mol^{-1}	λmax(nm) (THF)	β†	Low Molar Mass Equivalent (°C)
P(1)	85	S_A	165	2.2	378	29.1	K105N106I
P(2)	75	S_A	118	3.4	377	21.6	K89I
P(3)	85	S_A	151	1.7	378	28.9	K98N100I
P(4)	65	S_A	159	3.8	378	29.3	K111S_A111N114I
P(5)	65	S_A	119	4.8	377	16.0	K63S_A78N86I
P(6)	70	S_A	151	3.6	378	28.5	K86S_A96N98I
P(7)	50	S_A	155	4.4	378	24.2	K97S_A116I
P(8)	40	S_A	101	4.1	377	17.2	K66S_A93I
P(9)	50	—	—	—	378	23.5	K90S_A97I
P(10)	90	—	—	—	378	31.2	—

† $\times 10^{-30}$ cm^{5}esu at 1.91 μm. β values were estimated by a solvatochromic technique using the solvent shift between THF and hexane.

OPTICAL MICROSCOPY

In general, textural analysis of the polymers was very difficult, due mainly to the high viscosities of the polymers even just below the clearing point. This is typical of high molecular weight smectic polymers. After periods of annealing of up to 3 days at temperatures of about 1°C below T_{cl}, small textural regions could be seen for stilbene and imine polymers with 10 methylene unit spacer length. These both exhibited the distinctive focal conic texture of the S_A phase. For the other polymers only a fine grained texture was observed. All polymers were birefringent below a reversible clearing temperature indicating some degree of anisotropy and is itself evidence of liquid crystallinity. This occurred even for P(9) which did not show a distinctive melt.

DIFFERENTIAL SCAN CALORIMETRY

All the polymers exhibit a glass transition and all except P(9) and P(10) exhibit a melting endotherm at the clearing temperature. The glass transitions were observed to decrease as the methylene spacer group increased. For example, P(1) with a six carbon spacer group has a T_g of 85°C, whereas the ten carbon spacer equivalent P(3) has a T_g of only 50°C. (Note, the unfunctionalised poly-4-hydroxystyrene has a glass transition of 120°C.) This trend is caused by internal plasticisation by the spacer group.

The stilbene polymers all exhibited the highest clearing temperatures when compared to azo and imine polymers of equivalent spacer length. This has been shown to be similar to their low molar mass analogues. In general, as the spacer length increased, a slight decrease in the clearing temperature was observed, indicating a slight lowering of mesophase stability.

No crystallization transitions were observed. Examination of the values obtained for heats and entropies of the clearing transition show that they increase as the length of spacer group increases. This has also been reported by Wunderlich *et al.*,[5] and is believed to be due to an increase in decoupling of the mesogens from the main chain. The results also agree with other smectic polymer systems in that both heats and entropies of transition are much higher than nematic polymers. This is due to a large increase in disorder at the clearing temperature in going from a highly ordered smectic state to the disordered isotropic state. The transition values from nematic to isotropic states are much smaller as the nematic state is less ordered.

The polymers were all tested as a thin film on the pan base prepared by heat treatment, and the glass transition was taken as the point of inflection of the DSC curve.

X-RAY ANALYSIS

Sample X-Ray Results

Sample	Temp°C	Phase Comments	*d* spacings *A*°
P(1)	100	S_A or S_C	36.7
P(1)	140	S_A or S_C	36.1
P(8)	115	S_A or S_C	—
P(8)	146	S_A or S_C	—
P(10)	75	S_A or S_C	
P(10)	100	No sharp peaks, nematic or amorphous	

X-ray photographs were taken of fibres pulled from the mesophases of the polymers by tweezers. Any small angle reflections in the form of identifiable spots, crescents or rings would identify a smectic phase from a nematic. Photographs were also taken of unoriented samples quenched from the mesophase to freeze the structural order into the glassy state.

The diffraction photographs obtained showed mainly a diffuse halo (or partial crescents in ordered fibres) at wide angles. This corresponded to a distance of about 4.4 *A*° and is related to the spacings between the parallel mesogens.

At small angles, all polymers tested, except P(10), exhibited an inner ring corresponding to reflections between the regularly packed smectic layers. In all cases, the layer thickness was greater than the calculated chain lengths implying that a bilayer structure exists. This is thought to be due to the antiparallel interdigitised alignment favoured by highly polar mesogens and has also been observed by other research workers.[6] Although fibres were pulled from the mesophase, no great ordering was achieved.

UV-VIS AND SOLVATOCHROMISM

Within the limits of accuracy of the experiment, it was shown that both the azo and stilbene link units exhibit a greater solvatochromic shift than their imine counterpart. This manifests as a larger molecular hyperpolarisability and is due to the two aromatic rings being twisted out of plane, thus reducing the π-orbital overlap.

All polymers have similar absorption maxima. The azo polymers however have larger oscillator strengths and a larger tail into the lower energy wavelengths. This gives rise to their red colour in comparison to the yellow of both the stilbene and imine analogues.

THIN FILMS

The evaluation of the thin film properties of these materials is in its early stages, but some results can be reported

Loss Measurements

Sample	n_{1047}	Scatter loss ($dBcm^{-1}$)	n_{1321}	Scatter loss ($dBcm^{-1}$)
P(1)	1.65	20	1.633	7
P(3)	1.65	high	1.631	high
P(9)	1.62	very high	—	very high
P(10)	1.63	8	1.612	3

The polymers were extremely soluble in organic solvents such as chloroform and cyclopentanone (over 30% w/v) and were spin-coated to give good quality films. Loss measurements were carried out and indicated that as the spacer length increased, so did the loss. This was felt to be due to scatter at liquid crystalline domain boundaries. For the 3 methylene unit spacer P(10), a loss of 3 $dBcm^{-1}$ was observed. However as the polymers were heated above their T_g they became opaque on the formation of their liquid crystalline phases.

SHG Measurements

Sample	Optimum poling temperature (°C)	Maximum d_{33} during poling (pmV^{-1})
P(1)	50	8.4
P(2)	50	1.1
P(10)	50	1.4

Some preliminary measurements on electric field induced orientation of these polymers has been carried out. Poling of the films was carried out by corona discharge of -12 kV (1 cm from film). Optical nonlinearity was determined by *in situ* Maker fringe analysis at 1.319 μm during poling. The d_{33} coefficients (measured in the direction of poling) reflected a number of competing factors. Those included chromophore number density, its effective hyperpolarisability and also film quality and conductivity. For this work it seems apparent that the films must be scrupulously dried and free from inorganic ions which can lead to dielectric breakdown. This work is continuing.

Acknowledgment

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