Synthesis and characterisation of laterally substituted noncentrosymmetric main chain hydrogen-bonded polymers

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A series of laterally substituted noncentrosymmetric hydrogen-bonded liquid crystalline polymers which incorporate stilbazole acceptor units, alkyl or ethylene glycol linkers units, and benzoic acid or phenol donor units were prepared and investigated for their hydrogen bonding behaviour and phase transitions. Fourier transform infrared (FTIR) indicated that these polymers possess strong intermolecular donor–acceptor hydrogen bonding. These polymers have lower melting points than their non-substituted analogue, and some of the polymers are mesomorphic.

Keywords: hydrogen bonding; liquid crystalline polymers; polymorphism

1. Introduction

Polar materials have numerous applications including nonlinear optics,[1–4] piezoelectrics[5–7] and pyroelectrics.[8,9] For these applications, poled organic thin films have several advantages over traditional inorganic polar crystals including ease of processing,[10] larger second order susceptibilities,[11] an intrinsically low dielectric constant[10] and significantly faster responses.[12–15] One of the largest obstacles in the fabrication of polar organic materials is obtaining an acentric (polar) order in the material.[16] Main chain hydrogen-bonded liquid crystals are ideal for these films due to their tunable properties[17,18] and high quality polymer films formed by self-assembly of the monomer units.[19,20] Additionally, the inherent order in the liquid crystalline phase[21,22] of these polymers can aid in the polar alignment of these polymer chains.

The fields of dimeric and trimeric hydrogen-bonded liquid crystals have been extensively researched and several reviews have been published on these topics.[23–25] Hydrogen-bonded liquid crystals have been formed from self-dimerisation of molecules.[26–28] 1:1 dimeric hydrogen bond donor: hydrogen bond acceptor complexes,[29–33] as well as complexes formed from bifunctional hydrogen bond acceptors with monofunctional hydrogen bond donors[34,35] and bifunctional hydrogen bond donors with monofunctional hydrogen bond acceptors.[36,37]

Extensive research has also been focused on the field of hydrogen-bonded liquid crystalline polymers.[38,39] Hydrogen bonding between a liquid crystal and a polymer chain has been used to produce side-chain hydrogen-bonded liquid crystalline polymer.[40–42] Intermolecular hydrogen bonding between difunctionalised hydrogen bond donors and difunctionalised hydrogen bond acceptor molecules has been used to produce centrosymmetric main chain hydrogen-bonded polymers.[43–47]

Fabrication of polar films of side chain hydrogen-bonded liquid crystalline polymers is difficult due to dissociation of the hydrogen bond[48] when the polymer is heated above the glass transition temperature of the polymer. Additionally, the dipoles of the resulting polymer will reorient to a random distribution over time.[16] Centrosymmetric main chain hydrogen-bonded polymers have an average dipole moment of zero along the polymer chain and thus cannot be fabricated into polar films.

Our approach to polar organic films involves polar alignment of noncentrosymmetric main chain liquid crystalline polymers. In the polymers, a hydrogen bond donor and hydrogen bond acceptor are located on the same monomer. When these monomers self-assemble in to polymer chains, all dipoles along the polymer chains point in the same direction; therefore, the chains have a net polarisation.[16]

We have previously synthesised several first generation noncentrosymmetric hydrogen-bonded polymers which incorporate carboxylic acid hydrogen bond donors and stilbazole hydrogen bond acceptors.[16,49] Unfortunately, these polymers have high melting points, low solubilities in organic media and only a
few possesses a liquid crystalline phase. Our approaches to lowering the melting points of our first generation polymers involve lateral substitution, incorporating glycol chains (as linker units) into the monomer units and incorporating weaker hydrogen bond donors into the monomer unit. These strategies have been shown to be effective in reducing the melting points of liquid crystals.[50–55] Here, we report the effect of lateral substitution and incorporation of glycol linker chains on the intermolecular hydrogen bonding and phase transitions in stilbazole containing noncentrosymmetric main chain hydrogen-bonded polymers.

2. Experimental details
Chemicals were of pure grades and purchased from Fisher, Acros or Aldrich Chemical Company and used as received. Tetrahydrofuran (THF) was distilled over sodium-benzophenone under an argon atmosphere. Dichloromethane was distilled over calcium hydride under an argon atmosphere. Column chromatography was performed using Sorbent Technology 60 Angstrom, 63–200 μm mesh silica. Thin layer chromatography was performed using Whatman flexible plates with a 250 μm layer of fluorescent silica gel (UV254). All final products were dried at appropriate temperatures below their melting or decomposition temperatures in a vacuum oven prior to final analysis.

2.1 Equipment
Infrared spectroscopy was performed on a Thermo-Nicolet Nexus 670-FTIR (Thermo Fisher Scientific) using an Avatar multi-bounce HATR accessory. Differential scanning calorimetry (DSC) was performed on a Mettler Toledo DSC 821e (Mettler-Toledo Inc., Columbus, OH, USA) equipped with a Julabo FT 900 (JULABO USA Inc., Allentown, PA, USA) cooling unit using heating and cooling rates of 10°C/min; all reported transition temperatures are from the second cycle of a DSC scan unless otherwise noted. All DSC transition temperatures reported are the mid-points of the transitions and enthalpies of the transitions are reported in parentheses following the transition temperature. Polarised optical microscopy was performed using an Olympus BXP polarising microscope (Olympus Inc., Center Valley, PA, USA) equipped with an Instec HCS400 (Instec Inc., Boulder, CO, USA) heating stage. Heating and cooling rates varied between 1°C/min and 5°C/min.

2.2 Preparation of model mixtures
A total of 50–100 mg of one component was weighed into a vial. The appropriate amount of the second component (to obtain the desired mole ratio) was weighed into the vial. The vial was immersed in a silicon oil bath (150°C) until the contents were visibly melted. The vial was removed from the oil bath and allowed to cool to room temperature during which time the mixture crystallised. This melt/crystallise procedure was repeated two additional times and the resulting solid was analysed.

2.3 Synthesis procedures
Detailed syntheses of all compounds can be found in the supplemental data. The syntheses of polymers 1–8 have been reported previously.[16] The syntheses of compounds 12–15,[56–59] compound 31,[60] compound 40,[61] compound 49[62] and compound 64[63] have been reported previously.

2.3.1 Syntheses of stilbazoles
A mixture of 4-substituted pyridine (1.2 eq), the appropriate benzaldehyde (1 eq) and acetic anhydride (0.23 mL/mmol 4-substituted pyridine) was heated at 120°C for 48 hours. The solution was cooled, quenched with 5N NaOH (1.25 mL/mmol 4-substituted pyridine) and stirred at room temperature overnight. The solution was neutralised with 10% aqueous HCl.

2.3.2 Mitsunobu coupling of substituted phenols with alcohols
A mixture of substituted phenol (1 eq), triphenylphosphine (1 eq), and alcohol (0.9 eq) in THF (2.3 mL/mmole triphenylphosphine) was treated with diethylazodicarboxylate (1.1 eq) and the reaction was stirred at room temperature for 6–12 hours. The solvent was evaporated and the resulting solid was slurried in 95/5 (v/v, hexane/ethyl acetate). The mixture was filtered to remove triphenylphosphine oxide. The filtrate was concentrated and purified via silica gel column chromatography.

2.3.3 Basic alkylation of stilbazoles
A mixture of the stilbazole (1 eq), base (2–3 eq) and alkyl halide (1 eq) in anhydrous dimethylformamide (DMF) (6.1 eq/mmole stilbazole) was heated at 120°C for 7–12 hours and cooled to room temperature. Water was added and the solution was extracted with ethyl acetate. The organic layer was dried over sodium sulphate and filtered. The filtrate was evaporated and purified via column chromatography.
2.3.4 Basic cleavage of esters
A mixture of the ester (1 eq), 5N NaOH (100 mL/mmol ester) and THF (20 mL/mmol ester) was refluxed for 48 hours and cooled to room temperature. The solution was neutralised with 50% HCl. The solution was either filtered to obtain product or the product was extracted into ethyl acetate and purified via column chromatography. Final acids were recrystallised in appropriate solvents.

2.3.5 Acidic hydrolysis of THP ethers
A mixture of THP ether, THF (15 mL/mmol protected compound), methanol (15 mL/mmol protected compound) and concentrated HCl (10 mL/mmol protected compound) was stirred overnight at room temperature. The mixture was neutralised with saturated sodium bicarbonate and filtered. Final products were recrystallised in appropriate solvents.

3. Results and discussion
3.1 Synthesis of noncentrosymmetric hydrogen-bonded polymers
Polymers 25–30 were synthesised according to Scheme 1. Stilbazoles 9–11 were synthesised from the appropriate 4-hydroxy-benzaldehydes and 4-alkyl pyridines using literature methods.[64] Esters 14, 15 and methyl-4-hydroxybenzoate were coupled

Scheme 1. Syntheses of polymers 25–30. (i) 4-picoline or 4-ethyl pyridine, Ac2O; (ii) MeOH, cat. H2SO4 or NaHCO3, MeI; (iii) TPP, 10-chloro-1-decanol; (iv) K2CO3, 9, 10 or 11; (v) NaOH, THF, MeOH.

Scheme 2. Syntheses of polymers 38 and 39. (i) DHP, TsOH; (ii) NaH, decylbromide; (iii) THF, HCl; (iv) NaH, 33; (v) 4-picoline, Ac2O; (vi) NaOH, THF, MeOH.
with 10-chloro-1-decanol to afford 16–18. Compounds 16–18 were coupled with stilbazoles 9–11 under basic conditions to afford compounds 19–24. These esters were hydrolysed in basic media.

Table 1. Carbonyl C=O stretches of acid containing model compounds, model mixtures and polymers.

| Compound or Mixture | α acid C=O (cm⁻¹) |
|---------------------|-------------------|
| C₆H₅CO₂H | 1666 |
| C₅H₇CO₂H | 1681 |
| C₅H₇CO₂H |  |  |
| 1:1 (mol: mol) 57:60 (A) | 1:1 (mol: mol) 58:61 (B) | 1:1 (mol: mol) 59:60 (C) |
| 1693 (A) | 1691 (B) | 1690 (C) |
| 1:1 (mol: mol) 57:61 (D) | 1:1 (mol: mol) 58:61 (E) |
| 1670 (D) | 1678 (E) |
| 1:1 (mol: mol) 57:63 (F) | 1:1 (mol: mol) 58:63 (G) |
| 1693 (F) | 1692 (G) |
| 1:1 (mol: mol) 57:62 (H) | 1:1 (mol: mol) 58:62 (I) |
| 1670 (H) | 1692 (I) |

Scheme 3. Syntheses of polymers 47 and 48. (i) SOCl₂; (ii) NaH, 14 or methyl 4-hydroxybenzoate; (iii) K₂CO₃, 4-hydroxybenzaldehyde, NaI; (iv) 4-picoline, Ac₂O; (v) NaOH, MeOH, THF.

Scheme 4. Syntheses of polymers 55 and 56. (i) DHP, TsOH; (ii) NaH, 1,10-dichlorodecane; (iii) K₂CO₃, 9; (iv) HCl, THF.
to afford compounds 25–30, which are soluble in hot (120°C) DMF and hot (120°C) dimethyl sulfoxide (DMSO), but insoluble in other solvents.

Polymers 38 and 39 were prepared from 2-decylloxy-4-hydroxybenzaldehyde according to Scheme 2. Compound 33 was coupled with compounds 16 and 17 under basic conditions to afford compounds 34 and 35 which were subsequently treated with 4-picoline and acetic anhydride to afford compounds 36 and 37. Esters 36 and 37 were hydrolysed under basic conditions to afford polymers 38 and 39, which had similar solubilities to polymers 25–30.

Glycol containing polymers 47 and 48 were synthesised from tetraethylene glycol according to Scheme 3. Compound 40 was coupled with methyl-4-hydroxybenzoate and 14 to afford compounds 41 and 42 which were coupled with 4-hydroxybenzaldehyde to afford compounds 43 and 44. Compounds 43 and 44 were coupled with 4-picoline to afford esters 45 and 46. Esters 45 and 46 were hydrolysed to afford polymers 47 and 48. Unlike our other polymers, 47 and 48 are soluble at room temperature in DMSO and DMF and in hot (60°C) methanol.

Phenol containing polymers 55 and 56 were synthesised according to Scheme 4. Compounds 49 and 50 were coupled with 1,10-dichlorodecane to afford compounds 51 and 52. Compounds 51 and 52 were coupled with stilbazole 9 under basic conditions to afford esters 53 and 54. THP esters 53 and 54 were hydrolysed in acidic media to afford polymers 55 and 56. These polymers had similar solubilities to those of polymers 19–24.

3.2 Hydrogen bonding in noncentrosymmetric main chain polymers

Attenuated total reflectance Fourier transform infrared (FTIR) spectroscopy was used to study the intermolecular hydrogen bonding in our polymers. Select FTIR stretches (which are most sensitive to hydrogen bonding [65,66]) for model compounds, model mixtures and our polymers are shown in Tables 1 and 2.

Table 2. O–H stretches of model compounds, model mixtures and polymers.

| Compound or Mixture | O–H (cm$^{-1}$) |
|---------------------|----------------|
| C$_{10}$H$_{21}$O        | 3358           |
| C$_{10}$H$_{21}$O        | 3205           |
| J                   | 3073*           |
| K                   | 3073*           |
| L                   | 3078†           |

Note: * = center of a broad peak spanning 30–50 cm$^{-1}$; † = no peak in the region commonly associated with this stretch.

3.3 Phase transition of noncentrosymmetric hydrogen bonding polymers

The phase transitions of our polymers are summarised in Table 3 and the polarised optical microscopy images of liquid crystalline phases of these polymers are shown in Figure 1. The melting point of polymer 25 (198°C) is 46°C lower than that of polymer 2.[67] Additionally, polymer 25 has an enantiotropic nematic phase instead of the high temperature smectic phases in polymer 2. These phenomena can be attributed to disruption of chain packing by ortho to the acid unit in decyloxy containing polymer 38 results in a blue shift in the C=O frequency in polymer 39. Since a similar shifting pattern is observed in model mixtures H and I, we attribute this blue shift to electronic effects from the C10 alkoxy substituent.

While the O–H stretch in polymer 55 is red shifted with respect to those in compounds 64 and 65, no O–H peak was observed in the ATR spectrum of polymer 56. These phenomena suggest the presence of strong intermolecular phenol-stilbazole hydrogen bonding in these model mixtures and polymers.
the methyl substituent. Unlike polymer 25, polymer 26 does not possess any liquid crystalline phases and has a melting point only 15°C lower than that of polymer 25. This suggests that single ortho substitution is the most effective strategy at lowering the melting point and liquid crystalline phase transition temperatures of the resulting polymers.

Methoxy substituted polymers 27 and 28 both have significantly lower melting points than that of 2 (244°C). Additionally, polymer 28 possesses a monotropic nematic phase (on the cooling cycle) while polymer 27 has no liquid crystalline phases. Alkene substituted polymers 29 and 30 both have significantly lower melting points than that of compound 2 and both of these molecules possess nematic liquid crystalline phases. We attribute this large melting point depression and nematic phases in polymers 29 and 30 to disruption of intermolecular hydrogen bonding and disruption of the chain packing as a result of ring twisting (from steric hindrance) in the stilbazole unit in these polymers. While polymers 38 and 39 have much lower melting points than our other polymers, they do not possess any liquid crystalline phases. This can be attributed to disruption of chain packing by the decyloxy substituents.

Glycol containing polymers 47 and 48 had much lower melting points and liquid crystalline phase transitions their alkyl analogues.[67] Similar to polymer 25, the ortho methyl substituent in polymer 48 results in the loss of the smectic phase in polymer 47. The nematic of polymer 48 is stable when cooled to room temperature and slowly crystallizes at room temperature.

While phenol containing polymers 55 and 56 have much lower melting points than polymer 2, neither of these polymers have liquid crystalline phases. The absence of mesogenic phases and the relatively smaller melting point depression observed upon lateral substitution in polymer 55 relative to polymer 56 can be attributed to the relatively weaker phenol-stilbazole hydrogen bond (compared to the acid-stilbazole hydrogen bond).[68,69]
4. Conclusions

The syntheses of several laterally substituted noncentrosymmetric main chain hydrogen-bonded polymers which incorporate stilbazole acceptors and benzoic acid and phenol hydrogen bond donors are described. While all of these polymers possess strong intermolecular hydrogen bonding, laterally substituting the monomer units disrupts the hydrogen bonding in these polymers. Lateral substitution lowers the melting point of the resulting polymers (relative to non-substituted analogues) and, in some cases, induces mesomorphic behaviour in the resulting polymers. Incorporating glycol chains and single methyl substituents ortho to the acid functionalities in our polymers is the most effective strategy for lowering the melting points and inducing mesomorphic behaviour in the resulting polymers.

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Supplemental data

Detailed synthesis procedures are available in the supplemental data.

Supplemental data for this article can be accessed here.
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