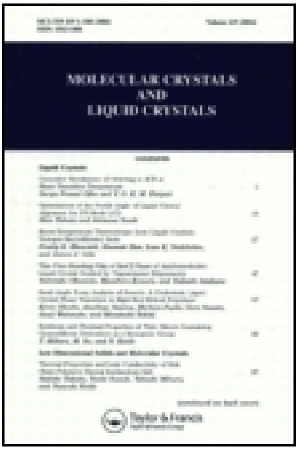

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Hyperbranched Architectures for NLO Polymers

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Hyperbranched Architectures for NLO Polymers

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A new approach to NLO polymer architecture is investigated. A hyperbranched polymer containing NLO chromophores is synthesised in three steps. Measurement of the NLO response indicates a $\chi^{(2)}$ value of 5 pm/V. Possible reasons for not achieving even higher values are discussed.

Keywords: Hyperbranched polymer; non-linear optics; electrical poling; electrooptical response

INTRODUCTION

Second-order non-linear optical chromophores are usually blended with a suitable polymer to allow poling, to hinder crystallisation, and allow reorientation of the chromophore in a supportive matrix.[1] The thermal stability of the poling in the film is then limited by the glass transition temperature (Tg) of the host polymer. Another common approach has been to covalently attach the chromophore onto the polymer, either as a side chain or as part of the main chain.[2] This approach has its advantages, such as ensuring good mixing of the polymer and chromophore, and the prevention of crystallisation. Main chain polymers do not seem to offer any immediate advantages, and poling of the main chain can be much more difficult than the local reorientation of a side-chain substituent. Thus, most NLO polymer tend to be of the side-chain type.

One problem with NLO chromophore systems has only recently been properly identified and studied. Typical second-order NLO molecules tend to be elongated and have large dipole moments (μ) to enhance the molecular hyperpolarisability ($\mu\beta$) and poling tendency (μ/Kt). At high concentrations these molecules can aggregate in a centrosymmetrical fashion, leading to poorer than expected NLO performance.[3,4] This then requires the use of higher electrical fields to overcome, potentially leading to damage of the organic material. One approach is to redesign the chromophore to prevent aggregation through the use of bulky side-groups.[3,4] A drawback to this approach is that the extra bulk of these groups dilutes the effective concentration of the active part of chromophore.

COLLECTIVE POLING

Several groups have investigated the idea of collective poling using a main chain polymer approach, which offers the possibility of an enhancement in poling, especially at low fields.[5] The idea is that by arranging the chromophores in a head to tail fashion (Figure 1), then poling might occur in a collective fashion. However, in practice such polymers do not perform very well. If the spacer groups are too long, this leads to a decoupling of the chromophore responses. However, if they are too short then the polymer is possibly too entangled to pole properly. In practice, even very short spacers can have very high conformational mobility, leading to decoupling of the chromophore responses. A collective response has been shown for oligomers with rigid linkers.[6]

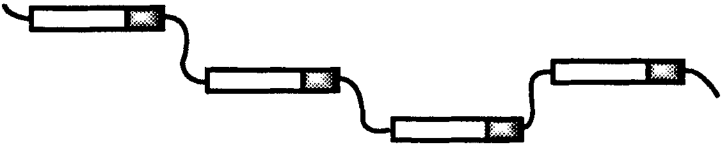


FIGURE 1 Section of main-chain polymer with chromophores arranged in a head-to-tail fashion

In a theoretical paper by Gunn and Warner,[7] it was shown that a main chain polymer in a liquid-crystalline nematic state with the chromophores arranged in a head to tail fashion should have an effective *collective* poling response as long as the persistence length of the polymer was greater than one monomer unit. Indeed, this was shown to be the case by Heldman and Warner[8] who synthesised such a main-chain nematic polymer. As predicted, the NLO response was increased significantly over a similar but non-LC polymer (though a part of the increase could be assigned to the effect of the director alignment[9] rather than to a collective poling response).

One drawback to the nematic main chain approach is that it requires the chromophore to perform several roles at once: to have a high molecular hyperpolarisability, to be a good nematogen, possess good optical and thermal stability, and also be capable of being linked into a main-chain polymer in a head to tail fashion. Thus, the actual system used is often a compromise between these requirements, and the NLO performance may not be optimal as a consequence.

While the long shape of typical NLO chromophores is also similar to that found in most nematic molecules, the functional groups found in each differ in their requirements. NLO chromophores require a strong donor group (such as amino) and a strong acceptor group (such as nitro or tricyanoethene) at the other. In particular, standard acceptor functionalities are often not well set up to be incorporated either as a linker in a polymer or a useful nematogenic group. As a compromise, Carsten and Warner used an ester functionality as the acceptor and linker group, but the resulting hyperpolarisability of the chromophore was probably only a half to a quarter of that which could have been obtained with either a nitro- or tricyanoethenyl-group.

EVALUATION OF A HYPERBRANCHED POLYMER

We have been interested in looking at some other potential architectures that might also offer the possibility of collective poling. Zhang et al first suggested the possibility of using a head to tail hyperbranched polymer architecture.[10] The simplified schematic shown in Figure 2 for a hypothetical hyperbranched materials shows a high degree of anisotropy, and thus may show a collective macromolecular poling response. Hyperbranched polymers[11] often have quite different properties to main chain materials. They are usually very soluble, non crystalline materials due to their branched nature and lack of entanglement in the solid state. This latter factor may also be very useful in the poling response. As well, there should be much fewer intermolecular chromophore-chromophore interactions, leading to lower aggregation effects. However, the only literature example of a hyperbranched polymer in a second-order NLO system did not show any obvious extra enhancement,[10] and we were interested in investigating this further.

It has been found that the carbodiimide promoted coupling between an aromatic carboxylic acids and phenols to be a mild, high yielding way of producing polyesters.[12] This system was successfully used in the synthesis of the original nematic NLO polymers,[8] this time using non-phenolic hydroxyl groups. However, when trying to reproduce this work, the molecular weights obtained were sometimes lower than expected, and there seemed to be a problem that needed to be investigated before extending it to hyperbranched polymers. By the use of model compounds we found the problem to be formation of a tosyl ester resulting from an unwanted side-reaction between the alcohol and the catalyst, which upset the 1:1 stoichiometry needed to produce high molecular weights. This was solved by changing the counter ion in the dimethylaminopyridinium catalyst from tosylate to the less nucleophilic tetrafluoroborate.

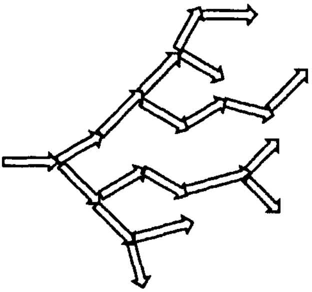
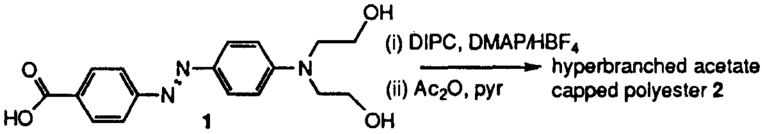


FIGURE 2 Representation of a hyperbranched polymer where each arrow represents a chromophore

The synthesis of the hyperbranched polymer was fairly straightforward. Amino-benzoic acid was diazotised and coupled with N-phenyldiethanolamine to produce the azo-containing AB_2 monomer 1. This was then polymerised using diisopropylcarbodiimide and dimethylaminopyridinium tetrafluoroborate in DMF to produce a hyperbranched polymer. Due to the large number of hydroxyl-groups in this polymer, it was only soluble in very polar organic solvents such as DMF and DMSO. The hydroxyl groups were then acetylated in order to produce a less polar polymer **2** for characterisation and solution processing (scheme 1)



SCHEME 1

Polymer **2** was soluble in standard organic solvents such as THF and chloroform and had a weight average molecular weight by gel permeation chromatography (GPC) of 5700 (polystyrene standards). However, GPC significantly underestimates the molecular weight of highly branched polymers[13] and it is likely that the real molecular weight is much higher. The polymer has a maximum in the UV-VIS spectrum of 432 nm.

Measurements of NLO response at 632 nm indicated that the hyperbranched polymer had an electro-optical response $\chi^{(2)}$ of 5 pm/V. This is similar to a non-LC crystalline main chain polymer containing the same chromophore, and indicates a lack of a collective poling response, mirroring the results of Zhang et al.[10] There are several possible reasons for this lack of enhancement. It is very likely in a hyperbranched system for loops to occur.[14] This reduces or eliminates the non-centrosymmetric structure (Figure 3a), leading to a large loss in any possible collective poling response. Another strong possibility is that the 5 atom linker between the chromophore molecules is long enough to decouple the response between the groups. Indeed, molecular modelling shows that the bent conformation (figure

3b) is as stable as the hoped for extended structure, and indeed may even be more stable if the overall dipoles of neighbouring chromophores are taken into account.

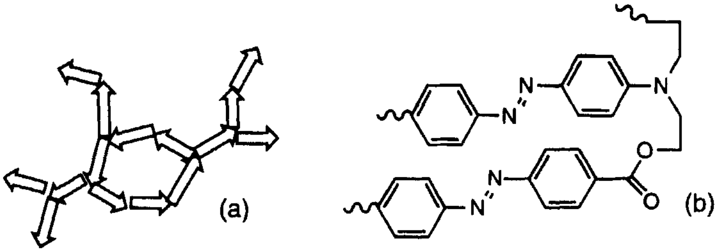


FIGURE 3 Postulated substructures responsible for lowering the NLO response.

Future work will be directed to the synthesis of hyperbranched systems with more rigid spacers, and to controlling the occurrence of cyclisation.

EXPERIMENTAL

Descriptions of the poling techniques and procedures for measurement of the $\chi^{(2)}$ values can be found in previous papers.[8,15]

Synthesis of Monomer 1

To a solution of 4-aminobenzoic acid (6.17 g, 0.45 mol) in aq. HCl (45 ml, 3N) at 0-5 °C was added slowly a solution of $NaNO_2$ (3.11g) in 18 ml water. After 30 min at 0 °C, the diazonium salt solution was then added slowly with stirring to a solution of N-phenyldiethanolamine (8.15 g, 0.045 mol) and sodium acetate (7.38 g) in water (90 mL), the temperature being maintained between -5 and 0 °C. After 30 min at this temperature, the reaction was poured into 1.5 L water containing 10 g sodium acetate., and the orange precipitate was collected by filtration, washed with water and dried. Recrystallisation from acetone yielded **1**, 11 g (80%); m.p. 246-246.5 °C; Calc for $C_{17}H_{19}N_3O_4$ C 62.0, H 5.8, N 12.8, Found: C 61.8, H 5.8, N 12.6 %; IR (KBr) 1673, 1588 cm^{-1}; ^1H; NMR (DMSO) 3.1-3.4 (2H, br s, OH), 3.48-3.72 (8 H, m, CH_2), 6.85 (2H, d, J=9 Hz), 6.86(2H, d, J=9 Hz,), 7.77 (2H, d, J=8 Hz), 7.80 (2H, d, J=8 Hz), 8.04 (2H, d, J=8.5Hz); UV λ_{max} (film) 206, 274, 426 nm.

Polymerisation of **1**.

To a solution of monomer 1 (0.43 g, 1.32 mmol) and dimethylaminopyridinium tetrafluoroborate (0.39 g, 1.32 mmol) in DMF (dry, 20 ml) was added diisopropylcarbodiimide (0.3 ml, 0.24 g, 1.9 mmol). After 1 day another 0.3 ml of DIPC was added and stirring continued for 2 more days. The mixture was poured into water (100 mL) and the polymer collected by filtration, washed with methanol and dried. To increase the solubility, a portion of the solid was acetylated in a mixture of acetic anhydride (50 mL) and sulfuric acid (conc., 2 drops) for 24 h, and the reaction mixture was poured into water (300 ml). The polymer was collected by filtration, washed with water and dried to yield **2**, Found: C 66.2, H 5.5, N 12.9%; IR (KBr) 1716, 1588, 1368 cm^{-1} H NMR ($CDCl_3$) 2.01 (3H, s), 3.80 (2H, d, J 7, CH_2), 3.85 (2H, d, J 7, CH_2), 4.29 (4H, m, CH_2), 4.58 (2H, m, CH_2), 6.87 (2H, d, J 10), 7.88 (4H, m), 8.10 (2H, bs). GPC ($CDCl_3$) M_n 3100, M_w 5700 (vs. polystyrene by GPC). UV (film) 276, 432 nm.

Acknowledgements

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