polymer reports

Second-harmonic generation in poly(α-amino acid) and poly(isocyanate) films

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Films of poly(γ-benzyl-L-glutamate) (PBLG) and poly(hexylisocyanate) (PHIC) were cast from solution whilst under electric fields generated between parallel strip electrodes placed at the surface. Because of their chain rigidity and large macromolecular dipole moments, this procedure induces some parallel chain alignments in the field direction, even if the fields are low ($\leqslant 300$ V mm^{-1}). The field induces a degree of non-centrosymmetric order in the films which is retained after the field is removed. In these ordered states such films were found to have second-harmonic generating (SHG) ability under 1.06 μm irradiation and this ability did not age over a period of 6 months. The SHG activity varied with the angle of polarized radiation relative to the poling direction, showing a single maximum and minimum for PHIC (uniaxial symmetry) and double maxima and minima for PBLG (biaxial symmetry) over π radians. Optical microscopy of the PBLG films formed under electric fields showed regions of nematic as well as cholesteric order.

(Keywords: poly(γ-benzyl-L-glutamate); poly(hexylisocyanate); α-helix; poled films; second-harmonic generation)

INTRODUCTION

There is a growing interest in materials, both inorganic and organic, which have non-linear optical (NLO) responses to electrical and optical stimuli. Such materials require non-zero second- or third-order hyperpolarizabilities, both at the molecular level and in the bulk. One necessary requirement for second-order effects is a lack of a centre of symmetry either at the molecular level or in the bulk material state. This constraint has led to most device materials requiring second-order effects being based on single crystals belonging to a non-centrosymmetric point group. Large NLO efficiencies also depend on large molecular hyperpolarizabilities (β, γ, etc.) for which the molecular architectures are now well understood.

It has been recognized that in some respects organic crystals could prove superior to inorganic ceramics for NLO applications and that efficient and stable NLO active polymers would be very attractive for use in many devices[1-12]. Fabrications involving NLO wave-guides is one such area in which single crystal substrates are very difficult to manufacture. The problem with polymers in a second-order NLO role is that without some form of chain ordering, there is random order within the dimensions of the optical coherence length and in consequence a zero bulk second-order hyperpolarizability. Poling polymer films during a thermal cycle from above to below the glass transition temperature (T_g) has been used to induce the necessary alignment using either the side chain as the source for high β[4-6] or including a small guest molecule with high β in the polymer to be ordered by the constraining influence of field induced chain arrangements[4,6,9,10]. Liquid crystal side chain polymers with their greater ease of field switching have found particular favour[4,9-11]. It has also been found possible to develop orientated SHG active organic crystallites within a polymer matrix by zone melting to give a composite material[12]. The NLO activity was found to be long lived but the composites did scatter light strongly, particularly along the draw axis.

However, it has not been found easy to produce poled polymer films by thermal cycling which retain their second-harmonic generating (SHG) efficiency on long storage, even when kept at ambient temperatures[4-6,11]. The reason for this decay lies in there being some molecular motion involving the NLO active moieties even when the T_g is well above ambient. Attachment of the active group to the polymer rather than using dissolved but unattached molecules is a preferable strategy, but even then there are few polymeric systems which show stability over months, and most lose efficiency over periods ranging from hours to weeks. Using high T_g polymers often presents problems of thermal stability and of obtaining and maintaining effective aligning fields at elevated temperatures: thermal motion of chains and impurity conductance conspire to make such conditions difficult.

We report below the outcome of another stratagem to achieve poled sheets of certain polymers. It is based upon the field (E) alignment of certain macromolecules with large dipole moments (μ) when in solution, and maintaining that alignment during solvent evaporation to produce a frozen uni- or biaxially ordered film, and only then removing the field. Solvation rather than temperature provides the freedom for macromolecular motion during poling. In order to achieve any significant level of order at realizable and reasonable fields ($E \sim$ kV mm^{-1}), macromolecules with large values of

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μ ($\sim 4 \times 10^{-27}$ C m) are needed so that $\mu E \sim kT$. This requires inflexible macromolecules of the rigid-rod-type for which there is direct additivity of a component of residue dipoles along the chain. Furthermore, such rigid rod-like molecules are ideal in that in the solid state there is little or no free movement of such long inflexible and very anisometric macromolecules. Particularly suitable polymers for this purpose are the poly(isocyanates)[13] and the α-helical forms of the poly(α-amino acids), for example those based upon the γ-esters of glutamic acid[14] which tend to have high solubilities for the α-helical forms. Below we report on the preparation of such poled films of poly(γ-benzyl-L-glutamate) (PBLG) and poly(hexylisocyanate) (PHIC), their SHG generating characteristics and their long term stability.

EXPERIMENTAL

PHIC (g.p.c. determined weight average molar mass = 108 000) was prepared by the method of Shashoua *et al.*[15] using sodium cyanide initiation of the distilled monomer in dry *N*,*N*-dimethylformamide at −55°C. High molecular weight PBLG was synthesized by the tributylamine initiated polymerization of freshly prepared and recrystallized γ-benzyl-L-glutamate *N*-carboxyanhydride using the method previously described[16]. PHIC was cast from toluene solution and PBLG from either chloroform or dioxan. Films were obtained by evaporating aliquots of such solutions under ambient temperatures and pressures in a channel formed between parallel stainless steel electrodes mounted on the upper surface of glass slides. At this stage the assembly was mounted horizontally and with the upper surface of the channel open to allow unimpeded evaporation (for SHG measurement the assembly with its attached film was mounted vertically in the laser beam as shown in *Figure 1*). The edges of the electrodes served to prevent lateral spreading of the polymer solutions. It was not found necessary to block the channel ends because there was little seepage of the viscous polymer solutions from there. An adjustable d.c. supply of maximum rating 3 kV at 6 mA was used to supply the field which acted over a 3 mm electrode separation.

The SHG generating ability of film samples was measured using 5 ns pulses of 1.06 μm radiation generated from a Nd–YAG laser. The radiation passed through a goniometer mounted polarizer and then a beam splitter with one branch passing through a Y-cut quartz plate acting as reference standard and the other through the films mounted with their faces normal to the beam as shown in *Figure 1* which also defines the polarization angle. The sample beam was made convergent with a 25 cm focal length lens to give a spot diameter of ~0.3 mm at the film surface. Two matched photomultipliers with apertures covered by 532 nm narrow band pass filters were used as detectors and the ratio of sample to reference signal averaged over a selectable number of pulses using a digitizing oscilloscope. To eliminate systems variations in laser energy output or photomultiplier gain settings which may be subject to long term drift or vary between runs, the signal ratio from any sample is processed as a value relative to the signal ratio from a standard 2 mm thick Y-cut quartz plate replacing the sample. The quartz plate was mounted with its major optic axis parallel to the polarization plane of the beam. The derived ratio of sample to standard signal ratio is referred to as the relative intensity.

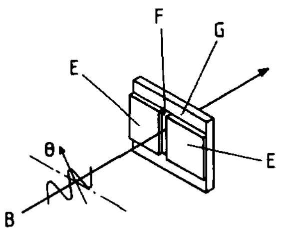

Figure 1 Film assembly in its vertical position in the laser beam (B) showing the polarization angle (θ) between the beam and the poling direction. Electrodes (E) are mounted on a glass slide (G) and contain the film (F) which is solution cast with the assembly horizontal

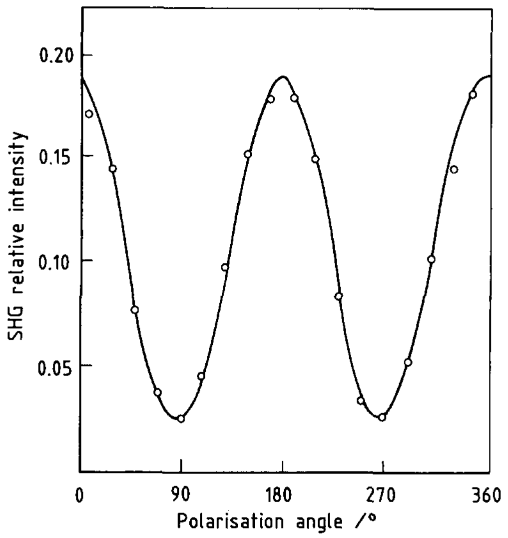

Figure 2 SHG intensity generated from a 6 μm film of PHIC cast under a field of 266 V mm^{-1} as a function of polarization angle

Film thicknesses and their variance were measured using a Rank Taylor Hobson Talysurf surface profilimeter with a 0.2 μm head and magnifications set to a vertical resolution of ±1 μm and a horizontal scaling factor of 50 μm mm^{-1}.

RESULTS AND DISCUSSION

PHIC

Figure 2 shows the SHG signal under polarized radiation from a 6 μm film of PHIC cast under a field of 266 V mm^{-1} with various angles of polarization relative to the poling-axis. In conformity with uniaxial symmetry, there are maxima at 0 and 180° and minima at 90 and 270°. No SHG signal was observed for unpoled films, whilst the strength of signals given by films cast under various fields but otherwise set conditions to provide films of approximately constant film thickness (20 ± 5 μm) appear to show a threshold field of ~150 V mm^{-1} for switching the chain alignment (*Figure 3*).

The SHG signal from a poled film was monitored periodically using identical mounting conditions in the beam in order to study its ageing. No significant drop in signal intensity (*Table 1*) was observed over a period of 6 months.

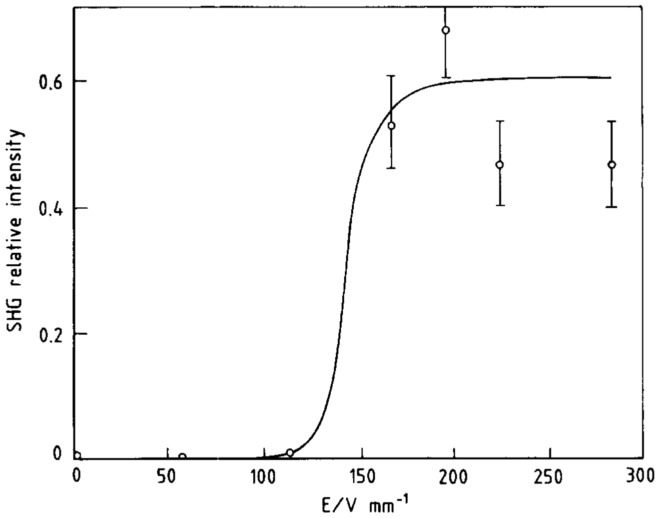

Figure 3 SHG intensity generated by irradiating 20 ± 5 μm PHIC films prepared under various aligning fields (E). Polarization angle set at 0°

Table 1 Ageing of SHG activity in PHIC and PBLG films

	Comparative SHG intensity[a]	
Age of film (days)	PHIC (228 V mm^{-1})	PBLG (133 V mm^{-1})
30	0.935	0.937
90	0.984	0.979
150	0.887	0.947
180	0.968	0.968
R.m.s. values	0.955 ± 0.045	0.966 ± 0.025
Decay/month[b]	<0.003	<0.003

[a] Measured at the same position and fixed polarizer angle (0 and 45° for PHIC and PBLG, respectively) and quoted as the ratio of current relative intensity to the value shortly after formation. Poling fields quoted in parentheses

[b] Obtained by linear regression

PBLG

The angular dependence of the SHG signal from a poled (300 V mm^{-1}) film of PBLG irradiated with polarized 1.06 μm light is shown in *Figure 4* and exhibits four maxima and minima over 2π radians. This suggests biaxial symmetry for the film which could be a consequence of the chirality of the macromolecules[17]. PBLG in its α-helical form is known to form films containing regions of rod-like suprastructures when solvent cast in the absence of fields[18]. These arise from the cholesteric mesophase which forms in solutions of PBLG in helecogenic solvents at particular concentrations[19]. It is known that electric fields can readily orientate the PBLG macromolecule when in dilute solution, and when in the lyotropic liquid crystal state such fields change the mesophase from cholesteric to nematic[14]. Within the nematic domains, which tend to align with their director in the field direction, there is then also a significant preponderance of dipoles which pole into that direction[20]. There is evidence that during evaporation of PBLG solutions under fields, when the concentration increases through the lyotropic phase to the solid film, the morphological changes are at least partially maintained. Thus, microscopic examination under polarized light of poled films prepared by the above methods showed aligned rod-like texture as well as some cholesteric regions.

The SHG ability of such poled films showed considerable variation when the ~0.3 mm exciting beam, polarized at a fixed angle, fell on different regions of the film, even for films prepared under set conditions of field, aliquot volume, solvent and concentration. There was no regular variation or trend in traversing the beam along or across the film. Films did however show consistency in the angular dependence of the SHG efficiency with the maxima and minima occurring at the same position of the polarizer, regardless of where the beam struck the film. Talysurf measurements showed that variation in film thickness could not account for the observed spatial variation of SHG activity. The SHG results and the microscopic examination, showed that the small laser spot could easily sample regions of different morphologies shown by the films (also observed by Iizuka *et al.*[20]), and this could account for the variation. The complex morphology could well result from non-uniform evaporation causing differing macromolecular mobility effecting alignment rates, or differential solvent losses might induce non-uniform fields, including the occasionally non-aligned region. Whatever the cause of the spatial variation of SHG activity, the variation of intensity with film thickness for films individually poled at a set field only show trends when maximum values are compared. Furthermore, there are grounds for such a comparison since it is arguable that, provided there is enough data collected to ensure a maximum or near maximum value, then that value would reflect the full thermodynamic level of order. Other lower levels have only achieved partial and variable alignment or dipole–dipole decoupling and cannot therefore be compared. *Figure 5* shows the expected square root dependence of this maximum measured SHG signal on film thickness and implies that the optical coherence length is >22 μm.

An ageing test similar to that undertaken for PHIC was made on a PBLG film which again showed no measurable decay in SHG efficiency over a period of 6 months (*Table 1*).

CONCLUSIONS

Both PHIC and PBLG films formed by aligning in electric fields during solvent casting show SHG activity which is greater for the former than for the latter. Neither

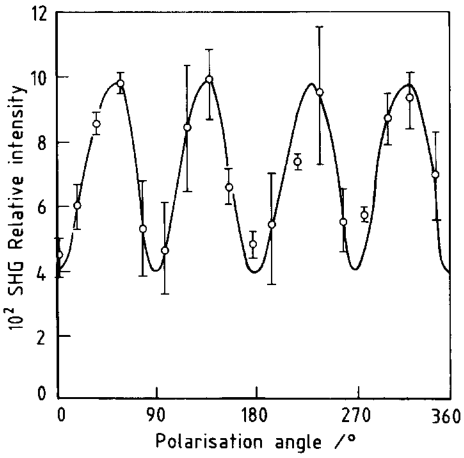

Figure 4 SHG intensity generated from a 20 μm film of PBLG cast under a field of 300 V mm^{-1} as a function of polarization angle

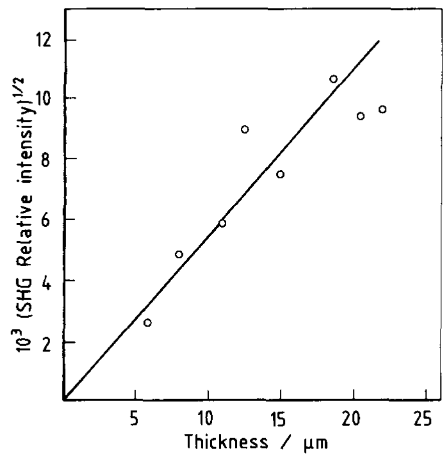

Figure 5 Variation of the maximum SHG activity found over the film area for PBLG films as a function of film thickness with data showing the square root dependence. Fields during film formation ~100 V mm^{-1}. Surface variation of film thickness <20%

polymer is as active as some other polymer systems tailored to have high molecular β values, although it is noteworthy that PHIC, being a polymeric urea, is fairly active, as indeed is urea. The electron delocalization in the urea group in PHIC is absent in the peptide bond of PBLG and it would appear that the intra-hydrogen bonding in the α-helix does not provide any large non-linearity. Electric field induced second harmonic generation (EFISH) experiments[21] have established a significant β for PBLG but this is its value per macromolecule and the second-order hyperpolarizability per peptide residue is not high.

However, the retention with time of the SHG activity of both systems is impressive and suggests the approach reported here for achieving SHG active polymer systems could overcome the problems of the 'thermal cycle' approach. Introducing chemical groupings with higher molecular hyperpolarizability should improve the level of SHG activity and other NLO properties. Devising improved methods of casting under electric fields to provide more uniform films is another area which requires further work. We are currently investigating both kinds of improvement.

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