Determination of the electro-optical coefficient r_{33} and refractive index of *para*-substituted poly(γ-benzyl-L-glutamate) derivatives

Dong-Hoon Choi† and Robert Zand*
Macromolecular Science and Engineering Center† and Biophysics Research Division, Institute of Science and Technology, Department of Biological Chemistry*, The University of Michigan, Ann Arbor, MI 48109-1055, USA*

(Received 8 September 1992; revised 16 April 1993)

The electro-optical coefficient r_{33} and refractive index of films of poly(γ-benzyl-L-glutamate) and the *p*-nitro, *p*-fluoro and *p*-trifluoromethyl derivatives were determined as a way to assess the non-linear optical behaviour of these organic polymers. The *p*-fluoro-γ-benzyl and *p*-trifluoromethyl-γ-benzyl ester polymers are new materials synthesized for this study. The electro-optical coefficient $r_{33} = 5.2 \times 10^{-2}$ pm V^{-1} for the unsubstituted polymer, 13.9×10^{-2} pm V^{-1} for the *p*-nitro polymer, 3.0×10^{2} pm V^{-1} for the *p*-fluoro polymer, and 1.6×10^{-2} pm V^{-1} for the *p*-trifluoromethyl polymer. The refractive indices, at a wavelength of 488 nm, of films of the polymer were determined to be 1.60, 1.61, 1.59, and 1.70, respectively, for the unsubstituted polymer and the *p*-nitro, *p*-fluoro, and *p*-trifluoromethyl derivatives. The frequency dependence of the dielectric constant, from 10 kHz to 4 MHz, for each of the polymer films was also determined. The waveguiding and other properties of each of the polymers were assessed in terms of the polymer structure.

(Keywords: poly(γ-benzyl-L-glutamate); electro-optical coefficient; refractive index)

INTRODUCTION

Non-linear optical behaviour is strongly dependent upon the magnitude of the molecular orientational polarization and the opposing counterforce due to thermal randomization of the dipole-containing group. Synthetic polypeptides and poly(amino acid)s, consisting of the appropriate amino acid sequence, can have a repetitive secondary structure of the backbone such as the 3_{10} or the α helix (a 3.6_{13} helix). In this helical structure, the orientational polarization, once aligned, is less likely to be easily thermally randomized. The helix is stabilized by intramolecular hydrogen bonds which result in a rigid rod-like molecule with an enormous dipole moment whose vector is oriented along the backbone of the polymer chain. Wada[1], in a theoretical treatment of the dielectric properties and dipole moment of poly(γ-benzyl-L-glutamate), had implied that it might be possible to enhance further the dipole moment of the helical backbone in this polymer by modification of the amino acid monomer.

Studies of the non-linear optical behaviour of solutions of unsubstituted poly(γ-benzyl-L-glutamate) had been reported as far back as 1975 by Levine and Bethea[2,3]. The most recent review of the literature on non-linear optical studies of poly(γ-benzyl-L-glutamate) that we could find was published in 1983 by Williams[4]. Of the factors that contribute to the non-linear behaviour of this molecule, the α-helical backbone conformation that is acquired by poly(γ-benzyl-L-glutamate) in certain environments permits the dipole moments of the peptide units to be summed so that the molecule can be viewed as a large, rigid dipole. The presence of a liquid crystalline structure, under certain conditions, can also function to enhance the non-linear optical properties of such polymers.

Inorganic compounds, such as lithium niobate, potassium dihydrogen phosphate, and ammonium dihydrogen phosphate, etc., exhibit non-linear optical properties that find application in areas such as optical communication and optical switching devices.

The advantage of the organic polymer systems over the inorganic systems is that they can be spin cast into optical quality films directly onto the desired substrate. A number of organic polymer systems that exhibit non-linear optical properties have been synthesized as potential alternatives to the inorganic compounds[5-7].

The disadvantage of the organic polymer systems is that the majority of the common organic polymers are amorphous materials, lacking long-range order, and are typically centrosymmetric. Some investigators, in order to compensate for the lack of long-range order in amorphous organic polymers, doped low-molecular-weight molecules which possessed large, microscopic non-linear optical properties into isotropic amorphous media, such as poly(methyl methacrylate) and polystyrene[1,4,5]. Electrical poling or mechanical orientation of these dopant molecules could arrange them into some form of long-range order.

---

* To whom correspondence should be addressed

0032-3861/94/010023-07

Levine and Bethea[2,3] measured the molecular hyperpolarizability β and the third-order hyperpolarizability γ of poly(γ-benzyl-L-glutamate) and assessed the non-linear optical behaviour of this polymer in solution. Their measurements utilized a technique for investigating the electric field induced second harmonic generation (EFISH) properties of molecules in solution[3]. The purely electronic, second-order hyperpolarizability β was reported to be 5×10^{-28} esu ± 50%.

Many of the studies of non-linear optical behaviour in synthetic polymers involve systems in which the non-linear optical unit is resident in the side-chain moiety of the polymer. The present study investigated the non-linear optical properties of poly(γ-benzyl-L-glutamate) (PBLG) and some *para*-substituted γ-benzyl esters that have strong dipole strengths in both the backbone chain and the side chain.

In this study we synthesized the known polymers poly(γ-benzyl-L-glutamate) (PBLG) and poly(γ-*p*-nitrobenzyl-L-glutamate) (PGLU(*p*NB)), in addition to the two new polymers poly(γ-*p*-fluorobenzyl-L-glutamate) (PGLU(*p*FB)) and poly(γ-*p*-trifluoromethylbenzyl-L-glutamate) (PGLU(*p*TFMB)), and investigated their non-linear optical behaviour.

This communication reports the results of our investigation on films of the four polyglutamates. We have determined the influence of γ-benzyl ester *para* substituents on the electro-optical coefficient r_{33}, the refractive index, and the dielectric properties of the four polyglutamate systems.

EXPERIMENTAL

The protocols for the synthesis of poly(γ-*p*-fluorobenzyl-L-glutamate) and poly(γ-*p*-trifluoromethylbenzyl-L-glutamate), as well as the two known polymers poly(γ-benzyl-L-glutamate) and poly(γ-*p*-nitrobenzyl-L-glutamate), are described in a paper that reports the liquid crystalline properties of these polymers[8].

The molecular weight of each of the polymers was estimated from the intrinsic viscosity using the Mark–Houwink equation with k and α values for the unsubstituted polymer as reported by Doty *et al.*[9]. The use of the k and α values of the unsubstituted poly(γ-benzyl-L-glutamate) for the *para*-substituted polymers assumes that these values will not change significantly for the *para*-substituted polymers. The solvent used for the viscosity measurements was dichloroacetic acid.

The thermal properties of the powdered polymers over the temperature range from −40 to 350°C were determined with a Perkin–Elmer model DSC7 differential scanning calorimeter. The rate of heating was 10–20°C min^{-1}.

Solutions of each polymer, in an appropriate solvent, were filtered through a 0.45 μm pore size microfilter (Whatman Puradisc 25TF). For PBLG and PGLU(*p*FB) two different solvent systems were used. These were dimethylformamide (DMF) and cyclohexanone. For PGLU(*p*NB) the solvent was 1-methyl-2-pyrrolidinone (NMP), and for PGLU(*p*TFMB) the solvent was cyclohexanone. Films of the four polymers were prepared on indium–tin oxide conducting glass by spin coating and were used in the determination of the dielectric constant. Typical drying conditions involved drying at room temperature *in vacuo* for 24 h and then at 100°C *in vacuo* for 24 h. The dried film sample was then coated with a gold–palladium layer of 1000 Å thickness with a Hummer IV sputtering machine. The capacitance of each polymer film was measured using a Hewlett–Packard model 4275A multifrequency LCR meter. The frequency was varied incrementally from 10 kHz to 4 MHz. From the capacitance measured at each frequency, the dielectric constant was obtained from equation (1). The film thickness was adjusted within the range 10–22.4 μm. Film thickness was measured with a Sloan Dektak IID wafer inspection system. The vertical resolution was 5 Å.

$$k = \frac{Cd}{\varepsilon_0 A} \qquad (1)$$

where C (C V^{-1}) is the measured capacitance, d (m) is the thickness of the polymer film, ε_0 is the permittivity constant (8.85×10^{-12} C V^{-1} m^{-1}), A (m^2) is the area of the electrode, and k is the dielectric constant (dimensionless).

The prism–film coupling technique was used to measure the refractive index and the film thickness. This method uses films on any substrate whose refractive index is already known. For the determination of the film refractive index, a single rutile (TiO_2) prism with a refractive index of 3.06 at 488 nm for light polarized along the extraordinary axis of the crystal was used. The light source was an argon ion laser.

The method for measuring the electro-optical coefficient was based on the procedure developed by Teng and Man[10]. The thin film was prepared using either spin coating or normal casting of the solution onto indium–tin oxide (ITO) coated conducting glass. The film surface was then coated with semi-transparent gold–palladium or another transparent conductor at a wavelength of 488 nm (*Figure 1*).

After deposition of a 700–1000 Å thick gold–palladium coating on the surface of the film, an electric field induced alignment of the side-chain dipoles in the polymer was carried out. The poling conditions for each polymer are given in *Table 1*.

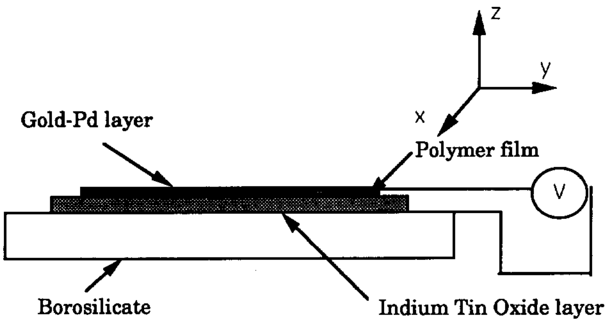

Figure 1 Schematic diagram of the polymer film on indium–tin oxide glass as used to determine the electro-optical coefficient

Table 1 The poling conditions of PBLG and its synthetic analogues

Polymer	Temperature (°C)	Maximum poling voltage[a] (V μm^{-1})
PBLG	130	26
PGLU(*p*FB)	175	100
PGLU(*p*NB)	145	6
PGLU(*p*TFMB)	135	20

[a] The maximum poling voltage was set as the voltage just before dielectric breakdown

In determining the electro-optical coefficient by Teng and Man's procedure[10], the small modulating amplitude signal was monitored with a lock-in amplifier. Since the other parameters were known, once the values of I and I_c were measured the electro-optical coefficient r_{33} could be calculated by means of

$$\frac{I}{I_c} \approx \delta\psi_{sp} \tag{2}$$

$$r_{33} = \frac{3\lambda I_m}{4\pi V_m I_c n^2} \frac{(n^2 - \sin^2\theta)^{3/2}}{(n^2 - 2\sin^2\theta)} \frac{1}{\sin^2\theta} \tag{3}$$

where I_m is the amplitude of modulation, V_m is the modulating voltage applied to the sample, and I_c is half the maximum intensity of modulation. The value determined will correspond to r_{33} provided that the electro-optical coefficient is dispersionless and the poled polymer belongs to the point group (α, ∞, ∞).

RESULTS

Assessment of optical waveguiding properties

Films of PBLG and *para*-substituted PBLGs were cast from a solvent mixture of chloroform and 1% *m*-cresol or DMF (v/v). The films prepared from this solvent permitted the observation of three or four modes (*Table 2*). The PBLG polymer crystallizes readily during solution casting at room temperature, resulting in some scattering of the incident laser beam. Although several modes and synchronous angles were observed, the streak lines did not appear clearly on the screen and showed larger line widths than the *p*-fluoro and *p*-nitro polymers. Film-casting conditions of appropriate solvents and drying conditions were found that retarded polymer crystallization in the films and minimized the incident light scattering.

When used as a waveguide medium, a 3 μm thick film of poly(γ-*p*-fluorobenzyl-L-glutamate) (molecular weight 45 000) coated on a glass slide (borosilicate, $n = 1.52$ at 488 nm) clearly showed six modes corresponding to six synchronous angles (*Table 3*). The refractive index was determined to be 1.59 ~ 1.60.

A similar film of poly(γ-*p*-nitrobenzyl-L-glutamate) (molecular weight 45 000) was prepared from a 5–7% (w/v) solution of 1-methyl-2-pyrrolidinone (NMP). When films were cast from the solvent 1,1,1,3,3,3-hexafluoro-2-propanol, rapid crystal formation occurred during the drying process. The film cast from NMP exhibited five modes corresponding to the variation of the incident angle. These data are presented in *Table 4*.

Table 2 A comparison of the computed effective refractive indices with the experimentally obtained values for PBLG[a]

Mode	Synchronous angle (°)	θ	N_{eff}(comp)	N_{eff}(exp)	$10^{-3}\Delta$
0	332.1	47.0	1.5772	1.5839	−6.7
1	333.5	48.4	1.5686	1.5694	−0.7
2	335.4	50.3	1.5545	1.5502	4.3
3	337.7	52.6	1.5352	1.5278	7.3
0	331.7	46.2	1.5911	1.5923	−1.3
1	333.5	48.0	1.5733	1.5735	−0.2
2	336.3	50.8	1.5444	1.5452	−0.9

[a] Film thickness = 2.33 μm, 1.55 μm; substrate index $n_a = 1.52$; film index $n_f = 1.58$, 1.60; reference angle $\theta = 285.1°$, 285.5°

Table 3 A comparison of the computed effective refractive indices with the experimentally obtained values for PGLU(*p*FB)[a]

Mode	Synchronous angle (°)	θ	N_{eff}(comp)	N_{eff}(exp)	$10^{-3}\Delta$
0	332.1	47.4	1.58630	1.57897	7.33
1	333.5	47.8	1.58120	1.57670	4.50
2	333.2	48.5	1.57280	1.56830	4.50
3	334.1	49.4	1.56100	1.55920	1.80
4	335.3	50.6	1.54590	1.54720	−1.30
5	336.6	51.9	1.52790	1.53450	−6.6

[a] Film thickness = 3.0 μm; substrate index $n_a = 1.52$; film index $n_f = 1.59$; reference angle $\theta = 284.7°$

Table 4 A comparison of the computed effective refractive indices with the experimentally obtained values for PGLU(*p*NB)[a]

Mode	Synchronous angle (°)	θ	N_{eff}(comp)	N_{eff}(exp)	$10^{-3}\Delta$
0	330.2	44.5	1.6068	1.6106	−3.8
1	331.1	45.4	1.5972	1.6009	−3.6
2	332.6	46.9	1.5813	1.5849	−3.7
3	334.8	49.1	1.5590	1.5622	−3.2
4	337.7	52.0	1.5312	1.5336	−2.3

[a] Film thickness = 2.3 μm; substrate index $n_a = 1.52$; film index $n_f = 1.61$; reference angle $\theta = 284.5°$

Electro-optical properties of para-*substituted poly(γ-benzyl-L-glutamate)s*

The electro-optical coefficients r_{33} of the poled and unpoled polymers were determined by using the reflection technique in which the polarization rotation of a laser beam due to the electro-optical effect is determined. The results of these measurements permitted the polymers to be classified into two groups (see *Figure 3*). One group consists of PGLU(*p*FB) and PGLU(*p*TFMB) and the other group consists of PBLG and PGLU(*p*NB). The former group exhibited dielectric constants approaching 4.0 until the frequency reached 1 MHz. The latter group, PBLG and PGLU(*p*NB), exhibited lower dielectric constants. The dielectric constant range for PBLG is 3.42–2.53 for frequencies lower than 1 MHz. The *p*-nitro polymer PGLU(*p*NB) does not show any dielectric relaxation behaviour in the frequency range from 10 kHz to 4 MHz. Over this frequency range it gives a static dielectric constant with a value of 1.41–1.48. These results are interpreted as showing that the latter group has a faster response time than the former group. Consequently, the former group, PGLU(*p*FB) and PGLU(*p*TFMB), would not be as effective in applications involving electro-optical devices.

The electro-optical coefficient of PBLG poled at 26 V mm^{-1} and 120°C was determined to be 5.2×10^{-2} pm V^{-1}. Relative to PBLG, the fluoro derivatives PGLU(*p*FB) and PGLU(*p*TFMB) had lower electro-optical coefficients. Even when poled at 100 V mm^{-1} and 175°C, PGLU(*p*FB) had an electro-optical coefficient of 3.0×10^{-2} pm V^{-1} and PGLU(*p*TFMB) poled at 20 V mm^{-1} and 135°C had a coefficient of 1.6×10^{-2} pm V^{-1}. These values correspond to reductions of 57.7% and 30.8% relative to PBLG. Of the four poly(amino acid)s, PGLU(*p*NB) poled at 6 V mm^{-1} and 145°C had the highest electro-optical coefficient of 13.9×10^{-2} pm V^{-1}, equivalent to a 267% increase over PBLG.

DISCUSSION

The propagation of guided waves in thin-film waveguides can be described by an equation that is obtained from Maxwell's equations by applying boundary conditions at the air–film and film–substrate interfaces[11,12]. It is possible to compare the effective refractive index from the experimental results with that from the eigenvalue equation (4)[11,12] by means of a calculation that utilizes the known values of refractive index and film thickness[13,14]

$$k_x T = (m+1)\pi - \tan^{-1}\left(\frac{k_x}{\gamma_s}\right) - \tan^{-1}\left(\frac{k_x}{\gamma_c}\right) \qquad (4)$$

where

$$\gamma_c = k_0\sqrt{N^2 - n_c^2}$$
$$\gamma_s = k_0\sqrt{N^2 - n_s^2}$$

with $k_0 = 2\pi/\lambda$. Here, n_c and n_s are the refractive indices of the cladding and substrate layers, N is the effective refractive index of the guided node, k_x, γ_s and γ_c are the propagation constants of each layer, m is the mode number, and T is the guide thickness.

The value of N_{eff}(comp) was calculated from equation (4) using an iterative method. The value of N_{eff}(exp) was obtained directly from equation (5). A single rutile (TiO_2) prism with a refractive index of 3.06 in the transverse electric (TE) mode was used throughout the study. The relationship between the value of N_{eff}(exp) and the incident angle t_i is

$$N_{\mathrm{eff}}(\mathrm{exp}) = n_p \sin[45 - \sin^{-1}(\sin t_i/n_p)] \qquad (5)$$

where n_p is the refractive index of the prism and t_i is the incident angle[15].

The comparison between the effective refractive index from the characteristic equation (4) and that from the experimental results using equation (5) exhibits consistency within an error of the order of ±0.01. This small error range is indicative of a greater reliability in the data obtained by the method used in the present study than by alternative methods.

Two sample films of PBLG were used in order to average the measured refractive indices. The polymer provides a weak waveguide mode at each measurement so that an accurate determination of the synchronous angle is difficult. Despite the difficulties caused by scattering losses, the refractive index of PBLG was determined to be in the range 1.59–1.60.

Of the four polymers investigated in this study, PGLU(*p*FB) shows good transparency in the visible region and some unique optical properties when compared to the other polymers. The difference between PGLU(*p*NB) and PGLU(*p*FB) is that at 488 nm the extent of absorption of PGLU(*p*NB) is slightly higher than that of PGLU(*p*FB). Each streak line is narrow and sharp, permitting the observation of the synchronous angle at each mode.

Electro-optical properties of para-*substituted poly(γ-benzyl-L-glutamate)s*

The α-helical backbone is a non-centrosymmetric structure that inherently shows electro-optical activity. In contrast to the α-helical backbone, the side-chain functions are normally composed of centrosymmetric structures that show no electro-optical effect. For highly helical poly(amino acid) systems such as PBLG, the side-chain contribution to an electro-optical effect is negligible. Assuming that the polymeric thin-film system was centrosymmetric due to the isotropic structure of the side-chain moiety, poling the film under a high electric field can remove the centrosymmetry. Orienting the side chain removes the inversion symmetry of the grouping chain.

As part of the present investigation, comparisons of the electro-optical coefficients were made between PBLG and the *para*-substituted benzyl PBLG derivatives. The rationale for such a comparison is that in rigid, rod-like polymers, such as PBLG and its *para*-substituted derivatives, the electro-optical coefficient or second harmonic generation properties are, in large part, dependent on the dipole moment of the polymer structure. By orienting the side-chain dipole either to reinforce or diminish the backbone dipole, the electro-optical behaviour could be modified. Determining the electro-optical coefficients of the *para*-substituted PBLG polymers makes it possible to assess the side-chain contribution to the total electro-optical coefficient.

Differential thermal analysis (*Figure 2*) revealed two transitions below the melting temperature. At temperatures in the region of 120–160°C, all PBLG analogues show a transition (T_b) which we interpret as arising from the intermolecular or intramolecular breakdown of the benzyl ring stacking. In the present study the temperature T_b was used as the poling temperature to provide some degree of rotational freedom in the side-chain functions and to allow for dipole reorientation. Most of the polymers show an almost zero output amplitude of the modulating signal before the poling process. However, there is a very small value for the electro-optical coefficient before the poling process that is attributed to the non-centrosymmetric nature of the stiff main chain.

For PBLG and PGLU(*p*NB), the poling field is low relative to that for the fluorine-containing polymers PGLU(*p*FB) and PGLU(*p*TFMB). The polymers PGLU(*p*FB) and PGLU(*p*TFMB) have much higher dielectric breakdown strengths than do PBLG and PGLU(*p*NB). The role of the poling field is much more important in its effect on the *r* value than the poling temperature. Once the poling temperature is set just below the melting point of these polyglutamates, the alignment of the non-linear groups becomes largely dependent on the poling field. It is possible to estimate the dielectric breakdown strength of each polymer from the poling process. For these polyglutamates we estimate that the temperature at which the breakdown of the dielectric will occur lies in the region of 120 ~ 175°C. This temperature coincides with the onset of some degree of rotational freedom of the side-chain moiety in these polymers.

For the polymers PBLG and PGLU(*p*NB), the applied direct current (d.c.) voltages approached the values of their dielectric breakdown voltages. Available equipment did not allow for sufficiently high d.c. poling voltages to be applied to the PGLU(*p*FB) and PGLU(*p*TFMB) films.

Poled and unpoled samples of the polymers show a significant difference in their electro-optical coefficients. The fluorine-containing polymers PGLU(*p*FB) and PGLU(*p*TFMB) have values for their electro-optical coefficients which are even lower than that of PBLG. Although the polymers PBLG and PGLU(*p*NB) could be oriented by the application of a high voltage that was

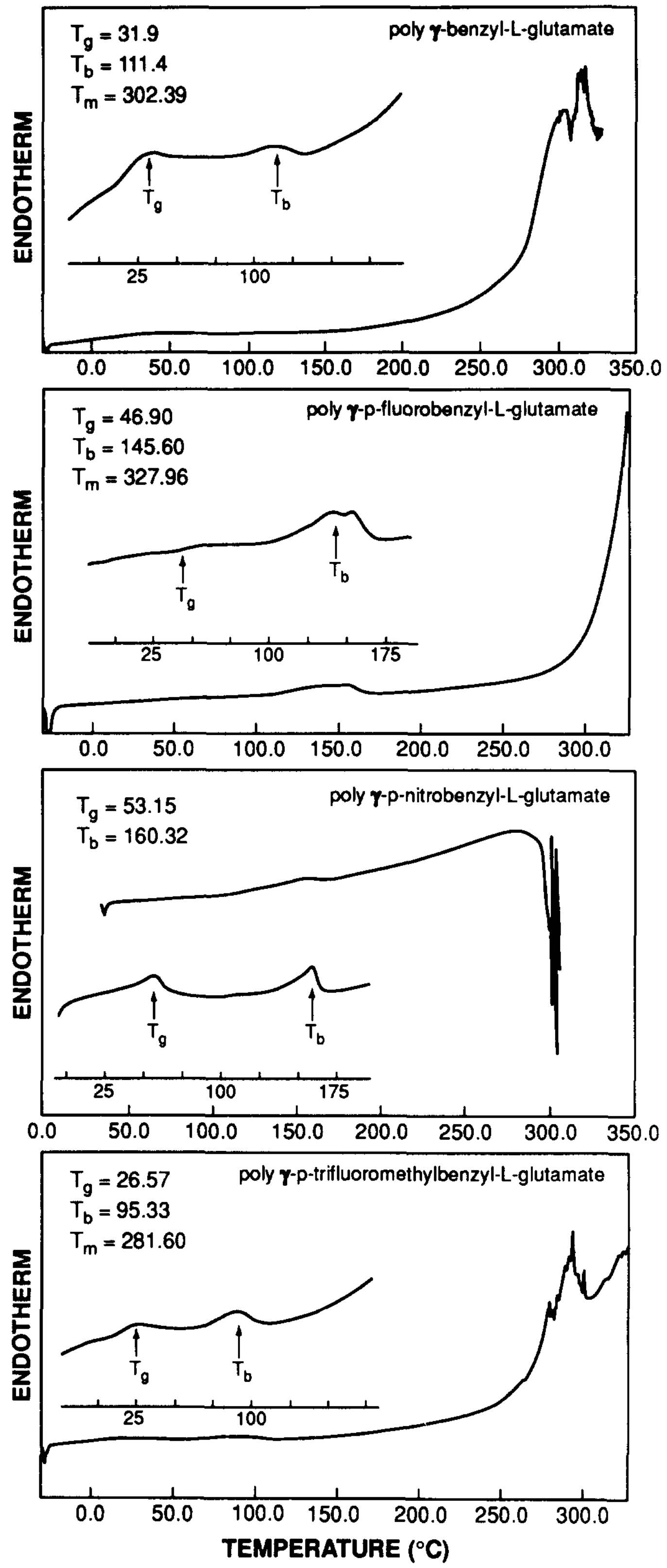

Figure 2 D.s.c. curves for the polymers poly(γ-benzyl-L-glutamate), poly(γ-*p*-fluorobenzyl-L-glutamate), poly(γ-*p*-nitrobenzyl-L-glutamate), and poly(γ-*p*-trifluoromethylbenzyl-L-glutamate) over the temperature range −40 to 350°C

Side-chain orientation in PGLU(pFB)

The *r* value for PGLU(*p*FB) is not as high as the *r* values for PGLU(*p*NB) and PBLG. Differential scanning calorimetry (d.s.c.) revealed a second transition peak T_b at approximately 150°C. The area under the peak is much larger than that under the first transition peak, and the peak is much broader. We interpret this as indicating that PGLU(*p*FB) has a larger heat capacity which contributes to maintaining a constant temperature in the polymer. The ability to store this heat energy implies that PGLU(*p*FB) requires a much higher thermal energy input, relative to the other polymers, in order to disrupt the benzene ring stacking and polar interactions. Therefore, it appears that PGLU(*p*FB) consists of a more stable helical structure than the other glutamate ester polymers used in the present study. The increased difficulty in orienting the PGLU(*p*FB) side-chain groupings is attributed to the stacking of the side chain and the restriction of the chain motion. This structural feature suggests that the polymer would be a good insulator with a high dielectric breakdown strength (>1 MV cm^{-1} at 160°C). Our measured dielectric strength data on this polymer are comparable to those for organic and inorganic insulators such as Teflon (0.39 MV cm^{-1}) and mica (1.46 MV cm^{-1})[17]. The PGLU(*p*FB) polymer has a dielectric constant of 4.6 until the frequency approaches 1 MHz. Additional data supporting the prediction of such electrical insulating properties are presented in *Figure 3*.

Side-chain orientation in PGLU(pTFMB)

The application of an electric field of 20 V μm^{-1} to PGLU(*p*TFMB) resulted in a significant increase in the electro-optical coefficient, although the poling efficiency is less than that for PBLG and PGLU(*p*NB). The PGLU(*p*TFMB) side chain contains a trifluoromethyl group and each monomer unit has a dipole moment of 2.54 D[18]. This polymer should exhibit a higher electro-optical coefficient than poly(γ-benzyl-L-glutamate). However, the measured *r* value for this polymer is lower than the *r* values of even PBLG and PGLU(*p*FB). This indicates that the polymer has a high dielectric breakdown strength and that the applied voltage for the poling process was insufficient to reorient the side chains. The dielectric constant for each of these polymers is given in *Figure 3*. Analogous to PGLU(*p*FB), PGLU(*p*TFMB) is also a good electrical insulator. Imposition of side-chain reorientation in this polymer very close to the dielectric breakdown voltage, the polymers PGLU(*p*FB) and PGLU(*p*TFMB) could not be adequately oriented by the highest voltage that was accessible. Since the known poling efficiency is of the order of 10–20%, only a small fraction of the side chains could be aligned and it was not possible to remove the centre of inversion symmetry by the poling process[16].

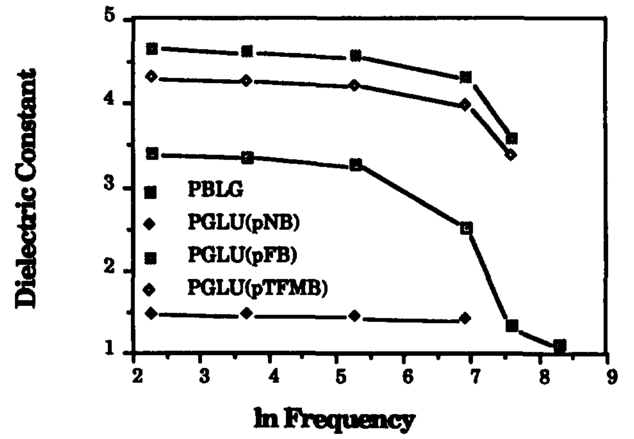

Figure 3 Plots of the dielectric constant against ln(frequency) for PBLG and the *para*-substituted polymers

under mild poling conditions could not be achieved. Although a high poling electric field ($20\,\mathrm{V\,mm^{-1}}$) was applied to the film at 150°C, the centre of inversion symmetry was still present in the side-chain structure.

The infra-red spectrum of PGLU(*p*TFMB) shows amide I bands at 1624 and $1656\,\mathrm{cm^{-1}}$, indicating the presence of both α-helical and β structures[19]. It has been suggested that polypeptides that normally form α-helical secondary structures tend to form β structures when the molecular weight of the polypeptide is sufficiently low[20]. The spectrum for PGLU(*p*TFMB), along with the intrinsic viscosity data, indicate that this polymer has a relatively low molecular weight and this could be responsible for the presence of a β-structure component. D.s.c. thermograms revealed that the T_g value for PGLU(*p*TFMB) was the lowest (26.6°C) of the four polymers. Since T_g is only 26.6°C, the side-chain functions can undergo extensive relaxation to a random orientation after the sample is poled and returned to room temperature. Consequently, the additivity of the dipole moments of the side-chain groups is broken and the total molecular dipole moment is not enhanced.

The infra-red spectroscopic data indicate that PGLU(*p*FB) and PGLU(*p*TFMB) have a longitudinal side-chain orientation in the solid state. This is a significant factor that contributes to the low r values for these polymers. Because of the random orientation and the low T_g values, the side-chain structures in these polymers require higher levels of thermal and electrical energy for reorientation of the side chain and its associated dipole than do those in PBLG and PGLU(*p*NB).

If the electro-optical coefficients of PGLU(*p*FB) and PGLU(*p*TFMB) are compared, it is apparent that the electro-optical coefficient for PGLU(*p*FB) is almost twice as large as the coefficient for PGLU(*p*TFMB). We attribute this to the difference in the ease of side-chain orientation between the two polymers.

Wada[1] has shown that the normal right-hand α helix of PBLG has a side-chain dipole moment direction that is in the opposite direction to the dipole of the α helix. Because the side chain is oriented longitudinally in right-handed polyglutamates, its dipole moment does not reinforce the helical backbone dipole moment. Since the dipole moment of the side-chain group in PGLU(*p*TFMB) is greater than that of PGLU(*p*FB), the total dipole moment that can contribute to the electro-optical properties of PGLU(*p*TFMB) can be presumed to be smaller than that of PGLU(*p*FB). If this assessment is correct, it would result in a smaller electro-optical coefficient for PGLU(*p*TFMB) than for PGLU(*p*FB). Both PGLU(*p*FB) and PGLU(*p*TFMB) have an almost zero value for the lock-in signal I in the unpoled samples, as compared to PBLG and PGLU(*p*NB). When poled at $20\text{–}38\,\mathrm{V\,\mu m^{-1}}$, PGLU(*p*FB) shows an r value equal to $3.0\times10^{-2}\,\mathrm{pm\,V^{-1}}$, whereas PGLU(*p*TFMB) has an r value of $1.6\times10^{-2}\,\mathrm{pm\,V^{-1}}$ at $20\,\mathrm{V\,\mu m^{-1}}$. Therefore, these polymers did not show an enhanced electro-optical effect relative to PBLG under our poling conditions.

Of the four polyglutamates, PGLU(*p*NB) had the highest electro-optical coefficient at $13.87\times10^{-2}\,\mathrm{pm\,V^{-1}}$ and required a relatively low poling voltage ($6\,\mathrm{V\,\mu m^{-1}}$). When poled at $26\,\mathrm{V\,\mu m^{-1}}$, PBLG was found to have an electro-optical coefficient of $5.2\times10^{-2}\,\mathrm{pm\,V^{-1}}$. PGLU(*p*NB), poled at this low voltage, had an electro-optical coefficient almost three times higher than the electro-optical coefficient for PBLG. This is attributed to the high electronegativity of the nitro group. If the molecule is oriented so that the vector for the dipole moment of the side-chain group can be added to the total electronic polarization, there is an enhancement of the non-linear properties. However, the PBLG side-chain vector does not contribute to the total electronic polarization to the same degree as the nitro side chain; therefore, it cannot be additive to the same degree.

A plot of the electro-optical coefficient against the poling field shows that the slope for PGLU(*p*NB) in *Figure 4* is much higher than that for the other polymers. We interpret this as indicating that PGLU(*p*NB) has the highest poling efficiency. If the poling does not orient the side-chain dipole in the direction of the α-helix dipole, the total dipole moment along the α-helix axis would be reduced by the vector sum of the side-chain dipole moments. The dipole moment of the ester group in PBLG has a negligible effect on the entire molecular dipole system. However, under the usual poling conditions, the electro-optical coefficient of PBLG is higher than the coefficients of PGLU(*p*FB) and PGLU(*p*TFMB). This implies that the effect of the ester group in PBLG is much smaller than the effects of the substituted side-chain groups in PGLU(*p*FB) and PGLU(*p*TFMB). In contrast to PGLU(*p*FB) and PGLU(*p*TFMB), PBLG also has a finite value of r prior to the poling process. The explanation for this is that, despite the small effect on the dipole moment of the side-chain dipoles of the ester group, PBLG still lacks some centrosymmetry owing to the main-chain crystal structure. Consequently, the transverse orientation of the side chain in PGLU(*p*NB) makes it much easier than for any other similar polymer of this type which has a longitudinal side-chain orientation to reorient the side chain by poling and to enhance the electro-optical effect.

Another way to compare PBLG and PGLU(*p*NB) to the fluorine-containing polymers PGLU(*p*FB) and PGLU(*p*TFMB) is in terms of the electrical insulating property against high temperatures and high electric fields. This implies that the stability of the molecular motion is important for poling efficiency under severe environmental conditions such as high temperature and high electric fields. Compared to the fluorine-containing polymers, PBLG and PGLU(*p*NB) have a relatively low dielectric breakdown strength, which was noted during the poling process. As can be seen in *Figure 3*,

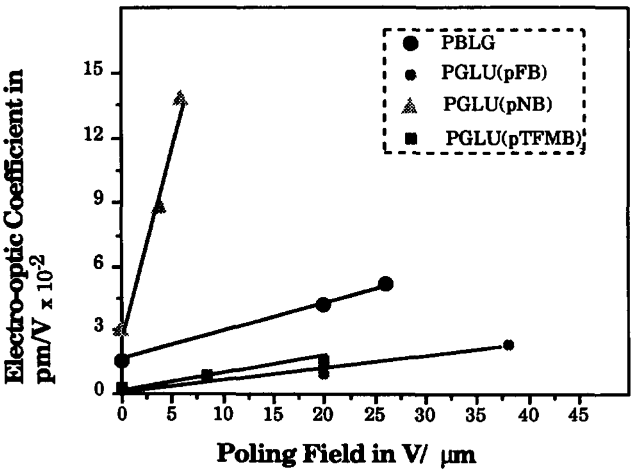

Figure 4 Plots of the electro-optical coefficient against the poling field for PBLG and the *para*-substituted polymers

the dielectric constants at various frequencies for PGLU(*p*NB) and PBLG are much smaller than those for PGLU(*p*FB) and PGLU(*p*TFMB). PGLU(*p*NB) exhibited almost no variation in its dielectric constant until the frequency was increased to 4 MHz. Thus, this polymer has the fastest response time relative to the other three polymers investigated.

The results of this study have demonstrated that specific *para*-substituted poly(γ-benzyl-L-glutamate)s in the α-helix conformation can be electrically poled to orient the side chain so that its dipole moment influences the dipole moment of the backbone. To our knowledge, this is the first demonstration of electrical poling of the side chain in poly(γ-benzyl-L-glutamate) and its derivatives. The poling has the consequence of yielding a bio-organic polymer with enhanced non-linear optical properties.

ACKNOWLEDGEMENTS

The authors thank Mr Jose Rimone and Dr Kim Winick for technical assistance with this study.

REFERENCES

1 Wada, A. in 'Polyamino Acids, Polypeptides, and Proteins' (Ed. M. A. Stahman), University of Wisconsin Press, Madison, 1962, pp. 131–146
2 Levine, B. F. and Bethea, C. G. *J. Chem. Phys.* 1976, **65**, 1989
3 Levine, B. F. and Bethea, C. G. *J. Chem. Phys.* 1975, **63**, 2666
4 Williams, D. J. (Ed.) 'Nonlinear Optical Properties of Organic and Polymeric Materials', Am. Chem. Soc., Washington, DC, 1983, p. 405
5 Singer, K. D., Sohn, J. E. and Lalama, S. J. *Appl. Phys. Lett.* 1986, **49**, 248
6 Watanabe, T., Yoshinaga, K., Fichou, D. and Miyata, S. *J. Chem. Soc., Chem. Commun.* 1988, 250
7 Ye, C., Marks, T., Yang, J. and Wong, G. K. *Macromolecules* 1987, **20**, 2324
8 Choi, D.-H. and Zand, R. *Mol. Cryst. Liq. Cryst.* in press
9 Doty, P., Bradbury, J. H. and Holtzer, A. M. *J. Am. Chem. Soc.* 1956, **78**, 947
10 Teng, C. C. and Man, H. T. *Appl. Phys. Lett.* 1990, **56** (18), 30
11 Nishihara, H., Haruna, M. and Suhara, T. 'Optical Integrated Circuits', McGraw-Hill, New York, 1985, Ch. 2
12 Nishihara, H., Haruna, M. and Suhara, T. 'Optical Integrated Circuits', McGraw-Hill, New York, 1985, Ch. 8
13 Tien, P. K. and Ulrich, R. *J. Opt. Soc. Am.* 1968, **58**, 551
14 Ulrich, R. and Torge, R. *Appl. Opt.* 1973, **12**, 2901
15 Kaminow, I. P. 'An Introduction to Electro-optic Devices', Academic Press, New York, 1974, pp. 49–51
16 Mortazawi, M. A., Knosen, A. and Kowel, S. J. *J. Opt. Soc. Am. B* 1989, **6**, 633
17 'ARRL Handbook', The American Radio Relay League, Newington, CT, 1987, Ch. 2
18 Ku, C. C. and Liepins, R. 'Electrical Properties of Polymers', Hanser, New York, 1990, p. 43
19 Bamford, C. H., Elliot, A. and Markey, W. Z. 'Synthetic Polypeptides', Academic Press, New York, 1958, pp. 143–167
20 Blout, E. R. and Asadourian, A. *J. Am. Chem. Soc.* 1956, **78**, 955