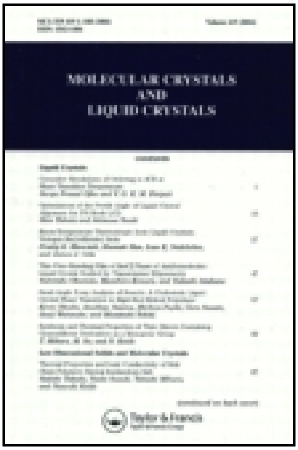

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Charge Injection Induced Optical Nonlinearity of 'In-Plane' Poled Polymer Films : Effects of Host Polymer, Substrate and Electrodes

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CHARGE INJECTION INDUCED OPTICAL NONLINEARITY OF 'IN-PLANE' POLED POLYMER FILMS : EFFECTS OF HOST POLYMER, SUBSTRATE AND ELECTRODES

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Abstract 'In plane' poling of polymer films containing hyperpolarizable dye molecules can lead to large optical nonlinearities along a direction perpendicular to that of the applied field. The magnitude of this nonlinearity depends on the polymer host, substrate and electrode metal. After removal of the field, decay of the nonlinearity also varies considerably from host to host. Measurement of the current flow during poling is consistent with a model for formation of the perpendicular nonlinearity via charge injection from the electrodes, diffusion into the bulk polymer and charging of the dye.

Keywords: polymers, poling, nonlinear optics

INTRODUCTION

Much research is currently being carried out with the aim of producing cheap and efficient second-order nonlinear optical materials. In particular, electric field poling of polymer blends or co-polymers incorporating hyperpolarizable dye molecules has received considerable attention.[1-5]

The "conventional" approach to polymer poling has involved contact or corona discharge poling of thin films in a "sandwich" type geometry *i.e.* the electric field is applied perpendicularly to the plane of the polymer film.[1-5] The electric field is applied when the polymer is close to the glass transition temperature, to align the dipolar dyes. The polymer becomes asymmetric along the direction of the applied field, and consequently it exhibits optical nonlinearity along this direction.

Poling studies in which the electric field is applied parallel to the plane of the film are much less common.[6-8] Our group[9] has concentrated on phenomena occurring during poling under conditions of charge injection, using a special 'in-plane' geometry. In this arrangement, the electric field is applied parallel to the film plane, and specifically uses electrodes which are much thinner than the polymeric film (see Figure 1). We have studied in greatest detail[9b,c] the 'model' system of a 2% blend of dimethylamino nitrostilbene (DANS) in poly methyl methacrylate (PMMA). The remarkable result of these studies was that this 'in-plane' poling produced not only nonlinearity along the electric field direction, but also a much stronger nonlinearity perpendicular to the film plane (*i.e.* perpendicular to the applied field).

Further experiments, detailed in earlier papers, led[9c] to the postulate of a new, different mechanism for production of second order nonlinearity in poled polymer films. In contrast to dipolar alignment, the dominant mechanism for producing nonlinearity in our 'in-plane' films is assumed to arise from the following sequence of steps:

(a) charge injection into the polymer when the electric field is applied

(b) conduction of charge basically along the substrate surface, but with some diffusion perpendicular to the surface

(c) trapping of charges on dye molecules, including dye dimers, thus creating an asymmetric distribution of charged dye species along the direction perpendicular to the film plane. It was then postulated[9c] that a charged dimer is hyperpolarizable along its stack axis, in order to fully explain the net nonlinearity perpendicular to the field.

In the present communication we wish to report further manifestations of this interesting new nonlinear effect, including enhanced control of the phenomenon, both in magnitude and stability, with particular reference to the electrical properties of the host polymer employed. Variation of the polymer matrix can lead to much longer retention (i.e. slower decay) of the nonlinearity both parallel and perpendicular to the applied field. The polymer matrix, the substrate and the metallic electrode material can all strongly affect the nonlinearity induced by in-plane poling, in contrast to their rather minor effect on the conventional dipolar poling mechanism. These influences can be related to the charge injection and retention properties of the media. Our results show that the magnitude and stability of the NLO coefficients which can be produced by charge injection in the 'in-plane' geometry can potentially rival those produced by poling in sandwich geometries, despite the much weaker poling fields employed.

EXPERIMENTAL

Our experimental techniques have been described fully in earlier publications.[9] Parallel strip electrodes, 2mm apart, are evaporated onto cleaned glass slides to a thickness of about 500 Å. (In experiments described in section C the glass slides were precoated in order to modify the substrate surface - see Fig. 1). The standard electrode material is aluminium, and we also present for comparison results using other metals. The slides were then coated by dipping into the appropriate polymer/dye solution (solvent THF) and drying under reduced pressure at 60°C for 24 h, and then at room temperature for another week. All polymers employed were samples of commercial origin.

Samples were activated for second harmonic generation (SHG) measurement only by application of high voltage (2 kV) across the electrodes at room temperature for 10 minutes. The current flow through the sample during the application of the voltage was recorded. SHG measurements, using a pulsed Nd:YAG laser, were performed on completion of the charging process, and at later times to monitor the SHG decay. By placing the sample plane at 45° to the laser propagation, the nonlinearity parallel and perpendicular to the direction of the DC electric field is measured using s- and p-polarized laser light respectively.[9c] The magnitude of the SHG response is converted to a nonlinear susceptibility by the accepted procedure of calibration against quartz. In accordance with our convention,[9] the x direction in the sample is the direction along which the DC electric field is applied, and the z direction, normal to the film plane, is that along which this new phenomenon of charge injection induced SHG is observed.

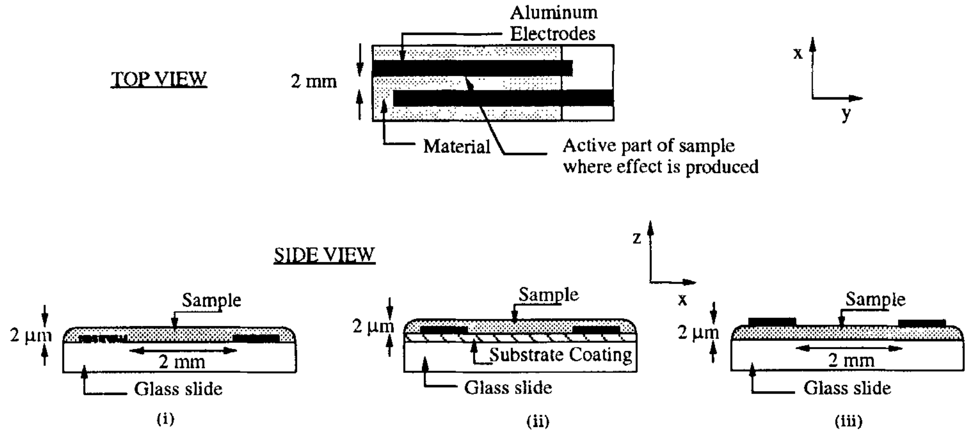

FIGURE 1 Top and side views of the sample geometries used for 'in-plane' poling of polymer-dye films. Side views are shown for samples: (i) cast directly on glass slides, (ii) in which the glass is pre-coated with a different substrate, and (iii) in the "reverse geometry" with the electrodes at the polymer/air interface.

RESULTS

A. Magnitude of SHG of films containing DANS dissolved in different polymers.

The efficiency of various polymeric hosts in producing nonlinearity perpendicular to the applied field is demonstrated here. Films containing 2% by weight DANS were prepared in : Polymethyl-methacrylate (PMMA), Polycarbonate (PC), Polystyrene (PS), Polyvinyl-chloride (PVC), and Polysulphone (P.Sul).

After applying the DC field of 10^4 V/cm at room temperature, the SHG measurements were performed (Table 1); nonlinearity perpendicular to the applied field is designated by $\chi^{(2)}_{zzz}$, and nonlinearity parallel to the field is given by $\chi^{(2)}_{xxx}$. Application of the field only at RT (as compared to T_g) may somewhat facilitate[9b,c] the charge injection induced nonlinearity ($\chi^{(2)}_{zzz}$) as opposed to the dipolar nonlinearity ($\chi^{(2)}_{xxx}$).

Generally the SHG signals along the z-direction ($\chi^{(2)}_{zzz}$) are higher by the order of 20-40 compared to the x-direction ($\chi^{(2)}_{xxx}$). Polymers with higher or lower glass transition temperatures (T_g) than PMMA show smaller $\chi^{(2)}$ values. We also see that the absorption maximum of the DANS varies somewhat from host to host; all these absorptions are red-shifted with respect to the solution maximum in THF (430 nm).

As noted earlier,[9b,c] the magnitude of the $\chi^{(2)}_{zzz}$ nonlinearity ($2*10^{-8}$ esu) appears to be the highest ever reported for polymers exposed to a field of only 10^4 V/cm.

MATRICES	T_g [°C]	λ_{max} [nm]	$\chi^{(2)}_{zzz}$ [10^{-9} esu]	$\chi^{(2)}_{xxx}$ [10^{-9} esu]
Poly methyl methacrylate (PMMA)	109	438	15	0.40
Poly vinyl chloride (PVC)	88	448	11	0.27
Polycarbonate (PC)	149	442	8	0.21
Polystyrene (PS)	92	437	6	0.13
Polysulphone (P.Sul)	188	447	5	0.16

TABLE 1. Comparison of the nonlinearity induced by 'in-plane' poling of blends of 2% DANS in various polymers. The pure polymer glass transition temperature and the absorption maximum of DANS in each matrix are also given. Note that addition of DANS caused a small change in T_g.

B. Decay of SHG of DANS in polymeric matrices.

After removing the field, the poled film is not at thermodynamic equilibrium, and generally the SHG will decay due to the tendency of the system to relax to equilibrium. However, the rate of SHG decay is controlled by kinetic factors. In conventional poling (nonlinearity induced by dipolar alignment of the dyes), once the DC electric field is removed, dopants in the regions of sufficient mobility and local free volume are free to rotate out of the imposed orientation,[10] thus diminishing the symmetry breaking.

For $\chi^{(2)}_{zzz}$ nonlinearity, which is attributed to an asymmetric distribution of charged dye species, nonlinearity is lost after removal of the field due to current discharge.[9b]

The SHG decay was measured for the different polymer matrices. Figure 2 illustrates the $\chi^{(2)}_{zzz}$ decay, showing that the decay in four polymer hosts (P.Sul, PC, PS and PVC) is much slower than in the "model" host PMMA. Decay cannot be fitted by simple exponential behavior (see Discussion). In the normalized $\chi^{(2)}_{xxx}$ decay illustrated in figure 3, the decay curves are qualitatively similar, but not identical.

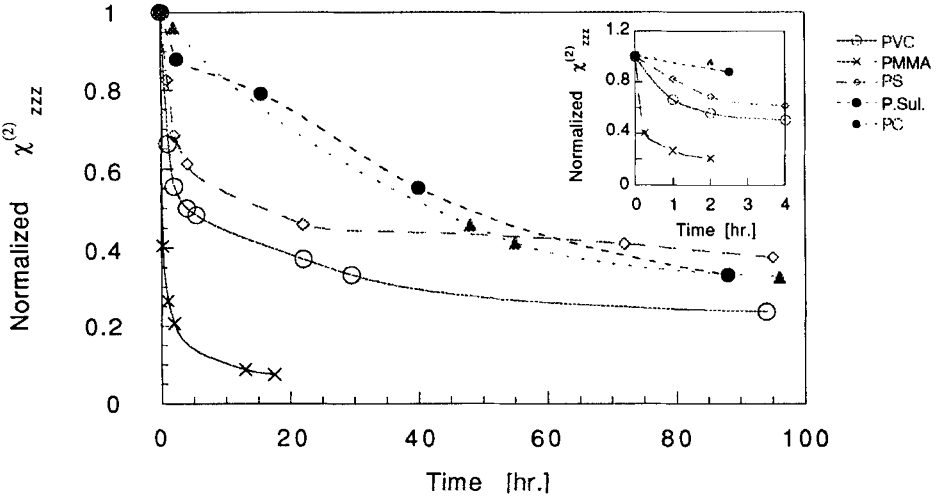

FIGURE 2. Decay of the $\chi^{(2)}_{zzz}$ nonlinearity of 2% DANS in various polymer matrices. For each matrix, the decay is normalized relative to the value of the nonlinearity recorded immediately after turning off the high voltage. The decay during the first 4 hours is shown in more detail in the insert. Curves joining the data points are for guidance only.

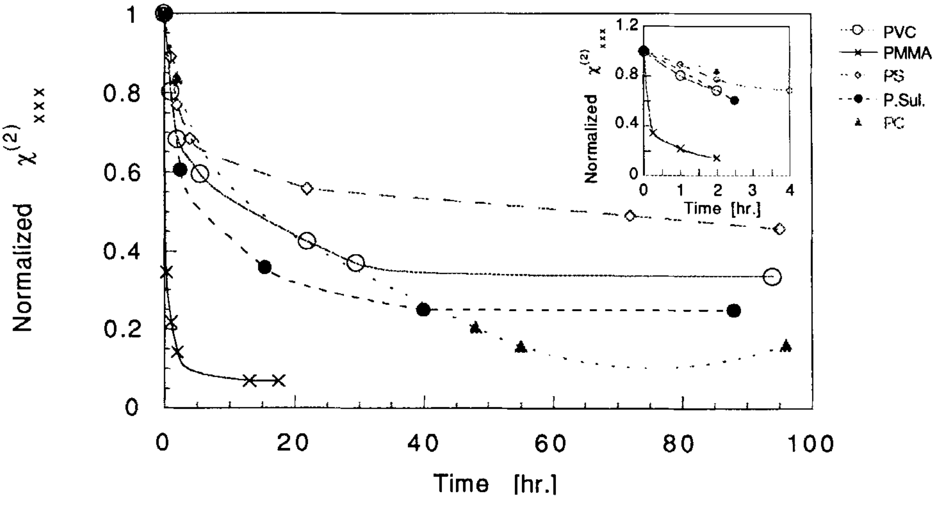

FIGURE 3. Decay of the $\chi^{(2)}_{xxx}$ nonlinearity of 2% DANS in various polymer matrices. For each matrix, the decay is normalized relative to the value of the nonlinearity recorded immediately after turning off the high voltage. Curves joining the data points are for guidance only.

C. Effect of different substrates and charging current in the 'in-plane' geometry

In this section we show how changing the substrate onto which a 2% blend of DANS/ PMMA is cast can drastically change the $\chi^{(2)}_{zzz}$ nonlinearity. We further show how these differences can be correlated with the charging current which flows along the substrate surface during the application of the high voltage.

Our starting point for examining the effect of different substrates was the comparison of two glass slides obtained from different manufacturers - Herenz and Knittel Glaser - and denoted type I and type II respectively. (Experiments described in other sections of this paper were performed on the type I glass). Samples were prepared by casting 2% DANS/PMMA on both types of glass. It was observed that after application of the high voltage, samples on type II glass yielded very low $\chi^{(2)}_{zzz}$ nonlinearity as opposed to the high $\chi^{(2)}_{zzz}$ nonlinearity on type I glass.

In order to examine more fully substrate effects we also prepared samples on the following substrates (see Figure 1):

- type I glass coated with 2% by weight tetramethylammonium-bromide, which has been shown[9b,c] to inhibit $\chi^{(2)}_{zzz}$ formation by charge 'scavenging'.

- type II glass covered with an approximately 1000 Å thick layer of Polyimide (PI), octadecyl-trichloro-silane (OTS), Nylon 6, Polyamide-Urea (PAUrea) or Polyamide-Urethane (PAUrethane).

- a "reverse geometry" where the DANS/PMMA film was cast on plain glass, and electrodes were evaporated on top of the film. This enables us to compare charge injection along the PMMA/air interface to that along the PMMA/substrate interface.

Table 2 presents the results of these experiments. Glass type I is an efficient substrate for producing strong $\chi^{(2)}_{zzz}$.Treating it with a surface scavenger reduces the $\chi^{(2)}_{zzz}$ values by two orders of magnitude, from $20*10^{-9}$ esu to $0.2*10^{-9}$ esu. Glass type II is a "bad" substrate with $\chi^{(2)}_{zzz} = 0.08*10^{-9}$ esu, but coating it with Polyimide converted it into a "good" substrate with $\chi^{(2)}_{zzz}$ of $15*10^{-9}$ esu. So by simply modifying the sample substrate we can drastically change the nonlinear response. A "good" substrate can be converted into "bad" substrate and vice versa. The different behavior of the two glass types, I and II, can be attributed to different surface conductivities, which we assume to arise from different manufacturing and cleaning procedures in the two glass samples.

A connection exists between the charging current and the nonlinearity in the z-direction. In the first and fourth substrates (glass type I, and type II coated with PI) the charging current is high and so is $\chi^{(2)}_{zzz}$. In the slide covered with the surface scavenger the nonlinear response is only moderate, as is the current, while on type II glass the current is so low that the $\chi^{(2)}_{xxx}$ ($=0.1*10^{-9}$ esu) is even higher than $\chi^{(2)}_{zzz}$.

On OTS, Nylon, PAUrea and PAUrethane substrates, the current is similarly too small to induce an effective charge gradient. In those samples we also measured higher values of $\chi^{(2)}_{xxx}$ than of $\chi^{(2)}_{zzz}$. On the other hand, substantial current is observed in the "reverse geometry" i.e. along the PMMA/air interface, and a significant $\chi^{(2)}_{zzz}$ is obtained.

Substrate	Current [μA] after charging for					$\chi^{(2)}_{zzz}$ [10^{-9} esu]	$\chi^{(2)}_{xxx}$ [10^{-9} esu]
	1/2 min.	1 min.	2 min.	5 min.	10 min.		
Glass type I	16.2	15.1	13.4	12.2	10.7	20	0.3
Glass type I + surface scavenger	4.2	3.9	3.0	2.4	1.9	0.2	
Glass type II	0.64	0.18	0.23	0.19	0.22	0.08	0.1
Glass type II + PI	10.4	6.1	2.8	1.2	0.9	15	0.4
OTS	0.03	0.03	0.03	0.02	0.02	0.06	0.07
Nylon 6	1.2	0.95	0.64	0.42	0.28	0.04	0.08
PAUrea	0.26	0.24	0.20	0.16	0.13	0.04	0.06
PAUrethane	0.74	0.60	0.44	0.29	0.20	0.03	0.07
"Reverse Geometry"	30	15.5	7.0	2.4		3.4	0.04

TABLE 2 Charging current measured at various times during the application of 2000V to various samples. The nonlinear susceptibilities were measured at the conclusion of the charging process (10 minutes). The "reverse geometry" is as depicted in Figure 1.

A comparison between the charging currents shows that the current in the first 30 seconds should be about 10μA in order to gain effective SHG signals. In all the examined samples covered with PMMA + DANS, the building up of the SHG signal took about 20 to 30 sec., and another 30 sec. were needed to reach equilibrium values.

In samples containing the PI substrates, high nonlinearities were observed by 'in-plane' poling at room temperature, whereas application of the field at 100°C produced a low $\chi^{(2)}_{zzz}$ value ($0.37*10^{-9}$ esu). Although current measurement at 100°C showed that the PI layer has a higher conductivity than at 20°C, the higher temperature appears to adversely affect the efficiency of charge diffusion and trapping on the dyes.

In conclusion we postulate that a current of 5-20μA, after 30 sec. of charging, is needed for producing a strong $\chi^{(2)}_{zzz}$ response. This current is much stronger than the discharge currents (pA) measured after turning off the field.[9b] A comparison of the charging current integrated over the 10 minute charging time to that of the integrated dischage current[9b] indicates that only a small fraction of the injected charge actually becomes trapped inside the polymer.

D. Effect of electrode metals on the SHG signals

The effect of the electrode metal on the SHG signals is examined here. The electrodes were evaporated on glass slides covered with polyimide (PI), as illustrated in Figure 1, followed by casting of the 2% DANS/PMMA. Measurements were made after exposing to an electric field of 10^4 V/cm at room temperature for 5 minutes. Results are given in Table 3, along with the work function of each metal ; there does not appear to be any direct correlation between the work function and the magnitude of the $\chi^{(2)}_{zzz}$ nonlinearity.

Metal	Work function[a] [ev]	$\chi^{(2)}_{zzz}$ [10^{-9} esu]	$\chi^{(2)}_{xxx}$ [10^{-9}esu]
Al	4.28	28	0.67
Cu	4.65	17	0.56
Au	5.10	12	0.24
80% Ni +20% Cr	5.15(Ni) , 4.50(Cr)	12	0.46
Ag	4.26	1	0.05

[a] "Handbook of Chemistry and Physics", 65th. edition, p.E-76,77 , CRC Press (1985).

TABLE 3 Effect of different electrode metals on the nonlinear susceptibilities of films of 2% DANS in PMMA cast on polyimide covered glass.

DISCUSSION

The experimental results presented above clearly demonstrate the connection between charge injection and formation of $\chi^{(2)}_{zzz}$ nonlinearity perpendicular to the applied field direction. Consequently, factors such as the type of host polymer, substrate and metal electrode material can have a strong effect on the magnitude of the nonlinearity. Such parameters are expected to have only small indirect effects (if any) on the formation of nonlinearity by the conventional dipolar alignment mechanism in poled polymers.

The magnitude of the observed $\chi^{(2)}_{zzz}$ nonlinearity in the various host polymers should be considered at this stage as an empirical observation. It is difficult to associate the observed trends with any particular single property of the polymer. According to our model,[9b,c] this nonlinearity depends on several effects such as charge diffusion, charge retention and tendency of the dye to aggregate, which may all vary independently from polymer to polymer.

It is therefore more worthwhile to consider the different decay rates in the various polymer hosts. Decay of nonlinearity induced by dipole alignment has been analyzed in terms of bi-exponential decay[11] or stretched exponentials.[12] Bi-exponential decays suggest[11] that the dye is usually found in either of two environments - such as inside the bulk polymer or on grain boundaries - while the stretched exponential model[12] suggests more complex kinetics. Attempts to fit our data to these kinetics were more successful using stretched exponentials, indicating that the decay mechanisms are quite complex. At a practical and more qualitative level, it is desirable to correlate the decay time to physical properties of the host polymer. As such, we ask why the $\chi^{(2)}_{zzz}$ decay was so much faster in PMMA than in the other 4 polymer hosts tested. There does not seem to be any simple connection with the T_g values, as two host polymers (PS and PVC) with lower T_g exhibit slower decay. Polymer relaxation below T_g occurs[13] down to a temperature T_β which is around or below room temperature for all these polymers.[14] In PMMA, which has the smallest aging range (T_g -T_β),[14] polymer relaxation rates around room temperature are observed[13,15] to be faster than in the other polymer hosts we have employed in this study. This may explain our observation that the highest decay rates of $\chi^{(2)}_{zzz}$ nonlinearity are observed in PMMA compared to the other matrices.

In general, the decay rates of $\chi^{(2)}_{zzz}$ and $\chi^{(2)}_{xxx}$ in the same polymer are different. For example, in PC and P.Sul, $\chi^{(2)}_{xxx}$ decays faster than $\chi^{(2)}_{zzz}$, especially in the initial stages. In accord with our model that $\chi^{(2)}_{zzz}$ nonlinearity arises from charged aggregates and $\chi^{(2)}_{xxx}$ from aligned monomers, we can suggest that the different behavior can be explained by the polymer structure. In PC and P.Sul the polymer backbones contain benzene rings that can freely interact with the aggregates, and thus can increase the aggregate's stability. This point may be important when choosing the polymer backbone for synthesis of nonlinear optical polymers for optimizing $\chi^{(2)}_{zzz}$ nonlinearity.

We have also observed that for a given polymer (PMMA) we can induce significantly different $\chi^{(2)}_{zzz}$ nonlinearity by varying the metal forming the electrode. It would be expected that different metal types would inject different amounts of charge into the polymer, and if electron injection will be dominant, the $\chi^{(2)}$ values should be related to the work function of the metal. However, this is only one part of the picture, since the nature of the Metal/Polymer/Glass interface must also be taken into account in order to predict the amount of charge storage in the polymer.

Gross[16] proposed that the total charge storage in a charged polymer ("electret") is the algebraic sum of charges (electrons and holes) existing in it. Mehendru *et al*[17] have shown that for the metals we have used, aluminium shows the highest density of charges injected into poly vinyl acetate, while copper and gold have similar charge density, and silver shows the lowest charge storage. These results correlate quite well with the relative magnitudes of $\chi^{(2)}_{zzz}$ we have observed using these metals for electrodes.

CONCLUSION

'In-plane' poling with thin electrodes can lead, via charge injection and diffusion, to large optical nonlinearities along a direction perpendicular to the applied field. The amount of charge injection and subsequent nonlinearity depends very strongly on the host polymer, substrate and electrode metal, while retention times vary from host to host. Empirical measurements of the effects of these parameters correlate with the conductivity of the substrate, the amount of charge injection from both the electrodes and equilibration rates of the polymer after removal of the electric field. The magnitudes and temporal stabilities of the nonlinearities perpendicular to the field reported here are slightly inferior to those reported for 'conventional' poling at much higher fields of optimized co-polymers. However, our results indicate that 'in-plane' poling depends on many parameters, optimization of which may yield superior and commercially viable nonlinear optical materials.

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