

Large Second Harmonic Generation in Electrically Ordered *p*-Nitroaniline–Poly(oxyethylene) 'Guest–Host' Systems

Toshiyuki Watanabe, Kazuo Yoshinaga,† Denis Fichou,‡ and Seizo Miyata*

Department of Material Systems Engineering, Faculty of Engineering, Tokyo University of Agriculture and Technology, Koganei, Tokyo 184, Japan

Molecular doping of poly(oxyethylene) by *p*-nitroaniline, followed by a polarising–freezing process, yields a material which exhibits large second harmonic generation (20–30 times that of urea).

Owing to their unusually large nonlinear optical second and third order susceptibilities [respectively, $\chi^{(2)}$ and $\chi^{(3)}$] as well as their ultrafast response times in the femtosecond time domain, organic nonlinear optical materials are of increasing interest for applications in optical devices. As for every second order nonlinear optical process, second harmonic generation (S.H.G.) can only be observed in media lacking any centre of symmetry inversion, and noncentrosymmetric organic crystals are the most promising materials with S.H.G. properties. Nevertheless, even though single crystals may have the high optical quality required for applications, they are difficult to prepare and show weak mechanical properties. For these reasons, materials with potential S.H.G. activity have been designed in a large number of other phases, including, recently, molecularly doped polymers.^{1,2} In this case, the nonlinear doping molecules are partially aligned inside the polymer matrix with the help of an intense electric field. For thermodynamic reasons, molecular relaxation occurs gradually after the electric field is removed and the nonlinear optical susceptibilities induced by this method always proved to be rather small.¹

We report the S.H.G. properties of *p*-nitroaniline (*p*-NA)–poly(oxyethylene) (POE) systems, where *p*-NA is the nonlinear optical doping molecule and POE is the matrix material, as a result of a polarising–freezing process. Both *p*-NA and

POE (MW 5000000) were dissolved in acetonitrile or benzene, and films were obtained by casting onto glass substrates. These films can be stretched and hot-pressed, since they have a good mechanical strength. The fairly good miscibility of *p*-NA in POE allows us to prepare materials with *p*-NA:POE molar compositions up to 1:4, differential scanning calorimetry (D.S.C.) showing a single phase for each composition. This study presents the results, only for molar compositions of 1:8 and 1:16. The *p*-NA/POE films were heated at 80 °C, allowing the doping molecules to rotate freely inside the polymer. Alignment was then achieved by applying a low intensity electric field ($\sim 10^{-2}$ mV/cm) between two conducting plates sandwiching the films (thickness ~ 0.5 mm). The systems were cooled to room temperature while still being polarised. Finally, the field was removed, leaving cloudy crystallised films which have acentric structures due to the alignment of the *p*-NA molecules along their polar axis.

The S.H.G. measurements were carried out by reflection by the classical powder technique.³ The films were held between two glass plates and irradiated with a pulsed Nd:YAG laser at 1.064 μm (10 ns, 5 mJ). The reflected second harmonic light was focused on a monochromator (532 nm) and a photomultiplier. The intensity of the S.H.G. is always referred to that of urea in powder form.

Figure 1 shows the time dependence of the S.H.G. intensity for *p*-NA/POE systems for the two compositions. For the 1:8 system the initial S.H.G. intensity is 20–30 times that of urea, and similar to that of 2-methyl-4-nitroaniline (MNA). The initial S.H.G. intensity is independent of the cooling rate in the polarising–freezing process. Figure 1 also shows that if the *p*-NA doping is halved (1:16 system), the S.H.G. intensity is

† On leave from the Canon Research Center, 5-1 Morinosato Wakamiya, Ateugi-shi, Kanagawa-Ken 243-01, Japan.

‡ On leave from C.N.R.S., Equipe de Recherche 241, 2–8, rue Henry Dunant, 94320 Thiais, France.

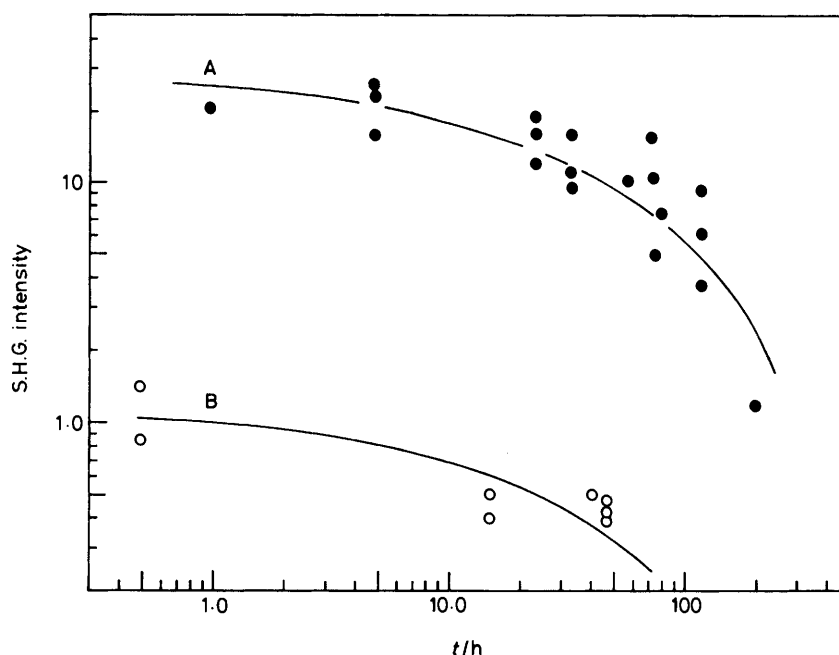


Figure 1. Time dependence of the S.H.G. intensity (relative to urea) for *p*-NA-POE systems. (A) *p*-NA-POE 1 : 8; (B) *p*-NA/POE 1 : 16 (molar ratio).

drastically reduced to values comparable to that for urea. Furthermore, the very high S.H.G. intensity of the 1 : 8 system persists over a long period and starts to decrease slowly only after 10 h, reaching half-intensity after ~ 100 h. This gradual decrease of S.H.G. intensity is due to the decomposition of the new crystalline complex into its components. This is confirmed by X-ray powder diffraction; the peaks arising from *p*-NA increase with time, while those due to the complex decrease; details will be described elsewhere.

The unexpectedly favourable S.H.G. properties of these *p*-NA/POE systems need some explanation. If we assume these systems to be a simple mixture of *p*-NA and POE, the theoretical second-order nonlinear coefficient, d_{33} , can be estimated by using the procedure of Singer *et al.*¹ The second order nonlinear optical coefficient is expressed by equation (1), where N is the number density of nonlinear optical molecules, and L_3 is the third order Langevin function. The function assumed, when the molecular polarisation anisotropy is small, is given by equation (2), p being given by equation (3), ϵ being the static dielectric constant, n the refractive index, and E the applied electric field. β is the molecular nonlinear optical susceptibility. Appropriate local field factors for the optical field, f^ω , are Lorentz-Lorentz type, $(n_\omega^2 + 2)/3$, and for the polarising field in equation (3) are Onsager type. Here we use the following values: $N = 1.54 \times 10^{21}/\text{cm}^3$ (POE-*p*-NA 8 : 1), $E = 50 \text{ kV/cm}$, $n = 1.5$, $\epsilon = 4.0$, $\beta = 34.5 \times 10^{-30} \text{ e.s.u.}$, and $\mu = 6.2 \times 10^{-18} \text{ e.s.u.-cm}$, respectively. From equation (2), the value of L_3 is calculated as 7.6×10^{-3} . The second harmonic coefficient d_{33} may be estimated by using equations (1)–(3) as $1.2 \times 10^{-9} \text{ e.s.u.}$ This value is one half of that for urea ($d_{36} 2.3 \times 10^{-9} \text{ e.s.u.}$).

$$d_{33}(-2\omega; \omega, \omega) = N f^{\omega} f^{\omega} f^{\omega} \beta_{ZZZ}(-2\omega; \omega, \omega) L_3(p) \quad (1)$$

$$L_3(p) = (p/5) - (p^3/105) + \dots \quad (2)$$

$$p = [\epsilon(n^2 + 2)] / (n^2 + 2\epsilon) \mu E / kT \quad (3)$$

This value is thus far too small to account for observed high S.H.G. intensity. Furthermore, if we assume the system to be a simple mixture of both components, the *p*-NA alignment is expected to relax rapidly after the electric field has been removed.

Therefore, the highly oriented nature of the *p*-NA is presumably induced by co-operative phenomena, *e.g.* oriented crystal growth in an electric field. These two unusual observations also show that the two components of the 1 : 8 *p*-NA-POE systems interact strongly so as to form a new phase, as occurs, for example, for dibromobenzene⁴ and resorcinol⁵ inside POE. In conclusion, the 1 : 8 *p*-NA-POE system, when submitted to a polarising-freezing process, has proved to exhibit intense and long-term S.H.G. activity under i.r. irradiation. These properties are due not only to the expected alignment of *p*-NA molecules under the effect of the electrical field, but also to a great extent to the formation of *p*-NA-POE complexes. The good mechanical strength together with the small optical damage observed under repeated pulsing make this new organic nonlinear optical material a good candidate for application in opto-electronic technologies.

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