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Optimisation of Photo-induced Geometric Isomerisation of Azobenzene Derivatives in Dye-doped Polymer Films for Enhanced Photo-induced Poling

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Summary: Photo-induced geometric isomerisation of azobenzene based chromophores can be utilised in a variety of molecular control procedures including photo-induced poling. In such processes additional mobility is imparted to chromophores trapped in a glassy matrix through the photo-induced *trans-cis-trans* cycle. We show that by using selected narrow wavelength bands of light to induce the isomerisation cycle during photo-induced poling, enhanced levels of polar order can be obtained in comparison to those obtained with monochromatic light. We attribute this to an increase in the fraction of chromophores which undergo isomerisation via an inversion mechanism. As a result, a higher proportion of the chromophores are able to participate in the photo-induced poling process since the free volume for isomerisation is reduced from that required for the rotation mechanism.

Introduction

Photo-induced poling [1-3] is one of a family of procedures which exploit the process of photo-induced geometric isomerisation in order to control and manipulate the molecular organisation in polymer and liquid crystal matrices. Central to such procedures is the availability of molecular units, most notably azobenzene moieties, which exhibit two inter-convertible geometric isomers. These procedures may exploit the presence of a thermally stable *cis* isomer to yield substantial shifts in isomer populations as in photo-induced isothermal phase transitions in liquid crystal systems [4,5] or utilise a rapidly cycling of *trans-cis-trans* isomers to provide molecular mobility within a glassy matrix as in both writing polarisation gratings [6] and photo-induced poling [1,2]. This contribution is concerned with molecular control procedures which involve the latter approach. In particular, we consider how the spectral characteristics of the incident light can be tuned to yield an optimum response in terms of the efficiency of the *trans-cis-trans* cycle and the influence of these characteristics on the molecular reorganisation process which accompanies the photo-induced

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geometric isomerisation. Although, this optimisation process is discussed in terms of photo-induced poling, the results have general application to all photo-induced isomerisation processes.

Photoisomerisation

Stilbene and pseudo-stilbene (azobenzenes and benzylidine anilines) chromophores are photochromic, showing significant changes in their optical absorption spectra when irradiated at a certain wavelengths. This response arises because they have two geometric isomers which may be inter-converted through the absorption of light and which exhibit different absorption spectra. The process of photo-induced inter-conversion is known as photoisomerisation. The two geometric isomers, *trans* and *cis*, for azobenzene are shown schematically as part of Figure 1. The precise mechanism of photoisomerisation is still not fully understood, with models predicting isomerisation via singlet-singlet state excitations or via singlet-triplet-singlet state excitations (Figure 2) 7). Within the stilbene family, it has been shown that some molecules utilise the singlet-singlet state route, while others such as 4-nitrostilbene isomerise via single-triplet-singlet states. For azobenzene based chromophores, the experimental evidence for these differing mechanisms is not conclusive 8). However, recent work 9) on the influence of the solvent on photoisomerisation of azobenzene based chromophores suggests that such molecules exhibit a similar behaviour to the stilbenes. In terms of molecular mechanisms, photoisomerisation in azobenzenes can occur through rotation about the -N=N- bond or by an inversion process involving a rehybridisation mechanism of one of the nitrogen atoms 8,10). These two routes are shown schematically in Figure 1. It is widely accepted that the thermally driven conversion of the *cis* isomer of an azobenzene-based chromophore to the trans isomer involves the inversion mechanism 11). Less definite are the mechanisms for the photoisomerisation of the *trans* isomer to the *cis* isomer. Most evidence suggests that the π-π* excitation is responsible for the rotation mechanism and the weaker n-π* excitation may be responsible, in some systems, for the inversion mechanism 10).

Figure 3 shows the optical absorption spectra for a number of different azobenzene based chromophores in a non-polar solvent. Azobenzene shows a maximum absorption at ~ 318 nm which corresponds to the π-π* excitation and a much weaker peak at ~ 450nm which relates to the n-π* excitation. Para-substitution of electron acceptor/donor groups in the basic azobenzene chromophore results in substantial shifts of the π-π* peak in to the visible part of the electromagnetic spectra. In contrast the n-π* peaks are not significantly affected by such substitutions as shown in Figure 3. In Figure 4, we compare the absorption spectra of disperse red 1 (DSR1) in a polymethylmethacrylate (PMMA) host with the absorption spectra of azobenzene. For the DSR1 spectra we are not able to resolve the n-π* peak. However, if we assume that there is little shift in the n-π* peak for the DSR1 chromophore from the parent azobenzene, then the n-π* excitation peak for DSR1 is at a lower wavelength ~ 450nm) than the π-π* excitation. This is different to the behaviour of chromophores with weaker electron acceptor/donor group substitution in which the n-π* excitation is often resolvable on the high wavelength size of the π-π* excitation.

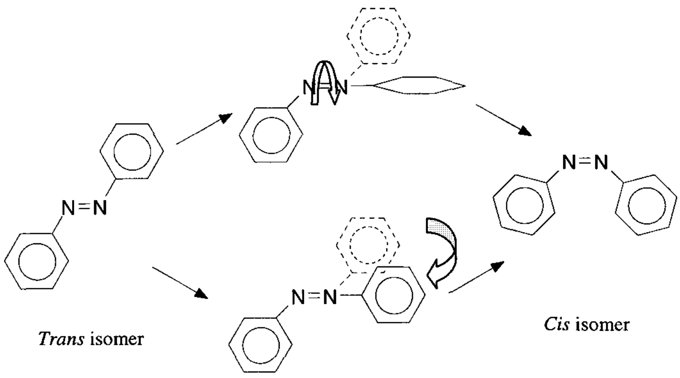
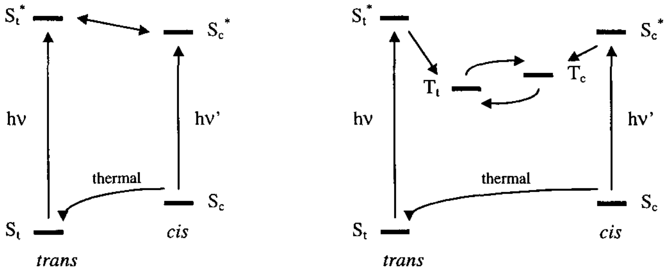


Figure 1: The inversion (bottom) and rotation (top) mechanisms possible for the photoisomerisation of the *trans* and *cis* isomers of azobenzene.



(a) *Singlet-singlet transitions*

(b) *Singlet-triplet-singlet transitions*

Figure 2: Schematic diagrams of the electronic states involved in the photoisomerisation of different stilbene chromophores, (a) cyanostilbene based chromophores, and (b) nitro based chromophores.

It is clear from this brief overview of photoisomerisation that the mechanisms may be complex and that the effects of minor variations in substituents or the matrix may be quite marked.

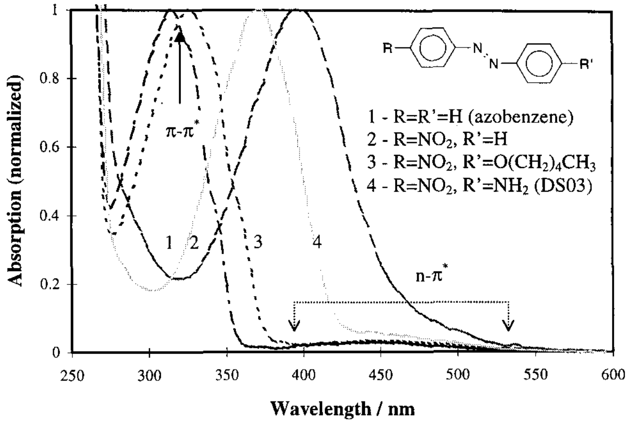


Figure 3: UV-visible absorption spectra of azobenzene based chromophores with different electron acceptor/donor groups at the para positions of the basic azobenzene molecule. The spectra were recorded for dilute solutions of the chromophores in methylcyclohexane at room temperature.

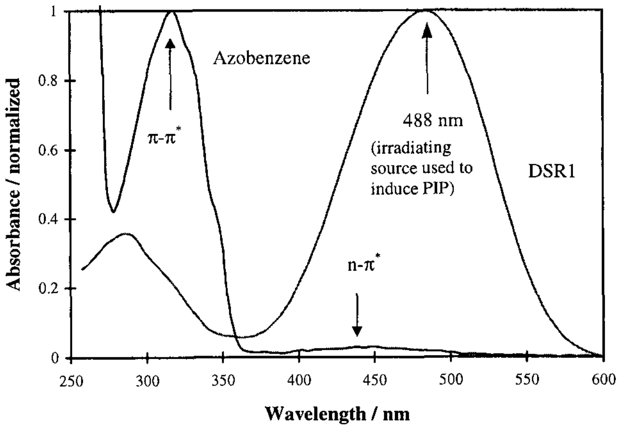


Figure 4: UV-visible absorption of DSR1 in the host polymer PMMA. Also shown is the absorption spectra of azobenzene in methylcyclohexane, and the positions of its π-π^* and n-π^* absorption peaks.

Experimental Procedures

The majority of the experiments described in this contribution were performed on a guest host system consisting of the chromophore Disperse Red 1 (Aldrich) (7% w/w) and a polymethylmethacrylate host (Aldrich M_w ~101,000). Although such films are unsuitable for technological devices due to the limited chromophore loading and long-term alignment stability, they provide a convenient system with which to explore the various photo-induced poling processing parameters. Thin films were prepared using a dip coating procedure from a 10% w/v solution of the chromophore and polymer in dichloromethane. The films of thickness 2μm were prepared in a sandwich structure with glass substrates coated with indium tin oxide (Balzers Z20) which acted as electrodes during the poling procedure. The extent of polar order was measured through the level of second harmonic generation *in-situ* during photo-induced poling using standard procedures with 1064nm as the fundamental beam. All values of the intensity of second harmonic are reported as a ratio to the equivalent intensity from an Y cut quartz crystal. A variety of radiation sources were employed for the photo-induced poling procedures including an argon-ion laser as a quasi-monochromatic source at 488nm and a xenon arc lamp equipped with optical filters to provide a selective broad-band source.

Photo-induced Poling

Photo-induced poling (PIP) is a technique that may be used to induce a polar alignment of non-linear optical chromophores which form part of a glassy guest-host or functionalised polymer system. The technique uses an external poling electric field which couples to the ground state dipole moments of the chromophore. In the glassy state, the chromophores are unable to respond to this applied electric field due to the restricted mobility within the glassy matrix. Irradiation at a wavelength which induces photoisomerisation, in particular the *trans-cis-trans* isomerisation cycle, provides additional mobility to the chromophores. As a consequence the chromophores adopt a statistical polar orientation distribution in a similar manner to that observed if the poling was performed at temperatures above the glass transition. PIP offers the particular advantage of enabling selected regions to be poled without the need for complex electrode patterns [1,12)]. Figure 5 shows a schematic of the PIP process. A more complete description is provided elsewhere [1-3,12,13)] and quantitative models have been developed by Dumont et al [14-17)]. Figure 6 shows the results of a simple PIP experiment performed at room temperature using 488nm light as the irradiating or pump light source. Application of the dc electric field alone results in a small level of second harmonic generation ($I_{2\omega}$) which arises principally from a third order interaction and not from any chromophore alignment. Irradiation at 488nm yields a substantial increase in the level of $I_{2\omega}$ which develops at a rate which is inversely proportional to the irradiation intensity. The plateau level of the second harmonic intensity is determined by the strength of the poling field and by parameters related to the matrix and chromophore. It is convenient during PIP to employ a laser as the irradiation source, partly since an argon ion laser conveniently provides light at a wavelength which corresponds to the wavelength of maximum absorption in a DSR1/PMMA film. In the next section we will explore the effect of varying the wavelength distribution of the irradiation source, building on previous studies using broad band irradiation [18].

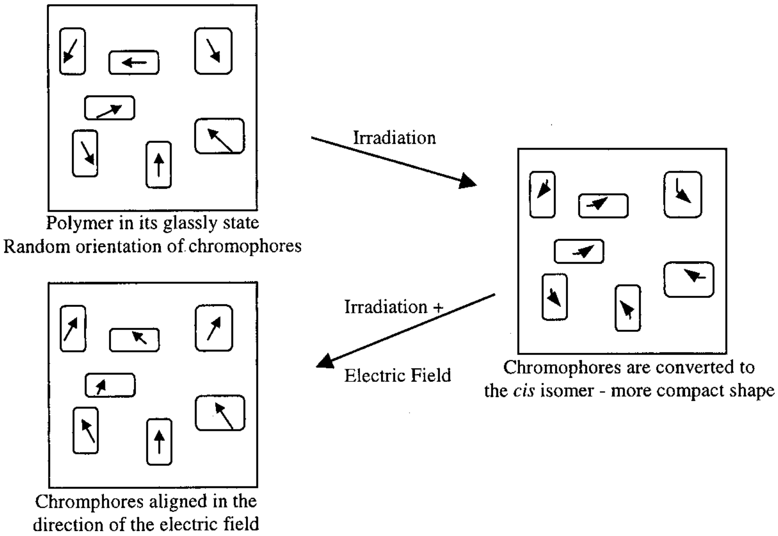


Figure 5: Schematic diagram of the PIP procedure in a guest-host polymer system.

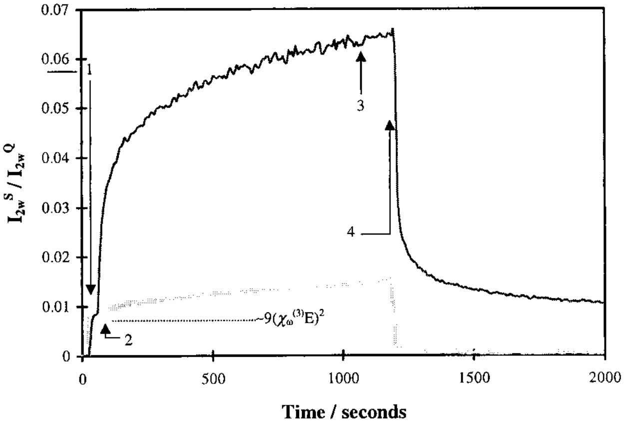


Figure 6: In-situ measurement of $I_{2\omega}$ for a DSR1/PMMA polymer film irradiated at 488 nm (34 mWcm^{-2}), and poled with an electric field of 50 Vμm^{-1} at room temperature. The broken line is the response when only an electric field is applied. [1 - Electric field On, 2 - Irradiation, 3 - Irradiation Off, 4 - Electric field Off].

Enhanced Photo-Induced Poling

We have explored the influence of the spectral characteristics of the irradiation source on the PIP process by selecting three narrow wavelength bands of ~ 40nm width which bridge the principal optical absorption feature of the DSR1/PMMA film as shown in Figure 7. Figure 8 shows plots of the second harmonic intensity recorded during the PIP process for each of the wavelength bands shown in Figure 7. In order to ensure that each sample was in a similar state, the films were first irradiated at room temperature with 488nm light until a plateau in terms of the second harmonic intensity was reached. At which point a narrow band of light centered at either 450nm (14mWcm^{-1}), 500nm (21mWcm^{-1}) or 550nm (32mWcm^{-1}) was employed instead of the 488nm light. Throughout the entire irradiation period a constant dc electric field was applied. It is clear that in the case of the second stage irradiation involving either 450nm or 500nm bands, there is a significant increase in the intensity of the second harmonic reflecting an increase in the level of polar order. It is noticeable that the band at 550nm which does not overlap with the n-π* peak does not lead to enhanced levels of poling. It is clear that the wavelength characteristics of the irradiation source strongly affects the PIP process. The power of the radiation source does not directly influence the steady state level of polar order achieved using PIP. In these studies the highest level of polar order is achieved using the 450nm centered band which had the lowest power density.

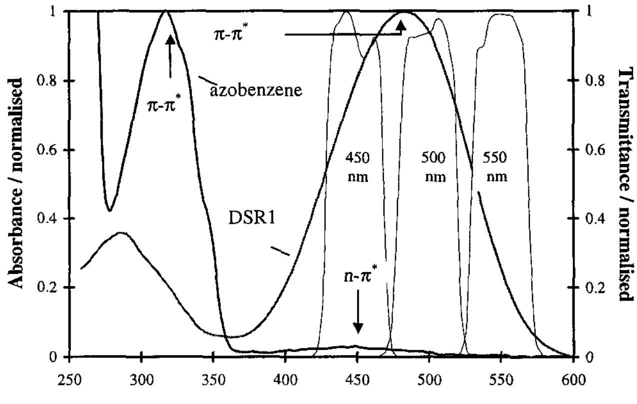


Figure 7: The absorption spectra of DSR1 in the host polymer PMMA, and azobenzene in methylcyclohexane. Also shown are the transmission spectra of the narrow-band filters used to irradiate the sample of DSR1/PMMA.

Without the irradiation field, few of the chromophores are able to rotate in response to the dc electric field. This lack of mobility can be related to the restricted free volume available to the chromophores during the rotation mechanism from *trans* to *cis*. The irradiating field, through the *trans-cis-trans* cycle, enables the chromophores to access a greater proportion of the free volume in the glassy matrix. This is because the *cis* isomer has a more compact shape. The PIP process involves the complete *trans-cis-trans* cycle and hence the level of polar order that can be achieved depends on the fraction of chromophores which have sufficient free volume to undergo isomerisation and to rotate under the influence of the poling field. The initial PIP stage using 488nm light stimulated isomerisation through the rotation mechanism. Simple inspection of molecular models reveals that isomerisation which proceeds through the inversion mechanism requires a small volume than the mechanism of isomerisation via rotation. As a consequence the level of polar order which can be achieved through PIP depends on the number of chromophores which be addressed using the irradiation field, on the precise mechanism of photoisomerisation from *trans* to *cis* and from *cis* to *trans* and on the mechanism of thermal relaxation from *cis* to *trans*. We attribute the differing levels of polar order for each of the different wavelength bands (Figure 7) to the details of the photoisomerisation process. The use of 40 nm bands of light centered at 450nm and 500nm increases the fraction of isomerisation processes which takes place through the inversion mechanism as a consequence of n-π* excitation. Previous studies of molecular mobility have assumed that the distribution of the size of free volume in a glassy polymer follows the gamma function 19). As a consequence most of the free volume is localised in small volumes relative to the polymer segment, with relatively little free volume distributed in large contiguous volumes. Since the inversion mechanism requires a smaller volume, increasing the fraction of chromophores absorbing at the n-π* excitation will enable a greater proportion of the chromophores to respond to the poling field. In other words, the level of enhancement is related both to the varying fraction of chromophores which undergo isomerisation through rotation and inversion and to the distribution of free volume in the sample and its relationship to the molecular volumes required for isomerisation.

It is possible that the bands at 450nm and 500nm stimulate photo-induced *cis-trans* isomerisation, since the π-π* excitation for the *cis* isomer is at ~ 360nm 13) and there may be some overlapping in the tail of the absorbtion maxima. To test the photophysics aspects of this model and to discount the photo-induced *cis-trans* stimulation, we have studied the process of PIP in guest host films based on PMMA and 4-cyano-4'-pentyloxyazobenzene. Inspection of the optical absorption of such films (Figure 9) shows that, due to the reduced strength of the electron donor/acceptor substituents, the π-π* excitation is situated at 375nm. This absorption maximum has a tail which extends to longer wavelengths which we associated with a partially resolved n-π* excitation. The absorption curve for azobenzene, in which the n-π* excitation is completely resolved, is shown for comparison. Clearly the absorption maxima for the n-π* excitation and the π-π* for the *cis* isomer are widely separated in terms of wavelength. Figure 10 shows the results of the PIP experiment using 4-cyano-4'-pentyloxyazobenzene as the chromophore. This chromophore has a small second order susceptibility compared with DSR1 and hence the intensity of the second harmonic is much reduced to that observed with the DSR1/PMMA films. The first stage involves PIP using a narrow wavelength band centered on 369nm which is close to the wavelength of maximum absorption for the π-π* excitation. The second stage involves irradiation with a narrow band centered on 450nm. It is clear that there is a significant increase in the level of polar order when the longer wavelength of light is used. This provides strong evidence for the model of enhancement described above.

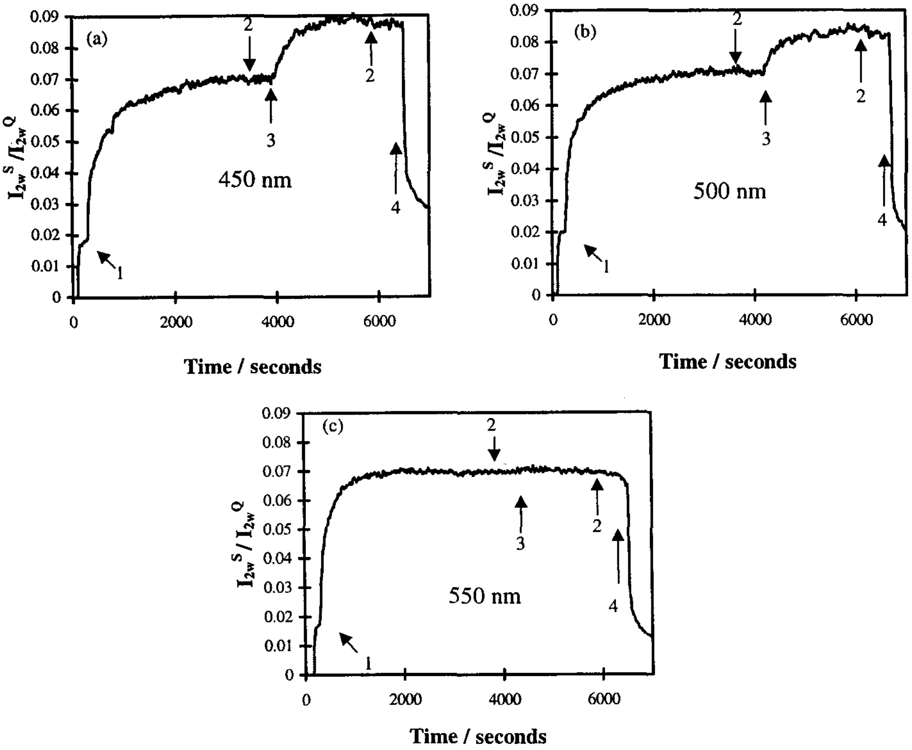


Figure 8: Three graphs showing the effect of different narrowband irradiating sources on the level of $I_{2\omega}^S/I_{2w}^Q$ for a DSR1/PMMA sample after initially being poled with an electric field of 50 Vμm^{-1} and irradiating at 488 nm (filter, bandwidth ~2 nm). The narrowband irradiation sources used were centred at (a) 450 nm, (b) 500 nm, and (c) 550 nm. [1- Irradiation at 488 nm, 2 - Irradiation Stopped, 3 - Filtered Irradiation On, 4 - Electric Field Off].

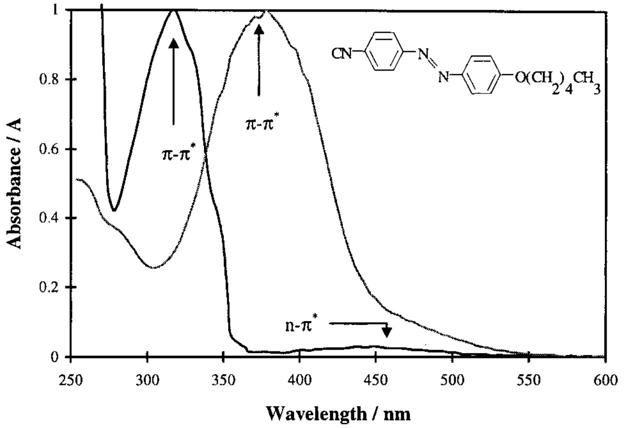


Figure 9: UV-visible absorption spectra of a film of 4-cyano-4'-pentyloxyazobenzene in PMMA. Also shown is the absorption spectra of azobenzene in methylcyclohexane, and the positions of the π-π^* and n-π^* absorption peaks.

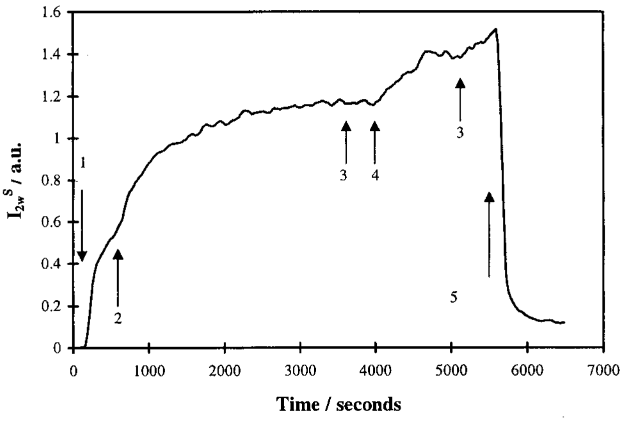


Figure 10: The variation of $I_{2\omega}^S$ with time of a 4-cyano-4'-pentyloxyazobenzene /PMMA sample poled using PIP when irradiated with a source centred at 369 nm until a photo-stationary level of $I_{2\omega}^S$ had been reached, and then irradiated at 450 nm. [1 - E-Field On, 2 - 369 nm On, 3 - Irradiation stopped, 4 - 450 nm On, 5 - Electric Field Off].

Conclusions

Photo-induced poling provides a direct route to the generation of selected areas of polar order in both guest-host and functionalised polymer systems. We have shown that the effectiveness of the photo-induced poling depends on the wavelength characteristics of the irradiating field and its relationship to the optical absorption spectrum of the chromophore. The number of chromophores which can respond to the poling field is directly related to the distribution of accessible free volume. By selecting an irradiating field which activates both the π-π* and n-π* excitations an enhanced level of polar order results. We attribute this to an increase in the fraction of chromophores which undergo isomerisation via an inversion mechanism and as a result a higher proportion of the chromophores are involved in the photo-induced poling process.

Acknowledgements

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