

Applied Photochromic Polymer Systems

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Preface

Photochromic polymer systems are of two main types: those which are merely solid solutions of photochromes in polymeric matrices and those custom-designed polymers which inherently exhibit photochromism. This book provides a concise review of developments in such systems over the past two decades. The coverage has been limited specifically to applied systems, or areas with potential applications, although over 500 references cite much of the literature on the fundamentals of the subject.

In general, non-biological organic photochromism in organic matrices has been covered. However, the unique properties of polysiloxanes merit special mention in Chapter 4, because of the attributes that such inorganic polymers can provide in certain systems such as liquid crystalline photochromic polymers, where two extremely interesting phenomena are combined. In addition to outlets in polarization-sensitive holographic recording media, such materials exhibit interesting non-linear optical effects suitable for optical switching and rheo-optical phenomena which may find application in mechano-optic transduction. Within this framework examples of all the important photochromic mechanisms are covered by authors from both the industrial and the academic sectors.

Given the photonic nature of the phenomenon under discussion, it is not surprising that many optical applications have been proposed. It is perhaps more surprising, however, that, until recently, no large scale markets had been identified that could commercially exploit photochromic phenomena. Invariably, the better candidates for exploitation involve photochromic polymer systems. Many arguments can be put forward to explain this slow uptake of photochromic 'device' application. These would include poor performance with regard to fatigue, thermal reversibility, light fastness, viable systems integration as well as market strategies which may question the very need for reversion of an initially useful/exploitable photochemical conversion reaction. Chapters 1, 2 and 3 of this book broadly address such issues and illustrate that a choice of materials currently exists, for example, to provide stable photochromic systems which may not thermally revert, as for fulgides and related species, and that high performance reversible spiroxazines in appropriate matrices are available which address specific

large volume markets, e.g. ophthalmic lenses, only because the combination of all of the properties unique to such systems conform to market needs. These chapters also include a critical analysis of digital, analog and holographic optical storage applications and describe materials suited to passive component fabrication in guided wave optics and active media for optical signal processing.

Chapters 5 and 6 complement earlier chapters in the book by dealing with areas which require research investment for future applications. The penultimate chapter broadly discusses photoresponse in polymers, from conceptual perspectives through to impressive working examples, and allows the reader to follow experimental strategy clearly throughout. This leads, ultimately, to identification of the somewhat previously neglected triphenylmethane-type photochromism in polymers, as exemplary candidates for the demonstration of large (field-assisted) genuine photomechanical responses which may have future applications, e.g. in novel photomechanical transducers. Chapter 6 provides a definitive overview of redox photochromism in viologen-based solid state systems. From an applications standpoint, such systems already describe impressive photochromism which gives rise to absorption at near infrared wavelengths, a region easily accessible to current laser diode technology. This chapter should stimulate new research in a less common area of photoresponsive polymers, so that, when combined with the other chromogenic phenomena available to such systems, new applications may emerge.

This volume complements existing and recent books on photochromism, which deal with low molecular weight photochromic systems mainly from a more fundamental perspective. It should appeal to industrial and academic researchers in materials science, chemistry, physics and electronics.

The editor is indebted to the contributors, experts in their field, for their superb co-operation throughout this project. Finally, as always the editor warmly acknowledges the encouragement given by his wife.

C.B.McA.

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Contents

1 Optical applications of organic photochromic polymer systems	1
C.B. McARDLE	
1.1 Introduction	1
1.2 Potential for erasable optical storage in photochromic polymer systems	3
1.3 Photochromic imaging in ordered systems or in systems exploiting ordering effects	12
1.4 Applications in optical signal processing and in integrated optics	21
1.5 Conclusions	26
References	27
2 Spiroxazines and their use in photochromic lenses	31
J.C. CRANO, W.S. KWAK and C.N. WELCH	
2.1 Introduction	31
2.2 Chemistry of spiroxazines, spiropyrans and related organic photochromic compounds	31
2.2.1 Nomenclature	31
2.2.2 Synthesis	33
2.2.3 Photochemistry of the spiropphotochromics	34
2.3 Required properties of photochromic systems for eyewear	40
2.3.1 General	41
2.3.2 Absorption spectra of unactivated and activated states	42
2.3.3 Kinetics of photochromic lens processes	45
2.3.4 Fatigue resistance (eyewear lifetime)	46
2.4 Structure–property relationships of spiroxazines	48
2.4.1 Indolinospiroxazines	49
2.4.2 Other spiroxazines	60
2.5 Stabilization of spiroxazines	61
2.6 Development of a commercial system for plastic photochromic eyewear	63
2.6.1 Plastic lens manufacturing	63
2.6.2 Processes for photochrome incorporation	67
2.6.3 The finished lens	71
References	77
3 Fulgides and fulgimides — a promising class of photochromics for application	80
J. WHITTAL	
3.1 Introduction to fulgides and fulgimides	80

3.2	Aryl fulgides	82
3.2.1	Introduction	82
3.2.2	Spectroscopic properties	83
3.2.3	Photochromism	87
3.2.4	Fatigue resistance	93
3.3	Fulgides with heteroaromatic groups — fatigue-resistant fulides	94
3.3.1	(E)- α -2,5-dimethyl-3-furylethylidene (isopropylidene)succinic anhydride	94
3.3.2	Structural modification of fulgides with heteroaromatic groups	97
3.4	Heliochromic compounds	107
3.4.1	Definition	107
3.4.2	Development of heliochromic fulgide derivatives	107
3.5	Fulgides and fulgimides in polymer matrices	110
3.5.1	Introduction	110
3.5.2	Investigations of photochemistry of fulgides in polymers	110
3.6	Applications of fulgides and fulgimides	114
3.6.1	Introduction	114
	References	118
4	Photochromic liquid crystal polymers	121
	V. KRONGAUZ	
4.1	Introduction	121
4.1.1	Mesomorphic phases	121
4.1.2	Important photochromic systems	123
4.2	Search for photochromic mesophases — Quasiliquid crystals (QLCs)	125
4.3	Photochromic liquid crystal polymers	135
4.3.1	Synthesis of copolymers	136
4.3.2	Thermodynamic properties	139
4.3.3	Thermochromism	142
4.3.4	Photochromism	145
4.4	Non-linear optical properties	157
4.4.1	Basic concepts	157
4.4.2	Theory of SHG from a mesophase containing high- β dye	159
4.4.3	Non-linear optical susceptibility measurements	161
4.4.4	Two-dimensional asymmetry and optical non-linearity upon poling by an electrostatic field	164
4.5	Optical information recording and storage	169
	References	171
5	Photoresponsive polymers: reversible control of polymer conformation in solution and gel phases	174
	M. IRIE	
5.1	Introduction	174
5.2	Photostimulated conformation changes of polymers in solution	175
5.3	Photostimulated phase separation of polymer solutions — another approach to induce the conformation changes of polymers	185
5.4	Photostimulated shape changes of polymer gels — continuous change	194
5.5	Photostimulated volume phase transition of gels — discontinuous change	203
	References	205

6 High and low molecular weight photochromic viologen-based systems	207
H. KAMOGAWA	
6.1 Introduction	207
6.2 Synthesis of viologens bearing vinyl groups and their polymers	208
6.3 Reversible colour development (photochromism) of viologens by photoreduction mechanisms (in matrices)	211
6.4 Generation of viologen radical cations in solution	216
6.5 Photochromism of viologen crystals	219
6.6 Preparation of polar aprotic viologen copolymers and their photochromic behaviour	223
6.7 Photochromism of <i>N</i> -aryl viologens	231
6.8 Viologens developing infrared absorption peaks (near 800 nm) by redox photochromism	234
6.9 Comparison of various viologens and photochromic reaction mechanism in the poly(<i>N</i> -vinyl-2-pyrrolidone) (PVP) matrix	239
6.10 Photomemories based on viologen photochromism.	243
References	245
Index	247

1 Optical applications of organic photochromic polymer systems

C.B. McARDLE

1.1 Introduction

Photochromism is a reversible transformation of a chemical system between two states whose absorption spectra are distinguishably different, the change being induced in at least one direction by electromagnetic radiation. This is illustrated schematically in Figure 1.1.

Radiation λ_1 , acting on species A, generates species B until a photostationary state is reached. In the dark, the photogenerated B forms may thermally revert to parent A forms. This back reaction can also be driven photochemically by irradiating with the wavelength at the maximum absorption of B, whence a new photostationary state will be achieved. The most common photochromic reactions are of the positive or normal type, in which the initial chemical system comprises a unimolecular A form which absorbs at a shorter wavelength (usually near UV/blue) and a B (or coloured) form that absorbs at wavelengths in the visible spectrum. Bimolecular chemical systems as well as negative or reverse photochromism ($\lambda_{\max}^A > \lambda_{\max}^B$) are also possible in organic systems. Unless otherwise stated this chapter is presently concerned with unimolecular, positively photochromic systems confined within amorphous or ordered solid or liquid crystalline states.

It is important to note that photochemically produced B forms need not be susceptible to thermal reversion to A in the dark. Whilst the former is quite a common feature, it is those systems which have been specifically molecularly engineered to be thermally stable in the B form, and reverted exclusively by photochemistry (driven by λ_2 irradiation), which have the greatest potential for practical device application.

The simplistic notion given thus far for $A \rightleftharpoons B$ interconversion ignores the fact that further undesirable side reactions involving the reactivity of B with active species, e.g. H_2O , O_2 , etc., can result in photoinduced decomposition and ultimately fatigue and loss of photochromism in the system. Fatigue and cyclability, i.e. the number of times the interconversion can be made without significant performance loss, as well as the photochemical quantum efficiency for forward and reverse (and decomposition) reactions,

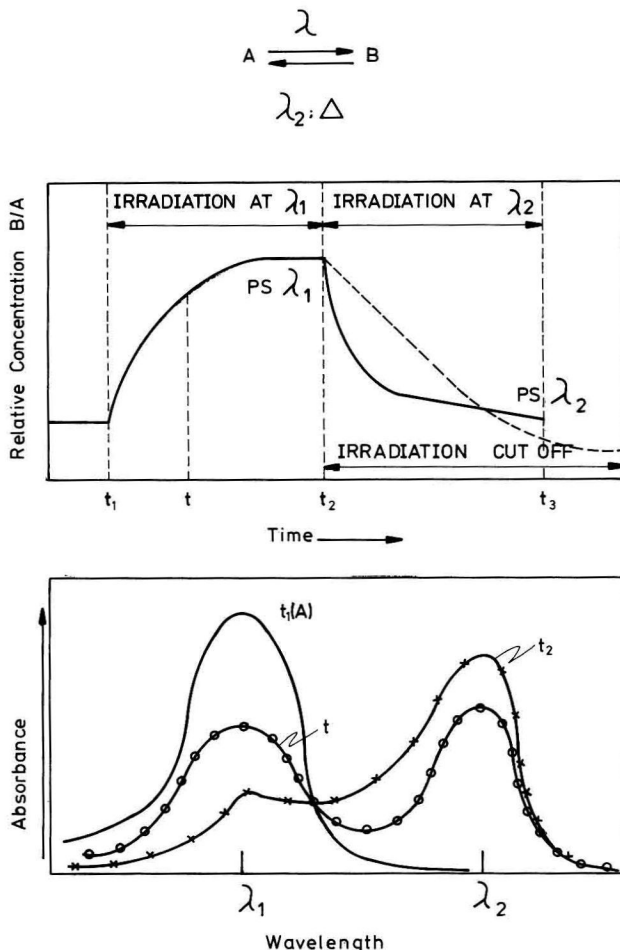


Figure 1.1 Schematic representation of the typical behaviour of a positively photochromic unimolecular reaction. A converts to photostationary state $PS\lambda_1$ on irradiation at λ_1 with concomitant spectral change described over time period t_1 to t_2 . The intermediate stage t recorded before the photostationary state $PS\lambda_1$ is also shown. (Redrawn from Eisenbach, 1979.)

are all important physical parameters which require characterization for device application.

Many organic (and inorganic) systems exhibiting photochromism as well as interesting chromogenic phenomena such as thermochromism (thermally-induced reversible colour change), solvatochromism (solvent-induced change), piezo- or barochromism (pressure-induced change), sorpto-chromism (acid-base-induced change), electrochromism (E-field-induced change) and

magnetochromism (H-field-induced change) have been detailed or reported in the literature (Brown, 1971; Lampert and Granqvist, 1990).

With regard to photochromic phenomena in organic molecules, six general categories may be used to classify the mechanisms responsible for the effect in the majority of cases, *viz.* heterolytic/homolytic bond cleavage, *cis-trans* isomerization, valence tautomerism, electron transfer systems, pericyclic reactions and triplet-triplet absorption. Several of these systems will be discussed throughout this text, particularly as inherent parts or components within macromolecular systems.

In this chapter it is assumed that the reader is familiar with the basic photochromic reactions of spiropyrans (heterolytic cleavage), fulgides (tautomerism) and azobenzenes (*cis-trans* isomerization). Extensive fundamental studies on these and other systems are documented in the works of Brown (1971), Japaridze (1979), Dürr (1989) and El'tsov (1990), and spiropyran-like and fulgide-fulgimide systems are further detailed in Chapters 2 and 3 of this book. From an applications standpoint the texts of Dorion and Wiebe (1970), Brown (1971) and Barachevskii *et al.* (1977) are also recommended.

The purpose of the present chapter is to comment on selected aspects of photochrome confinement in polymer matrices from a device viewpoint, as well as critically to review selected aspects of proposed optical applications for photochromic polymer and related systems over the last two decades. Because of the dramatic and reversible changes in the optical properties (absorption, refractive index) of a photochromic material on excitation, it is not surprising that much international research effort has centred on applications aimed at optical recording as well as in light attenuation control, for example in architectural and automotive glazing as well as in eyeglass wear. The latter area is close to commercialization and is described in detail in Chapter 2. Optical recording exploiting photochromic polymer systems has not, however, made an impact in the marketplace, and some of the reasons for this are alluded to in the present chapter, wherein systems considerations and competitive technologies are taken into account. It would appear, however, that the prospects for application in specialized holographic outlets, where hardware constraints are not so severe and photochemical reversibility and high resolution can all be used to full advantage, might become important in the future.

1.2 Potential for erasable optical storage in photochromic polymer systems

From the two available states (nominally colourless and coloured) associated with common photochromic processes, it will be clear that there is a basis for erasable optical storage/imaging systems which exploit this phenomenon.

Photochromic media for this application may be conveniently prepared by incorporation of the photochrome into a polymer binder in the form of a solid solution; alternatively, the polymer itself may be inherently photochromic. The former represents a facile low-cost option, whilst the latter may offer advantages from a stability viewpoint as well as the possibility of systems advantages (see p. 8). In either case, well-known techniques for high-quality film preparation used in the coatings industry should be directly applicable to photochromic media preparation.

In glassy solid solutions absorbances of 2 or more can be realized in films a few microns thick and at low photochrome loadings (approx. 2–3%). Nevertheless, care should be taken to avoid aggregation effects which can adversely influence kinetic behaviour as well as the spectral characteristics of the media. For example, Jones *et al.* (1989) noted that an approximately 2% solution of fulgides in toluene developed an additional absorption band on standing and have tentatively assumed this to be the result of dimerization. In their studies on photoanisotropic effects in solid poly(methyl methacrylate) (PMMA) solutions they have used approximately 0.25% fulgide levels to avoid potential problems.

Krongauz and his co-workers (Goldburt *et al.*, 1984; Goldburt and Krongauz, 1986) have reported new crystallization phenomena in atactic vinyl polymers bearing spiropyran groups in films cast by evaporation from methyltetrahydrofuran solutions. The so-called 'zipper crystallization' results from the mutual stimulation of solvatochromatically induced spiro \rightarrow merocyanine interconversion and crystallization. There appears to be no reason to assume that this phenomenon does not occur in simple solid solutions of spiropyranes in polymer matrices (Ekhardt *et al.*, 1987). The presence of such aggregates formed by antiparallel dipole–dipole interaction in merocyanines can occur at relatively low loadings (approx. 5%) and has a pronounced effect on decolourization kinetics (retardation) and causes hypsochromic shifts in the absorption maximum of coloured forms. Merocyanine association phenomena can lead to very stable coloured forms in crystalline (Goldburt *et al.*, 1984) and liquid crystalline polymeric systems (Yitzchaik *et al.*, 1990) (see also Chapter 5).

Aggregation effects are also known in azobenzene systems, so that while it is true to say that solid solutions of a variety of photochromes in polymer binders can be conveniently prepared care should nevertheless be taken to avoid association phenomena and their consequences on kinetics and wavelength tuning-in devices.

Although the concept of memory devices based on photochromism was proposed more than 30 years ago (Hirshberg, 1956), photochromic recording media have only reached the marketplace in an intermediary capacity via an early micrographics system [PCM I (NCR Co.), see Carlson *et al.*, 1962] and in small market niches for specialized films used in graphics work, etc. (e.g. Kodak photochromic film SO-548, Cyanamid films 43–540 (A),

51–142). There have been applications exploiting a single cycle from a photochromic reaction in instant imaging (Böttcher and Epperlein, 1983) but none has been realized in, for example, erasable digital storage despite the intense international research in photochrome development and the encouraging characteristics of write once–read–many (WORM) as well as some erasable alternative dye-in-polymer systems (Alexandru *et al.*, 1984; Gupta and Strome, 1985; Hartman and Lind, 1987). The principal reason for this situation would appear to relate to systems constraints since modern photochromes that exhibit good intrinsic fatigue characteristics and possess thermally stable coloured forms have been developed (see Chapter 3).

It is pertinent to consider briefly some of the very fundamental requirements, or highly desirable characteristics, for commercially viable, digital, bit-oriented optical memories in order to assess how likely photochromic polymer systems may conform. Desirable features include: high-integrity media (preferably with threshold characteristics) capable of facile mass production and of being handled under normal ambient conditions (light, O_2/H_2O , room temperature, etc.) without loss of performance (or data); simple optical systems, preferably using a single, low-power (approx. 5–10 mW), near-infrared (approx. 780–850 nm), directly modulated laser diode capable of providing all write, non-destructive read as well as tracking and focus error correction functions; high data rates (10 Mbits/s); high sensitivity ($\leq \text{nJ}/\mu\text{m}^2$); high bit resolution (approx. $1 \mu\text{m}^2/\text{bit}$); low bit error rates ($\leq 10^{-7}$); efficient implementation of fast data verification techniques such as direct read after or during write (DRAW or DRDW respectively); long-term bit stability (~ 10 years), etc. (see Bouwhuis *et al.*, 1985). Erasable media further require high cyclability ($\sim 10^6$ cycles) and preferably single-laser operation and similar kinetics for write and erase functions.

Notwithstanding the non-exhaustive list of requirements set out above, there is some question as to the relative virtues of erasable optical storage. The impetus to consider optical-based technology in the first instance was founded largely on the huge storage capabilities available to such systems resulting from focused coherent monochromatic light. Thus, WORM optical discs offer massive redundancy in memory which somewhat negates the need for erasability whilst at the same time offering the decided advantage of archivability.

At present it is impossible for photochromic media to fulfil many of the basic requirements for erasable digital recording in a commercially viable system. Even if ideal absorption characteristics and convenient wavelengths are assumed, many fundamental problems still remain, particularly from a kinetics standpoint. The kinetics of photochromic reactions (primarily thermal decolourization) in glassy polymer matrices has been extensively studied and comprehensively reviewed (Smets, 1983). Various studies have revealed that above the glass transition temperature (T_g), thermal back reactions obey a single first-order rate, whilst below T_g the behaviour is usually more

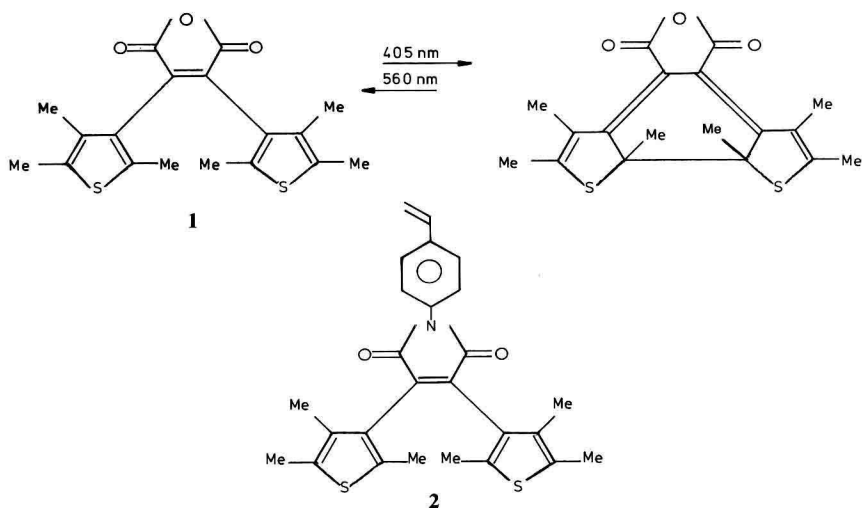
complex. It is generally accepted that this is the result of an inhomogeneous distribution of free volume within the matrices [Smets (1983) and references therein], although other possible mechanisms have been proposed (Goldburt *et al.*, 1986). The findings of Eisenbach (1979, 1980) pertaining to the dependence of photochromic processes in bulk polymers on free volume and their control by molecular motions within the polymer matrix itself has led to the conclusion that it is unlikely that the phenomenon has a good future in (rapid, reversible) photoimaging processes since reaction rate is determined by the mobility of the matrix surrounding the chromophore. However, in alternative types of photochromic imaging systems this may not be so serious a problem. More recently, several detailed studies on photochrome kinetics and on probing the size and distribution of free volume in glassy polymers and the effects of annealing photochromic polymer systems have been published (Lamarre and Sung, 1983; Sung *et al.*, 1984; Richert and Baessler, 1985; Victor and Torkelson, 1987a,b, 1988; Richert, 1988; Yu and Sung, 1988; Tsai *et al.*, 1990).

It is somewhat surprising that, in spite of the wealth of kinetics studies on photochromics in polymer matrices and the apparent interest in the exploitation of such materials in erasable optical storage, relatively few studies on photoinduced decolourization (even in systems with thermally stable coloured forms), especially in experimental arrangements which might simulate a practical optical system design, have been undertaken. Horrie *et al.* (1985) have, however, studied pulsed laser (337 nm) induced colouration with (continuous) visible light (filtered, 560 nm) decolouration for a spiropyran solid solution in a polycarbonate matrix. Such a study reveals much information for a systems engineer, e.g. write times in the nanosecond time regime (2.5 mJ, 10-ns pulse) are apparent, as is fluorescence emission occurring during the write pulse, which could in principle be useful as a DRDW verification system technique. However, the erase times are disappointing, occurring on the millisecond time scale, even if it is assumed that the majority of photoinduced decolourization occurs at elevated temperatures because of laser heating. It would not be anticipated that pulsed rather than continuous irradiation would improve this situation dramatically. Furthermore, it is already known that the quantum yields for photodecolourization (at erase wavelengths) for spiropyrans are generally orders of magnitude lower than for photocolouration (Bertleson, 1971; Wu and Yunfei, 1988).

Tomlinson (1984) has analysed the potential of model-generalized photochromic media for bit-oriented memory and has highlighted a significant number of deficiencies, most notably relating to lack of threshold for the phenomenon, erase power requirements, destructive read-out and the system requirements for tracking and focus control, the latter dictating the use of an additional laser at a medium-insensitive wavelength.

Notwithstanding the difficulties in this area, some of which have been highlighted above, the combined developments in photochrome design and

electro-optics technologies may change this perspective in the future. A detailed description of a promising class of photochromes developed by Heller and co-workers is given in Chapter 3. Together with high intrinsic fatigue characteristics, fulgide derivatives may be made thermally stable so that interconversion between the two forms is via purely photonic processes. This class of molecules exploits a tautomerism mechanism in its photochromism and has a minimum of steric requirements. Irie (1987) and Irie and Mohri (1988) have developed related photochromes such as 2,3-bis-(2,3,5-trimethyl-3-thienyl)-maleic anhydride, the photochromic reaction and derivatives of which are shown in structures **1** and **2** below.



Molecules of this type do not exhibit thermochromic reactions at high temperature (300°C), unlike certain fulgides which become thermochromic above 120°C. However, the quantum yields for the thienyl-type materials' reversible reactions are low. Irie and Mohri (1988a) have shown that the activated forms of dithienylethene derivatives have absorption tails extending to 700 nm and can be bleached with HeNe laser light at 633 nm. Development work continues to provide increased sensitivity in these systems at common laser diode wavelengths. Vinyl functionalized versions (**2**) have also been prepared (Irie, 1988) to provide photochromic homo- and copolymers with spectral characteristics similar to the present molecule. In copolymer films, photoinduced tautomeric ring closure is more efficient at elevated temperature because of increased mobility in the polymeric system, and it has been suggested that this temperature dependence might be exploited in a non-destructive read-out capability.