Macromolecules
ARTICLE

Macromolecules **2010**, *43*, 7073–7081 **7073**
DOI: 10.1021/ma101331u

Multiresponsive Spiropyran-Based Copolymers Synthesized by Atom Transfer Radical Polymerization

Demetra S. Achilleos and Maria Vamvakaki*

Institute of Electronic Structure and Laser Foundation for Research and Technology - Hellas, P.O. Box 1527, 711 10 Heraklion, Crete, Greece, and Department of Materials Science and Technology, University of Crete, P.O. Box 2208, 710 03 Heraklion, Crete, Greece

Received June 15, 2010; Revised Manuscript Received July 28, 2010

ABSTRACT: Multiresponsive spiropyran-based random copolymers were synthesized by atom transfer radical polymerization. The polymers were prepared by the copolymerization of 2-(dimethylamino)ethyl methacrylate (DMAEMA) with the photochromic monomer 1′,3′,3′-trimethyl-6-methacryloyloxyspiro-(2*H*-1-benzopyran-2,2′-indoline) (SP). The solvatochromic, pH, temperature, and light responsive behavior of the PDMAEMA-*co*-PSP polymers in solution was monitored by UV/vis spectroscopy. The copolymers exhibited "reverse photochromism" and stabilized the planar zwitterionic form of the chromophore, leading to "negative solvatochromism" upon increasing the polarity of the solvent, in contrast to a poly(methyl methacrylate)-*co*-PSP analogue which stabilized a nonpolar photoisomer and exhibited negligible sensitivity to the polarity of the surrounding medium, before irradiation. Moreover, the PDMAEMA-*co*-PSP copolymers exhibited a reversible pH-responsive character in aqueous media; the addition of a strong acid induced the SP-to-merocyanine (MC) isomerization, the formation of $[MC-OH]^+$ and $[SP-NH]^+$ species, and the disappearance of the H-type aggregates, whereas the initial SP moieties were recovered in alkaline media. The chromophore content and the photoinduced MC-to-SP isomerization affected the transition temperature of the PDMAEMA-*co*-PSP polymers. The lower critical solution temperature (LCST) of the copolymers increased with their content in hydrophilic MC moieties, while the MC-to-SP photoinduced isomerization decreased significantly the LCST due to the hydrophobic character of the SP units. Finally, the copolymers exhibited a first-order photoinduced bleaching of the chromophore units in water and acetonitrile, with a slower decoloration rate in the aqueous medium due to the effective stabilization of the bipolar MC form in the polar environment.

Introduction

"Bistable" compounds that can be interconverted, under certain external stimuli, to two thermodynamically stable states of different color have attracted considerable attention lately.[1] The interconversion can be induced by different stimuli and is defined as photochromism, thermochromism, electrochromism, and solvatochromism.[1] Photochromism is the light-induced reversible intramolecular rearrangement between two isomeric conformations with different absorption spectra.[2] Organic molecules exhibiting reversible photochromism include azobenzenes, spiropyrans (SPs), spirooxazimes, and naphthopyrans[3] with the former being the most extensively studied family of photochromic compounds. Lately, SP molecules, which consist of two orthogonal π-networks that are connected by a tetrahedral carbon center, have also attracted great interest.[1] Upon UV irradiation, the nonpolar, colorless SP molecule undergoes heterolytic cleavage of the C−O bond to form the polar, colored *cisoid* isomer of merocyanine (MC) (see Figure S1, Supporting Information). The *cisoid* form then isomerizes spontaneously to the thermodynamically stable *transoid* MC form, which is an extended π-conjugated system and absorbs in the visible region. The MC isomer can be converted back to the original SP state either thermally or upon irradiation with visible light. The SP-to-MC interconversion has been investigated for use in various applications, such as in data recording and optical data storage,[4] sensors,[5−7] microfluidics,[8,9] smart surfaces,[10−15] and bioseparation.[16]

The photochromism of SP depends on the polarity of the surrounding medium (solvent or polymer matrix), the solution pH, and the presence of ions.[17] Media of low polarity promote the photoinduced isomerization of MC to SP.[18] Moreover, polar media favor the formation of the zwitterionic MC form over the quinoidal isomer.[15] Both of these MC forms exhibit solvatochromism, which is changes in the position and the intensity of their absorption bands induced by variations in the polarity of the surrounding medium. In particular, when the oxygen is in the ionic form, the zwitterionic MC exhibits negative solvatochromism upon increasing the polarity of the medium, i.e., a shift of the λ_{max} of MC to shorter wavelengths,[15] accompanied by band broadening and attenuation of the extinction coefficient.[19] However, if the MC oxygen possesses a quinodial character, the MC isomer exhibits positive solvatochromism and the λ_{max} is red-shifted.[20] The solution pH also affects the SP-to-MC transformation; low solution pH favors the isomerization of SP to MC and leads to the protonation of the open form, which is accompanied by changes in the absorption spectra of the chromophore, while the SP isomer is recovered in alkaline media.[21,22] The MC form can also bind metal cations or undergo nucleophilic addition by CN^-, which lead to the appearance of blue-shifted MC bands.[5,23−25]

Photochromic copolymers carrying spiropyran side groups have attracted particular attention lately.[26−30] The chemical linking of the SP moieties can been achieved by two different

---

*To whom correspondence should be addressed. E-mail: vamvakak@iesl.forth.gr.

methods: the covalent attachment of photosensitive dyes to preformed polymer chains[31] or the copolymerization of photosensitive compounds carrying polymerizable groups with other vinyl monomers.[32,33] These materials allow to overcome many of the limitations inherent in traditional SP doped polymers such as the phase separation of the colorant and the retardation of the decoloration of the open form.[32,34,35] Matsushima et al. showed that the immobilization of the SP groups onto a polymer backbone suppressed their aggregation and reduced their photodegradation.[36] This is particularly attractive for electronic applications that require high contents of photosensitive compounds and stable performance.[37] Besides, the decoloration rate has been shown to depend on the rigidity, the free volume, and the polarity of the polymeric matrix.[19,38] For example, a low-T_g oligomer enhanced the photoswitching rate due to the flexibility of the polymer matrix.[39] At high SP contents the attachment of the photochromic side groups via a long, flexible spacer[40] minimized the retardation of the decoloration which was observed in short spacer systems due to the lack of free volume.[41,42]

The introduction of light-sensitive moieties within responsive polymers has led to the development of sophisticated multiresponsive systems.[26] Spiropyran monomer repeat units have been incorporated within temperature-responsive poly(*N*-isopropylacrylamide) (PNIPAM) chains. The photochromic molecules influenced the phase transition behavior of PNIPAM and reduced its cloud point by more than 10 °C.[29] On the other hand, PNIPAM-SP microgels were shown to alter their volume phase upon light irradiation.[43] Sumaru et al. reported that the sensitivity of a PNIPAM-*co*-PSP copolymer to light irradiation and temperature changes was dependent on the solution pH.[26] Recently, the photoinduced hydration of the polymer was found to be effective only at low temperatures when the PNIPAM component was sufficiently hydrophilic.[44] This property was applied to develop a colorimetric thermometer based on a PNIPAM-*co*-PSP copolymer, which upon UV irradiation exhibited a continuous bathochromic shift as the temperature increased. The change in the absorption was attributed to the zwitterionic-to-quinodal MC isomerization, induced by the less-polar environment which surrounded the chromophore moieties at higher temperatures.[28]

In this study, we report the synthesis of poly[2-(dimethylamino)ethyl methacrylate]-*co*-poly[1′,3′,3′-trimethyl-6-methacryloyloxyspiro(2*H*-1-benzopyran-2,2′-indoline)] (PDMAEMA-*co*-PSP) copolymers that are sensitive to the solvent polarity, temperature, pH, and light irradiation. Four different PDMAEMA-*co*-PSP copolymers in which the content of the photosensitive moieties was varied between 1.3 and 10 mol % were prepared by atom transfer radical polymerization (ATRP). A poly(methyl methacrylate)-*co*-PSP (PMMA-*co*-PSP) copolymer containing 19 mol % SP was also synthesized by the same method. The effect of the polarity of the comonomer on the isomerization mechanism of the spiropyran groups was evaluated by comparing the solvatochromic behavior of the PDMAEMA-*co*-PSP and PMMA-*co*-PSP copolymers. To the best of our knowledge, this is the first time that "reverse photochromism" of the chromophore units, induced by the polarity of the comonomer, is reported. The reversible acid-catalyzed ring-opening process of the photosensitive component of the PDMAEMA-*co*-PSP copolymers in aqueous media was studied. The influence of the copolymer composition and the photoinduced MC-to-SP isomerization on the phase transition temperature of the PDMAEMA-*co*-PSP copolymers was investigated. Finally, the photoinduced decoloration rates of the chromophore moieties of the PDMAEMA-*co*-PSP copolymers were determined in solvents of different polarity. The multiresponsive behavior of the PDMAEMA-*co*-PSP copolymers in addition to their cationic character at low pH, which can induce attractive electrostatic interactions with DNA, enzymes, and polyanionic drugs, are very important and open up new applications of these materials in the areas of chemical and biochemical gates, gene transfer, programmed adsorption of proteins, and drug delivery.

Experimental Section

Materials. The monomer DMAEMA (98%, hydrophilic and ionizable), the ligand *N,N,N′,N″,N″*-pentamethyldiethylenetriamine (99%, PMDETA), the initiator ethyl 2-bromoisobutyrate (98%), triethylamine (99%, TEA), the metal salt copper(I) bromide (99.9%, $Cu^{I}Br$), and chloroform (99.8%, $CDCl_3$) were purchased from Aldrich, Germany. The monomer MMA (99%, hydrophobic), dichloromethane (99.8%, DCM), and methacryloyl (97%) and acryloyl (96%) chlorides were purchased from Fluka, Germany. The photochromic spiropyran molecule, 1′,3′,3′-trimethyl-6-hydroxyspiro(2*H*-1-benzopyran-2,2′-indoline) (99%, HBPS), was purchased from Acros Organics, Germany, and was used without further purification. Toluene (99.7%) and tetrahydrofuran (THF, 99.9%) were purchased from Riedel-de Haën, Germany.

Methods. The monomers were passed through basic alumina columns to remove inhibitors. The polymerization solvent, THF, was dried by refluxing it over potassium for 3 days. All reagents used for the monomer synthesis were stirred over CaH_2, were freshly distilled under vacuum, and were kept under a dry nitrogen atmosphere until use. All glassware was dried overnight at 160 °C prior to use.

Synthesis of the Spirobenzopyran Methacrylate Monomer. The synthesis involved an esterification reaction to produce a spiropyran-based molecule carrying a polymerizable methacrylate moiety. In a typical reaction, HBPS (1.0 g, 3.4 mmol) was transferred in a 250 mL flask and was dried under vacuum for 2 h. Dry dichloromethane (29 mL) was injected in the reaction flask under nitrogen. Next, TEA (1.4 mL, 0.010 mol) was added followed by the dropwise addition of methacryloyl chloride (0.50 mL, 5.2 mmol). The reaction was allowed to proceed for 3 days at room temperature (RT). The triethylamine bromide salt produced was removed by filtration under nitrogen, while the solvent and the excess amounts of the reagents were eliminated under reduced pressure. The product (1 g, yield: 85%) was dried in a vacuum oven at RT and was characterized by ^1H NMR.

The following peaks were identified in the proton nuclear magnetic resonance (^1H NMR) spectrum of the synthesized monomer (500 MHz, $CDCl_3$) (see Figure S2, Supporting Information): δ 1.16 (3H, H-3′), 1.31 (3H, H-3′), 2.05 (3H, H-11) 2.73 (3H, H-1′), 5.70 (1H, $=CH_2$, H-9), 5.73 (1H, H-3), 6.31 (1H, $=CH_2$, H-10), 6.52 (1H, H-4), 6.71 (1H, H-7′), 6.79−6.85 (4H, H-5, H-5′, H-7, H-8), 7.08 (1H, H-4′), 7.18 (1H, H-6′).

Polymerizations. A typical polymerization procedure followed for the synthesis of the copolymers is described below (see Scheme 1). The initiator ethyl 2-bromoisobutyrate (14.7 μL, 9.87×10^{-5} mol), 1′,3′,3′-trimethyl-6-methacryloyloxyspiro-(2*H*-1-benzopyran-2,2′-indoline) (0.080 g, 2.21×10^{-4} mol), and DMAEMA (0.147 g, 9.35×10^{-4} mol) were transferred in a 100 mL round-bottom flask containing 6 mL of dry THF. The reaction was set under a nitrogen atmosphere, and subsequently, the ligand PMDETA (124 μL, 5.94×10^{-4} mol) and CuBr (0.0141 g, 9.83×10^{-5} mol) were added under continuous stirring. The polymerization flask was inserted in an oil bath at 60 °C, and the polymerization was allowed to proceed for 24 h. The product was isolated by precipitation in hexane and was dried under vacuum at RT. This procedure resulted in a PDMAEMA-*co*-PSP random copolymer containing 10 mol % PSP, with an M_n of around 5900 g/mol and M_w/M_n equal to 1.56 by gel permeation chromatography (see entry 4, Table 1) at 84% yield. The other three PDMAEMA-*co*-PSP copolymers were prepared by varying the comonomer ratio at a fixed initiator concentration. A similar procedure was followed for the

Scheme 1. Reaction Scheme for the ATRP Copolymerization of 1′,3′,3′-Trimethyl-6-methacryloyloxyspiro(2*H*-1-benzopyran-2,2′-indoline) with DMAEMA and MMA

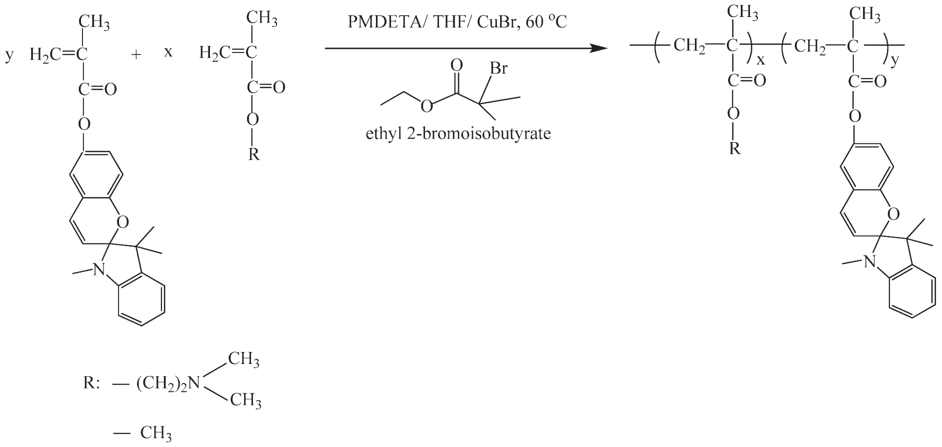


Table 1. GPC and ^{1}H NMR Characterization Data of the Spiropyran-Based Copolymers

	GPC results			
copolymer	M_n	M_w	M_w/M_n	composition by ^{1}H NMR (mol % SP)
PDMAEMA-*co*-PSP1	8900	13 000	1.46	1.3
PDMAEMA-*co*-PSP3	6600	10 000	1.51	3.0
PDMAEMA-*co*-PSP6	8300	12 300	1.48	6.0
PDMAEMA-*co*-PSP10	5900	9 200	1.56	10.0
PMMA-*co*-PSP19	4200	7 700	1.84	19.0

synthesis of the PMMA-*co*-PSP copolymer which was recovered by precipitation in water.

Characterization of the Copolymers. *Gel Permeation Chromatography* (*GPC*). The molecular weights (MWs) and the molecular weight distributions (MWDs) of the random copolymers were determined by GPC using a mixed-D and a mixed-E column. The mobile phase was THF, delivered at a flow rate of 1 mL min^{-1}. The refractive index signal was measured using a Shodex RI-101 refractive index detector. The calibration curve was based on six narrow MW linear polystyrene standards ranging from 1310 to 299 000 g mol^{-1}.

^{1}H NMR Spectroscopy. The composition of the copolymers was determined by ^{1}H NMR spectroscopy using a 500 MHz Avance Bruker NMR spectrometer. The solvent used was $CDCl_3$ containing tetramethylsilane (TMS) which served as an internal reference. The absolute molecular weight of the PMMA-*co*-PSP copolymer was also determined by ^{1}H NMR.

UV/vis Absorption Studies. The solvatochromism of the copolymers in a range of solvents of different polarity was monitored by UV/vis spectroscopy. The absorption spectra of 3.3×10^{-2} wt % copolymer solutions in toluene, chloroform, tetrahydrofuran, dichloromethane, and water were recorded using a Lambda 25 Perkin-Elmer UV/vis spectrophotometer in the wavelength range 250−850 nm.

The effect of the addition of acid or base on the absorption properties of the PDMAEMA-*co*-PSP3 copolymer in aqueous media was studied. A 1.2×10^{-2} wt % aqueous solution of the photosensitive copolymer was prepared by dissolving the appropriate amount of polymer in Milli-Q water prefiltered through a 0.2 μm syringe filter. The UV/vis spectra of the aqueous solution were recorded upon the addition of 2.4 μL aliquots of 0.1 M HCl or NaOH solution.

The temperature-induced phase transition behavior of the PDMAEMA-*co*-PSP copolymers was investigated by recording the absorbance of 1 wt % aqueous solutions of the copolymers at 750 nm, while the solution temperature was raised from 25 to 90 °C at a heating rate of 1 °C/min.

The photoinduced bleaching of the chromophore moieties of the PDMAEMA-*co*-PSP1 copolymer was studied in solvents of different polarity by UV/vis spectroscopy in the wavelength range 250−850 nm. A 5×10^{-2} wt % solution of the copolymer in water and in acetonitrile was prepared, and the samples were irradiated with visible light utilizing a Nd:yttrium aluminum garnet (YAG) laser operating at the second harmonic, $\lambda = 532$ nm (B.M. Industries, Series 5000). The ~100 mJ laser beam was focused in the cuvette to ensure the homogeneous irradiation of the sample. The decoloration rate, k_{obs}, of the chromophore units of the copolymer was calculated by fitting the experimental data to the following equation:[45]

$$\ln(A_t - A_e) = -k_{obs}t + \ln(A_0 - A_e) \qquad (1)$$

where A_0, A_t, and A_e are the absorbance at the λ_{max} of the MC form at time 0, t, and ∞ (taken as the absorbance of the visible irradiation photostationary state), respectively.

Results and Discussion

Synthesis of the Random Copolymers by ATRP. Random copolymers carrying photochromic spiropyran moieties were synthesized by ATRP. A photosensitive molecule exhibiting a singlet excited state was chosen instead of that with a triplet state, i.e., nitrospiropyrans, because the latter accelerates the photodegradation process.[46] The polymerizable spiropyran molecule was prepared first. The successful synthesis was confirmed by ^{1}H NMR spectroscopy due to the absence of the peak at 4.26 ppm attributed to the −OH group of the precursor alcohol and the appearance of two new peaks at 5.7 and 6.3 ppm assigned to the protons of the carbon−carbon double bond and a peak at 2.04 ppm which corresponds to the methyl group of the methacryloyl moiety.[47] The peaks attributed to the aromatic protons next to the ester group were also shifted to lower fields following the esterification reaction and verified the synthesis of the monomer.

Next, the dye monomer was copolymerized with DMAEMA or MMA by ATRP. Four different copolymers of 1′,3′,3′-trimethyl-6-methacryloyloxyspiro(2*H*-1-benzopyran-2,2′-indoline) with DMAEMA and one with MMA were prepared in THF (see Table 1). The presence of the peaks due to both monomer repeat units and the significant broadening of the peaks in the ^{1}H NMR spectra of the products (see Figure S3, Supporting Information) verified the synthesis of the copolymers. The absolute molecular weight of the PMMA-*co*-PSP copolymer was calculated by ^{1}H NMR by ratioing the peak integrals at 3.59 ppm attributed to the

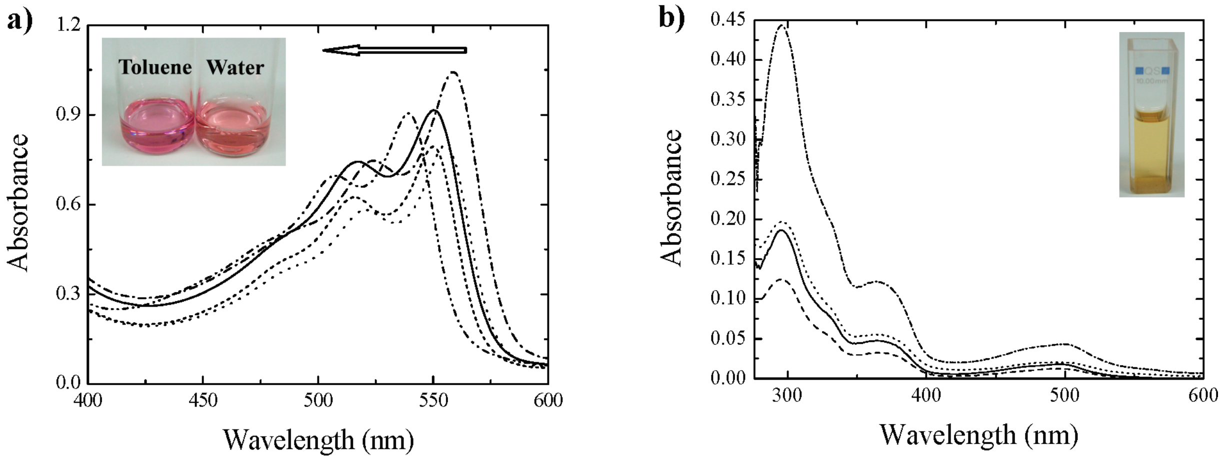


Figure 1. UV/vis absorption spectra of the PDMAEMA-*co*-PSP3 (a) and PMMA-*co*-PSP (b) copolymers in solvents of different polarity: toluene (-··-), chloroform (···), tetrahydrofuran (—), dichloromethane (---), and water (-···-).

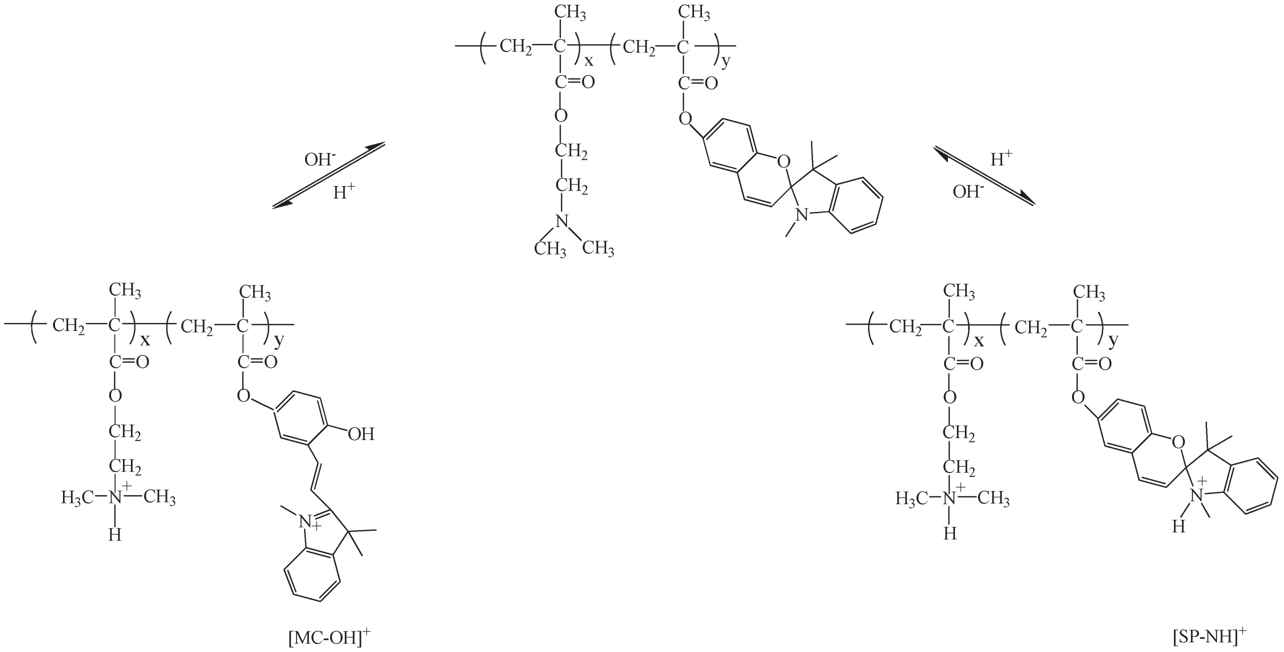
methoxy protons of the PMMA and at 5.7 ppm due to the proton of the benzopyran phenyl group next to the spiro tetrahydral linkage over that at 4.1 ppm, which corresponds to the methylene protons of the initiator. The actual molecular weight of the copolymer was found 1360 g/mol, which is in good agreement with the theoretical value of 1840 g/mol, suggesting the "controlled/living" character of the polymerization. However, the actual molecular weights of the PDMAEMA-*co*-PSP copolymers could not be determined by ^{1}H NMR due to the overlap of the peaks attributed to the methylene protons of the initiator and the methylene protons next to the ester group of the DMAEMA monomer repeat units at 3.95−4.35 ppm (see Figure S3). The apparent molecular weights (M_n's) and the molecular weight distributions (M_w/M_n's, PDIs) of the copolymers were determined by GPC (see Table 1). The M_n's of the photoresponsive copolymers were found between 4200 and 8900 g/mol, while their PDIs ranged between 1.46 and 1.84, which are lower than those reported for spiropyran-based copolymers synthesized by conventional free radical polymerization.[26,48,49] The slightly higher molecular weight distributions of the copolymers, compared to those reported for the controlled polymerization of styrenic and methacrylate monomers,[50,51] are attributed to the low molecular weights of the polymers and the polymerization of highly functional monomers (DMAEMA and SP) and are similar to those reported in the literature for PMMA-*co*-PSP copolymer analogues synthesized by ATRP.[30]

The copolymer composition (see Table 1) was calculated from the ratio of the peak integrals attributed to the methylene protons next to the ester group of DMAEMA (see Figure S3, H-13) and the proton of the benzopyran phenyl group next to the spiro tetrahydral linkage (see Figure S3, H-3) for the PDMAEMA-*co*-PSP copolymers, while the integrals of the peaks corresponding to the methoxy protons of MMA and the benzopyran protons of SP next to the spiro tetrahydral linkage were ratioed to calculate the composition of the PMMA-*co*-PSP copolymer.

Solvatochromic Behavior of the Copolymers. The solvatochromic behavior of the copolymers in solvents of different polarity was examined before irradiation. The polarity of the solvent has been shown to influence the isomerization of the photochromic molecules between the different MC forms and the thermal fading of the MC isomers to the SP form.[52,53] Figure 1a shows the UV/vis spectra for five PDMAEMA-*co*-PSP3 copolymer solutions in toluene, chloroform, THF, DCM, and water. The absorption band observed in toluene at 558 nm was attributed to the planar zwitterionic MC form. The formation of the colored zwitterionic MC form before irradiation was attributed to the "reverse photochromism", that is, the stabilization of the open zwitterionic form of the chromophore in polar media before irradiation, induced by the polar DMAEMA comonomer units.[54,55] Upon increasing the solvent polarity a shift of the MC peak to shorter wavelengths was observed from 558 nm for toluene (SPP scale = 0.655) to 555 nm for chloroform (SPP scale = 0.786), 551 nm for THF (SPP scale = 0.838), and 549 nm for DCM (SPP scale = 0.876), while the lowest value was found for water (539 nm, SPP scale = 0.962). This phenomenon, which is known as "negative" solvatochromism, is related to the stabilization of the planar zwitterionic MC form in the solvent medium and is common in spiropyrans disposing electron-withdrawing groups on the benzopyran moiety, known as pull-type photochromic compounds, such as the molecule used in this study.[20] In polar media, the ground state of the bipolar colored form[56] is stabilized more effectively compared to the excited state ($\mu_{\text{ground}} > \mu_{\text{excited}}$).[15] This results in a greater energy gap between the two MC states and to a hypsochromic shift of the absorption bands. A peak with an absorption maximum at 524 nm was also observed in the spectrum in toluene and was attributed to SP-MC and intramolecular MC_n stacks which are of H-type and thus blue-shifted compared to the free MC.[34] These aggregation phenomena are strongly enhanced in systems with high chromophore contents and under conditions which stabilize the planar zwitterionic MC molecules.[57] The H-stacks exhibited a "negative" solvatochromism similar to that of the free MC form, and a blue shift of the peak was observed upon increasing the polarity of the solvent (524 nm for toluene, 521 nm for chloroform, 517 nm for THF, 515 nm for DCM, and 506 nm for water). The "negative" solvatochromism of the photochromic species of the PDMAEMA-*co*-PSP3 copolymer upon increasing the polarity of the medium was also observed visually as a small change in the color of the solution from light pink in toluene to light orange in water (see Figure 1a inset).

In contrast to the PDMAEMA-*co*-PSP copolymer, the absorption properties of the PMMA-*co*-PSP analogue were not influenced by the solvent medium before irradiation (see Figure 1b). The absorption bands observed in toluene at 296 and 323 nm (shoulder) were attributed to the closed form of the spiropyran molecule. The two halves of the photochromic molecule in the closed form are topologically

Scheme 2. Reversible Protonation/Deprotonation of the PDMAEMA-*co*-PSP Copolymers in Acidic/Basic Media



orthogonal; hence, the π-absorption spectrum consists of two localized transitions rather than a single delocalized transition for the molecule as a whole.[58] The former intense peak (296 nm) was attributed to the indoline part, and the latter shoulder (323 nm) was assigned to the chromene moiety. However, no peak assigned to the free MC form at 558 nm was observed for this copolymer. This was attributed to the nonpolar character of the MMA comonomer which does not stabilize the open MC form and thus favors the "normal photochromism". The very low intensity band at ~500 nm was attributed to the formation of a few H-stacks as discussed above for the PDMAEMA-*co*-PSP copolymer. However, a new peak at 366 nm was observed attributed to a nonpolar MC isomer. It is noted that this peak was not observed for the PDMAEMA-*co*-PSP copolymers, suggesting that the nonpolar photoisomer was stabilized by the less polar MMA units. These species showed negligible sensitivity to the polarity of the surrounding medium and the λ_{max} of the peak remained at 366 nm, while a yellow color polymer solution was obtained (see Figure 1b inset) for all solvents. The above results suggest that the polarity of the comonomer affects the solvatochromic properties of the polymer by the selective stabilization of a particular photoisomer. The colored MC form is stabilized by polar comonomers, resulting in copolymers which exhibit "reverse photochromism" and "negative solvatochromism", whereas "normal photochromism" is favored by comonomers of lower polarity. The stabilization of specific chromophore isomers by tuning the polarity of the comonomer can be very promising for the development of materials with high specificity in terms of optical properties.

Acidochromic Properties of the Spiropyran-Based Copolymers. The effect of the solution pH on the SP-to-MC isomerization of the chromophore units of the PDMAEMA-*co*-PSP3 copolymer was also investigated. The closed SP form isomerizes to the open MC form and becomes protonated upon the addition of acid leading to the formation of $[MC-OH]^+$ species. A competitive process also takes place, that is the protonation of the closed SP moieties leading to the formation of the positively charged $[SP-NH]^+$ species (see Scheme 2). Both processes are fully reversible, and the closed SP form is recovered upon the addition of base.[22] Figure 2a shows the absorption spectra of an aqueous solution of the PDMAEMA-*co*-PSP3 copolymer upon the gradual addition of acid. The protonation of both the DMAEMA ($pK_a = 7.0$)[59] and the MC ($pK_a = 6-7$)[26] monomer repeat units (see Scheme 2) was taken into account for the addition of a stoichiometric amount of HCl to fully protonate the copolymer. For low acid contents (<9.6 μL) the intensity of the absorption band at 296 nm, assigned to the closed SP form, decreased gradually, while the intensity of the absorption peak at 538 nm, which corresponds to the open MC form, increased (see Figure 2a inset), suggesting the acid-catalyzed ring-opening of SP to the MC isomer.[60,61] Further addition of HCl (>9.6 μL) resulted in the decrease of the intensity of the peak at 538 nm (see Figure 2a inset) and the appearance of a new absorption band at 423 nm attributed to the protonated colored MC form.[62,63] This is consistent with the protonation of the open MC species and the formation of the *trans*-$[MC-OH]^+$ form at higher acid concentration. In a competing process, the closed SP species became protonated as evidenced by the appearance of an absorption peak at 316 nm attributed to the protonated closed SP form. It is also noted that the intensity of the peak attributed to the MC-MC H-type stacks (498 nm) decreased upon the addition of acid. The suppression of aggregate formation via intramolecular interactions in acidic media was attributed to two synergetic effects: the first is the protonation of the phenolate anions of the open MC form which led to a positive net charge on the photochromic side groups, and the second is the protonation of the tertiary amine groups of DMAEMA, both of which resulted in repulsive forces along the polymer chain and prohibited the formation of stacks. The acid-induced process discussed above was fully reversible; addition of base resulted initially to the deprotonation of the $[MC-OH]^+$ and $[SP-NH]^+$ species, signified by the decrease of the intensity of the peaks at 423 and 316 nm, respectively (see Figure 2b), while at higher base concentration the closed SP species were recovered due to the MC-to-SP isomerization, leading to an increase of the intensity of the band at 296 nm and a simultaneous decrease of the MC peak at 538 nm (see Figure 2b inset).

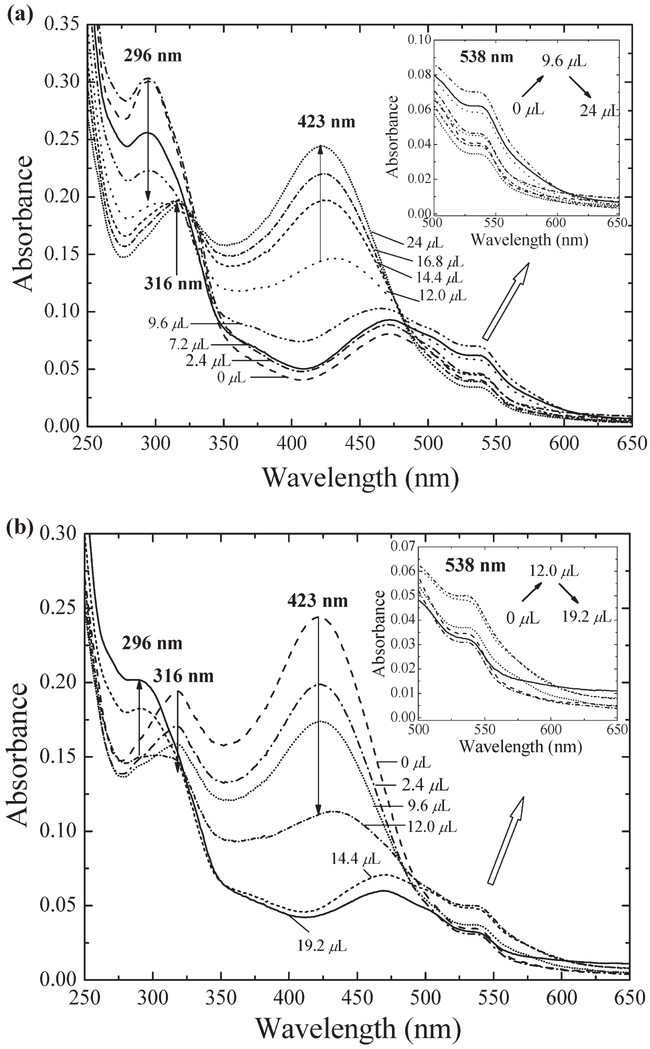


Figure 2. UV/vis absorption spectra of an aqueous PDMAEMA-*co*-PSP3 copolymer solution upon the addition of acid (HCl) (a) and following the neutralization of (a) with base (NaOH) (b).

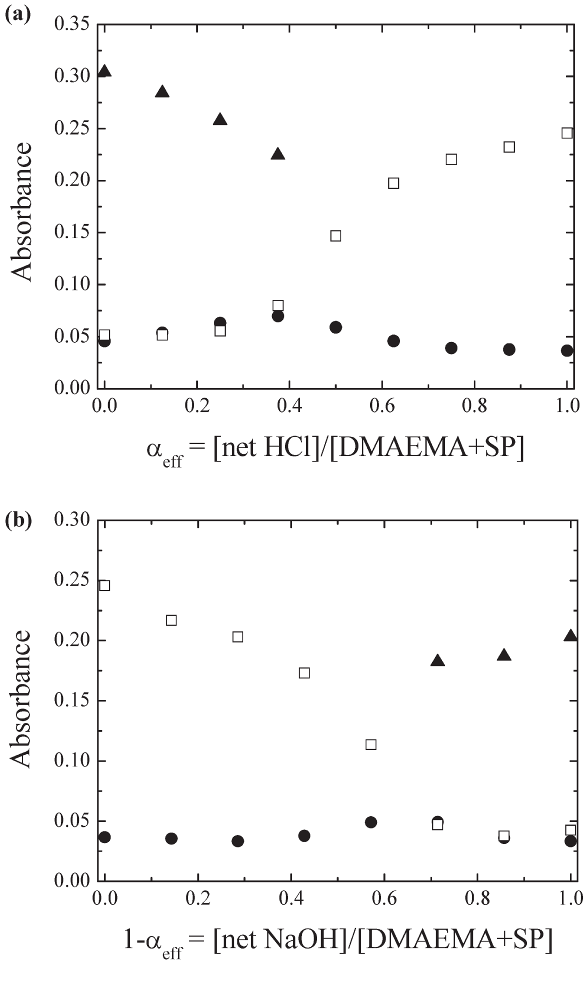


Figure 3. Absorption intensities of the chromophore species in an aqueous solution of the PDMAEMA-*co*-PSP3 copolymer as a function of the ratio α_{eff} = [HCl]/[DMAEMA + SP monomer units] (a) and ($1 - \alpha_{eff}$) = [NaOH]/ [DMAEMA + SP monomer units] (b): SP (▲), MC (●), and $[MC-OH]^+$ (□).

Figures 3a and 3b summarize the absorbance intensity changes for the PDMAEMA-*co*-PSP3 copolymer solution upon the addition of acid and base, respectively. The concentration of acid in the solution is normalized over the total concentration of ionizable species (DMAEMA and SP) defined as α_{eff} = [HCl]/[DMAEMA + SP monomer units]. α_{eff} represents the theoretical fraction of protonated DMAEMA and SP monomer repeat units, if one assumes that all H^+ from the added HCl protonate the DMAEMA and SP species of the copolymer, and takes values in the range $0 < \alpha_{eff} < 1$ (see Figure 3a).[64] For the addition of base (see Figure 3b) $1 - \alpha_{eff}$ = [NaOH]/[DMAEMA + SP monomer units] is defined as the fraction of the deprotonated ionizable groups (DMAEMA and SP), assuming that all OH^- from the added NaOH deprotonate the monomer repeat units, and takes values in the range $0 < (1 - \alpha_{eff}) < 1$. As shown in Figure 3a, the addition of HCl resulted initially ($0 < \alpha_{eff} < 0.4$) in a decrease of the SP species accompanied by a simultaneous increase of the MC moieties due to the acid-induced isomerization of SP to the open MC form. Further addition of acid ($0.4 < \alpha_{eff} < 1$) gave rise to a sharp increase of the intensity of the $[MC-OH]^+$ species accompanied by a decrease of the intensity of the MC units, suggesting the protonation of the latter moieties. On the other hand, Figure 3b shows that the addition of base resulted in a completely reversible process; first, the neutralization of the protonated MC species by NaOH and the formation of the open MC moieties took place for $0 < 1 - \alpha_{eff} < 0.6$, followed by the isomerization of MC to the closed SP species in strong alkaline media ($0.6 < 1 - \alpha_{eff} < 1$).

The reversible acidochromic behavior of the PDMAEMA-*co*-PSP3 copolymer in water was also observed visually. At high acid concentration the formation of the $[MC-OH]^+$ moieties was evidenced by the appearance of a yellow color attributed to the absorption of the protonated MC form at 423 nm, while upon addition of base the deprotonation of the $[MC-OH]^+$ species resulted in a light red color attributed to a low concentration of remaining MC species in the solution.

Temperature-Induced Phase Transition of the PDMAEMA-*co*-PSP Copolymers. PDMAEMA is a well-known temperature-sensitive polymer which exhibits a LCST in the range between 32 and 46 °C.[59,65] In this study we investigated the effect of the photosensitive comonomer on the LCST of the PDMAEMA-*co*-PSP copolymers. The phase transition behavior of the four copolymers containing 1.3, 3, 6, and 10 mol % chromophore units was studied in water. Figure 4 shows the absorbance at 750 nm for the four copolymer solutions in the temperature range 30−90 °C. The PDMAEMA-*co*-PSP1 copolymer exhibited a LCST of 44 °C. Furthermore, an increase of the chromophore content of the copolymer to 3 mol % resulted in a 14 °C increase of

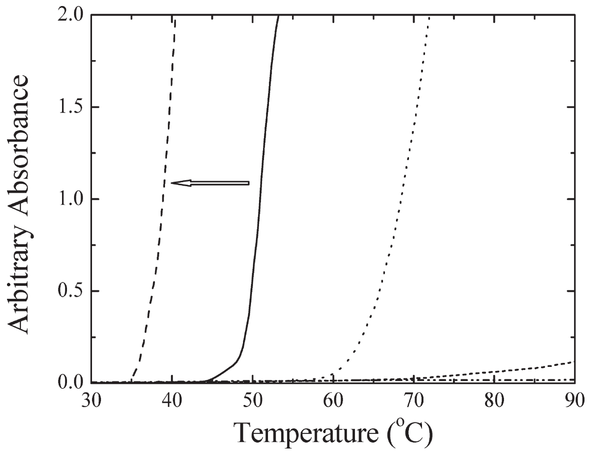


Figure 4. Turbidimetry vs temperature curves obtained for aqueous solutions of the PDMAEMA-*co*-PSP copolymers at neutral pH: PDMAEMA-*co*-PSP1 (—), PDMAEMA-*co*-PSP3 (···), PDMAEMA-*co*-PSP6 (---), PDMAEMA-*co*-PSP10 (-···-), PDMAEMA-*co*-PSP1 following irradiation with visible light (— — —). The cloud points were determined from tangents constructed from the turbidimetry curves.

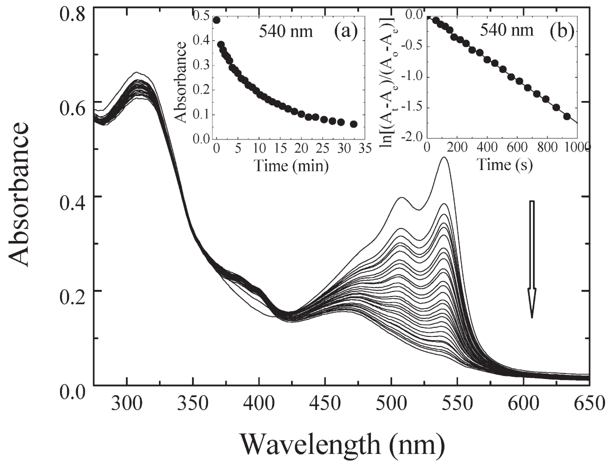


Figure 5. UV/vis absorption spectra of an aqueous PDMAEMA-*co*-PSP1 copolymer solution upon successive irradiation with visible light. Inset (a) shows the decay of the absorption at the MC maximum (λ = 540 nm) as a function of irradiation time. Inset (b) is the rate constant plot for the first-order decoloration reaction of the photochromic MC moieties of the copolymer.

the LCST, while for chromophore contents above 6 mol % the LCST was eliminated and the copolymers remained soluble in the aqueous medium over the whole temperature range. The increase in the LCST of the copolymer with the chromophore content was attributed to the hydrophilic open MC form of the photosensitive moieties the presence of which was verified by UV/vis spectroscopy (data not shown). The polar MC species increase the hydrophilicity of the copolymer and hence the LCST of the polymer.[43] Sumaru and co-workers reported that the MC-to-SP conversion in thermally responsive PNIPAM-*co*-PSP copolymers can become very important in the dark as the temperature increases and can hinder the tuning of the LCST of the copolymers.[26] However, the stabilization of the open MC form by the polar DMAEMA comonomer units in the PDMAEMA-*co*-PSP copolymers is believed to retard the thermal fading of the chromophore units in the dark and allow tuning the phase transition temperature of the copolymers. Moreover, irradiation of the PDMAEMA-*co*-PSP1 copolymer with visible light resulted in the significant decrease of the LCST to 34 °C (see Figure 4), which is lower compared to that reported in the literature for a PDMAEMA homopolymer of similar molecular weight.[59,65] This is attributed to the hybrophobic SP moieties formed upon irradiation of the copolymer with visible light (see discussion below), which increase the hydrophobicity of the copolymer.[43] Therefore, the photoinduced MC-to-SP isomerization of the chromophore units of the copolymers can be conveniently used to tune their phase transition behavior, which could be particularly advantageous for certain applications such as catalyst recovery, waste capture, and others.

Photoresponsive Behavior of the PDMAEMA-*co*-PSP Copolymer. Figure 5 shows the UV/vis spectra for an aqueous PDMAEMA-*co*-PSP1 copolymer solution upon successive visible light irradiation. A gradual decrease of the intensity of the absorption band at 540 nm, attributed to the bipolar MC isomer, was observed due to the isomerization of MC to the colorless SP form. A simultaneous decrease of the intensity of the absorption band at 507 nm, attributed to the H-type MC aggregates, was also observed, upon irradiation with visible light, suggesting the effective MC-to-SP isomerization of the MC moieties of the aggregates. Inset (a) in Figure 5 shows the intensity of the absorption band at 540 nm as a function of irradiation time. After 32 min of irradiation the absorbance at 540 nm reached a plateau, suggesting that the chromophores attained a photostationary state.[66] Similar results were obtained upon irradiating a PDMAEMA-*co*-PSP1 copolymer solution in acetonitrile with visible light (see Figure S4, Supporting Information); the intensity of the absorption bands at 509 nm (see Figure S4, inset (a)) and 542 nm (see Figure S4, inset (b)) attributed to the H-type MC stacks and the MC isomer, respectively, decreased progressively with irradiation time. However, the photostationary state was reached only after 17 min of irradiation in acetonitrile (see Figure S4, insets (a) and (b)). The rate constants for the visible bleaching, k_{obs}, of the colored MC moieties of the copolymer in water and in acetonitrile were calculated by fitting the experimental data to eq 1 (see Figure 5, inset (b)). k_{obs} in water was calculated to be 1.8×10^{-3} s^{-1}, whereas in acetonitrile the photobleaching process exhibited a higher kinetic value of 3.4×10^{-3} s^{-1}. The lower kinetic constant found in water suggests that the ring-closing process is suppressed in the polar aqueous environment (SPP scale = 0.962) due to the effective stabilization of the MC isomer. The latter results in a higher energy barrier for the MC-to-SP isomerization which requires an energerically unfavored rotation around the central double bond of the molecules.[15,18] On the contrary, acetonitrile is a less polar solvent (SPP scale = 0.895) compared to water, and thus, the MC form is less effectively stabilized and the MC-to-SP isomerization is energetically favored, resulting in a higher kinetic value. Similar results have been reported in the literature for spiropyran molecules in organic solvents of different polarity.[15]

Conclusions

In this study, we report the synthesis of multiresponsive spiropyran-based copolymers by ATRP. The polarity of the comonomer affected the stabilization of a certain isomer of the photosensitive moieties and thus the "normal" vs "reverse" photochromism of the PSP-based copolymers. In particular, DMAEMA, a polar comonomer, induced "reverse photochromism" and stabilized the planar zwitterionic form which exhibited a hypsochromic shift upon increasing the solvent polarity, known as "negative solvatochromism". On the other hand, the less polar MMA comonomer, exhibited "normal" photochromism and stabilized a nonpolar photoisomer, before irradiation, which was not affected by the polarity of the solvent. The PDMAEMA-*co*-PSP copolymers also exhibited a reversible pH-induced SP-to-MC isomerization and protonation/deprotonation of the MC form accompanied by a color change of the polymer solution. A strong influence of the copolymer composition and the photoinduced MC-to-SP isomerization of the chromophore moieties on the phase transition behavior of the PDMAEMA-*co*-PSP copolymers was found, with an increase of the LCST with the hydrophilic MC chromophore content and a decrease of the transition temperature following the photoinduced MC-to-SP isomerization of the chromophores due to the hydrophobic character of the SP moieties. Finally, the PDMAEMA-*co*-PSP copolymers exhibited a photoinduced decoloration, upon irradiation with visible light, which was faster in acetonitrile compared to water due to the more effective stabilization of the bipolar MC isomer in polar media. These multisensitive polymers create new perspectives for the development of multiresponsive materials for biological and environmental applications.

Acknowledgment. The general Secretariat for Research and Technology − Hellas is acknowledged for funding D. S. Achilleos' work (PENED 2003, programme 03EΔ581).

Supporting Information Available: Schematic representation of the reversible photoinduced SP-to-MC isomerization; ^{1}H NMR spectra of the 1′,3′,3′-trimethyl-6-methacryloyloxyspiro-(2*H*-1-benzopyran-2,2′-indoline) monomer and the PDMAEMA-*co*-PSP6 copolymer; UV/vis spectra of the PDMAEMA-*co*-PSP1 copolymer solution in acetonitrile upon successive irradiation with visible light. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Minkin, V. *Chem. Rev.* **2004**, *104*, 2751–2776.
(2) Minkin, V. I. *Theor. Exp. Chem.* **1995**, *31*, 140–152.
(3) Kobatake, S.; Irie, M. *Annu. Rep. Prog. Chem., Sect. C: Phys. Chem.* **2003**, *99*, 277–313.
(4) Bobrovsky, Y.; Boiko, N. I.; Shibaev, V. P. *Liq. Cryst.* **2000**, *27*, 57–62.
(5) Shao, N.; Zhang, Y.; Cheung, S.; Yang, R.; Chan, W.; Mo, T.; Li, K.; Liu, F. *Anal. Chem.* **2005**, *77*, 7294–7303.
(6) Voloshin, N. A.; Chernyshev, A. V.; Metelitsa, A. V.; Besugliy, S. O.; Voloshina, E. N.; Sadimenko, L. P.; Minkin, V. I. *ARKIVOC* **2004**, *xi*, 16–24.
(7) Radu, A.; Scarmagnani, S.; Byrne, R.; Slater, C.; Lau, K.; Diamond, D. *J. Phys. D: Appl. Phys.* **2007**, *40*, 7238–7244.
(8) Caprioli, L.; Mele, E.; Angilè, F. E.; Girardo, S.; Athanassiou, A.; Camposeo, A.; Cingolani, R.; Pisignano, D. *Appl. Phys. Lett.* **2007**, *91*, art. no. 113113
(9) Koide, T.; Takei, G.; Kitamori, T.; Kim, H.-B. 7th international Conference on Miniaturized Chemical and Blochemlcal Analysts Systems, Oct 5−9, 2003, Squaw Valley, CA, **2003**; pp 769−772.
(10) Lahann, J.; Langer, R. *MRS Bull.* **2005**, *30*, 185–188.
(11) Athanassiou, A.; Lygeraki, M.; Pisignano, D.; Lakiotaki, K.; Varda, M.; Mele, E.; Fotakis, C.; Cingolani, R.; Anastasiadis, S. *Langmuir* **2006**, *22*, 2329–2333.
(12) Mele, E.; Pisignano, D.; Varda, M.; Farsari, M.; Filippidis, G.; Fotakis, C.; Athanassiou, A.; Cingolani, R. *Appl. Phys. Lett.* **2006**, *88*, 203124.
(13) Wang, S.; Song, Y.; Jiang, L. *J. Photochem. Photobiol., C* **2007**, *8*, 18–29.
(14) Gras, S.; Mahmud, T.; Rosengarten, G.; Mitchell, A.; Kalantar-Zadeh, K. *ChemPhysChem* **2007**, *8*, 2036–2050.
(15) Wojtyk, J. T. C.; Wasey, A.; Kazmaier, P. M.; Hoz, S.; Buncel, E. *J. Phys. Chem. A* **2000**, *104*, 9046–9055.
(16) Nayak, A.; Liu, H.; Belfort, G. *Angew. Chem., Int. Ed.* **2006**, *45*, 4094–4098.
(17) *Chemistry and Applications of Leuco Dyes*, 1st ed.; Nakazumi, H., Ed.; Springer: New York, 1997.
(18) Sheng, Y.; Leszczynski, J.; Garcia, A. A.; Rosario, R.; Gust, D.; Springer, J. *J. Phys. Chem. B* **2004**, *108*, 16233–16243.
(19) Guglielmetti, R. In *Elsevier Science*, 2nd ed.; Dürr, H., Bous-Laurent, H., Eds.; Elsevier Science Publishing House: Amsterdam, 2003; Vol. *40*, pp 314−466.
(20) Ortica, F.; Favaro, G. *J. Phys. Chem. B* **2000**, *104*, 12179–12183.
(21) Raymo, F. M.; Giordani, S. *J. Am. Chem. Soc.* **2001**, *123*, 4651–4652.
(22) Wojtyk, J. T. C.; Wasey, A.; Xiao, N. N.; Kazmaier, P. M.; Hoz, S.; Yu, C.; Lemieux, R. P.; Buncel, E. *J. Phys. Chem. A* **2007**, *111*, 2511–2516.
(23) Chibisov, A. K.; Görner, H. *Chem. Phys.* **1998**, *237*, 425–442.
(24) Wojtyk, J. T. C.; Kazmaier, P. M.; Buncel, E. *Chem. Commun.* **1998**, 1703–1704.
(25) Shiraishi, Y.; Adachi, K.; Itoh, M.; Hirai, T. *Org. Lett.* **2009**, *11*, 3482–3485.
(26) Sumaru, K.; Kameda, M.; Kanamori, T.; Shinbo, T. *Macromolecules* **2004**, *37*, 4949–4955.
(27) Kameda, M.; Sumaru, K.; Kanamori, T.; Shinbo, T. *Langmuir* **2004**, *20*, 9315–9319.
(28) Shiraishi, Y.; Miyamoto, R.; Hirai, T. *Org. Lett.* **2009**, *11*, 1571–1574.
(29) Ivanov, A. E.; Eremeev, N. L.; Wahlund, P. O.; Galaev, I. Y.; Mattiasson, B. *Polymer* **2002**, *43*, 3819–3823.
(30) Piech, M.; Bell, N. S. *Macromolecules* **2006**, *39*, 915–922.
(31) Labsky, J.; Koropecky, I.; Nespurek, S.; Kalal, J. *Eur. Polym. J.* **1981**, *17*, 309–313.
(32) Hu, A.; Wang, W.-H.; Lee, H.-J. *J. Macromol. Sci., Part A: Pure Appl. Chem.* **1996**, *33*, 803–810.
(33) Davis, D. A.; Hamilton, A.; Yang, J.; Cremar, L. D.; Van Gough, D.; Potisek, S. L.; Ong, M. T.; Braun, P. V.; Martinez, T. J.; White, S. R.; Moore, J. S.; Sottos, N. R. *Nature* **2009**, *459*, 68–72.
(34) Krongauz, V. A.; Goldburt, E. S. *Macromolecules* **1981**, *14*, 1382–1386.
(35) Lukyanov, B. S.; Metelitsa, A. V.; Voloshin, N. A.; Alexeenko, Y.; Lukyanova, M. B.; Vasilyuk, G. T.; Maskevich, S. A.; Mukhanov, E. L. *Int. J. Photoenergy* **2005**, *7*, 17–22.
(36) Matsushima, R.; Nishiyama, M.; Doi, M. *J. Photochem. Photobiol., A* **2001**, *139*, 63–69.
(37) Krongauz, V.; Zelichonok, A.; Buchholz, F.; Ratner, J. US Patent 5905148, 1999, 5,322,945.
(38) Such, G.; Evans, R. A.; Yee, L. H.; Davis, T. P. *J. Macromol. Sci., Polym. Rev.* **2003**, *43*, 547–579.
(39) Evans, R.; Hanley, T.; Skidmore, M.; Davis, T.; Such, G.; Yee, L.; Ball, G.; Lewis, D. *Nature Mater.* **2005**, *4*, 249–253.
(40) Krongauz, V. *Mol. Cryst. Liq. Cryst.* **1994**, *246*, 339–346.
(41) Zelichenok, A.; Buchholtz, F.; Yitzchaik, S.; Ratner, J.; Safro, M.; Krongauz, V. *Macromolecules* **1992**, *25*, 3179–3183.
(42) Goldburt, E.; Shvartsman, F.; Fishman, S.; Krongauz, V. *Macromolecules* **1984**, *17*, 1225–1230.
(43) Garcia, A.; Marquez, M.; Cai, T.; Rosario, R.; Hu, Z.; Gust, D.; Hayes, M.; Vail, S.; Park, C.-D. *Langmuir* **2007**, *23*, 224–229.
(44) Edahiro, J. i.; Sumaru, K.; Takagi, T.; Shinbo, T.; Kanamori, T.; Sudoh, M. *Eur. Polym. J.* **2008**, *44*, 300–307.
(45) Drummond, C. J.; Furlong, D. N. *J. Chem. Soc., Faraday Trans.* **1990**, *86*, 3613–3621.
(46) Malkin, Y. N.; Krasieva, T. B.; Kuzmin, V. A. *J. Photochem. Photobiol., A* **1989**, *49*, 75–88.
(47) Moniruzzaman, M.; Fernando, G. F.; Bellamy, A. J. *Eur. Polym. J.* **2006**, *42*, 1455–1466.
(48) Bobrovsky, A. Y.; Boiko, N. I.; Shibaev, V. P. *Adv. Mater.* **1999**, *11*, 1025–1028.
(49) Kim, C.-H.; Kim, D.; Lee, J.; Lee, K.-S. *Mol. Cryst. Liq. Cryst.* **2001**, *370*, 131–134.
(50) Ohno, K.; Morinaga, T.; Koh, K.; Tsujii, Y.; Fukuda, T. *Macromolecules* **2005**, *38*, 2137–2142.
(51) Kwak, Y.; Matyjaszewski, K. *Macromolecules* **2008**, *41*, 6627–6635.
(52) Kojima, K.; Hayashi, N.; Toriumi, M. *J. Photopolym. Sci. Technol.* **1995**, *8*, 47–54.
(53) Semyakina, G. M.; Samedova, T. G.; Popova, N. I.; Zakhs; Malkin, Y.; Martynova, V. P.; Barachevskii, V. A.; Topchiev, D. A.; Kabanov, V. A. *Russ. Chem. Bull.* **1983**, *32*, 1153–1157.
(54) Biteau, J.; Chaput, F.; Boilot, J.-P. *J. Phys. Chem.* **1996**, *100*, 9024–9031.
(55) Schaudel, B.; Guermeur, C.; Sanchez, C.; Nakatani, K.; Delaire, J. A. *J. Mater. Chem.* **1997**, *7*, 61–65.

(56) Metelitsa, A. V.; Lokshin, V.; Micheau, J. C.; Samat, A.; Guglielmetti, R.; Minkin, V. I. *Phys. Chem. Chem. Phys.* **2002**, *4*, 4340–4345.
(57) Eckhardt, H.; Bose, A.; Krongauz, V. *Polymer* **1987**, *28*, 1959–1964.
(58) Tyer, N.; Becker, R. *J. Am. Chem. Soc.* **1970**, *92*, 1289–1294.
(59) Bütün, V.; Armes, S. P.; Billingham, N. C. *Polymer* **2001**, *42*, 5993–6008.
(60) Raymo, F.; Giordani, S. *J. Am. Chem. Soc.* **2001**, *123*, 4651–4652.
(61) Keum, S. R.; Lee, K. B.; Kazmaier, P. M.; Buncel, E. *Tetrahedron Lett.* **1994**, *35*, 1015–1018.
(62) Zhou, J.; Lia, Y.; Tanga, Y.; Zhaoa, F.; Songa, X.; Lib, E. *J. Photochem. Photobiol., A* **1995**, *90*, 117–123.
(63) Roxburgh, C. J.; Sammes, P. G. *Dyes Pigm.* **1995**, *27*, 63–69.
(64) Vamvakaki, M.; Papoutsakis, L.; Katsamanis, V.; Afchoudia, T.; Fragouli, P. G.; Iatrou, H.; Hadjichristidis, N.; Armes, S. P.; Sidorov, S.; Zhirov, D.; Zhirov, V.; Kostylev, M.; Bronstein, L. M.; Anastasiadis, S. H. *Faraday Discuss. Chem. Soc.* **2005**, *128*, 129–147.
(65) Fournier, D.; Hoogenboom, R.; Thijs, H. M. L.; Paulus, R. M.; Schubert, U. S. *Macromolecules* **2007**, *40*, 915–920.
(66) Yoshida, T.; Morinaka, A.; Funakoshi, N. *J. Chem. Soc., Chem. Commun.* **1986**, 437–438.