Articles

Reversible Photoinduced Chiral Structure in Amorphous Polymer for Light Polarization Control

Gabriella Cipparrone,*,† Pasquale Pagliusi,† Clementina Provenzano,† and Valery P. Shibaev‡

Licryl Laboratory CNR-INFM, Excellence Centre CEMIF.CAL and Physics Department, University of Calabria, Ponte P. Bucci, Cubo 33B, 87036 Rende-CS, Italy, and Chemistry Department, M.V. Lomonosov Moscow State University, Moscow 119991, Russia

Received May 7, 2008; Revised Manuscript Received June 25, 2008

ABSTRACT: Photoinduced supramolecular chiral structures in amorphous and nonchiral azo copolymer are demonstrated using circularly polarized light. The polymeric film undergoes a light-guided inhomogeneous supramolecular modification, both in the transverse and longitudinal directions. The photoinduced structure strongly affects the polarization state of the light propagating in it. Conversion from circular toward linear polarization occurs, and optical activity of the material arises. The direction of the optical rotation (clockwise or anticlockwise) can be controlled by means of the handedness of the inducing CPL. The resulting chiral structures, circular and spiral, exhibits interesting possibility to manipulate the light polarization, showing long-time stability and full reconfigurability.

Introduction

Recently, special attention was addressed toward the supramolecular approach to organic electronics, photonics, and nanotechnologies.[1−3] Several strategies, including supramolecular chemistry, self-assembly, or external stimuli, make possible to create architectures at different length scales that provided access to increasing complex functionalities.[1−5]

Chirality is a fundamental aspect in several systems and is also receiving a growing attention for the feasible technological applications.[6−8] There is a lot of interest in the control of chirality at different hierarchical levels because of the great potential for new approaches in asymmetric synthesis, the understanding of molecular communication processes, and the development of molecular memory systems and smart materials. The new generation of chiral materials stimulated the last years research of optics and materials communities. Chiral materials have been comprehensively studied having in mind to use them for creation of novel photonic devices.[9] Large interest was, for example, addressed toward chiral metamaterials that exhibit very impressive effects inducing relevant changes of the polarization state of the light propagating in them.[9]

On the other hand, chirality is an intriguing functionality of the soft matter systems, where it may be present at two different levels: molecular and supramolecular. While in the first case, chirality of the molecules is required, in the second case, a chiral superstructural organization of the molecules could be created even if the chirality at the molecular level does not exist. It is beyond question that the possibilities provided by molecular and supramolecular chirality could lead to the experimental findings of novel hierarchically ordered mesophase structures. To design materials with these properties, several strategies have been adopted mainly exploiting supramolecular chemistry.[10−13]

Photochromic organic materials, primarily polymers, have attracted much attention because of the ability to change their molecular structure and modify their macroscopic properties through interaction with light.[14−24] The “key point” is that they allow to perform a dynamical manipulation of the materials properties using an external stimulus. Depending on the involved photo-physicochemical processes, the intensity, the wavelength, and the polarization state of the light can be exploited to perform the control of the proper functionality. Photoinduced rotation effects via transfer of the angular momentum, both “spin” and “orbital”, from light to matter have been demonstrated in transparent and absorbing systems.[25−29] These phenomena clearly demonstrate that irradiation with circularly polarized light (CPL) is another possibility to induce and control the chirality in soft matter systems, in a fully reversible way. In this framework, the combination of photochromic and chiral functionality in polymers has been investigated for the chirality control by means of the light. Photoinduced modification of the chirality, as amplification, reversible switching, and photoresolution of racemic systems, has been reported in several papers.[29−31]

Recently some authors have reported that CPL and elliptically polarized light (EPL) irradiation can induce a supramolecular chirality inside polymers without chiral centers, but having photoisomerizable moieties.[21,22,30,32−39] Because of the photoinduced trans−cis isomerization, the side chain azo polymers are polarization-sensitive materials, where the appearance of a photoinduced linear birefringence and dichroism has been widely reported.[19,20,22−24] The appearance of the light-induced chiral properties in such materials has an intriguing aspect: they organize their environment in response to the external stimulus acquiring a new functionality. From the literature, the chirality induced by means of CPL has been observed in LC polymers,

---

* Corresponding author: e-mail cipparrone@fis.unical.it, Ph +39-0984-496148, Fax +39-0984-494401.

† University of Calabria.

‡ Moscow State University.

10.1021/ma801030b CCC: $40.75

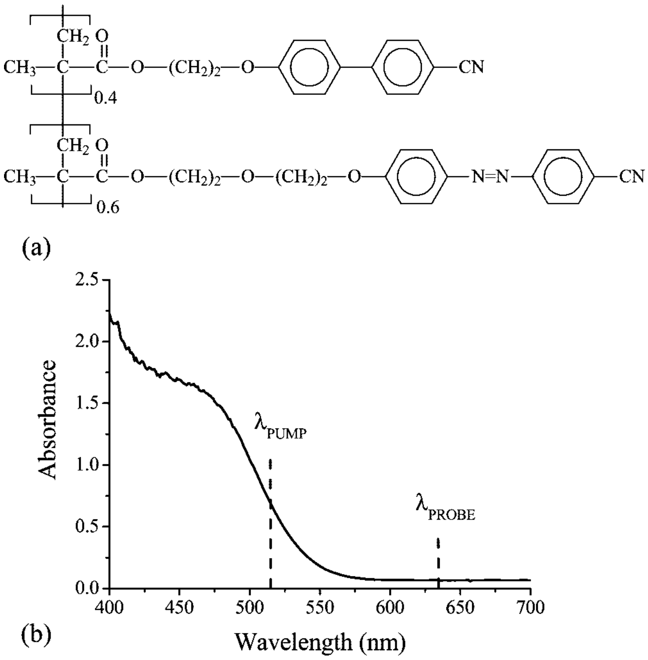

Figure 1. (a) Chemical formula of the polymethacrylic copolymer and (b) visible absorption spectrum of a polymer film. Pump and probe beam wavelengths are shown in the graph.

where an optical axis naturally exists, and in amorphous polymers only after a prealignment procedure that creates an optical axis. In both LC and amorphous polymers photoinduced chirality has been observed using EPL even without prealignment. The published results suggest that the phenomenon occurs when a macroscopic linear anisotropy is present in the light or in the medium.[21,30,32,34,36−39]

The experimental investigation reported here demonstrates that even in an amorphous, nonchiral polymer film without any prealignment, a CPL beam can induce a reorganization of the material related to the light chirality. The new structure of the material strongly affects the polarization state of the light propagating in it. Conversion from circular toward linear polarization occurs during the irradiation, and optical activity of the material arises, as the large rotation of the major axis of the ellipse demonstrates. The direction of the optical rotation (clockwise or anticlockwise) can be controlled by means of the handedness of the inducing CPL. The system preserves the imprinted chiral properties for several months or even longer due to a memory effect. Nevertheless, it allows to perform the light polarization management, controlling the exposure time, or even subsequent irradiations.

Experimental Section

The polymer used to perform the investigation is a side-chain polymethacrylic copolymer with 60 mol % content of oxycyanoazobenzene fragments in the side chains of the macromolecule.[19] The synthesis of the copolymer (polymerization degree $\bar{P}_n = 43$; polydispersity = 2.44) is described in ref 40. The glass transition temperature of the polymer is $T_g = 77$ °C. Figure 1 shows the chemical structure of the polymer (a) and the visible absorption spectrum of the isotropic film (b) measured at room temperature. The sample is a 30 μm thick film, prepared melting the polymer between two glass substrates.

To investigate the photoinduced effects, a pump−probe technique has been used. The polymer film has been exposed to a CPL beam at 514 nm. A probe beam at 633 nm, where the material practically does not absorb, has been used to investigate the photoinduced birefringence effect. The pump and probe beams are provided by linearly polarized argon ion laser (Innova 90C, Coherent) and helium−neon laser (05-LHP-201, MellesGriot). Both the pump and probe beam passes through the proper quarter-wavelength plate to convert linear into circular polarization. The pump beam is expanded to a spot size of 5 mm and overlaps with the probe beam in the polymer layer at a small angle. The spot size of probe beam on the sample is smaller than the pump beam one (2 mm) in order to investigate the central part of the irradiated area. A rotating analyzer placed on the probe beam path, between the sample and a photodetector, has been used to characterize the polarization state of the transmitted probe beam.

Results and Discussion

In the experiments, the pump and the probe beams are L-CP, with a measured ellipticity $e = -0.97 \pm 0.01$. In Figure 2a−e we report the polar plots of the intensity of the probe beam at the exit of the sample versus the analyzer angle for increasing pump beam exposure times.

As is seen from Figure 2a, the ellipticity value of the probe transmitted beam, before the pump irradiation, is −0.97. This value is equal to the ellipticity of the probe incident beam, indicating that the polymer film is optically isotropic before irradiation. The successive measurements were performed, stopping the pump beam; at any time the system reaches a steady state, no depolarization of the transmitted light is observed, and the polarization state remains stable for long time (several months). As shown in Figure 2, a continuous decrease of the ellipticity ($|e|$ down to 0.5) and rotation of the azimuth angle (about 250°) has been observed during the 5 min irradiation. Using R-CP pump beam on an unirradiated region of the sample, the absolute value of the ellipticity behaves likewise, while the azimuth angle of the ellipse rotates in the opposite direction (clockwise), proving that the effect depends on the handedness of the exciting beam. It is worth noting that a complete reconfigurability of the system can be achieved through thermal annealing above the glass transition temperature of the polymer.

The time evolution of the ellipticity of the transmitted beams (probe or pump) during the irradiation has been investigated exploiting a polarization grating. This optical device allows to have information on the R-CP and L-CP components of the wave impinging on it. Only first-order diffracted beams are generated whose intensities can be used to evaluate the ellipticity.[41,42]

In Figure 3a the time evolution of the L-CP and R-CP components of the transmitted probe beam are reported. Since the absorption is negligible at the probe wavelength, symmetric exchange between the left and the right component of the wave passing through the sample is observed during the irradiation. A clear conversion from the L-CP to the R-CP component is revealed, indicating the appearance of the anisotropy. From these results we evaluate that the probe beam at the exit of the sample reduces the ellipticity and reaches a value of −0.50 (Figure 3b).

Significant results were obtained studying the polarization state of the pump beam propagating through the sample, where a conversion from circular polarization toward linear polarization is observed. In Figure 3c,d is reported the time evolution of both the intensities of the L-CP and R-CP components and the ellipticity value. Starting from a good circular polarization state ($e = -0.97$, L-CP), the transmitted beam becomes almost linear, $e = -0.10$. Moreover, the effect of the absorption also needs to be considered, as suggested by the asymmetric energy exchange between the L-CP and R-CP components (Figure 3c). The left component experiences an increasing absorption with respect to the growing right component during the illumination, which is in agreement with the appearance of a circular dichroism.

The reported results provide the experimental evidence of the occurrence of two new properties of the material: the chirality, responsible of the optical rotation, and the linear

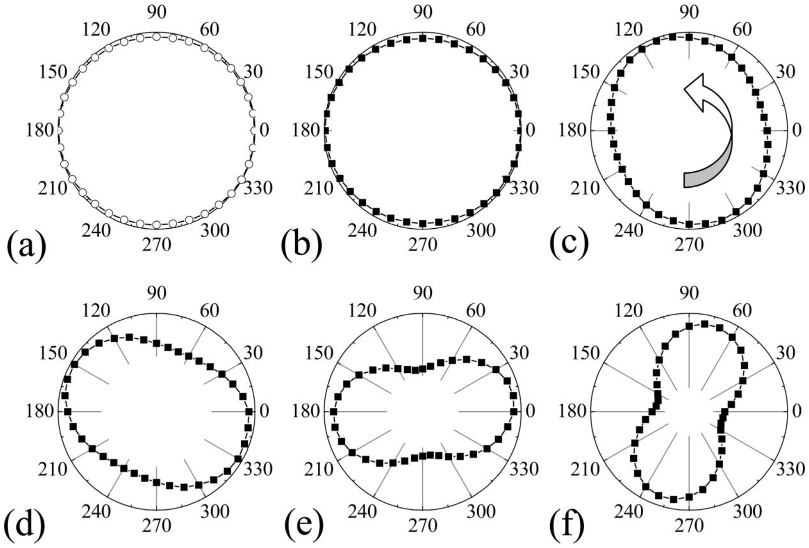

Figure 2. (a) Polar plot of the incident exciting beam ($e = -0.97$). Polar plots of the transmitted probe beam (b) before the illumination ($e = -0.97$), (c) after 60 s ($e = -0.89$), (d) after 100 s ($e = -0.80$), (e) after 150 s ($e = -0.65$), and (f) after 300 s ($e = -0.55$). The arrow in (c) denotes the sense of rotation of the azimuth (anticlockwise).

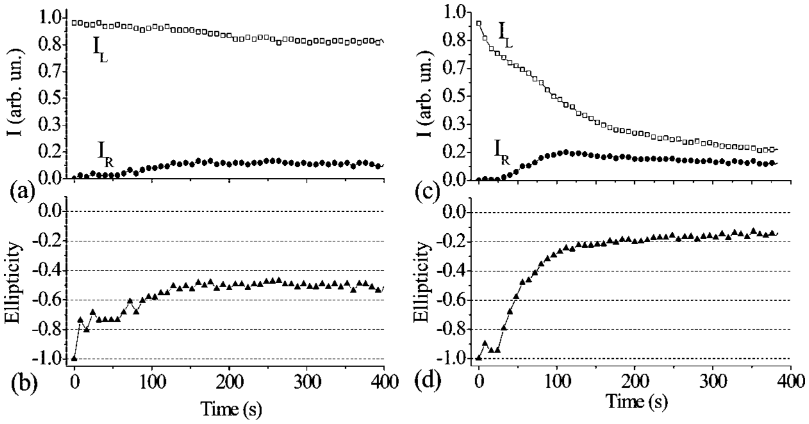

Figure 3. Polarization analysis of the probe (a, b) and pump (c, d) beams. Time evolution of the (a, c) L-CP and R-CP components and (b, d) ellipticity of the transmitted probe and pump beams.

anisotropy, responsible of the change in the ellipticity. The main point is to understand how, in the present case, a CPL can induce simultaneously both effects in an amorphous isotropic polymer.

Additional interesting suggestions are given by the observation of the irradiated region of the sample at the optical microscope between crossed polarizers. The structures observed at the microscope are bright and dark rings (see Figure 4) that exhibit a particular behavior when the sample is rotated around an axis perpendicular to it. During the rotation, in fact, the rings collapse toward the center or reopen from the center toward the outside region, depending on the rotation sense of the sample (anticlockwise or clockwise). A reversed behavior can be observed examining the regions of the sample irradiated with the opposite CPL. In Figure 4 are reported the images of the region of the sample previously exposed to a L-CP laser beam at an intensity of 100 mW cm^{-2} for few seconds. Starting from a position in which one dark ring and a dark central spot appear (Figure 4a), an anticlockwise rotation of about 40° determines an enlargement of the dark ring toward the external isotropic region and the opening of the dark spot into a dark ring (Figure 4b). Further rotation up to 90° produces a new dark spot arising in the central part of the bright region, while the dark ring enlarges toward the outside region (Figure 4c).

Although the ring structures can be related to the intensity Gaussian profile of the exciting laser beam, their behavior during the sample rotation can be accounted for the presence of optical chiral structures. The microscope investigations suggest that the exposed spot works as a birefringent system having a transversely inhomogeneous optical axis distribution, as in Figure 4d. Considering the *xy* reference frame of the sample, the angle between the local optical axis and the *x* axis changes versus the radius *r* of the Gaussian laser beam (green profile in Figure 4d), and at the same time, the birefringence reduces toward zero at the isotropic nonirradiated region of the sample.

The same dark and bright rings and similar dynamical behavior can be observed during the irradiation of the sample with CP pump beam, looking at the far field pattern of the LPL probe beam through a crossed analyzer. Starting the irradiation, a bright spot appears in the center of the beam and then opens toward the outside region, leaving a dark spot in the center; subsequently, a new bright spot arises in the center and so on.

The analogy in the dynamics with respect to the rotation of the irradiated spot under the microscope suggests a simultaneous rotation of the rising circular structures (Figure 4d) during the irradiation with the CP pump beam. Locally, the photoinduced birefringence increases and the optical axis rotates according to the light intensity and handedness.

Because of the absorption of the medium at the pump beam wavelength, a decreasing rotation of the transversal structures occurs versus the film depth. As a consequence, a rotation of

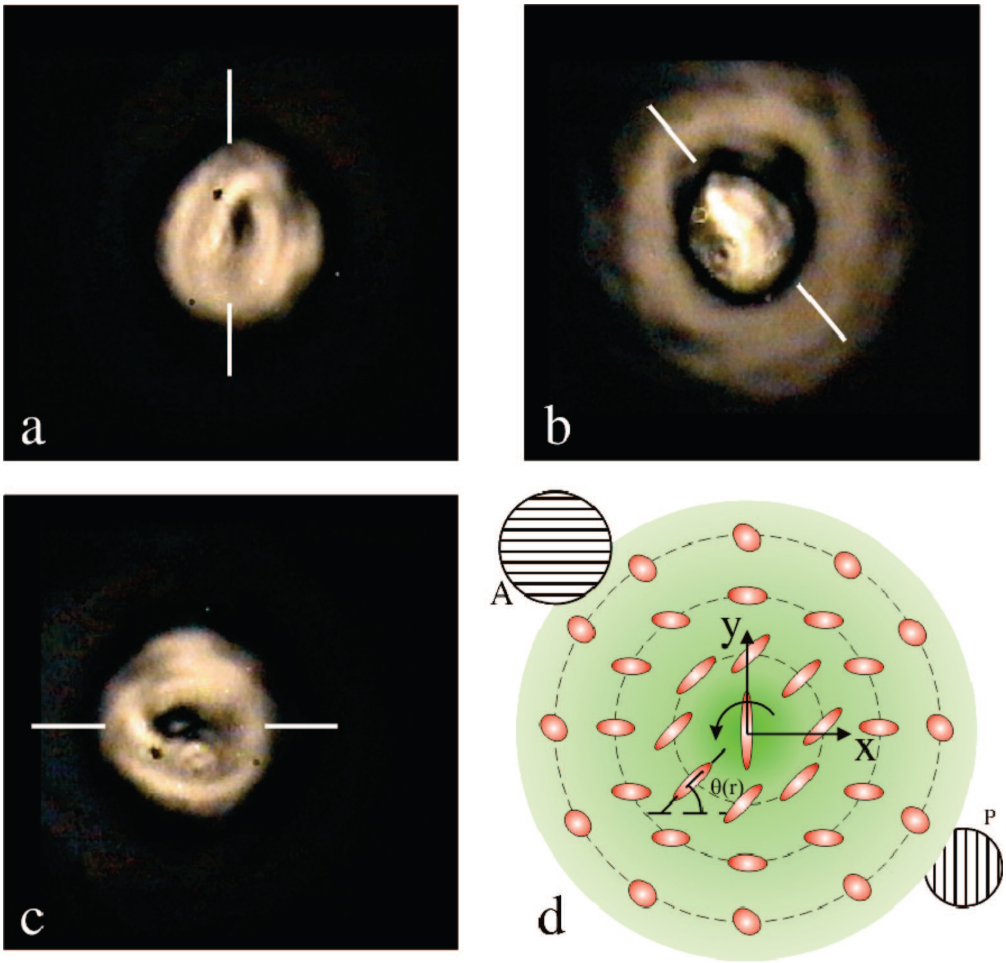

Figure 4. Optical microscope images of the sample between crossed polarizers. The region was irradiated for 10 s with a Gaussian pump beam (average intensity 100 mW/cm^2). The pictures are taken for anticlockwise rotation of the sample at angles (a) 0°, (b) 40°, and (c) 90° with respect to the polarizer. (d) Scheme of the transversal local optical axis and birefringence in the irradiated region. The green area represents the intensity spatial distribution of Gaussian laser beam; A and P are the microscope's analyzer and polarizer, respectively.

the optical axis and the decreasing of the birefringence along the longitudinal (z axis) direction is also expected.

The formation and the dynamics of such chiral structures support also the results reported in Figures 2 and 3. Then we can conclude that also these observations sustain the idea that both linear anisotropy and chirality are needed to explain experimental results.

For longer exposure time (several minutes) the structures observed at the microscope between crossed polarizers become much more complex, even if they preserve the main features of the former structures: circular and linear anisotropy. In Figure 5 the typical images of the spots irradiated for a long time are reported, showing spiral patterns with opposite handedness depending on the helicity of the pump beam.

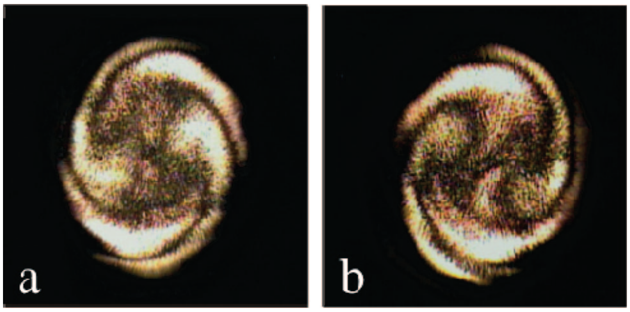

Figure 5. Optical microscope images, between crossed polarizers, of the spot irradiated with (a) L-CP and (b) R-CP pump beam (average intensity of 100 mW/cm^2) for several minutes.

It is difficult to explain how these structures can be created starting from an isotropic medium irradiated with CPL; nevertheless, we can find some suggestions considering the main peculiarities of the two interacting systems: the light and the medium. The CP state of the light possess a chirality that can be transferred to the absorbing material through the transfer of angular momentum. On the other hand, the material, amorphous and isotropic at the macroscopic level, is anisotropic on the molecular level, for both the anisometric azo- and cyanobiphenyl fragments in the side chains and their intermolecular interaction. We believe that the local optical axes, as depicted in Figure 4d, arise from the orientation of the side chains as a result of the coupling between the light-driven rotation of the azochromophores and their anisotropic interaction with the neighboring cyanobiphenyl groups. When the copolymer is irradiated with the Gaussian CPL beam, the photoalignment of the side chains starts at the beam center, where the intensity is higher. The rotation of the local optical axis, according to the handedness of the light, immediately takes place due to the transfer of angular momentum. Finally, a long-range correlation of the local optical axes would be responsible of the observed chiral structures.

Conclusions

We show the experimental evidence of supramolecular chirality induced in an amorphous and nonchiral copolymer film by mere CPL irradiation. Fascinating structures, from circular to spiral, have been created, through which different polarization states of the transmitted light can be achieved. A full reconfigurability is guaranteed by the intrinsic reversibility of the photoinduced processes. The effects clearly depend on the chirality of the light and are compatible with a light-induced transversely and longitudinally inhomogeneous modification of the polymer structure at the supramolecular level, including chirality and linear anisotropy. Although the involved mechanisms are not clearly understood, the material exhibits several intriguing advantages for manipulating light polarization and developing of new light-driven devices.

Acknowledgment. The authors deeply thank Dr. Sergey Kostromin for the synthesis of copolymer and its characterization as well as Prof. Lev M. Blinov and Prof. Roberto Bartolino for useful discussions. This work was partially supported by CNR-INFM, CEMIF.CAL, and the Russian Foundation for basic Research (Project No. 08-03-00481).

Supporting Information Available: Method for dynamic ellipticity measurement. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Samorì, P.; Cacialli, F.; Anderson, H. L.; Rowan, A. E. *Adv. Mater.* **2006**, *18*, 1235–1238.
(2) Davis, J. T.; Spada, G. *Chem. Soc. Rev.* **2007**, *36*, 296–3.
(3) Barth, J. V.; Costantini, G.; Kem, K. *Nature (London)* **2005**, *437*, 671–679.
(4) Nguyen, T. D.; Leung, K. C.-F.; Liong, M.; Liu, Y.; Stoddart, J. F.; Zink, J. I. *Adv. Funct. Mater.* **2007**, *17*, 2101–2110.
(5) Kocer, A.; Walko, M.; Meijberg, W.; Feringa, B. L. *Science* **2005**, *309*, 755–758.
(6) Muroaka, T.; Kinbara, K.; Aida, T. *Nature (London)* **2006**, *440*, 512–515.
(7) Ward, M. D. *Nature (London)* **2003**, *426*, 615–616.
(8) Purrello, R. *Nat. Mater.* **2003**, *2*, 216–217.
(9) Fedotov, V. A.; Mladyonov, P. L.; Prosvirnin, S. L.; Rogacheva, A. V.; Chen, Y.; Zheludevl, N. I. *Phys. Rev. Lett.* **2006**, *97*, 167401.
(10) Rikken, G. L. J. A.; Raupach, E. *Nature (London)* **2000**, *405*, 932–935.
(11) Hough, L. E.; Clark, N. A. *Phys. Rev. Lett.* **2005**, *95*, 107802.
(12) Perez-Garcia, L.; Amabilino, D. B. *Chem. Soc. Rev.* **2002**, *31*, 342–356.
(13) Link, D. R.; Natale, G.; Shao, R.; Maclennan, J. E.; Clark, N. A.; Korblova, E.; Walba, D. M. *Science* **1997**, *278*, 1924–1927.
(14) Berkovuch, G.; Krongauz, V.; Weiss, V. *Chem. Rev.* **2000**, *100*, 1741–1753.
(15) Delaire, J. A.; Nakatani, K. *Chem. Rev.* **2000**, *100*, 1817–1845.
(16) Ikeda, T.; Tsutsumi, O. *Science* **1995**, *268*, 1873–1875.
(17) Irie, M. *Chem. Rev.* **2000**, *100*, 1683–1684.
(18) Bobrovsky, A.; Shibaev, V. P. *Polymer* **2006**, *47*, 4310–4317.
(19) Simonov, A. N.; Uraev, D. V.; Kostromin, S. G.; Shibaev, V. P.; Stakhanov, A. I. *Laser Phys.* **2002**, *12*, 1294–1302.
(20) Fukuda, T.; Kim, J. Y.; Barada, D.; Yase, K. *J. Photochem. Photobiol., A* **2006**, *183*, 273–279.
(21) Tejedor, R. M.; Millaruelo, M.; Oriol, L.; Serrano, J. L.; Alcalà, R.; Rodrıguez, F. J.; Villacampa, B. *J. Mater. Chem.* **2006**, *16*, 1674–1680.
(22) Natansohn, A.; Rochon, P. *Chem. Rev.* **2002**, *102*, 4139–4175.
(23) Yager, K. G.; Barrett, C. J. *J. Photochem. Photobiol., A* **2006**, *182*, 250–261.
(24) Todorov, T.; Nikolova, L.; Tomova, N. *Appl. Opt.* **1984**, *23*, 4309–4312.
(25) Brasselet, E.; Galstian, T. V. *Opt. Commun.* **2001**, *200*, 241–248.
(26) Santamato, E.; Daino, E.; Romagnoli, M.; Settembre, M.; Shen, Y. R. *Phys. Rev. Lett.* **1986**, *57*, 2423–2426.
(27) Piccirillo, B.; Toscano, C.; Vetrano, F.; Santamato, E. *Phys. Rev. Lett.* **2001**, *86*, 2285–2288.
(28) He, H.; Friese, M. E. J.; Heckenberg, N. R.; Rubinsztein-Dunlop, R. *Phys. Rev. Lett.* **1995**, *75*, 826–829.
(29) Galstyan, T. V.; Drnoyan, V. *Phys. Rev. Lett.* **1997**, *78*, 2760–2763.
(30) Kim, M. J.; Yoo, S. J.; Kim, D. Y. *Adv. Funct. Mater.* **2006**, *16*, 2089–2094.
(31) Tamaoki, N.; Wada, M. *J. Am. Chem. Soc.* **2006**, *128*, 6284–6285.
(32) Choi, S. W.; Kawauchi, S.; Ha, N. Y.; Takezoe, H. *Phys. Chem. Chem. Phys.* **2007**, *9*, 3671–3681.
(33) Shibaev, V.; Bobrovsky, A.; Boiko, N. *Prog. Polym. Sci.* **2003**, *28*, 729–836.
(34) Pagès, S.; Lagugné-Labarthet, F.; Buffeteau, T.; Sourisseau, C. *Appl. Phys. B: Laser Opt.* **2002**, *75*, 541–548.
(35) Nedelchev, L.; Nikolova, L.; Todorov, T.; Petrova, T.; Tomova, N.; Dragostinova, V.; Ramanujam, P. S.; Hvilsted, S. *J. Opt. A: Pure Appl. Opt.* **2001**, *3*, 304–310.
(36) Nikolova, L.; Nedelchev, L.; Todorov, T.; Petrova, T.; Tomova, N.; Dragostinova, V. *Appl. Phys. Lett.* **2000**, *77*, 657–659.
(37) Sumimura, H.; Fukuda, T.; Kim, J. Y.; Barada, D.; Itoh, M.; Yatagai, T. *Jpn. J. Appl. Phys., Part 1* **2006**, *45*, 451–455.
(38) Iftime, G.; Lagugné-Labarthet, F.; Natansohn, A.; Rochon, P. *J. Am. Chem. Soc.* **2000**, *122*, 12646–12650.
(39) Choi, S. W.; Ha, N. Y.; Shiromo, K.; Rao, N. V. S.; Paul, M. Kr.; Toyooka, T.; Nishimura, S.; Wu, J. W.; Park, B.; Takanishi, Y.; Ishikawa, K.; Takezoe, H. *Phys. Rev. E* **2006**, *73*, 021702.
(40) Belayev, S.; Zvetkova, T.; Panarin, Yu.; Kostromin, S.; Shibaev, V. *Vysokomolek. Soedin., Ser. B* **1986**, *28*, 789–793.
(41) Cipparrone, G.; Mazzulla, A.; Blinov, L. M. *J. Opt. Soc. Am. B* **2002**, *19*, 1157–1161.
(42) Provenzano, C.; Cipparrone, G.; Mazzulla, A. *Appl. Opt.* **2006**, *45*, 3929–3934.

MA801030B