

We are IntechOpen, the world's leading publisher of Open Access books Built by scientists, for scientists

4,800

Open access books available

122,000

International authors and editors

135M

Downloads

Our authors are among the

154

Countries delivered to

TOP 1%

most cited scientists

12.2%

Contributors from top 500 universities



WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index
in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.

For more information visit www.intechopen.com



Side-Chain Multifunctional Photoresponsive Polymeric Materials

Luigi Angiolini¹, Tiziana Benelli¹, Loris Giorgini¹,
Attilio Golemme², Elisabetta Salatelli¹ and Roberto Termine²

¹Dipartimento di Chimica Industriale e dei Materiali, Università di Bologna,

²CNR-IPCF UOS di Cosenza-LiCryL, INSTM UdR Calabria,

Centro di Eccellenza CEMIF CAL, Dipartimento di Chimica,

Università di Calabria,

Italy

1. Introduction

Several potential advantages are connected to the availability of functional organic polymeric materials for advanced applications with respect to inorganic materials. They include structural flexibility (i.e. the possibility to achieve by synthetic methods different composition features, as well as molecular and physical properties), lighter weight, thermoplastic behaviour (allowing to prepare stable thin films), possibility of being processed by different procedures, potential low cost etc. Further advantages are also given by the chemical anchorage of the photoactive moieties to the macromolecular structure, thus avoiding several drawbacks deriving from crystallization, inhomogeneity in the bulk, phase segregation etc. which are present when small active molecules are dispersed into a plastic matrix.

Indeed, since several decades a very wide academic and industrial interest has arisen around this topic, as demonstrated by the huge amount of publications appeared in the literature. We shall limit here to review the recent literature concerning the state-of-the-art of the research on amorphous polymeric derivatives bearing side-chain photoactive moieties such as the azo-aromatic and the carbazole chromophore as functional groups, in addition to the presence of structural or chemical features suitable to also provide the macromolecules of chiral properties.

2. Functional polymers containing side-chain azoaromatic moieties

Azobenzene derivatives represent a most widely investigated chromophoric system, due in particular to their photochromic properties. When submitted to irradiation with appropriate light, the more stable azo-*trans* form isomerizes reversibly to the azo-*cis* form, possessing higher dipole moment and free volume requirement (Fig. 1), with several relevant consequences if the moiety is incorporated into polymers or other materials. The azo-*cis* form gives again the *trans* isomer thermally or by light irradiation.

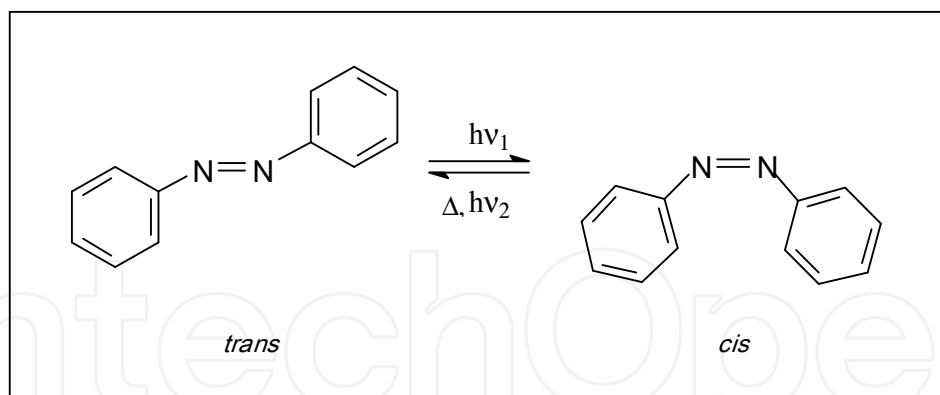


Fig. 1. Photoisomerization of azobenzene

Thus, the light-induced geometric change allows these systems to be used as photoswitches, with important effects on various chemical, mechanical, electronic and optical properties of the material. An exhaustive review paper focused on the photoinduced motions in azo-containing polymers covering the literature up to 2001, has been published by Natansohn and Rochon (Natansohn & Rochon, 2002). Recently, a book devoted to azobenzene-containing polymers and liquid crystals as light-responsive materials has appeared (Zhao & Ikeda, 2009).

Three levels of induced motions, at molecular, domain and mass (macroscopic) level, in order of increasing size scale, are considered in connection with polarization and power of incident light, although the motion at any scale invariably affects the other scales (Fig. 2).

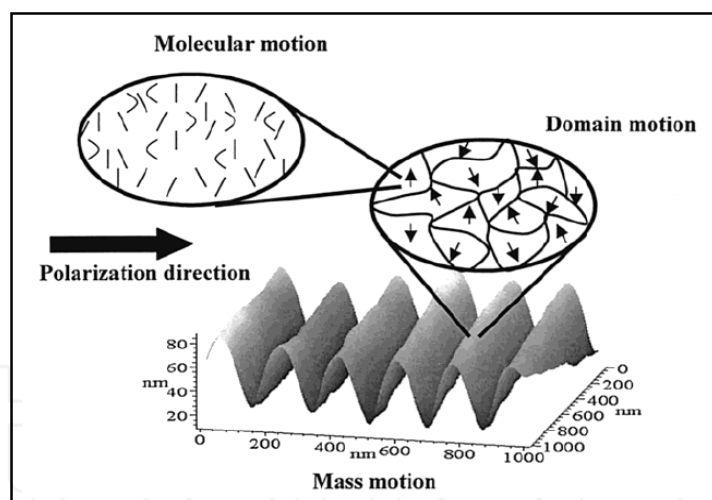


Fig. 2. Illustration of the three levels of polymer motion produced with light (Reprinted with permission from ref. Natansohn & Rochon 2002. Copyright 2002 American Chemical Society)

At the first scale level, this behaviour can be exploited in the optical storage of information, as optical birefringence in the material can be induced in consequence of a statistical process based on the absorption of linearly polarized (LP) light, *trans-cis-trans* isomerisation and reorientation of the azo groups. As the groups which reorient with their electronic transition dipole moments along a direction perpendicular to the light electric field, are unable to absorb again the radiation, a net excess of chromophores oriented in that direction, and consequently birefringence, is produced in the material (Fig. 3a).

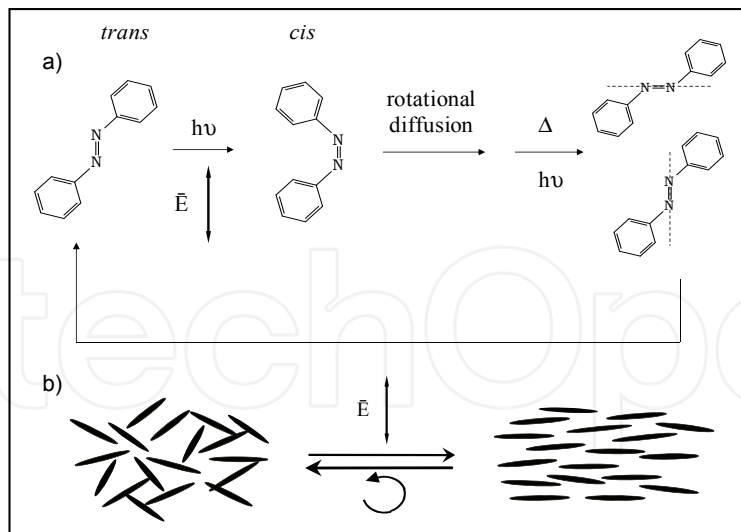


Fig. 3. Statistical photoorientation of azomolecules

The photoinduced birefringence can then be erased by irradiation with depolarized or circularly polarized (CP) light (Fig. 3b), thus recreating the original isotropic arrangement of the dipoles in the material. This reversible process can be repeated many times (up to hundred thousands of times). The application has been reported for poly(meth)acrylates functionalized in the side chain with the Disperse Red 1 (**DR1**) dye (Fig.4) (Natansohn et al., 1992; Ho et al., 1995) and demonstrated for rewritable optical disk systems (Sabi et al., 2001 as cited in Natansohn & Rochon, 2002).

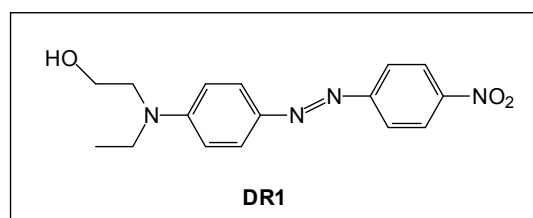


Fig. 4. Chemical structure of **DR1** molecule

More recently, enhanced photoinduced linear birefringence, lower relaxation after pump removal and long-term storage stability, although with lower stability to repeated cycles of irradiation with respect to **DR1** functionalized polymers, has been reported for side-chain azoaromatic polymethacrylates characterized by the presence of a chiral moiety with one prevailing absolute configuration interposed between the main chain and the chromophore (poly[(S)-**MAP-N**] Fig. 5).

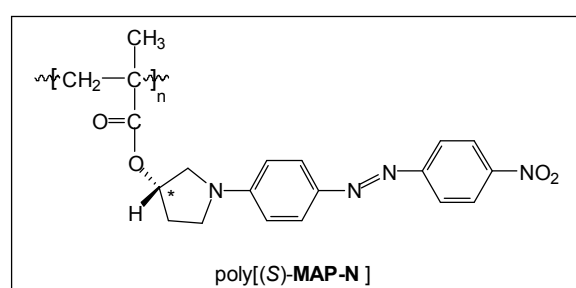


Fig. 5. Chemical structure of poly[(S)-**MAP-N**]

The presence of a chiral moiety in the material allows also the photomodulation of the chiroptical properties of the film at the domain level, upon irradiation with CP light of one single, L or R, rotation sense, with the possibility to reversibly invert the original supramolecular helical handedness of the native material without any need of preorientation with linearly polarized (LP) light for the circular dichroism to be photoinduced (Angiolini et al., 2002, 2003a, 2003b).

A similar intriguing phenomenon was previously observed in achiral smectic liquid crystalline side-chain azopolymers already possessing a supramolecular conformational order (Naydenova et al., 1999) and also in an achiral amorphous MMA azo-copolymer (**1**, Fig. 6) upon irradiation with L- or R-CP light, after preorientation by LP light (Ivanov et al., 2000). This was interpreted on the basis of circular momentum transfer from the CP light to the azobenzene chromophores (Nikolova et al., 2000).

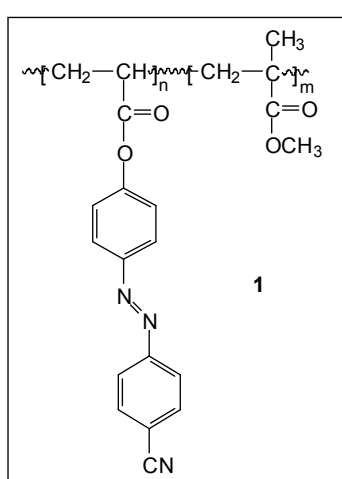


Fig. 6. Chemical structure of an achiral amorphous MMA azo-copolymer

The methacrylic copolymers bearing in the side chain both the above mentioned chiral moiety [(S)-MAP-N] and the DR1 methacrylate (DR1M) moiety (Fig. 7) display intermediate birefringence properties and increased stability at low content of chiral co-units (Angiolini et al., 2006).

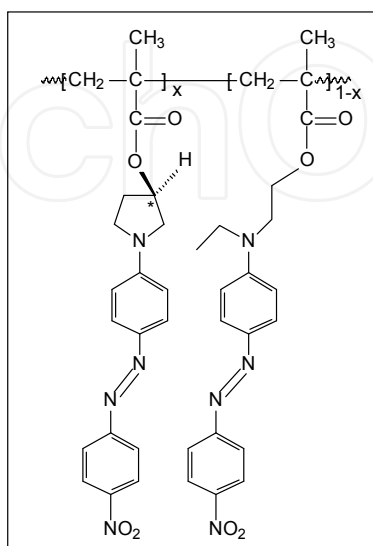


Fig. 7. Chemical structure of the copolymeric system poly[(S)-MAP-N-co-DR1M]

Side-chain bis-azo chromophores (Fig. 8) afford higher birefringence with respect to mono-azo ones, but limited solubility (Meng et al. 1997; J. Wang et al., 2003) and their isomerization mechanism was investigated (Jin et al., 2004). The application of these polymeric materials as rewritable digital data carriers and for optical recording has been patented (Hagen et al., 2003; Berneth et al., 2003).

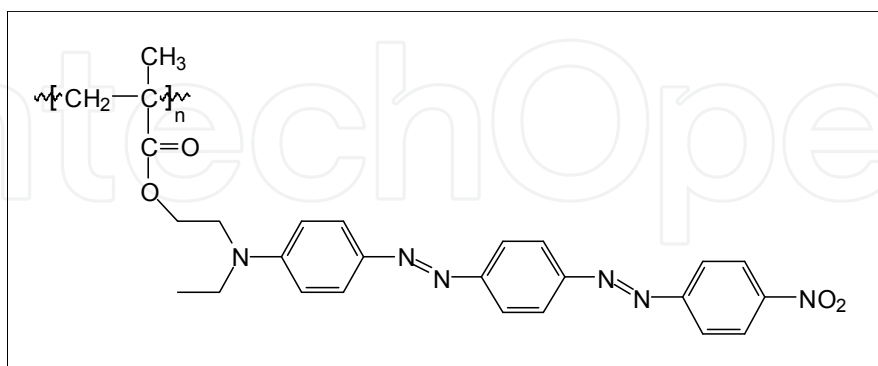


Fig. 8. Chemical structure of side-chain bis-azo chromophore

Experiments of photoinduced birefringence on chiral, optically active bis-azo homo- and copolymers with MMA (**2**, Fig. 9) (Angiolini et al., 2007a) show that, although these copolymers display slower optical response rates in comparison to similar derivatives containing only one azo bond (Angiolini et al., 2002), large and relatively stable birefringence and all-optical switching effects can be achieved with polymer films having a low content of photochromic co-units, along with better solubility and processability.

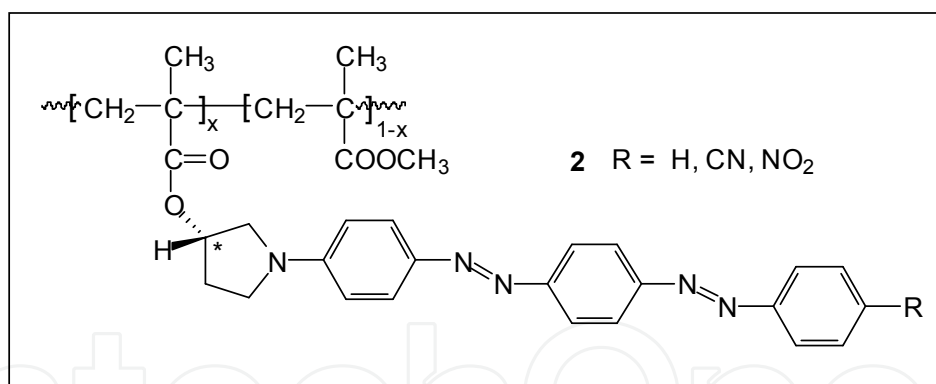


Fig. 9. Chemical structure of optically active bis-azo homo- and co-polymers with MMA

Non linear optical (NLO) properties, requiring an asymmetric response by the electronic system, can be achieved with push-pull substituents giving strongly differentiated electron distribution, and overall noncentrosymmetry in the bulk. They are based on electric field poling of dipoles in the material spin coated over a conducting substrate and then heated at a temperature above the glass transition temperature (T_g) (corona-poling), or submitted to photoassisted alignment in order to improve the electric field poling (Sekkat & Dumont, 1992). Azoaromatic derivatives are natural candidates to this application due to their large second-order NLO properties, ease of processing and architectural versatility with respect to inorganic counterparts such as LiNbO_3 . Of course, for achieving temporal stability of the system, the polar alignment has to be maintained at the working temperature of the material and a high value of T_g , well above the room temperature, is required. The NLO response is

usually assessed by measuring the second harmonic generation (SHG), i.e. the emission of light at a double frequency of the incident beam, the electrooptic (EO) effect (change of refractive index under an electric field), or through wave-mixing experiments (generation of various frequencies of light), all of these being also related to the main applications of NLO materials (Zhao & Ikeda, 2009).

A significant number of polymers functionalized, in particular, with **DR1** dye in the side chain are reported (Blanchard et al. 1993a, 1993b as cited in Natansohn & Rochon, 2002; Loucif-Saibi et al., 1993 as cited in Natansohn & Rochon, 2002; Hill et al., 1995 as cited in Natansohn & Rochon, 2002) to have been submitted to photoassisted alignment, thus achieving improved NLO properties. An all-optical poling, in which the aligning electric field is actually generated by the laser light has also been envisaged since 1993 on **DR1M-MMA** copolymer (Charra et al., 1993; Chalupczak et al., 1996) and subsequently applied to a new phosphine oxide azo-dye-MMA copolymer (Fiorini et al., 1997) achieving increased transparency with respect to the **DR1** functionalized material, together with large second-order properties. Differently from the polymeric **DR1M-MMA** material, efficient optical poling of thin films of norbornene functionalized with azo-dye have also been achieved, but without appreciable enhancement of second-order susceptibility, however, in the related polymeric poly-norbornene derivative, due probably to the increased rigidity of the poly-norbornene backbone with respect to the poly-MMA backbone (Churikov et al., 2000). Accordingly, copolymers based on side-chain push-pull azobenzene grafted to poly(N-methacryloyl-N'-phenylpiperazine) (**3**, Fig. 10) displayed much lower orientability and stability of the polar order with respect to the related guest-host systems having the chromophore physically dispersed into the unfunctionalized polymer. In addition, flexible structures gave better results than the rigid ones (Tirelli et al., 2000).

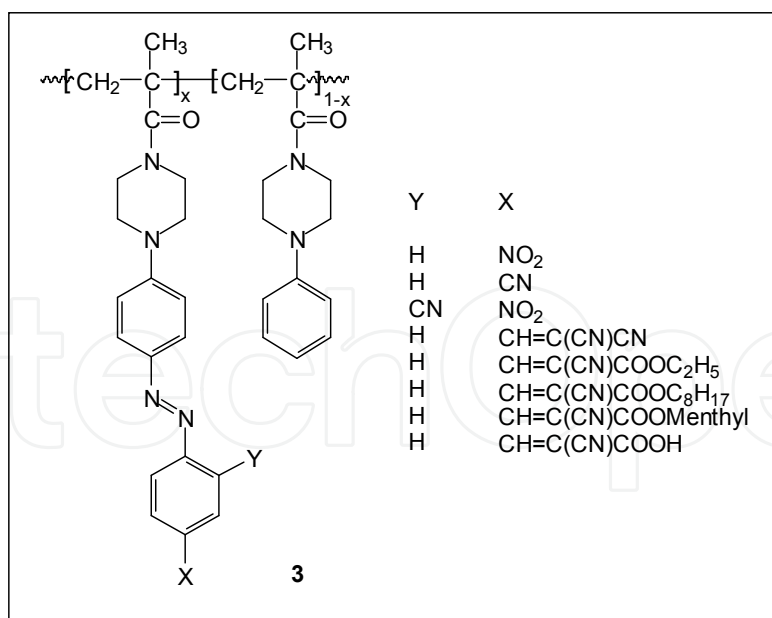


Fig. 10. Chemical structure of copolymers based on side-chain push-pull azobenzene grafted to poly(N-methacryloyl-N'-phenylpiperazine)

The influence of main-chain mobility on the effectiveness of optical or thermal poling is witnessed by many literature examples. For instance, the all-optical poling of a side-chain poly(urethane-imide) film containing the azobenzene chromophore displayed less surface

defects with respect to traditional corona poling (Sui et al., 2001), however in the case of crosslinkable polymeric thick films of isocyanate prepolymer functionalized with push-pull azobenzene moieties, corona-poling appears to be more efficient with respect to optical poling (Xu et al., 1999).

An interesting review paper on the state of the art in the field of second-order NLO polymers is reported by Samyn (Samyn et al., 2000), where a comparison is made among several side-chain azopolymers differing in the main chain structure. It turns out that poly(methacrylate) appears as the most favourable backbone in terms of second-harmonic coefficient values and temporal stability with respect to the related poly(alkyl vinyl ether)s and poly(styrene)s.

Chiral polymers, being inherently non-centrosymmetric on the molecular and macroscopic scale, could in principle not require poling in order to display NLO properties, but their symmetry in the bulk is high enough to prevent the production of frequency doubling. However it is sufficient for obtaining EO effect and frequency mixing (Beljonne et al., 1998). Recently, corona-poled chiral side-chain azobenzene polymethacrylates of various composition (**4**, Fig. 11) have been reported (Angiolini et al., 2008a) to afford higher values of their second-order coefficients with respect to similar achiral materials (S'Heeren et al., 1993) and confirmed that the best compromise between content and orientational mobility of the push-pull chromophore is obtained in the copolymers containing the 20-40% molar concentration of azo-chromophore.

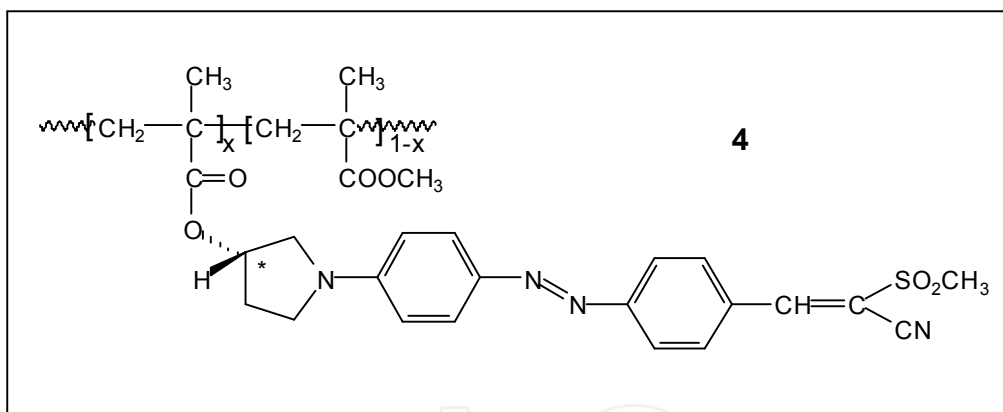


Fig. 11. Chemical structure of corona-poled chiral side-chain azobenzene polymethacrylates

When two interfering coherent laser beams are used as irradiation source on azobenzene polymeric films for a period of time longer than that required for photoinduced orientation, a motion at macroscopic level may be produced with formation of stable surface relief gratings (SRG) spatially modulated of the order of hundreds of nanometers (Fig. 12).

The first reports on this behaviour of azobenzene polymers appeared in 1995 (Rochon et al., 1995; Kim et al., 1995) and the phenomenon was accurately investigated (Viswanathan et al., 1999). These structures behave as holographic diffraction gratings, thus allowing to record polarization holograms in polymeric films (Nikolova et al., 1996 as cited in Natansohn & Rochon, 2002). Accordingly, holographic phase grating can be rapidly produced, erased and switched in polymeric azobenzene liquid crystals (Yamamoto et al., 2001) by irradiation with CP light or heating the material above its glass transition temperature. Interestingly, when the **DR1** polymethacrylate, which is known to not display, under normal conditions,

the presence of mesophases, is submitted, subsequently to the photoinduced grating, to annealing above its glass transition temperature accompanied by irradiation with He-Ne laser light, a “buried density grating” is observed immediately below the film surface (Pietsch & Rochon, 2003). This finding has been interpreted by the authors as the first case of photoinduction of liquid-crystalline properties in a material lacking of thermotropic properties.

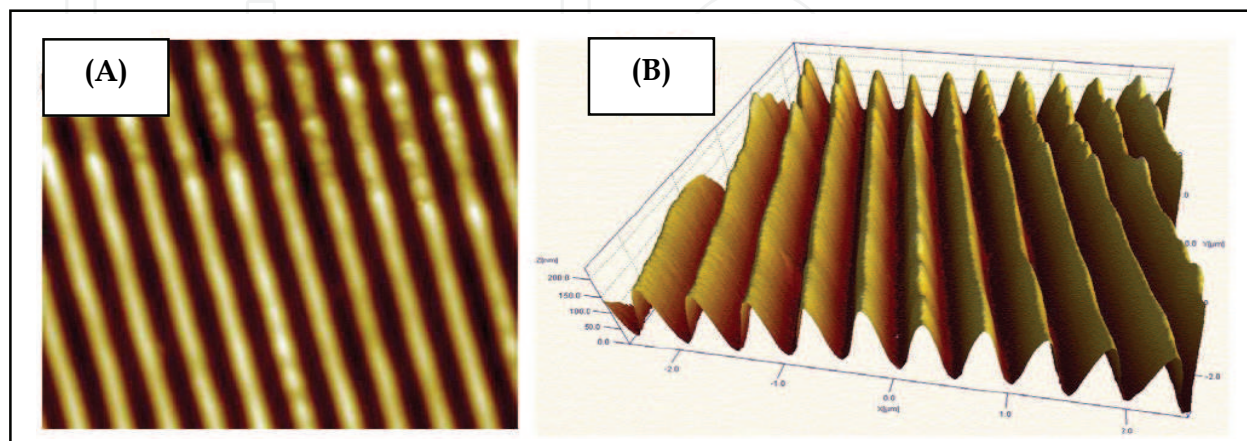


Fig. 12. Bidimensional (A) and tridimensional (B) AFM 5x5 μm surface profile of an optically inscribed grating on a film of azobenzene polymer

Applications of SRG on azobenzene polymers have been investigated for rewritable optical recording (Fukuda, 2004; Ramos et al., 2004; Raschellà et al., 2004) and optical devices (Viswanathan et al. 1999; Ramanujam et al., 1999; Dantsker et al., 2001; Matsui et al., 2002; Ubukata et al., 2005).

3. Functional polymers containing side-chain carbazole moieties

Since the discovery of photoconductivity in poly(N-vinylcarbazole) (Fig. 13) sensitized with suitable electron acceptors (Hoegl, 1965), an intense interest has grown around this topic, which has been subsequently dedicated to the development of polymeric light emitting diodes, organic photorefractive materials and photovoltaic devices (Grazulevicius et al., 2003).

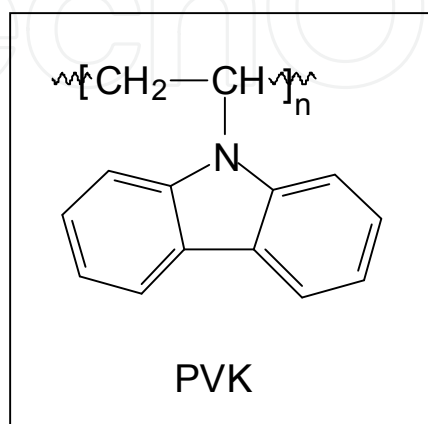


Fig. 13. Chemical structure of poly(N-vinylcarbazole) (PVK)

Photoconduction is promoted by initial light absorption producing charge photogeneration followed by charge transport upon action of an electrical field, in which the carbazole behaves as electron donor moiety (hole or radical cation) moving through a hopping process from one localized site to another in the general direction of the electric field (Naarmann & Strohmriegl, 1992). To improve photoconductivity, **PVK** can be chemically modified in order to increase the absorption in the visible region by linkage to moieties such as phthalimide (Biswas & Das, 1982), Cu phthalocyanine (H.Z. Chen et al., 1993; M. Wang et al., 1995), fullerene C₆₀ (Y. Chen et al., 1996a, 1996b).

However **PVK**, formerly used as charge transporting host in pristine photorefractive polymer composites in combination with a push-pull azoaromatic molecule as EO chromophore, 2,4,7-trinitro-9-fluorenone (**TNF**) as photosensitizer and N-ethylcarbazole added to lower the T_g of the material (Meerholz, 1994), displays a severely restricted conformational mobility of the macromolecules, due to the steric hindrance between neighbouring carbazole groups, originating the presence of undesired excimer-forming sites which give radiative decay as a loss process in charge photogeneration and mobility. Lowering the T_g by addition of a plasticizer or introducing a spacer between the main chain and the chromophore may improve the photorefractive performance, although the relative content of chromophore is diminished. Indeed, poly(2-(N-carbazolyl)ethyl methacrylate) exhibits charge carrier mobility comparable to that of **PVK**, despite the lower chromophore concentration (Keyanpour-Rad et al., 1978) and the photophysical properties of similar carbazolyl polymethacrylates indicate the absence of excimer-forming sites when the carbazole unit is not directly bound to the polymer main chain (Ledwith et al., 1981). Accordingly, the photoconductive properties of poly(N-epoxypropyl-carbazole) (**PEPK**) are comparable or even better than those of **PVK** (Gaidelis et al., 1976).

A significant number of other polymers containing side-chain carbazole moieties are reported and discussed with reference to the influence of the macromolecular rigid main chain and the side-chain mobility on their photoresponsive properties: polystyrenes (Kanbara et al. 2000; C. Chang et al. 2010), poly(*p*-phenylenevinylene) (Vellis et al., 2008; Ravindranath et al., 2007), polyisocyanides (Schwartz et al., 2010) and poly((amino)amide)s (Thomas et al., 2001; Liou et al., 2006), polythiophenes (W. Li et al., 2010) and polyimides (Ghaemy et al., 2009).

In connection with studies concerning the amplification of chirality in polymeric materials, helical polyacetylenes (Fujii et al., 2007; Qu et al., 2007a, 2007b) and vinyl polymers bearing in the side chain the carbazole group functionalized with chiral moieties (Chiellini et al., 1977, 1978, 1980, 1984) have been investigated and characterized in terms of optical activity of the macromolecules originated by ordered chiral arrangements. In this context, a new class of functional polymers possessing an optically active chiral functionality interposed between the polymethacrylic backbone and the carbazole moiety have also been tested for photoconductivity (Fig. 14).

These materials do not require the presence of a dopant in order to exhibit photoconductivity, but poly[(*S*)-**MECP**], bearing the electron donor pyrrolidine ring, favours the formation of a charge transfer complex with carbazole more effectively than poly[(*S*)-**MECSI**], where the electron acceptor succinimide ring is linked to carbazole (Angiolini et al., 2008b).

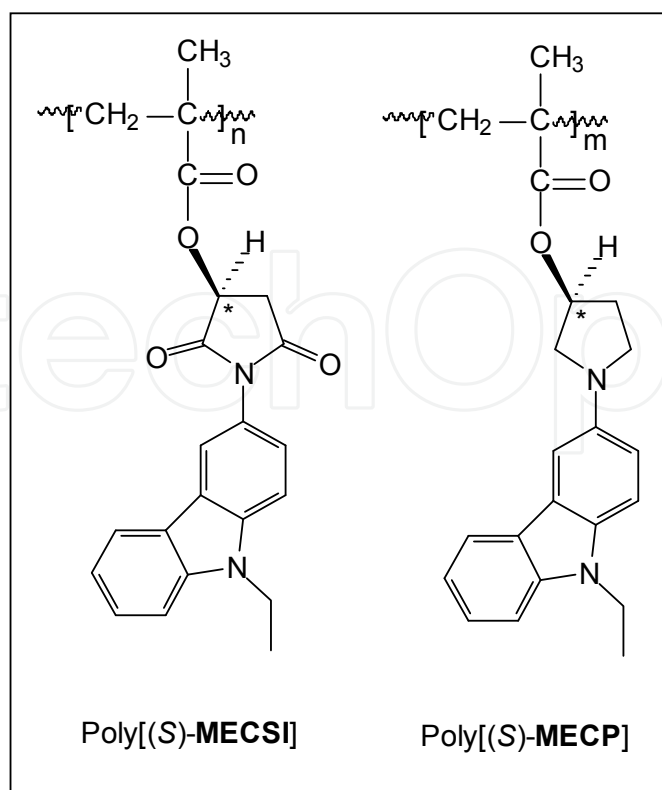


Fig. 14. Chemical structures of poly[(S)-MECSI] and poly[(S)-MECP]

Accordingly, poly[(S)-MCPP] (Fig. 15) exhibits higher photoconductivity than poly[(S)-MCPS], whereas the achiral sample poly[MCPE] displays even higher photoconductivity, attributed to the flexible spacer favouring a more convenient mutual arrangement of the chromophores (Angiolini et al., 2010).

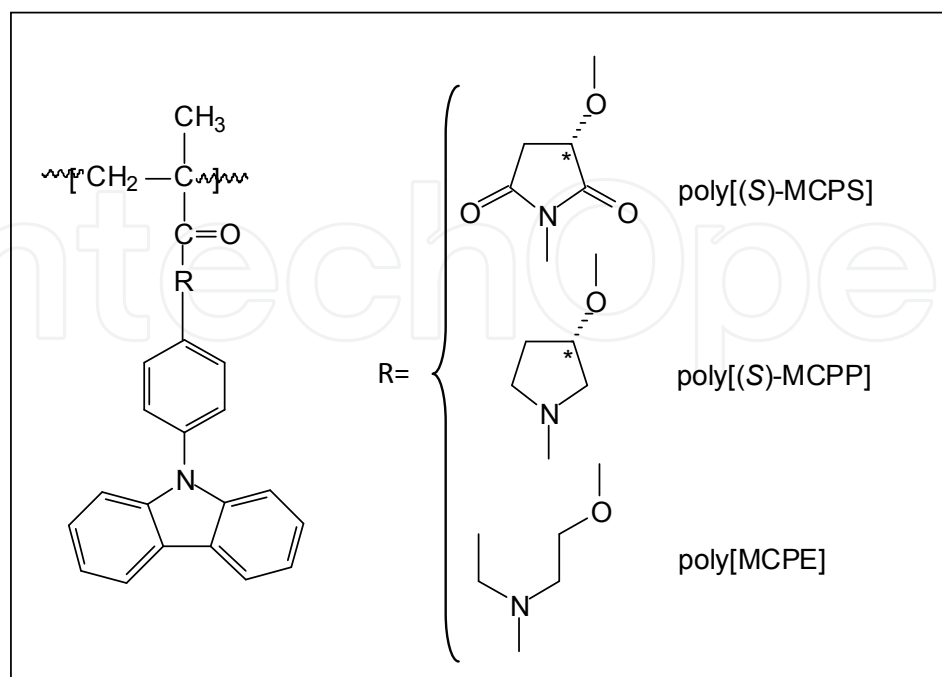


Fig. 15. Chemical structure of poly[(S)-MCPS], poly[(S)-MCPP] and poly[MCPE]

4. Multifunctional polymers containing side-chain azoaromatic and carbazole moieties

When azoaromatic chromophores and carbazole moieties are combined together in a photoresponsive system, further properties may be generated, among which photorefractivity, in addition to those mentioned above. Photorefractive materials are those in which charges photogenerated by a non-uniform light pattern redistribute in space, setting up an internal electric field that, in turn, changes the refractive index: the resulting hologram is a replica of the original light distribution. To be photorefractive, a material must display photoinduced charge generation, charge transporting, charge trapping and an EO response (electric field dependent refractive index, or Pockels effect) (Y. Zhang et al., 1998). The last three conditions may be satisfied by second order NLO chromophores, such as, e.g., push-pull conjugated azoaromatic derivatives, which can be submitted to orientation by suitable light irradiation, while the first condition requires the presence of a photosensitive component capable of charge generation. Photoconduction is also an important requirement in order to observe photorefractivity, a phenomenon widely studied for its applications in different areas, such as image treatment, optical limiting and amplification, dynamic holography.

Consequently, organic materials require the presence of different functionalities in order to achieve photorefractivity, including photosensitivity, photoconductivity and EO response.

In this context, bifunctional photorefractive polymers, possessing both photoconductivity and EO response, have been largely investigated, in particular polymers functionalized with pendant azoaromatic and carbazole moieties respectively located on different repeating units or linked to each other by a covalent bond. An additional functionality, constituted by the presence of asymmetric centers providing chirality to the macromolecule, may also participate to the system.

4.1 Copolymers containing side-chain azoaromatic and carbazole moieties

The presence of both the conductive and the EO moiety linked to the same backbone appears to give better results in comparison to the physical dispersion of chromophoric molecules into a carbazole-functionalized polymeric matrix. For instance, low T_g multifunctional copolymers constituted by polymethacrylates bearing in the side chain the carbazole moiety and a push-pull azoaromatic dye spaced from the main chain by methylene groups have been reported (Maertens et al., 2000) to display photoinduced orientation more than three orders of magnitude higher in the grafted material as compared to the dispersion of the azo dye in PVK and N-ethylcarbazole. However, the T_g of the functional copolymer appears to play a predominant role in the optical properties of the material.

A new class of high- T_g multifunctional photorefractive polymers obtained from a rigid maleimide monomer bearing differently spaced hole transporting carbazole moieties, by alternating copolymerization with methyl vinyl isocyanate, followed by functionalization of the isocyanate groups with different amounts of methanol and hydroxyalkyl NLO chromophores ($D\pi A$), including DR1 dye, (5, Fig. 16), has been reported (Hattemer et al., 2000). The sample with T_g ca. 80°C, containing the DR1 dye, added with TNF and N-ethylcarbazole as plasticizer, investigated by two-beam coupling (2BC) and degenerate four-wave mixing experiments, displayed response times in the order of 100 ms, a value very low for high T_g systems, comparable to those of low- T_g photorefractive materials.

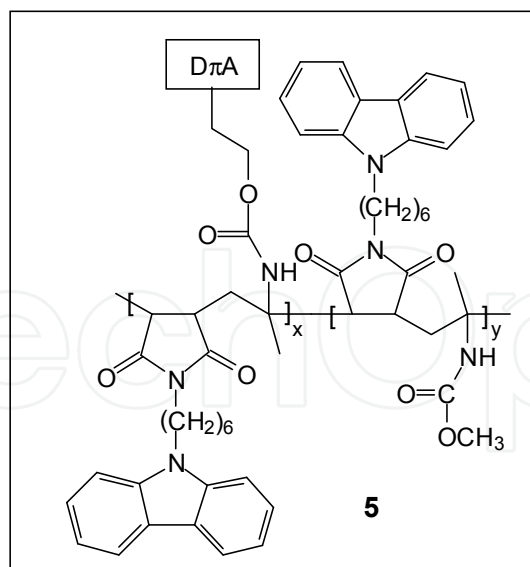


Fig. 16. Chemical structure of multifunctional photorefractive polymers

Copolymers of N-hydroxyethyl carbazole acrylate with azoaromatic push-pull acrylate (**6**, Fig. 17) of various compositions, possessing T_g values much over 200°C , mixed with N-ethylcarbazole as plasticizer and doped with TNF, have been prepared and investigated for EO properties and photorefractivity by 2BC experiments (Y. Chen et al., 2001).

Interesting alternating copolymers obtained by radical copolymerization between N-vinyl carbazole and azoaromatic acrylate having elevated T_g values have also been synthesized and characterized (Altomare et al., 2004).

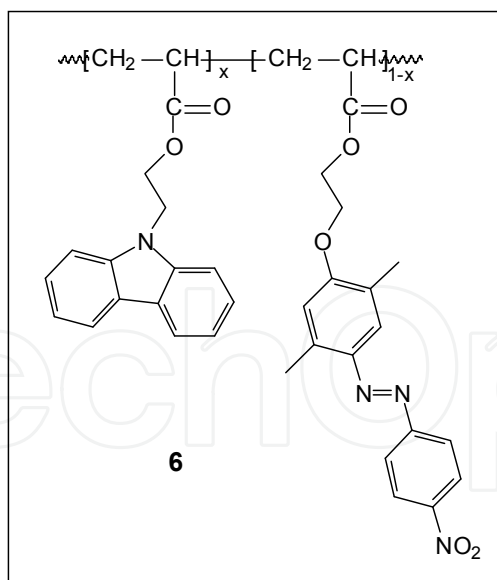


Fig. 17. Chemical structure of copolymers of N-hydroxyethyl carbazole acrylate with azoaromatic push-pull acrylate

A further functionality, chirality, is present in methacrylic copolymers bearing a side-chain chiral rigid group with one prevailing absolute configuration interposed between the backbone and the photoactive moiety (carbazole and azoaromatic), possessing T_g values above 200°C (Angiolini et al., 2007b; H. Li et al., 2009) (Fig. 18).

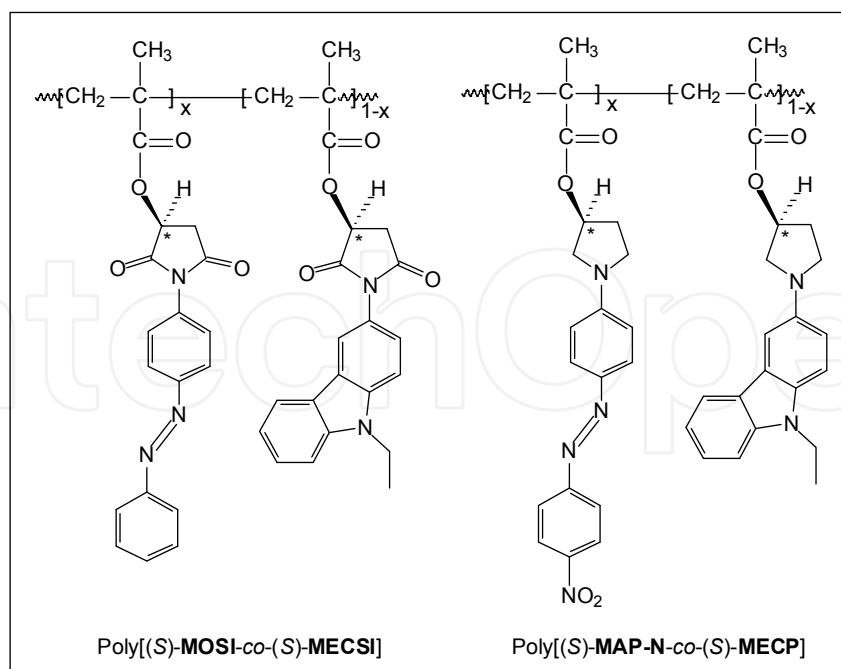


Fig. 18. Chemical structures of copolymers poly[(S)-**MOSI-co-(S)-MECSI**] and poly[(S)-**MAP-N-co-(S)-MECP**]

The additional functionality allows to obtain informations by Circular Dichroism (CD) spectroscopy about the presence of ordered helix-type structures of the macromolecules and of cooperative interactions between chromophores (Angiolini et al., 2009b), opening the possibility to use these polymeric derivatives as chiroptical switches, too (Angiolini et al., 2002, 2003a, 2003b). Differently from literature reports concerning amorphous systems containing azo-compounds, where electrically prepoled materials or an operating temperature close to T_g was required, the photorefractivity of these materials was achieved at room temperature without prepoling. This behaviour is attributed to a chromophore reorientation process induced by the electric field applied during the measurements, which is assisted by photoisomerization of the azo-chromophore.

The first photorefractive sol-gel material, constituted by the NLO chromophore **DR1** and carbazole grafted to the polysiloxane backbone in variable ratios, has also been reported (Chaput et al., 1996). In the presence of a small amount of **TNF**, the material displays photorefractivity, upon 2BC measurements, and NLO properties, as deduced from SHG measurements.

Macromolecular architectures other than linear polymers such as hyperbranched polyisophthalate containing pendant carbazoly and azobenzene groups as terminal moieties, having very low T_g (21°C), in the presence of C₆₀ as photosensitizer, displayed photorefractive and electrooptical properties, with fast response time (Kou & Shi, 2004).

4.2 Polymers containing side-chain carbazole moieties covalently linked to azoaromatic groups

The required components for photorefractivity (EO chromophore, charge traps and possibility of photopoling) may also be satisfied when both azo-chromophore and carbazole moiety are directly bonded together into a single multifunctional (monolithic) unit located in the polymeric side chain (Fig. 19).

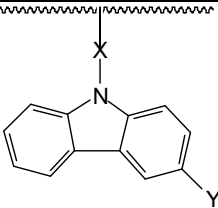
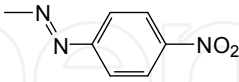
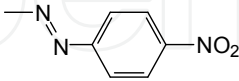
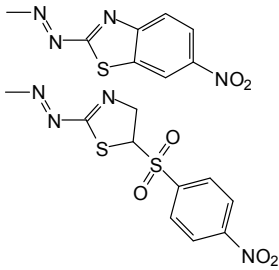
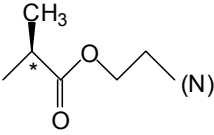
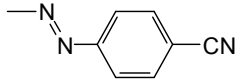
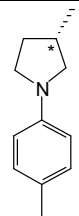
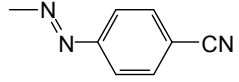
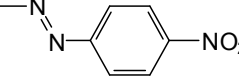
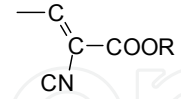
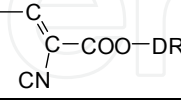
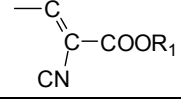
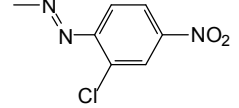
			
Derivative	Main chain	X	Y
C1	polymethacrylate	$-(CH_2)_n-$	
C2	polyacrylate	$-(CH_2)_6-$	
C3	polymethacrylate	$-(CH_2)_2-$	
C4	polymethacrylate		
C5	polymethacrylate		
C6	polyphosphazene	$-(CH_2)_3-$	
C7	polymethylsiloxane	$-(CH_2)_3-$	
C8	polyvinyl	$-(CH_2)_0-$	
C9	polyvinyl	$-(CH_2)_0-$	
C10	epoxy resin	$-\text{CH}_2-$	

Fig. 19. Chemical structure of side-chain carbazole-azoaromatic polymers

The first report concerning this class of materials appeared in 1996 (Ho et al., 1996), dedicated to the synthesis and optical properties of the methacrylic polymer obtained by

polymerization of N-hydroxyethyl carbazole methacrylate bearing the p-nitro phenylazo moiety linked to the position 3 of carbazole ring (**C1**, $n=2$, Fig.19). This material proved to be suitable to produce optically induced birefringence, surface gratings and photorefractivity. Subsequently, polymethacrylates prepared similarly with various spacer length ($n = 3-6, 8-10$) and T_g values ranging gradually from 127 to 65°C, were investigated (Barrett et al., 1998) (**C1**, $n=3-6, 8-10$, Fig. 19) confirming the previous findings and that the orientational order photoinduced in the material is higher with the derivatives possessing lower spacer length. Relevant thermal stability of the photoinduced surface gratings and high stability of the birefringence was also observed in polyimides bearing the carbazole group in the main chain linked to pendant azo chromophore (J.P. Chen et al., 1999).

An investigation on a series of copolymeric polyacrylates constituted by butyl acrylate and various monolithic chromophores, including azocarbazole (**C2**, Fig. 19) with molar composition photorefractive monomer/butyl acrylate 1:2.2, suggested that the photorefractivity was strongly dependent on the NLO property of the chromophore rather than photoconductivity, and, additionally, that the charge transporting species in these materials could be altered (hole or electron) according to the chromophore structure (Hwang et al., 2003).

Monolithic photorefractive polymethacrylates bearing side-chain azo-carbazole (**C3**, Fig. 19) were shown to display a much more significant photoconductivity with respect to the related copolymers with butyl methacrylate in the ratio 1:1 and a considerable increase of photoconductivity (one order of magnitude) in the presence of **TNF** as photosensitizer, due to efficient charge transfer between carbazole and **TNF** (Diduch et al., 2003).

An optically active methacrylic side-chain azocarbazole homopolymer containing a chiral moiety interposed between the main chain and the azocarbazole moiety, characterized by high T_g value (147°C) (**C4**, Fig. 19) displayed photorefractive and photoconductive properties at room temperature without pre-poling, with high optical gain, as noticed for the above mentioned copolymeric samples (poly[(*S*)-**MAP-N-co-(S)**-**MECP**]) (Fig. 18), which were similarly interpreted on the basis of a field-induced chromophore reorientation mechanism (Angiolini et al., 2007c; H. Li et al., 2009). In addition, **C4** was also apt to produce photoinduced SRG as well as birefringence, thus demonstrating several features typical of a multifunctional photoresponsive material. Besides the assessment of chirooptical properties investigated by CD, optically induced linear dichroism and birefringence, as well as SRG, were also produced without pre-poling on thin films of side-chain azocarbazole polymers containing the chiral pyrrolidine moiety (**C5**, Fig. 19), although the T_g values of these materials were very high (between 160 and 200°C), demonstrating the possibility to obtain temporally stable photoinduced anisotropy, particularly with the more conformationally rigid system containing the pyrrolidine ring (Angiolini et al., 2009a).

An alternative synthetic access to side-chain azo-carbazole moieties involves the functionalization of side-chain carbazole groups by coupling with a p-nitrophenyl diazonium salt to give the corresponding azo-derivative located at the position 3 of carbazole. In this case, being the functionalization reaction incomplete, a copolymeric product is obtained containing actually a molar amount of 20% of azocarbazole moiety (**C1**, $n=3$, Fig. 19) (Y. Chen et al. 2000). To achieve filmability, it is needed to add N-ethyl carbazole as a plasticizer, in addition to a small amount of **TNF** as a photosensitizer. However, both photorefractivity and EO response are observed in the material. Improved functionalization extent up to 67% was instead obtained by azo-coupling on carbazole

polymethacrylates with shorter spacer length (**C1**, $n=2$, Fig. 19), thus allowing the availability of polymeric derivatives with higher molecular mass with respect to those obtained by direct polymerization of the monolithic functional monomer (Shi et al., 2004a). The material with 32% of functionalization and longer spacer length (**C1**, $n=10$, Fig. 19) (Shi et al., 2004b) displayed appreciable optical gain coefficient, comparable to that obtained previously by Barrett (Barret et al., 1998) for the same material with homopolymeric structure, but lower molecular mass.

The post-polymerization azo-coupling procedure has also been applied to polyphosphazenes bearing side-chain carbazole moieties (L. Zhang et al. 2006) with formation of a copolymeric product possessing 29% of functionalization degree of the two carbazole moieties present in each repeating unit (**C6**, Fig. 19). The material displays a low T_g value (50°C) and photorefractivity without any added plasticizer or sensitizer. Polymethylsiloxane bearing side-chain carbazole groups was also submitted to functionalization with EO chromophores (Hua et al., 2007). In this case, a different approach to the synthesis of multifunctional polymeric derivatives has been followed, the EO chromophore resulting electronically isolated from the side-chain carbazole moiety. Thus, the carbazole was firstly formylated at the position 3, then treated with the cyanoacetyl derivative of push-pull azobenzenes (**C7**, Fig. 19) to afford up to a 32% molar functionalization with the EO chromophore. Although possessing a rather low molecular mass, these materials displayed, upon doping with TNF, SHG comparable to those of polymers containing **DR1** chromophores.

Similarly, partially formylated (50%) **PVK** was functionalized with the cyanoacetyl derivative of **DR1** (**C8**, Fig. 19) (Zhuang et al., 2010) or of push-pull azobenzene bearing additional N-alkyl carbazole linked to the aromatic ring (**C9**, Fig. 19) (Z. Li et al., 2010). The former derivative displayed capability to produce inter- or intra-chain donor (carbazole)-acceptor (**DR1**) nanoaggregated assemblies with good memory performance, the latter displayed relatively large SHG in the NLO field.

The advantages of azo-carbazole moieties chemically bound to polymer matrix for NLO applications by Maker-fringe technique were also demonstrated with regard to the third harmonic generation (THG) by bisphenolic epoxy resins containing 3-(2'-chloro-4'-nitrophenylazo-)N-(2,3-epoxypropyl)-carbazole (**C10**, Fig. 19) (Niziol et al., 2009).

5. Conclusion

In the recent years photoresponsive polymeric materials based on azoaromatic and carbazole moieties have generated a quite remarkable research interest, which has led to envisage a wide range of potential applications in advanced technologies achievable by using the same multifunctional material. As most of the properties are originated by the arrangement assumed by the chromophores at the "domain" level, roughly at the nanoscale level, through cooperative motions, the presence in the material of sufficiently organized macromolecular structures plays a major role. To this regard, the control of architecture, molecular mass and polydispersity of the macromolecular material, in addition to the presence of suitable functionalities, is predicted to assume increasing relevance. In particular, several synthetic procedures, allowing a "living"/controlled free-radical polymerization (LFRP), such as atom transfer radical polymerization (ATRP), reversible addition-fragmentation chain transfer (RAFT) polymerization and nitroxide-mediated free-

radical polymerization (NMP), could be conveniently adopted in order to obtain derivatives (block copolymers, multiarms architectures of appropriate size etc.) conveniently tailored to the use. In this context, the presence of helical structures of one prevailing sense of the macromolecules could play an important role in photoinduced phase transitions, amplification phenomena and photoswitched chirality.

To positively conclude the present note, photoresponsive polymeric materials are finding new opportunities in applications that in the past seemed only idealistic. This has arisen along with recent developments in nanosciences and nanotechnologies, opening new ways to make engineered polymers as novel macromolecular structures. Improvements in the design of multifunctional photoresponsive systems in which the relevant functionalities (photochromic and photoconductive) can be located within specialized nanoenvironments are presently worth of investigation.

Above all, collaborative efforts among different scientific disciplines will be the major factor that will develop the full potential of any photoresponsive system.

6. Acknowledgment

The financial support by MIUR (PRIN 2007) and INSTM Consortium is gratefully acknowledged.

7. References

- Altomare, A., Ciardelli, F., Mellini, L., & Solaro, R. (2004). Photoactive Azobenzene Polymers Containing Carbazole Chromophores (pages 1611–1619). *Macromol. Chem. Phys.*, Vol.205, No. 12, (August 2004), pp.1611-1619, ISSN 1521-3935
- Angiolini, L., Bozio, R., Giorgini, L., Pedron, D., Turco, G., & Daurù, A. (2002). Photomodulation of the chiroptical properties of new chiral methacrylic polymers with side chain azobenzene moieties. *Chem. Europ. J.*, Vol.8, No.18, (September 2002), pp. 4241-4247, ISSN 1521-3765
- Angiolini, L., Giorgini, L., Bozio, R., & Pedron, D. (2003a). Reversible chirality inversion of photochromic methacrylic polymers upon irradiation with one-handed circularly polarized light. *Synth. Met.*, Vol.138, No.1-2, (June 2003), pp. 375-379, ISSN 0379-6779
- Angiolini, L., Benelli, T., Bozio, R., Daurù, A., Giorgini, L., & Pedron, D. (2003b). Photoinduced chiroptical bistability in new chiral methacrylic azobenzene-containing polymers. *Synth. Met.*, Vol.139, No.3, (October 2003), pp. 743-746, ISSN 0379-6779
- Angiolini, L., Benelli, T., Giorgini, L., Salatelli, E., Bozio, R., Daurù, A., & Pedron, D. (2006). Improvement of photoinduced birefringence properties of optically active methacrylic polymers through copolymerization of monomers bearing azoaromatic moieties. *Macromolecules*, Vol.39, No.2, (January 2006), pp. 489-497, ISSN 0024-9929
- Angiolini, L., Benelli, T., Giorgini, L., Mauriello, F., Salatelli, E., Bozio, R., Daurù, A., & Pedron, D. (2007a). Synthesis, chiroptical properties and photoinduced birefringence of optically active methacrylic copolymers bearing side-chain bisazoaromatic moieties. *Europ. Polym. J.* Vol.43, No.8, (August 2007), pp. 3550–3561, ISSN 0014-3057

- Angiolini, L., Benelli, T., Giorgini, L., Mauriello, F., & Salatelli E. (2007b). Synthesis and chiroptical properties of copolymers containing in side-chain optically active carbazole and azochromophores. *Proc. of SPIE*, Vol.6653, (September 2007), pp. 66531C-1-6653C-8, ISSN 1996-756X
- Angiolini, L., Bozio, R., Dainese, T., Giorgini, L., Golemme, A., Mauriello, F., Pedron, D., & Termine, R. (2007c). Photoresponsive polymers containing side-chain chiral azocarbazole chromophores as multifunctional materials. *Proc. of SPIE*, Vol. 6653, (September 2007), pp. 665305-1, ISSN 1996-756X
- Angiolini, L., Benelli, T., Bozio, R., Cozzuol, M., Giorgini, L., Pedron, D., & Salatelli, E. (2008a). Second order nonlinear optical properties of multifunctional chiral azobenzene polymers. *e-Polymers*, No.13, ISSN 1618-7229
- Angiolini, L., Benelli, T., Giorgini, L., Golemme, A., Mauriello, F., Salatelli, E., & Termine, R. (2008b). Methacrylic Polymers Containing Optically Active Side-Chain Carbazole: Synthesis, Characterization and Photoconductive Properties *Macromol. Chem. Phys.*, Vol.209, No.9, (May 2008), pp. 944-956, ISSN 1521-3935
- Angiolini, L., Giorgini, L., Mauriello, F., & Rochon, P. (2009a). Synthesis and photoresponsive properties of optically active methacrylic polymers bearing side-chain azocarbazole moieties. *Macromol. Chem. Phys.*, Vol.210, No.1, (January 2009), pp. 77-89, ISSN 1521-3935
- Angiolini, L., Benelli, T., Giorgini, L., Mauriello, F., & Salatelli, E. (2009b). Relevant chiroptical and thermal properties in optically active methacrylic copolymers containing carbazole and azoaromatic chromophores in the side-chain. *React. Funct. Polym.*, Vol.69, No.12, (December 2009), pp. 898-904, ISSN 1381-5148
- Angiolini, L., Giorgini, L., Li, H., Golemme, A., Mauriello, F., & Termine, R. (2010). Synthesis, characterization and photoconductive properties of optically active methacrylic polymers bearing side-chain 9-phenylcarbazole moieties *Polymer*, Vol.51, No.2, (January 2010), pp. 368-377, ISSN 0032-3861
- Barrett, C., Choudhury, B., Natansohn, A., & Rochon, P. (1998). Azocarbazole polymethacrylates as single-component electrooptic materials. *Macromolecules*, Vol.31, No.15, (July 1998), pp. 4845-4851, 1520-5835
- Beljonne, D., Shuai, Z., Brédas, J.L., Kauranen, M., Verbiest, T., & Persoons A. (1998). Electro-optic response of chiral helicenes in isotropic media. *J. Chem. Phys.*, Vol.108, No.4, (January 1998), pp. 1301-1304, ISSN 1089-7690
- Berneth, H., Bieringer, T., Hagen, R., & Kostromine, S. (Bayer AG, Germany) (2003). United States Patent no. 2003113664 A1. Re-inscribable optical recording materials with good solubility, 2003
- Biswas, M., & Das, S.K. (1982). Chemical modification of poly(N-vinylcarbazole). II. Some properties of poly(N-vinylcarbazole-3,6-diphthalimide). *J. Polym. Sci., Polym. Lett. Ed.*, Vol.20, No.6, (June 1982), pp.333-339, ISSN 1543-0472
- Blanchard, P.M., & Mitchell, G.R. (1993a). Localized room temperature photo-induced poling of azo-dye-doped polymer films for second-order nonlinear optical phenomena. *J. Phys. D: Appl. Phys.*, Vol.26, No.3, (March 1993), pp. 500-503, ISSN 1361-6463 6463
- Blanchard, P.M., & Mitchell, G.R. (1993b). A comparison of photoinduced poling and thermal poling of azo-dye-doped polymer films for second order nonlinear optical

- applications. *Appl. Phys. Lett.*, Vol.63, No.15, (October 1993), pp. 2038-2040, ISSN 1077-3118 6463
- Chalupczak, W., Fiorini, C., Charra, F., Nunzi, J.M., & Raimond, P. (1996). Efficient all-optical poling of an azo-dye copolymer using a low power laser. *Opt. Commun.*, Vol.126, No.1-3, (May 1996), pp. 103-107, ISSN 1873-0310
- Chang, C., Zhu, J., Zhang, Z., Zhou, N., Cheng, Z., & Zhu, X. (2010). Synthesizing and characterization of comb-shaped carbazole containing copolymer via combination of ring opening polymerization and nitroxide-mediated polymerization. *Polymer*, Vol.51, No.9, (April 2010), pp. 1947-1953, ISSN 0032-3861
- Chaput, F., Riehl, D., Boilot, J.P., Cargnelli, K., Canva, M., Le'vy, Y., & Brun, A. (1996). New nonlinear sol-gel films exhibiting photorefractivity. *Chem. Mater.*, Vol.8, No.2, (February 1996), pp. 312-314, ISSN 1520-5002.
- Charra, F., Kajzar, F., Nunzi, J.M., Raimond, P., & Idiart, E. (1993). Light-induced second-harmonic generation in azo-dye polymers. *Opt. Lett.*, Vol.18, No.12, (June 1993), pp. 941- 943, ISSN 1539-4794
- Chen, H.Z., Wang, M., Feng, L.X., & Yang, S. (1993). Synthesis and photoconductivity study of phthalocyanine polymers. II. PVK-co-CuPc (COOH)₃. *J. Polym. Sci., Part A: Polym. Chem.*, Vol.31, No.5, (April 1993), pp. 1165-1170, ISSN 1099-0518
- Chen, J.P., Labarthe, F.L., Natansohn, A., & Rochon, P. (1999). Highly stable optically induced birefringence and holographic surface gratings on a new azocarbazole-based polyimide. *Macromolecules*, Vol.32, No.25, (December 1999), pp. 8572-8579, ISSN 1520-5835
- Chen, Y., Cai, R.F., Huang, Z.E., Bai, X., Yu, B.C., Jin, W., Pan, D.C., & Wang, S. (1996a). Researches on the photoconductivity and UV-visible absorption spectra of the first C₆₀-chemically modified poly(N-vinylcarbazole). *Polym. Bull.*, Vol.36, No.2, (February 1996), pp. 203-208, ISSN 1436-2449
- Chen, Y., Huang, Z.E., Cai, R., Fan, D., Hou, X., Yan, X., Chen, S., Jin, W., Pan, D., & Wang, S. (1996b). Photoconductivity and paramagnetism of fullerene chemically modified polymers. *J. Appl. Polym. Sci.*, Vol.61, No.12, (September 1996), pp. 2185-2190, ISSN 1097-4628
- Chen, Y., He, Y., Chen, H., Wang, F., Chen, Z., & Gong, Q. (2000). Photorefractive effect in a new composite based on bifunctional host polymer. *J. Appl. Polym. Sci.*, Vol.77, No.1, (July 2000), pp. 189-194, ISSN 1097-4628
- Chen, Y., He, Y., Wang, F., Chen, H., & Gong, Q. (2001). Synthesis and characterization of bifunctional photorefractive polymers. *Polymer*, Vol.42, No.3, (February 2001), pp. 1101-1107, ISSN 0032-3861
- Chiellini, E., Solaro, R., & Ledwith, A. (1977). Optically active vinyl polymers containing fluorescent groups. 2. Synthesis of optically active vinylcarbazole derivatives. *Makromol. Chem.*, Vol.178, pp. 701-713, ISSN 0025-116X
- Chiellini, E., Solaro, R., & Ledwith, A. (1978). Optically active vinyl polymers containing fluorescent groups. 3. Synthesis and characterization of optically active polymers containing carbazolyl groups. *Makromol. Chem.*, Vol.179, pp. 1929-1937, ISSN 0025-116X
- Chiellini, E., Galli, G., Solaro, R., & Ledwith, A. (1980). Optically active vinyl polymers containing fluorescent groups. 8. Synthesis and properties of copolymers of N-

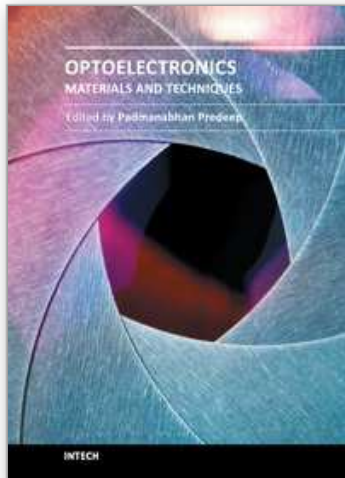
- vinylcarbazole and (-)-menthyl acrylate and (-)-menthyl methacrylate. *Macromolecules*, Vol.13, No.6, (November 1980), pp. 1654-1660, ISSN 1520-5835
- Chiellini, E., Galli, G., Solaro, R., & Ledwith, A. (1984). Optically active synthetic polymers containing pendant carbazolyl groups. *Adv. Polym. Sci.*, Vol.62, pp. 143-169, ISSN 0065-3195
- Churikov, V.M., Hung, M.F., Hsu, C.C., Shiau, C.W., & Luh, T.Y. (2000). Encoding of macroscopic second-order non-linearity via all-optical polar alignment in substituted norbornene polymer thin films. *Chem. Phys. Lett.*, Vol.332, No.1-2, (December 2000), pp. 19-25, ISSN 1873-4448
- Dantsker, D., Kumar, J., Tripathy, S.K. (2001). Optical alignment of liquid crystals. *J. Appl. Phys.*, Vol.89, No.8, (April 2001), pp. 4318-4325, ISSN 1089-7550
- Diduch, K., Wubbenhorst, M., & Kucharski, S. (2003). Photocurrent generation of bi-functional carbazole containing polymers. *Synth. Met.*, Vol.139, No.2, (September 2003), pp. 515-520, ISSN 1879-3290
- Fiorini, C., Nunzi, J.M., Charra, F., Kajzar, F., Lequan, M., Lequan, R.M., & Chane-Ching, K. (1997). Light-induced orientation of a low absorbing phosphine oxide azo-dye/PMMA copolymer: towards a trade-off between transparency and photoinduced non-linearity. *Chem. Phys. Lett.*, Vol.271, No.4-6, (June 1997), pp. 335-340, ISSN 1873-4448
- Fukuda T. (2004). Re-writable high-density optical recording on azobenzene thin film. *Optics in Information System*, Vol.15, No.1, (February 2004)
- Fujii, T., Shiotsuki, M., Inai, Y., Sanda, F., & Masuda, T. (2007). Synthesis of helical poly(N-propargylamides) carrying azobenzene moieties in side chains. Reversible arrangement-disarrangement of helical side chain arrays upon photoirradiation keeping helical main chain intact. *Macromolecules*, Vol.40, No.20, (October 2007), pp. 7079-7088, ISSN 1520-5835
- Gaidelis, V., Krisciunas, V., & Montrimas, E. (1976). Optical and photoelectric properties of thin layers of poly-n-epoxypropylcarbazole. *Thin Solid Films*, Vol.38, No.1, (October 1976), pp. 9-14, ISSN 1879-2731
- Ghaemy, M., Alizadeh, R., & Behmadi, H. (2009). Synthesis of soluble and thermally stable polyimide from new diamine bearing N-[4-(9H-carbazol-9-yl)phenyl] formamide pendent group. *European Polymer Journal*, Vol.45, No.11, (November 2009), pp. 3108-3115, ISSN 0014-3057
- Grazulevicius J. V., Strohriegel P., Pielichowski J., Pielichowski K. (2003). Carbazole-containing polymers: synthesis, properties and applications. *Progress Polym. Sci.*, Vol.28, No.9, (September 2003), pp. 1297-1353, ISSN 1873-1619
- Hagen, R., Bieringer, T., Kostromine, S., & Berneth, H. (Bayer AG, Germany) (2003). United States Patent no. 2003049549 A1. Optical storage method for rewritable digital data carriers, 2003
- Hattemer, E., Zentel, R., Mecher, E., & Meerholz K. (2000). Synthesis and Characterization of Novel Multifunctional High- T_g Photorefractive Materials Obtained via Reactive Precursor Polymers. *Macromolecules*, Vol.33, No.6, (March 2000), pp. 1972-1977, ISSN 1520-5835
- Hill, R.A., Dreher, S., Knoesen, A., & Yankelevich, D.R. (1995). Reversible optical storage utilizing pulsed, photoinduced, electric - field - assisted reorientation of

- azobenzenes. *Appl. Phys. Lett.*, Vol.66, No.17, (April 1995), pp. 2156-2158, ISSN 1077-3118
- Ho, M.S., Natansohn, A., & Rochon, P. (1995). Azo polymers for reversible optical storage. 7. The effect of the size of the photochromic groups. *Macromolecules*, Vol.28, No.18, (August 1995), pp. 6124-6127, ISSN 0024-99297
- Ho, M.S., Barrett, C., Paterson, J., Esteghamatian, M., Natansohn, A., & Rochon P. (1996). Synthesis and optical properties of poly{(4-nitrophenyl)-[3-[N-[2-(methacryloyloxy)ethyl]-carbazolyl]]diazene}. *Macromolecules*, Vol.29, No.13, (June 1996), pp. 4613-4618, ISSN 1520-5835
- Hoegl, H. (1965). On photoelectric effects in polymers and their sensitization by dopants. *J. Phys. Chem.*, Vol.69, No.3, (March 1965), pp. 755-766, ISSN 1541-5740
- Hua, J., Li, Z., Qin, J., Li, S., Ye, C., & Lu, Z. (2007). Synthesis and characterization, second-order nonlinear optical and photorefractive properties of new multifunctional polysiloxane with broad optical transparent pentafluorophenyl azo chromophore. *React. Funct. Polym.*, Vol.67, No.1, (January 2007), pp. 25-32, ISSN 1873-166X
- Hwang, J., Sohn, J., & Park, S.Y. (2003). Synthesis and structural effect of multifunctional photorefractive polymers containing monolithic chromophores. *Macromolecules*, Vol.36, No.21, (October 2003), pp. 7970-7976, ISSN 1520-5835
- Ivanov, M., Naydenova, I., Todorov, T., Nikolova, L., Petrova, T., Tomova, N., & Dragostinova, V. (2000). Light-induced optical activity in optically ordered amorphous side-chain azobenzene containing polymer. *J. Mod. Opt.*, Vol.47, No.5, (April 2000), pp. 861-867, ISSN 1362-3044
- Jin, M., Yang, Q.X., Lu, R., Xu, T.H., & Zhao, Y.Y. (2004). Syntheses of bisazo-containing polymethacrylates using atom transfer radical polymerization and the photoalignment behavior. *Journ. Polym. Sci., Part A: Polym. Chem.*, Vol.42, No.17, (September 2004), pp. 4237-4247, ISSN 1099-0518
- Kanbara, T., Yokokawa, Y., & Hasegawa, K. (2000). *J. Polym. Sci. Part A: Polym. Chem.*, Vol.38, No.1, (January 2000), pp. 28-34, ISSN 1099-0518.
- Keyanpour-Rad, M., Ledwith, A., Hallam, A., North, A. M., Breton, M., Hoyle, C., & Guillet J.E. (1978). Some photophysical properties of five new carbazole-containing methacrylate polymers. *Macromolecules*, Vol.11, No.6, (November 1978), pp. 1114-1118, ISSN 1520-5835
- Kim, D.Y., Tripathy, S.K., Li, L., & Kumar, J. (1995). Laser - induced holographic surface relief gratings on nonlinear optical polymer films. *Appl. Phys. Lett.*, Vol.66, No.10, (March 1995), pp. 1166-1168, ISSN 1077-3118
- Kou, H., & Shi W. (2004). Photorefractivity of hyperbranched polyisophthalate endcapped with pendant carbazolyl and azobenzene groups. *Eur. Polym. J.*, Vol.40, No.7, (July 2004), pp. 1337-1342, ISSN 0014-3057
- Ledwith, A., Rawley, N.J., & Walker, S.M. (1981). Fluorescence emission from poly[2-(9-ethyl)carbazolyl-methylmethacrylate]. *Polymer*, Vol.22, No.4, (April 1981), pp. 435-436, ISSN 0032-3861
- Li, H., Termine, R., Angiolini, L., Giorgini, L., Mauriello, F., & Golemme, A. (2009). High Tg, nonpoled photorefractive polymers. *Chem. Mat.*, Vol.21, No.12, (June 2009), pp. 2403-2409, ISSN 1520-5002

- Li, W., Han, Y., Chen, Y., Li, C., Li, B., & Bo, Z. (2010). Polythiophenes with carbazole side chains: design, synthesis and their application in organic solar cells. *Macromol. Chem. Phys.*, Vol.211, No.8, (April 2010), pp. 948-955, ISSN 1521-3935
- Li, Z., Wang, L., Xiong, B., Ye, C., Qin, J., & Li, Z. (2010). Novel, side-on, PVK-based nonlinear optical polymers: Synthesis and NLO properties. *Dyes and Pigments*, Vol.84, No.1, (January 2010), pp. 134-139, ISSN 1873-3743
- Liou, G.S., Hsiao, S.H., Huang, N.K., & Yang, Y.L. (2006). *Macromolecules*, Vol.39, No.16, (August 2006), pp. 5337-5346, ISSN 0024-9297
- Loucif-Saïbi, R., Nakatani, K., Delaire, J.A., Dumont, M., & Sekkat, Z. (1993). Photoisomerization and second harmonic generation in disperse red one-doped and -functionalized poly(methyl methacrylate) films. *Chem. Mater.*, Vol.5, No.2, (February 1993), pp. 229-236, ISSN 1520-5002 6463
- Maertens, C., Dubois, P., Jérôme, R., Blanche, P.-A., & Lemaire Ph.C. (2000). Synthesis and polarized light-induced birefringence of new polymethacrylates containing carbazolyl and azobenzene pendant groups. *J. Polym. Sci.: Part B: Polym. Phys.*, Vol.38, No.1, (January 2000), pp. 205-213, ISSN 1099-0488
- Matsui, T., Ozaki, M., Yoshino, K., & Kajzar, F. (2002). Fabrication of flexible distributed feedback laser using photoinduced SRG on azo-polymer film as a template. *Jpn. J. Appl. Phys.*, Vol.41, part 2, No. 12A, (2002), pp. L1386-L1388, ISSN 0021-4922
- Meerholz, K., Volodin, B.L., Kippelen, B., & Peyghambarian, N. (1994). A photorefractive polymer with high optical gain and diffraction efficiency near 100%. *Nature*, Vol.371, (October 1994), pp. 497-500, ISSN 1476-4687
- Meng, X., Natansohn, A., & Rochon, P. (1997). Azo polymers for reversible optical storage: 13. Photoorientation of rigid side groups containing two azo bonds. *Polymer*, Vol.38, No.11, (May 1997), pp. 2677-2682, ISSN 0032-3861
- Naarmann, H., & Strohriegl, P. (1992). *Handbook of Polymer Synthesis, Part B* (Kricheldorf H. R., ed.), New York: Marcel Dekker; p. 1353, ISBN 0824754735
- Natansohn, A., Rochon, P., Gosselin, J., & Xie, S. (1992). Azo polymers for reversible optical storage. 1. Poly[4'-[[2-(acryloyloxy)ethyl]ethylamino]-4-nitroazobenzene]. *Macromolecules*, Vol.25, No.8, (April 1992), pp. 2268-2273, ISSN 0024-9297
- Natansohn, A., & Rochon, P. (2002). Photoinduced Motions in Azo-Containing Polymers. *Chem. Rev.*, Vol.102, No.11, (October 2002), pp. 4139-4175, ISSN 0009-2665
- Naydenova, I., Nikolova, L., Ramanujam, P.S., & Hvilsted, S. (1999). Light-induced circular birefringence in cyanoazobenzene side-chain liquid-crystalline polyester films. *J. Opt. A: Pure Appl. Opt.*, Vol.1, No.4, (July 1999), pp. 438-441, ISSN 1741-3567
- Nikolova L., Todorov T., Ivanov M., Andruzzi F., Hvilsted S., Ramanujam P. (1996). Polarization holographic gratings in side-chain azobenzene polyesters with linear and circular photoanisotropy. *Appl. Opt.* 1996, Vol.35, No.20, (July 1996), pp. 3835-3840, ISSN 1539-4522
- Nikolova, L., Nedelchev, L., Todorov, T., Petrova, Tz., Tomova, N., Dragostinova, V., Ramanujam, P.S., & Hvilsted, S. (2000). Self-induced light polarization rotation in azobenzene-containing polymers. *Appl. Phys. Lett.*, Vol.77, No.5, (July 2000), pp. 657-659, ISSN 1077-3118 6463
- Nizioł, J., Essaïdi, Z., Bednarz, M., & Sahraoui, B. (2009). Thermal stability of blends containing azo-carbazole derivatives and epoxy resin, designed for nonlinear

- optical applications. *Opt. Mat.*, Vol.31, No.3, (January 2009), pp. 501-504, ISSN 1873-1252
- Pietsch, U., & Rochon, P. (2003). Evidence of a density grating under light induced formation of SRG at polymers containing azobenzene moieties. *J. Appl. Phys.*, Vol.94, No.2, (July 2003), pp. 963-967, ISSN 1089-7550
- Qu, J., Kawasaki, R., Shiotsuki, M., Sanda, F., & Masuda, T. (2007a). Synthesis and properties of helical polyacetylenes containing carbazole. *Polymer*, Vol.48, No.2, (January 2007), pp. 467-476, ISSN 0032-3861
- Qu, J., Suzuki, Y., Shiotsuki, M., Sanda, F., & Masuda, T. (2007b). Synthesis and electro-optical properties of helical polyacetylenes carrying carbazole and triphenylamine moieties. *Polymer*, Vol.48, No.16, (July 2007), pp. 4628-4636, ISSN 0032-3861
- Ramanujam, P.S., Pedersen, & M., Hvilsted, S. (1999). Instant holography. *Appl. Phys. Lett.*, Vol.74, No.21, (May 1999), pp. 3227-3230, ISSN 1077-3118
- Ramos, G., Herrero, A.A., Belenguer, T., Nùñez, A., del Monte, F., & Levy, D. (2004). Photopolymerizable hybrid sol-gel materials for holographic recording. *Optics in Information System*, Vol.15, No.8
- Raschellà, R., Marino, I., Lottici, P., Bersani, D., Lorenzi, A., & Montenero, A. (2004). Photorefractive gratings in DR1-doped hybrid sol-gel. *Opt. Mater.*, Vol.25, No.4, (May 2004), pp. 419-423, ISSN 0925-3467
- Ravindranath, R., Ajikumar, P.K., Bahulayan, S., Hanafiah, N.B.M., Baba, A., Advincula, R.C., Knoll, W., & Valiyaveetil, S.J. (2007). *J. Phys. Chem. B*, Vol.111, No.23, (June 2007), pp. 6336-6343, ISSN 1520-5207
- Rochon, P., Batalla, E., & Natansohn, A. (1995). Optically induced surface gratings on azoaromatic polymer films. *Appl. Phys. Lett.*, Vol.66, No.2, (January 1995), pp. 136-138, ISSN 1077-3118
- Sabi, Y., Yamamoto, Y., Watanabe, H., Bieringer, T., Haarer, D., Hagen, R., Kostromine, S.G., & Berneth, H. (2001). Photoaddressable polymers for rewritable optical disc systems. *Jpn. J. Appl. Phys.*, Vol.40, No.3B, (2001), pp. 1613-1618, ISSN 0021-4922 6463
- Samyn, C., Verbiest, T., & Persoons, A. (2000). Second-order non-linear optical polymers. *Macrom. Rapid Commun.* Vol.21, No.1, (January 2000), pp. 1-15, ISSN 1521-3927
- Schwartz, E., Lim, E., Gowda, C.M., Liscio, A., Fenwick, O., Tu, G., Palermo, V., de Gelder, R., Cornelissen, J.J.L.M., Van Eck, E.R.H., Kentgens, A.P.M., Cacialli, F., Nolte, R.J.M., Samori, P., Huck, W.T.S., & Rowan, A.E. (2010). *Chem. Mat.*, Vol.22, No.8, (April 2010), pp. 2597-2607, ISSN 1520-5002
- Sekkat, Z., & Dumont, M. (1992). Photoassisted poling of azo dye doped polymeric films at room temperature. *Appl. Phys. B*, Vol.54, No.6, (May 1992), pp. 486-489, ISSN 1432-0649
- S'Heeren, G., Persoons, A., Rondou, P., Wiersman, J., Van Beylen, M., & Samyn, C. (1993). Synthesis of nonlinear optical polymers functionalized with 4-amino-4'-cyanostilbene and -azobenzene dyes. Second harmonic generation in corona-poled thin films. *Makromol. Chem.* Vol.194, No.6, (March 2003), pp. 1733-1744, ISSN 0025-116X
- Shi, J., Jiang, Z., & Cao, S. Synthesis of carbazole-based photorefractive polymers via post-azo-coupling reaction. *React. Funct. Polym.*, Vol.59, No.1, (May 2004a), pp. 87-91, ISSN 1873-166X

- Shi, J., Huang, M., Chen, Z., Gong, Q., & Cao, S. (2004b). Carbazole-based azo group-containing single component polymer exhibiting photorefractive performance. *J. Mat. Sci.*, Vol.39, No.11, (June 2004), pp. 3783-3785, ISSN 1573-4803
- Sui, Y., Yu, X., Yin, J., Zhong, X., Li, Q., Chen, Y., Zhu, Z., & Wang, Z. (2001). All-optical poling of a side-chain poly(urethane-imide) film and surface morphology studies. *Opt. Commun.*, Vol.191, No.3-6, (May 2001), pp. 439-444, ISSN 1873-0310
- Thomas, K.R.J., Lin, J.T., Tao, Y.T., & Ko, C.W. (2001). *J. Am. Chem. Soc.*, Vol.123, No.38, (September 2001), pp. 9404-9411, ISSN 1520-5126
- Tirelli, N., Altomare, A., Solaro, R., Ciardelli, F., Follonier, S., Bosshard, C., & Günter, P. (2000). Structure-activity relationship of new NLO organic materials based on push-pull azodyes: 4. Side chain polymers. *Polymer*, Vol.41, No.2, (January 2000), pp. 415-421, ISSN 0032-3861
- Ubukata, T., Isoshima, T., & Hara, M. (2005). Wavelength-programmable organic DFB laser based on a photoassisted polymer-migration system. *Adv. Mater.*, Vol.17, No.13, (July 2005), pp. 1630-1633, ISSN 1521-4095
- Vellis, P.D., Mikroyannidis, J.A., Cho, M.J., & Choi, D.H.J. (2008). *Polym. Sci., Part A: Polym. Chem.*, Vol.46, No.16, (August 2008), pp. 5592-5603, ISSN 1099-0518
- Viswanathan, N.K., Kim, D.Y., Bian, S., Williams, J., Liu, W., Li, L., Samuelson, L., Kumar, J., Tripathy, S.K. (1999). Surface relief structures on azo polymer films. *J. Mater. Chem.*, Vol.9, pp. 1941-1955, ISSN 1364-5501
- Wang, M., Chen, H.Z., & Yang, S.L. (1995). Synthesis and photoconductivity study of VK-AA copolymer containing CuPc. *J. Photochem. Photobiol., Part A: Chem.*, Vol.88, No.2-3, pp. 183-186, ISSN 1873-2666
- Wang, J., Zhang, L., Niu, Y., Liang, Z., Chen, Y., Huang, Y., Wang, H., & Lin, W. (2003). Photo-induced birefringence phenomenon of a double azo polymer. *Polym. Intern.*, Vol.52, No.7, (July 2003) pp. 1165-1168, ISSN 1097-0126
- Xu, G., Liu, X., Si, J., Ye, P., Li, Z., & Shen, Y. (1999). Optical poling in a crosslinkable polymer system. *Appl. Phys. B.*, Vol.68, No.4, (April 1999), pp. 693-696, ISSN 1432-0649
- Yamamoto, T., Ohashi, A., Yoneyama, S., Hasegawa, M., Tsutsumi, O., Kanazawa, A., Shiono, T., & Ikeda, T. (2001). Phase-type gratings formed by photochemical phase transition of polymer azobenzene liquid crystal. 2. Rapid switching of diffraction beams in thin films. *J. Phys. Chem. B*, Vol.105, No.12, (March 2001), pp. 2308-2313, ISSN 1520-5207
- Zhang, Y., Wada, T., & Sasabe, H. (1998). Carbazole photorefractive materials. *J. Mater. Chem.*, Vol.8, No.4, pp. 809-828, ISSN 1364-5501
- Zhang, L., Huang, M., Jiang, Z., Yang, Z., Chen, Z., Gong, Q., & Cao, S. (2006). A carbazole-based photorefractive polyphosphazene prepared via post-azo-coupling reaction. *React. Funct. Polym.*, Vol.66, No.12, (December 2006), pp. 1404-1410, ISSN 1873-166X
- Zhao, Y., & Ikeda, T. (2009). *Smart Light-Responsive Materials*, Wiley & Sons, ISBN 978-0-470-17578-1, Hoboken, New Jersey
- Zhuang, X.-D., Chen, Y., Liu, G., Zhang, B., Neoh, K.-G., Kang, E.-T., Zhu, C.-X., Li, Y.-X., & Niu, L.-J. (2010). Preparation and memory performance of a nanoaggregated dispersed red 1-functionalized poly (*N*-vinylcarbazole) film via solution-phase self-assembly. *Adv. Funct. Mat.*, Vol.20, No.17, (July 2010), pp. 2916-2922, ISSN 1616-3028



Optoelectronics - Materials and Techniques

Edited by Prof. P. Predeep

ISBN 978-953-307-276-0

Hard cover, 484 pages

Publisher InTech

Published online 26, September, 2011

Published in print edition September, 2011

Optoelectronics - Materials and Techniques is the first part of an edited anthology on the multifaceted areas of optoelectronics by a selected group of authors including promising novices to the experts in the field. Photonics and optoelectronics are making an impact multiple times the semiconductor revolution made on the quality of our life. In telecommunication, entertainment devices, computational techniques, clean energy harvesting, medical instrumentation, materials and device characterization and scores of other areas of R&D the science of optics and electronics get coupled by fine technology advances to make incredibly large strides. The technology of light has advanced to a stage where disciplines sans boundaries are finding it indispensable. Smart materials and devices are fast emerging and being tested and applications developed in an unimaginable pace and speed. Here has been made an attempt to capture some of the materials and techniques and underlying physical and technical phenomena that make such developments possible through some real time players in the field contributing their work and this is sure to make this collection of essays extremely useful to students and other stake holders such as researchers and materials scientists in the area of optoelectronics.

How to reference

In order to correctly reference this scholarly work, feel free to copy and paste the following:

Luigi Angiolini, Tiziana Benelli, Loris Giorgini, Attilio Golemme, Elisabetta Salatelli and Roberto Termine (2011). Side-Chain Multifunctional Photoresponsive Polymeric Materials, Optoelectronics - Materials and Techniques, Prof. P. Predeep (Ed.), ISBN: 978-953-307-276-0, InTech, Available from:
<http://www.intechopen.com/books/optoelectronics-materials-and-techniques/side-chain-multifunctional-photoresponsive-polymeric-materials>

INTECH
open science | open minds

InTech Europe

University Campus STeP Ri
Slavka Krautzeka 83/A
51000 Rijeka, Croatia
Phone: +385 (51) 770 447
Fax: +385 (51) 686 166
www.intechopen.com

InTech China

Unit 405, Office Block, Hotel Equatorial Shanghai
No.65, Yan An Road (West), Shanghai, 200040, China
中国上海市延安西路65号上海国际贵都大饭店办公楼405单元
Phone: +86-21-62489820
Fax: +86-21-62489821

© 2011 The Author(s). Licensee IntechOpen. This chapter is distributed under the terms of the [Creative Commons Attribution-NonCommercial-ShareAlike-3.0 License](#), which permits use, distribution and reproduction for non-commercial purposes, provided the original is properly cited and derivative works building on this content are distributed under the same license.

IntechOpen

IntechOpen