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# Side-Chain Multifunctional Photoresponsive Polymeric Materials

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## 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.

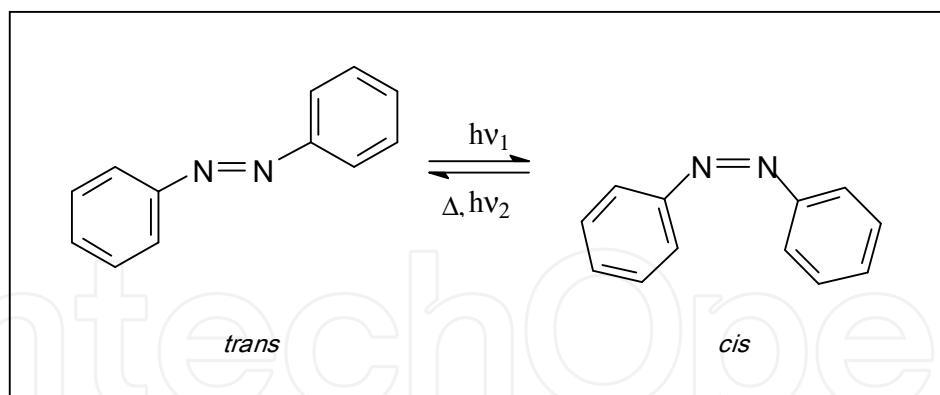


Fig. 1. Photoisomerization of azobenzene

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).

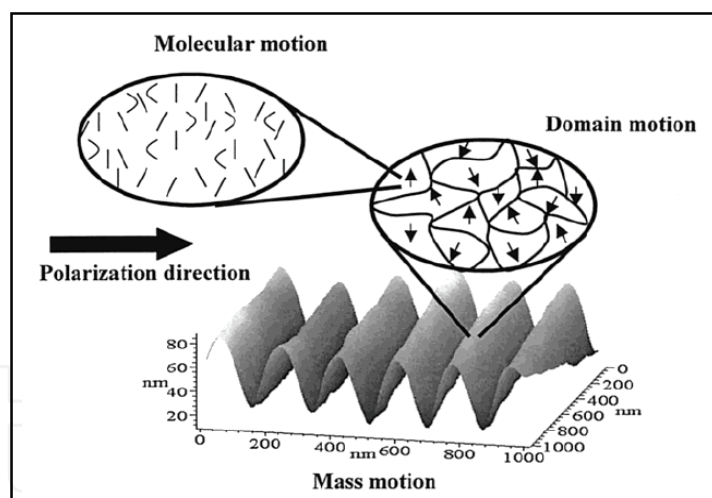


Fig. 2. Illustration of the three levels of polymer motion produced with light (Reprinted with permission from ref. Natansohn & Rochon 2002. Copyright 2002 American Chemical Society)

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).

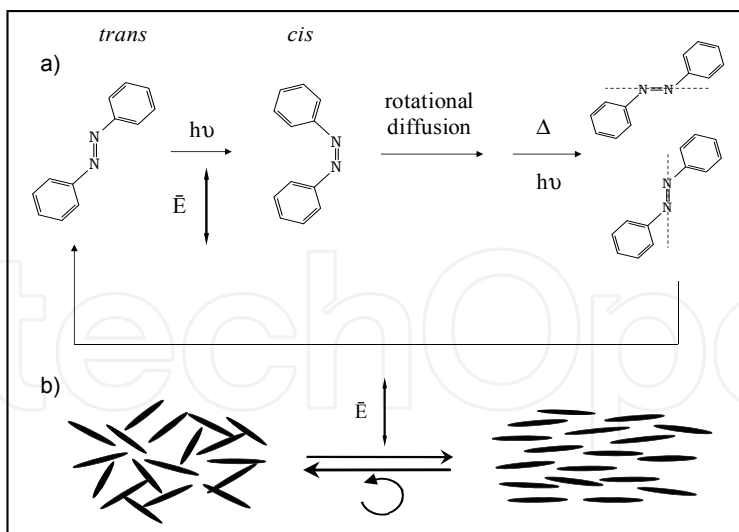


Fig. 3. Statistical photoorientation of azomolecules

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).

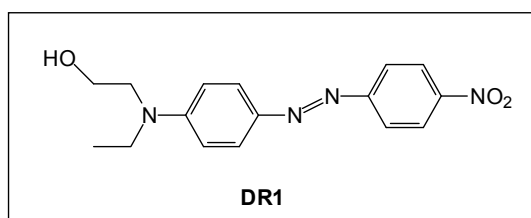


Fig. 4. Chemical structure of **DR1** molecule

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).

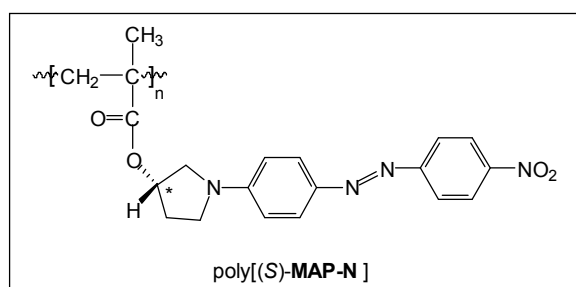


Fig. 5. Chemical structure of poly[(S)-**MAP-N**]

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).

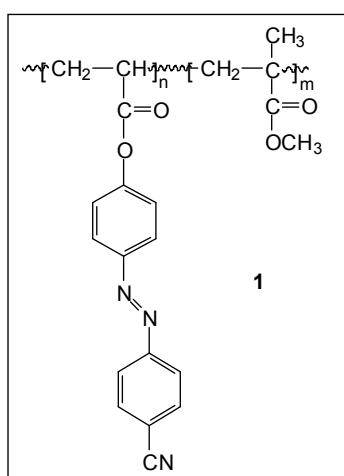


Fig. 6. Chemical structure of an achiral amorphous MMA azo-copolymer

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).

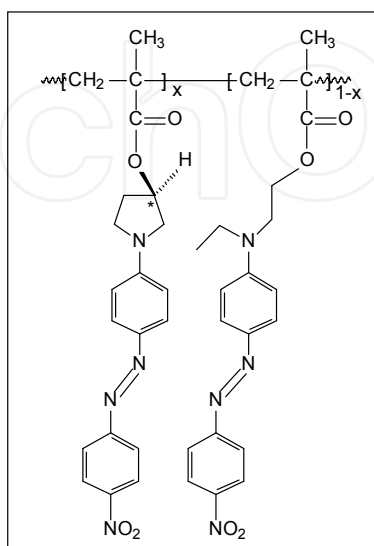


Fig. 7. Chemical structure of the copolymeric system poly[(S)-MAP-N-co-DR1M]

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).

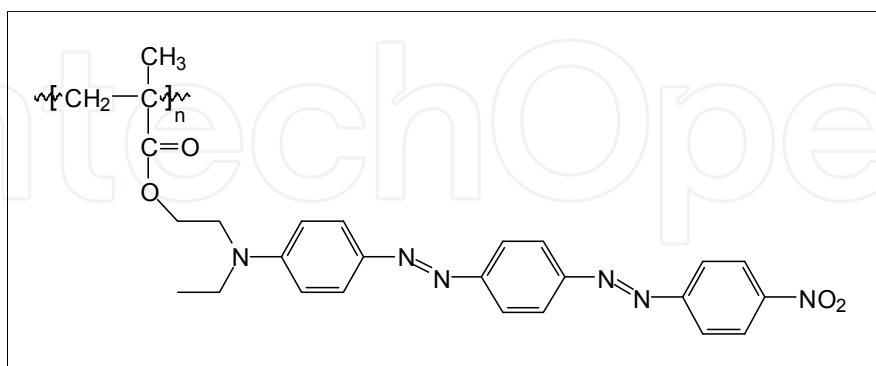


Fig. 8. Chemical structure of side-chain bis-azo chromophore

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.

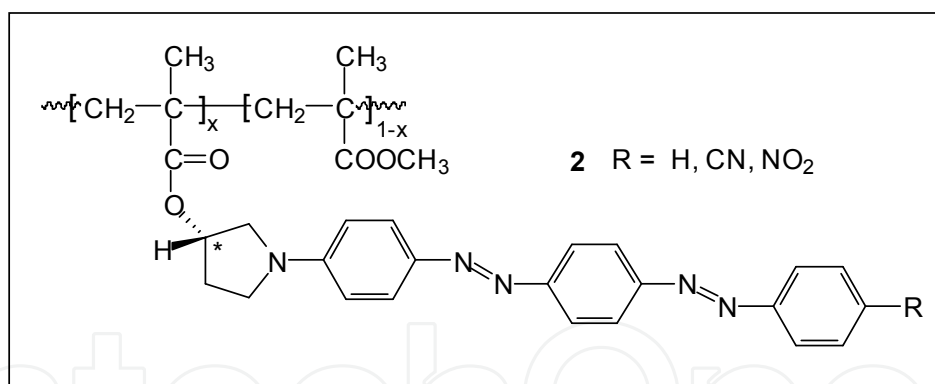


Fig. 9. Chemical structure of optically active bis-azo homo- and co-polymers with MMA

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 (Sekkati & 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  $\text{LiNbO}_3$ . 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).

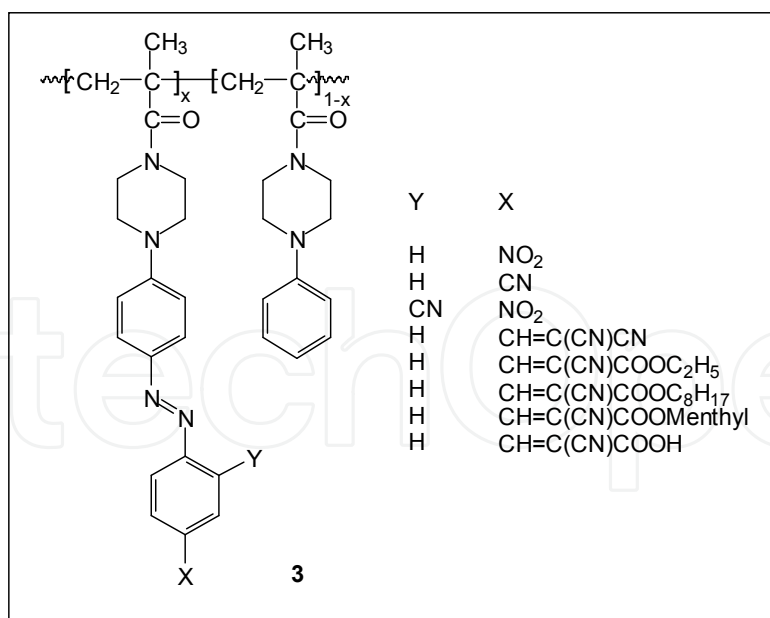


Fig. 10. Chemical structure of copolymers based on side-chain push-pull azobenzene grafted to poly(N-methacryloyl-N'-phenylpiperazine)

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.

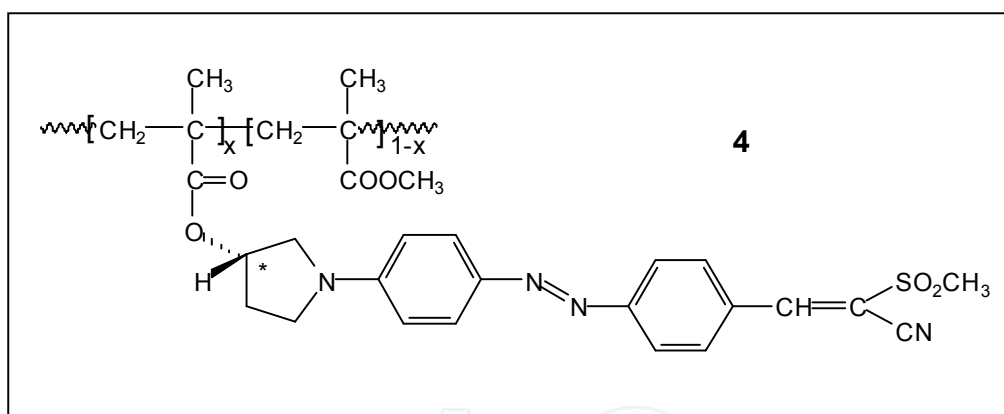


Fig. 11. Chemical structure of corona-poled chiral side-chain azobenzene polymethacrylates

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.

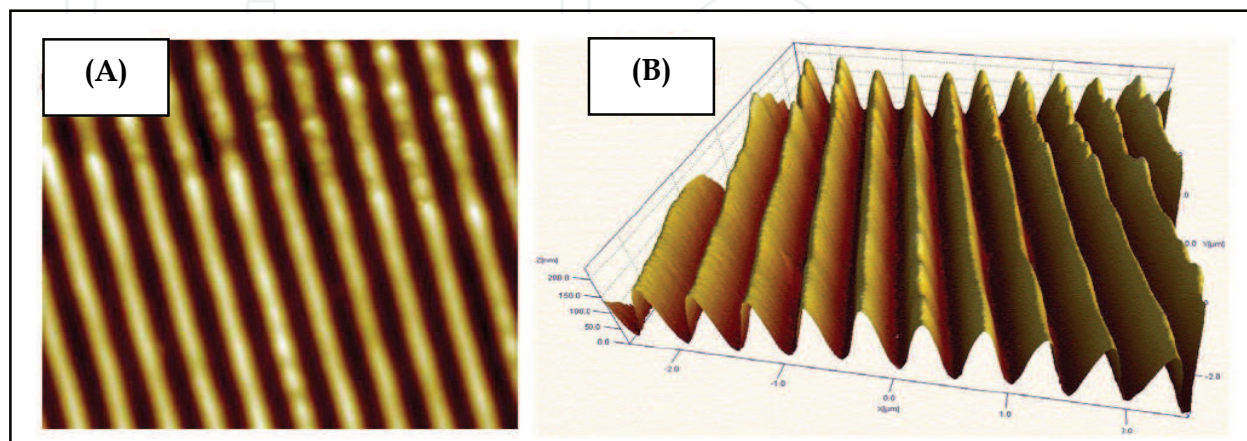


Fig. 12. Bidimensional (A) and tridimensional (B) AFM 5x5  $\mu\text{m}$  surface profile of an optically inscribed grating on a film of azobenzene polymer

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).

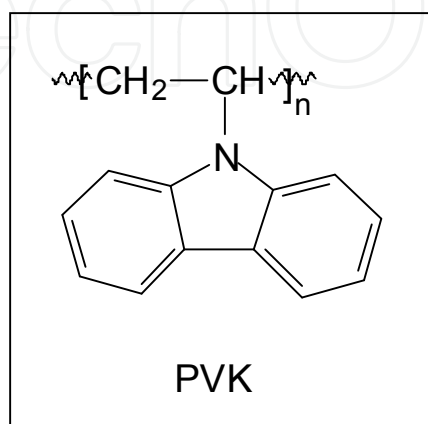


Fig. 13. Chemical structure of poly(N-vinylcarbazole) (PVK)

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 Tg 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 Tg 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).

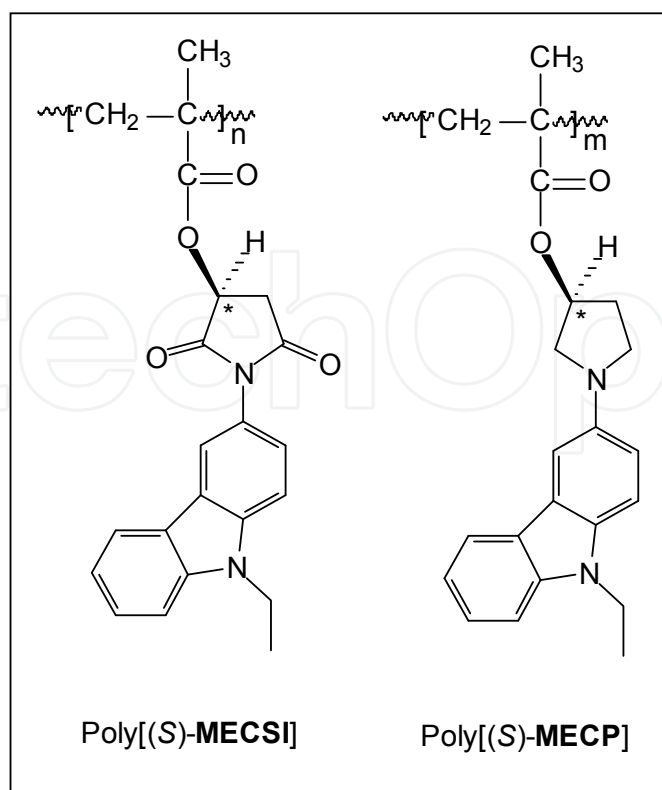


Fig. 14. Chemical structures of poly[(S)-MECSI] and poly[(S)-MECP]

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).

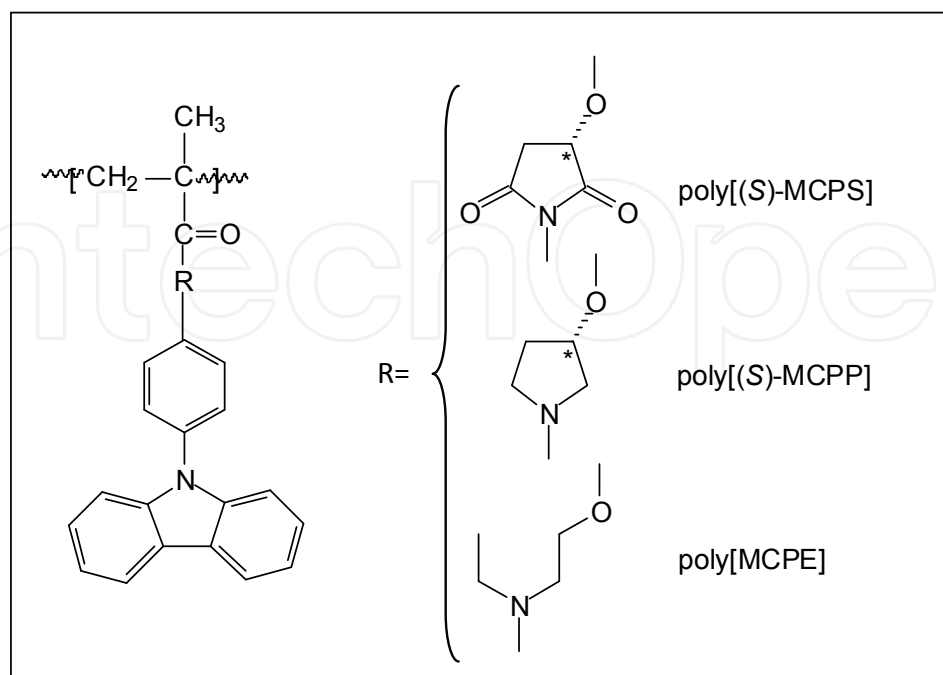


Fig. 15. Chemical structure of poly[(S)-MCPS], poly[(S)-MCPP] and poly[MCPE]

#### 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 co-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.

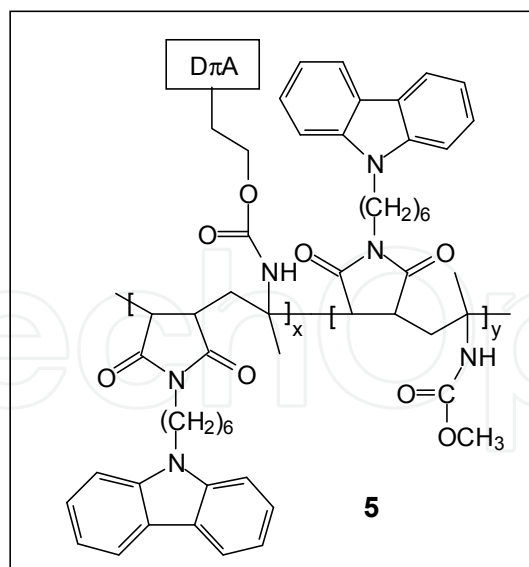


Fig. 16. Chemical structure of multifunctional photorefractive polymers

Copolymers of N-hydroxyethyl carbazole acrylate with azoaromatic push-pull acrylate (6, Fig. 17) of various compositions, possessing  $T_g$  values much over  $200^\circ\text{C}$ , 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).

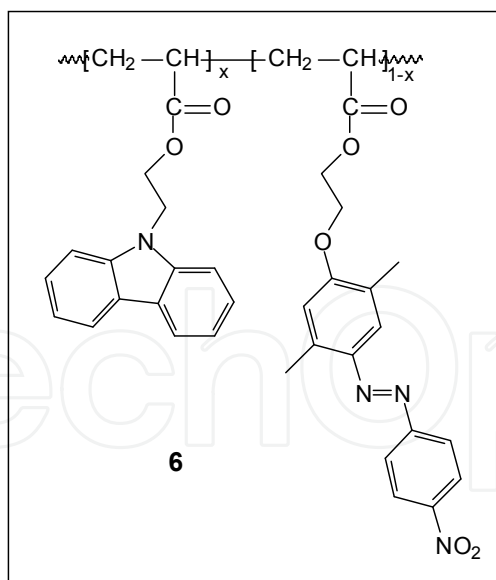


Fig. 17. Chemical structure of copolymers of N-hydroxyethyl carbazole acrylate with azoaromatic push-pull acrylate

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  $200^\circ\text{C}$  (Angiolini et al., 2007b; H. Li et al., 2009) (Fig. 18).



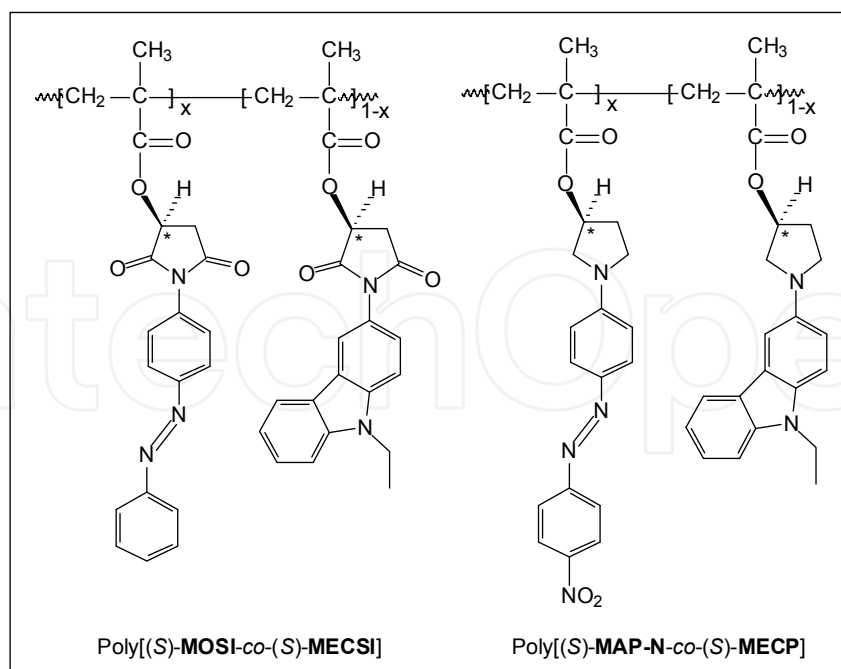


Fig. 18. Chemical structures of copolymers poly[(S)-**MOSI-co-(S)-MECSI**] and poly[(S)-**MAP-N-co-(S)-MECP**]

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 carbazoyl and azobenzene groups as terminal moieties, having very low  $T_g$  (21°C), in the presence of  $C_{60}$  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).

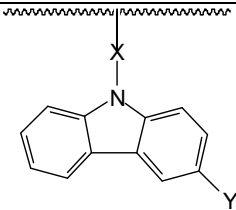
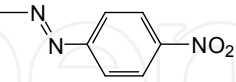
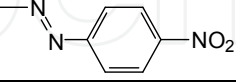
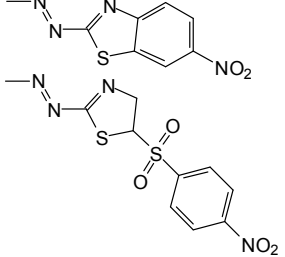
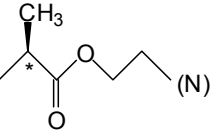
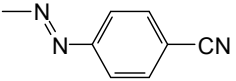
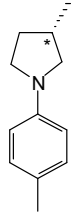
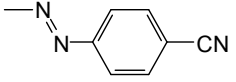
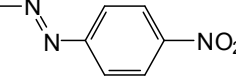
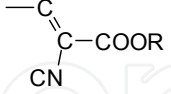
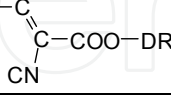
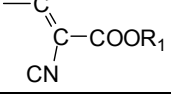
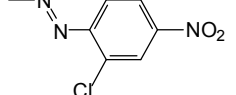
			
Derivative	Main chain	X	Y
C1	polymethacrylate	$-(CH_2)_n-$	
C2	polyacrylate	$-(CH_2)_6-$	
C3	polymethacrylate	$-(CH_2)_2-$	
C4	polymethacrylate		
C5	polymethacrylate		
C6	polyphosphazene	$-(CH_2)_3-$	
C7	polymethylsiloxane	$-(CH_2)_3-$	
C8	polyvinyl	$-(CH_2)_0-$	
C9	polyvinyl	$-(CH_2)_0-$	
C10	epoxy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

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 ( $50^\circ\text{C}$ ) 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

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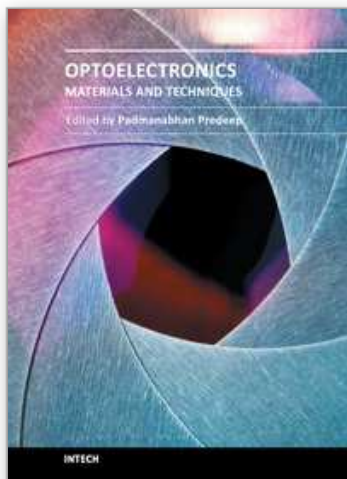
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