Preparation of Side-Chain Liquid Crystalline Azopolymers by CuAAC Postfunctionalization Using Bifunctional Azides: Induction of Chirality Using Circularly Polarized Light

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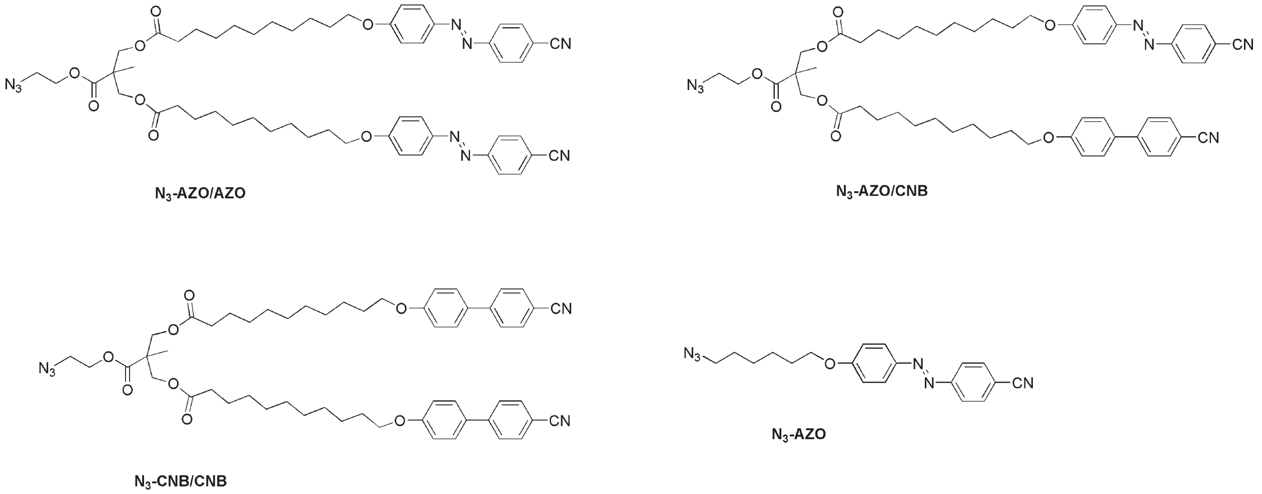
ABSTRACT: Well-defined side-chain liquid crystal azopolymers have been synthesized by click chemistry of poly(propargyl methacrylate) with bifunctional liquid crystalline azides to produce materials with large degrees of functionalization. A polymeric scaffold having pendant alkyne groups was prepared by atom transfer radical polymerization (ATRP) and postfunctionalized by copper(I)-catalyzed azide-alkyne cycloaddition (CuAAC) using homo- and heterobifunctional azides. The azides are derivatives of 2,2-bis(hydroxymethyl)propanoic acid (bis-MPA) containing photoresponsive azobenzene and/or liquid crystalline biphenyl moieties. The approach is a convenient alternative to increase the density of functional units in side-chain polymers having moderate polymerization degrees and to modulate the properties of the final material. The article describes the synthesis, characterization, and liquid crystalline properties of the obtained polymers. The effect of the chemical structure and the possible cooperative effects between functional units in the photo-induction of chirality are also evaluated. A switchable photo-transference of chirality from the circularly polarized light (CPL) to material has been achieved.

INTRODUCTION The preparation of macromolecules with well-defined structures carrying tailored functional units for a range of potential applications is a very active field of research because it is possible to establish better structure-properties relationship leading to a new generation of materials rationally designed in the function of the desired properties. Side-chain polymers for specific applications can be approached by two general synthetic strategies, either by polymerization of an appropriate monomer or by appending a functional unit onto an existing polymer. The first methodology provides a precise structural control over the final polymer. However, the preparation of polymers with high and controlled levels of functional groups by polymerization of monomers bearing specific functionalities often encounters that the availability and reactivity of monomers is limited. An attractive and versatile alternative to circumvent the problem is the postmodification of a polymeric precursor. In this case, an incomplete functionalization of the polymeric skeleton is the major disadvantage.Postpolymerization functionalization strategies have been expanded by using chemical transformations of the so-called click chemistry due to their versatility and high efficiency under mild reaction conditions.[1–3] In particular, modular synthetic strategies that sequentially combine controlled rad-ical polymerizations (CRP) with click chemistry techniques have broadened the access to well-defined macromolecules with precise composition, microstructure, functionality, and architecture.[4–8] From all the click reactions, the copper(I)-catalyzed azide-alkyne cycloadditions (CuAAC) is recurrently described in the literature as an effective instrument to improve the synthesis of complex architectures and/or functionalization of macromolecules due to its high selectivity and almost quantitative conversion under mild reaction conditions.[9–12]



N_3-AZO/AZO

N_3-AZO/CNB

N_3-CNB/CNB

N_3-AZO

CHART 1 Chemical structure of the target azido compounds.

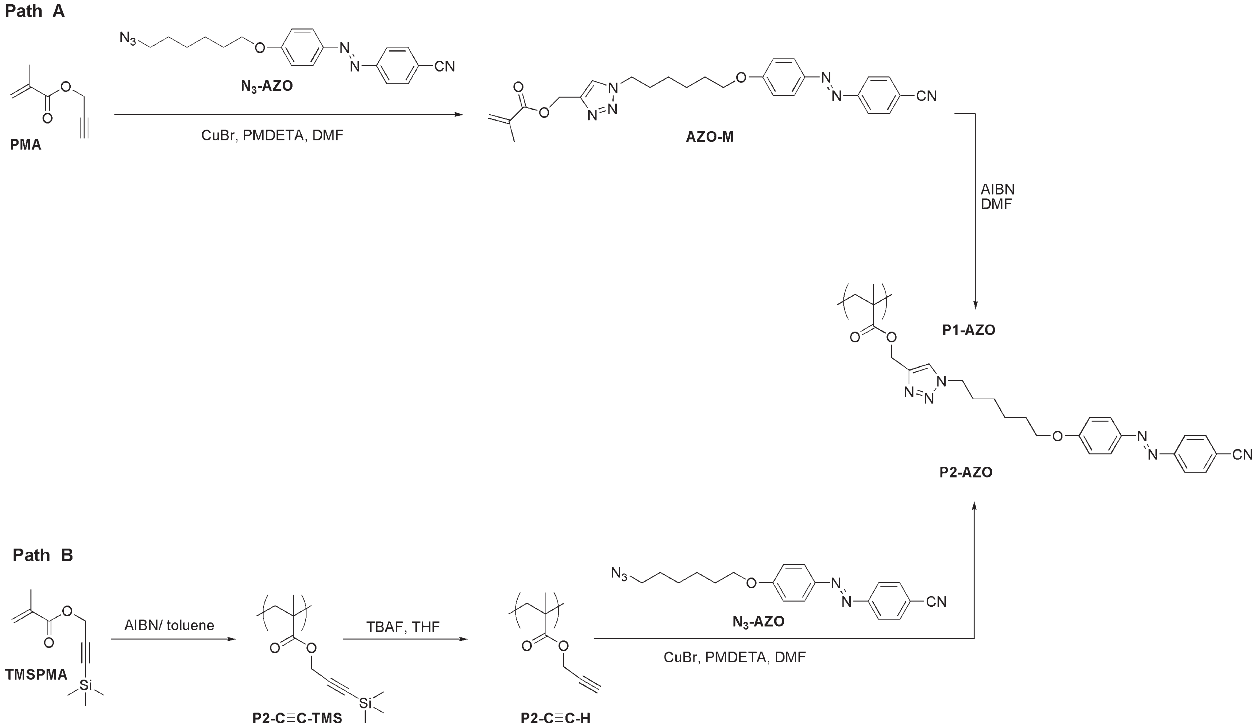
Postfunctionalization of a polymer side-chain via CuAAC requires the direct polymerization of monomers with pendant azido or alkyne groups that can be further conjugated with a desired functional unit. Therefore, methacrylic monomers with pendant azides have been polymerized and subsequently "clicked" to alkynes;[13] nevertheless, it has been reported that azides might give side reactions during polymerization.[14] Propargyl methacrylate can be polymerized by ATRP to yield a polymer with pendant alkyne groups; in this case, the alkyne function have to be protected with the trimethylsilyl-protecting group and deprotected after polymerization otherwise the alkyne interferes in the polymerization.[15] References can be found in the literature regarding the CuAAC postfunctionalization of poly(propargyl methacrylate) to achieve, for example, glycopolymers,[15] cyclodextrin side-chain polymers,[16] or polymers for nonlinear optics.[17]

Azobenzene polymers have been deeply investigated for optical applications due to its photo-responsive properties, in particular, polymethacrylates and polyacrylates, because of their suitable film-forming properties. Upon irradiation with light of different wavelengths they show a reversible *trans-cis* isomerization, which is the origin of a large number of applications ranging from optical storage media to photomechanical actuators.[18–20]

In earlier works, we have approached the preparation of liquid crystalline side-chain azobenzene polymethacrylates by polymerization of azobenzene monomers, either by free radical polymerization in solution or by ATRP.[21–23] It is known that radical polymerization is affected by the azobenzene group and molecular weights are only moderate.[24] Therefore, the click methodology can facilitate the access to well-defined azobenzene polymethacrylates where, in addition, polymer composition and properties can be adjusted using a common polymer scaffold that can serve to attach multiple functionalities. To date, there are reports on azobenzene polymers and dendrimers grown by repetitive CuAAC such as main chain azopolymers,[25] multiblock copolymers,[26] or azobenzene dendrons.[27] The general concept of postfunctionalization by click chemistry has also been applied to attach azobenzene units to different polymeric backbones[28,29] including poly(propargyl methacrylate) to produce random copolymers[17] or merely homopolymers showing the feasibility of the methodology.[30]

In this article, we report on the postpolymerization modification of poly(propargyl methacrylate) by CuAAC using homo- and heterobifunctional azides (see Chart 1) as a strategy to modulate the properties of the final polymer. The functional units are the photoresponsive 4-cyanoazobenzene and the liquid crystalline 4-cyanobiphenyl units. The first one is capable of photoinduced isomerization accompanied by a molecular reorientation on using linearly or circularly polarized light. The second one is transparent in the excitation region of the azobenzene but is capable of cooperative reorientation stabilizing the response of the photochromic azobenzene units contributing, for example, to the birefringence of the material in copolymers or tuning the physical and thermal properties in codendrimers.[23,31,32] Unlike the random copolymers, the proposed strategy provides a family of functional materials where the final properties can be modulated not only by the nature of the functional units but also by the density, the regularity on their position, and distribution along the polymeric chain as the polymer repeating unit is constituted by two functional moieties.

The liquid crystalline properties and photo-induced chiroptical behavior under circularly polarized light irradiation are described. In particular, our interest is focussed on the photoinduction of chirality in polymeric achiral materials when they are put onto a chiral stimulus. This photoinduction of chirality can be achieved by irradiating a photoactive material with circularly polarized light (CPL). Recently, we have proved the induction of chiral supramolecular order in achiral conventional polymethacrylates with pendant azobenzene units by irradiation with a chiral light source as CLP.[33] Moreover, we have investigated the effect of the glass transition



SCHEME 1 Path A: synthesis of **P1-AZO** by preparation of an azobenzene methacrylic monomer and its subsequent radical polymerization in solution. Path B: synthesis of **P2-AZO** by radical polymerization in solution of the protected propargyl methacrylate followed by deprotection of the alkyne group and CuAAC with the corresponding azide.

temperature as well as the different substituents at the azobenzene units on the chiral induction.[21,34] Here, we explore the photoinduction of a chiral supramolecular order in new architectures which include azobenzene units or azobenzene-containing bifunctional units connected to the polymethacrylic main chain by a 1,2,3-triazole built up in the CuAAC reaction.

RESULTS AND DISCUSSION

Synthesis and Thermal Characterization of Azides and Polymers

The click methodology was first verified using a monofunctional azobenzene azide **N_3-AZO** (see Chart 1 and Scheme 1).[16,30,35] The CuAAC reaction was assayed on propargyl methacrylate that was subsequently polymerized (**P1-AZO** in Scheme 1, path A) and then the same azo polymer was obtained by the CuAAC reaction on poly(propargyl methacrylate) (**P2-AZO** in Scheme 1, path B). Full experimental details are given in the Supporting Information.

Therefore, the methacrylate **AZO-M** was prepared by CuAAC reaction between the azide **N_3-AZO** and propargyl methacrylate (**PMA**) using the CuBr/PMDETA catalytic system in DMF at 35 °C.[36,37] The conversion of the alkyne and azido functional groups into a 1,2,3-triazole unit was confirmed by ^{1}H NMR and FTIR analysis. The polymerization of **AZO-M** was carried out by a conventional free radical polymerization in solution, using AIBN as a thermal initiator in DMF as the solvent, to yield the corresponding side-chain polymer **P1-AZO**. The physical characterization was undertaken by FTIR, ^{1}H NMR, and elemental analysis, the data being consistent with the expected structure. Number–average molecular weight (M_n) and polydispersity (M_w/M_n) were determined for **P1-AZO** by SEC with $M_n = 16{,}000$ g/mol and $M_w/M_n = 1.28$ relative to poly(methyl methacrylate) (PMMA) standards (see Table 1).

Therefore, a polymer of similar characteristics was approached by postfunctionalization. **P2-AZO** was prepared from trimethylsilylpropargyl methacrylate (**TMSPMA**) that was polymerized also by free radical polymerization in solution, using AIBN in toluene. Subsequent removal of the protecting group rendered the corresponding alkyne precursor **P2-C≡C—H** ($M_n = 6300$ g/mol, $M_n/M_w = 1.20$).[15] Finally, the target azopolymer **P2-AZO** was obtained by postfunctionalization via CuAAC reaction between the **P2-C≡C—H** and the azide **N_3-AZO**. Evidence of the described sequence of reactions was gained by FTIR, ^{1}H NMR and also SEC analysis. Residual alkyne groups were not evident either by ^{1}H NMR or FTIR spectroscopies. As it was pursued, the apparent molecular weight and polydispersity determined by SEC for **P2-AZO**, $M_n = 14{,}500$ g/mol, $M_w/M_n = 1.18$ are similar to those of **P1-AZO**. Considering that M_n values are given relative to PMMA standards (elution time is based on the hydrodynamic volume of the polymer) and the structural similarities of PMMA reference standards and **P2-C≡C—H**, we can estimate an average polymerization degree for

TABLE 1 Size Exclusion Chromatography (SEC) Data and Thermal Characterization of the Synthesized Azopolymers

Polymer	M_n	M_w/M_n	TGA[a]	DTGA[a]	Residue$_{600}$[a]	T_g[b]	$T_i(\Delta H_i)$[b]
P1-AZO	16,000	1.28	321	338, 418, 445^{sh}	21	76	130 (2.1)
P2-AZO	14,500	1.18	316	338, 408, 441	25	68	127 (1.7)
P3-AZO/AZO	37,900	1.46	309	337, 420, 457	15	28	143 (9.6)
P3-AZO/CNB	38,200	1.45	300	335, 360^{sh}, 424	12	19	115 (8.6)
P3-CNB/CNB	37,700	1.28	341	372, 405^{sh}, 442^{sh}	3	18	98 (8.9)

[a] TGA: decomposition temperature given in °C at the onset of the weight loss curve; DTGA: maxima of the weight loss curve first derivative; Residue$_{600}$: pyrolysis residue at 600 °C given in % determined from the weight loss curve.

[b] T_g: glass transition temperature; T_i and ΔH_i: isotropization temperature and associate enthalpy. Temperatures are given in °C and correspond to a second heating of the sample at 10 °C/min, enthalpy transitions are given in kJ per mole of repeating unit.

P2-C≡C—H of ≈50. Accordingly, the theoretical average-molecular weight of **P2-AZO** should be about 23,700 g/mol indicating that values obtained by SEC for these azopolymers are underestimated.

The similarities also account for the thermal properties (see Table 1). Thermal stability of the polymers was assessed by TGA in nitrogen atmosphere. Both azopolymers have an optimal thermal stability with loss temperatures associated with thermal degradation of the material above 315 °C. A combined study by DSC and POM shows that both polymers are glassy materials with liquid crystal properties between the glass transition, T_g, and the isotropization temperature, T_i. On cooling the isotropic liquid, a mesophase growth in the form of classical batônnets is associated with the development of a smectic A phase. From the DSC scans corresponding to the second heating, a weak and wide T_g is calculated at 76 and 68 °C for models **P1-AZO** and **P2-AZO**, and isotropization at 130 and 127 °C, respectively. This closely related thermal behavior can be associated to their intimate structural correspondence concluding that by click postfunctionalization we attain almost the same material than by direct polymerization of the corresponding monomer as it has also been reported for related nitroazobenzenes.[30]

In order to gain information on the effect of the generated 1,2,3-triazole linking group, it should be interesting to compare the thermal behavior of the polymers with that of the poly(methyl methacrylate) azobenzene having a decyloxy spacer, **PC10** (see Chart 2).[21] In both cases separation of the azo moiety from the polymeric chain is of similar length. There are not differences on thermal stabilities, **PC10** has a decomposition temperature of 320 °C calculated from TGA curve, proving the stability of the triazole covalent linkage.[38] **PC10** shows a smectic A mesophase between $T_g = 28$ °C and $T_i = 131$ °C. Therefore, the most remarkable difference is that the presence of the 1,2,3-triazole increases the T_g about 40 °C. This is not unexpected as the bulky and rigid triazole aromatic unit close to the polymeric chain should restrict rotational freedom and therefore increase T_g.

Once the postfunctionalization via CuAAC as an adequate alternative is checked out, the main goal of the work was approached, which is the functionalization of poly(propargyl methacrylate) with bifunctional azides. Dimers based on 2,2-bis(hydroxymethyl)propionic acid (bis-MPA) bearing an azido group at the focal point (Chart 1) were prepared according to the reported procedure for **N$_3$-AZO/AZO** (Scheme 2).[37] The chemical structure of these azides was fully confirmed by FTIR, ^{1}H NMR, and elemental analysis techniques. Details on the synthesis and the characterization of the azides are described in the Supporting Information.

The polyalkyne precursor was prepared in two steps starting from the **TMSPMA** (Scheme 3). To have a better control over the final material, **TMSPMA** was polymerized by a controlled radical polymerization method, ATRP, using ethyl 2-bromoisobutyrate (EBB) as the initiator and in the presence of the catalytic system CuBr/PMDETA in anisole was used to obtain the corresponding polymer that after deprotection rendered the desired poly(propargyl methacrylate) **P3-C≡C—H**. CuAAC reaction was carried out using ~2.5% molar excess of the azide to drive the reaction to completion and 0.1 equiv. of the catalytic system CuBr/PMDETA. The unreacted azide detected by ^{1}H NMR and SEC analysis was readily removed by size exclusion chromatography (SEC) using BioBeads® SX-1. Analysis of the purified polymers demonstrated the complete removal of the bifunctional azide as it is shown for **P3-AZO/AZO** in Figures 1 and 2. Thus, the band at ≈2100 cm^{-1} in the FTIR spectrum corresponding to the N_3 stretching mode and the triplet at 3.47 ppm in the ^{1}H NMR spectrum due to the proton in the α-position to the azido group ($—CH_2—N_3$) have disappeared. Again, there is no evidence of residual alkyne functions either by FTIR or

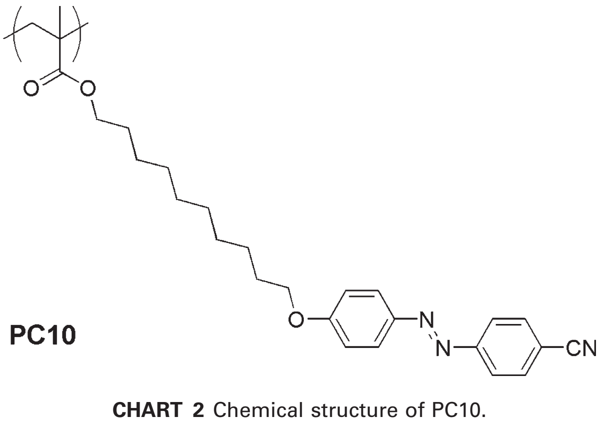
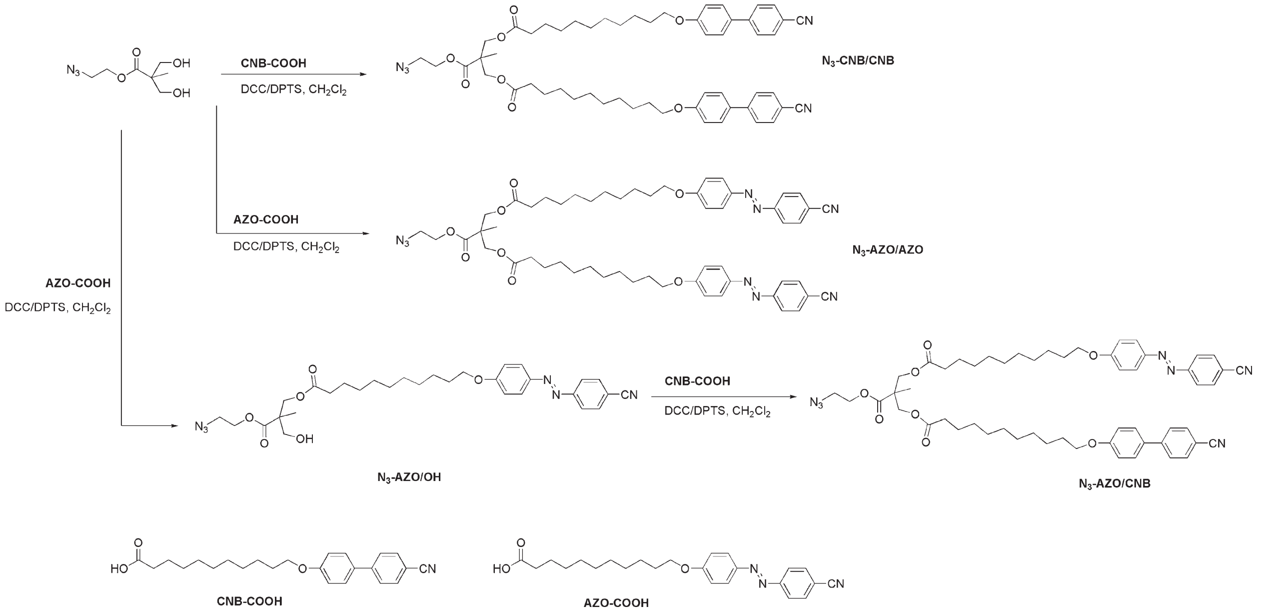


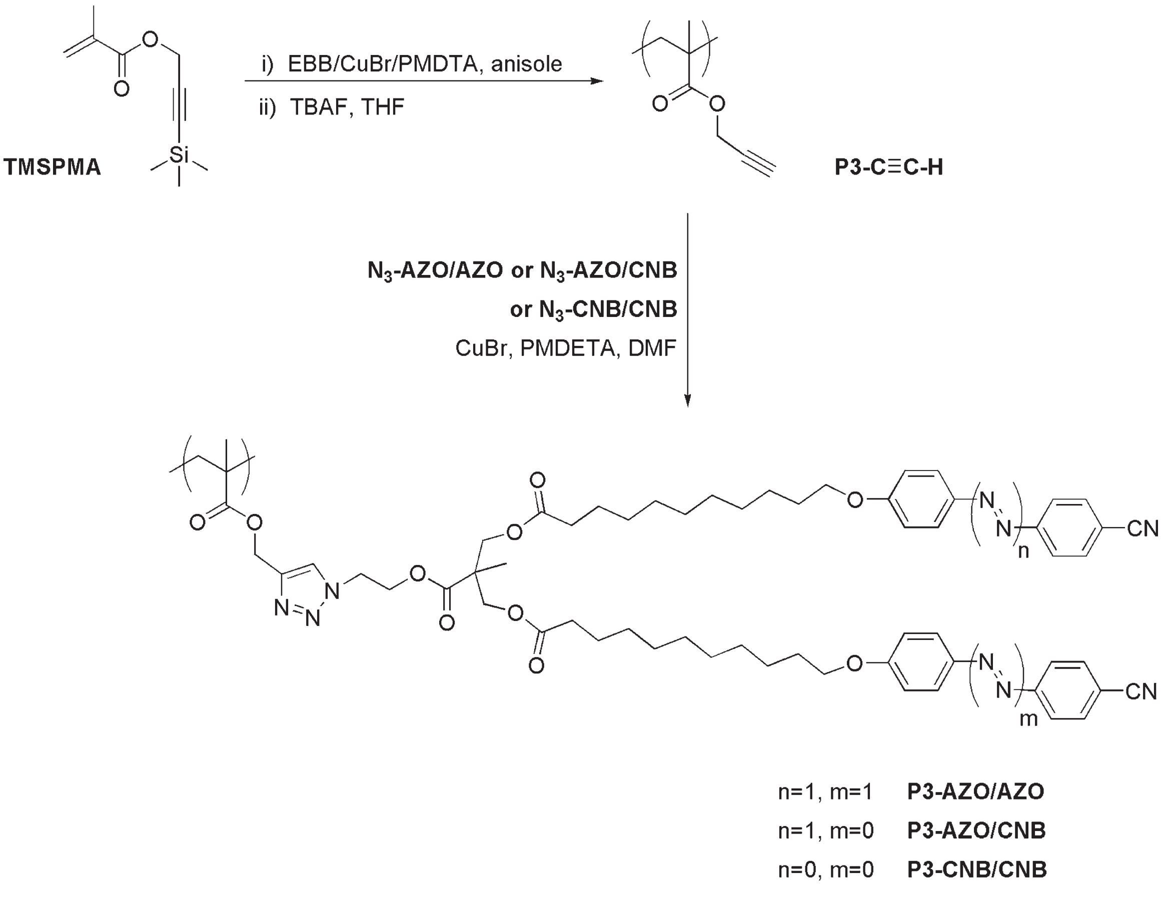
CHART 2 Chemical structure of PC10.



SCHEME 2 Synthesis of bifunctional azides.

^{1}H NMR, and the reaction was considered complete within the detection limits of the techniques, which is above 95% for ^{1}H NMR.

Formation of the triazole ring is only obvious in the NMR spectra of **P3-CNB/CNB** (see Supporting Information Fig. S4). A broad signal at 7.95 ppm in the ^{1}H NMR spectrum



SCHEME 3 Synthesis of bifunctional polymers (**P3-AZO/AZO, P3-AZO/CNB, P3-CNB/CNB**) by ATRP and CuAAC postfunctionalization.

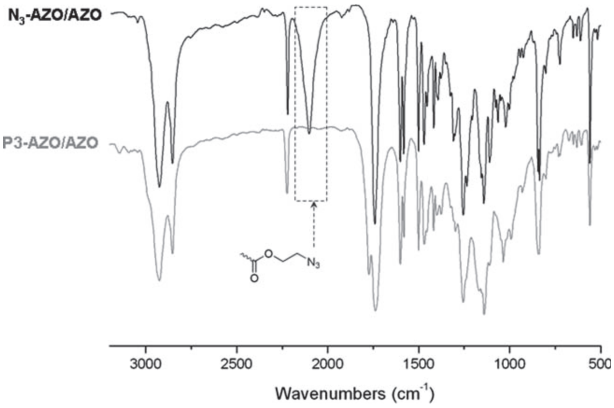


FIGURE 1 FTIR spectra of the polymer **P3-AZO/AZO** and the bifunctional azide **N_3-AZO/AZO** taken in KBr pellets.

was assigned to the proton in the triazol ring (the proton bonded to C5: *H*-C5). This peak is masked by the azobenzene aromatic protons in **P3-AZO/AZO** and **P3-AZO/CNB** (see Fig. 2). This assignment was confirmed by ^{13}C NMR as it correlated in the ^1H-^{13}C-HSQC spectrum with the carbon at 125.1 ppm corresponding to a C of the triazole ring (see Supporting Information Fig. S6). It is well established that one of the characteristics of the CuAAC is its regiospecificity and the formation of 1,4-regioisomer is favored over the 1,5 one.[3,11] This was distinguished by ^1H NOESY experiments where correlation was found between the proton of the triazol ring (*H*-C5) and the methylenic protons in α to C4 ($-CH_2-C4$) and in α to N1 ($-CH_2-N1$), which indicates the proximity in space of these protons (see Supporting Information Fig. S7).

Based on SEC data for **P3-C≡C—H**, $M_n = 11{,}000$ g/mol, $M_n/M_w = 1.21$, we can estimate an average polymerization degree of ≈ 88. This, added to the fact that we are using bifunctional azides, we can go up to ≈ 176 functional side units, almost three-fold times the number attained by conventional free radical polymerization in solution. This average degree of side-chain functionalization is also higher than values achieved by ATRP of azobenzene methacrylates.[23,39]

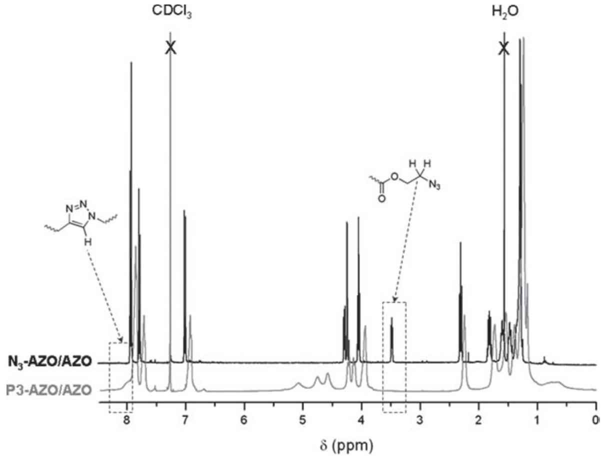


FIGURE 2 ^1H NMR spectra in $CDCl_3$ of the polymer **P3-AZO/AZO** and its bifunctional azide precursor **N_3-AZO/AZO**.

Thermal stability of the polymers was assessed by TGA in nitrogen atmosphere (Table 1). All these polymers present thermal degradation above 300 °C; however, the azopolymers **P3-AZO/AZO** and **P3-AZO/CNB** show lower stability than the corresponding **P3-CNB/CNB**, with onset decomposition temperatures of 309 and 300 °C versus 341 °C, respectively. Differences in the thermal stability on homo- and co-dendrimers based on poly(propylene imine) containing the 4-cyanoazobenzene and 4-cyanobiphenyl units have already been described.[32,40]

Mesomorphic properties of the azides were evaluated by DSC and POM, and the results are collected in Table 2, Figure 3(a), and Supporting Information Figure S8. **N_3-AZO** shows a Nematic mesophase easily identified from its Schlieren texture between 76 and 120 °C [see Fig. 4(a)]. The bifunctional azides exhibit a smectic A mesophase that has been assigned on the basis of its distinctive fan-shaped and homeotropic textures [see Fig. 4(b)]. The mesogenic properties of **N_3-AZO/AZO** have already been reported.[37] From the data, it is clear that the 4-cyanobiphenyl unit decreases both melting and clearing temperatures. On comparing the behavior of **N_3-AZO/AZO** and **N_3-CNB/CNB**, they both form a mesophase, on cooling from the isotropic liquid, which is stable below room temperature and crystallizes at 12 and 8 °C, respectively. The heterobifunctional azide **N_3-AZO/CNB** has a melting temperature that is intermediate between those of the homofunctionalized azides. However, on cooling, the compound does not crystallize; instead it forms a supercooled smectic glass. The DSC corresponding to the subsequent heating of the sample shows a glass transition at −6 °C followed by a cold crystallization process at 12 °C. The low crystallization tendency of the heterobifunctional **N_3-AZO/CNB** can be associated to the disturbance of structural uniformity when compared to the homobifunctional azides.

TABLE 2 Transition Temperatures and Enthalpies Data for the Monomer and Azide Precursors[a]

Compound	Transition Temperatures and Enthalpies
AZO-M	Cr 134 (88.1) I[b]
N_3-AZO	Cr 76 (32.7) N 120 (1.9) I
N_3-AZO/AZO	Cr 71 (57.4) SmA 85 (7.4) I
N_3-CNB/AZO	Cr 33 (38.5) SmA 70 (6.8) I[c]
N_3-CNB/CNB	Cr 36 (40.8) SmA 53 (5.3) I

[a] g: glass; Cr: crystal; I: isotropic liquid; N: nematic; SmA: smectic A. Data corresponding to the second heating scan at 10 °C/min heating rate. Temperatures are given in °C, values in brackets correspond to the associated enthalpy transition given in kJ/mol.

[b] Data corresponding to the first heating. Polymerization of the sample is detected when heating above the melting point.

[c] On cooling the molten isotropic liquid, the compound forms a smectic glass. A glass transition is observed at −6 °C and a cold crystallization process at 12 °C with an associated enthalpy of −31 kJ/mol.

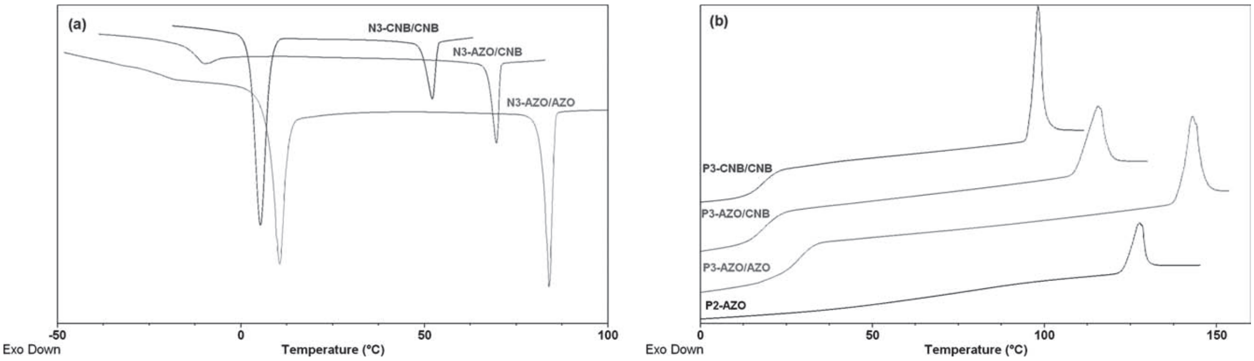


FIGURE 3 DSC traces of (a) bifunctional azides recorded during the cooling scan (10 °C/min cooling rate) and (b) the functional polymers recorded during the heating scan (10 °C/min heating rate).

The polymers are glassy materials with liquid crystal properties. The DSC traces of the samples corresponding to heating scans at 10 °C/min rate show a very clear jump of the baseline due to the glass transition and an exothermic peak due to the isotropization [Fig. 3(b)]. As it was observed for the corresponding azides, the incorporation of the 4-cyanobiphenyl unit provokes a decrease in the transition temperatures, that is more evident for T_i than for T_g. Therefore, **P3-AZO/AZO** has a $T_\mathrm{g} = 28$ °C and $T_\mathrm{i} = 143$ °C and the temperatures decrease for **P3-CNB/CNB** to $T_\mathrm{g} = 18$ °C and $T_\mathrm{i} = 98$ °C. For **P3-AZO/CNB**, T_i had an intermediate value, $T_\mathrm{i} = 115$ °C, but the T_g was lower and close to **P3-CNB/CNB**. All these polymers show liquid crystalline behavior and the nature of the smectic A mesophase was assigned according to X-ray diffraction and POM techniques [see Fig. 4(c,d) and Supporting Information Fig. S9). In this context, dendritic polymethacrylates bearing dimeric azobenzene moieties based on benzyl ether have been reported by free radical polymerization of the appropriate methacrylic monomer which show calamitic phases.[41,42]

Optical Properties and Chiral Induction

The UV–vis spectra of precursors and polymers were obtained for ~10^{-5} M solutions in THF. Relevant data are

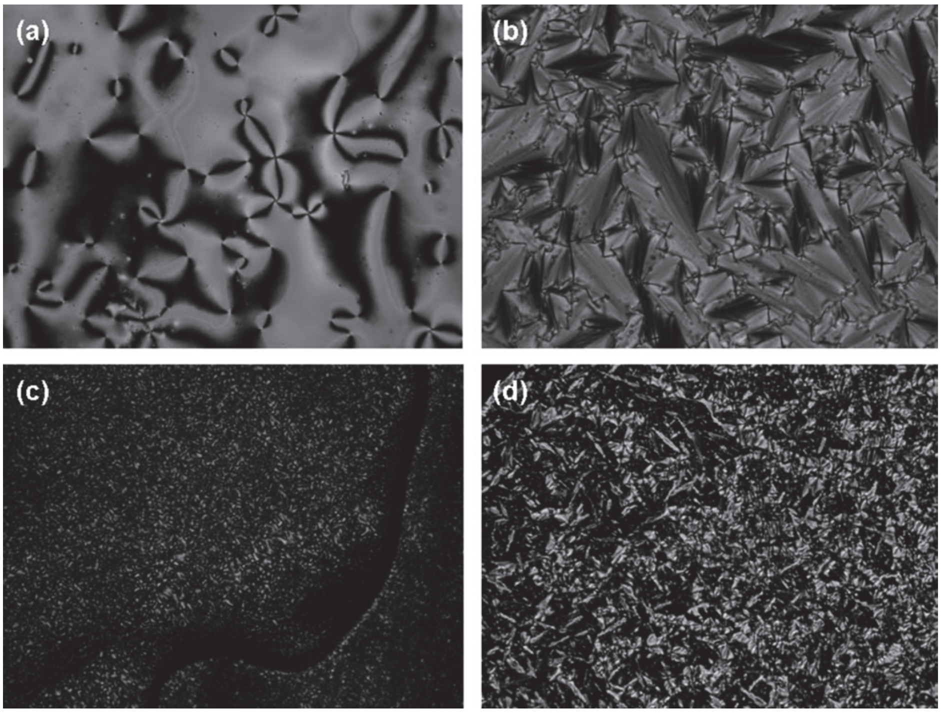


FIGURE 4 POM images of (a) Schlieren texture of the Nematic mesophase observed on cooling at 101 °C for **N_3-AZO**, (b) fan-shaped texture of the smectic mesophase observed for **N_3-CNB/CNB** cooling at 34 °C, (c) **P3-AZO/AZO** observed on cooling at 0.5 °C/min to 137 °C after annealing for 36 h, and (d) mesophase growth on cooling the isotropic liquid at 0.2 °C/min to 94 °C and annealing for 1 h for **P3-CNB/CNB**.

TABLE 3 UV–vis Data of the Azides and Polymers

Azide	λ (log ε)/THF Solution[a]	Polymer	λ (log ε)/THF Solution[a]	λ/Film[b]
N_3-AZO	364 (4.32)	**P2-AZO**	365 (4.26)	352
N_3-AZO/AZO	366 (4.39)	**P3-AZO/AZO**	365 (4.34)	346
N_3-CNB/AZO	291 (4.88), 365 (4.51)	**P3-CNB/AZO**	298 (4.49), 365 (4.32)	297/364
N_3-CNB/CNB	297 (4.42)	**P3-CNB/CNB**	297 (4.40)	–

[a] λ is given in nm and corresponds to the maximum of the absorption band. ε is given in M^{-1} cm^{-1} and has been calculated using the concentration of the corresponding chromophore AZO or CNB in solution.

[b] λ is given in nm and corresponds to the maximum of the absorption band.

collected in Table 3 and Figure 5(a). **P3-AZO/AZO** shows an intense absorption band at 365 nm related to the π–π* transition together with a weak absorption band about 450 nm corresponding to the symmetry forbidden n–π* transition of the (E)-4-cyanoazobenzene unit.[43] These optical features are also distinctive in the azido derivatives **N_3-AZO** and **N_3-AZO/AZO** or in the related **AZO-M** monomer, and **P1-AZO** or **P2-AZO** polymers. **P3-CNB/CNB** shows an intense band at 297 nm due to π–π* transition of the 4-cyanobiphenyl unit, similar to the corresponding azide **N_3-CNB/CNB**. The spectra of the bifunctional azide **N_3-AZO/CNB** and the polymer **P3-AZO/CNB** are, within experimental error, a combination of the spectra of the 4-cyanoazobenzene and 4-cyanobiphenyl units. The fact that the λ_{max} values of the bands do not vary significantly when compared with those of the azides indicates that the functional units attached to the polymer behave independently in solution.

The UV–vis spectra of azo-polymers films [Table 3 and Fig. 5(b)] were registered after thermal treatment by annealing first in isotropic state following at mesophase temperature and subsequent fast cooling to room temperature. The absorption maximum of the main π–π* transition band of **P2-AZO** and **P3-AZO/AZO** films is shifted to shorter wavelength when compared to THF solution, from 365 to 352 nm and 346 nm, respectively, which proves the H-aggregation of the azobenzene units.[44] The hypsochromic shift of the main band of the **P3-AZO/AZO** compared to **P2-AZO** can be related with a stronger coupling of the azochromophores probably imposed by a higher concentration of the azobenzene units into the material.[40] The UV–vis data of **P3-AZO/CNB** film repeat the absorption maximum of the THF solution data for both 4-cyanobiphenyl and 4-cyanoazobenzene; consequently, the precise alternation between different moieties prevented an effective aggregation among chromophores.

In order to photo-induce a chiroptical response, as-casted films of the cited polymers were prepared. Previous to irradiation, the polymer films were annealed first in the isotropic state for 5 min, then at the mesophase temperature for 15 min, and finally quenched to room temperature. The annealed films were irradiated with r-CPL or l-CPL at 488 nm (Ar^+, 20 mW/cm^2) for 30 min. The CD and UV–vis spectra of the films were registered before and after irradiation. A control experiment was initially performed by irradiation of **P3-CNB/CNB**. As expected, nonirradiated and r- and l-CPL irradiated films of **P3-CNB/CNB** were CD silent. These preliminary experiments implied that azobenzene units are required for the chiral transfer between light and material. Therefore, Figure 6 collects the UV–vis and CD spectra of irradiated films of azo polymers **P2-AZO**, **P3-AZO/AZO**, and **P3-AZO/CNB**. All the nonirradiated films are CD-silent but after irradiation intense and well-defined CD signals were detected. Moreover, the CD spectra recorded at different positions rotating around the light beam have the same shape and approximately the same intensity; consequently, the contribution of the linear dichroism to the CD spectra can be considered insignificant.

After CPL irradiation, the CD spectrum of the polymer containing a monofunctional unit, **P2-AZO**, showed a strong exciton couplet associated to the π–π* absorption that indicated a chiral arrangement between the achiral azobenzene

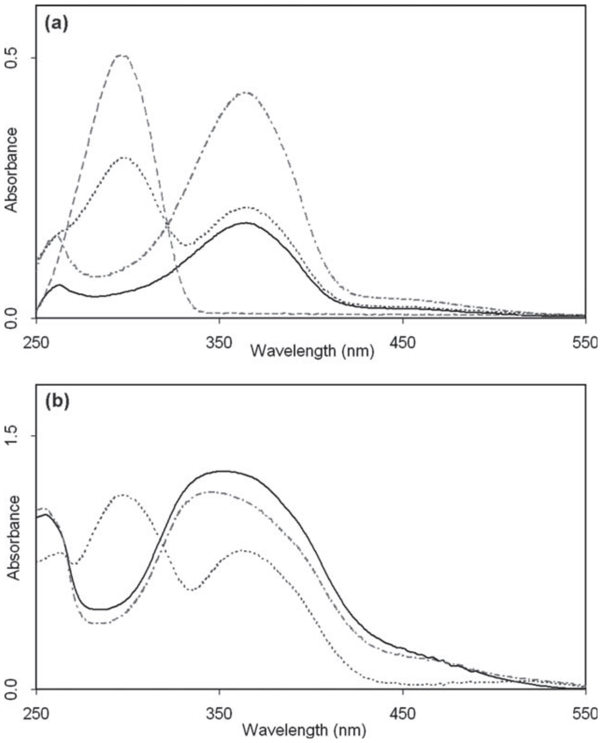


FIGURE 5 UV–vis spectra in THF solution (a) and annealed film (b) of **P2-AZO** (—), **P3-AZO/AZO** (– · –), **P3-AZO/CNB** (- - -), and **P3-CNB/CNB** (– –).

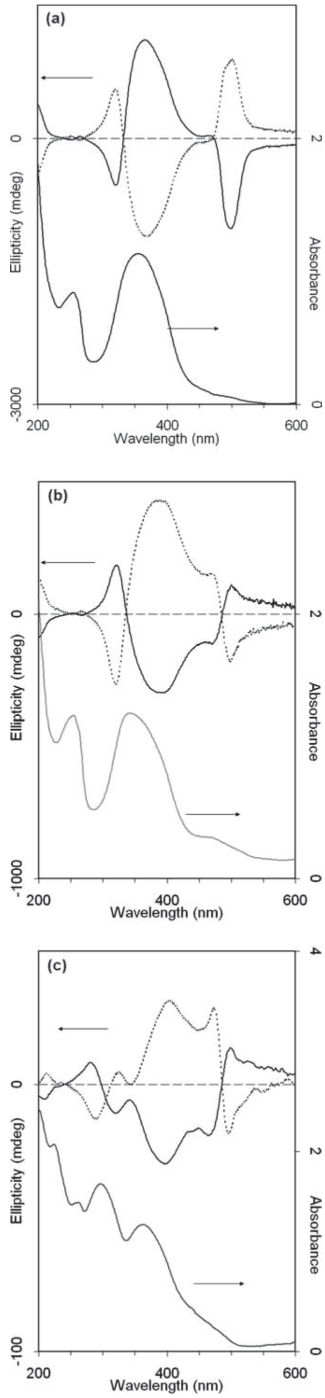


FIGURE 6 UV–vis (—) and CD spectra of r-CPL (—) and l-CPL (• • •) irradiated films of (a) **P2-AZO**, (b) **P3-AZO/AZO**, and (c) **P3-AZO/CNB**.

units and a slight Cotton effect corresponding to the ϕ–ϕ* band. Moreover, a nonabsorptive signal appeared around 500 nm probably due to a selective reflection caused by a long range helical organization.[34] The light handedness determines the sign of the CD response. Accordingly, r-CPL transfers a chiral order to the azobenzene units which yields a positive exciton couplet of the π–π* band while l-CPL generates the opposite chiral order and, thus, a negative exciton couplet. The CPL irradiation modified noticeably the UV–vis spectra of **P2-AZO**. Moreover, any modification of the photo-induced chiral response was not detected on the irradiated film after the storage at 30 °C for two months. The behavior of **P2-AZO** is similar to what we have previously reported for liquid crystalline side-chain poly(methyl methacrylate)s with pendant azobenzene moieties and comparable glass transition temperature.[21]

The behavior of the polymers with bifunctional units is slightly different than for **P2-AZO** and other related compounds. As expected, **P3-AZO/AZO** and **P3-AZO/CNB** showed a chiral response under CPL irradiation and the sense of the CD spectra depends on the handedness of the CPL. The most intense CD band of the **P3-AZO/AZO** spectrum is the exciton couplet corresponding to the π–π* transition of the azobenzene units, which proves a chiral order between azobenzene chromophores. For **P3-AZO/CNB** the exciton couplet due to 4-cyanoazobenzene moieties is overlapped with the one corresponding to the π–π* band of the 4-cyanobiphenyl, which points to a chiral arrangement of the nonphotosensitive biphenyl units induced by CPL through azobenzene organization.[45] After storing at room temperature for 24 h, the CD signal of the irradiated **P3-AZO/AZO** decreases a 50% while the CD response of **P3-AZO/CNB** disappears. The glass transition temperatures of these polymers are around room temperature (28 and 19 °C, respectively); thus, according to reported results, the stability of the CD signals on storage at room temperature depends on the ratio between T_g of the material and room temperature.[21] The CD spectra of the irradiated polymers with bifunctional units around 500 nm seems to point to an exciton couplet of the n–π* band better than a nonabsorptive band due to a selective reflection. This difference between monofunctional and bifunctional side-chain azo polymer suggests that the photo-induced chiral supramolecular arrangement is affected by the density of the chromophores which imposes a close packing. This preliminary result is currently under investigation with the aim of clarifying the photo-induced chiral order in high concentrated azo polymers and the origin of the exciton couplet of the n–π* band.

EXPERIMENTAL

Synthesis of Bifunctional Azides by Sequential ATRP and CuAAC

Synthesis of Poly(propargyl methacrylate) by ATRP

To a Schlenk charged with CuBr (42.90 mg, 0.30 mmol) under argon atmosphere was added (trimethylsilyl)propargyl methacrylate (TMSPMA) (9.00 g, 45.92 mmol), distilled anisole (60 mL), 1,1,4,7,7-pentamethyldiethylenetriamine (PMDETA) (63 μL, 0.30 mmol), and ethyl 2-bromoisobutyrate (EBB) (45 μL, 0.30 mmol). Oxygen was removed by successive pump-thaw cycles by applying vacuum and backfilling with argon. Polymerization was carried out at 90 °C for 24 h. Cu(I) complex was removed by treatment with the acid ion-exchange resin Dowex® Marathon MSC. The resin was filtered off, and the solution was poured into cold methanol to isolate the poly(trimethylsilylpropargyl methacrylate) (**P3-C≡C—TMS**) as a white solid that was dried under vacuum (50% yield). IR (KBr disk, cm^{-1}): 2190 (C≡C st), 1741 (C=O st), 1253, 850 (Si—C st). ^{1}H NMR (400 MHz, CDCl$_3$, δ, ppm): 4.59, 1.89, 1.08–0.92, 0.18. Anal. Calcd. for $C_{10}H_{16}O_2Si$: C, 61.18; H 8.21 Found: C, 59.56; H, 8.59. SEC (THF) $M_w = 11{,}400$, $M_w/M_n = 1.26$. To a solution of the polymer **P3-C≡C—TMS** (400 mg, 2.04 mmol) in THF (100 mL) cooled in an isopropanol/liquid nitrogen bath was added dropwise a solution of tetrabutylammonium fluoride (TBAF) (960 mg, 3.67 mmol) in THF (3 mL). The solution was warmed to room temperature and stirred overnight. The reaction was vacuum concentrated and the polymer was precipitated by pouring the mixture into cold methanol/water (10:2 v/v). The polymer was recovered by filtration and dried under vacuum (52% yield). IR (KBr disk, cm^{-1}): 3301 (≡C—H st), 2136 (C≡C st), 1739 (C=O st). ^{1}H NMR (400 MHz, CDCl$_3$, δ, ppm): 4.61, 2.50, 1.89, 1.25, 1.09. Anal. Calcd. for $C_7H_8O_2$: C, 67.73; H, 6.50. Found: C, 67.00; H, 7.47. SEC (THF) $M_n = 11{,}000$, $M_w/M_n = 1.24$.

General Procedure for the Synthesis of Bifunctional Polymers by CuAAC

A mixture of the polymer bearing alkyne groups **P3-C≡C—H** (50 mg, 0.42 mmol), the azide **N$_3$-AZO/AZO** (0.43 mmol, 2.5% molar excess), CuBr (6.03 mg, 0.04 mmol), and PMDETA (8.87 μL, 0.04 mmol) in deoxygenated DMF (3 mL) was placed in a Schlenk tube under argon atmosphere. The reaction was stirred at 50 °C for 3 days and then Cu(I) cations were removed by stirring with the ion-exchange resin (400 mg) Dowex®Marathon MSC. The resin was filtered off and the solution was evaporated to dryness. The residue was taken with a minimum amount of THF and the polymer was precipitated by pouring the solution into cold methanol. The residual azide was removed by SEC using Bio-Beads® S-X1. The precipitate was again dissolved in a minimum amount of THF and precipitated into cold methanol to yield the desired polymer (the polymer was recovered in 70–80% weight yield assuming the complete coupling reaction).

Physical Characterization Data of P3-AZO/AZO

IR (KBr disk, cm^{-1}): 2223 (C≡N st), 1774 (C=O st), 1738 (C=O st), 1601, 1501. ^{1}H NMR (400 MHz, CDCl$_3$, δ ppm): 7.85, 7.71, 7.59, 6.92, 5.08, 4.75, 4.57, 4.23–4.11, 3.93, 2.24, 1.72–1.17. Anal. Calcd. for $C_{62}H_{75}N_9O_{10}$: C, 67.31; H, 6.83; N, 11.39. Found: C, 67.47; H, 6.92; N, 11.59. SEC (THF) $M_n = 37{,}900$, $M_w/M_n = 1.46$.

Physical Characterization Data of P3-CNB/CNB

IR (KBr disk, cm^{-1}) 2225 (C≡N st), 1776 (C=O st), 1733 (C=O st), 1603. ^{1}H NMR (400 MHz, CDCl$_3$, δ ppm): 7.96, 7.58, 7.45, 6.90, 5.07, 4.73, 4.56, 4.22–4.10, 3.91, 2.23, 1.72–1.16. Anal. Calcd. for $C_{62}H_{75}N_5O_{10}$: C, 70.90; H, 7.20; N, 6.67. Found: C 70.48; H, 7.41; N, 6.71. SEC (THF) $M_n = 37{,}700$, $M_w/M_n = 1.28$.

Physical Characterization Data of P3-AZO/CNB

IR (KBr disk, cm^{-1}) 2226 (C≡N st), 1772 (C=O st), 1736 (C=O st), 1603. ^{1}H NMR (400 MHz, CDCl$_3$, δ ppm): 7.88, 7.74, 7.61–7.57, 7.47, 6.93, 5.11, 4.76, 4.59, 4.23–4.15, 3.96, 2.27, 1.75–1.19. Anal. Calcd. for $C_{62}H_{75}N_7O_{10}$: C, 69.06; H, 7.01; N, 9.09. Found: C, 68.03; H, 7.11; N, 8.73. SEC (THF) $M_n = 38{,}200$, $M_w/M_n = 1.45$.

Techniques

Infrared spectra were measured on an ATI-Matsson Genesis Series FTIR using KBr pellets. NMR spectra were recorded on a Bruker AV-400 spectrometer operating at 400 MHz for ^{1}H and 100 MHz for ^{13}C or on a Bruker AV-500 spectrometer operating at 500.13 MHz for ^{1}H and at 125.7 MHz for ^{13}C. Elemental analysis was performed with a Perkin-Elmer 240C microanalyzer. Molecular weight and polydispersity were measured by size exclusion chromatography (SEC) using a Waters 2695 liquid chromatography system equipped with a Waters 2420 evaporation light scattering detector using a combination of two Ultrastyragel columns with pore size of 500 and 10^4 Å, calibrated using poly(methyl methacrylate) standards and THF as solvent.

The optical textures of the mesophases were studied with an Olympus BH-2 polarizing microscope equipped with a Linkam THMS600 hot stage and a CS196 cooling system. Differential scanning calorimetry (DSC) was performed using a DSC Q2000 from TA Instruments with samples ($\approx$3 mg) sealed in aluminium pans at a scanning rate of 10 or 20 °C min^{-1} under a nitrogen atmosphere. Temperatures were read at the maximum of the transition peaks, and the glass transition temperature was read at the midpoint of the heat capacity increase. Thermogravimetric analysis (TGA) was performed at 10 °C/min under nitrogen atmosphere using a TGA Q5000IR from TA Instruments. TGA data are given as the onset of the decomposition curve, and DTGA data are given at the maxima of the weight derivative curve peaks.

UV–vis absorption spectra were measured with a UV4-200 from ATI-Unicam using 10^{-4} to 10^{-5} M solutions in THF.

Film Processing and Irradiation

Polymer films were prepared by casting a chloroform solution of the polymers onto clean, fused silica slides. The absorbance of as-casted films at the π–π* transition of the azobenzene units was around 1.2. The films showed a good transparency, and no noticeable scattering was detected either by optical or thermal treatments. The circular dichroism (CD) and UV–vis spectra of the polymer films were obtained using a Jasco J-810 spectropolarimeter. The CD spectra of the films were registered by rotating the samples every 60 degrees around the light beam axis in order to verify that linear dichroism contribution to CD responses is insignificant. Before irradiation with circularly polarized light (CPL), films were thermally treated by annealing in the isotropic state for 5 min followed by annealing at the mesophase temperature for 15 min and subsequent rapid cooling to room temperature (rt). Irradiation with left-circularly polarized light (l-CPL) or right-circularly polarized light (r-CPL) was carried out using the 488-nm line of an Ar^+ laser (power 20 mW/cm^2).

CONCLUSIONS

Free radical polymerization in a solution of azobenzene methacrylates mostly yields low to moderate molecular weight polymers with wide molecular weight distributions. Even polymerization of methacrylates by controlled radical polymerization techniques such as ATRP or RAFT produces better defined polymers but still, most of them with moderate molecular weights.[22,39,46] Therefore, combining ATRP and CuAAC methodologies is a versatile and efficient strategy to attain degrees of functionalization that cannot easily reach by direct polymerization of azobenzene methacrylates. In particular, postfunctionalization of a common polymeric skeleton of moderate M_n poly(propargyl methacrylate) with bifunctional azides brings in densely functionalized polymers. In addition, the use of heterofunctionalized azides allows the modulation of the polymer properties. For instance, incorporation of the 4-cyanobiphenyl unit decreases the glass transition temperature and the mesophase to isotropic transition temperature.

The characterization of the materials has demonstrated that the 1,2,3-triazole heterocycle formed by CuAAC has a remarkable influence on the thermal behavior by increasing the T_g of the polymer but does not alter any other properties such as the thermal stability, the mesomorphic properties, or the optical properties of the photoresponse to CPL.

Besides, this polymer architecture obtained by a combination of ATRP and click chemistry is compatible with the transfer of the chirality from light to material using the azobenzene units as chiral mediator.

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