

Communication

A bifunctional amorphous polymer exhibiting equal linear and circular photo-induced birefringences.^a

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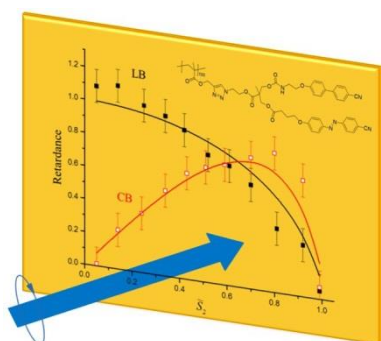
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The large and reversible photo-induced linear and circular birefringences in azo-compounds are at the basis of the interest in these materials which are potentially useful for several applications. Since the onset of the linear and circular anisotropies relies on orientational processes which typically occur on molecular and supramolecular length scale respectively, a circular birefringence at least one order of magnitude lower than the linear one is usually observed. Here the synthesis and the characterization of an amorphous polymer with a dimeric repeating unit containing a cyanoazobenzene and a cyanobiphenyl moieties is reported, in which identical optical linear and circular birefringences are induced for proper light dose and ellipticity. A pump-probe technique and an analytical method based on the Stokes-Mueller formalism have been used to investigate the photo-induced effects and to

^a **Supporting Information** is available online from the Wiley Online Library or from the author.

evaluate the anisotropies. The peculiar photo-response of the polymer makes it a good candidate for applications in smart functional devices.

FIGURE FOR ToC_ABSTRACT



1. Introduction

Azobenzene-containing materials have been widely studied during the last three decades because of the feasibility of manipulating their optical properties by light.^[1-4] They have provided the basis for several relevant phenomena in light-matter interactions, such as photo-induced anisotropy,^[5] light initiated mass transport,^[6,7] polarization dependent chiral structures^[8] and polarization holography.^[9] Despite many years of research effort, these materials continue to reveal new phenomena both in the inter-intra molecular interactions and in the light-matter interactions. The appearance of spiral-shaped relief patterns under the illumination of focused Laguerre–Gauss beams^[10] and a photo-induced anisotropy with a radial contribution^[11] are some examples. Azobenzene molecules undergo a reversible *trans-cis-trans* photo-isomerization by irradiating them with light of appropriate wavelength.^[12] As a consequence, complex photomechanical effects occur giving rise to anisotropic alignment perpendicular to the polarization of the incident light as well as important molecular mass transport. Another property of azobenzene compounds is the appearance of significant circular anisotropy on irradiation with circularly polarized light.^[8,13-16] This phenomenon is connected to the angular momentum transfer from the light to the chromophores; being these latter attached to the material backbones, they rotate around to the light propagation direction, inducing chirality of the whole structure with a sense which depends on the handedness of the exciting light.^[17] Thereby, the possibility to orient azo-materials in nearly any direction and their light-induced molecular displacement, enables them to be transformed into sophisticated shapes^[12], providing new opportunities for the fabrication of micro- and nano-architectures.^[18] Large and reversible photo-induced linear (*LB*) and circular birefringences (*CB*) make azo-materials very attractive for optical data storage and, more particularly, for holographic recording applications, which enable optical devices whose properties strongly depend on the relative values of *LB* and *CB* ^[9].

The possibility to induce *LB* and *CB* in azo-materials by irradiation with properly polarized light has been widely demonstrated, but a *CB* at least one order of magnitude lower than the linear one is usually observed.^[19, 20] Indeed *LB* and *CB* occur at molecular and supramolecular level respectively,^[21, 22] and as a consequence, a different growth rate versus the radiation dose is generally observed.^[23] Moreover, the photo-induced anisotropies are associated not only to the reorientation of the azobenzene moieties, but also to the organization of the whole polymer chain.^[24, 25] In this regard, the macromolecular backbone plays an important role.

Here we report the synthesis and the characterization of an amorphous side-chain azobenzene polymer **P-CNB/AZO** with a repeating unit containing calamitic 4-cyano-4'-oxyazobenzene and 4-cyano-4'-oxybiphenyl moieties (**Figure 1**) which has a densely functionalized and regular structure with the two units precisely positioned along the macromolecular chain. The polymer has been prepared by post-functionalization of poly(propargyl methacrylate) (**PPMA**) skeleton with an azide *via* a copper(I)-catalyzed azide-alkyne cycloaddition: a straight way to get densely functionalized polymers with a controlled monomer sequence where the use of heterobifunctional azides also allows the modulation of the thermal and the optical properties.^[26]

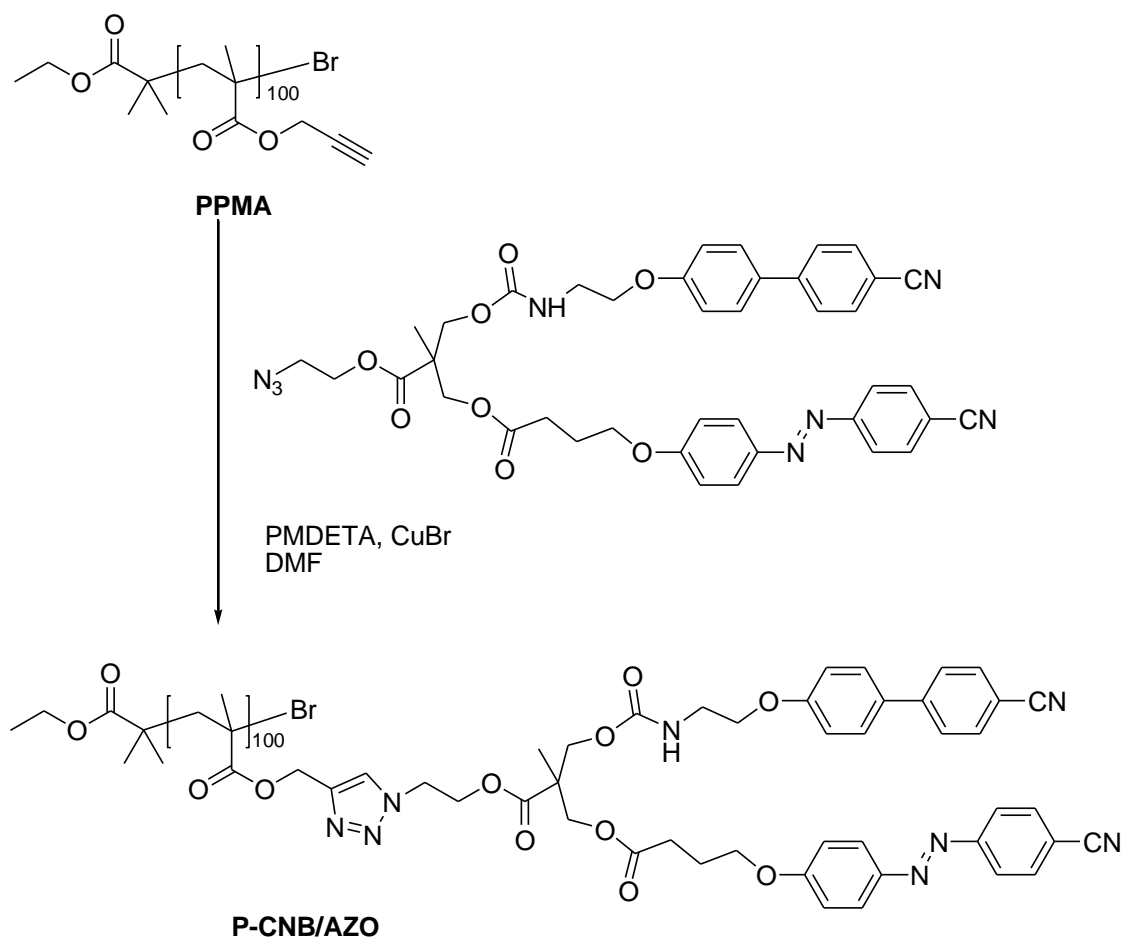


Figure 1. Synthesis and chemical structure of the target P-CNB/AZO polymer.

A pump-probe technique has been used to investigate the photo-induced effects, and an analytical method based on the Mueller matrix formulation and the Stokes parameters has been adopted in order to evaluate LB and CB . The analyses demonstrate the possibility for obtaining $LB \approx CB$, for proper light ellipticity and dose. Moreover, in contrast with the conventional assumption of CB proportional to the ellipticity the exciting light,^[9, 19] an alternative dependence is proposed which accounts for the reported non-monotonous behavior of CB , that reaches its maximum for an ellipticity $e \cong 0.8$ and decreases for larger ellipticity, down to zero at $e \cong 1$.

2. Experimental section

Full details for the synthesis and characterization of the intermediates as well as the characterization techniques are available online in the supporting information.

Synthesis of functionalized poly(propargyl methacrylate) P-CNB/AZO. A Schlenk flask was charged with poly(propargyl methacrylate) (PPMA) (31.0 mg, 0.3 mmol), the azide (10) (0.372 g, 0.5 mmol) and CuBr (3.6 mg, 0.03 mmol) under argon atmosphere. *N,N,N',N'',N'''*-pentamethyldiethylenetriamine (PMDETA) (5.2 μ L, 0.03 mmol) and *N,N*-dimethylformamide (2.5 mL) were added and the flask evacuated via three freeze-pump-thaw cycles. The reaction mixture was heated to 35°C and stirred for 3 days. The reaction was poured into THF (20 mL) and filtered through neutral alumina pad. DOWEX Marathon acid exchange resin was added and the dispersion was stirred for 4 h at room temperature. The resin was filtered off and the volatiles were removed in a rotary-evaporator. Residual azide was removed by preparative SEC and the polymer precipitated in cold methanol. The desired polymer P-CNB/AZO was isolated as a fine orange solid (0.178 g, 81% yield). IR (KBr) ν = 3418 (N–H), 2230 (C \equiv N), 1746 (C=O). ^1H NMR (400 MHz, CDCl_3 , δ): 8.11–7.71, 7.71–7.58, 7.58–7.50, 7.49–7.42, 7.41–7.28, 6.95–6.76, 5.81–5.50, 5.24–4.83, 4.70–4.52, 4.52–4.30, 4.25–4.03, 4.01–3.85, 3.57–3.30, 2.57–2.31, 2.08–1.88, 1.84 –1.43, 1.25–1.00, 1.00–0.57; Anal. calcd. for $\text{C}_{47}\text{H}_{46}\text{N}_8\text{O}_9$, C 63.94 H 5.52 N 12.69; found, 63.97, H 5.23, N 12.90; $M_n^{\text{NMR}} = 87000 \text{ g mol}^{-1}$; $M_n^{\text{SEC}}(\text{DMF}) = 89000 \text{ g mol}^{-1}$, $D^{\text{SEC}} = 1.15$.

Optical Characterization. The sample used in the experiment is a 20 μm -thick polymer film confined between two glass plates, prepared by melting the polymer above the T_g and cooling it down to room temperature. The sample has been exposed to a single pump beam at $\lambda_{\text{pump}} = 488 \text{ nm}$ (Ar^+ laser Innova 90C, Coherent Inc.) and a probe beam at $\lambda_{\text{probe}} = 633 \text{ nm}$ (He-Ne laser 05-LHP-201, Melles-Griot), far from the absorption band of the polymer, has been used to investigate the photo-induced anisotropies. Both the pump and probe beams pass

through the proper quarter-wavelength plate in order to span the ellipticity range, from $e = 0.01$ (linear) to $e = 0.99$ (circular), keeping the major axis of the ellipse along the y -axis and the radiation dose at 5 J/cm^2 . The pump beam is expanded to a spot size of 4 mm and overlaps at a small angle with the probe beam in the polymer layer (see **Figure 2**). The spot size of probe beam on the sample is smaller than the pump beam one (2 mm) in order to investigate the central part of the irradiated area. The sample is placed in an oven and the measurements are carried out at the same temperature (25°C), after thermal annealing above the T_g and controlled cooling down to bring the sample back to the amorphous state.

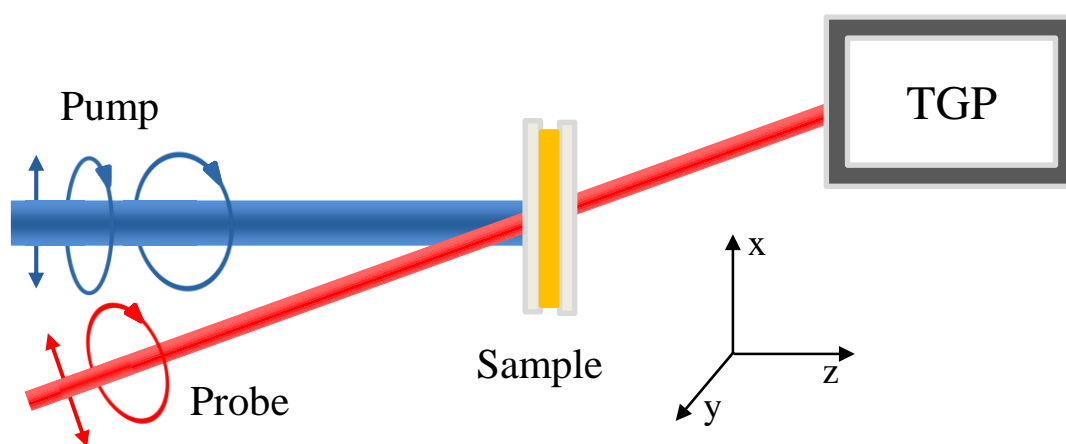


Figure 2. Scheme of the experimental set-up. TGP, two gratings polarimeter.

3. Results and Discussion

Modular synthetic strategies that combine controlled radical polymerizations with highly efficient ligation methodologies are a convenient and versatile approach to simplify the access to rationally designed polymeric materials with a precise level of control over composition, functionality or architecture.^[27] Accordingly, the target polymer P-CNB/AZO was prepared as outlined in Figure 1 by post-functionalization of PPMA, obtained by atom transfer radical polymerization, using a heterobifunctional azide obtained from a cyclic carbonate precursor

from 2,2-bis(hydroxymethyl)propionic acid (bis-MPA) (full characterization details are given in the supporting information). To impede the formation of liquid crystalline phases on the target polymer, linking spacers were shortened to a three atoms length. In differential scanning calorimetry (DSC), polarizing optical microscopy (POM) and X-ray diffraction (XRD) the polymer was confirmed as amorphous with a T_g at 67 °C, well-above room temperature, and no liquid crystalline properties were observed (see supporting information). The photo-induced linear and circular birefringence has been evaluated by means of a two gratings polarimeter (TGP) ^[28], adopting the Mueller matrix formulation^[29].

The Stokes vector

$$\vec{S} = \begin{bmatrix} S_0 \\ S_1 \\ S_2 \\ S_3 \end{bmatrix} = S_0 \begin{bmatrix} 1 \\ \tilde{S}_1 \\ \tilde{S}_2 \\ \tilde{S}_3 \end{bmatrix} = \begin{bmatrix} I_x + I_y \\ I_{+45^\circ} - I_{-45^\circ} \\ I_{LC} - I_{RC} \\ I_x - I_y \end{bmatrix} \quad (1)$$

completely describe the polarization state of a light beam, where S_0 represents the total light intensity, S_1 , S_2 and S_3 are the difference between the +45° and -45°, left- and right-circularly components, horizontal (x -axis) and vertical (y -axis) linearly polarized components, respectively. \tilde{S}_1 , \tilde{S}_2 and \tilde{S}_3 are the normalized Stokes parameters. A 4x4 Mueller matrix \vec{M} describes how an optical medium influences the light beam that passes through it, according to $\vec{S}_{OUT} = \vec{M} \times \vec{S}_{IN}$, where \vec{S}_{IN} and \vec{S}_{OUT} represent the incident and the transmitted beam.^[30] In the case of a medium exhibiting linear and circular birefringence, with optical axis parallel to the x -axis, the Mueller matrix $\vec{M}_{LB,CB}$ is ^[31]

$$\vec{M}_{LB,CB} \cong \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 - \frac{1}{2}(CB^2 + LB^2) & -LB + \frac{1}{6}(CB^2LB + LB^3) & -CB + \frac{1}{6}(CBLB^2 + CB^3) \\ 0 & LB - \frac{1}{6}(CB^2LB + LB^3) & 1 - \frac{1}{2}LB^2 & -\frac{1}{2}CBLB \\ 0 & CB - \frac{1}{6}(CBLB^2 + CB^3) & -\frac{1}{2}CBLB & 1 - \frac{1}{2}CB^2 \end{bmatrix} \quad (2)$$

where $LB = (\pi \Delta n_{lin} d) / \lambda$, $CB = (\pi \Delta n_{circ} d) / \lambda$, d is the thickness of the material, λ the probe wavelength and Δn_{lin} and Δn_{circ} are the linear and the circular birefringence, respectively.

$\vec{M}_{LB,CB}$ in (2) well represents the optical response of azo-compounds, in which the chromophores and, consequently, the optical axis align perpendicularly to the major axis of polarization ellipse of the pump beam (i.e. y -axis). The values of LB and CB can be calculated, independently from each other, from \vec{S}_{OUT} for two different input polarization states of the probe beam, i.e. linear polarization parallel to the x -axis (\vec{S}_{IN}^x) and a left circular polarization (\vec{S}_{IN}^{LC}). In the first case

$$\vec{S}_{OUT}^x = \vec{M}_{LB,CB} \times \vec{S}_{IN}^x = \vec{M}_{LB,CB} \times S_0 \begin{bmatrix} 1 \\ 0 \\ 0 \\ 1 \end{bmatrix} = S_0 \begin{bmatrix} 1 \\ -CB + \frac{1}{6}(CBLB^2 + CB^3) \\ -\frac{1}{2}CBLB \\ 1 - \frac{1}{2}CB^2 \end{bmatrix} \quad (3)$$

for which it is easy to calculate $CB = \sqrt{2(1 - \tilde{S}_{OUT,3}^x)}$ after the measuring of $\tilde{S}_{OUT,3}^x$ by means of the TGP. With the left circular polarization

$$\vec{S}_{OUT}^{LC} = \vec{M}_{LB,CB} \times \vec{S}_{IN}^{LC} = \vec{M}_{LB,CB} \times S_0 \begin{bmatrix} 1 \\ 0 \\ 1 \\ 0 \end{bmatrix} = S_0 \begin{bmatrix} 1 \\ -LB + \frac{1}{6}(CB^2 LB + LB^3) \\ 1 - \frac{1}{2}LB^2 \\ -\frac{1}{2}CBLB \end{bmatrix}, \quad (4)$$

it is possible to evaluate $LB = \sqrt{2(1 - \tilde{S}_{OUT,2}^{LC})}$.

In **Figure 3** we report the values of LB and CB induced by an elliptically polarized pump beam with the major axis parallel to the y -axis, versus the ellipticity $e \equiv \tilde{S}_{pump,2}$ of the pump beam ($\tilde{S}_{pump,1} = 0$ and $\tilde{S}_{pump,3} = \sqrt{1 - e^2}$). LB exhibits a conventional trend being proportional

to the difference of the intensities of light components polarized along and perpendicular to the axis of the polarization ellipse of the exciting light

$$LB = k_L \tilde{S}_{pump,3} = k_L \sqrt{1 - e^2}, \quad (5)$$

where $k_L = k_L(S_{pump,0})$ is the intensity dependent photo-response parameter of the medium for linear anisotropy.^[9]

On the contrary CB shows an unusual non-monotonous behavior, increasing up to its maximum value at $e \cong 0.8$ and decreasing for larger ellipticity, down to zero at $e \cong 1$. This trend is not accounted for by the conventional dependence, according to which $CB \propto e$,^[9, 19] therefore, here we propose

$$CB = k_C 2|\tilde{S}_{pump,3}|e, \quad (6)$$

where $k_C = k_C(S_{pump,0})$ is the intensity dependent photo-response parameter of the medium for circular anisotropy. This hypothesis has been validated by fitting the experimental data in Figure 3 with the Equation (5) and (6), where solid lines represent the fitting curve.

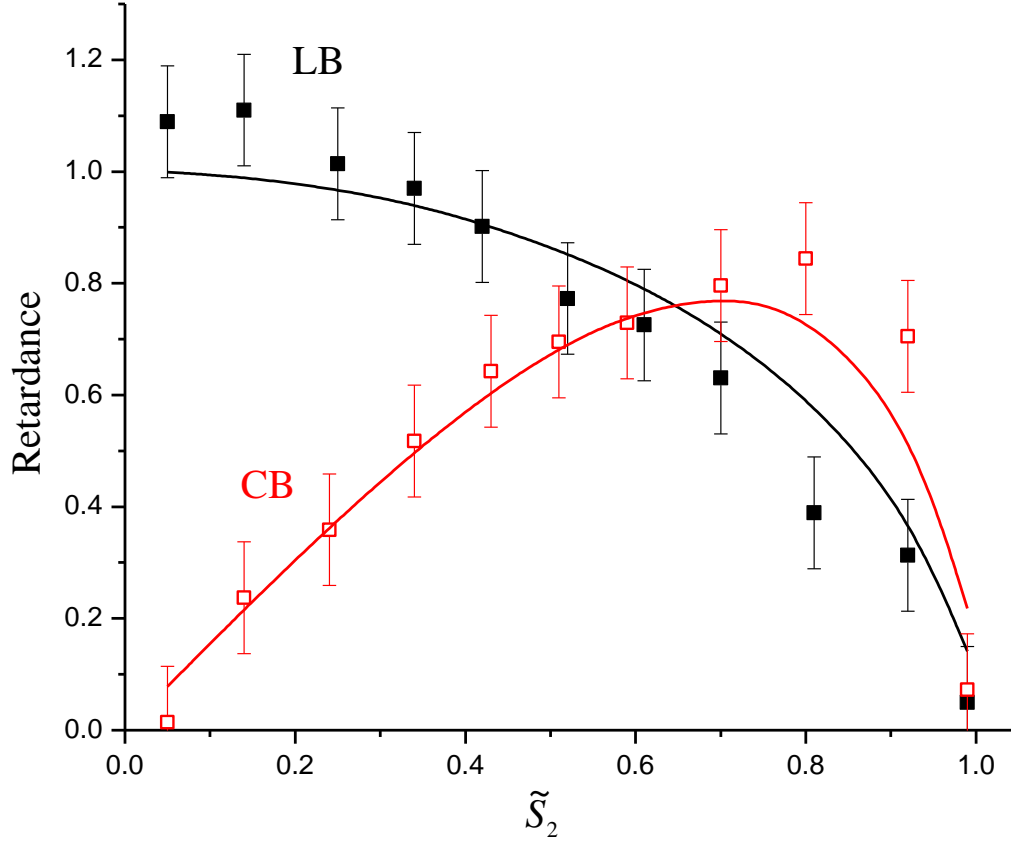


Figure 3. *LB* (black close squares) and *CB* (red open squares) photo-induced by an elliptically polarized pump beam with the major axis parallel to the x -axis, versus the ellipticity $e = \tilde{S}_2$ of the pump beam ($\tilde{S}_{pump,1} = 0$ and $\tilde{S}_{pump,3} = \sqrt{1 - e^2}$).

It is worth noting that, for $e = 0.6$ and a radiation dose of 5 J/cm^2 the values of *LB* and *CB* are equal. Also the maximum values $LB_{max}=1.1$ and $CB_{max}=0.8$, obtained at $e = 0$ and $e = 0.8$ respectively, are of the same order of magnitude. In addition, controlling also the dosage, we succeeded in making $LB_{max}=CB_{max}=1.0$ at 25 J/cm^2 . This is a remarkable result considering that the onset of the linear and circular birefringences in such class of materials rely on orientational processes which typically occur on molecular and supramolecular length scale, respectively.

Since the propagation of elliptically polarized light and the consequent formation of the chiral structures strongly depends on the material backbone, we believe that the structure of the side-chain amorphous polymer **P-CNB/AZO** characterized by a constitutional repeating unit containing both a 4-cyanoazobenzene moiety and a promesogenic 4-cyanobiphenyl moiety plays a fundamental role in determining its unique photo-induced response.

4. Conclusions

We report the synthesis and an optical study of a light responsive amorphous side-chain polymethacrylate polymer, whose repeating unit contains both cyanoazobenzene and cyanobiphenyl moieties. An investigation, based on uniform polarized light irradiation in pump-probe configuration, reveals the potential for obtaining comparable values of linear and circular photo-induced birefringences for proper light dose and ellipticity. The ordered arrangement of azobenzene and cyanobiphenyl moieties along the polymeric structure should play a crucial role with respect to its photo-induced optical properties. Considering the long time stability, the full reconfigurability related to the intrinsic reversibility of the photo-induced processes, the polymer can be considered a good candidate for applications in smart functional devices. In particular a polarization holographic recording based on the interference of two waves with orthogonal linear polarization could demonstrate the possibility to obtain a polarization hologram able to decompose an incident light field into a set of linear basis that it is possible only if $LB=CB$. Because of the strict required features of the material related to identical optical birefringences, this optical device, to the best of our knowledge, has not yet attained.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author

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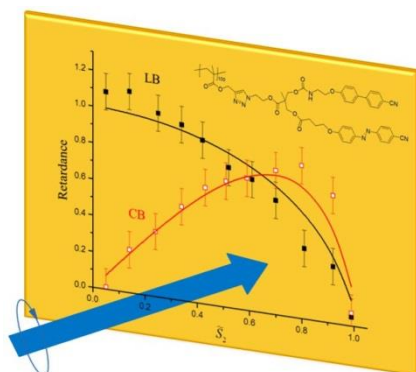
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A bifunctional polymer characterized by a regular arrangement of the azobenzene and cyanobiphenyl moieties along the macromolecular chain has been synthesized. An optical investigation of the material reveals the potential for obtaining equal values of linear and circular photo-induced anisotropies. This peculiar aptitude makes the material a good candidate for smart optical devices.

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1. Experimental procedures and materials

Reagents were purchased either from Sigma-Aldrich or TCI Company and used as received. Tetrahydrofuran (THF) and dichloromethane were dried using Innovative technologies PureSolv[®] system, toluene was dried over calcium hydride and distilled, *N,N*-dimethylformamide (DMF) was dried over anhydrous calcium sulfate for 72 h, distilled at reduced pressure and deoxygenated by bubbling argon through before use. 4-(Dimethylamino)pyridinium *p*-toluenesulfonate (DPTS) was prepared from 4-(dimethylamino)pyridine and *p*-toluenesulfonic acid in THF.

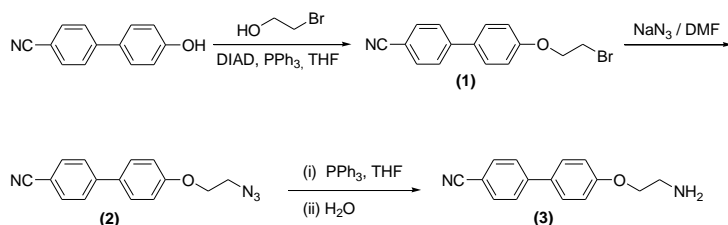
Medium pressure liquid chromatography (MPLC) was performed using a BUCHI C-605 pump module and C-615 pump manager. Silica gel 60Å pore size, 70-230 mesh particle size, was used for the stationary phase. Preparative size exclusion chromatography (SEC) was performed using Bio-Beads[®] SX-1 (approx. 10 g of resin / 150 mg of polymer) as the stationary phase and THF as eluent.

The functionalized polymer **P-CNB/AZO** was by prepared by combining a radical controlled polymerization by atom transfer radical polymerization (ATRP) with a highly efficient ligation reaction copper(I)-catalyzed azide-alkyne cycloaddition (CuAAC). The precursor, poly(propargyl methacrylate) (PPMA) was obtained by ATRP of triethylsilylpropargyl methacrylate and subsequent deprotection of the alkyne group. It had an average polymerization degree of 100 estimated by ¹H NMR spectroscopy and dispersity (*D*) of 1.15

determined by size exclusion chromatography. In contrast to previous report, to simplify the preparation of the target heterobifunctional azide, a cyclic carbonate precursor of bis-MPA was used as proposed by Fréchet and co-workers. CuAAC post-functionalization was carried out using CuBr/*N,N,N',N'',N''*-pentamethyldiethylenetriamine catalytic system in *N,N*-dimethylformamide and an azide/alkyne 2:1 molar ratio to assure the completeness of the reaction. Excess of azide was easily removed by size exclusion chromatography and ¹H-NMR and FT-IR spectroscopies gave no evidence of unreacted alkyne groups in the post-functionalized polymer.

1.1. Synthesis of the amino and carboxylic acid precursors of the azide

The required amino derivative was prepared following the reactions sequence shown in Scheme S1. The carboxylic acid was prepared as outlined in Scheme S2.



Scheme S1. Synthesis of the 4-(2-aminoethoxy)-4'-cyanobiphenyl (**3**)

1.1.1. Synthesis of 4-(2-bromoethoxy)-4'-cyanobiphenyl (**1**)

2-Bromoethanol (3.749 g, 30.0 mmol) and diisopropyl azodicarboxylate (DIAD) (6.066 g, 30.0 mmol) were added to a solution of 4-hydroxy-4'-cyanobiphenyl (6.066 g, 30.0 mmol) in anhydrous THF (20 mL) under argon atmosphere and cooled down to 0 °C. Then, a triphenylphosphine (PPh₃) (7.864 g, 30.0 mmol) solution in anhydrous THF (15 mL) was added dropwise. The reaction mixture was stirred for 18 h at room temperature. The solvent was rotary-evaporated and the residue extracted with hexane/ethyl acetate (7:3 v/v) (320 mL).

The remaining solid was discarded and the organic solution washed with a saturated aqueous NaHCO₃ solution (2×100 mL), a saturated aqueous NaCl solution (100 mL) and dried over anhydrous MgSO₄. The solvent was evaporated and the product purified by flash column chromatography using silica gel and hexane/ethyl acetate (9:1) as eluent (R_f = 0.38) to render the target product (**1**) as a white solid (6.175 g, 69% yield); mp = 79 °C; IR (KBr): ν = 2228 (C≡N); ¹H NMR (400 MHz, CDCl₃, δ): 7.75–7.66 (m, 2H), 7.66–7.60 (m, 2H), 7.58–7.49 (m, 2H), 7.07–6.96 (m, 2H), 4.35 (t, *J* = 6.2 Hz, 2H), 3.67 (t, *J* = 6.2 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃, δ): 158.7, 145.0, 132.6, 132.3, 128.5, 127.2, 119.1, 115.3, 110.3, 68.0, 29.0.

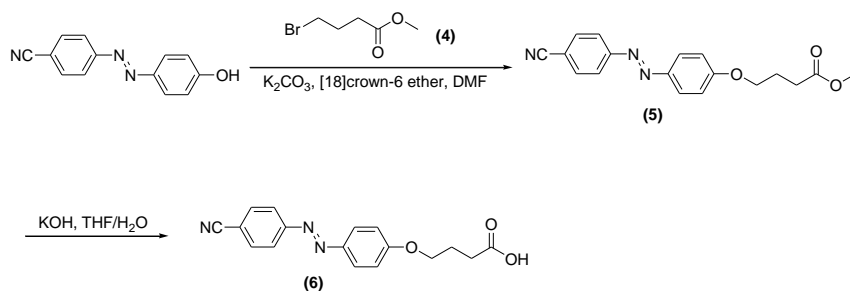
1.1.2. Synthesis of 4-(2-azidoethoxy)-4'-cyanobiphenyl (**2**)

A mixture of (**1**) (5.000 g, 16.5 mmol) and sodium azide (3.230 g, 49.6 mmol) in DMF (20 mL) was stirred at 120 °C for 24 h. The reaction was then quenched by water addition (250 mL) and the product extracted with hexane/ethyl acetate (1:1) (3×200 mL). The combined organic phases were washed with water (2×200 mL) and a saturated aqueous NaCl solution (200 mL), and dried over anhydrous MgSO₄. The solvent was distilled off and the residue purified by recrystallization in absolute ethanol to yield the desired azido compound (**2**) as white crystals (4.151 g, 95% yield); mp = 74 °C; IR (KBr) ν = 2225 (C≡N), 2112 (N₃); ¹H NMR (400 MHz, CDCl₃, δ): 7.75–7.67 (m, 2H), 7.66–7.60 (m, 2H), 7.58–7.50 (m, 2H), 7.10–6.97 (m, 2H), 4.21 (t, *J* = 5.0 Hz, 2H), 3.64 (t, *J* = 5.0 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃, δ): 158.8, 145.0, 132.6, 132.2, 128.5, 127.2, 119.0, 115.2, 110.3, 67.1, 50.1.

1.1.3. Synthesis of 4-(2-aminoethoxy)-4'-biphenyl (**3**)

A solution of (**2**) (3.964 g, 15.0 mmol) and PPh₃ (4.721 g, 12.0 mmol) in anhydrous THF (300 mL) was stirred at reflux temperature while the reaction progress was monitored by thin layer chromatography (TLC) using dichloromethane as eluent (R_f = 0.12). After 3 h, distilled water was added (10 mL) and the mixture refluxed for additional 3 h. The solvent was evaporated and the target isolated white solid thoroughly washed with hexane/ethyl acetate (7:3) (3.503 g, 98%); mp = 102 °C; IR (KBr) ν = 3374 (N–H), 2227 (C≡N) ¹H-NMR (400

MHz, CDCl₃, δ): 7.72–7.67 (m, 2H), 7.66–7.61 (m, 2H), 7.57–7.51 (m, 2H), 7.05–6.98 (m, 2H), 4.05 (t, *J* = 5.2 Hz, 2H), 3.13 (t, *J* = 5.2 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃, δ): 159.5, 145.2, 132.6, 131.7, 128.4, 127.1, 119.1, 115.1, 110.1, 70.2, 41.5.



Scheme S2. Synthesis of 4-(4'-cyanophenylazo-4-phenoxy)butanoic acid (**6**)

1.1.4. Synthesis of methyl 4-bromobutanoate (**4**)

H₂SO₄ (conc) (65 mL) was added dropwise over a solution of 4-bromobutanoic acid (4.177 g, 25.0 mmol) in methanol (375 mL) that was then stirred at reflux temperature for 24 h. Afterwards, the solvent was removed in a rotary-evaporator, the residue taken into distilled water (150 mL) and extracted with dichloromethane (3×100 mL). The combined organic extracts were washed with a saturated aqueous NaHCO₃ solution (60 mL), dried over Na₂SO₄ and evaporated to yield the desired compound (**4**) as a yellowish oil (3.792 g, 84% yield); IR (NaCl) ν = 1739 (C=O), 1211, 1088, 773; ¹H NMR (400 MHz, CDCl₃, δ): 3.69 (s, 3H), 3.47 (t, *J* = 6.5 Hz, 2H), 2.51 (t, *J* = 7.2 Hz, 3H), 2.22–2.1.3 (m, 2H). ¹³C NMR (100 MHz, CDCl₃, δ): 173.0, 51.7, 32.7, 32.2, 27.7.

1.1.5. Synthesis of methyl 4-(4'-cyanophenylazo-4-phenoxy)butanoate (**5**)

A mixture of 4-cyano-4'-hydroxyazobenzene (3.840 g, 17.2 mmol), [18]crown-6 ether (0.185 g, 0.7 mmol) and K₂CO₃ (3.870 g, 28.0 mmol) in DMF (10 mL) was heated at 120 °C and then a solution of methyl 4-bromobutanoate (**4**) (2.600 g, 14.0 mmol) in DMF (10 mL) was added. After 24 h, the reaction was cooled to room temperature and distilled water was added

(200 mL). The reaction mixture was extracted with dichloromethane (3×100 mL) and the combined organic extracts subsequently washed with water (200 mL) and a saturated aqueous NaCl solution (200 mL), dried over anhydrous MgSO₄ and evaporated to dryness. The crude product was purified by flash column chromatography on silica gel using dichloromethane as eluent and recrystallization on methanol to yield the required product (**5**) (3.357 g, 75% yield); mp = 118 °C; IR (KBr) ν = 2220 (C≡N), 1732 (C=O); ¹H NMR (400 MHz, CDCl₃, δ): 7.97–7.90 (m, 4H), 7.83–7.76 (m, 2H), 7.05–6.97 (m, 2H), 4.12 (t, *J* = 6.1 Hz, 2H), 3.71 (s, 3H), 2.57 (t, *J* = 7.3 Hz, 2H), 2.21–2.12 (m, 2H); ¹³C NMR (100 MHz, CDCl₃, δ): 173.5, 162.3, 154.8, 146.9, 133.2, 125.5, 123.1, 118.7, 114.9, 113.2, 67.1, 51.7, 30.4, 24.5.

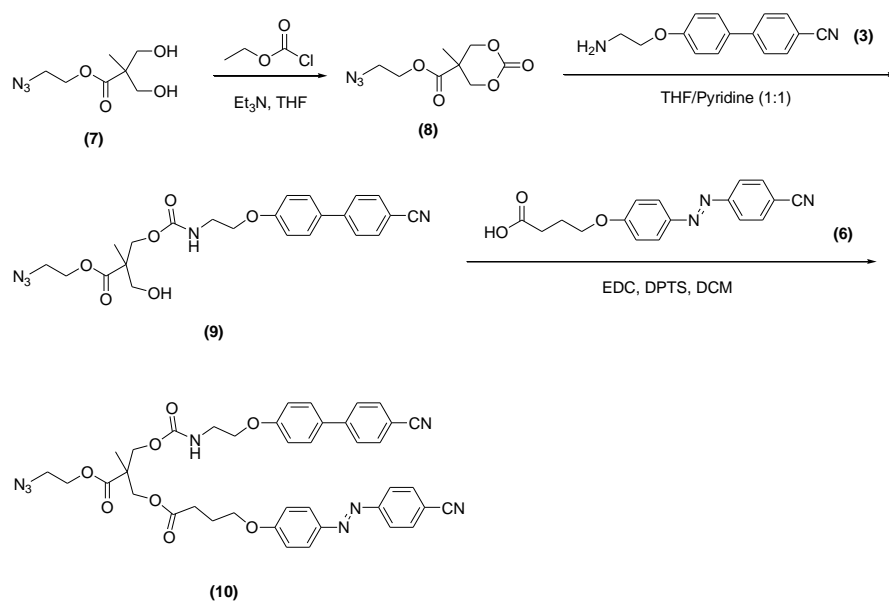
1.1.6. Synthesis of 4-[4'-cyanophenylazophenyl]butanoic acid (**6**)

An aqueous solution of KOH (7.670 g, 153.0 mmol of KOH in 50 mL of water) was added over a solution of (**5**) (2.900 g, 9.0 mmol) and [18]crown-6 ether (0.240 g, 0.9 mmol) in THF (50 mL). The reaction was stirred at room temperature for 72 h while the progress was monitored by TLC using hexane/ethyl acetate as eluent (4:1) (*R_f* = 0.05). Then the reaction was cooled into an ice bath and taken to pH=7 using HCl (conc). The orange precipitate was isolated by filtration, thoroughly washed with water and recrystallized in ethanol to give the desired product (**6**) as crystals (2.514, 90% yield); mp = 236 °C; IR (KBr) ν = 3227 (O–H), 2237 (C≡N), 1742 (C=O); ¹H NMR (400 MHz, DMSO-d₆, δ): 8.19–8.00 (m, 2H), 8.0–7.88 (m, 4H), 7.20–7.07 (m, 2H), 4.12 (t, *J* = 6.4 Hz, 2H), 2.41 (t, *J* = 7.3 Hz, 2H), 2.04–1.93 (m, 2H); ¹³C NMR (100 MHz, DMSO-d₆, δ): 174.1, 162.3, 154.2, 146.2, 133.8, 125.4, 123.0, 118.6, 115.3, 112.6, 67.4, 30.1, 24.2.

1.2. Synthesis of the azide

The target azide (**10**) was prepared as outlined in Scheme S3. This heterobifunctional azide was prepared from the 2,2-bis(hydroxymethyl)propionic acid precursor (**7**) whose details of synthesis and characterization have been previously reported.^[1] Because the introduction of

two different functional moieties in the bis-MPA derivative (**7**) might be complicated by the equal reactivity of its two hydroxyl groups, a cyclic carbonate (**8**) has been employed as proposed by Fréchet and coworkers.^[2] This symmetric carbonate substrate (**8**) can give a heterobifunctional azide by reacting sequentially with an amine, forming a carbamate linkage, and then with a carboxylic acid forming, an ester linkage.



Scheme S3. Synthesis of the target azide (**10**)

1.2.1. Synthesis of 5-(2-azidoethoxy)carbonyl-5-methyl-1,3-dioxan-2-one (**8**)

A solution of (**7**) (7.112 g, 35.0 mmol), ethyl chloroformate (22.790 g, 210.0 mmol) in THF (425 mL) was cooled to 0 °C. Then, triethylamine (Et₃N) (30.3 mL, 217.0 mmol) was added dropwise and the reaction stirred at room temperature overnight. The formed solid was filtered off and the solution evaporated to yield a liquid that was purified by flash column chromatography using silica gel and dichloromethane as eluent (*R_f* = 0.37) to yield the target compound (**8**) as a viscous oil (7.427 g, 93% yield); IR (NaCl) ν = 2104 (N₃), 1734 (C=O carbonate), 1700 (C=O ester); ¹H NMR (400 MHz, CDCl₃, δ): 4.72 (d, *J* = 11.0 Hz, 2H), 4.37 (t, *J* = 4.9 Hz, 2H), 4.22 (d, *J* = 11.0 Hz, 2H), 3.53 (t, *J* = 4.9 Hz, 2H), 1.36 (s, 3H); ¹³C NMR (100 MHz, CDCl₃, δ): 170.9, 147.3, 72.8, 64.7, 49.5, 40.3, 17.4.

1.2.2. Synthesis of 2-azidoethyl 3-(2-(4'-cyanobiphenyl-4-yloxy)ethylcarbamoyloxy)-2-(hydroxymethyl)-2-methylpropanoate (9)

A solution of (3) (3.574 g, 15.0 mmol) and pyridine (15 mL) in anhydrous THF (30 mL) was added dropwise to a solution (8) (3.438 g, 15.0 mmol) and pyridine (30 mL) in anhydrous THF (15 mL) stirred under argon atmosphere. The reaction mixture was stirred at room temperature overnight. Then, ethyl acetate (500 mL) was added and the resulting solution washed with NaHSO₄ 1M (2×300 mL), saturated aqueous NaCl solution (200 mL) and dried over anhydrous MgSO₄. The volatiles were removed in a rotary-evaporator and the crude purified by flash column chromatography using silica gel and dichloromethane/ethyl acetate (9:1) as eluent (R_f = 0.17) to give compound (9) as a waxy white solid (4.343 g, 62% yield); IR (KBr) ν = 3374 (N–H), 2226 (C≡N), 2107 (N₃), 1727 (C=O); ¹H NMR (400 MHz, CDCl₃, δ): 7.72–7.60 (m, 4H), 7.58–7.50 (m, 2H), 7.03–6.94 (m, 2H), 5.33 (t, *J* = 5.3 Hz, 1H), 4.38 (d, *J* = 11.5 Hz, 1H), 4.33 – 4.28 (m, 2H), 4.26 (d, *J* = 11.5 Hz, 1H), 4.09 (t, *J* = 5.1 Hz, 2H), 3.71 (d, *J* = 11.9 Hz, 1H), 3.65 (d, *J* = 11.9 Hz, 1H), 3.64 – 3.57 (m, 2H), 3.48 (t, *J* = 5.1 Hz, 2H), 2.28 (broad s, 1H), 1.22 (s, 3H); ¹³C NMR (100 MHz, CDCl₃, δ): 174.1, 159.0, 156.9, 145.0, 132.6, 132.2, 132.1, 132.0, 131.9, 131.8, 128.6, 128.4, 127.1, 119.0, 115.0, 110.2, 66.9, 66.0, 64.2, 63.5, 49.8, 48.8, 40.6, 17.4.

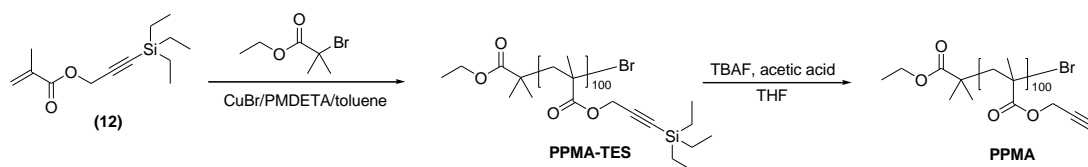
1.2.3. Synthesis of 3-(2-azidoethoxy)-2-((2-(4'-cyanobiphenyl-4-yloxy)ethylcarbamoyloxy)methyl)-2-methyl-3-oxopropyl 4-(4'-cyanophenylazo-4-phenoxy)butanoate (10)

A solution of (9) (2.524 g, 5.4 mmol), (6) (2.001 g, 6.5 mmol) and DPTS (0.314 g, 1.1 mmol) in anhydrous dichloromethane (60 mL) was cooled with an ice-salt bath under argon atmosphere for 20 min, and then a dispersion of 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDC) (1.242 g, 6.5 mmol) in anhydrous dichloromethane (40 mL) was added dropwise. Once addition was completed, the reaction mixture was allowed to warm to room temperature and stirred for 24 h while the reaction was

monitored by TLC using dichloromethane/ethyl acetate (9:1) as eluent ($R_f = 0.56$). The reaction mixture was diluted with dichloromethane (200 mL) and washed with distilled water (2×200 mL) and saturated aqueous NaCl solution (200 mL), and dried over $MgSO_4$. The volatiles were removed and the solid obtained was purified by MPLC, using silica gel and dichloromethane/ethyl acetate (9:1) as eluent. Subsequent recrystallization in absolute ethanol yielded the target compound (**10**) as an orange powder (3.758 g, 50% yield); mp = 44 °C; IR (KBr) $\nu = 3400$ (N–H), 2225 (C≡N), 2114 (N₃), 1740 (C=O); ¹H NMR (400 MHz, CDCl₃, δ): 7.96–7.90 (m, 4H), 7.81–7.75 (m, 2H), 7.71–7.65 (m, 2H), 7.64–7.59 (m, 2H), 7.55–7.48 (m, 2H), 7.05–6.94 (m, 4H), 5.23 (t, $J = 5.8$ Hz, 1H), 4.36–4.23 (m, 6H), 4.14 – 4.01 (m, 4H), 3.60 (td, $J = 5.8, 5.3$ Hz, 2H), 3.45 (t, $J = 5.1$ Hz, 2H), 2.57 (t, $J = 7.3$ Hz, 2H), 2.21–2.09 (m, 2H), 1.28 (s, 3H); ¹³C NMR (100 MHz, CDCl₃, δ): 172.7, 172.5, 162.3, 159.0, 154.7, 146.9, 145.0, 133.2, 132.6, 132.0, 128.5, 127.1, 125.5, 123.1, 119.0, 118.6, 115.0, 114.9, 113.2, 110.3, 67.0, 66.9, 66.0, 65.4, 63.8, 49.7, 46.7, 40.6, 30.5, 24.4, 17.7; HRMS (ESI) m/z : $[M+H]^+$ calcd for C₄₀H₃₉N₈O₈, 759.2885; found, 759.2835; calcd. for C₄₀H₃₈N₈NaO₈, 781.2705; found, 781.2658. Anal. calcd for C₄₀H₃₈N₈O₈: C 62.90, H 4.87, N 15.05; found, C 62.87, H 5.05, N 14.68.

1.3. Synthesis of the polymer

The polymerization of PPMA and post-functionalization via CuAAC is outlined in Scheme S4. Poly(propargyl methacrylate) (**PPMA**) was prepared by atom transfer radical polymerization (ATRP) from triethylsilylpropargyl methacrylate. It has been reported that it is necessary to protect the alkyne groups to prevent side reactions and loss of control during the polymerization reaction.^[3] Examples in the literature have successfully used the trimethylsilyl group (TMS) to protect the alkyne functional group, however, it has been described to be labile under common ATRP conditions.^[4] Consequently, we have used the more stable triethylsilyl protecting group.^[5]



Scheme S4. Synthesis of the poly(propargyl methacrylate) (PPMA)

1.3.1. Synthesis of triethylsilylpropargyl alcohol (11)

A solution of propargyl alcohol (7.840 g, 135.0 mmol) in THF (200 mL) was cooled to $-78\text{ }^{\circ}\text{C}$ under argon atmosphere. Then, a solution of *n*-butyllithium 2.5 M in hexane (120.0 mL) was added dropwise and, the mixture warmed to room temperature and stirred for 1 h. The mixture was again cooled to $-78\text{ }^{\circ}\text{C}$ and a solution of triethylsilane chloride (50.0 mL, 298.0 mmol) in anhydrous THF (150 mL) was added, finally the reaction was stirred at room temperature overnight. The reaction was cooled into an ice bath, quenched adding aqueous H_2SO_4 5M (100 mL) and stirred for 1 h at room temperature. The mixture was extracted with diethyl ether ($3\times 75\text{ mL}$) and the combined organic extracts washed with water ($2\times 100\text{ mL}$), saturated aqueous NaCl solution (100 mL) and dried over MgSO_4 . The volatiles were removed and the crude purified by reduced pressure distillation (bp = $64\text{ }^{\circ}\text{C}$, 5 torr) yielding the target triethylsilylpropargyl alcohol (**11**) as a colorless oil (20.670 g, 90% yield). IR (NaCl) $\nu = 3853$ (O–H), 2175 ($\text{C}\equiv\text{C}$). ^1H NMR (400 MHz, CDCl_3 , δ): 4.29 (d, $J = 6.2\text{ Hz}$, 2H), 1.54 (t, $J = 6.2\text{ Hz}$, 1H), 1.06–0.86 (m, 9H), 0.69–0.45 (m, 6H). ^{13}C NMR (100 MHz, CDCl_3 , δ): 104.9 , 100.0 , 51.8 , 7.37, 4.21.

1.3.2. Synthesis of triethylsilylpropargyl methacrylate (12)

Triethylsilylpropargyl alcohol (**11**) (20.000 g, 117.0 mmol), 2,6-di(*tert*-butyl)-4-methylphenol (35 mg, 0.3 mmol) and Et_3N (32.6 mL) were dissolved in anhydrous dichloromethane (240 mL) and cooled to $0\text{ }^{\circ}\text{C}$ under argon atmosphere. Methacryloyl chloride (10.5 mL, 140.0 mmol) in anhydrous dichloromethane (10 mL) was added dropwise and the reaction stirred at

room temperature overnight. The resulting precipitate was filtered off and the organic solution washed with water (250 mL), aqueous saturated NaHCO₃ (250 mL) and aqueous saturated NaCl solution (250 mL), and dried over anhydrous MgSO₄. Once the solvent was evaporated, the resulting yellowish oil was purified by flash column chromatography using silica gel and hexane/ethyl acetate (9:1) as eluent (R_f = 0.83). The recovered oil was distilled under reduced pressure (bp = 64 °C, 5 torr) obtaining triethylsilylpropargyl methacrylate (**12**) as a colorless oil (22.872 g, 82% yield); IR (NaCl) ν = 2184 (C≡C), 1723 (C=O); ¹H-NMR (400 MHz, CDCl₃, δ): 6.16 (dq, *J* = 2.4, 1.1 Hz, 1H), 5.61 (dq, *J* = 2.4, 1.6 Hz, 1H), 4.77 (s, 2H), 1.96 (dd, *J* = 1.6, 1.1 Hz, 3H), 0.99 (t, *J* = 7.9 Hz, 9H), 0.61 (q, *J* = 7.9 Hz, 6H); ¹³C NMR (100 MHz, CDCl₃, δ): 166.6, 135.8, 126.3, 100.3, 89.5, 53.0, 18.3, 7.3, 4.1.

1.3.3. Synthesis of poly(triethylsilylpropargyl methacrylate) (PPMA-TES)

A Schlenk flask charged with a solution of trimethylsilylpropargyl methacrylate (**12**) (10.000 g, 42.0 mmol), ethyl 2-bromoisobutyrate (EBB) (45.7 μ L, 0.3 mmol) and *N,N,N',N'',N''*-pentamethyldiethylenetriamine (PMDETA) (64.3 μ L, 0.3 mmol) in distilled toluene (16.0 mL) was degassed via three freeze-pump-thaw cycles and flushed with argon. This solution was transferred to an oxygen evacuated Schlenk flask containing copper(I) bromide (44.2 mg, 0.3 mmol) and the system was further degassed via additional freeze-pump-thaw cycles. The polymerization mixture was heated to 70 °C and stirred for 24 h. Then, the reaction mixture was poured into THF (50 mL) and the solution filtered through a pad of neutral alumina pad. DOWEX Marathon[®] acid exchange resin was added and the dispersion was stirred for 4 h at room temperature. The resin was filtered off and the volatiles removed in a rotary-evaporator. The residue was taken into the minimum amount of THF and precipitated in a cold methanol/water (10:2) mixture giving **PPMA-TES** as a fine white powder (8.467 g, 73% yield); IR (KBr) ν = 2187 (C≡C), 1746 (C=O); ¹H-NMR (400 MHz, CDCl₃, δ): 4.72–4.56, 2.14–1.69, 1.45–1.06, 1.06–0.84, 0.73–0.47; M_n^{NMR} = 25000 g mol⁻¹; $M_n^{SEC(THF)}$ = 18000 g mol⁻¹, D^{SEC} = 1.16.

1.3.4. Synthesis of poly(propargyl methacrylate) (PPMA)

A solution containing **PPMA-TES** (2.000 g, 8.4 mmol) and glacial acetic acid (0.7 mL, 12.6 mmol) in anhydrous THF (100 mL) was cooled to 0 °C under argon atmosphere. A solution of tetra-*n*-butylammonium fluoride in THF 0.2 M (63 mL) was added dropwise and the mixture stirred at room temperature for 4 h. The solution was filtered through a pad of silica gel and the solvent evaporated. The residue was dissolved in the minimum amount of THF and precipitated in cold methanol to yield **PPMA** as a fine white powder (1.035 g, 99% yield). IR (KBr) $\nu = 3298$ ($\equiv\text{C-H}$), 2133 ($\text{C}\equiv\text{C}$), 1738 (C=O); ^1H NMR (400 MHz, CDCl_3 , δ): 4.74–4.48, 2.62–2.40, 2.08–1.74, 1.60–0.77; $M_n^{\text{NMR}} = 10000 \text{ g mol}^{-1}$; $M_n^{\text{SEC(THF)}} = 14000 \text{ g mol}^{-1}$, $D^{\text{SEC}} = 1.14$

2. Characterization techniques

IR spectra were measured on a Bruker Tensor 27 spectrometer using KBr pellets or NaCl discs for solid or for liquid samples, respectively. NMR spectra were recorded on a Bruker AV-400 spectrometer operating at 400 MHz for ^1H and 100 MHz for ^{13}C . Mass spectrometry data were determined using a Bruker MicroTof-Q equipped high resolution hybrid Q-TOF analyzer. Elemental analysis was performed with a Perkin-Elmer 240C microanalyzer. Number average molecular weights (M_n) and polydispersities (D) were determined by size exclusion chromatography (SEC) on a Waters 2695 liquid chromatography system using Styragel guard column (30 mm \times 4.6 mmID) and a combination of two Styragel columns (300 mm \times 7.8 mmID) from Waters. When THF (1.0 mL min $^{-1}$) was used as mobile phase, the system was equipped with Styragel HR1 and HR4 columns, a Waters 2420 evaporation light scattering detector was used and the SEC system was calibrated using poly(methyl methacrylate) standards. When DMF/LiBr 50 mM (0.5 mL min $^{-1}$) was used as the mobile phase, the system was equipped with Styragel HR1 and HR3 columns, a Waters 2998 photodiode array detector was used and the SEC system was calibrated using polystyrene standards. Alternatively, M_n for **PPMA-TES** and **PPMA** was calculated by end-group

analysis using ^1H NMR and the relative integration of the terminal end group coming from the 2-bromoisobutyrate initiator and the methylenic protons of the propargyl radical of the repetitive unit (see **figure S5**).

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 $20\text{ }^\circ\text{C min}^{-1}$ under a nitrogen atmosphere. Melting temperatures were read at the maximum of the transition peaks, and glass transition temperatures were read at the midpoint of the heat capacity increase. Thermogravimetric analysis (TGA) was performed at $10\text{ }^\circ\text{C min}^{-1}$ under nitrogen atmosphere using a TGA Q5000IR from TA Instruments. TGA data were given as the onset of the decomposition curve.

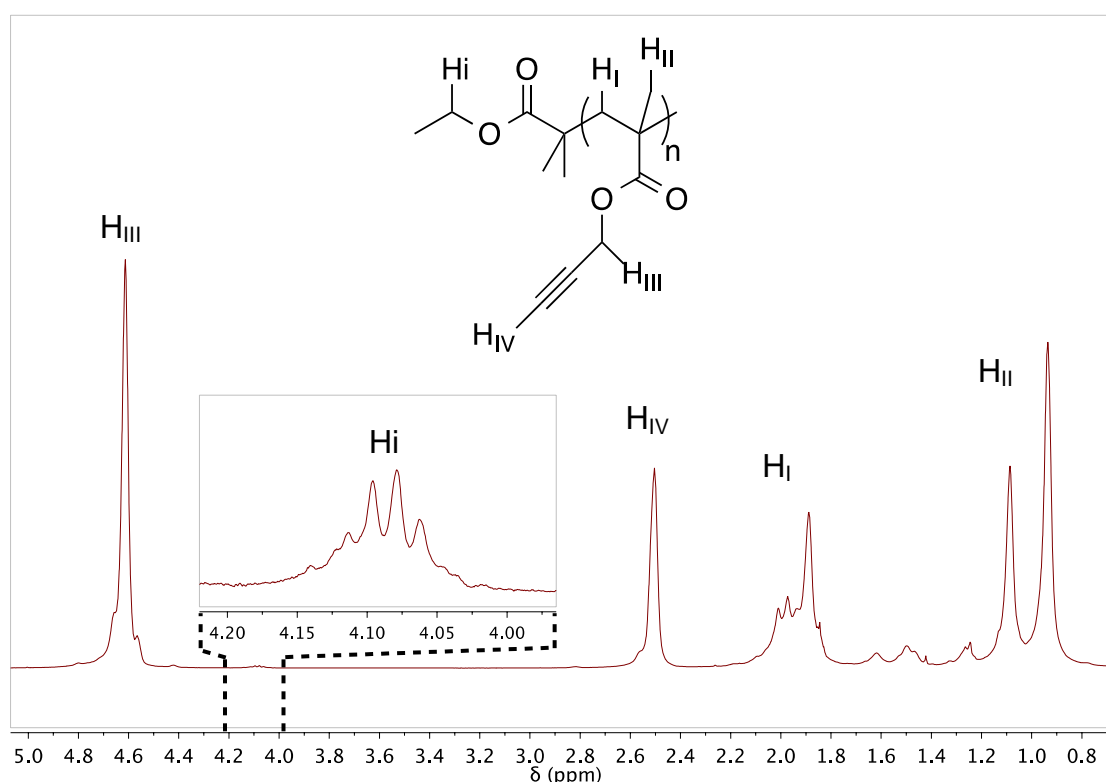


Figure S5. ^1H NMR (CDCl_3 , 400 MHz) of PPMA. The inset shows the methylenic protons of the end-chain group.

Size: 2.4570 mg

TGA

Run Date: 03-Jul-2012 13:25
Instrument: TGA Q5000 V3.15 Build 263

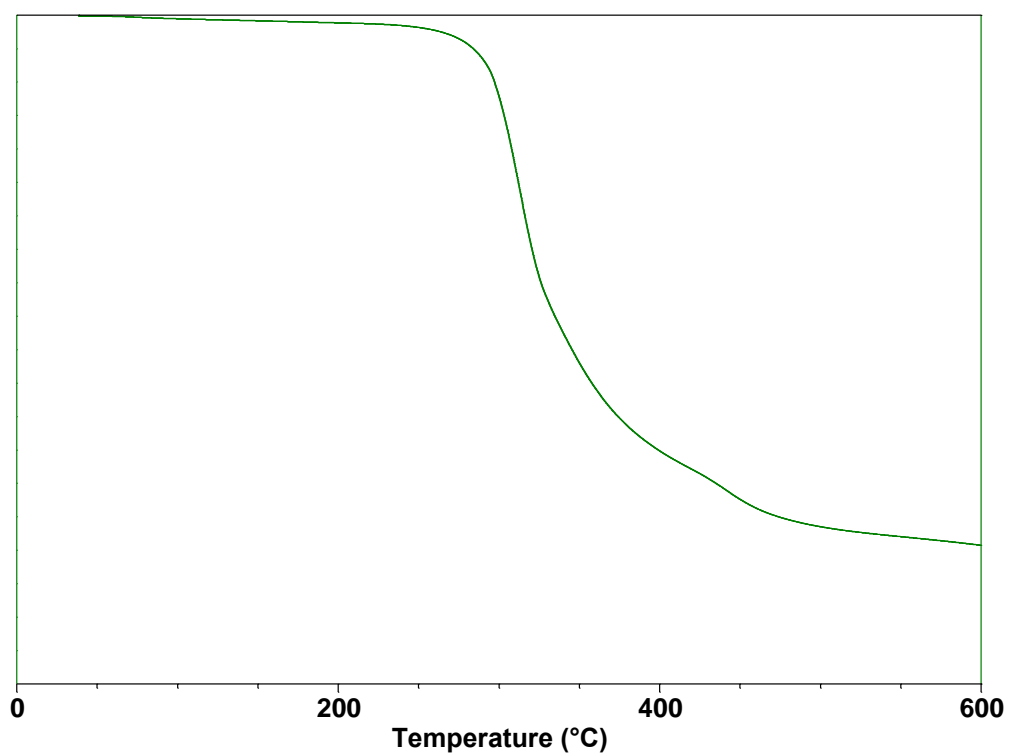


Figure S6. TGA curve of **P-CNB/AZO** recorded on heating at $10\text{ }^{\circ}\text{C min}^{-1}$

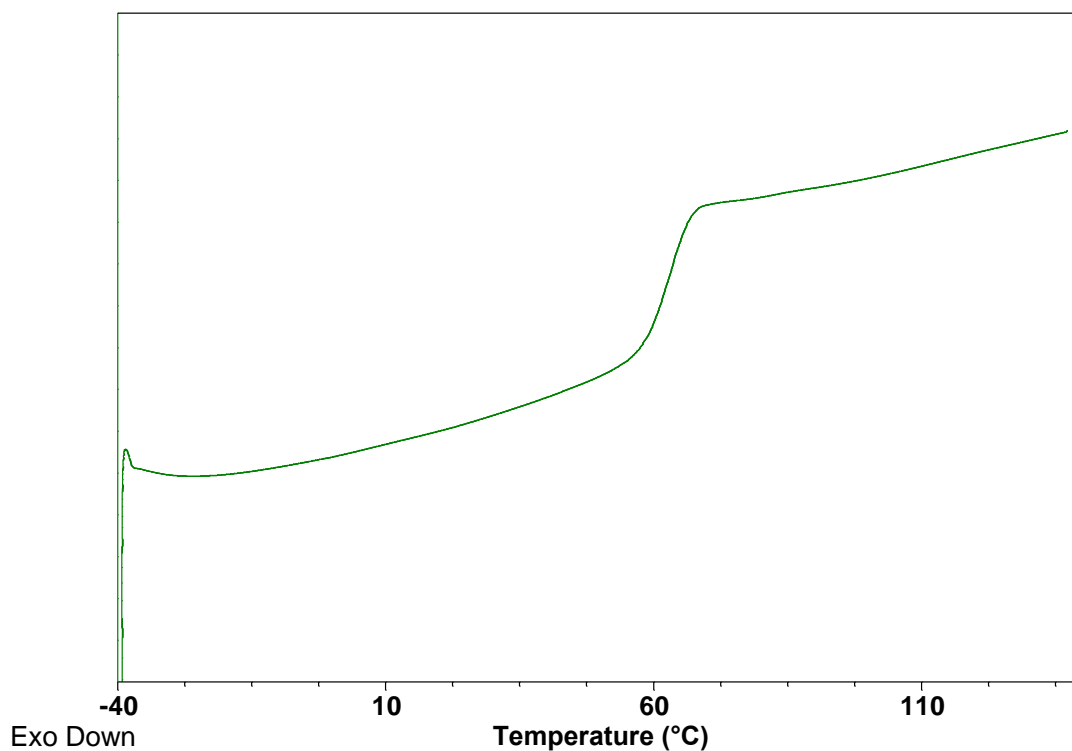


Figure S7. DSC scan of **P-CNB/AZO** recorded on heating at $20\text{ }^{\circ}\text{C min}^{-1}$

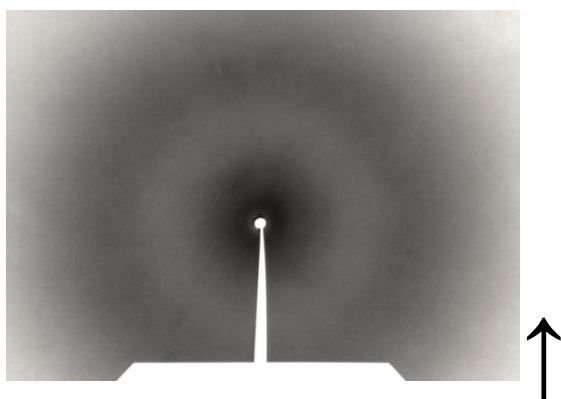


Figure S8. Ray scattering pattern registered at room temperature of a **P-CNB/AZO** fibre processed from the molten state at $120\text{ }^{\circ}\text{C}$. The arrow indicates the longitudinal axis of the fibre.

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