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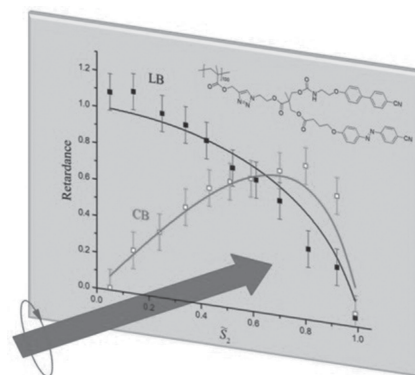
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# A Bifunctional Amorphous Polymer Exhibiting Equal Linear and Circular Photoinduced Birefringences

Jorge Royes, Clementina Provenzano,\* Pasquale Pagliusi, Rosa M. Tejedor, Milagros Piñol, Luis Oriol\*

The large and reversible photoinduced 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 the 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 characterization of an amorphous polymer with a dimeric repeating unit containing a cyanoazobenzene and a cyanobiphenyl moiety are 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 are used to investigate the photoinduced effects and to evaluate the anisotropies. The peculiar photoresponse of the polymer makes it a good candidate for applications in smart functional devices.



## 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.<sup>[1–4]</sup> They have provided the basis for several relevant

phenomena in light–matter interactions, such as photoinduced anisotropy,<sup>[5]</sup> light-initiated mass transport,<sup>[6,7]</sup> polarization-dependent chiral structures,<sup>[8]</sup> and polarization holography.<sup>[9]</sup> 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<sup>[10]</sup> and a photoinduced anisotropy with a radial contribution<sup>[11]</sup> are some examples. Azobenzene molecules undergo a reversible *trans*–*cis*–*trans*-photoisomerization by irradiating them with light of appropriate wavelength.<sup>[12]</sup> 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

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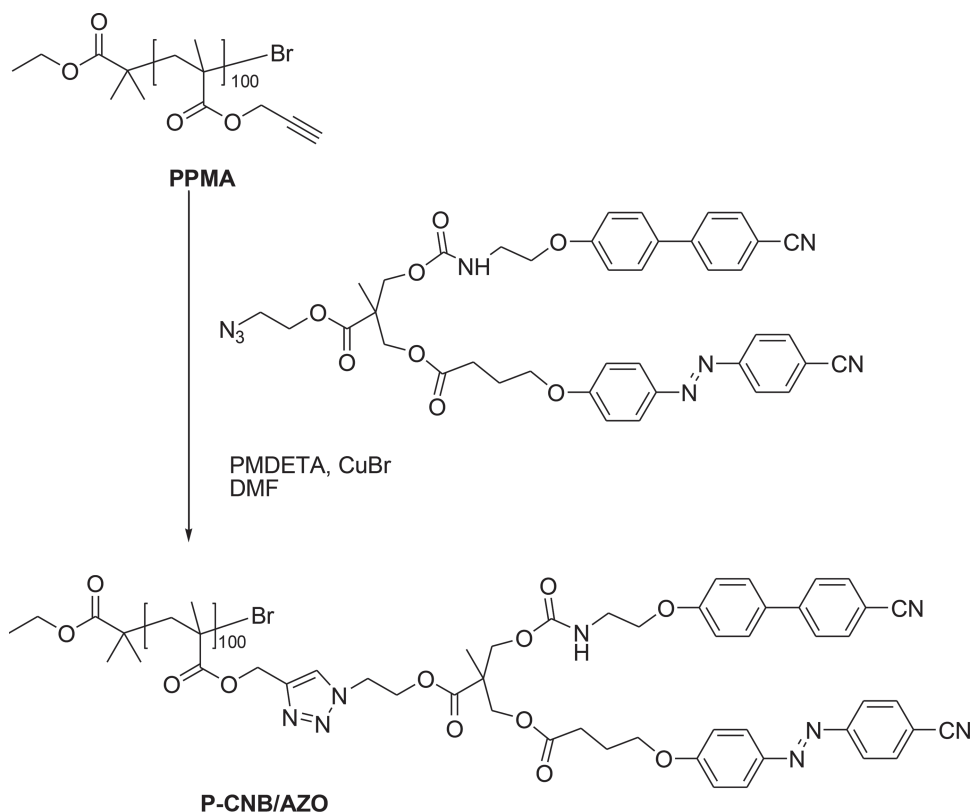
polarized light.<sup>[8,13–16]</sup> This phenomenon is connected to the angular momentum transfer from the light to the chromophores; being these latter attached to the material backbones, they rotate around to the light propagation direction, inducing chirality of the whole structure with a sense, which depends on the handedness of the exciting light.<sup>[17]</sup> 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,<sup>[12]</sup> providing new opportunities for the fabrication of micro- and nanoarchitectures.<sup>[18]</sup> Large and reversible photoinduced 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.<sup>[9]</sup>

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.<sup>[19,20]</sup> Indeed LB and CB occur at molecular and supramolecular level, respectively,<sup>[21,22]</sup> and as a consequence, a different growth rate versus the radiation dose is generally observed.<sup>[23]</sup> Moreover, the photoinduced anisotropies are associated not only to the reorientation of the azobenzene

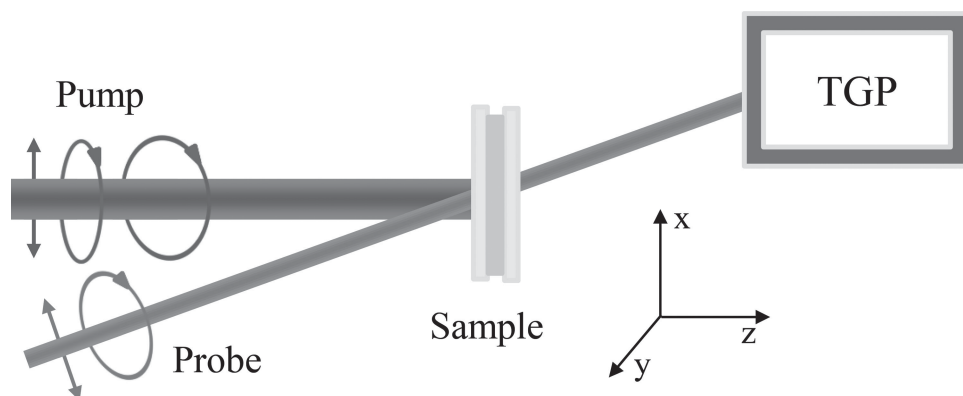
moieties, but also to the organization of the whole polymer chain.<sup>[24,25]</sup> In this regard, the macromolecular backbone plays an important role.

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.<sup>[26]</sup>

A pump-probe technique has been used to investigate the photoinduced 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,<sup>[9,19]</sup> an alternative dependence is proposed, which accounts for the



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



■ Figure 2. Scheme of the experimental set-up (top view). TGP, two gratings polarimeter.

reported non-monotonous behavior of CB, that reaches its maximum for an ellipticity  $e \approx 0.8$  and decreases for larger ellipticity, down to zero at  $e \approx 1$ .

## 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.

### 2.1. Synthesis of Functionalized Poly(propargyl methacrylate) P-CNB/AZO

A Schlenk flask was charged with 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''*-pentamethyldiethylenetriamine (PMDETA) (5.2  $\mu$ L, 0.03 mmol) and *N,N*-dimethylformamide (2.5 mL) were added and the flask was evacuated via three freeze–pump–thaw cycles. The reaction mixture was heated to 35 °C and stirred for 3 d. 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 was precipitated in cold methanol. The desired polymer P-CNB/AZO was isolated as a fine orange solid (0.178 g, 81% yield). IR (KBr)  $\nu$  = 3418 (N–H), 2230 (C $\equiv$ N), 1746 (C=O).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 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  $\text{C}_{47}\text{H}_{46}\text{N}_9\text{O}_9$ , C 63.94 H 5.52 N 12.69; found, 63.97, H 5.23, N 12.90;  $\bar{M}_n^{\text{NMR}} = 87\,000\text{ g mol}^{-1}$ ;  $\bar{M}_n^{\text{SEC}}(\text{DMF}) = 89\,000\text{ g mol}^{-1}$ ,  $D^{\text{SEC}} = 1.15$ .

### 2.2. Optical Characterization

The sample used in the experiment is a 20  $\mu\text{m}$  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 photoinduced 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  $5\text{ J cm}^{-2}$ . The pump beam is expanded to a spot size of 4 mm and overlaps at a small angle with the probe beam (1 mW) 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.

## 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.<sup>[27]</sup> 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 photoinduced linear and circular birefringence has been evaluated by means of a two gratings polarimeter (TGP),<sup>[28]</sup> adopting the Mueller matrix formulation.<sup>[29]</sup>

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  $+45^\circ$  and  $-45^\circ$ , 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  $4 \times 4$  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.<sup>[30]</sup> 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<sup>[31]</sup>

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

where  $LB = (\pi \Delta n_{lin} d) / \lambda$  and  $CB = (\pi \Delta n_{circ} d) / \lambda$  are the optical retardances,  $d$  is the thickness of the material,  $\lambda$  the probe wavelength and  $\Delta n_{lin}$  and  $\Delta n_{circ}$  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

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

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

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

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.<sup>[9]</sup>

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

It is worth noting that, for  $e = 0.6$  and a radiation dose of  $5 \text{ J cm}^{-2}$  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  $25 \text{ J cm}^{-2}$ . 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

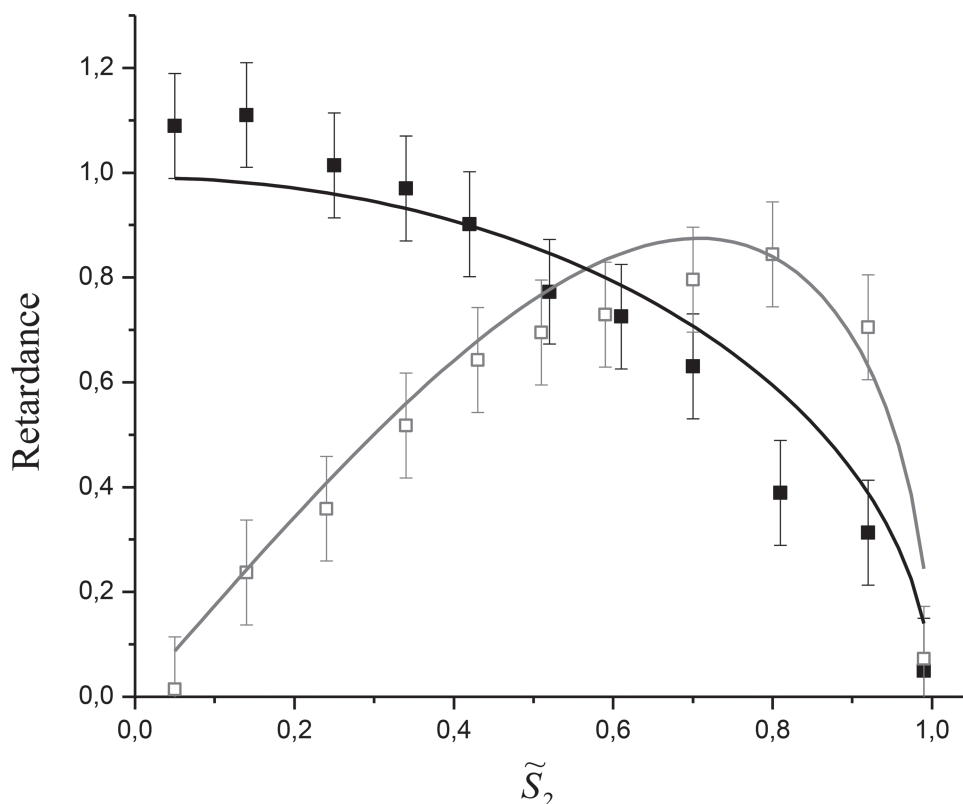


Figure 3. LB (close squares) and CB (open squares) photo-induced by an elliptically polarized pump beam with the major axis parallel to the x-axis, versus the ellipticity  $e = \tilde{S}_2$  of the pump beam ( $\tilde{S}_{\text{pump},1} = 0$  and  $\tilde{S}_{\text{pump},3} = \sqrt{1 - e^2}$ ). The values of the fitting parameters are  $k_L = 0.99 \pm 0.04$  and  $k_C = 0.9 \pm 0.2$ .

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 photoinduced 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 photoinduced 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 photoinduced optical properties. Considering the

long time stability, the full reconfigurability related to the intrinsic reversibility of the photoinduced 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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