Polymer 53 (2012) 2049–2061

Contents lists available at SciVerse ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer

Liquid-crystalline polymers bearing phenylene(azobenzene) moieties substituted with an electron-donor or electron-acceptor lateral group. Synthesis, mesomorphic behavior and photo-induced isomerization

Tonatiuh García [a], Leticia Larios-López [a], Rosa Julia Rodríguez-González [a], Geminiano Martínez-Ponce [b], Cristina Solano [b], Dámaso Navarro-Rodríguez [a,*]

[a] Centro de Investigación en Química Aplicada, Blvd. Enrique Reyna H. 140, 25253 Saltillo Coahuila, México
[b] Centro de Investigaciones en Óptica A. C. Apdo. Postal 1-948, 37000 León Guanajuato, México

ARTICLE INFO

Article history:
Received 20 January 2012
Received in revised form
7 March 2012
Accepted 10 March 2012
Available online 16 March 2012

Keywords:
Azobenzene
Liquid crystal polymers
Photo-induced isomerization

ABSTRACT

Methacrylic polymers bearing phenylene(azobenzene) moieties substituted with a OCH_3 (electron-donor) or a CN (electron-acceptor) lateral group were synthesized and their liquid-crystalline (LC) and photo-induced isomerization properties were studied. The thermotropic LC properties were analyzed by DSC, POM, and XRD. All polymers showed a mesomorphic behavior that extends over wide temperature ranges (>100 °C) displaying smectic type mesophases. The effect of the lateral group was reflected in the packing of mesogens in the smectic phases; the polar interactions of the CN groups seem to counterbalance the hindering effects of this lateral group. On the other hand, the photoisomerization of all polymers was induced in dilute solution and films (spin coated and casted). All polymers photoisomerize relatively fast with the CN-substituted polymers reaching high *cis*-isomer contents (>95%) at the photostationary state. Light induced birefringence experiments indicated a tight interplay between the photo-induced orientation and the LC intrinsic order. Homogeneous sinusoidal surface relief gratings were obtained.

1. Introduction

Over the last 25 years, liquid-crystalline polymers (LCPs) bearing azobenzene moieties have attracted much attention because of synergistic effects produced by coupling the spontaneous molecular order of liquid crystals with the photo-sensitive response of azocompounds [1]. The interplay between these two physical properties has been of great interest for applications in optics [2], photonics [3], photo-mechanics [4,5], among others [6,7]. One of the main characteristics of azobenzenes is their clean photoisomerization produced under a specific UV–Vis irradiation [8]. Depending on the material and irradiation conditions, the *trans* ↔ *cis* cyclic photoisomerization can induce motions at molecular, nanometric (domain), and micrometric (mass motion) levels [9].

In 1987, Wendorff et al. synthesized LC polymers bearing azobenzene mesogens whose cooperative motion (nanometric level) lead to a significant molecular photo-alignment, which turned out to be stable once the irradiation was stopped [10,11]. Moreover, the attachment of azobenzene moieties to a polymer backbone gives rise to a photo-induced mass migration, which at that time was unknown and became a promising tool for the fabrication of regular micro scale surface relief gratings (SRG) [12–14]. More recently, several groups have synthesized new LCPs aiming to improve the photo-induced properties taking advantage of the intrinsic molecular order of liquid crystals [15–19]. It is noteworthy that the higher birefringence values so far reported for azocompounds belong to LCPs. Ikeda et al reported in 2006 remarkably high birefringence values ($\Delta n = 0.48{-}0.76$) for LCPs bearing side chain azotolane moieties [20]. Such outstanding birefringence values were associated not only with the long π-conjugation of the azotolanes but also to their LC order [11]. In these moieties, the additional rigid group, which is directly linked to the azobenzene moiety, maintains the linearity of the mesogen and increases the lateral cohesive interaction between molecules in the mesophase. This increased molecular anisotropy may induce a richer polymorphism, and higher thermal and mesophase stabilities. These

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[*] Corresponding author. Tel.: +52 844 4389846; fax: +52 844 4389839.
E-mail addresses: tonatiuhgarcia@gmail.com (T. García), llarios@ciqa.mx (L. Larios-López), rjrodrig@ciqa.mx (R.J. Rodríguez-González), geminis@cio.mx (G. Martínez-Ponce), csolano@cio.mx (C. Solano), damaso@ciqa.mx (D. Navarro-Rodríguez).

0032-3861/$ – see front matter © 2012 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2012.03.024

effects were also demonstrated in azobenene derivatives substituted with a biphenylene group, which display a mesomorphic behavior that extends over 200 °C [21]. In spite of such remarkable results, there are few reports on side-chain liquid-crystalline polymers (SCLCPs) bearing highly anisotropic azobenzene mesogens and this is probably due to solubility (or processing) problems. Rigid rodlike molecules are insoluble in most common solvents and this is normally associated to the strong π–π lateral interactions that maintain the molecules close together. A common practice to reduce such interactions is the introduction of relatively small lateral groups like Cl, Br, OCH_3, among others [22]. The presence of such lateral groups not only improves the solubility of the rigid rodlike azobenzenes but also influences their mesomorphic behavior [23]. Moreover, if such groups are polar in nature they may have important effects on the spectroscopic properties [8] as well as on the photoisomerization process [24]. In the present work, the synthesis, the liquid-crystalline properties and the photoisomerization of new side-chain liquid-crystalline polymers bearing phenylene(azobenzene) moieties substituted with a OCH_3 or a CN group is presented and discussed.

2. Experimental

2.1. Materials

All reagents were purchased from Aldrich and used without further purification unless otherwise noted. Azobisisobutyronitrile (AIBN) was recrystallized from methanol (MeOH). Reactive grade acetone, methanol, chloroform ($CHCl_3$), and hexanes were purchased from J. T. Baker and were used without further purification. Tetrahydrofuran (THF) was dried over a sodium/benzophenone complex and distilled prior to use.

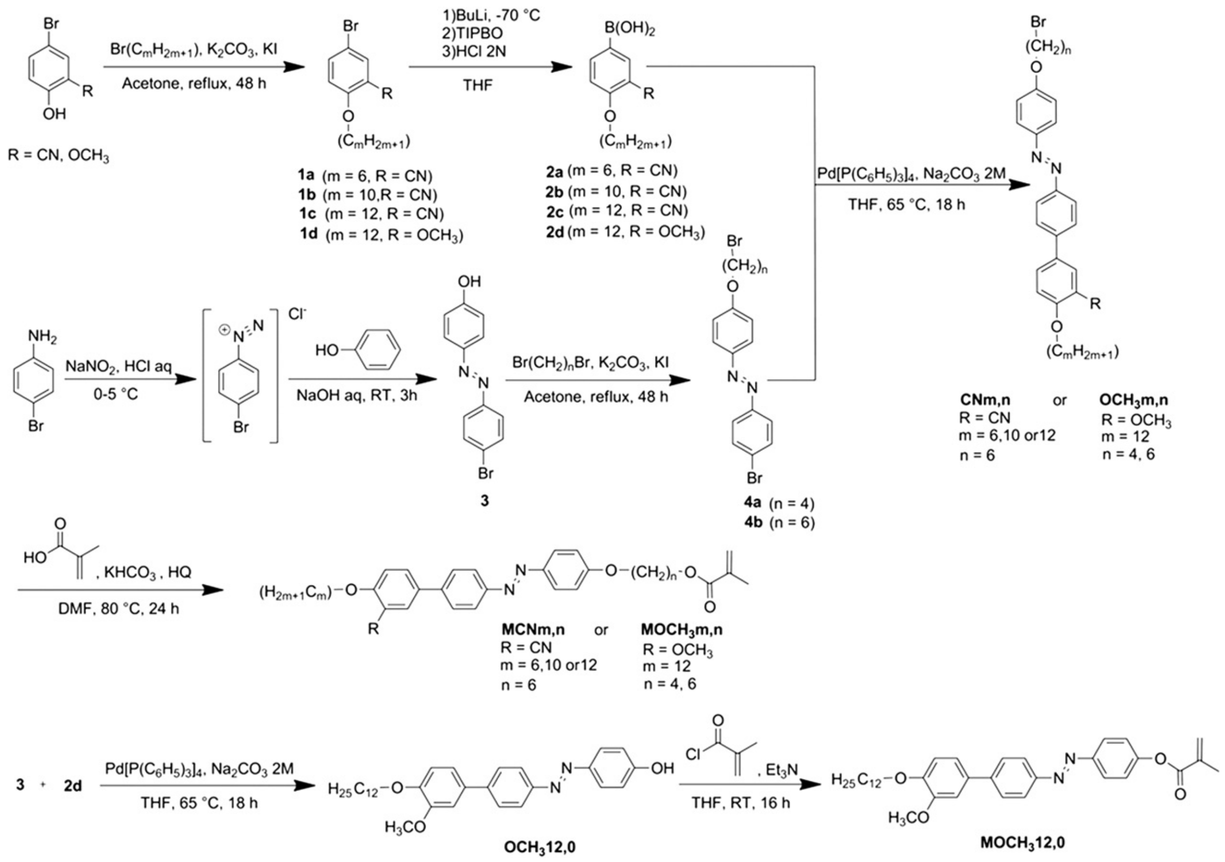
2.2. Synthesis

Two groups of azopolymers were prepared from monomers obtained following the synthetic route outlined in Scheme 1. The first group corresponds to polymers having phenylene(azobenzene) moieties substituted with a lateral OCH_3 group. In these polymers the length of the spacer is 0, 4 and 6 methylene groups, whereas the length of the tail (terminal chain) is kept constant (12 carbon atoms). These polymers were named p$OCH_3$12,0, p$OCH_3$12,4 and p$OCH_3$12,6, respectively. The second group corresponds to polymers bearing phenylene(azobenzene) moieties substituted with a lateral CN group. In these polymers the length of the tail is 6, 10 or 12 carbon atoms, whereas the flexible spacer is kept constant (6 methylene groups). These polymers were named pCN6,6, pCN10,6 and pCN12,6, respectively.

Intermediates **1a**–**d**, **3**, **4a** and **4b** were synthesized according to known procedures [21,24–26]. For the other precursors typical procedures are presented below.

2.2.1. 3-Cyano-4-(decyloxy)phenylboronic acid. (**2b**)

In a 250 mL three-neck round-bottom flask, equipped with two addition funnels (100 mL) and septa, 3 g (8.87 mmol) of **1b** were dissolved in about 120 mL of freshly distilled THF. The solution was cooled down to −78 °C and then 6.2 mL (9.92 mmol) of BuLi in hexanes 1.6 M was added dropwise keeping the temperature below −70 °C. The reaction mixture was stirred for 90 min and then 4.5 mL (19.57 mmol) of triisopropyl borate (TIPBO) were added



Scheme 1. Synthesis route for the preparation of the phenylene(azobenzene) monomers.