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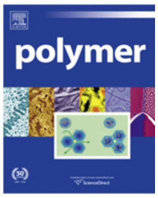

Synthesis and characterization of side-chain liquid-crystalline block-copolymers containing laterally attached photoluminescent quinquephenyl units via ATRP

Ling-Yung Wang, Kuang-Chieh Li, Hong-Cheu Lin*

Department of Materials Science and Engineering, National Chiao Tung University, 1001 Ta Hsueh Road, Hsinchu, Taiwan 30049, ROC

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A series of novel side-chain liquid-crystalline polymers (SCLCPs) consisting of laterally attached photoluminescent *p*-quinquephenyl (**QQP**) pendants with different flexible terminal- and/or side-alkoxy chains were synthesized via atom transfer radical polymerization (ATRP). Homopolymers (**HP1**–**HP3**) and block-copolymers (**PSP1**–**PSP3** and **PEOP1**–**PEOP3**), where **QQP** units were copolymerized with styrene or ethylene oxide monomers, possessed the number average molecular weights (M_n) of 8.7–26.0 × 10^3 with narrow PDI values of 1.08–1.26. Various characterization techniques of polarized optical microscopy (POM), differential scanning calorimetry (DSC), and X-ray diffraction (XRD) were used to investigate their mesomorphic properties, and all homopolymers and block-copolymers exhibited the nematic phase affected by the flexible terminal- and/or side-alkoxy chains of the conjugated rod-like pendants. In addition, the photophysical properties of these polymers were measured by UV–vis and photoluminescence (PL) spectroscopies, which showed blue PL emissions with rather high fluorescence quantum yields in solutions.

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1. Introduction

Self-organization into a particular order is a general phenomenon in nature. Block-copolymers (BCPs) present one of the most straightforward models to achieve self-organized nanostructures, which can lead to the formation of a variety of structures such as cylinders, lamellas, and spheres, etc [1]. There are several major classes of synthetic materials that can readily accomplish BCPs with various phase structures, such as amorphous (coil–coil) [2,3], crystalline–amorphous (or crystalline–crystalline) [4–6], and liquid-crystalline (LC) structures [7,8]. LC BCPs have been an active research target in creating different hierarchical structures with unique mesomorphic and mechanical behaviors for several past decades. Numerous LC BCPs have been focused on the LC molecular architectures, which can be divided into main-chain [9–11] and side-chain LC BCPs [12–23], as well as BCPs made of mesogenic jacketed LC polymers (MJLCPs) [24–30]. However, most researches of LC BCPs concentrated on “longitudinally linked” side-chain liquid-crystalline polymers (LCPs) forming a comb-like fashion whose termini of rigid rods in mesogenic units were attached to the polymer backbones through completely flexible spacers [12–23]. Side-chain LCPs consisting of cyanophenyl [12–15], azobenzyl [16–19], and (*n*-alkoxyphenyl)benzyl [20–23] moieties have been usually studied in different applications of mesomorphic, electro-optical, and microphase-separated structural properties, respectively. For example, Yu et al. revealed that well-defined conjugated-LC block-copolymers with side-chain LCPs exhibited the properties that energy transfer from the LC mesogens to the conjugated oligomers [12]. Pugh et al. found that a series of polynorbornenes (PNBEs) laterally attached side-chain LC polymers by using different symmetrically di-substituted mesogens exhibited the tilted layer structure of a smectic C (S_C) phase at room temperature and a nematic (*N*) phase at higher temperatures, which were characterized by polarizing optical microscopy (POM) and X-ray diffraction (XRD) experiments [22]. Based on these concepts, the subject of functional materials can be set more clearly to be explored for new types of block-copolymers with novel mesomorphic and optical properties in this work.

To investigate the structures of LC block-copolymers, many research groups have synthesized several varieties of living or controlled polymerization methods, such as cationic, ring-opening metathesis, and anionic living polymerizations [31–34]. Recently, the controlled (“living”) radical polymerizations of atom transfer radical polymerization (ATRP) and nitroxide-mediated radical polymerization have been used to synthesize side-chain LCPs [25–37]. Because the ATRP method can be handled easily and applied to a wide number of monomers and lead to special polymer architectures with narrow polydispersities [38–40], the successful

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* Corresponding author. Tel.: +8863 5712121x55305; fax: +8863 5724727.
E-mail addresses: linhc@mail.nctu.edu.tw, linhc@cc.nctu.edu.tw (H.-C. Lin).

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polymerization technique was chosen to develop new functional block-copolymers for this research. For instance, a new class of side-on LCP-containing block-copolymers with different hydrophilic/hydrophobic ratios were developed by Li et al. via ATRP method [65].

An approach to increase the rigidity of the polymers, particularly at high temperatures, was to introduce oligo-phenyl segments into the rigid cores of the polymer backbones [41–49]. Thus, the presence of *p*-quinquephenyl (**QQP**) chromophores in the polymer structures was of considerable interest for the creation of new promising multifunctional (including photoluminescent) materials. Besides, such chromophores bearing alkoxy-substituted side groups not only showed increased solubility and high modulus at high temperatures but also exhibited a different phase behavior [44]. For example, Zhou et al. reported that *p*-terphenyl groups with different symmetrical alkoxy terminal substituents exhibited different mesophases, regardless of the lengths of the tails [26]. Furthermore, because of the strong π–π interactions between the conjugated benzene rings favoring the self-organization of molecules, these types of chromophores possessed the multiple properties of photoluminescence, thermally stable liquid crystallinity, and microphase-separated behavior in such systems [45–49].

Herein, we report the synthesis of novel photoluminescent monomers with laterally connected pendent **QQP** moieties substituted by different alkoxy groups at both ends and central sides, the ATRP polymerizations of LC homopolymers and their functional block-copolymers (Chart 1) with narrow polydispersities initiated by different flexible macroinitiators, i.e., poly(ethylene oxide) (**PEO**) and polystyrene (**PS**). The phase transition and mesomorphic properties (investigated by POM, DSC, and temperature-variable XRD) as well as the UV–vis and PL properties of the rod-coil block-copolymers will be evaluated.

2. Experimental

2.1. Measurements

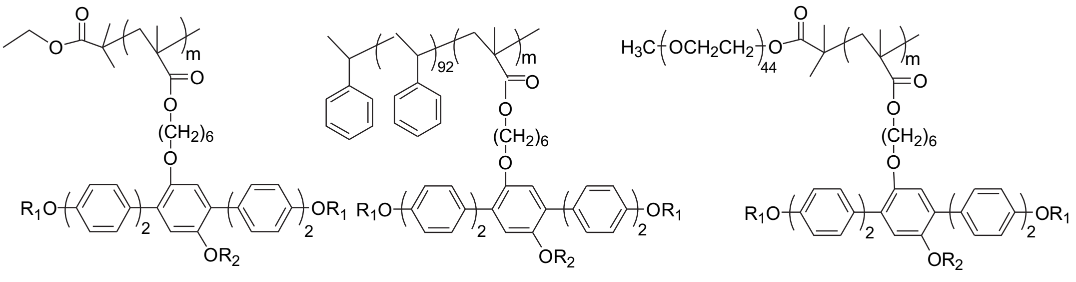
^{1}H NMR spectra were recorded on a Varian Unity 300 MHz spectrometer using $CDCl_3$ and DMSO solvent. Elemental analyses were performed on a HERAEUS CHN-OS RAPID elemental analyzer. Transition temperatures were determined by differential scanning calorimetry (Perkin–Elmer Pyris 7) with a heating and cooling rate of 5 °C/min. Thermogravimetric analysis (TGA) was conducted with a TA instrument Q500 at a heating rate of 20 °C/min under nitrogen. Gel permeation chromatography (GPC) analysis was conducted on a Waters 1515 separation module using polystyrene as a standard and THF as an eluent. UV–vis absorption spectra were recorded in dilute THF solutions (10^{-6} M) on a HPG1103A spectrophotometer, and fluorescence spectra were obtained on a Hitachi F-4500 spectrophotometer, where the excitation wavelengths of PL were ca. 290 nm. Fluorescence quantum yields were determined by using a 9,10-diphenylanthracene standard (10^{-6} M in cyclohexane, $\Phi_F = 90\%$) [50]. Polymer solid films were spin-coated (at 1000 rpm) on quartz substrates for 1 min from THF solutions with a concentration of 10 mg/mL and dried under vacuum at 50 °C for 3 h. LC textures were studied via a polarizing optical microscope (POM, model Leica DMLP) coupled with a hot stage. Synchrotron powder X-ray diffraction (XRD) measurements were performed at beamline BL17A of the National Synchrotron Radiation Research Center (NSRRC), Taiwan, where the wavelength of X-ray was 1.33361 Å. The XRD data were collected using Mar345 image plate detector mounted orthogonal to the beam with sample-to-detector distance of 250 mm, and the diffraction signals were accumulated for 3 min. The powder samples were packed into a capillary tube and heated by a heat gun, whose temperature controller is programmable by a PC with a PID feedback system. The scattering angle theta was calibrated by a mixture of silver behenate and silicon. The self-assembling surface morphology was investigated by the tapping mode of atomic force microscopy (AFM) at room temperature using a Digital Instruments Nanoscope IIIa microscope, where the sample was prepared by dipping a 0.5 wt% copolymer solution (in toluene) onto a Si wafer and then annealed under vacuum at 170 °C for 2 h then cooling slowly to 100 °C for 1 day.

2.2. Materials

Chemicals and solvents were reagent grades and purchased from Aldrich, ACROS, TCI, and Lancaster Chemical Co. Dichloromethane, THF, and triethylamine were distilled to keep anhydrous before use. Catalyst copper (I) bromide was purified successively by stirring in acetic acid and ethanol, and then dried [51]. Styrene monomers were distilled under nitrogen over calcium hydride and 2,6-di(*tert*-butyl-4-methyl)phenol as an inhibitor before use. All of the other chemicals and solvents were used as received.

2.3. Synthesis of polymers

The synthetic routes of macroinitiator **14**–**15** are shown in Scheme S1. Homopolymers (**HP1**–**HP3**) and diblock-copolymers (**PSP1**–**PSP3** and **PEOP1**–**PEOP3**) were synthesized by using the analogous procedure except for the utilization of different initiators and monomers via ATRP in Scheme 1.



HP1 : $R_1 = C_8H_{17}$; $R_2 = CH_3$

HP2 : $R_1 = C_8H_{17}$; $R_2 = C_8H_{17}$

HP3 : $R_1 = CH_3$; $R_2 = C_8H_{17}$

PSP1 : $R_1 = C_8H_{17}$; $R_2 = CH_3$

PSP2 : $R_1 = C_8H_{17}$; $R_2 = C_8H_{17}$

PSP3 : $R_1 = CH_3$; $R_2 = C_8H_{17}$

PEOP1 : $R_1 = C_8H_{17}$; $R_2 = CH_3$

PEOP2 : $R_1 = C_8H_{17}$; $R_2 = C_8H_{17}$

PEOP3 : $R_1 = CH_3$; $R_2 = C_8H_{17}$

Chart 1. Side-chain liquid-crystalline polymers (SCLCPs) with calamitic LC mesogens.

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