

Preparation of a New Polymer-Dispersed Liquid Crystal Film by Using Phthalocyanine-Functional Photocurable Copolymer

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ABSTRACT: A new, asymmetrical zinc phthalocyanine (aZnPc)-functional photocurable copolymer was prepared by the combination of atom transfer radical polymerization and copper (I)-catalyzed azide-alkyne cyclo-addition (CuAAC) click reaction and used as polymer matrix of polymer dispersed liquid crystal (PDLC) film. For this purpose, aZnPc was prepared through statistical condensation of 4-*tert*-butylphthalonitrile and 4-pent-4-ynoxyphthalonitrile. Double CuAAC click reaction between azido-functional poly(methyl methacrylate-*co*-2-(2-bromoisobutyryloxy)-ethyl methacrylate), terminal alkynyl-substituted aZnPc, and 4-ethynyl-*N,N*-dimethyl aniline yielded photocurable aZnPc-functional copolymer. Thereby, synthesized copolymer was crosslinked in the presence of liquid crystalline mesogen 4'-(octyloxy)-4-biphenylcarbonitrile by ultraviolet irradiation using benzophenone as initiator and ethylene glycol dimethacrylate as difunctional crosslinker. Thermal and optical properties of PDLC film were investigated by using differential scanning calorimetry and polarized optical microscopy. Smectic A liquid crystal mesophases were observed in both PDLC film and its mesogenic component 4'-(octyloxy)-4-biphenylcarbonitrile. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 41574.

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INTRODUCTION

Phthalocyanines consist of a planar macrocycle with an 18 π -electron system, which is responsible for their diverse functionality. They have increasing interest for applications in nonlinear optics,¹ molecular electronics,² photodynamic cancer therapy,³ solar energy conversion,⁴ various catalytic processes,⁵ electrochromic and electroluminescent displays,⁶ liquid crystals (LCs),^{7,8} and gas sensors.⁹ Pc containing polymers have been the focus of interest in recent years, which offer a unique combination of good properties of polymers and phthalocyanines for designing new materials with special properties.^{10–12} There are three general methods for the synthesis of side-chain polymers in which the Pc unit is attached to a polymer backbone via a single linking group. These are (i) the grafting of a preformed Pc derivative to a preformed polymer, (ii) a mixed cyclotetramerization involving a polymer bound precursor, and (iii) polymerization of a phthalocyanine containing monomer.¹³ Click chemistry is an attractive approach, allowing incorporation of Pc molecules onto preformed polymers.^{14–17} The combination of controlled/“living” polymerization (CRP) techniques especially with copper (I)-catalyzed azide alkyne cyclo-addition (CuAAC) click reaction have developed the available range of polymer architectures and functional materials.^{18–25}

Polymer dispersed liquid crystals (PDLCs) are formed when liquid crystalline material is dispersed within a polymer matrix.^{26,27} The best-known PDLCs can be used as optical devices.^{28–33} switchable windows,^{34,35} and displaces,^{36–38} The development of new polymeric matrices for PDLCs is an active area of research as the performance of PDLC is directly affected by polymer matrix properties. Graft structures having much lower solution and melt viscosities compared to linear polymers of the same molar mass are promising materials for PDLCs since they lead PDLCs with improved electric-optical properties via better phase separation. Furthermore, high concentration of functional terminal groups leads to significant changes of chemical and physical properties of highly grafted molecules as compared with their linear analogs.³⁹ In practical applications, acrylic resin is the most conventional polymer material in PIPS.⁴⁰ Also, it is reported that the presence of HEMA improves the contrast ratio of the PDLC film.⁴¹

Generally, phase separation techniques are used for the preparation PDLCs. In these techniques, the homogeneous system of LC, polymer or prepolymer phase separates by solvent evaporation (SIPS),^{42,43} melt cooling (TIPS),^{44,45} or polymerization (PIPS).^{46,47} Photo-polymerization induced phase separation (p-PIPS) of mixtures composed of reactive prepolymer and LC is

usually regarded as the most convenient and versatile method for the preparation of PDLCs with good electro-optical properties, stability, uniformity, and reproducibility due to an absence of solvents and room temperature of the process.

Recently, we have reported the syntheses of Pc-containing polystyrene (PS) and poly(*tert*-butyl acrylate) (PtBA) in which phthalocyanine compound is either end-group or core via CuAAC click reaction between asymmetrically and symmetrically terminalalkynyl substituted phthalocyanines and azide end-functional PS and PtBA.^{48,49}

In continuation of our recent studies on Pc-containing polymers, we present here for the first time the synthesis of asymmetrical zinc phthalocyanine (aZnPc)-functional photocurable copolymer by the combination of ATRP and CuAAC click reaction and the use of the functional copolymer as polymer matrix of PDLC film. We fabricated the PDLC film by p-PIPS technique in the presence of 4'-(octyloxy)-4-biphenylcarbonitrile (8OCB) LC using photocurable aZnPc-functional copolymer as co-initiator, ethylene glycol dimethacrylate (EGDMA) as difunctional crosslinker, benzophenone as initiator. Thermal and optical properties of PDLC film were investigated by using differential scanning calorimetry (DSC) and polarized optical microscopy (POM). To the best of our knowledge, this report is the first example on the use of Pc-functionalized polymer as matrix for PDLC film.

EXPERIMENTAL

The ¹H NMR and ¹³C NMR spectra were recorded on Agilent VNMRS (500 MHz for ¹H and 125 MHz for ¹³C). IR spectra were recorded on Perkin Elmer One FTIR (ATR sampling accessory) spectrophotometer and electronic spectra on a Unicam UV2 ultraviolet (UV)-vis spectrophotometer. Elemental analyses were performed on a Thermo Flash EA 1112. Mass spectra were performed on Bruker Microflex MALDI-TOF/MS and Perkin-Elmer Clarus 500 mass spectrometers. The gel permeation chromatography measurements of polymers were obtained from an Agilent instrument (Model 1100) consisting of a pump, a refractive index, and UV detectors, a column oven, and three Macherey Nagel columns (103S, 104S, 105S). About 0.01M LiBr/DMF was used as an eluent at a flow rate of 0.7 mL/min at 50°C. Toluene was used as an internal standard. The molecular weight of the polymers was calculated based on linear poly(methyl methacrylate) standards (Polymer Laboratories). PDLC film was prepared using Spectrolinker XL-1000A UV Crosslinker equipped with five 8W 365-nm tubes. DSC analyses were performed with TA Instruments, New Castle, Delaware, DSC Q10 at a heating rate of 5°C/min under nitrogen atmosphere. All data were collected from a second heating cycle and the glass transition temperatures (*T*_g) were calculated as a midpoint of thermogram. LC behavior of the materials was investigated by polarized light microscopy (POM) using Leica DM2500P equipped with a LTSE350 Liquid Crystal Prosystem TMS 94 Hot Stage at heating rate 5°C/dk.

2-Hydroxyethyl methacrylate (HEMA, 97%; Aldrich), and methyl methacrylate (MMA, 98.5%; Aldrich) were passed through a basic alumina column to remove the inhibitor and

then distilled over CaH₂ *in vacuo* before use. *N,N,N',N',N''*-Pentamethyldiethylenetriamine (PMDETA; 99%; Aldrich) was distilled over NaOH before use. All starting materials were purchased from major suppliers and used without any further purification. 4-Pent-4-ynyloxy-phthalonitrile was synthesized according to the literature.⁴⁹ 4-Nitro-phthalonitrile, 4-*tert*-butyl-phthalonitrile, 4-pentyne-1-ol, 1-pentanol, anhydrous K₂CO₃, 4'-hydroxy-4-biphenylcarbonitrile, and dimethyl sulfoxide (DMSO) were purchased commercially. All organic solvents used for the synthesis were of analytical grade. Column chromatography was performed on silica gel 60 for a proper purification [Merck Kieselgel 60 (0.040–0.063 mm)].

Synthesis

9,16,23-Tri-*tert*-butyl-2-(pent-4-ynoxy)phthalocyaninatozinc(II)

(1). aZnPc was prepared by a similar method reported in the literature.⁴⁹ 4-Pent-4-ynyloxyphthalonitrile (0.028 g, 0.133 mmol), 4-*tert*-butyl-phthalonitrile (0.074 g, 0.402 mmol), and Zn(CH₃COO)₂ (0.024 g, 0.133 mmol) were added to 1-pentanol (1 mL) and stirred for 0.5 h in succession. The reaction mixture was stirred for 24 h at 135°C under a nitrogen atmosphere. After cooling down, 1-pentanol was removed under reduced pressure. The collected solid was purified by column chromatography (silica gel/dioxane-petroleum ether 1 : 5) to afford desired aZnPc as a bluish green powder in 23% yield (25 mg).

FTIR γ (cm⁻¹): 3287 (\equiv C-H); 3072 (Ar-H); 2956–2861 (CH, aliphatic); 2112 (C \equiv C); 1391, 1362, 1331 (C(CH₃)₃). ¹H NMR (500 MHz, CDCl₃): δ ppm 8.44, 8.20, 7.86, 7.77, 7.66, 7.18 (Ar-H, m, 12H), 4.93 (CH₂-O-, m, 2H), 2.34 (CH₂, m, 2H), 2.20 (CH₂, m, 2H), 1.92 (C \equiv CH, m, 1H), 1.77–1.29 (C-(CH₃)₃, m, 27H). ¹³C NMR (500 MHz, CDCl₃): δ ppm 174.04, 168.21, 158.99, 152.18, 135.75, 131.34, 129.84, 126.61, 125.50, 123.36, 121.46, 120.65, 118.08 (Ar-C), 83.76 (C \equiv CH), 69.06 (CH₂-O), 66.63 (C \equiv CH), 38.62–34.21 (C(CH₃)₃), 31.94–29.07 ((CH₃)₃), 24.95–21.17 (CH₂), 15.23–10.96 (CH₂). MS: *m/z* (C₄₉H₄₆N₈OZn) found = 828.384 (calcd. for [M]⁺ 828.33). Anal. Calcd. for C₄₉H₄₆N₈OZn: C 71.05, H 5.60, N 13.53 %; found: C 70.43, H 5.65, N 13.87%. UV-vis (THF) λ_{\max} /nm: 673, 349.

Poly(methyl methacrylate-co-2-hydroxyethyl methacrylate)

(PMMA-co-PHEMA) (2). PMMA-co-PHEMA was prepared by ATRP with conditions modified from previously reported method.⁵⁰ HEMA (1.593 mL, 13.14 mmol), MMA (7.027 mL, 65.7 mmol), CuBr (0.0225 g, 0.157 mmol), 2,2'-bipyridine (bpy) (0.0490 g, 0.314 mmol), ethyl 2-bromoisobutyrate (EiBr) (0.0261 mL, 0.158 mmol), and methanol (7 mL) were added to a 25 mL of Schlenk tube. Nitrogen was bubbled through the solution for 40 min to remove the oxygen. The tube was then placed in an oil bath set at 50°C for 300 min. The reaction mixture was cooled to room temperature and the contents were diluted with THF and passed through a column of neutral alumina. The excess of THF was evaporated under reduced pressure. The polymer was precipitated in 10-fold excess hexane. The solid product was dried for 24 h in a vacuum oven at 40°C.

[MMA]₀: [HEMA]₀: [I]₀: [CuBr]₀: [bpy]₀ = 418 : 83 : 1 : 1 : 2. Yield = 38%. GPC: *M*_{n,GPC} = 36,500; *M*_w/*M*_n = 1.12. *T*_g = 79.8°C. ¹H NMR (500 MHz, CDCl₃): δ ppm 4.1 (HOCH₂CH₂OCO-,

$\text{CH}_3\text{CH}_2\text{OCO}-$), 3.8 ($\text{HOCH}_2\text{CH}_2\text{OCO}-$), 3.6 (CH_3OCO). FTIR γ (cm^{-1}): 3517, 2995, 2950, 1722, 1435, 1387, 1241, 1146.

Poly(methyl methacrylate-co-2-(2-bromoisobutyryloxy)-ethyl methacrylate) (PMMA-co-PBIEM) (3). PMMA-co-PHEMA (2) (2 g, 0.054 mmol), triethyl amine (753 μL , 5.40 mmol), and 20 mL dry THF were added to a 25 mL of Schlenk tube. Solution mixture was stirred at 0°C and then 2-bromoisobutyryl bromide (BrIB) (666 μL , 5.41 mmol) was added and mixture was stirred 24 h. Excess solvent was removed at rotary evaporator and polymer solution was precipitated in 10 times more methanol. The solid product was dried for 24 hr in a vacuum oven at 40°C .

Yield = 96%. ^1H NMR (500 MHz, $(\text{CD}_3)_2\text{SO}$): δ ppm 4.3 ($(\text{CH}_3)_2\text{BrCCOOCH}_2\text{CH}_2\text{OCO}-$), 4.1 ($(\text{CH}_3)_2\text{BrCCOOCH}_2\text{CH}_2\text{OCO}-$), 3.6 ($\text{CH}_3\text{OCO}-$), 1.9 ($(\text{CH}_3)_2\text{BrCCOO}-$). FTIR γ (cm^{-1}): 3021, 2943, 1724, 1441, 1266, 1241, 1144.

PMMA-co-PBIEM Copolymer with Pendant Azide Groups (PMMA-co-(PBIEM-g- N_3)) (4). PMMA-co-PBIEM (3) (1.5 g) and DMF (10 mL) were added to a 25 mL of Schlenk tube and stirred until a homogenous mixture is obtained and then added NaN_3 (4.03 g, 61.98 mmol) the mixture was stirred 24 hr. The excess of DMF was evaporated under reduced pressure. The polymer was precipitated in ten-fold excess methanol. The solid product was dried for 24 hr in a vacuum oven at 40°C .

Yield = 78%. ^1H NMR (500 MHz, CDCl_3): δ ppm 4.4 ($(\text{CH}_3)_2\text{N}_3\text{CCOOCH}_2\text{CH}_2\text{OCO}-$), 4.2 ($(\text{CH}_3)_2\text{N}_3\text{CCOOCH}_2\text{CH}_2\text{OCO}-$), 3.6 (CH_3OCO), 1.5 ($(\text{CH}_3)_2\text{N}_3\text{CCOO}-$). FTIR γ (cm^{-1}): 3017, 2948, 2110, 1724, 1438, 1242, 1140.

***N,N*-dimethylamino- and aZnPc- Functional Copolymer (5).** PMMA-co-(PBIEM- N_3) (4) (1 g), DMF (10 mL) were added to a 25 mL of Schlenk tube and stirred until a homogenous mixture is obtained and then added PMDETA (0.212 mL, 1.018 mmol), CuBr (0.0975 g, 0.679 mmol), aZnPc (1) (0.0225 g, 0.0272 mmol), 4-ethynyl-*N,N*-dimethyl aniline (0.0946 g, 0.6528 mmol). Oxygen was removed by bubbling nitrogen through the solution for 40 min. After 48 h at 40°C , solution was diluted with THF, filtered through a column filled with neutral alumina to remove copper complex and precipitated in hexane. The solid product was dried for 24 hr in a vacuum oven at 40°C .

Yield = 70%. GPC: $M_{n,\text{GPC}} = 43,500$; $M_w/M_n = 1.26$. $T_g = 88.9^\circ\text{C}$. ^1H NMR (500 MHz, CDCl_3): δ ppm 7.9 (ArH of Pc), 7.7 (CH of triazole), 6.7 (ArH of phenyl), 4.4 ($(\text{CH}_3)_2\text{N}_3\text{CCOOCH}_2\text{CH}_2\text{OCO}-$), 4.3 (-triazole- $(\text{CH}_3)_2\text{CCOOCH}_2\text{CH}_2\text{OCO}-$), 4.2 ($(\text{CH}_3)_2\text{N}_3\text{CCOOCH}_2\text{CH}_2\text{OCO}-$), 4.1 (-triazole- $(\text{CH}_3)_2\text{CCOOCH}_2\text{CH}_2\text{OCO}-$), 3.8 ($\text{CH}_3\text{CH}_2\text{OCO}$), 3.6 (CH_3OCO), 3.01 ($(\text{CH}_3)_2\text{N}-$). FTIR γ (cm^{-1}): 2997, 2927, 2348, 2111, 1725, 1619, 1481, 1388, 1241, 1145. UV-vis (THF) $\lambda_{\text{max}}/\text{nm}$: 674, 348.

4'-(octyloxy)-4-biphenylcarbonitrile (8OCB) (6). Under nitrogen atmosphere, 1-bromooctane (20 mmol, 3.5 mL) was added drop wise to a stirring mixture of 4'-hydroxy-4-biphenylcarbonitrile (15.4 mmol, 3 g) and anhydrous K_2CO_3 (14.5 mmol, 2 g) in 200 mL of anhydrous DMSO. The reaction

mixture was heated at 110°C for 3 h. After this process, the reaction mixture was added drop wise to 400 mL of 10% NaOH solution at room temperature and filtered. The resultant was dried in vacuum and crystallized from ethanol. White crystalline product was obtained and dried under vacuum.

Yield = 93%. FTIR (cm^{-1}): 2956- 2852 (CH, aliphatic), 2235 (CN), 1251, 1051 (C-O-C). ^1H NMR (500 MHz, CDCl_3): δ ppm 6.9-7.69 (Ar-H, 8H), 4.02 (CH_2-O , 2H), 1.29-1.80 ($-(\text{CH}_2)_6-$, 12H), 0.9 (CH_3-R , 3H).

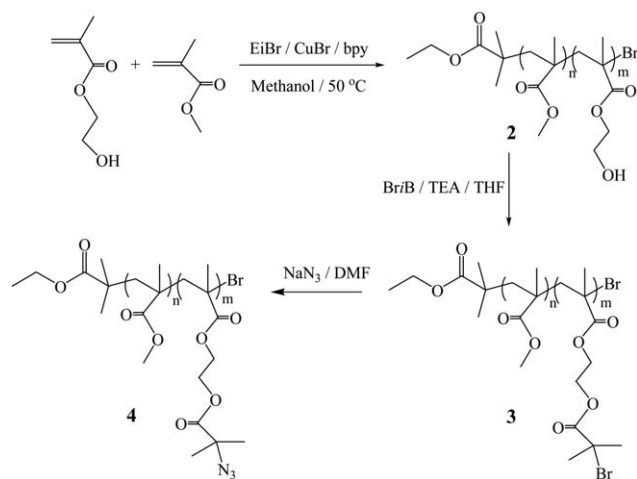
PDLC Film (7). A solution containing 70 mg (0.0016 mmol) *N,N*-dimethylamino- and aZnPc-functionalized copolymer, 2.9 mg (0.016 mmol) benzophenone, 0.1 g (0.33 mmol) 8OCB, and 5 mL (26.5 mmol) EGDMA in 0.5 mL of THF was placed on to glass surface to form a thin film and irradiated in UV crosslinker at 25°C for 5 h, leading to the formation of a PDLC film.

RESULTS AND DISCUSSION

Synthesis and Characterization of aZnPc-Functional Photocurable Copolymer

In this study, we describe the synthesis and characterization of a new aZnPc-functional photocurable copolymer and its utilization as matrix of PDLC film. For this purpose, we first prepared asymmetrical zinc Pc having one terminal alkynyl group and three *tert*-butyl groups through the statistical condensation of 4-*tert*-butylphthalonitrile and 4-pent-4-ynoxyphthalonitrile in the presence of template zinc acetate.⁴⁹ Characterization of the aZnPc was verified using elemental analysis, IR, ^1H , and ^{13}C NMR, UV-vis, and mass spectra. All data were consistent with the proposed structure and results were given in the experimental section. The yield of aZnPc is 23 % which is quite comparable to values reported in the literature.⁵¹⁻⁵³

The synthetic strategy for the synthesis of targeted PMMA-co-(PHEMA-g- N_3) copolymer was depicted in Scheme 1. First, PMMA-co-PHEMA (2) copolymer was synthesized using ethyl-2-bromoisobutyrate (EiBr) as the initiator and CuBr with bpy as the catalyst system at 50°C in methanol (MMA/methanol = 1, v/v). The polymerization was stopped at relatively low monomer conversion (<40%) to achieve good control over molecular weight. The molecular weight (M_n) and molecular weight distribution (MWD) of PMMA-co-PHEMA copolymer were determined by GPC on PMMA standards were 36.5 K and 1.12. The composition of 2 was determined by comparing the integral area of the ^1H NMR peak a at 3.6 ppm for MMA units with that of the peak c at 4.1 ppm for HEMA units [Figure 1(a)]. The molar ratio of HEMA to MMA in copolymer chain was calculated to be 0.28/1. Esterification reaction was performed between PMMA-co-PHEMA copolymer and 2-bromoisobutyrylbromide to yield PMMA-co-PBIEM (3). In the ^1H NMR spectra, for PMMA-co-PBIEM (3), a new peak appearing at 4.3 ppm, is assigned to $(\text{CH}_3)_2\text{BrCCOOCH}_2\text{CH}_2\text{OCO}-$ of BIEM units [Figure 1(b)]. Noteworthy, the integration of peaks at 4.3 and 4.1 ppm is almost equal indicating the complete esterification reaction was performed. Thereby synthesized PMMA-co-PBIEM was reacted with NaN_3 to give PMMA-co-(PHEMA-g- N_3) (4) copolymer. The characteristic peak of



Scheme 1. Synthesis of PMMA-*co*-PBIEM copolymer with pendant azide groups (PMMA-*co*-(PBIEM-*g*-N₃)).

methyl protons [peak d, in Figure 1(b)] next to the bromo group disappeared after azidation, and a new peak at 1.5 ppm corresponding to the methyl protons [peak d, in Figure 1(c)] was appeared. Azidation of PMMA-*co*-PBIEM was also confirmed with FTIR [Figure 2(c)]. The FT IR spectrum of PMMA-*co*-(PBIEM-*g*-N₃) (4) exhibited characteristic signal at 2111 cm⁻¹, due to -N₃ stretching vibration, hence confirming the presence of azido groups.

CuAAC click reaction was performed between PMMA-*co*-(PBIEM-*g*-N₃) (4), 4-ethynyl-*N,N*-dimethyl aniline, and aZnPc to yield aZnPc-functional photocurable copolymer (5) (Scheme 2). The reaction was conducted in DMF, a good solvent for 4, aZnPc (1), and 4-ethynyl-*N,N*-dimethylaniline

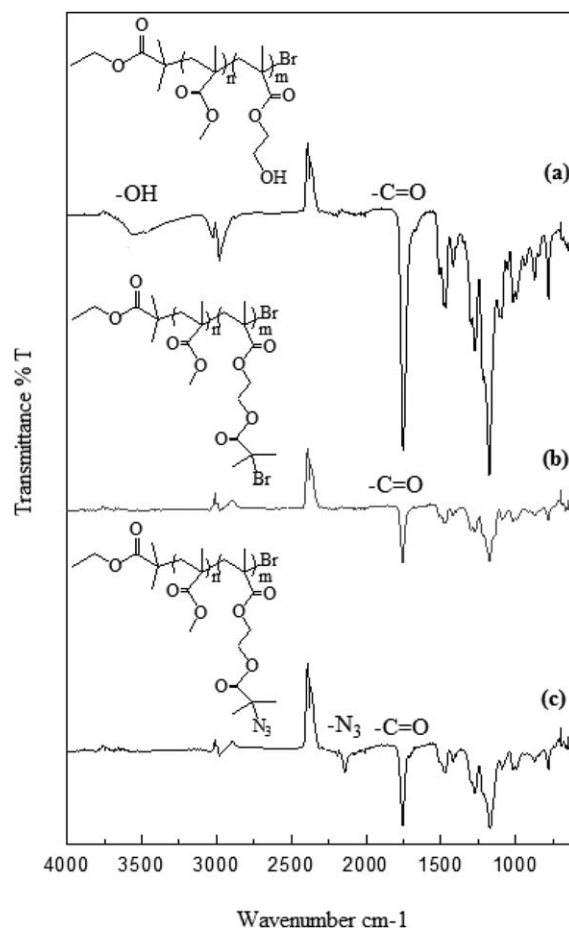


Figure 2. FTIR spectra of (a) 2, (b) 3, and (c) 4.

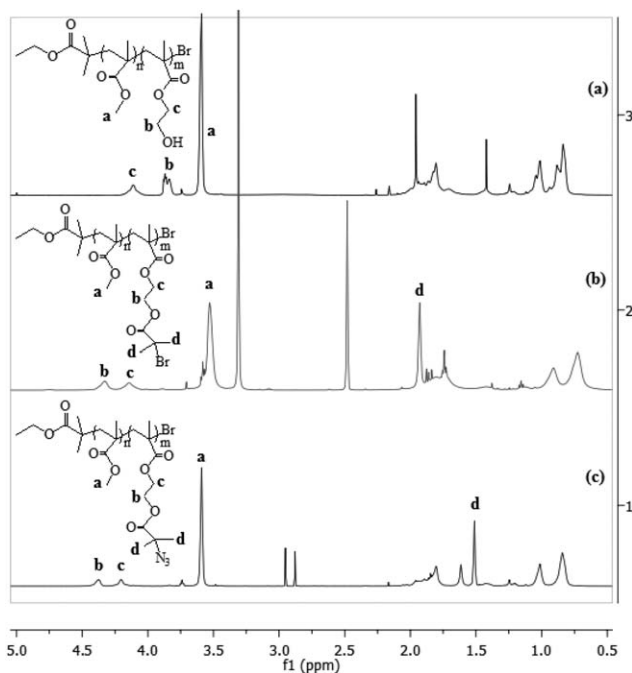
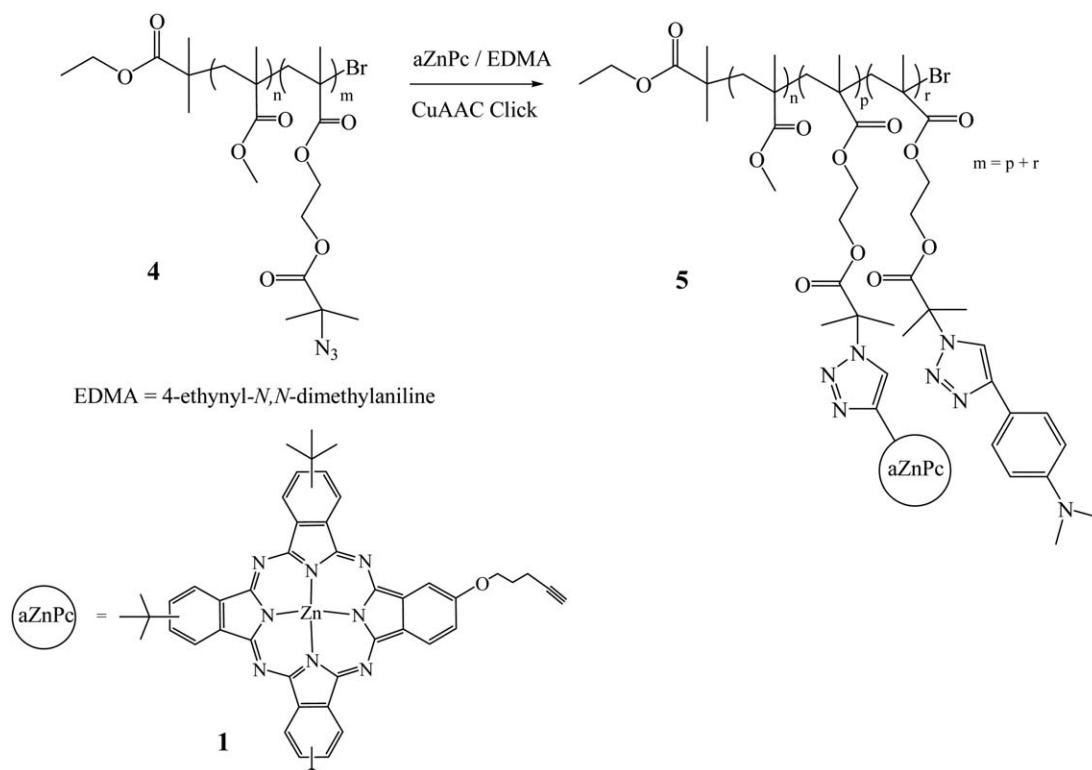


Figure 1. ¹H NMR spectra of (a) 2 in CDCl₃, (b) 3 in (CD₃)₂SO, and (c) 4 in CDCl₃.

(EDMA) with the molar ratio 1 : 24 for aZnPc : EDMA. The ¹H NMR spectrum of the CuAAC click product is presented in Figure 3. In comparison to its precursor 4 [Figure 1(c)], the characteristic peaks at 4.4 and 4.2 ppm corresponding to PMMA-*co*-(PBIEM-*g*-N₃), decreased and new peak appeared at 7.7 ppm indicating triazole formation. Due to steric hindrance of aZnPc (1) and EDMA not all the azide groups of 4 take part in CuAAC click reaction. However, the decrease in the intensity of the peak at 2111 cm⁻¹ corresponding to -N₃ stretching vibration have proved that CuAAC click reaction was occurred. Overlaid GPC chromatograms of 2, 3, 4, and 5 were presented in Figure 4. Change in *M_n* was not clearly observed through DMF GPC measurements which is consistent with literature.⁵⁴ Besides the shoulders in GPC chromatograms of 4 and 5 can be attributed to change in the polarity of the functional copolymers. Thermal properties of 2 and 5 were investigated by DSC measurements. It was found that the incorporation of bulky and rigid aZnPc and EDMA groups into the copolymer caused an increase in the glass transition temperature (*T_g*) from 79.8 to 88.9°C for the copolymers 2 and 5, respectively. UV-vis spectrum of aZnPc-functional photocurable copolymer (5) showed characteristic aZnPc-related signals, confirming the presence of aZnPc function. A similar electronic absorption spectra of 1 and 5 were observed in THF with intense sharp Q band at 674 nm and B band at 348 nm.



Scheme 2. Synthesis of aZnPc-functional photocurable copolymer.

Polymer Dispersed Liquid Crystal

The liquid crystalline nematic mesogen 8OCB was synthesized according to following reaction (Scheme 3) and used for the preparation of PDLC. The chemical structure of the 8OCB was characterized by FTIR and $^1\text{H-NMR}$. FTIR spectrum of 8OCB showed characteristic bands at 1251–1051, 2235, and 2956, 2920–2852 cm^{-1} attributed to aromatic ether C—O—C, —CN, and saturated —CH stretching bands, respectively. $^1\text{H-NMR}$ spectrum of 8OCB showed triplet peaks at 0.90 ppm, multiplet peaks at 1.29–1.80 ppm, triplet peaks at 4.02 ppm, and multiplet peaks at 6.99–7.69 ppm corresponding to —CH₃, —CH₂, —CH₂—O, and aromatic protons respectively.

PDLC has been obtained by UV curing at 365 nm of aZnPc and *N,N*-dimethylamino functional copolymer in the presence of EGDMA as a crosslinker, benzophenone as an initiator, and 8OCB as a liquid crystalline mesogen. Insoluble polymer in

THF showed the formation of cross linking during photo curing.

Thermal and Mesomorphic Properties of PDLC

The DSC heating and cooling scans for 8OCB are shown in Figure 5. Figure 5(a) exhibits two peaks at 59.5 and 83.4°C

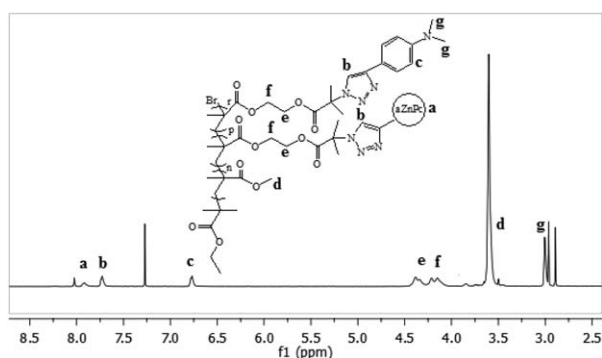


Figure 3. $^1\text{H NMR}$ spectrum of **5** in CDCl_3 .

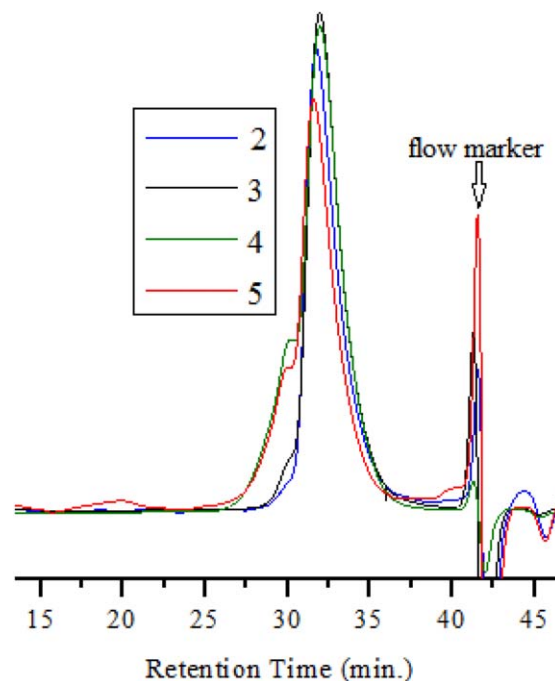
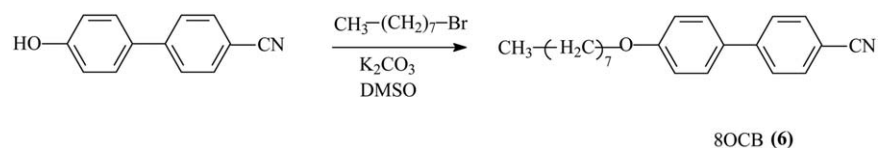


Figure 4. GPC curves of **2**, **3**, **4**, and **5**. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



Scheme 3. Synthesis of liquid crystalline mesogen 4'-(octyloxy)-4-biphenylcarbonitrile (8OCB).

corresponding to the crystal to Smectic A transition and isotropic transition, respectively. The DSC cooling scan [Figure 5(b)] exhibits two peaks at 82.4 and 36.17°C corresponding to the transition from isotropic phase to Smectic A phase and Smectic A transition to crystal. The phase diagram for the cooling process is not being identical to that for heating process. The cooling curve [Figure 5(b)] shows slight displacement of the isotropic transition, due to supercooling. The smectic A to crystal transition is depressed strongly due to supercooling of the smectic A phase.

Morphology of 8OCB was investigated by POM. During heating stage, the transition from the solid phase to a smectic A phase at 56°C [Figure 6(a)] and the smectic A transition to isotropic phase at 84.7°C [Figure 6(b)] were observed. During cooling stage, transition from isotropic phase to mesophase was observed at 82°C. Smectic A mesophase occurred at 63°C [Figure 6(c)] and the transition from smectic A to crystal phase was observed at 35.5°C.

The DSC heating scan for 8OCB dispersed *N,N*-dimethylamino- and aZnPc-functionalized copolymer matrix shown in Figure 7(a) shows a single peak at 56.6°C corresponding to transition from the solid phase to a Smectic A phase. A peak for the clearing temperature cannot be detected (Figure 7).

Through the use of POM, the dispersed liquid crystal domains were detected (Figure 8). The textures of the mesophase was identified during both heating and cooling cycles as being a Smectic A mesophase at 61.5°C and 52.5°C, respectively, and they are shown below in Figure 8(a,b).

CONCLUSIONS

Using click chemistry strategy aZnPc-functional photocurable copolymer was successfully prepared and used as matrix of

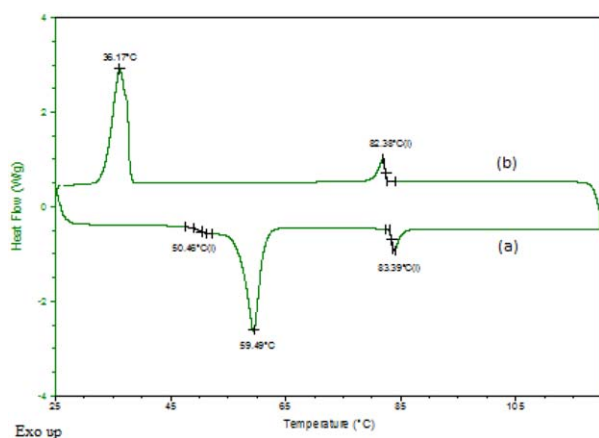


Figure 5. DSC thermograms of 6 at a rate 5 K min⁻¹. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

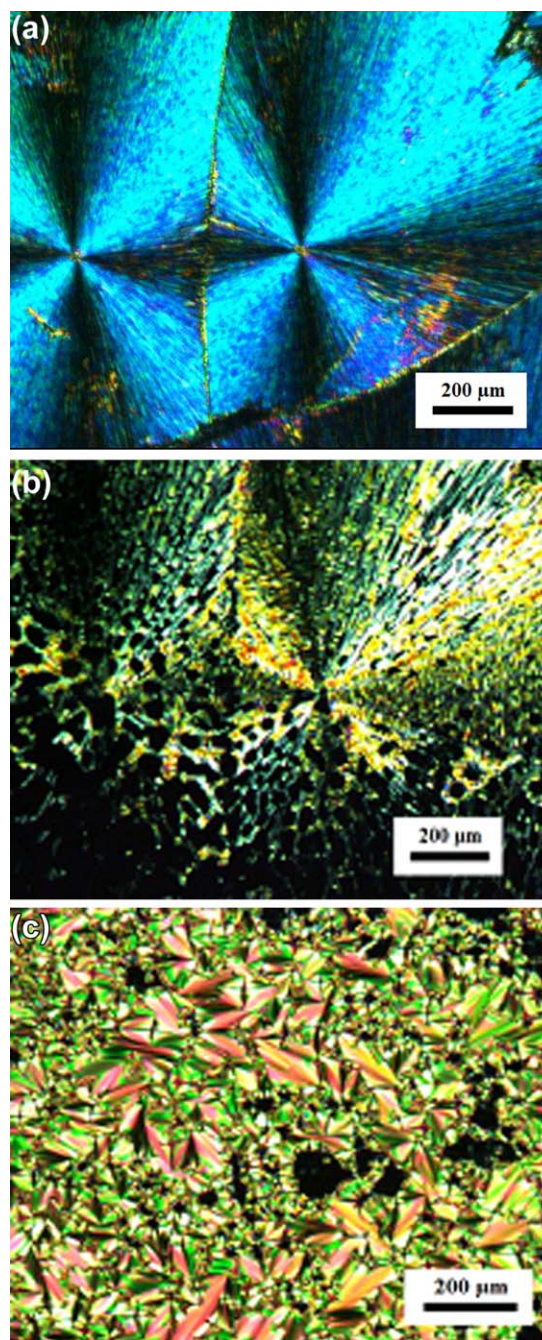


Figure 6. Polarized optical micrographs of 8OCB taken during heating from crystal to smectic A at 56°C (a), transition to isotropic phase at 84.7°C (b), and during cooling from the isotropic phase to smectic A at 63°C (c) at a rate 5 K min⁻¹ (250×). The scale bar in inset represents 200 μm. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

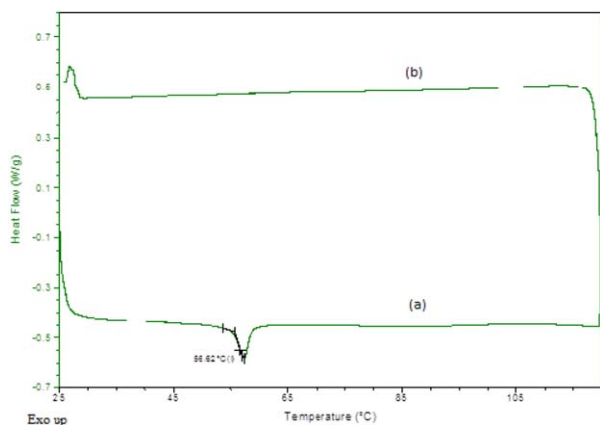


Figure 7. DSC thermograms of 7 at a rate 5 K min^{-1} . [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

PDLC film. The optical and thermal characterization of aZnPc-functionalized polymer-dispersed liquid crystal and its mesogenic component were characterized using DSC and POM. PDLC was prepared by p-PIPS technique.

The mesomorphic behaviours of 8OCB as dispersed droplets within the aZnPc-functionalized polymer exhibited differences

from those of the pure 8OCB. The purpose of using aZnPc-functional polymer was to improve the molecular orientation of mesogenic units in the PDLCs and investigate the influence of interactions between aZnPc and mesogenic moiety on the nematic-isotropic phase transition temperature of the pure LC. As a result of interaction between Pc groups and mesogenic units of 8OCB in the polymer matrix, polymer-dispersed 8OCB exhibited more stable liquid crystal mesophase in the lower temperature and the broader temperature range than its mesogenic component. Smectic A liquid crystal mesophases were observed in both polymer dispersed 8OCB and its mesogenic component 8OCB.

This newly prepared aZnPc-functional PDLC film (7) is potentially useful in electro-optic devices. Therefore, electro-optical investigations are under consideration.

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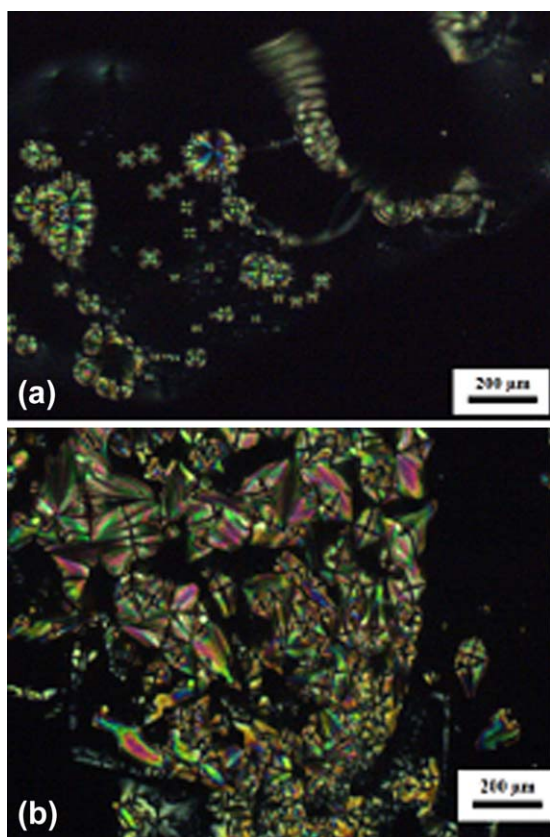


Figure 8. Polarized optical micrographs of 7 taken during heating at 61.5°C (a) and cooling at 52.5°C (b) at a rate 5 K min^{-1} ($250\times$). The scale bar in inset represents $200 \mu\text{m}$. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

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