Synthesis, Characterization and Self-Assembly Properties of a New Copper-Phthalocyanine Core Acrylate Block Copolymer

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Abstract
A new di-block acrylate copolymer with a Copper-Phthalocyanine (CuPc) core has been synthesized via a multi-step reaction scheme involving the atom-transfer radical polymerization. This material displayed amphiphilic character and consists of a CuPc core with eight copolymer arms. This new amphiphilic material and related intermediates have been characterized by UV-Vis, FT-IR, 'H-NMR and elemental analysis. A preliminary study involving self-assembly properties of this material by optical, atomic force and scanning electron microscopies is presented.

Keywords: Copper-phthalocyanine, Amphiphilic materials, Atom-transfer radical polymerization, Aggregates, Self-assembled properties.

Abbreviations: CuPc—Copper-Phthalocyanine, Por-Porphyrins, Pc-Phthalocyanines, DMF-Dimethylformamide, DCM-Dichloromethane, FT-IR-Fourier-Transform Infrared Spectroscopy, TLC-Thin Layer Chromatography, tBA-tert-Butyl Acrylate, TEGA-Tri(ethylene glycol) monomethyl ether

Introduction
In the past decade, the synthesis of functional nano-architectures, aimed at designing electronic and photonic nano-devices to perform specific functions, such as catalysis, chemical sensing, electrical conductivity, photodynamic therapy, etc., has been an intense area of research [1-10]. Most of these activities are driven by the self-assembly and self-organization properties of molecules and require the incorporation of functional building blocks through a well-defined controlled process. Porphyrins (Por), tetraazaporphyrins, Phthalocyanines (Pc) and porphyrines are examples of tetrpyrrole macrocyclic ring systems, through which mutual non-covalent recognition of specific structural properties, can self-assemble and act as building blocks for self-organized architectures.

Phthalocyanines possess an extended flat hydrophobic aromatic surface and the disc-shaped rigid Pc rings can easily stack through strong intermolecular arene-arene (π-π) interactions, leading to aggregation [11-13]. Other molecular recognition motifs that can self-aggregate are metal-ligand and donor-acceptor interactions and hydrogen bonding [14-16]. Various approaches have been explored in order to control the self-organization of Pc molecules to form well-defined nano-objects. One such approach is the incorporation of these molecules in amphiphilic polymers [17-20].
Pcs have been incorporated in such systems as a side group, as a terminal group, in the main chain and in a polymeric network [21-26]. Kimura et al studied the self-assembly properties of ZnPc-terminated Butyl Acrylate (BA) and Tri(Ethylene Glycol)Methyl Ether Acrylate (TEGA) polymers and have reported formation of nanofibers through self-organization [18]. This group also studied the aggregation behavior of the amphiphilic block copolymer of poly(norbornene)s containing Pc moieties as a side chain of the polymer backbone that formed spherical micelles in an alkaline aqueous solution [19]. In addition, ordered stacked Pc polymers were prepared in which the Pc moieties were contained in the polymer network and in the main chain of the Pc polymers with reported rod-like nanostructures [20]. Similar polymer systems have also been developed using Por moieties [27-30]. In most cases, the polymerization step has been achieved by controlled/living radical polymerization, such as metathesis polymerization and Atom Transfer Radical Polymerization (ATRP) [18-20, 27-30].
Pcs have mostly been incorporated in amphiphilic polymers as a side group; a terminal group, or in the main chain [31-34]. Although polymer amphiphiles with Por cores have been designed and reported, amphiphilic polymers especially block copolymers with Pc cores; have not been studied well due to synthetic challenges. We report here the synthesis and characterization of a new di-block acrylate copolymer with CuPc core, having a distinct hydrophobic segment composed of tert-Butyl Acrylate (tBA) units, and a hydrophilic segment having Tri(Ethylene Glycol)Monomethyl Ether Acrylate (TEGA) units.

Experimental

Materials and Methods
Unless mentioned otherwise, all reagents were used as received from commercial suppliers without further purification. Dimethylformamide (DMF) used in these reactions was purchased as anhydrous grade

stored in a Sure-Seal™ bottle. Toluene was dried by distillation over freshly cut sodium metal cubes. All reactions involving moisture- and air-sensitive reagents were carried out under an inert atmosphere using high-purity grade argon that was first passed through a column of anhydrous calcium sulfate. Thin Layer Chromatography (TLC) was done on 60, 200 μm thick silica gel flexible plates and 250 μm aluminum oxide flexible plates. Gravity-flow column chromatography was performed on 70-230-mesh, 60Å silica gel or 150-mesh, 58Å activated neutral aluminum oxide.

Structural characterization by Fourier-Transform Infrared spectroscopy (FT-IR) was carried out using a Thermo Nicolet Nexus 470 FT-IR spectrometer and a Perkin-Elmer System 2000 instrument. The electronic absorption spectra were recorded on a Perkin Elmer (UV/VIS/NIR) spectrometer Lambda-19. 1H-NMR and 13C-NMR spectra were recorded by a 300 MHz Bruker instrument. Elemental analyses were performed on a Perkin-Elmer Series II CHNS/O Analyzer 2400 machine. Scanning Electron Microscopy (SEM) was performed by a JEOL JSM5900-LV instrument and Atomic Force Microscopy (AFM) by Picoscan 3000 AFM (Agilent Technology).

**Synthesis of the Phthalocyanine Precursor, 2,3-Dicyano-1,4-bis-[2-(2-hydroxyethoxy)-ethoxy]-ethoxy]benzene (1)**

2,3-dicyano-1,4-dihydroquinone (11.3958 g, 71.1659 mmol) in 100 mL anhydrous DMF was added to a stirred suspension of K₂CO₃ (29.5075 g, 213.5 mmol) and KI (2.9834 g, 18 mmol) in 150 mL anhydrous DMF under inert atmosphere in a 500 mL 3 neck round bottom flask. A solution of 2-(2-(2-chloroethoxy)-ethoxy)ethanol (30 g, 170.7982 mmol) in 10 mL anhydrous DMF was added to it. The reaction mixture was stirred at 70°C for 10 days. It was then cooled to room temperature and filtered. The filtrate was poured into a Teflon petri dish and DMF was allowed to evaporate. When it was dry, it was kept in the oven at 50°C under vacuum for 2 hours. The brown solid was stirred with water and extracted with chloroform. The organic layer was collected, dried over anhydrous MgSO₄, filtered and chloroform was evaporated in a rotary evaporator to give orange colored solid. The solid was purified by column chromatography, using alumina column, eluting with first with DCM and then with 5% methanol in DCM. The color of the reaction mixture turned green. The reaction mixture was cooled to room temperature and 40 mL of methanol was added to it. It was stirred overnight and filtered under vacuum. Methanol was evaporated in a rotary evaporator to give green solid. It was purified by column chromatography using alumina. The solvent systems used were DCM, followed by 2-5% methanol in DCM. TLC showed that the product is still not pure. So the fractions that eluted with 2-5% methanol in DCM, were combined and subjected to another column chromatography, with a solvent system of DCM, again followed by 2-5% methanol in DCM. The fractions obtained with the last eluent system were checked with TLC and were found to be pure.

**Synthesis of Copper Phthalocyanine (CuPc) (2)** 1 (2.682 g, 6.32 mmol) and copper powder (0.8 g, 12.59 mmol) were added sequentially.

4b was made following the same procedure as the synthesis of 4a. In this case, 4a itself was used as the macroinitiator for the polymerization reaction.

**Synthesis of ATRP macroinitiator (3)**

Compound 2 (0.5 g, 0.2765 mmol) was dissolved in 8 mL pyridine in a 25 mL round bottom flask in presence of argon. 2-Bromoisoobutyryl bromide (7 g, large excess) was dissolved in 5 mL chloroform and added drop wise to a vigorously stirred solution of 11 at 0°C over a period of 1 hour under inert atmosphere. The temperature gradually rose to room temperature and the reaction was allowed to proceed for 24 hours. Chloroform was evaporated in a rotary evaporator. The reaction mixture was then added drop wise to a large excess of water when green solid separated out. It was washed thoroughly with hexane in order to remove unreacted 2-bromoisoobutyryl bromide. It was then extracted with chloroform and the organic layer was washed thoroughly with water, a saturated solution of K₂CO₃ and a saturated solution of NaCl, twice each.

**Synthesis of the polymer, CuPc-core-poly-(BA) (4a)**

The macroinitiator for the polymerization was 4a (0.0367 mmol) and Cu(I)Br (0.0552 mmol) were added to it. The reaction mixture was then heated under vacuum at 90°C for 4 hours under argon atmosphere. Toluene was evaporated. The mixture was washed several times with hexane to remove unreacted PMDETA and the monomer. After each washing, it was centrifuged and hexane was decanted. The green solid was dissolved in chloroform and filtered. The residue is unreacted Cu(I)Br.

**Synthesis of the polymeric CuPc core (4b)**

4b was made following the same procedure as the synthesis of 4a. In this case, 4a itself was used as the macroinitiator for the polymerization reaction.

**Synthesis of TEGA monomer (5)**

Triethylene glycol monomethyl ether (1.5 g, 9.1352 mmol) was dissolved in 5 mL anhydrous THF. Acryloyl chloride (1.5 g, 16.5727 mmol) and triethyl amine (3.18 mL, 22.838 mmol) were added to it. The reaction mixture was stirred under argon atmosphere overnight at

room temperature. It was then poured into water and extracted with chloroform. The organic layer was washed several times with a saturated solution of Na₂CO₃ and a saturated solution of NaCl. It was dried over anhydrous MgSO₄. filtered and chloroform was evaporated from the filtrate to yield the TEGA monomer (5) as a colorless liquid. 5 were purified by column chromatography using alumina. 2% methanol in chloroform was used to elute the pure fraction.

FT-IR (KBr): 2872, 1722, 1631, 1455, 1411, 1269, 1195, 1113, 987, 853, 806 cm⁻¹; ¹H-NMR (300 MHz, CDCl₃ δ=7.26): δ=6.35 (dd, 1H), δ=6.1 (dd, 1H), δ=5.79 (dd, 1H), δ=4.25 (t, 2H), δ=3.46-3.7 (m, 10H), δ=3.33 (s, 3H).

Results and Discussion

Retro-synthetic Analysis

The two key components of the retro-synthetic design for this project are (i) an appropriate core molecule functionalized with initiator groups and (ii) polymerization to form the arms. Therefore, in order to make CuPc core functionalized polymer arms (4a and 4b), a CuPc derivative containing eight bromoisobutyryl initiator moieties (3) must be synthesized first. This macro-initiator could be made from a CuPc-centered tri(ethyleneoxy) intermediate (2), a CuPc derivative with peripherally substituted hydroxyl (OH) functional groups. That leaves 2 to be constructed by cyclo-tetramerization of a phthalonitrile precursor (1).

Synthesis and Characterization

Phthalonitriles are the most commonly used precursors for the synthesis of phthalocyanine derivatives. A disubstituted phthalonitrile derivative (1) was synthesized as the precursor of 2 by an O-alkylation reaction in which 2,3-dicyanohydroquinone was alkylated by treatment with 2-[2-(2-chloroethoxy)-ethoxy]ethanol in the presence of anhydrous potassium carbonate and a catalytic amount of potassium iodide (Scheme 1). The reaction was carried out in anhydrous DMF. The same reaction conditions were followed as reported by Xue et al., [16]. After evaporation of DMF, the crude product was extracted with chloroform and purified by column chromatography to afford pure 1 as a white solid.

The first attempt to synthesize CuPc was by refluxing 1 in 2-(dimethylamino)ethanol in the presence of copper acetate under an argon atmosphere, but no characteristic green color of Pc was obtained, even after 3 days. Next, we tried to synthesize the CuPc via its LiPc [35]. After purification, the desired CuPc was obtained, but in very low yield (12%). The next attempt was via the isoindoline route where 1 was first converted into its isoindolene by treating with ammonia in the presence of sodium methoxide in methanol, followed by self-condensation of the isoindolene into CuPc, in the presence of copper acetate, but without success. Another attempted route to 2 was by reacting 1 with copper acetate in dry quinoline at 220°C for 3 hours, but the characteristic green color of Pc was not observed. Finally, we succeeded in synthesizing 2 from 1 by a solvent-free method [36]. The phthalonitrile derivative was stirred with Cu powder at a very high temperature [36]. The optimum temperature for our system was found to be 170°C under vacuum for 3 hours (Scheme 1). Unreacted Cu powder was filtered off and pure 2 were obtained as a sticky green solid after column chromatography. The macroinitiator 3, with bromoisobutyryl initiating sites, was synthesized by acylation of the peripheral hydroxyl groups in 1 with a large excess of 2-bromoisobutyryl bromide. The reaction was carried out in a mixture of chloroform and pyridine and the temperature was allowed to rise from 0°C to room temperature and maintained there for 24 hours (Scheme 2). The crude product was extracted with chloroform and washed thoroughly with saturated solutions of Potassium Carbonate (K₂CO₃) and Sodium Chloride (NaCl). Pure 3 was obtained as a bright green solid after column chromatography.

The polymerization reactions were performed under ATRP conditions (Scheme-3). Two monomers were chosen: (i) tert-Butylacrylate (t-BA) and (ii) Tri(ethylene glycol)Monomethyl Ether Acrylate (TEGA). While the polymer chain composed of t-BA units imparts hydrophobicity to the system, the one composed of TEGA monomers provides hydrophilicity. Accordingly, the CuPc-core block copolymer poly-(t-BA)-poly-(TEGA) will be amphiphilic in nature. The monomer TEGA (5) was obtained from tri(ethylene glycol)monomethyl ether and acryloyl chloride following the conditions previously reported for the preparation of acylated PEG derivatives [37]. Copper (I) Bromide ([CuBr]₃) was used as the catalyst and N,N,N',N''-Pentamethylidihydropyridine (PMDETA) as the ligand. In a typical polymerization procedure, the Pc-core macroinitiator: CuBr: ligand ratio was 1:8.2:8.2 and the amount of monomer added was 5 times the weight of the initiator. Polymerization reactions were carried out in
solution with toluene as solvent under argon atmosphere. The purification procedure was modified, by first extracting with chloroform and then purified by column chromatography.

The FT-IR spectrum of the phthalonitrile precursor (1) showed strong O-H stretching at 3410 cm⁻¹ and aromatic C-H stretch at 3092 cm⁻¹. Bands at 2907 cm⁻¹ and 2876 cm⁻¹ are indicative of CH₂ asymmetric and CH₂ symmetric stretching frequencies. The strong peak at 2228 cm⁻¹ is typical of C≡N stretching in aromatic nitriles. The presence of both aromatic and aliphatic C-H vibrations proves that the O-alkylation step was been successful. The C≡N peak at 2228 cm⁻¹ was completely disappeared in the spectrum of CuPc (2), indicating complete cyclotetramerization of 1. The strong peak at 3390 cm⁻¹ is due to O-H stretching. The aromatic C-H stretching vibration is seen at 3080 cm⁻¹ and the positions of symmetric and asymmetric aliphatic C-H stretching vibrations remain the same as those for compound 1. In the FTIR spectrum of the macroinitiator 3, successful acylation with 2-bromoisobutyryl bromide is evident from the disappearance of the O-H and the formation of the ester linkage comes from the strong ester carbonyl peak at 1732 cm⁻¹. The FT-IR spectrum of the homopolymer, 4a, had characteristic peaks similar to those of 3, with the common features being (i) absence of O-H, (ii) presence of CH₂ asymmetric and CH₃ symmetric frequencies, and (iii) >C=O around 1730 cm⁻¹.

Formation of TEGA was also confirmed by FT-IR from the aliphatic CH₂ peaks around 2900 cm⁻¹ and the ester carbonyl peak at 1722 cm⁻¹.

\[^1\text{H}\text{NMR}\] of the phthalonitrile precursor 1 in DMSO-d₆ shows chemical shifts for the aromatic protons at δ=7.62 (m), for the OH protons at δ=4.56 (t), for the ArOCH₂ protons at δ=4.28 as a triplet and for all the other CH₂O protons at δ=3.39-3.77 as multiplet. The chemical shifts for these protons remain almost the same in the CuPc (2), with the aromatic protons at δ=7.4, OH protons at δ=4.25, ArOCH₂ protons at δ=3.91 and CH₂O protons at δ=3.6-3.8. In the \[^1\text{H}\text{NMR}\] spectrum of the macroinitiator 3, the presence of a singlet at δ=1.86, due to the chemical shift of the protons in the CH₃ groups at the end of the side chains, proves that the esterification step has been successful.

The peaks for the ArOCH₂ protons are at δ=4.22 and for the CH₂O protons at δ=3.75. Besides the aromatic protons and the ArOCH₂ protons at δ=7.26 and δ=4.22, respectively, the \[^1\text{H}\text{NMR}\] spectrum of the poly-t-BA (4a) exhibits peaks at δ=2.2 for CH protons of the polymer backbone, at δ=1.9 for the CH₂ of the polymer backbone and at δ=1.43 (CH₃)C protons of the t-BA ester group. The success of the copolymerization reactions to synthesize 4b is conspicuous from its \[^1\text{H}\text{NMR}\] spectra. It shows peaks attributed to the tert-butyl resonance (δ=1.44) as well as the to the OCH₃ resonance (δ=3.38, singlet). The \[^1\text{H}\text{NMR}\] spectrum of TEGA monomer (5) shows three doublets of doublet for the three protons in the C≡C at δ=6.35, δ=6.1 and δ=5.79 and the OCH₃ resonance at δ=3.33.

The UV-Vis spectroscopy of compounds 2-4 was performed in DCM. All exhibit the characteristic Q band of Pc molecules. Further study was carried out with the homopolymer (4a) and the copolymer (4b) in order to investigate their aggregation properties at low concentrations. This was done by studying their UV-Vis absorption behavior at different concentrations and plotting the intensity of their Q-bands at different concentrations against the sample concentration at selected absorption wavelength (corresponding to the wavelength of the Q bands). The linear relationship between concentration and absorbance, as displayed in Figure 1 and Figure 2, strictly follows the Lambert-Beer Law, suggesting that neither of them form aggregates at low concentrations.

![Figure 1](image1.png)  
**Figure 1:** Plot of UV-Vis Absorption Spectra of Poly-t-BA (4a) at Different Concentrations against Wavelength in DCM. Inset: Plot of the Q Band Absorbance versus Concentration at 735 nm.

![Figure 2](image2.png)  
**Figure 2:** Plot of UV-Vis Absorption Spectra of Poly-t-BA-poly-TEGA (4b) at Different Concentrations against Wavelength in DCM. Inset: Plot of the Q Band Absorbance versus Concentration at 735 nm.

The solubility properties of compounds (1-4), summarized in Table 1, indicating that the copolymers are soluble in polar solvents.

**Study of Self-Assembly Properties**

A preliminary study was carried out to investigate the self-assembly properties of the CuPc-core block copolymer poly-(t-BA)-poly-

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(TEGA) (4b), using optical microscopy, AFM and SEM. The copolymer was dissolved in methanol (10 mg per mL). A drop of it was placed on the substrate and the solvent was allowed to evaporate completely.

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<th>Diethyl ether</th>
<th>THF</th>
<th>Hexane</th>
<th>Acetone</th>
<th>Ethyl acetate</th>
<th>CHClCN</th>
<th>DCM</th>
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Note: +: Soluble on warming. ++: Highly Soluble. --: Insoluble

Table 1: Solubility Characteristics of Compounds 1-4.

Figures 3-5 show images from an optical microscope at 10x, 20x and 40x magnifications, on days 1, 3 and 7. A glass was used as the substrate. The images of days 1 and 3 show that the polymer is in the process of self-assembling (Figure 3 and Figure 4). By the day 7, this process was complete and fibrous assemblies can be observed (Figure 5).

The substrate used for SEM study was silicon wafer. The sample studied was day 7 after evaporation of the solvent. Again, self-assembled fibrous structures, with fiber width of ~2 micron, were observed (Figure 6). Tapping mode AFM of the sample on Highly Ordered Pyrolytic Graphite (HOPG) on day 7 showed spherical assemblies with diameters 2.5–3.8 μm. (Figure 7).

In conclusion, we believe that since the copolymer has a hydrophilic segment at the peripheral sites, it forms spherical assemblies on hydrophobic substrate HOPG, whereas on hydrophilic substrates, e. g., silicon wafer and glass, it forms fibrous assemblies.

References


