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Novel Azobenzene-Functionalized Polyelectrolytes of Different Substituted Head Groups 1: Synthesis, Characterization and Absorption Spectroscopy Studies

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A new class of a series of amphiphilic polyelectrolytes functionalized with azobenzene chromophores have been synthesized and thoroughly characterized by various techniques. A facile two stage strategy is developed, and first involved the preparation of a precursor base polymer, designated as P(APEA), by the free-radical copolymerization of the monomers of acrylic acid (AA) and 2-(phenylethylamino)ethyl acrylate (PEA). In the second step, precursor PAPEA polymers are reacted and post-polymer modified with the diazonium salts to synthesize azobenzene polyelectrolyte, PAPEA-R with different substituted R-groups present on the para position of the aromatic ring of the azo chromophores. The PAPEA-R polyelectrolytes are same in their degree of polymerization and repeat unit compositions of AA and PEA monomers, and only differ from each other by the type of R-groups. The copolymers were classified on the basis of the characteristics of their R-groups into the hydrophilic-ionizeable smaller pair of $-SO_3H$ and $-COOH$, the hydrophobic-non-ionizeable smaller pair of $-H$ and $-OC_2H_5$, and the hydrophobic-non-ionizeable larger octyl pair of $-C_8H_{17}$ and $-C_8F_{17}$. The prepared copolymers are also characterized by NMR spectroscopy for structure, GPC for molecular weight, and UV-Visible spectroscopy for absorption determination. In DMF solvent, approximately similar absorption maxima, (λ_{max}) values were observed for azo chromophore-containing monomers and after incorporating these into their corresponding polymers structures. However, for the self-assembled multilayer thin films, λ_{max} moved to lower wavelengths to exhibit a blue shift with hydrophobic R-group of $-C_8H_{17}$, while this behaviour was not observed for hydrophilic R-group of $-COOH$. The shift in λ_{max} is found to be highly dependent on the type of substituted R-group, and attributed to aggregation of hydrophobic azo chromophores in DMF:H_2O mixture employed for self-assembly. The presence of the ionizeable AA and light-sensitive azo-chromophore functionalized PEA monomers in the PAPEA-R polyelectrolytes impart self-assembling and photoswitchable characteristics, respectively. Through understanding and controlling the solubility and complex solution aggregation behaviour of the different substituted R-groups of azo PEL, their adsorption, thickness, morphology, wetting, molecular-control, and photoresponsiveness can be tailored to enhance the capabilities of the self-assembled multilayer film process in diversified areas of microfluidics, sensing, and controlled release.

Keywords: amphiphilic polymers, azobenzene, polyelectrolytes, self-assembly, hydrophilic, hydrophobic, aggregation

1 Introduction

Recent progress in different technological fields, such as microfluidics, tissue engineering, and cellular biology, has created a great demand for materials that can undergo defined remodeling with time (1, 2). As a result, the latest research on materials with dynamically controllable properties has led to the design and synthesis of a variety of novel smart materials and surfaces (3). These materials possess properties that can be significantly changed in a controlled fashion by external stimuli, such as stress, temperature, moisture, pH, and electricity (4, 5). A few examples of such materials include piezoelectric materials (voltage responsive) (6), shape memory alloys (thermoresponsive materials) (7), electrochromic materials (change their color or opacity on the application of a voltage) (8), pH-sensitive polymers (9), and temperature-responsive polymers (10).

In addition to these materials, novel optical and photonic materials based on polymers containing azobenzene chromophores have attracted great attention for diverse potential applications (11–15). Azobenzene and its derivatives (azo) upon exposure to light undergo efficient

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*Address correspondence to: Nasir M. Ahmad, School of Chemical and Materials Engineering, National University of Sciences and Technology (NUST), Islamabad, Pakistan. Tel: +92+5190855213; E-mail: nasir.ahmad-scme@nust.edu.pk photo-induceable and reversible *trans-cis* isomerization (16). This isomerization can be induced in a well-defined manner in space and time, and capable of producing reversible changes in the optical, geometrical, and electronic properties. Such photoinduced changes can significantly affect the bulk and surface characteristics of the polymers. Furthermore, the rate and extent of isomerization from relatively more stable *trans*-isomer to less stable *cis* isomer are strongly rely on the structure of the azo chromophores and their incorporating matrixes. Due to such fascinating switchable characteristics, photoresponsive azo polymers are now considered important to many technological and biological processes and applications. Many of these applications require materials with optimized properties and functions, which can be met largely through the versatility by which the azobenzene chromophores can be incorporated into a polymer structure (17, 18). In this regard, two major classes of azo polymers have been prepared by introducing the azo group as a linking unit or as a pendant groups in the polymer main-chain. The main-chain polymers are mostly prepared by carrying out polycondensation of an aromatic azo group monomer having two functional groups with other di-functional monomers (19). The polymers with side-chain azo chromophores have been synthesized mainly by radical polymerization. The vinyl monomers with the pendant azo chromophore can be homopolymerized or copolymerized with the othervinyl monomers (20, 21).

Given the considerable interest generated in recent years, it is of great scientific and technical significance to design and synthesize novel photoresponsive azobenzene-functionalized polymeric materials. In this regard, the radical polymerization technique has been widely reported in literature for the synthesis of azo polymers of novel structures and characteristics. However, there are few studies which described in detail the synthesis and characterization of azo polymers. In addition, detailed studies about the effect of the azo chromophores incorporated into PEL, which differs in terms of their hydrophilicity/hydophobicity, degree of ionization, and sizes on their solution properties and self-assembled layers-by-layers multilayers (SAMU) thin films formation are still lacking. Considering the importance of the parameters which control the growth and properties of the SAMU film, therefore, it is necessary to understand the role played by the type of azo-chromophores present in the polymer chain. Such study will assist to fabricate thin films of optimized performance through clever synthetics design and development of the azo-polymers. Our current research efforts attempt to provide answers to few of these vital questions, and this paper presents work to describe the synthesis, characterization, and UV-visible solution spectroscopy studies of a novel series of copolymers with various types of azo-containing monomer and acrylic acid (AA) repeat units. The principal objective of this work is to develop a facile strategy to combine self-assembly with photo-switchable characters of the azo to prepare a wide range of amphiphilic azo-PEL by (i) preparing a base precursor-copolymers by radical polymerization, and then (ii) through post azo-functionalization reactions incorporate chromophores onto the precursor polymers. A main advantage of this approach is that the precursor polymers are of similar molecular weight, MWD, and only differ in terms of the chromophore types introduced in the post-polymerization step at the substituted para position. Further, such conditions are expected to provide functionalized polymers by avoiding their degradation. This strategy is of particular advantage to study and compare the photoresponsive property of polymers functionalized with different azo-chromophores. More work is underway to investigate the effect of the type of substituted R-group of an azo-chromophores to control the solubility, aggregation and self-assembly in solution, which subsequently affect the inter- and intra-polymeric interactions to control the self-assembled multilayers characteristics such as their wetting and its switchability, surface morphology, layers interpenetration, chromophores distribution/aggregation, absorption shift and thickness. General structures and classifications of the azo-PEL prepared and studied in the current work are given in Figure 1 and their preparation is represented in Reaction Scheme 1 and 2. The prepared PEL are classified into three pairs based on the type of the substituted azo-chromophores R-groups, and designated as the shorter-ionized hydrophilic R-groups of SO_3H and COOH, shorter-nonionized hydrophobic H and OC_2H_5, and larger-nonionized hydrophobic octyl C_8H_{17} and C_8F_{17}. The UV-Visible solution and self-assembled multilayers thin films characteristics of the prepared azo polymers have also been investigated.

2 Experimental

2.1 Materials

Chemicals were purchased from Aldrich (98–99% purity) and used as such unless specified. THF (Fischer Scientific 98%) solvent was distilled over sodium under N_2 gas, and used within 24 h. Methylene chloride (Fischer Scientific 98%) solvent was distilled over CaH_2 under N_2 gas and used within 24 h. Azobisisobutyronitrile (AIBN) free-radical initiator (Chem Serve 98%) was recrystallized by dissolving it in hot toluene at 30°C followed by cooling and collecting of the AIBN crystals by filtration. The AIBN initiator was finally dried in a vacuum desicator. Acrylic acid monomer contained inhibitor which was removed by allowing the monomer to stand over silica gel (Aldrich chromatographic grade) for 24 h in a refrigerator at 4°C. The following materials were used as received: acryloyl chloride monomer, diethyl ether (Fisher Scientific 98%), N,N-dimethylformamide (DMF) (Fischer Scientific 98%), triethylamine, N-ethylanilino ethanol, poly(diallydimethyllammonium chloride) (PDAC)

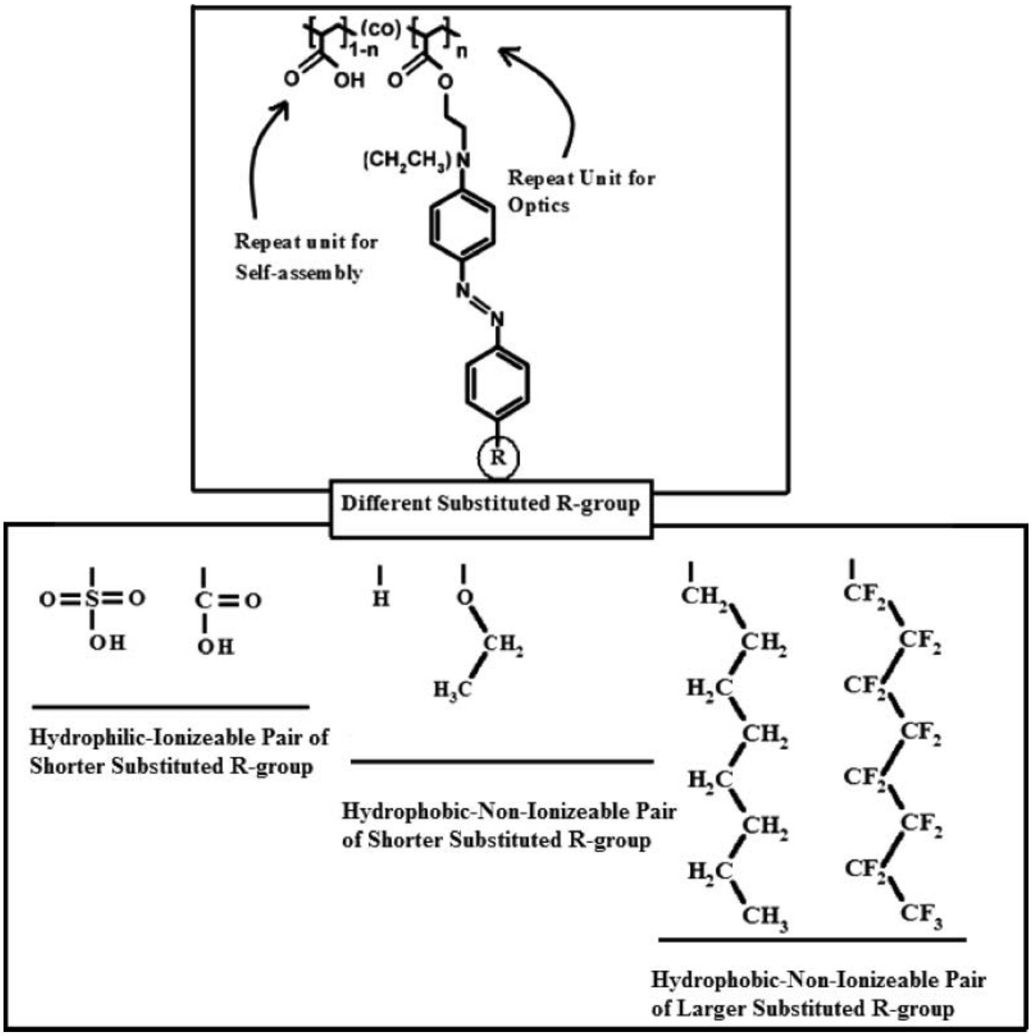
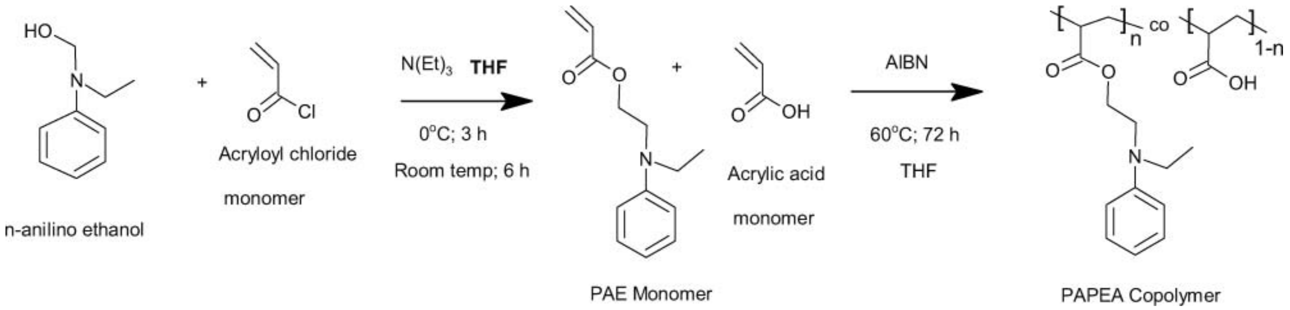


Fig. 1. General structures and classifications of the synthesized azo polyelectrolytes based on the monomer of acrylic acid and monomer functionalized with azobenzene. The different substituted R-groups presnt on the para position of the aromatic ring of the azo chromophores are also presented.

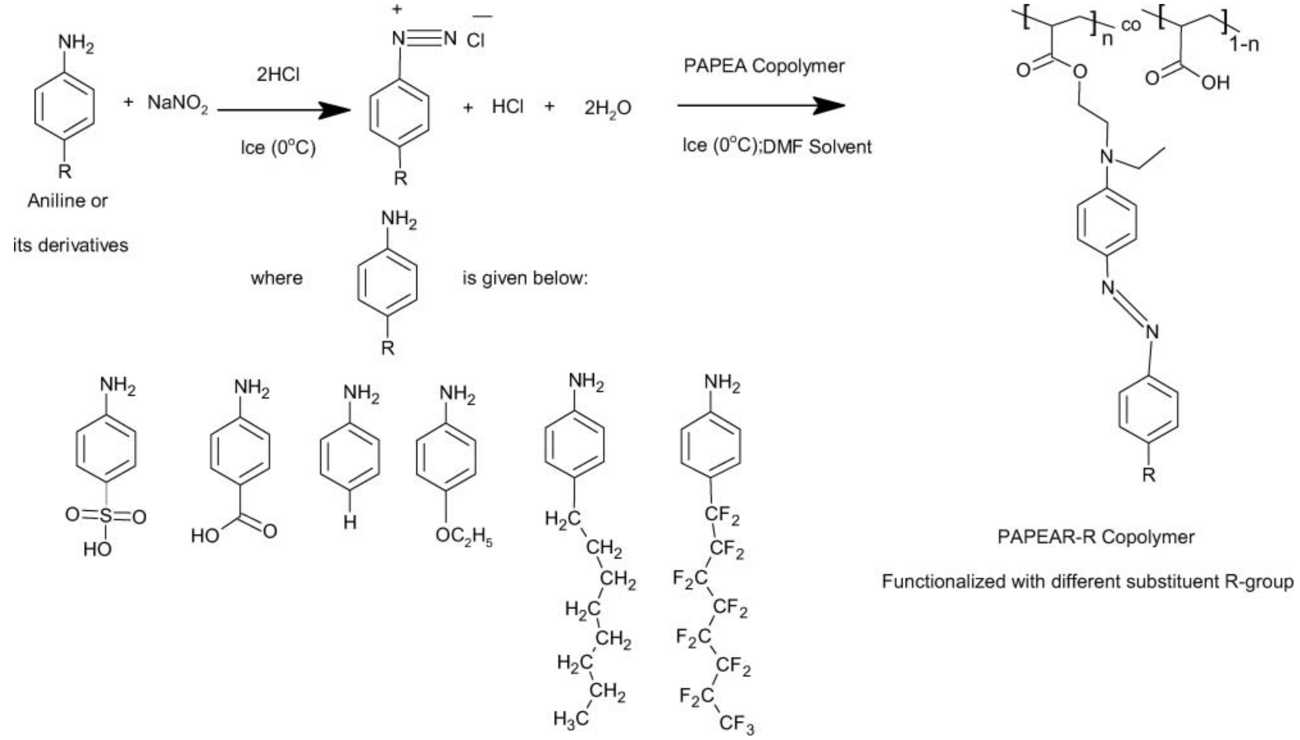
(MW = 200 K–350 K, 20% solution), sodium nitrite ($NaNO_2$), p-anilinesulfonic acid (Na-salt), p-aminobenzoic acid (Na-salt), aniline, p-ethoxyaniline, p-octylaniline, and p-(perfluoro octyl)aniline.

2.2 Monomer Synthesis

Reaction Schemes 1 and 2 describe the various steps involved in the monomer and polymer synthesis. The precursor monomer, 2-(phenylethylamino)ethyl acrylate (PEA),



Sch. 1. Reaction steps and conditions to synthesize PAE monomer and precursor copolymer of P(PEA-co-AA) or PAPEA by free-radical polymerization by using AIBN initiator.



Sch. 2. Reaction steps and conditions to preprare diazonium salt and its reaction with precursor PAPEA copolymer to synthesize azobenzene functionalized copolymers of P(PEA-co-AA)-R or PAPEA-R with different substitutent R-groups.

was synthesized by Schotten-Baumann reaction procedure (22). For example; anhydrous methylene chloride (100 ml) was taken into a 250 ml 2-necked flask, followed by the addition of n-ethyl-n-hydroxyethylaniline (8.25 g; 0.05 moles) and triethylamine (7.58 g; 0.075 moles). The prepared solution was then kept at around 0 °C for 15 minutes by placing the flask in an ice bath. To the cold solution, a mixture of acryloyl chloride (9.1 g; 0.10 mole) and methylene chloride (50 ml) was added dropwise with continuous stirring. The reaction temperature was maintained at 0°C for 3 h and then continued at room temperature for a further duration of 6 h. The reaction product was purified by several steps, which included filtration, washing with water and extraction with methylene chloride, and silica gel column chromatography. Finally, the purified monomer was obtained using rotary evaporation and vacuum distillation. The purity of the prepared monomer was confirmed by thin-layer chromatography using ethyl acetate:methylene chloride solvent mixture (5:95 vol. ratios), and also by ^{1}H-NMR spectroscopy. ^{1}H-NMR (d-$CDCl_3$, ppm): $\delta = 1.19$, 3.42, 3.60, 4.33, 5.80–5.86, 6.06–6.15, 6.37–6.42, 6.73, 7.23.

2.3 Precursor Polymers Synthesis

Homopolymerization of PAE monomer and its copolymerization with desired concentrations of acrylic acid (AA) (Aldrich) to prepare homopolymer P(PEA) and copolymer P(AA-co-PEA) or PAPEA (see Figure 1 for structure) were performed in THF at 60°C for 48 h. Total concentration of the monomers in the solution was kept at approximately 0.5 M and AIBN initiator was used with a concentration of 7.5% (w/w) with respect to the monomer concentration. Typically, polymerizations were carried out in custom made Rota-Flo tap glass ampoules by keeping 15 mol% of PEA and 85 mol% AA monomers. Air from the polymerization solutions was removed by 3 times freeze-thaw cycling procedure and bubbling the solution with N_2 gas for 5 min. After polymerization, solutions were concentrated up to 10–15% (w/w) in THF, and precipitated with continuous stirring in diethyl ether cooled in dry-ice/acetone. The synthesized precursor polymers were dried at 40°C under vacuum for 24 h. Yield = 70% (gravimetric analysis). GPC: Mn = 1637, Mw = 5400, MWD 3.24. ^{1}H-NMR (DMSO-d6, ppm): $\delta = 0.95$, 1.20–2.40, 3.20–3.50, 4.12, 6.52, 6.58, 7.05, 11.97–12.85.

2.4 Diazonium Salt Preparation

The diazonium salts were prepared in order to perform post-polymerization functionalization via azo-coupling reaction on the PAPEA copolymers. A typical diazonium salt synthesis involved the dissolution of aniline (5.0 g, 0.054 moles) by stirring in a mixture of 15 ml of concentrated HCl and 15 ml of anhydrous DMF contained in a 2-neck 250 ml round-bottom flask equipped with a thermometer and a magnetic stirrer. The aniline-hydrochloride mixture was cooled to 0°C by placing the flask in an ice-water bath. A chilled solution of $NaNO_2$ (4.0g; 0.058 mol) in 20 ml of

H_2O/DMF (1:1) was prepared, and added dropwise to the prepare mixture to diazotize it. Decomposition of nitrous acid and diazonium salt were avoided by vigorous stirring and not allowing the temperature to rise above 5–10°C by adding few grams of ice if necessary. The presence of excess amount of acid was tested by placing a drop of reaction product on a paper moist with starch-potassium iodide solution. If no immediate blue color is obtained at the point of contact with the paper, a further small amount of $NaNO_2$ solution was added, and tested again to detect the slight excess of nitrous acid.

By a similar procedure diazonium salt of 4-anilinesulfonic acid (Na salt), 4-aminobenzoic acid (Na salt), 4-ethoxyaniline, 4-octylaniline, and 4-(perfluorooctyl)aniline were prepared, and used for post-polymerization azo-coupling reactions to carry out post-polymer modifications. All the polymers prepared via post-azo coupling reaction were from the same batch of the precursor PAPEA polymers, and therefore expected to have the same degree of polymerization. This is due to that fact that the post-chemical modification is not expected to cleave the polymer backbone because of gentle reaction conditions employed here.

2.5 Post-polymer Azo-Functionalization

A general method involving post azo-functionalization, to prepare PAPEA-R polymers and analytical results are given below.

2.5.1. *PAPEA–H*

Poly{2-[4-phenylazophenylethylamino]ethyl acrylate-co-acrylic acid}, PAPEA-H with 15 mol% of PEA repeat unit was synthesized by the drop wise addition of the previously prepared diazonium salt solution of aniline into a solution of PAPEA (0.448 g total weight, and 0.15 molar fraction of PEA) in 20 ml of DMF at 0°C. After the solution was stirred at 0°C for 12 h, the mixture was poured into water under agitation while adding a few drops of hydrochloric acid. The precipitated PAPEA-H was collected by filtration and washed thoroughly with water until neutral stage was achieved. The product obtained was dried under vacuum, for 24 h at 40°C. Further purification was carried out by dissolving the polymer in small amount of DMF (15 ml) and then added dropwise into an excess amount of ether with continuous stirring. The re-precipitated polymers product then dried under high vacuum for at least 24 h at 40°C. ^1H-NMR (DMSO-d_6, ppm): $\delta = 0.98$, 1.21–2.42, 3.15–3.87, 4.13, 7.08, 7.46, 7.78. λ_{max} (DMF) = 418 nm.

2.5.2. *PAPEA-SO₃H*

Poly{2-[4-(4′-(sulfonic acid)phenylazophenylethylamino] ethyl acrylate-co-acrylic acid}, PAPEA-SO_3H was synthesized by using diazonium salt of 4-anilinesulfonic acid via a procedure similar to that described above for PAPEA-H. ^1H NMR (DMSO-d_6, ppm): δ= 1.00, 1.20–2.43, 3.14–3.86, 4.12, 6.71–6.40, 6.80, 7.01, 7.60, 8.01. λ_{max} (DMF) = 419 nm.

2.5.3. *PAPEA-COOH*

Poly{2-[4-(4′-(carboxylic acid)phenylazophenylethylamino] ethyl acrylate-co-acrylic acid}, PAPEA-COOH was synthesized by using diazonium salt of 4-aminobenzoic acid via a procedure similar to that described above for PAPEA-H. ^1H-NMR (DMSO-d_6, ppm): δ=.01, 1.21–2.44, 3.15–3.87, 4.11, 6.40-6.70, 7.05, 7.68, 8.05. λ_{max} (DMF) = 439 nm.

2.5.4. *PAPEA-OC₂H₅*

Poly{2-[4-(4′-(ethoxy)phenylazophenylethylamino]ethyl acrylate-co-acrylic acid}, PAPEA-OC_2H_5 was synthesized by using diazonium salt of 4-ethoxyaniline via a procedure similar to that described above for PAPEA-H. ^1H NMR (DMSO-d_6, ppm): $\delta = 1.01$, 1.21–2.42, 4.12, 4.92, 6.42–6.73, 6.80, 7.16, 7.75, 8.05. λ_{max} (DMF) = 422 nm.

2.5.5. *PAPEA-C₈H₁₇*

Poly{2-[4-(4′-(octyl)phenylazophenylethylamino]ethyl acrylate-co-acrylic acid}, PAPEA-C_8H_{17} was synthesized by using diazonium salt of 4-octylaniline via a procedure similar to that described above for PAM-H. ^1H-NMR (DMSO-d_6, ppm): $\delta = 1.01$, 1.22–2.43, 3.15–3.84, 4.11, 7.05, 7.45, 7.76, λ_{max} (DMF) = 423 nm.

2.5.6. *PAPEA-C₈F₁₇*

Poly{2-[4-(4′-(perfluorooctyl)phenylazophenylethylamino] ethyl acrylate-co-acrylic acid}, PAPEA-C_8F_{17} was synthesized by using diazonium salt of 4-(perfluorooctyl)aniline via a procedure similar to that described above for PAPEA-H. ^1H NMR (DMSO-d6, ppm): $\delta = 1.01$, 1.21–2.44, 3.13–3.84, 4.10, 6.42–6.71, 7.15, 7.48, 8.12. λ_{max} (DMF) = 445 nm.

2.6 Monomer Azo-Functionalization

This was also carried out in order to compare the UV-Visible absorption spectra of azo-functionalized PAPEA-R polymers with their corresponding azo-functionalized PEA monomer. For this purpose, similar experimental approach was used as described above in the case of post-polymer azo-functionalization procedure.

2.7 Self-Assembled Multilayer Films (SAMU) Fabrication

Polished silicon wafers (Wafernet) and glass microscope slides (Fischerbrand) substrates were cleaned in a bath of 25% H_2SO_4 and 75% H_2CrO_4 for about 12 h. This was followed by thoroughly rinsing with neutral Milli-Q water prior to polymer adsorption. Polyelectrolyte multilayers films were assembled on the substrates with the aid of an automatic slide stainer (Varistain 24-4, Shandon). For self-assembled layer fabrication, Milli-Q water (resistivity >18 MΩ) was used. The 0.1 mmol/L concentrated solutions of poly(diallyldimethylammonium chloride) (PDAC) and azo polyelectrolytes (with respect to azo repeat units) were used as polycation and polyanions, respectively. Films were fabricated by alternate 20 min dipping in the aqueous PDAC solution and one of the azo polyanion solutions by usual layer-by-layer technique. If required, the solubility of azo-functionalized polyelectrolytes was increased by the addition of salt such as $NaHCO_3$ and about 15 vol% of DMF. After each polycation or polyanion dipping, the slides were washed by dipping for 10 min into 3 separate washing baths. After the desired numbers of layers were deposited, the coated films were dried under vacuum at 60°C for about 12 h.

2.8 Characterization

Synthesized polymers were studied and characterized by different techniques. Structures of the prepared polymers were confirmed by using NMR spectroscopy. A Varian Associate Unity 300 MHz spectrometer was used to obtain NMR spectra. Samples were prepared in 3 cm^3 of $CDCl_3$ or d-DMSO to give a solution of around 100 mg cm^{-3} concentration. NMR spectra were obtained by referring the chemical shift to solvent peak at 7.25 and 2.49 ppm for ^1H spectra in $CDCl_3$ or d-DMSO, respectively. By comparing the peak integral values, copolymer composition were obtained experimentally. UV-Visible spectroscopy was used to study the absorption characteristic of azo chromophore by using a Varian Carry 300 UV-Visible spectrophotometer. From these studies, absorption maxima, λ_{max} values due to π to π^* electronic transition of the azo-polymers were determined. Molar masses of the polymers were determined from gel permeation chromatography analysis (GPC). A GPC system equipped with Waters Associates 510 pump and Varian RI-4 detector was used under ambient conditions. THF solvent was used as an eluent at a flow rate of 1 mL/min. The concentration of injected polymer solution was about 2 mg/mL. The solution was filtered through membrane filters before injection. The GPC was calibrated with monodisperse PS standards obtained from Polyscience. Polymer molecules were separated on a series of three columns packed with 5 microns styragel. The chromatograms obtained were analyzed by the GPC software version, supplied by Polymer laboratories to calculate molar masses and molar mass distribution (MMD).

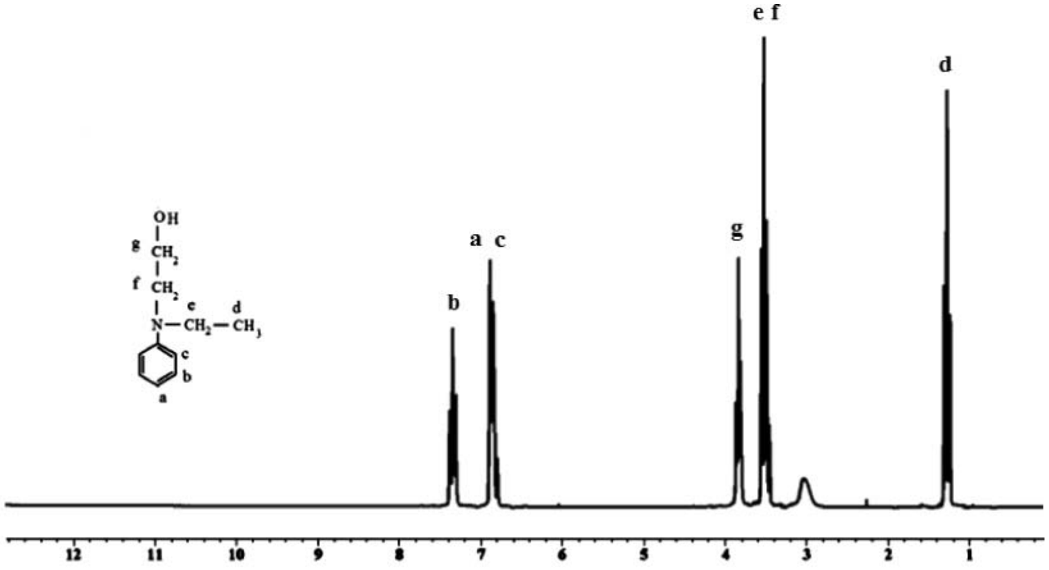
3 Results and Discussion

3.1 Synthesis and Characterization of Azo Polyelectrolytes

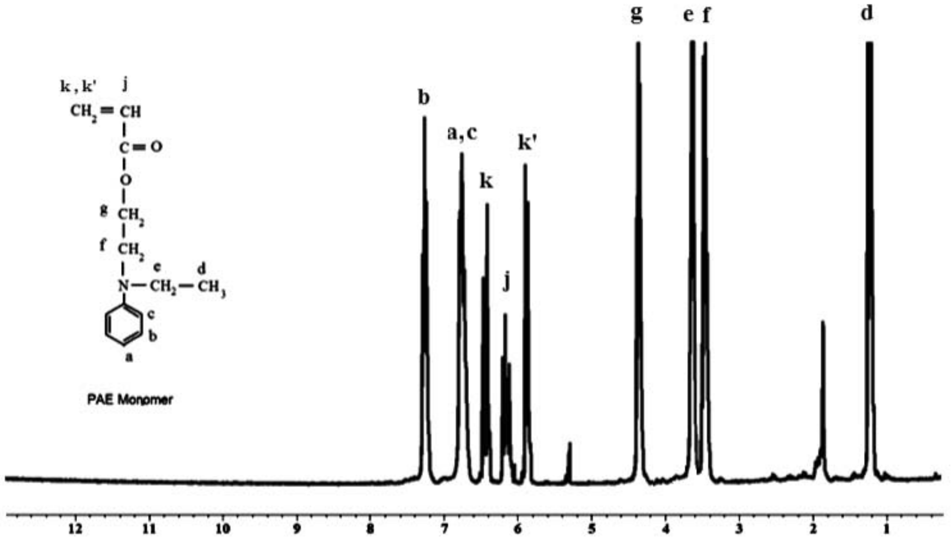
Reaction Schemes 1 and 2 represent various steps involved in preparation of azobenzene-functionalized polymers. Reaction procedure described in the experimental section gives precursor monomer, 2-(phenylethylamino)ethyl acrylate (PEA), due to a reaction of acryloyl chloride monomer with n-ethyl-n-hydroxyethylaniline under an anhydrous condition. Structure of the purified monomer was confirmed by ^1H NMR spectroscopy. The formation of the ether bond after an acyl group react with a hydroxyl group was confirmed by the disappearance of the $–CH_2$- peak of the hydroxyl group of an aniline moiety at 3.58 ppm, and the appearance of the $–CH_2$- peak of PEA monomer at 4.33 ppm. Furthermore, purification of the PEA monomer was confirmed by the presence of only single specie after performing the thin layer chromatography of a silica coated plate analysis under UV-illumination. The purified PEA monomer was polymerized with desired mole fractions of an acrylic acid monomer (AA) to prepare precursor polymers, P(PEA-co-AA), designated simply here as PAPEA. Under the experimental conditions employed, the monomers polymerized well to give high conversion of approximately 70%. Their polymerization can be attributed to the free-radical polymerization of acrylic monomers which are generally characterized by high rate of propagation due to their low steric bulk and high reactivity (23). For the copolymerization of these two acrylic monomers, relatively higher concentration of free-radical initiator was employed in order to obtain higher monomer conversions but broad molar mass distributions (MMD) and lower molar masses to attain the better aqueous solubility of amphiphilic copolymers. GPC analysis indicated the number average molar masses (M_n) of approximately 2500-8000, and with the MMD of 2.2–3.7. This corresponds to the low degree of polymerization and the broad MMD, both of them are expected to increase the aqueous solubility of a polymer. Furthermore, although reactivity of monomers of the AA and PEA are quite different, but their free radical solution polymerization is expected to produce the random distribution of comonomer repeat units in polymer chains. This is of significant importance to current work in terms of photoisomerization of azobenzene chromophores. Since upon post-azo functionalization, such polymers yield a distribution of chromophores with free volume available to undergo relatively efficient *trans* to *cis* isomerization due to their random packing density in the polymer chains. Considering such a requirement of availability of the free volume, the azo fraction is kept modest to 15 mol% in the polymer chains.

Representative ^1H NMR spectra for the prepared PAPEA copolymer are shown in Figure 2. The spectra of the PAPEA copolymers exhibited features common to those expected to be present in the homopolymers of P(PEA) and P(AA). Assignments of peaks were made by comparing spectra of the copolymers with the homopolymers and others similar copolymers (24–25). The aliphatic region (1–2.5 ppm) shows the disappearance of sharp vinylic proton peaks of the monomer on polymerization, and appearance of broad and overlapped resonances of backbone CH_2 and CH of monomers repeat units in the copolymers. The aromatic region (6–8 ppm) is simplified by the fact that it contains peaks present in the PEA monomer repeat unit only, and therefore this region is similar to its homopolymer of P(PEA). The intensity of the broad peak of an acrylic acid proton (12.2–12.8 ppm) is found to depend on the mole fraction of AA monomer in the copolymer. This peak broadening is because of rapid intermolecular proton exchange with d-DMSO. Another factor contributing to the peak broadening is H-bonding, which can take place with other polymer molecules or with the solvent molecules of d-DMSO. Both these factors may have resulted in the broadening of this peak.

The synthesized and characterized precursor PAPEA copolymers were azo-functionalized by a post-coupling technique by reacting with the diazonium salt of corresponding aniline compounds to incorporate different azobenzene chromophores in a final synthetic step. The diazonium salt is expected to act as an electrophile to readily attack the relatively higher electron density of para position of benzene ring of the aniline residue of a polymer. The electrophillic substitution is preferred to take place at the para position due to its less steric hindrance as compare

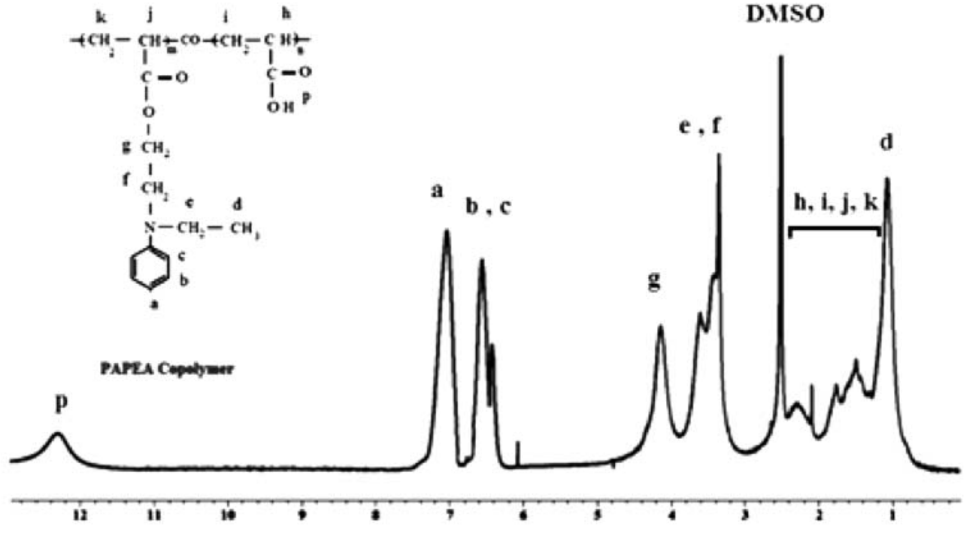


(i) NMR spectrum of n-anilino ethanol

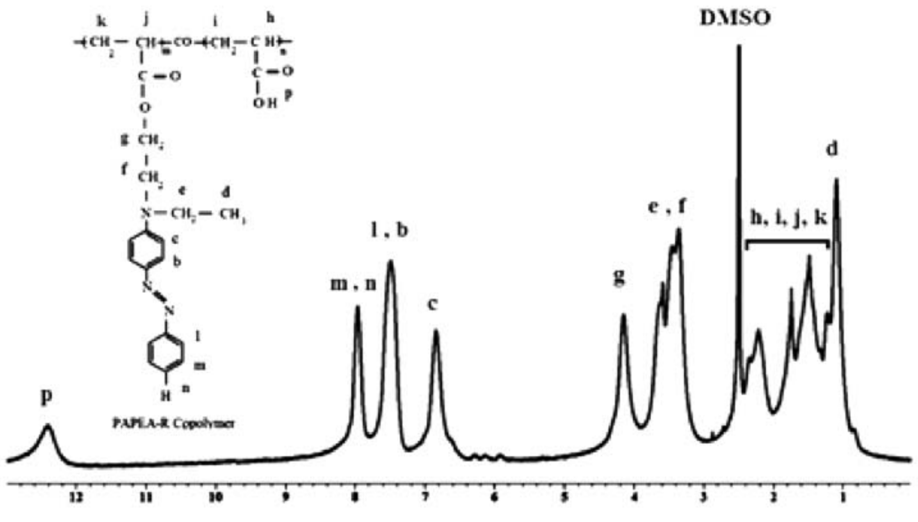


(ii) NMR spectrum of the precursor monomer, 2-(phenylethylamino)ethyl acrylate (PEA)

Fig. 2. Representative ^{1}H-NMR spectra: (i) n-anilino ethanol (ii) 2-(phenylethylamino)ethyl acrylate (PEA) prepared by Schotten-Baumann reaction procedure between acryloyl chloride and n-ethyl anilino ethanol, (iii) free radical polymerization gives precursor base polymer PAPEA with 15 mol% PEA monomer and 75 mol% AA and (iv) post-azo functionalized polymers PAPEA-R with substituent R-group as H. (*Continued*)



(iii) NMR spectrum of PAC-AN with 15mol% n-anilino ethanol



(iv) NMR spectrum of PAPEA-R copolymer with substituted R-group of H.

Fig. 2. (*Continued*).

to a relatively higher hindrance at an ortho position. In order to overcome any steric affect of the polymer chain to carry out an efficient post-modification functionalization reaction, the coupling reactions were performed in DMF, which was found to be a good solvent for all the constituents of the reaction. Under these conditions, the coupling reaction takes place almost instantly as indicated by the formation of a distinct azo-dye color upon dropwise addition of the diazonium salt. The procedure described in the experimental section can be used to conveniently control the degree of azo-coupling or functionalization by adding the desired molar amount of the diazonium salt and/or by controlling the amount of a PEA monomer copolymerized with other AA monomer followed by the azo coupling. Specifically the diazonium salt was added in an equivalent molar amount to that of the PEA monomer present in the PAPEA copolymers. The structures of the prepared polymers were again investigated and confirmed by NMR spectroscopy. Figure 2 (i,ii,iii,iv) represents the ^{1}H-NMR spectra of the prepared PAPEA-R azo functionalized copolymers. After the coupling reaction, the relatively sharp and separated proton resonances of the diazonium salts were replaced by broad and overlapped resonances of the azo chromophores functionalized to the polymer chain. The ^{1}H-NMR spectra of the post-functionalized polymers were also used to study the position of electrophillic substitution, and the degree

Table 1. UV-Visible absorption spectroscopy results of the absorption maxima, λ_{max}, of the prepared azobenzene monomer, PAPEA-R polyelectrolytes. Spectra are recorded in anhydrous DMF with 10^{-3} M concentration. The λ_{max}values of PAPEA-R groups for COOH, and C_8H_{17} measured in mixed solvent of DMF and H_2O are also given.

	Absorption Maxima, λ_{max}		
Substituted Head Group R	*Monomer DMF*	*Polymer DMF*	*Mixed Solvent Volume Ratio H_2O (1) : DMF(2)*
SO_3H	421	419	—
COOH	438	439	439
H	419	418	—
OC_2H_5	421	422	—
C_8H_{17}	429	423	395
C_8F_{17}	451	445	—

of functionalization. For example, the precursor polymers formed after the incorporation of aniline moieties, showed resonance of aromatic ortho, meta and para protons at 7.12, 6.67, and 6.50 ppm, respectively (see Figure 2 (iii) for PAPEA-H). As indicated by the NMR spectra, the post-functionalization of the precursor polymer preferentially occurred at the para position of aniline moieties. After the post-coupling reaction, the intensity of the resonance at 6.50 ppm corresponding to proton at the para position disappeared. Also after the azo coupling, the chemical shift of ortho and meta protons of the benzene ring shift to lower field due to presence of additional conjugation of benzenoid ring. The degree of post-azo-functionalization is found to be high for these copolymers, which was obtained by comparing the peak areas for the proton of the aniline prior to substitution and after azo-substitution.

3.2 UV-Visible Absorption Solution Spectroscopy Characteristics.

The λ_{max} values due to π to π^* transitions of the trans-azobenzene PEL of the PAPEA-R and their chromophores are summarized in Table 1. The representative UV-visible absorption spectra are shown in Figures 3 and 4. All the monomers and polymers exhibit symmetrical single strong broad absorption bands in the UV-visible range. Their distinct absorption characteristics can be explained in accordance to the Rau classification of azobenzene chromophores, which distinguished between three different types of aromatic azo molecules on the basis of the relative energetic order of their n to $\pi^*$and π to π^* transitions: molecules of azobenzene type, molecules of amino azobenzene type, and molecules of pseudo-stillbene type (26). The absorption spectra give rise to the particular colors of yellow, orange, and red, respectively. In the *trans* isomer, azobenzene chromophores exhibit a symmetrical forbidden low-intensity n to π^* band in the visible, and an allowed strong-intensity π to π^* band in the UV region.

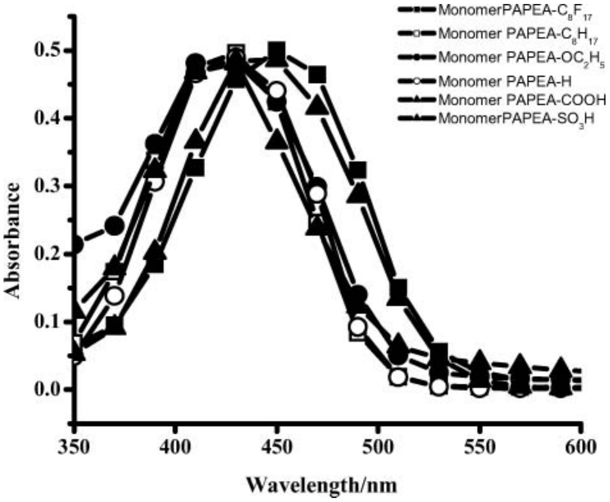


Fig. 3. UV-Visible absorption spectra recorded in DMF solvent of various azobenzene functionalized monomer employed for polymerization, where R-substituent designates the group which is present on the p-position of the aromatic ring of the azobenzene chromophores.

The azobenzene type exhibits rather slow thermal *cis-trans* isomerization rates, and therefore, the *cis* isomer can be isolated. In contrast to this, amino-azobenzene and pseudo-stillbene type molecules isomerize back quickly at room temperature. The presence of the electron donating or withdrawing R-groups, especially at the ortho and para position on the aromatic ring has a significant effect on the isomerization rate, intensity and position of the absorption band. In the present work, the polymers with R-group of H, OC_2H_5, and C_8H_{17}, and C_8F_{17} can be classified as the amino-azobenzene type of chromophores. Here, the presence of electron donating amino-type substituent at the

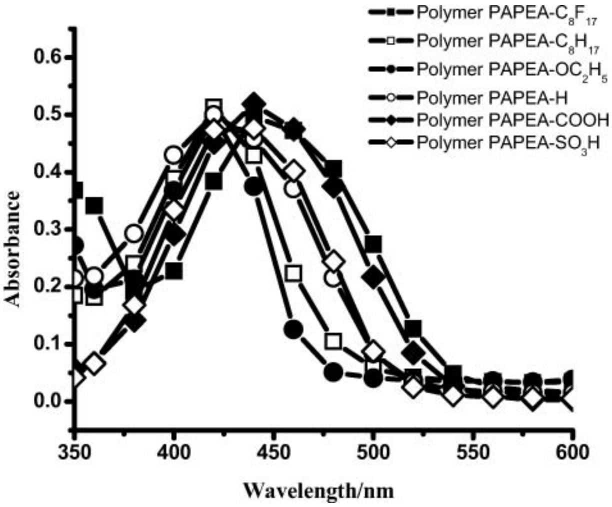


Fig. 4. UV-Visible absorption spectra in DMF solvent of the azobenzene polymer, PAPEA-R, where R-substituent designates a group which is present on the p-position of the aromatic ring of the azobenzene chromophores.

para-position of the azo chromophore results in weak n to π^* and intense π to π^* bands to become close due to an increase in the π orbital energy and a decrease in the energy of the π^* orbital. This leads the former band to be overlapped by the later to exhibit broad absorption band in the visible region. On the other hand, COOH and SO_3H groups known to possess electron resonance withdrawing group effect and H-bonding characters. These factors affect the transition band significantly by further decreasing the energy gap between π and π^* orbital and thus shifting absorption to lower energy, i.e., longer red wavelength, and past the n to π^*. Such types of chromophores are very sensitive to light, and exhibit non-linear electronic distribution due to the push/pull substitution system, and can be classified as pseudo-stillbene type. The wide ranges of λ_{max}which can be exhibited by different substituents demonstrate the versatility and applications of azobenzene chromophores. The aromatic ring substitution pattern employed here results in absorption spectra of trans- and cis-isomer to overlap. In such cases, a single wavelength of light can effectuates both the forward and reverse photo-reaction, leading to mixed stationary state, and continual interconversion of the molecules. The presence of different R-groups exhibits variation in their λ_{max}, and expect to isomerize with characteristic rates and extent. In general these will interact differently with light of a given wavelength when incorporated into polymers and thin films.

Absorption wavelength maxima (λ_{max}) of the chromophores and functionalized polymers were also found to be almost identical in DMF solutions (see Table 1 and Figure 5). It is well known that azo chromophores are sensitive to their environment.The distribution and aggregation of azos in the polymer structure can result in shifting of the absorption band as compared to the individual chromophore molecules. The shifting of band depends on the solubilization ability of a solvent and does not observe in the absence of molecular interactions which are attributed to possible aggregation of azo chromophores (27–32). The observation of the similar absorption spectra is attributed to DMF having better solvation properties, which behaves as an amphiphilic solvent for both hydrophilic and hydrophobic repeat units of acrylic acid and of azo chromophores, respectively. The solvent effect of DMF is effective to suppress band-shifting and introduce a cooperative effect between the adjacent azo chromophores which changes the excitation energy for the electronic transitions. However, λ_{max} is observed to be blue-shifted for the copolymers containing hydrophobic R-groups upon addition of water in the DMF, while no noticeable change is observed for the case of R-groups being hydrophilic. A representative example is shown in Figure 6 for PAPEA-C_8H_{17} and PAPEA-COOH azo polymers. These observations are not unusual and exciton molecular model proposed by McRae and Kasha can be used to quantitatively describe the absorption shift behavior (33–34).

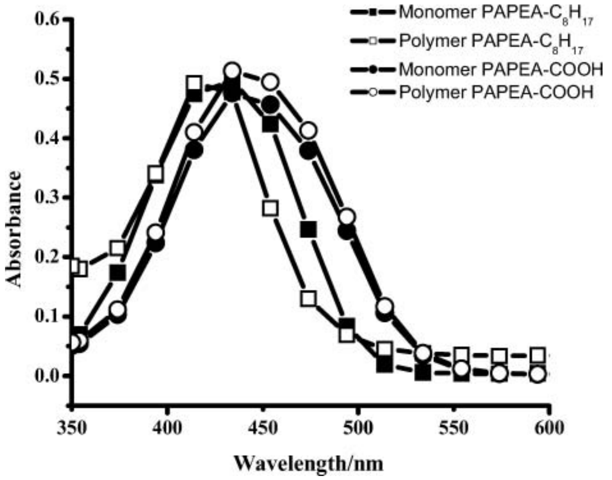


Fig. 5. UV-Visible absorption spectra exhibiting the approximately similar absorption maxima for the monomers and polymers in DMF solvent.

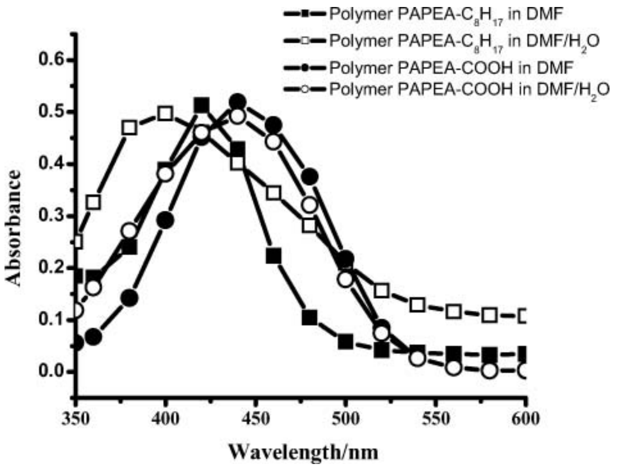


Fig. 6. Comparison of the UV-Visible absorption spectra of PAPEA-C_8H_{17} and PAPEA-COOH in DMF solvent and H_2O:DMF mixed solvents (1:2 volume ratio). Note the shift of λ_{max} to lower wavelength (blue shift) in the H_2O/DMF mixed solvent relative to that of in the DMF solvent for hydrophobic azo-PEL of PAPEA-C_8H_{17}.

The spectral shifts observed in the current work are rationalized by taking into account the factors such as hydrophilic or hydrophobic nature of the polyelectrolytes R-groups, properties of azo PEL such as their solubility, chromophore aggregation, and degree of ionic repeat unit presence in the chains. These inter-related factors influenced the nature and extent of localization or distribution of azobenzene chromophores in the solution. The azo PEL with COOH groups has good solubility in DMF/H_2O mixed solvent systems, while presence of aggregates is not ruled out due to relatively poor solubility in case of azo PEL of octyl group. This is indicated in Table 1 and supported by the UV-Visible spectrums of azo PEL of the

PAPEA-C_8H_{17} in DMF and in DMF/H_2O mixed solvent systems. The λ_{max} of this PEL moves to lower wavelength and exhibits blue shift upon addition of H_2O in DMF. For azo PEL with hydrophilic R-group of COOH, however, a shift in λ_{max} was not observed. Such groups are highly water soluble, and therefore may have resulted in virtually no aggregate formation in the solution. Further, the repeat units of PEL, such as PAPEA-COOH are fully ionized to repel each other as it contains anions of COO^- from acrylic acid monomer and azo co-monomer with substituted R-groups of COOH. This effect reduces chromophore interactions both intermolecularly as well as intramolecularly due to relatively even distribution of chromophores and suppression of their interactions to such extent that no shift was observed. On the other hand, PAPEA-R with hydrophobic R-groups on the azo chromophores they are not ionizeable, and therefore not expected to undergo such ionic repulsion in solution. In this case only the acrylic acid repeat units of the azo PEL involved in the interactions with solvent molecules of DMF and/or water to promote solubility, while the R-groups on the azo chromophores decrease it to produce aggregation.

3.3 UV-Visible Absorption Characteristics of Self-Assembled Multilayers Films

The electrostatic layer-by-layer (ELBL) self-assembled multilayer (SAMU) films deposition process was primarily investigated using UV-Visible absorption spectroscopy, and local structural information of the SAMU films were obtained. Absorption maxima, $\lambda_{max'}$ of thin films and spectral shifts of azo dyes are sensitive to medium effects and organization, and therefore, can be used as solvatochromic micro-reporter molecules. Representative UV-Visible spectra for the SAMU films based on PAPEA-COOH and PAPEA-C_8H_{17} are shown in Figure 7. The prepared films were clear and uniform with good optical quality. In the current study, PDAC polycation, which is known to promote good adhesion, was first deposited onto the substrate surface followed by the alternate deposition of polyanions and polycation. Both PDAC and azo polyanion used here are expected to be fully ionized under experimental conditions employed for the layer-by-layer process, and thus promote adsorption due to anionic and cationic charge interactions, and hence the charge density of the polyion pair was sufficient to proceed with charge overcompensation (reversal) during each subsequent adsorption step (34).

The preliminary results obtained from UV-Visible absorption spectra shown in Figure 7 indicate that SAMU films of azo PEL having hydrophobic R-groups of C_8H_{17} exhibit blue shifts or hypsochromic shifts. On the other hand, no noticeable shifts in λ_{max} are observed for COOH groups of the hydrophilic or ionizeable based films. As mentioned earlier, association of neighboring chromophore dipoles is a viable explanation for the shift observed in absorption. In fact, aggregation of chromophores typically results in marked spectral shift, however, whether a blue or red shift is observed depends on the detailed structure of aggregates and the resulting possibility of interactions between the chromophores. The presence of aggregation of the azobenzene chromophores in multilayers is further supported by comparison of the UV-Visible spectra of PAPEA-C_8H_{17} in DMF and DMF:H_2O mixture solution used for SAMU films fabrication as shown in Figure 5. It is evident that no shift in λ_{max} is observed for polyelectrolyte with hydrophilic COOH groups as these are highly water soluble, and therefore may have resulted in virtually no aggregate formation in solution used for self-assembly. On the other hand, λ_{max} moves to lower wavelength and exhibits a blue shift upon addition of water for hydrophobic -C_8H_{17} groups and also upon the SAMU film fabrication. Since R-groups of COOH and C_8H_{17} are different in terms of their electromagnetic characteristics, the variations in the hydrophobic/hydrophilic and ionization characters of their polyelectrolytes produce different extents of aggregates/non-aggregates in solution. This results in different solvation effects of these polyanions, and therefore affects their adsorption as thin films via the SAMU deposition process. The solvent effect on the SAMU film formation is complicated, and can influence growth of multilayer formation, morphology and organization through aggregation. The hydrophobic/hydrophilic character of the PEL investigated in the current work is important as these produce different extents of aggregates/non-aggregates in solution, and these can be manifested when adsorbed as thin films via self-assembled multilayers (SAMU) deposition process. More work is underway and will be reported to describe the results of contact angle, ellipsometry and AFM studies of the SAMU films fabricated using these azo polyelectrolytes to discuss the influence of the

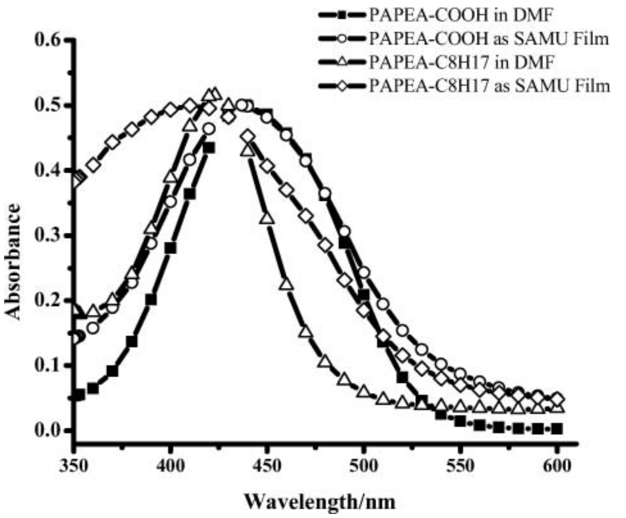


Fig. 7. UV-Visible absorption spectra of the 5-bilayer SAMU films of PAPEA-COOH and PAPEA-C_8H_{17} fabricated on glass slides, where R-substituent designates a group which is present on the p-position of the aromatic ring of azobenzene chromophores.

type of substituted R-groups on surface wetting, growth, morphology and organization through interpolymeric association and intrapolymeric aggregation.

4 Conclusions

A simple strategy was developed and used to synthesize a series of novel amphiphilic azobenzene-containing polyelectrolytes (azo PEL) which only differ from each other due to the presence of a substituted R-group on the p-position of the aromatic ring in the chromophores. The synthesized azo polyelectrolyte structures combine self-assembly with photoresponsivity due to the presence of acrylic acid and azobenzene chromophore repeat units, respectively. Synthetic procedures involved the preparation of a functionalized monomer, 2-(phenylethylamino)ethyl acrylate (PEA) by reacting acryloyl chloride with n-ethyl anilino ethanol via a Schotten-Baumann reaction procedure. The synthesized PEA monomer was then free-radically copolymerized with acrylic acid (AA) to prepare precursor base copolymers. The precursor polymer was designated as P(PAEA), and by reacting it with the diazonium salt of desired aniline or its derivatives, PAPEA-R functionalized azo-polyelectrolytes were synthesized with R being the para-substituted groups of $-SO_3H$, $-COOH$, $-H$, $-OC_2H_5$, $-C_8H_{17}$ and $-C_8F_{17}$. The PAPEA-R were classified on the basis of properties of R-groups into a hydrophilic-ionizeable pair of $-SO_3H$, and $-COOH$, hydrophobic-non-ionizeable smaller pair of $-H$, and $-OC_2H_5$, and hydrophobic-non-ionizeable larger octyl group pair of $-C_8H_{17}$ and $-C_8F_{17}$. NMR spectroscopy was used to determine the structures and compositions of the prepared PAPEA-R. UV-visible absorption spectroscopy was used to study absorption characteristics and absorption maxima (λ_{max}) found to be not significantly affected after incorporation of azo chromophore into the polymer structures as indicated by the similar λ_{max} values of the azo-functionalized monomers and their polymers in DMF solvent. All spectra exhibited broad single absorption bands. Prepared polymers were also employed to fabricate self-assembled multilayer thin films on glass substrates. The λ_{max} measured for the prepared SAMU films, however, were observed to shift to lower wavelength to exhibit a blue shift for hydrophobic R-groups such as $-C_8H_{17}$. This observation was attributed to the increase in chromophore interactions because of the aggregation of the hydrophobic azo chromophores on the surface of substrates. The work described here has provided a facile method to develop a broad range of photoresponsive azobenzene-functionalized polyelectrolytes and their self-assembled thin films of well defined compositions, structures and characteristics and therefore offers promise to design and develop novel types of optical-switchable materials for potential applications in microfluidics, biomedical and nanotechnology.

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