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CHROMIC TRANSITIONS IN POLYDIACETYLENES: POLY(1-(3-QUINOLYL)-4-((CH_2)$_N$OCONHCH_2OCO(CH_2)$_3$CH_3)–BUTA-1,3-DIYNE)

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This paper is dedicated to honor the memory of Professor Sukant K. Tripathy.

ABSTRACT

This paper describes solution electronic spectral properties and solvatochromic behavior of polydiacetylenes obtained from the solid state polymerization of a series of asymmetric quinolyl substituted diacetylenes with (CH_2)nnBCMU as the other substituent (where n = 2, 3, 4, and 9). The pristine polymers, upon dissolution in chloroform, exhibit blue shifted absorption. The addition of hexane to chloroform solutions of the polymers causes dramatic chromic changes and development of red shifted structured spectra. The spectral observations have been examined in terms of influence of substituents on the electronic absorption spectra.

Key Words: Polydiacetylenes; Chromic transitions; Solvatochromism; Coiling behavior; Conjugating side group; Substituent effects

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INTRODUCTION

Polydiacetylenes (PDAs), $(=CR-C\equiv C-CR'=)_n$ belong to a class of conjugated polymers, which have received considerable attention from scientists over the last three decades. This is due to their electronic, optical, and mechanical properties [1], as well as their potential applications in photonics [2] and sensing devices for molecular and biomolecular systems [3] The polymer structure consists of a sequence of conjugated alternate double and triple bonds with pendant groups attached to trigonal carbons in the backbone. Electronic and optical properties of these polymers are primarily determined by the conjugated backbone system of the polymer. However, these properties get modulated by theinteraction of the backbone with the pendant groups (R,R') [1]. Many PDAs exhibit color changes when subjected to changes in solvent quality [4, 5], temperature [6-8], pH, ionic strength [9], and pressure [10]. Chromatic transition behavior of polydiacetylenes in solution and various solid phase morphologies such as PDA crystals, cast and LB films, and vesicles has been the subject of much investigation [7, 8, 11, 12]. Supermolecular assemblies containing PDAs exhibit chromatic changes by specific interaction with a variety of biological analytes forming the basis of sensor applications [3]. These chromatic transitions are believed to arise from conformational changes affecting π conjugation in the conjugated polymer backbone induced by changes in the side group intramolecular interactions and associated conformational changes due to the stimulus.

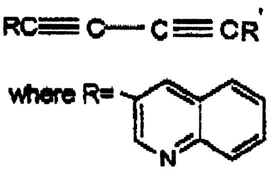
Most PDAs are insoluble even in exotic solvents. However, soluble polydiacetylenes have been prepared by introducing high internal entropy side groups such as long chain alkyl and alkyl urethane derivatives [4, 9, 13, 14, 15]. Solvatochromic and thermochromic behavior of symmetrically substituted poly(nBCMU) in solution and solid phase morphologies have been the subject of extensive study. Chromatic changes are observed in chloroform solutions of symmetrical poly(3- and 4-BCMU) upon the addition of a non-solvent like hexane [4, 5]. Typically, the blue pristine polymers, formed by polymerization of the monomers, dissolve in chloroform to form yellow solutions of the PDA. On addition of hexane, a red solution is obtained for poly(4-BCMU) and a blue solution results for PDA poly(3-BCMU) [6]. The chromic changes in solution have been shown to result from the distortion of the conjugated polymer backbone to folded structure on dissolution of the pristine polymer and disruption of intramolecular hydrogen bonds of urethane side groups due to solvent interaction with pendant groups [16]. The addition of a poor solvent like hexane is believed to restore the intraside group hydrogen bond interactions and extend the planarity of the conjugated backbone causing the shift of the absorption spectra to longer wavelengths akin to a crystallization process. Usually this reversible coil-rod transition is accompanied by aggregation of the rigid rods and subsequent precipitation of the polymer. The mechanism of this change has been much studied and debated [17-19]. Two types of mechanisms have been proposed. One view is that the coil to rod transition is essentially a single chain process and involves conformational changes within a chain [18]. The other view is that the conformational change is a consequence of aggregation of polymer chains [19]. There are increasing indications that coil-rod transition is a single chain process, which may get overlapped with aggregation of polymer chain depending on the experimental conditions such as concentration, solvent, and temperature [17].

Most of the early studies on solvatochromism have been done on PDAs with high internal entropy flexible pendant groups, which strongly influence the energetics and dynamics of the conformational change of the conjugated back bone responsible for the chromic transition. In recent years, synthesis of soluble polydiacetylenes with rigid aryl groups directly attached to the backbone has been achieved [20-23]. Aryl substituents directly attached to the conjugated backbone have been shown to modulate the properties of the PDAs through high π electron density per repeat unit and potential for π conjugation with the backbone [20]. Solvatochromic and thermochromic studies of such polydiacetylenes exhibit characteristics indicating distinctive influence of the aryl substituent on the coiling behavior of the polydiacetylene backbone [22-24]. Thus, for poly(1,4-bis(3-quinolyl)buta-1,3-diyne) abbreviated as PDQ, a PDA with symmetrically substituted rigid 3-quinolyl pendant group, unusually low energy electronic transitions were observed in phenol (λ_{max} ~656 nm), phenol-non solvent (λ_{max} ~694, ethanol, DMF, toluene etc.) and in phenol-acetonitrile (λ_{max} ~733 nm) solutions. These are some of the lowest energy electronic transition reported for PDA solutions [22, 24]. This implied that much longer effective conjugation lengths even for the coiled PDAs in good solution in comparison with poly(nBCMU) and other PDAs with entropy rich pendant groups with typical absorption λ_{max} ~470 nm. Thus, rigid 3-quinolyl pendant group seems to alter the coiling behavior and planarity of the PDA backbone both in the good solvent and in solutions containing non-solvents. Relatively low energy transitions in solution were attributed to a combination of electronic coupling of the aryl substituent with conjugated backbone and steric effect of the rigid of the side group and its hydrogen bonding interaction with the solvent on the worm coil conformation of the conjugated backbone in solution [22, 24]. Solvatochromism and thermochromic behavior of asymmetrically substituted PDAs with a rigid hetero aryl group and a flexible alkyl urethane side group also indicates a significant effect of the rigid aryl side group in influencing the solution electronic transition energies of the PDAs (Table 1, entries PQPU(R= 3-quinolyl, R'= CH_2OCOPh [22] and poly(BPOD), R=3-pyimidyl, R'= $(CH_2)_4OCONHCH_2OCO(CH_2)_3CH_3$) [24], although the influence was much attenuated. The magnitude of electronic transition energies observed in these PDAs also seems to depend on the structure of the rigid hetero aromatic, low entropic side group and the flexible side group. The modulation of the electronic spectra of PDAs in solution by manipulation of the rigidity and flexibility of the flexible pendant group would be of practical value besides providing a deeper insight into the significance of the pendant group backbone and solvent interactions. In this paper, we further explore the influence of the side group structure on the solution spectral behavior of PDAs.

In a project aimed at designing processable PDAs with aryl pendant groups for non-linear optical studies, synthesis of a series of asymmetrically substituted diacetylenes 1a–d (Scheme 1) and their polymerization was undertaken [25]. The -$(CH_2)_n$BCMU side group was chosen as one of the pendant groups because of its known propensity to enhance reactivity in the solid state reaction and to enhance polymer solubility in organic solvents. We report here the solution spectra and solvatochromic behavior of polymers of 1a—d, poly(QnBCMU) [26]. In these polymers, the change in the methylene chain length of the flexible pendant group would influence the entropy contribution to the solution and the chain folding processes. The results imply a role for both the rigid and the flexible pendant group molecular structure in defining the effective π-conjugation lengths of polymers in solutions.

EXPERIMENTAL

Details of the synthesis and polymerization of diacetylenes 1a—d will be published elsewhere. Polymers were obtained by gamma irradiation of the monomers in solid state. Monomer free polymers were obtained by extraction of the partial polymers with suitable solvents (hexane or benzene). These polymers are soluble in phenol and conc. sulphuric acid. In chloroform, only a fraction of the polymer was soluble, and chloroform soluble fractions were used for the solution studies. Weight average molecular weight M_w (dispersity), obtained by GPC analysis of the chloroform soluble fractions of poly(Q2BCMU) and poly (Q3BCMU) were estimated to be ~1.05×10^5(2.4) and 1.19×10^5 (3.4), respectively (polystyrene standards). For the solvatochromism study, chloroform solutions of polymers were used, in which chloroform served as a good solvent. Polymer solutions in various ratios of chloroform and hexane were prepared by mixing a stock solution of the polymer in chloroform and requisite amounts of the two solvents such that the final concentration (0.1- 0.01 mmole/l of the repeat unit) of the polymer was same in all the solutions for a particular polymer. The solutions were thoroughly mixed prior to recording of electronic absorption spectra. Electronic absorption spectra were recorded on Shimadzu Uv-vis 260 Spectrophotometer.



R' = (CH_2)nOCONHCH_2OCOCH_2CH_2CH_2CH_3 (nBCMU)

where n = 2 (1a, Q2BCMU); 3(1b, Q3BCMU); 4(1c, Q4BCMU); 9(1d, Q9BCMU)

Scheme 1. (1-(3-quinolyl)-4- R–buta-1, 3-diyne).

RESULTS AND DISCUSSION

Absorption spectra for poly(Q2BCMU) solutions in various solvent compositions are shown in Figure 1. Similar spectral behavior was noticed for poly(Q4BCMU) and poly(Q9BCMU) solutions. Spectral behavior observed for poly(Q3BCMU) solutions was somewhat different and is shown in Figure 2, and these results are discussed in a subsequent paragraph. The spectrum in the chloroform solution and that observed after the chromatic transition for each of the polymers in this study are presented in Figure 3. Relevant data about the chromic changes is summarized in Table 1, which also contains data on poly(nBCMU) and other PDAs from literature. Typically, the polymers dissolved in chloroform to form red-purple solutions, which exhibited broad absorptions with λ_{max} in the

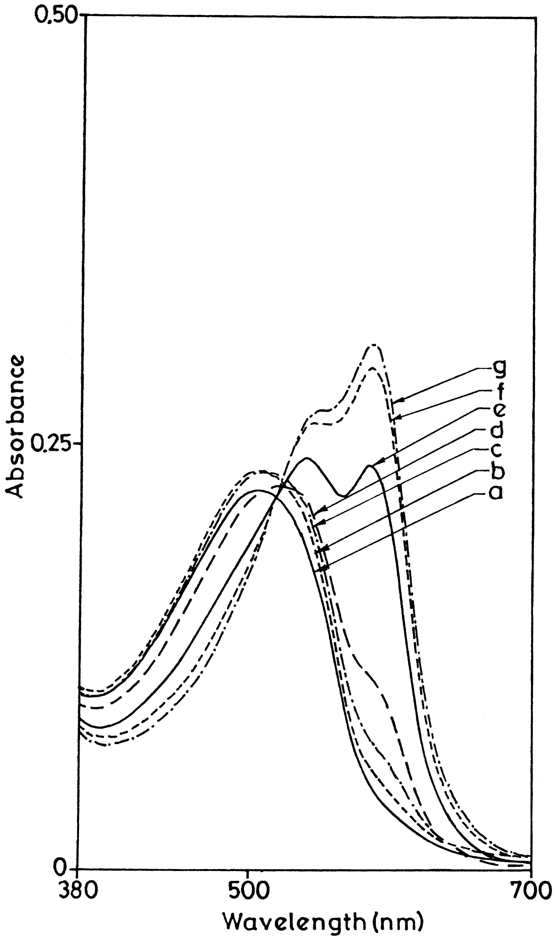


Figure 1. Absorption spectra of poly (Q2BCMU) solutions in various ratios of chloroform/hexane solvent mixtures (v/v): (a) 10/0; (b) 8/2; (c) 7/3; (d) 6/4; (e) 5/5; and (g) 3/7

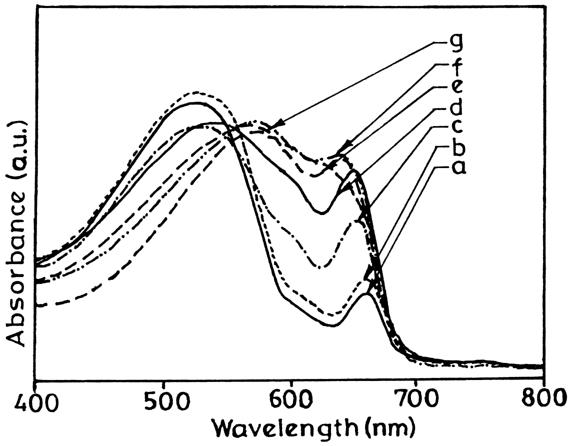


Figure 2. Absorption spectra of poly (Q3BCMU) solutions in various ratios of chloroform/hexane (v/v) solvent mixtures: (a) 10/0; (b) 8/2; (c) 6/4; (d) 5/5; (e) 4/6; (f) 3/7; and (g) 2/8.

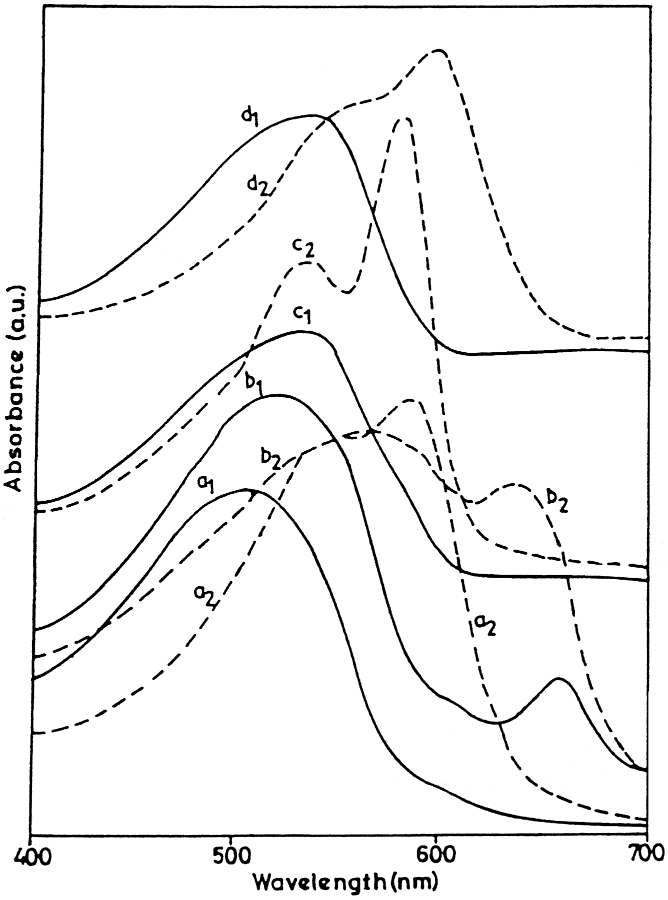


Figure 3. Absorption spectra of poly (QnBCMU) solutions in "good" (chloroform: C) and "poor solvent" (chloroform/hexane : CH) systems. (n : C : CH), 2 : a_1 : a_2, 3 : b_1 : b_2, 4: c_1: c_2, 9 : d_1: d_2.

Table 1. Electronic Absorption Spectral Data for Poly (QnBCMU), Poly (nBCMU), and Other Soluble Aryl Containing Polydiacetylenes in Solid Phase and in Solutions (Numbers Are ~ λmax in nm)

Polymer	Pristine Polymer	Polymer Film	Good Solvent (Chloroform)	Poor Solvent (Chloroform Hexane)	Xc at Color Transition Pt.
Poly(Q2BCMU)	552 purple	587 purple	500 pink	586,543 purple	0.71
Poly(Q3BCMU)	660 blue	660,570 blue	520(660)[a] red	649,571 blue	0.52
Poly(Q4BCMU)	600 purple	598 purple	540 red	582,540 purple	0.79
Poly(Q9BCMU)	670 blue	600 purple	540 red	600,550 purple	0.71
Poly(2BCMU)			465 yellow	545 red	
Poly(3BCMU)	635 blue	635 blue	469 yellow	630 blue	0.71
Poly(4BCMU)	620 blue	538 red	465 yellow	529 red	0.52
PDQ[b]	728	728	656 blue phenol	694 blue 96% toluene 4% phenol	
PQPU[c]	730,680		537	590,550	
Poly(BPOD)[d]	(red)		510 red	599 purple	

Note: Xc = Mole fraction of chloroform.

[a] See Figure 2.

[b] Reference 20.

[c] Reference 22.

[d] Reference 23.

505-540 nm region. These are quite blue shifted compared to excitonic transitions in the respective pristine solid polymers (Table 1). In hexane/chloroform mixtures, an increasing fraction of hexane caused development of new relatively sharp bands in the longer wavelength region causing the red solutions of polymer in chloroform to form purple or blue solutions. The absorption spectral change was usually complete in ~6:4(V/V) chloroform/hexane mixtures. A color change was noticed corresponding to mole fraction X_c of chloroform. The solutions were stable and no precipitation was noticed for at least 12 hours except for solutions with quite high fractions of hexane. For example, a poly(Q2BCMU) solution in 3:7(V/V) hexane-chloroform composition was stable for a month without precipitation. The conformational changes in solution, aggregation and precipitation were observed to occur at a rate that was hexane composition dependent. In solutions with lower fractions of a non-solvent like hexane, the conformational changes were slow and required several hours to complete and no precipitation was observed. At higher fractions of hexane, the changes were more rapid and precipitation from solutions happened in short time scales varying from few minutes to few hours. An isobestic point was observed in each of the cases, suggesting equilibration between two types of species, i.e., coiled and planar rigid backbone polymer, in various solvent compositions. The general pattern of solvatochromic behavior observed in this series of poly (QnBCMU) is similar to the reported solvatochromic behavior for other PDAs containing $(CH_2)_n$BCMU side groups. The results reflect the formation of polymer with extended π conjugation with an increase in the non-solvent fraction. The solutions are true solutions and inter chain interactions are probably not significant in the regime of concentrations used in this study. Considering the concentrations and the stability of solutions at which complete transformations occurred to the extended π-conjugated form, the transformations probably involve a single chain conformational change followed by aggregation and precipitation. However, simultaneous aggregation and conformational changes, especially at high non solvent fractions, cannot be ruled out.

Poly(Q3BCMU) dissolves in chloroform to form a red solution, and exhibits an absorption spectrum (Figure 2a) with a broad intense absorption band (λ_{max} ~ 520 nm) and a sharper weaker absorption band (λ_{max} ~660 nm). This indicates the presence of both the coiled and planar forms of the PDA in this solution. The pristine polymer of Q3BCMU showed a broad reflection spectra with a minimum at ~660 nm. Solution spectrum of this sample of the polymer remained unchanged on keeping the solution for several hours and subsequent filtration through a 0.5 μm filter. Probably chloroform does not function as 'true good solvent' for all of poly(Q3BCMU). Phenol solution of this polymer sample showed only a broadband λ_{max} ~520 nm suggesting that a fraction of the polymer requires stronger hydrogen bonding disrupter then chloroform. The addition of hexane to chloroform solution causes an increase in the intensity and broadening of the band in the ~660 nm region with a gradual blue shift of the long wavelength maximum to about 645 nm. Simultaneously, the broad band λ_{max} ~520 nm showed a gradual red shift to a very broad band with λ_{max} ~570 nm. The solution turned blue at 5:5 (V/V) cChloroform/hexane composition and the color transition was complete in 4:6 (V/V) chloroform/hexane composition. The absorption spectrum in 3:7 chloroform hexane mixture is similar to that in the previous spectrum, and the spectrum remained unchanged for at least 12 hours. However, in a solution containing higher hexane fraction, precipitation of the polymer was observed within minutes of the preparation of the solution with the precipitated polymer forming a film with absorption maxima at ~571 nm and ~658 nm, respectively. The precipitated film spectrum is quite similar to the solution spectrum at high hexane fraction. These complex changes probably arose due to the formation of an intermediate with a polymer chain conformation with effective conjugation length which lies between the fully coiled conformation (λ_{max} ~ 520nm) and fully extended conformation (λ_{max} ~ 660 nm) of the PDA. An intermediate metastable conformational state was established for symmetrical poly(3BCMU) in chloroform hexane mixtures [26]. Ease of formation of intramolecular hydrogen bonds between the carbonyl oxygen and the NH hydrogen of the adjacent urethane moiety in the 3BCMU side groups of the PDA may stabilize the intermediate conformation. The strong intra-side group hydrogen bonding may be responsible for only partial disruption of hydrogen bonds in chloroform solution noted above. Intermediate conformational state in PDA's has also been observed in poly(9BCMU) solutions [13]. A detailed study of the chromic behavior is being undertaken. Poly (Q4BCMU) and poly(Q9BCMU) solution spectral behavior was quite similar to that observed for poly(Q2BCMU) and is not discussed explicitly.

A closer examination of spectral results reveals some interesting features, which merit comment. Two points about the absorption spectra of poly(QnBCMU) in chloroform solutions may be noted. Firstly, the respective chloroform solution spectral maximuma isare red shifted by about 30-70 nm compared to those of poly(nBCMU) and are significantly blue shifted with respect to PDQ phenol solution spectral maximum (Table 1). Secondly, the broad spectral bands exhibit a finite red shift in their spectral maximum with increase in the number of methylene carbons in the pendant chain (Figure 3 curves a-d). Thus, while poly(Q2BCMU) absorption maximum appears at ~509 nm, poly(Q9BCMU), a polymer with a high internal entropy side chain, absorption maximum is red shifted and appears at ~540 nm. These observations suggest that structure of each side group, the rigid aryl and the flexible group, and their interaction with solvent affects the coiling behavior of the PDA backbone in a distinctive manner. The origin of the red shift in good solutions of PDAs with rigid heteroaryl groups has been discussed at some length and was briefly mentioned in the introduction. However, the red shift in the respective spectral maximum of poly(QnBCMU) despite increase in internal entropy of the pendant groups in this series of polymers is unexpected especially in view of observation that all symmetrical poly(nBCMU) with n = 2–9 and other PDA's with long chain alkyl side groups form yellow solutions in chloroform with λmax ~ 465-470 nm. Disruption of intramolecular intra side group hydrogen bonds by the solvent and hydrogen bond formation with quinolyl nitrogen and with –NH- and carbonyl groups in the $(CH_2)_n$BCMU side chain with chloroform areis primarily responsible for the dissolution of the poly(QnBCMU)'s. The side group (R, R')/solvent interactions control the coiling behavior and effective conjugation lengths observed in these solutions. If hydrogen bonding contribution to enthalpy changes associated with the dissolution may be taken to be approximately the same for all the four polymers under consideration, the changes in the position of the absorption maximum in chloroform solutions of these polymers must then be attributed to the differences in the Van der Waals interaction and solvation effects of the methylene chains. Importance of solvent effect and weak Van der Waals interaction was indicated in the coil-rod chromatic transition of poly(4BCMU) [27]. The results suggests that intramolecular side group interactions in the $(CH_2)_n$BCMU pendant groups and local solvation effects play small but finite role in extending effective conjugation length of the polymer backbone in these polymer solutions in synergy with the heteroaryl group.

It is also interesting to compare the absorption maximum in chloroform solution of poly(Q4BCMU), with absorption maximum of symmetrical substituted poly(4BCMU) which has no aryl group directly attached to the backbone and that of poly(BPOD). The respective λ_{max} are at ~540, 470, and 509 nm. This points to differences in the effective conjugation lengths for these PDAsADs in chloroform solution and role of the chemical structure of the low entropy rigid groups directly attached to the backbone and its interaction with the solvent in defining the conformation of the PDA in chloroform solutions. It may be inferred that the 3-quinolyl as a side group has a more pronounced effect on the conformational behavior of the PDA backbone than the 3-pyrimidyl group. Intensity of the effects may differ with solvent characteristics and solvent interaction with the other pendant groups and consequent effect on the orientation of the aromatic group relative to the conjugated polymer backbone.

Comparison of the electronic absorption spectrum of the solution of poly(Q2BCMU) with fully extended conformations and its cast film exhibit more structured absorption spectrum with λ_{max} at lower energy and thatn observed in the pristine polymer. This implies that cast film of poly(Q2BCMU) has greater degree of organization compared to pristine film (Table 1). Interestingly, excitonic transition in the pristine polymers and monomer free polymer show some dependence on the length of the methylene chain in the nBCMU side group (Table 1). PDAs with odd number of methylene groups in the side chain poly(Q3BCMU) and poly(Q9BCMU) exhibit excitonic transition at longer wavelengths i.e., λ_{max} ~ 660 and λ_{max} ~670 nm, respectively, in the pristine polymer. The processable nature and low electronic energy transitions in the processed films make these polymers potential candidates for non-linear optical studies.

CONCLUSION

The solvatochromicsm behavior and solution electronic spectra of a series of asymmetrical PDAs with a rigid aryl pendant substituent and a series of alkyl urethane substituents with varying flexibility have been examined. The results suggest finite role of the two types of pendant groups in defining the coiling behavior of the polymer and tuning the absorption spectra of the solutions of these polymers through their interactions with the solvent. The results also indicate that the size and structure of the rigid aryl group as well as the structure of the flexible group has significant bearing on the coiling behavior of the conjugated polymer chain in solution.

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