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Unusually Low Energy Electronic Transitions in Poly(diacetylene) Solutions: Solvato- and Thermochromic Behavior of Poly(1,4-bis(3-quinolyl)buta-1,3-diyne)

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ABSTRACT: Solutions of poly(1,4-bis(3-quinolyl)buta-1,3-diyne) (PDQ) have shown the lowest energy electronic transitions of all the reported poly(diacetylene)s. Unusual solvato- and thermochromic behavior of PDQ in various polar and nonpolar environments is discussed. The role of hydrogen bonding appears crucial to the solution and chromic behavior in these solutions. π-Conjugation between the polymer backbone and the cross-conjugated heteroaromatic side groups appears to lead to chain segments with unusually extensive electron delocalization. Stable (over a period of 2 years), dark green, true solutions in phenol-acetonitrile (nonsolvent) (λ_{max} = 733 nm) are obtained. The stability of charged and rigid rod-like PDQ macromolecules is explained in terms of screening of interchain Coulombic interactions.

Introduction

The study of reversible chromic transitions in poly(diacetylene)s (PDAs) have been a subject of great interest.[1-7] Poly(diacetylene) solutions are known to undergo reversible visual conformational transitions with changes in the solvent type or temperature.[8] Typically, red ($\lambda_{max} \sim 550$ nm) or blue solid PDAs ($\lambda_{max} \sim 630$ nm) furnish yellow solutions ($\lambda_{max} \sim 470$ nm) in good solvents and turn red or blue upon the addition of a nonsolvent (e.g., hexane) or by decreasing the temperature of the solution as in the case of the poly(*n*BCMU) series of poly(diacetylene)s.[9,10] Macroscopically, these transitions have been understood in terms of a reversible order-disorder phenomenon along the conjugated PDA backbone.[11,12] At a microscopic level, the origin of the chromic transitions is a subject of debate in spite of exhaustive experimental and theoretical investigations.[13-25]

One of the factors responsible for the ambiguity over the microscopic origin of the chromic transition is the inability to distinguish the energetics and dynamics associated with the long and flexible side groups from those associated with the backbone. In general, long and flexible side groups with high internal entropy have been employed to help dissolve poly(diacetylene)s.[8-10,13,14,26,27] The complex dynamical behavior of the side group and the backbone in solution also complicates the analysis of the origin of the chromic transitions. Side group related complications could, in principle, be overcome by employing short and rigid side groups that are so designed that solubilization of the resultant polymers is still possible.

Soluble PDAs in which aromatic side groups are directly attached to the backbone may be selected to simplify the study and analysis of the solvato- and thermochromic behavior. Rigid aromatic side groups are expected to greatly reduce the entropic and enthalpic contributions from the side groups to the overall energetics and dynamics of these chromic transitions. In addition, such side groups are capable of introducing a degree of cross-conjugation with the PDA backbone. This is expected to lead to novel and interesting conformation and dynamics dependent chromic characteristics of the PDA macromolecules in the solution and the solid state.

The influence of π-conjugated aromatic side groups in fine-tuning the electronic properties of the backbone in PDA was analyzed by Orchard and Tripathy.[28] Maximum cross-conjugation is anticipated when the side groups are coplanar with the backbone. Interesting electronic transport properties have been observed in these types of poly(diacetylene)s.[29,30] Dramatic changes in the chain dynamics and the optical properties of the PDA backbone are also expected in the solution state in this class of PDAs. However, these types of polymers are often obtained with very low monomer to polymer conversion. It has not been possible to dissolve them in any organic solvent or a combination of solvents.

Recently, a soluble poly(diacetylene) with rigid and formally π-conjugating quinolyl side groups, *viz.*, poly(1,4-bis(3-quinolyl)buta-1,3-diyne), was reported by Talwar *et al.*[31,32] Solvatochromic and thermochromic properties of PDQ were also discussed.[33] In the solid state, PDQ showed the longest wavelength absorption peak at 756 nm (λ_{max}) as compared to that of the prototypical poly(diacetylene) PTS at ~614 nm. Solutions of PDQ in thermodynamically good solvents showed the longest wavelength absorption maximum at 656 nm, which is the lowest energy electronic transition of all the PDA solutions reported to date. Thermodynamically good and poor solvents and solutions hereafter are simply referred to as good and poor solvents and solutions. The prototypical soluble poly(diacetylene)s poly(*n*BCMU)s in comparison show the longest wavelength absorption peak at ~470 nm in good solutions.[9] Cross-conjugation between the quinolyl side groups and the PDA backbone was believed to be responsible for such unusual changes in the electronic properties of PDQ in solution and in the solid state.

The importance of charge interactions in the solution dynamics of soluble polyacetylenes with charged side groups was recently established. Theoretical[34] and experimental studies[35] on a novel polyacetylene with charged

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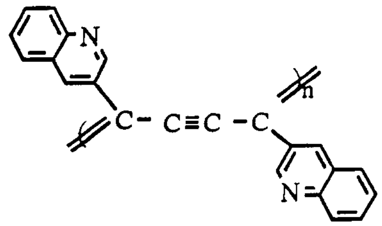

Figure 1. Chemical structure of PDQ.

(pyridinium) side groups revealed that intrachain Coulombic interactions play the dominant role in deciding the chain dynamics of these systems in solution. This water-soluble doped polyacetylene with charged side groups adopts an extensively conjugated, rod-like structure. It was also recently reported that the poly(*n*BCMU) PDA chains may exist as individual charged rigid rod-like structures in poor solutions.[36,37] PDQ provides intriguing possibilities as a polymer with a rigid backbone and side groups (Figure 1). The side groups are capable of forming extensive hydrogen bonding with an appropriate solvent and are highly polarizable. The solvatochromic characteristics of PDQ in various polar/nonpolar and ionic environments are expected to reveal new insights into its chain dynamics and electronic properties.

In this article, the influence of the polarity of the solvent environment and the role of hydrogen bonding on the details of the chromic transition is investigated. We present some unique observations on the solvatochromic transitions of PDQ in different solvent mixtures with varying degrees of polarity. Phenol is used as the good solvent as it is capable of extensive hydrogen bonding with the side groups. The range of nonsolvents is varied from toluene to acetonitrile, selected for their differing polarities. The use of acetonitrile as a nonsolvent resulted in a novel solvatochromic behavior. Solutions of PDQ in phenol/acetonitrile mixtures showed the lowest energy electronic transitions for any PDA in solution or in the solid state. The exciting and somewhat anomalous behavior of acetonitrile as a nonsolvent in the solvatochromic transition of PDQ solution is discussed in terms of the screening of Coulombic interactions between neighboring individual polymer chains.

Experimental Section

Materials. DQ monomer was synthesized according to the method of Talwar *et al.*[31] Partial polymerization was achieved by exposing freshly prepared polycrystalline monomer samples to γ-radiation from a ^{60}Co source.[38] A degree of polymerization of up to 25% is achieved. PDQ was obtained by extracting the unreacted monomer from the partially polymerized sample with dichloromethane.

Phenol and all the other solvents (spectroscopic grade) used in this study were obtained from Aldrich Chemical Co. and were used without any further purification. Acetonitrile used in the study of PDQ solutions in $AlCl_3$–CH_3CN was distilled over CaH_2 prior to use. Crystalline anhydrous $AlCl_3$ was purchased from Merck Sharp & Dohme Research Laboratories and was used without further purification. Thin films of PDQ were prepared by spin-coating the good solutions on glass slides at a speed of 1000 rpm. Polymer density was measured by the gradient column method.

Preparation of Standard Solutions. Phenol (mp 42 °C) is a good solvent for dissolving PDQ above its melting point. In this study, the standard solutions of PDQ were prepared at room temperature by dissolving a known amount of polymer in a 9:1 (v/v) mixture of phenol (good solvent) and the respective nonsolvent. Dilution of standard solutions with respective nonsolvents was performed in quartz cuvettes. Solvent–nonsolvent compositions at any given solvent mixture are represented by volume ratios as well as molar ratios of the individual components. The absorption spectrum of each solution was recorded immediately after each dilution. The spectra obtained were normalized with respect to the spectrum of the undiluted solution.

Table 1. Nonsolvents, Their Dielectric Constants (ϵ), Changes in the Absorption Maxima ($\Delta\lambda_{max}$), and Volume (v_S/v_N) and Molar (M_S/M_N) Ratios at the Point Where the Solvatochromic Transition Is Complete[a]

no.	nonsolvent	ϵ	$\Delta\lambda_{max}$ (nm)	v_S/v_N	M_S/M_N
1	toluene	2.4	656–694	1:49	0.025
2	chloroform	4.8	656–693	1:12	0.047
3	ethanol	24.6	660–693	1:3	0.454
4	DMF	36.7	662–698	1:3.4	0.33
5	acetonitrile	37.5	657–733	1:3.6	0.37

[a] S = solvent (phenol); N = nonsolvent.

$AlCl_3$–CH_3CN solvent mixtures of known strength were prepared by dissolving anhydrous $AlCl_3$ in anhydrous acetonitrile. Solutions of PDQ in $AlCl_3$–CH_3CN solvent mixture was prepared by stirring a known amount of PDQ in the solvent over a period of 12 h. The solutions were centrifuged to obtain a blue supernatant PDQ solution and to remove the undissolved PDQ. The exact strength of these solutions could not be estimated due to the incomplete solubility of the polymer in the $AlCl_3$–CH_3CN solvent mixture. Spectra obtained for PDQ/($AlCl_3$–CH_3CN) solutions were not normalized.

Instrumentation. The absorption spectra were recorded on a Perkin-Elmer Lambda 9 UV/vis/near-IR spectrophotometer for all the solutions except for the solutions with $AlCl_3$. Absorption spectra of solutions of PDQ/($AlCl_3$–CH_3CN) were recorded on a Shimadzu UV 260 UV–visible spectrophotometer. A liquid circulating thermostat was used to control the temperature in the sample compartment of the spectrophotometer.

Rayleigh scattering intensity distribution was recorded with a 20-mW diode laser with a circular beam operated at a wavelength of 830.0 nm as the light source. This wavelength is sufficiently away from the absorption edge of the polymer solutions. A circularly movable photodiode detector placed at a distance of 15 cm from the sample was used to monitor the scattered light intensity. This setup could easily measure picowatt levels of scattered light intensity. The polymer solutions were placed in glass vials, and the scattered intensity was measured at different angles. All the measurements were normalized with respect to the scattered intensity measured at an angle of 2°. At this angle, the intensity of the direct light beam in the absence of the sample was negligible.

Results and Discussion

Organic Solvents and Nonsolvents. PDQ was dissolved in a 9:1 (v/v) mixture of phenol and the respective nonsolvent to furnish blue solutions. Absorption spectra of solutions of PDQ showed long-wavelength absorption maxima in the range of 650–660 nm depending on the solvent (phenol) and the nature of the nonsolvent (Table 1). This is similar to the absorption spectra of PDQ in pure phenol solutions. The absorption maxima in these solutions are significantly red shifted in contrast to those exhibited by the good solutions ($\lambda_{max} \sim 470$ nm) of all the other reported soluble poly(diacetylene)s.[8-10,13,14,26,27] Extensive hydrogen bonding of the quinolyl side groups with the highly polar phenol is expected. A degree of cross-conjugation of the backbone electronic structure with the side groups is also anticipated.

The solvatochromic transitions in PDQ solutions have been investigated in this study with different nonsolvents whose polarities vary considerably. Table 1 presents the dielectric constants of each of the nonsolvents used[39] and the relative solvent–nonsolvent composition at which the transition is complete in the time frame of the experiment. The changes in the lowest energy electronic transitions before and after the solvatochromic transitions are noted. The dielectric constants of the solvents are

Table 2. θ-Solvents and the Spectral Features for PDQ[a]

good solvent	poor solvent	Θ-solvent (v/v)	λ_{max} (nm) at Θ-condition
phenol	toluene	1:49	694
phenol	chloroform	1:12	693
phenol	ethanol	1:3	693
phenol	DMF	1:3.4	698
phenol	acetonitrile	1:3.6	733
H_2SO_4	H_2O	1:1	670

[a] Phenol–acetonitrile: cloud point was not observed even after the chromic transition. The relative composition of the solvent components in the Θ-solvents was almost identical over 3 orders of magnitude of the polymer concentration (10^{-4}–10^{-7} M).

taken as a measure of their relative polarities. A large ratio of toluene to phenol was required to cause the expected solvatochromic shifts. At these nonsolvent concentrations it is expected that most phenol molecules in the vicinity of the polymer chains have exchanged with toluene to rob them of the favorable hydrogen-bonding interactions. Chains adopt a rigid extended conformation, interchain interactions help them form clusters, and the polymers slowly drop out of the solution. Similar observations are made when chloroform is the nonsolvent.

Among the three highly polar nonsolvents selected in this study, ethanol and dimethylformamide (DMF) are capable of forming strong hydrogen bonds and acetonitrile is a relatively poor hydrogen-bonding solvent (Table 4). An increase in the nonsolvent composition led to major bathochromic shifts in the long-wavelength absorption maximum in each of the solutions, which has been a common characteristic of all the reported soluble poly(diacetylene)s.

The Θ-solvents for PDQ were established qualitatively by observing the cloud point upon a gradual addition of the respective nonsolvent to solutions in thermodynamically good solvents over 3 orders of magnitude of the polymer concentration. Phenol and concentrated H_2SO_4 are two separate thermodynamically good solvents for PDQ. Toluene, chloroform, ethanol, DMF, and acetonitrile were used as the nonsolvents when phenol was the selected good solvent. The cloud point could be observed only after the spectral transitions occurred. In the case of acetonitrile as a nonsolvent, the cloud point was not observed even after the chromic transition had occurred. In principle, solutions of PDQ in phenol–acetonitrile may not be considered as poor solutions even after the chromic transition has occurred. H_2O was used as the nonsolvent when concentrated H_2SO_4 was used as the thermodynamically good solvent. The cloud point appeared at a H_2O composition of 0.5 (v/v). The Θ-conditions and the absorption maxima are presented in Table 2.

Absorption spectra of phenolic solutions of PDQ with increasing composition of the nonsolvent ethanol are shown in Figure 2. Initial solutions with a 9:1 (v/v) solvent to nonsolvent composition showed the absorption maximum at 660 nm. As the molar ratio of phenol to ethanol was increased to 0.454, a bathochromic shift to 693 nm was observed in the absorption maximum. A similar solvatochromic transition was observed when DMF was used as a nonsolvent (Figure 3). In this case, the solvatochromic transition occurred at the solvent to nonsolvent molar ratio of 0.33. PDQ is trapped upon passing these solutions through 1.0 μm filters (Gelman, Acrodisc cr PTFE) after the chromic transition. In the cases of both ethanol and DMF as the nonsolvent, the PDQ chains were noticed to aggregate and fall out of solution within a few hours (~2) after the observed spectral changes.

A significantly more dramatic solvatochromic transition was observed in phenol–acetonitrile solutions (Figure 4).

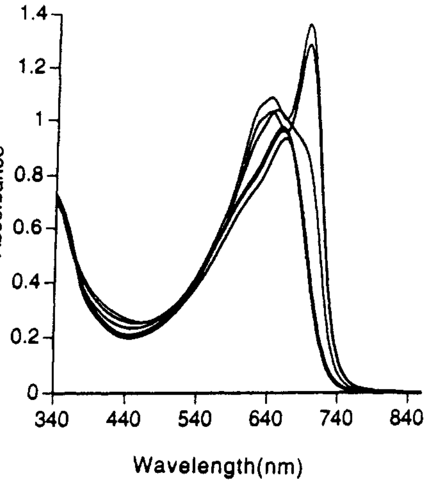

Figure 2. Normalized absorption spectra of the solutions of PDQ in 9:5, 9:14, 9:18, 9:20, 9:24, and 9:27 (v/v) (bottom to top) ratios of phenol and ethanol, respectively. The curve peaking at 660 nm represents the solution with high phenol content (9:5), and the curve peaking at 694 nm represents the solution with high ethanol content (9:27). Concentration of PDQ: 0.4 × 10^{-5} M.

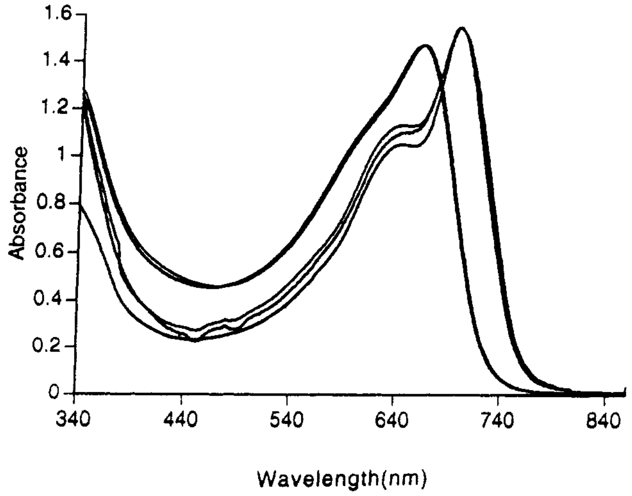

Figure 3. Normalized absorption spectra of the solutions of PDQ in 9:1, 9:7, 9:11, 9:21, and 9:31 (v/v) (left to right) ratios of phenol and DMF, respectively. The curve (top left) peaking at 660 nm represents the solution with high phenol content (9:1), and the sharper curve peaking at 694 nm represents the solution with high DMF content (9:31). Concentration of PDQ: 0.4 × 10^{-5} M.

The initial good solutions of PDQ in 9:1 (v/v) phenol–acetonitrile showed the longest wavelength absorption peak at 657 nm. Upon increasing the composition of acetonitrile to a relative molar ratio of 0.37, the absorption maximum shifted to 733 nm. This peak was accompanied by a second peak at 680 nm with the absorption edge extending up to 820 nm. This value of 733 nm is the lowest for an electronic transition of any PDA reported to date. Only the PDQ solid shows a lower energy electronic transition at such a long wavelength (from the diffuse reflectance spectrum).[33] Hence, it may be reasonable to infer that the PDQ chains in phenol–acetonitrile solutions are at least as ordered and extended as they are in the solid state before dissolution. Surprisingly, the PDQ solutions in phenol–acetonitrile sustained their true solution character with unreduced spectral intensity and were found to be stable to aggregation for more than 24 months (over which period they were observed) after the chromic transition. PDQ macromolecules filter through 1.0 μm filters, indicating the absence of aggregation in the poor

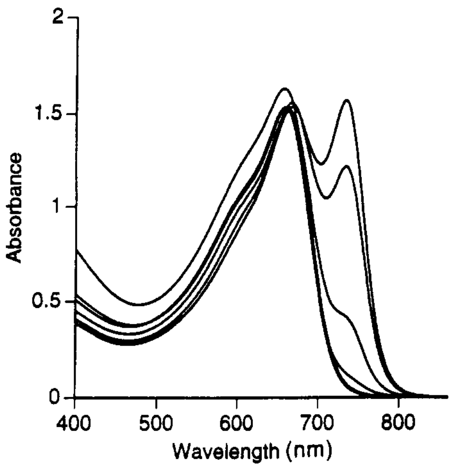

Figure 4. Normalized absorption spectra of the solutions of PDQ in 9:1, 9:11, 9:21, 9:27, 9:31, and 9:33 (v/v) ratios of phenol and acetonitrile, respectively. The curve (second from left) peaking at 660 nm represents the solution with high phenol content (9:1), and the curve (top right) peaking at 733 nm represents the solution with high acetonitrile content (9:33). Concentration of PDQ: 0.4×10^{-5} M.

Table 3. Changes in the λ_{max} of Poly(3BCMU), Poly(4BCMU), and PDQ during Chromic Transitions[a]

polymer	$\Delta\lambda_{max}$ (solid–good solv)	$\Delta\lambda_{max}$ (good–poor solv)
poly(3BCMU)	5300	5000
poly(4BCMU), blue	5000	2700
poly(4BCMU), red	2700	2700
PDQ (Ph–Acn)	1600	1600
PDQ (Ph–DMF)	1600	835

[a] $\Delta\lambda_{max}$ is expressed in cm^{-1}; Ph = phenol, Acn = acetonitrile, and DMF = dimethylformamide.

solution even after the solvatochromic transition is complete.

Structural ordering along the backbone is postulated to be responsible for the solvatochromic and thermochromic transitions in solutions of poly(*n*BCMU) and other types of soluble poly(diacetylene)s. In the starting good solutions, the PDA backbone is believed to exist in a worm-like coiled state.[23] As the composition of the nonsolvent is increased or the temperature of the solution is decreased, the polarity of the solvent medium changes and the solubilizing interactions between the PDA chains and the good solvent decrease. As a result, the polymer chains start stiffening and become ordered along the backbone (perhaps extended planar). In the case of poly(*n*BCMU) type of polymers, it was observed that the degree of intrachain inter side group hydrogen bonding increases during the process of and after the chromic transition.[8,9] It is also believed that certain ordered segments of the polymer backbone act as the nucleating sites for aggregation.[19] The aggregates fall out of solution as particles over a period of time.

The broad nature of the solvatochromic transitions in poly(4BCMU), poly(3BCMU), and PDQ are comparable. However, the details of the transitions are different from each other. Some of the differences are shown in Table 3. From the table, it can be seen that the change in the absorption maximum in the case of PDQ is much smaller than the corresponding changes in the poly(*n*BCMU)s. The smaller magnitude of these changes indicates that the extent of the conformational changes in the PDQ system is much smaller than that in the poly(*n*BCMU)s. In other words, upon dissolution in good solvents PDQ chains undergo a much smaller conformational disorder from the rod-like conformation (in the solid state) to the worm-like conformation (in the good solution state) compared with the poly(*n*BCMU) chains. It implies that the PDQ chains are much more ordered than their poly(*n*BCMU) counterparts even in thermodynamically good solutions. Similarly and consequently the extent of conformational ordering upon going from good solutions to poor solutions is much smaller in PDQ than that in poly(*n*BCMU)s.

Table 4. Numerical Solubility Parameters of Different Solvents and the Polymers Used in This Study[a]

compd	molar vol	δ_d	δ_p	δ_h	δ
toluene	106.8	18.0	1.4	2.0	18.6
$CHCl_3$	80.7	17.8	3.1	5.7	19.0
C_2H_5OH	58.5	15.8	8.8	19.4	26.6
DMF	77.0	17.4	13.7	11.3	24.8
CH_3CN	52.6	15.3	18.0	6.1	24.6
phenol	87.5	18.0	5.9	14.9	24.1
quinoline	118.0	19.4	7.0	7.6	22.1
PDQ					25.0
P(3BCMU)					18.5
P(4BCMU)					20.5

[a] δ = overall solubility parameter, δ_d = dispersive term, δ_p = polar term, and δ_h = hydrogen-bonding term. δ, δ_d, δ_p, and δ_h are expressed as $(MPa)^{1/2}$. Molar volume is expressed as cm^3/mol.

PDQ is soluble in phenol primarily because of the hydrogen-bonding interactions between phenol and the nitrogen atoms of the quinolyl side groups. Partial positive charges (δ+) and partial negative charges (δ−) are expected to develop on the nitrogen (quinolyl groups) and oxygen (phenol) atoms, respectively, as a result of hydrogen-bonding interactions. We expect the interaction between phenol and the nitrogens of the quinolyl side groups in PDQ to be classical hydrogen-bonding interactions. The attempts to study these interactions were unsuccessful primarily because of the overshadowing influence of phenol both in the IR and in the UV–vis spectroscopic studies. In the initial solvent mixtures, the PDQ chains are believed to exist in an extended worm-like coiled state with some degree of cross-conjugation between the backbone and the side groups.

The numerical values of the solubility parameter and dispersive, polar and hydrogen-bonding terms for different solvents and PDAs are given in Table 4. It should be noted that the contribution of the dispersive term from all the solvents to the solubility of the polymers is comparable. It appears that the polar interactions and the hydrogen-bonding interactions are responsible for all the differences in the solute–solvent and solvent–solvent interactions. The details of these interactions dictate the conformation of the polymer chains in different solvent mixtures. Among the solvents listed in the table, acetonitrile can be classified as a highly polar solvent and DMF and ethanol as moderately polar solvents. The rest of the solvents are weakly polar. Similarly, phenol and ethanol are strong hydrogen-bonding solvents, and DMF is only moderately capable of forming hydrogen bonds. An important feature to note is that the most polar solvent, acetonitrile, is a very poor hydrogen-bonding solvent. Quinoline, the side group in PDQ, is weakly polar and has a hydrogen-bonding capability similar to that of acetonitrile. We attempted to interpret the results on the chromic transitions of PDQ based on the complex interplay of all these interactions in the polymer solutions with different solvent compositions.

The solubility parameters of PDQ, poly(3BCMU), and poly(4BCMU) were calculated by the group contribution technique. The solubility parameter (δ_i) was obtained using the following relationship.

$$\delta_i = (\rho_{ij}\sum F_j)/M_i$$

where ρ_i is the polymer density, M_i is the molecular weight of the repeat unit, and F_j is the group molar attraction constant.[43] As shown in the table, the solubility parameters of PDQ, poly(3BCMU), and poly(4BCMU) were calculated to be approximately 25.0, 18.5, and 20.5 (MPa)$^{1/2}$, respectively.

Two important factors, *viz.*, (i) the hydrogen-bonding interactions between the solvent and the polymer and (ii) the influence of the changes in the dielectric constant of the solvent medium on the charge interactions between the polymer chains, seem to be playing a crucial role in the dynamics of the solvatochromic transitions in poor PDQ solutions. Ethanol (δ_h = 19.4 (MPa)$^{1/2}$) and DMF (δ_h = 11.3 (MPa)$^{1/2}$) are polar and are capable of forming strong hydrogen bonds with phenol (δ_h = 14.9 (MPa)$^{1/2}$).[43] Upon increasing the composition of ethanol or DMF in PDQ/phenol solutions, these nonsolvent molecules will compete with th quinolyl side groups (δ_h = 7.6 (MPa)$^{1/2}$) for hydrogen bonding to phenol. Hydrogen bonding between –O···H–O– (in the case of ethanol or DMF with phenol) is expected to be much stronger than that between –N···H–O– (in the case of PDQ with phenol). These stronger solvent–nonsolvent hydrogen-bonding interactions cause a reduction in the good solvent (phenol)–solute (PDQ) solubilizing hydrogen-bonding interactions even at relatively low nonsolvent compositions. The reduced phenol–PDQ solubilizing interactions seem to force the PDQ macromolecules to undergo a conformational transition into a more ordered backbone structure with the aid of a considerable degree of π-conjugation from the quinolyl side groups. This ordering at the molecular level is believed to be responsible for the bathochromic shift (650 to 693 nm) in the lowest energy electronic transition.

To understand the phenomenon of aggregation of PDQ macromolecules, it may be noteworthy to consider some of the recently reported results on the role of charges generated on the polymer chains during the solvatochromic transitions. Coulombic interactions among these charges are reported to play an important role in the chromic transitions in poly(diacetylene) solutions. It was shown that the coiled chains and rod-like segments coexist in the same polymer chain in poor solutions of poly(*n*BCMU). The coiled chains are electrically neutral and the rod-like chains have a net charge as a result of charge transfer between the stiff polymer chain and the solvent.[37] It is a general contention that the generation of a net charge on polymer chains in solutions is a typical colloidal effect. It implies that the aggregates of the polymer chains have to form first before any charge transfer takes place between the solvent and the polymer due to the phase boundary. Xu and Chu[37] have shown that the charge status of poly(4BCMU) in different solvent mixtures is related to the differences in the dielectric constants of the solvent mixture and the polymer. It was shown that the polymer becomes either positively charged or negatively charged depending on the dielectric constant of the solvent mixture in which the chromic transition is studied. Origination of charges from the aggregated particles of the polymer is an acceptable notion. We are intrigued by the possibility of charge generation on single chains as shown by Xu and Chu and find this to be a reasonable basis for understanding the behavior of PDQ in different solutions.

Charge transfer occurs because of the dielectric constant difference between the polymer and the solvent. Subsequently, the rod-like chains aggregate over a relatively short time scale and it results in the formation of aggregates with a net electrical charge. The net charge on the aggregates is neutralized by the surrounding polarized solvent molecules. Poly(3BCMU), poly(4BCMU), and poly(3-hexylthiophene) have been shown to be positively charged and poly(9PA) and poly(92NA) to be negatively charged after the chromic transition.[36]

In poor solutions of PDQ in phenol–ethanol and phenol–DMF, it is possible that the stiffening of segments of the PDQ macromolecules is accompanied with the development of a net charge as a result of charge transfer from or to the solvent medium. The charge transfer is primarily due to the vast differences in the dielectric constants of the solute and the solvent and also due to the absence of any significant solubilizing interactions. The rigid and charged segments of the PDQ chains act as the nucleating sites for the onset of aggregation even before the complete ordering of the individual chains has occurred. The fast and dynamic aggregation process relative to the process of intramolecular structural ordering in this system manifests itself in the formation of large aggregates (size >1.0 μm) in a short time period. These aggregates eventually fall out of the solution.

The unusually long wavelength absorption maximum and the resistance of PDQ in phenol–acetonitrile solutions to aggregation suggest that a different mechanism operates. In this system, more ordered individual PDQ chains seem to be responsible for the long-wavelength absorption, and acetonitrile solvent medium seems to be responsible for the long-term resistance of the solutions to aggregation. The good solvent–nonsolvent and the good solvent–solute interactions are expected to be different in the phenol–acetonitrile system as compared to those in the phenol–DMF and phenol–ethanol systems. This is due to the fact that acetonitrile (δ_p = 18.0, δ_h = 6.1 (MPa)$^{1/2}$), though highly polar, is a poor hydrogen-bonding nonsolvent whereas DMF and ethanol are moderately polar and strong hydrogen-bonding nonsolvents. An increase in the composition of acetonitrile in the solutions of PDQ/phenol results in an increase in the polarity of the solvent medium somewhat similar to that caused by DMF or ethanol. However, the change in the polarity of the medium resulting from the increased composition of acetonitrile is not expected to substantially reduce the solubilizing hydrogen-bonding interactions between phenol and PDQ. The extent and the strengtrh of –N···H–O– hydrogen-bonding interactions between PDQ and phenol and that between acetonitrile and phenol are comparable (δ_h values for acetonitrile and quinoline are comparable) since same atoms are involved in both cases, though in different environments. In other words, acetonitrile molecules are not capable of dislodging the phenol molecules from the polymer vicinity to the extent that ethanol or DMF can. The polymer thus remains in solution even in solutions with high acetonitrile composition.

There is a large difference in the polarizability and the dielectric constant of phenol (9.68 at 40 °C) and acetonitrile (37.5). An increase in the acetonitrile composition leads to a large difference in the dielectric constants of the solvent medium and the solute (PDQ). Even though the solubilizing hydrogen-bonding interactions in the close vicinity of the polymer chain remain unaffected, the vast difference in the dielectric constant of PDQ and the solvent medium can force the coiled PDQ macromolecules to undergo a conformational transition into an ordered (perhaps extended planar) form. The rigid and ordered PDQ macromolecules are expected to develop a net charge along the skeleton of the polymer chain.[37] Acetonitrile, being a highly polar and non-hydrogen-bonding solvent, can

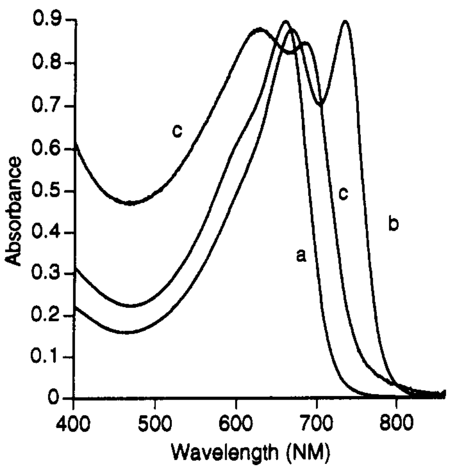

Figure 5. Absorption spectra of the solutions of PDQ in (a) 9:1 (v/v) phenol–acetonitrile, (b) 9:33 (v/v) phenol–acetonitrile, and (c) a thin solid film from a good solution.

screen the charge interactions between the rigid, extended, individual polymer chains. Screening of the net charges that develop on individual polymer chains by acetonitrile seems to prevent the ordered PDQ macromolecules from aggregation. The linear shape, smaller size (molar volume: 52.6 cm^3/mol), and large polarizability of acetonitrile molecules may be the reasons for their ability to act as effective charge screeners between neighboring polymer chains. In such an environment, PDQ macromolecules can undergo a complete conformational transition to a structure with a planar backbone without an appreciable degree of aggregation. The π-conjugating quinolyl side groups take up an optimum conformation so as to minimize the total energy of the system. This overall conformation of individual PDQ chains in poor solution of phenol–acetonitrile can be visualized as that seen in the monomer-free polymer crystals (before dissolution). Attempts to observe lyotropic liquid crystalline behavior in these solutions were unsuccessful at the concentrations studied.

The polymer chains in the partially polymerized crystals exist in an extended rigid rod conformation as the chains are formed through a lattice-controlled topochemical reaction process (expected on geometry consideration and inferred from experiments such as single-crystal X-ray structure determination). The dissolution of poly(*n*BCMU)s in thermodynamically good solvent forces the polymer chains to undergo conformational transition from an extended rod-like conformation to a "worm-like" coiled conformation (well established in ref 23). The diffuse reflectance spectrum of the polymer (PDQ) single crystals shows a minimum at 756 nm. The solutions of PDQ in thermodynamically good solvents undergo a hypsochromic shift in their spectrum compared with the single crystals. However, these shifts are not as large as those observed in the poly(*n*BCMU)s.

The solutions were spin-coated into thin films (opposite to the dissolution process) on glass substrates to investigate the conformational changes in the polymer chains upon going from solutions to solid thin films. The PDQ thin films showed the λ_{max} at 682 nm in contrast to the λ_{max} in acetonitrile–phenol solutions at 733 nm. If it is assumed that the spectral changes (from 656 to 733 nm) occur in the phenol–acetonitrile solutions only due to the aggregation of the worm-like coils (present in the good solutions), the spin-coated films also should have the absorption maximum very close to 733 nm. The absorption maximum at 682 nm in the thin films of the polymer reflects that the chains are not so ordered (extended conformations) as they are either in the phenol–acetonitrile solutions or in the undissolved polymer crystals. This observation also suggests that the polymer chains must undergo a conformational transition prior to aggregation to be able to show the absorption maximum at 733 nm. The diffuse reflectance spectrum of the monomer-free polymer (PDQ) shows a minimum at 756 nm. The fact that PDQ shows the maximum wavelength electronic transitions at comparable energies both in the ordered solid state (before dissolution) and in the phenol–acetonitrile solution is a strong indication that the polymer chains exist in extended rod-like conformation in both their environments.

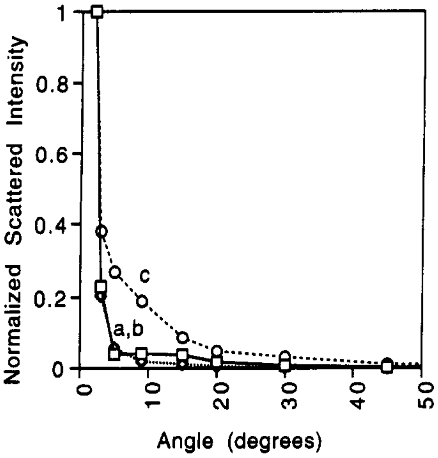

Figure 6. Angular distribution of the scattered light intensity from PDQ solutions in (a) 9:1 (v/v) phenol–acetonitrile, (b) 9:33 (v/v) phenol–acetonitrile, and (c) 9:31 (v/v) phenol–DMF. Solution c contains aggregates of PDQ.

The light scattering experiments showed little or no change in the scattering intensity distribution that will be consistent with aggregation immediately after the chromic transition has occurred (Figure 6). This may be due to the fact that the PDQ chains have undergone only a minor conformational change (835 cm^{-1}) as compared to that in the other soluble poly(diacetylene)s (Table 3). However, when toluene, chloroform, ethanol, and DMF are used as the nonsolvents, the polymer chains aggregate in about 2 h (in the concentration range studied). A substantial change in the scattering intensity distribution is seen only after the formation of the aggregates (Figure 6c). The polymer remained on the filter upon passing these solutions through a 1.0 μm filter. The solutions with acetonitrile as the nonsolvent did not show any aggregation or changes in the scattering intensity distribution with time even after the chromic transition occurred (Figure 6b). The solutions after passing through 1.0 μm filters retained the absorption spectral profile and the optical density. Similar observations were made with solution in which the polymer concentration was varied over 2 orders of magnitude.

These observations and the analysis focus on the conformational ordering of the backbone and the side groups as the origin of the chromic transitions in PDQ solutions. Such an ordering is probably accompanied with concerted rotation of the quinolyl side groups to an energy-optimized stack on either side of the backbone.[41] Large steric hindrance from bulkier side groups can prohibit any significant conformational ordering in the backbone. For example, in the case of poly(1-(trimethylsilyl)-1-propyne), a nonconjugated backbone conformation with jogs and kinds is "frozen" even in good solutions due to steric hindrance from bulky side groups.[40] Favorable side group–solvent interaction is responsible for the solubilization of these rigid backbone polymers. In the case of soluble poly(diacetylene)s, precipitation from solution has accompanied backbone conformational ordering and red-

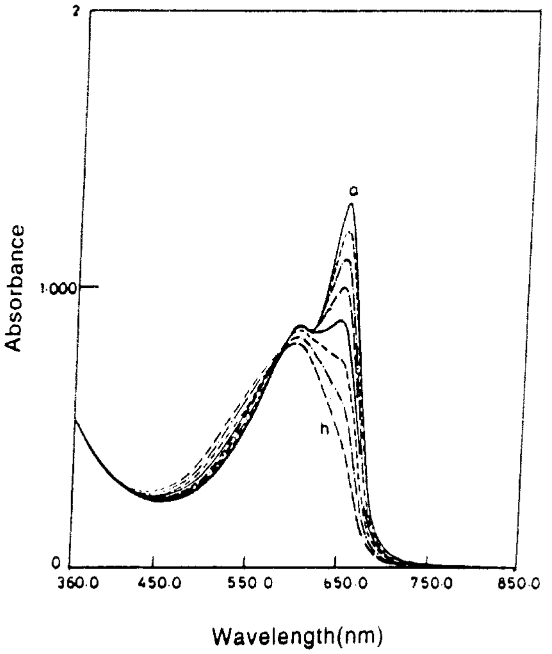

Figure 7. Absorption spectra of solutions of PDQ in $AlCl_3$–CH_3CN at 30, 40, 50, 60, 70, 80, 90, and 100 °C (a–h). The highest temperature data are represented by the dashed curve peaking at 590 nm. The lowest temperature data are shown as a solid curve peaking at 652 nm. Concentration of PDQ: $<3.0 \times 10^{-4}$ M. Concentration of $AlCl_3$: 0.26 M.

shifting of the absorption maximum. An interesting question to ponder is if it is possible to capture a poly(diacetylene) backbone in a good solution and cause it to precipitate without allowing structural ordering of the backbone. A solvent system with bulky interacting groups was envisioned to test this concept.

Inorganic Solvent–Organic Nonsolvent. We decided to investigate the chain dynamics of PDQ in such a constrained environment that prevents intrachain backbone mobility and yet maintains it in a good solution. Inorganic solvent systems where the side group can form a bulky complex are expected to provide such a constrained environment. The study of the absorption spectral changes in such a system is expected to provide interesting information about the chain dynamics during the solvato- and thermochromic transitions.

The quinolyl side group in PDQ is a Lewis base; thus Lewis acids might be expected to dissolve PDQ through acid–base interactions. PDQ is partially soluble in $AlCl_3$–acetonitrile mixtures to furnish blue polymer solutions. The dissolution of PDQ in this system is promoted by the formation of an acid–base complex between the quinolyl side groups and the $AlCl_3$ molecules. The absorption spectrum of this solution showed the longest wavelength absorption maximum at 653 nm, with another sharp peak at 600 nm, and the absorption edge extending to 720 nm (Figure 7a). The λ_{max} of PDQ in this novel reactive solvent system is comparable to that observed in the phenolic systems. This is an indication of similar backbone conformation in both these good solutions.

These solutions undergo reversible visual thermochromic transitions from blue to violet-purple with an isosbestic point at 585 nm (Figure 7). The peak at 653 nm almost vanished as the temperature was increased to 100 °C, and the intensity of the spectral profile below the 585 nm region increased. The solution turned violet-purple upon increasing the temperature to 100 °C. The original spectral profile and the color could be recovered upon cooling the solution to room temperature. This establishes the reversible nature of the thermochromic transition.

The presence of an isosbestic point indicates the coexistence of two types of thermally equilibrating species in solution. The two types of species may arise due to the varying degree of PDQ–$AlCl_3$ interactions or due to a different statistical distribution of segments with conjugation between the backbone and the side groups, or a combination of both. In the case of phenolic solutions, the reversible thermochromic changes in the absorption spectral profile are not as pronounced as they are in PDQ–$AlCl_3$ solutions.[33] Phenolic solutions do not show any visual thermochromic transitions, and the relative ratios of the equilibrating species do not seem to change much in the same temperature range (30–100 °C). A large variation in the extent of strong acid–base interaction with changes in the temperature may be causing such a dramatic thermochromic change in PDQ–$AlCl_3$ solutions. In the case of phenolic solutions, it was suggested that the two types of equilibrating species transform simultaneously into one species upon increasing the nonsolvent composition at room temperature. This leads to a solvatochromic transition.

As a mixture of $AlCl_3$ and acetonitrile is a good solvent and acetonitrile alone is a nonsolvent for PDQ, poor solutions of PDQ in $AlCl_3$–CH_3CN were prepared by addition of more acetonitrile to the initial solution to investigate the possibility of solvatochromic transitions in this novel solvent mixture. Upon 400% (by volume) dilution of the initial solution (concentration of PDQ $< 3.0 \times 10^{-4}$ M) with acetonitrile, the PDQ–$AlCl_3$ complex started precipitating out of solution accompanied by a nominal bathochromic shift of 10 nm (650 to 660 nm). As anticipated, the bulky $AlCl_3$ molecules that are complexed to quinolyl groups seem to be preventing the less than ordered polymer backbones from adopting an ordered structure upon dilution with the nonsolvent. As a result, the chains of the polymer–$AlCl_3$ complex aggregate without any substantial conformational changes. In spite of aggregation and precipitation of the PDQ–$AlCl_3$ complex, the change in the lowest energy electronic transition of the complex is not appreciable. This suggests that aggregation has occurred without appreciable change in the backbone conformation. Aggregation in a PDA solution is observed for the first time unaccompanied with a chromic transition. This observation may be generally applicable to the solutions of other soluble PDAs as well. The aggregated PDQ–$AlCl_3$ complex was purified by removing the free $AlCl_3$ by sublimation under vacuum. The complex is not an aqueous polyelectrolyte.

Preliminary studies[42] on solutions of poly(3BCMU) and poly(4BCMU) in an $AlCl_3$–acetonitrile solvent system showed that the polymer–$AlCl_3$ complex precipitates in the form of a yellow solid from yellow solutions. No change was observed in the long-wavelength absorption (470 nm) during the precipitation process. The estimation of the stoichiometry of the complex for different PDAs is in progress. The results of these studies will be communicated shortly. In all the reported solvatochromic studies of poly(*n*BCMU) solutions, precipitation upon the addition of nonsolvents resulted in significant bathochromic shifts. This result has important implications in addressing the ambiguity over the origin of the chromic transitions in PDA solutions, at least indirectly. The conclusions we would like to draw from these results are that (i) chromic transitions in PDQ do not occur without conformational changes in the polymer chains and (ii) aggregation of polymer chains, in general, need not necessarily be accompanied by chromic transitions.

Conclusions

The electronic nature and the hydrogen-bonding potential of the nonsolvent seem to play a crucial role in the details of the solvato- and thermochromic transitions in PDQ solutions. The nature of the nonsolvent is important in the case of the chromic transitions in other PDA solutions as well. The absence of any substantial change in the lowest energy electronic transition in PDQ–$AlCl_3$ complex before and after aggregation suggests that the notion that chromic transitions in PDA solutions are a consequence of aggregation should be carefully revisited.

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