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ARTICLE

Solvent Effects on Structure, Morphology, and Photophysical Properties of an Azo Chromophore-Functionalized Polydiacetylene

Si Wu,[†,‡] Qijin Zhang,*[,†] and Christoph Bubeck*[,‡]

[†]*CAS Key Laboratory of Soft Matter Chemistry, Department of Polymer Science and Engineering, University of Science and Technology of China, Key Laboratory of Optoelectronic Science and Technology in Anhui Province, Hefei, Anhui 230026 P.R. China, and* [‡]*Max Planck Institute for Polymer Research, Ackermannweg 10, 55128 Mainz, Germany*

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ABSTRACT: We investigate the effects of solvents on structure, morphology and photophysical properties of micelle-like assemblies of an azo chromophore-functionalized polydiacetylene (polyAzoDA) and polymerized tricosa-10,12-diynoic acid (polyTDA) for comparison. Using mixtures of water with glycol, DMSO, ethanol and THF, we systematically vary the solubility parameters and observe blue-to-red color changes of polydiacetylenes. Teas plots are used to estimate the strength of polymer−solvent interactions and explain the properties of polyAzoDA supramolecular assemblies in different solvent environments. In poor solvents, polyAzoDA forms rod-like micelles and the photoisomerization is strongly hindered by the aggregation of azo chromophores. At increasing content of organic solvents, polyAzoDA becomes gradually swollen, as indicated by the onsets of blue-to-red color changes, starting trans−cis isomerizations of the azo groups, and changes of the structures as seen in SEM images. At large ethanol content, we observe that photoisomerization of azobenzene groups induces a morphological transition and a color change of the polydiacetylene backbone.

1. Introduction

Conjugated polymers (CPs) are receiving much attention because of their unique optical, electrochemical and electrical properties and their applications as optoelectronic devices.[1,2] The introduction of photoresponsive azobenzene groups to CPs can modulate the properties of CPs by light.[3−10] Harbron et al reported that photoisomerization of azobenzene groups can modulate the fluorescent properties of azobenzene-functionalized poly(*p*-phenylenevinylene)s;[3−5] Leclerc et al reported that photoisomerization of azobenzene groups changes the conformation of the backbone of azobenzene-functionalized polythiophenes;[6,7] Mochizuki et al reported that photoisomerization of azobenzene groups can control conductivity of azobenzene-functionalized polythiophenes;[8] Izumi et al reported that photoisomerization of azobenzene groups can modulate the electrochemical property and hydrodynamic volume of CPs.[9,10]

Polydiacetylenes (PDAs) are conjugated polymers, which show intense colors due to their highly delocalized, one-dimensional π-electron system of their polymer backbone.[2] PDAs are well-known for the intriguing stimuli-responsive blue-to-red color changes.[2,11,12] In this work, we study the effects of solvents on structure, morphology and photophysical properties of an azo chromophore-functionalized PDA (polyAzoDA). For comparison, we also study polymerized tricosa-10,12-diynoic acid (polyTDA). The chemical structures of both monomers and polymers are shown in Scheme 1. We are interested in the effects of solvents on the properties of polyAzoDA for two reasons:

1. It is found that the solvent environment plays an important role on photoinduced modulations of properties of CPs.[3−7] For example, photoinduced modulations of the fluorescent properties of azobenzene-functionalized poly(*p*-phenylenevinylene)s occur in 30−60% methanol[3] and the dual photochromism of azobenzene-functionalized polythiophenes is observed in chloroform:methanol = 1:1 solution.[6,7] However, there is still a need of improved basic understanding of the effects of solvents on the photoinduced modulations of azobenzene-functionalized CPs. The azo chromophore-functionalized PDA system presented in this work can be used as a model system to quantitatively study the effects of solvents on the photoinduced modulations of properties of azobenzene-functionalized CPs.
2. In our previous work, we found that the photoisomerization of the azobenzene groups does not take place in the polyAzoDA assemblies because azobenzene groups form strong H- and J-like aggregates, which hinder the photoisomerization of azobenzene groups.[13] Many other groups also found that aggregation effects can strongly hinder the photoisomerization of azobenzene groups in close-packed structures.[14−18] This is a frequent problem for the construction of photoresponsive systems using azobenzenes. We found that the addition of a suitable organic solvent (DMSO) to a dispersion of polyAzoDA micelles can eliminate the aggregation without destroying the micelles.[13] So, adding some suitable solvents to azo aggregation-containing systems could be a general method to remove aggregation of azo chromophores without destroying the assemblies. However, a general understanding is still needed which solvents are suitable for a certain azobenzene-containing system to remove the aggregation.

Therefore, we need a common method to estimate the interactions between solvents and CPs or azobenzene-containing polymers which can be extended more generally to functional polymers. Solubility parameters and Teas plots can give

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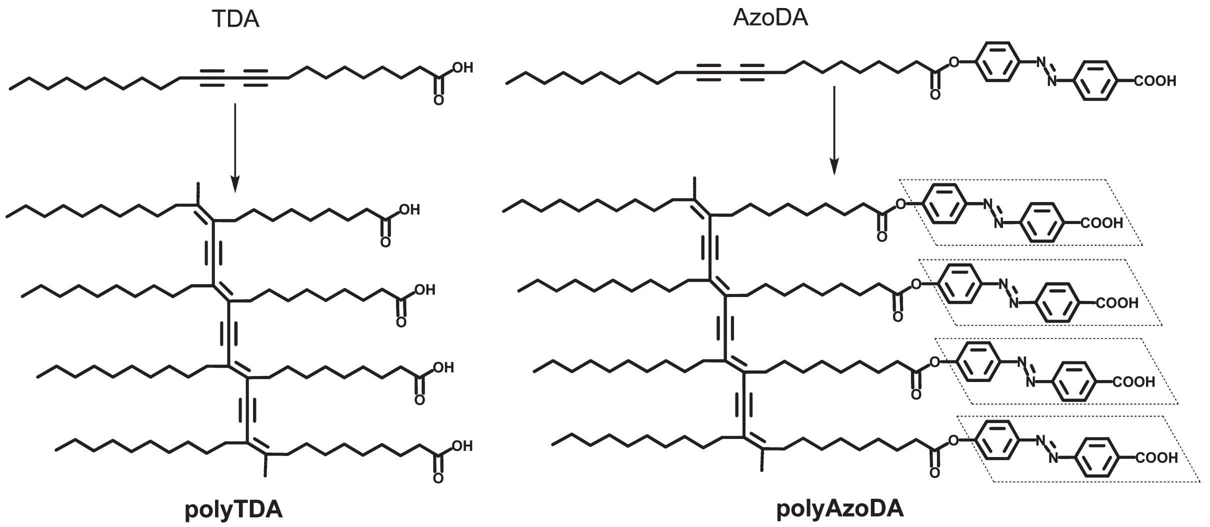
*Corresponding authors. E-mail: zqjm@ustc.edu.cn (Q. Z.); bubeck@mpip-mainz.mpg.de (C. B.).

Scheme 1. Chemical Structures of the Diacetylene Derivatives TDA and AzoDA and Their Corresponding Structures after Topochemical Photopolymerization[a]



[a] Micelles of polyAzoDA have H- and J-like aggregates of the azo chromophore as indicated by the dashed frames.

intuitive indication of solvent−polymer interactions and can help us to understand the properties of a polymer in different solvent environments.[19−23] In this work, we use solubility parameters and Teas plots to study the interactions between solvents and polyAzoDA quantitatively. We found the H- and J-like aggregates of azo chromophores can be removed by suitable organic solvents and the photoisomerization of azo chromophores is not hindered anymore after the aggregation is eliminated.

2. Experimental Section

2.1. Materials. Tricosa-10,12-diynoic acid (TDA) was obtained from Alfa Aesar and used without further purification. The synthesis of the azo chromophore-functionalized diacetylene molecule AzoDA was reported in our previous work.[13] The chemical structures of TDA and AzoDA and their corresponding polymers polyTDA and polyAzoDA are shown in Scheme 1.

We prepared micelle-like assemblies of polyTDA and polyAzoDA in the following way: 2 mg of the corresponding DA derivative was dissolved in 2 mL of THF in a flask. The solvent was removed by a stream of N_2 gas and then the flask was vacuum pumped for about 4 h to remove residual organic solvent. Subsequently, 6 mL of a 5 mM HEPES buffer solution (a buffer solution prepared from 4-(2-hydroxyethyl)piperazine-1-ethanesulfonic acid sodium salt) was added into the flask to hydrate the dry materials. The samples were sonicated at 80 °C for 30 min. The resulting dispersions were stored at 4 °C overnight. Polymerization was carried out at room temperature by irradiating the dispersions with an ordinary UV hand-lamp at 254 nm for 3 min. The dispersion was filtered through a 5 μm micropore filter before measurements. PolyTDA and polyAzoDA micelles with different contents of organic solvents were prepared by adding different amounts of Milli-Q water (18.2 MΩ cm) and organic solvents into the original micelle dispersion. We used the following analytical grade organic solvents: glycol, DMSO, ethanol and THF. We used specific mixing ratios of organic solvents and water which are shown in Table 1.

2.2. Measurements. UV−vis absorption spectra of the micelle dispersions were measured on a Perkin-Elmer Lambda 900 spectrophotometer. Scanning electron microscopy (SEM) images of polyAzoDA assemblies were obtained with a LEO Gemini 1530 system. The samples for SEM measurements were prepared by dropping the micelle dispersion onto a silicon wafer and leaving it dry in a fume hood. Photoisomerizations of azo chromophores were induced by a high-pressure mercury arc combined with water- and UG11-filters resulting in UV intensity (λ_{max} at 365 nm) at the sample position in the order of 21 mW cm^{-2}.

Table 1. Mixing Ratios of Original Micelle Dispersions in Buffer Solutions As Specified in the Experimental Section, Milli-Q Water and Organic Solvents, Respectively

solvent content (%)	0	16.7	33.3	50	66.7	83.3
original micelle (mL)	0.5	0.5	0.5	0.5	0.5	0.5
Milli-Q water (mL)	2.5	2	1.5	1	0.5	0
organic solvent (mL)	0	0.5	1	1.5	2	2.5

3. Results and Discussion

3.1. Blue-to-Red Color Transitions of Polydiacetylenes. The colors of PDAs may change after exposure to organic solvents.[12] The interactions between PDAs and the organic solvents can be studied by means of solvatochromism. We studied the solvatochromism of polyAzoDA micelles, which are stabilized by strongly aggregated azo chromophores.[13] The solvatochromism of the reference compound polyTDA without aggregation is also studied for comparison. We add glycol, DMSO, ethanol, and THF into the dispersions of polyTDA and polyAzoDA, whose colors are blue originally. As shown in Figure 1, the colors of polyTDA and polyAzoDA change at certain contents of organic solvents. The results of solvent induced color changes are listed in Table 2. From this simple approach, we know that the strength of the polyTDA-solvent interaction is in the following order: THF > ethanol > DMSO > glycol. THF is also a good solvent for polyAzoDA, as we observe blue-to-red color transitions of polyAzoDA in THF/water mixtures and we do not observe color transitions in the other solvents/water mixtures. Compared with polyTDA, polyAzoDA shows an improved stability to several solvents, which is apparently caused by the H- and J-like aggregates of azo chromophores in polyAzoDA.[13]

To have a deeper understanding of the PDA-solvent interactions, we use solubility parameters and Teas plots to show the polymer−solvent interactions quantitatively.[19−24] The total solubility parameter δ_t could be divided into three component Hansen parameters, δ_d, δ_p, and δ_h by considering the dispersion, polar and hydrogen bonding forces.[19−23] The Hansen parameters of the water/organic solvent mixtures

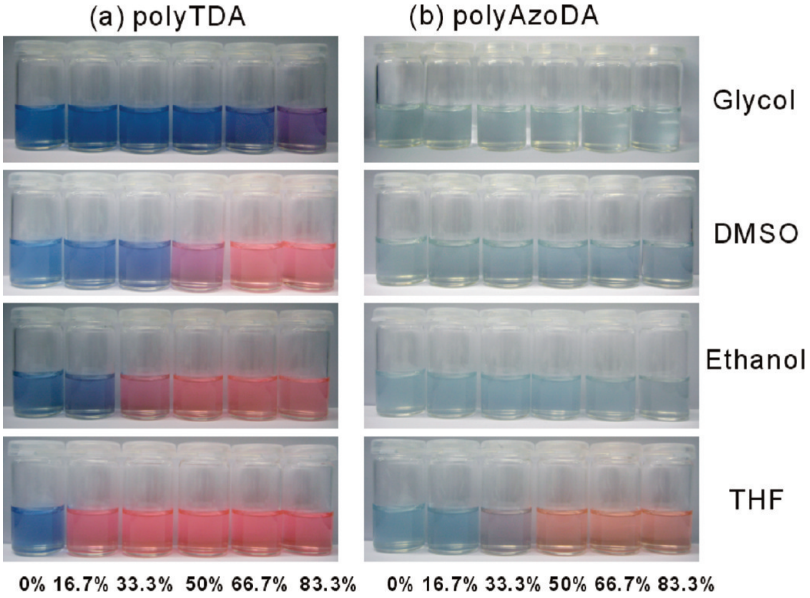


Figure 1. Photographs of micelle dispersions in different water-solvent mixtures as specified in Table 1. At increasing solvent content, the color of (a) polyTDA and (b) polyAzoDA changes from blue to purple/red depending on type of solvent and its relative content, respectively.

Table 2. First Appearance of Visual Color Changes of the Micelle Dispersions from Blue to Purple/Red at Increasing Solvent Content[a]

solvent mixture	polyTDA	polyAzoDA
% glycol content	83.3	-
% DMSO content	50	-
% ethanol content	33.3	-
% THF content	16.7	33.3

[a] The "-" indicates that no color change was observed at visual inspection.

can be estimated from the following equation:[20]

$$\delta_{\text{average}} = \Sigma\phi_i\delta_i \tag{1}$$

where δ_{average} is the average solubility parameter of the mixture and ϕ_i and δ_i are the volume fraction and solubility parameter of the component.

The Hansen parameters of PDAs and substituents of PDAs can be calculated according to a group-contribution method.[24] Hansen solubility parameters can also be used in the equivalent form of Teas parameters.[20−24] With these parameters, each compound is represented by a single point in a ternary plot. The Teas parameters of the water/organic solvent mixtures can be estimated from the following equations:[20−24]

$$f_{\text{d}} = \delta_{\text{d}}/(\delta_{\text{d}} + \delta_{\text{p}} + \delta_{\text{h}}) \tag{2}$$

$$f_{\text{p}} = \delta_{\text{p}}/(\delta_{\text{d}} + \delta_{\text{p}} + \delta_{\text{h}}) \tag{3}$$

$$f_{\text{h}} = \delta_{\text{h}}/(\delta_{\text{d}} + \delta_{\text{p}} + \delta_{\text{h}}) \tag{4}$$

where f_{d}, f_{p}, and f_{h} are the dispersion component, polar component, and hydrogen bonding component of Teas parameters, respectively.

The polymer−solvent interaction strength can be directly related to the difference of solubility parameters of a polymer and a solvent. Usually, with increasing difference between solubility parameters of a polymer and a solvent, the interactions between them decrease.[19−24] The solubility parameters of the solvents, PDAs and the substituents of PDAs are calculated as described above and presented in the Teas plots, see Figure 2. The solubility parameters of the mixed solvents extend to the lower right part of the Teas plots as the content of the organic solvents increases. The calculated parameters of the two PDAs and the substituents of the two PDAs are also located at lower right of the Teas plots. The parameters of the solvents and PDAs have a tendency to become more closely located in the Teas plots as the content of the organic solvent increases. So, as the content of the organic solvent increases, the interactions between the PDAs and the solvents increase. Although the critical color transition concentrations of polyTDA in different solvents are different, these critical color transition concentrations appear almost at the same place of the Teas plot (Figure 2a), indicating that the Teas plot describes the solvent−polymer interaction correctly for polyTDA. However, polyAzoDA shows solvatochromism in THF/water mixtures only. PolyAzoDA does not show solvatochromism in the other solvent/water mixtures, although the location of the mixtures of glycol/water, DMSO/water and ethanol/water appear similarly close to polyAzoDA. This behavior of polyAzoDA is different from polyTDA and might be related to the aggregation state of polyAzoDA. We note that the use of solubility parameters describes the swelling behaviors of polymers quite well but has limited suitability for crystallized or strongly aggregated systems.[20,22,23]

The polyAzoDA-solvent interactions are further studied by UV−vis absorption spectroscopy as shown in Figure 3. The absorption band around 650 nm does not shift as the contents of glycol, DMSO and ethanol increase. However, when the content of THF increases, the absorption band around 650 nm gradually decreases and the absorption band around 550 nm gradually increases. Besides the solvatochromism, two other effects of the solvents on the absorption spectra are found:

1. The apparent tails seen in the absorption spectra at $\lambda > 700$ nm are related to light scattering by the polyAzoDA dispersions. These tails gradually decrease as the contents of the organic solvents increase, indicating that structural transitions happen in the micelle-like assemblies.
2. The $\pi-\pi^*$ transition of trans azobenzene groups in the near UV range gradually changes from a broad band to a sharp band as the content of the organic solvents increases, indicating that the amount of

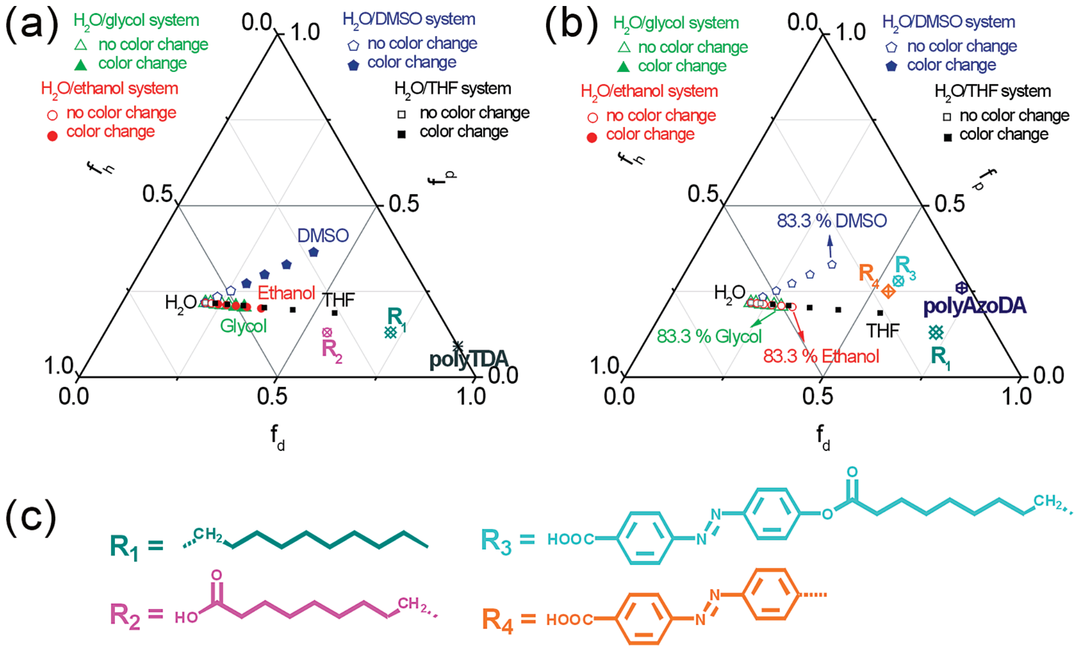


Figure 2. Teas plots of calculated solubility parameters of water-solvent mixtures, hydrophobic side chains (R_1), hydrophilic side chains (R_2, R_3), azo group (R_4), and of PDAs (a) polyTDA and (b) polyAzoDA. The symbols of the water-solvent mixtures represent visual color changes of the micelle dispersions; open symbols: no color change, full symbols: purple/red color is visible. (c) Chemical structures of the side chains of polyTDA and polyAzoDA.

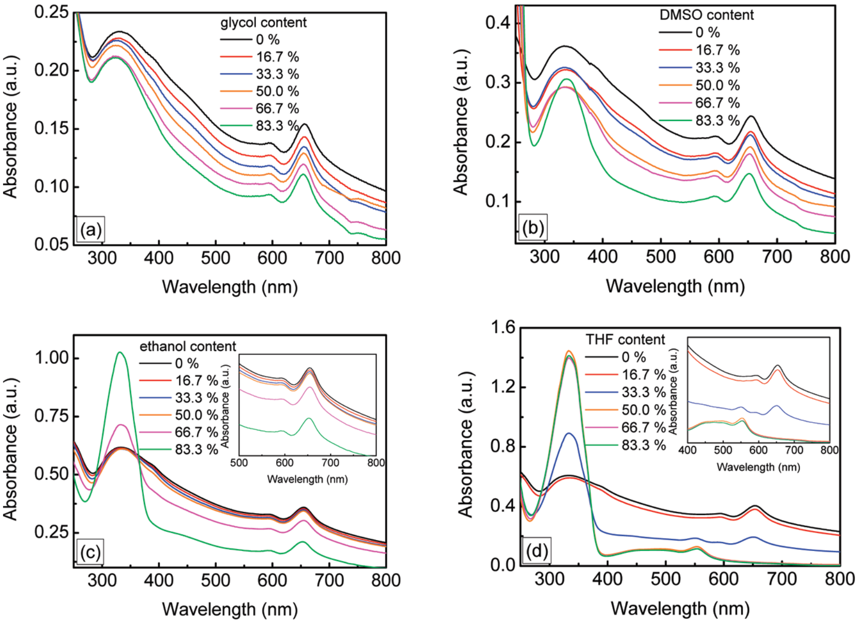


Figure 3. UV−vis absorption spectra of polyAzoDA in different amounts of (a) glycol, (b) DMSO, (c) ethanol, and (d) THF. The insets in parts c and d are the enlargements of the absorption bands of PDA backbone.

H- and J-like aggregates is gradually reduced by the organic solvents.

3.2. Morphological Transitions of polyAzoDA. Micelles of polyAzoDA may show changes of their size, shape, and amount after adding solvents to their dispersions, which are related to changes of their light scattering properties. The decrease of light scattering after addition of solvents to dispersion of polyAzoDA is most pronounced in the case of THF. Therefore, the measured transmittances of polyAzoDA dispersions at 800 nm indicate the amount of light scattering after adding THF. As shown in Figure 4, the transmittance of polyAzoDA increases significantly as the content of THF increases, which indicates structural transitions.

For comparison with the transmittance changes of polyAzoDA, the structures of polyAzoDA at different contents of THF are studied by SEM. In our previous work, we showed that the assemblies of polyAzoDA without organic solvents have a preferred cylindrical or rod-like shape.[13] The SEM images in Figure 5 show that the morphology of polyAzoDA changes from cylinders to spheres. Finally, the micelle-like assemblies are totally dissociated at large THF content.

We draw a schematic model in Scheme 2 and explain the morphological transitions by the critical packing parameter

v/a_0l_c of amphiphilic molecules,[25,26] where v is the volume of the hydrocarbon chain, a_0 is the optimal area of the hydrophilic group, and l_c is the critical chain length of the hydrophobic group. Cylindrical micelles are formed when v/a_0l_c is between $^1/_2$ and $^1/_3$, whereas spherical micelles are formed if v/a_0l_c is smaller than $^1/_3$.[25,26] Because polyAzoDA is formed by topochemical polymerization of AzoDA and AzoDA is a typical amphiphilic molecule, we use the critical packing parameters of the repeating unit of polyAzoDA to show the self-assembly properties of polyAzoDA.

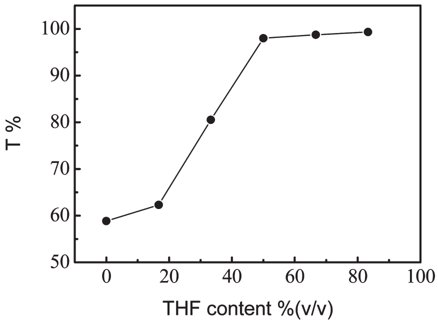


Figure 4. Transmittance of polyAzoDA at 800 nm as a function of the content of THF.

As shown in Figure 5a−d, without THF and with a small amount of THF (16.7%), cylindrical micelles are formed. Usually, cylindrical micelles are formed by single-chained lipids with small headgroup areas.[25] The optimal headgroup area a_0 is affected by two factors. One is attractive hydrophobic interactions of the hydrocarbon chain, which will decrease a_0 and the other is the repulsive interaction between the polar head groups, which will increase a_0.[25] In polyAzoDA, besides the normal hydrophobic interactions of the hydrocarbon chain, there is H- and J-like aggregation among azobenzene groups, which provides an additional attractive interaction. So, the optimal area a_0 of the hydrophilic group becomes even smaller and cylindrical micelles are formed.

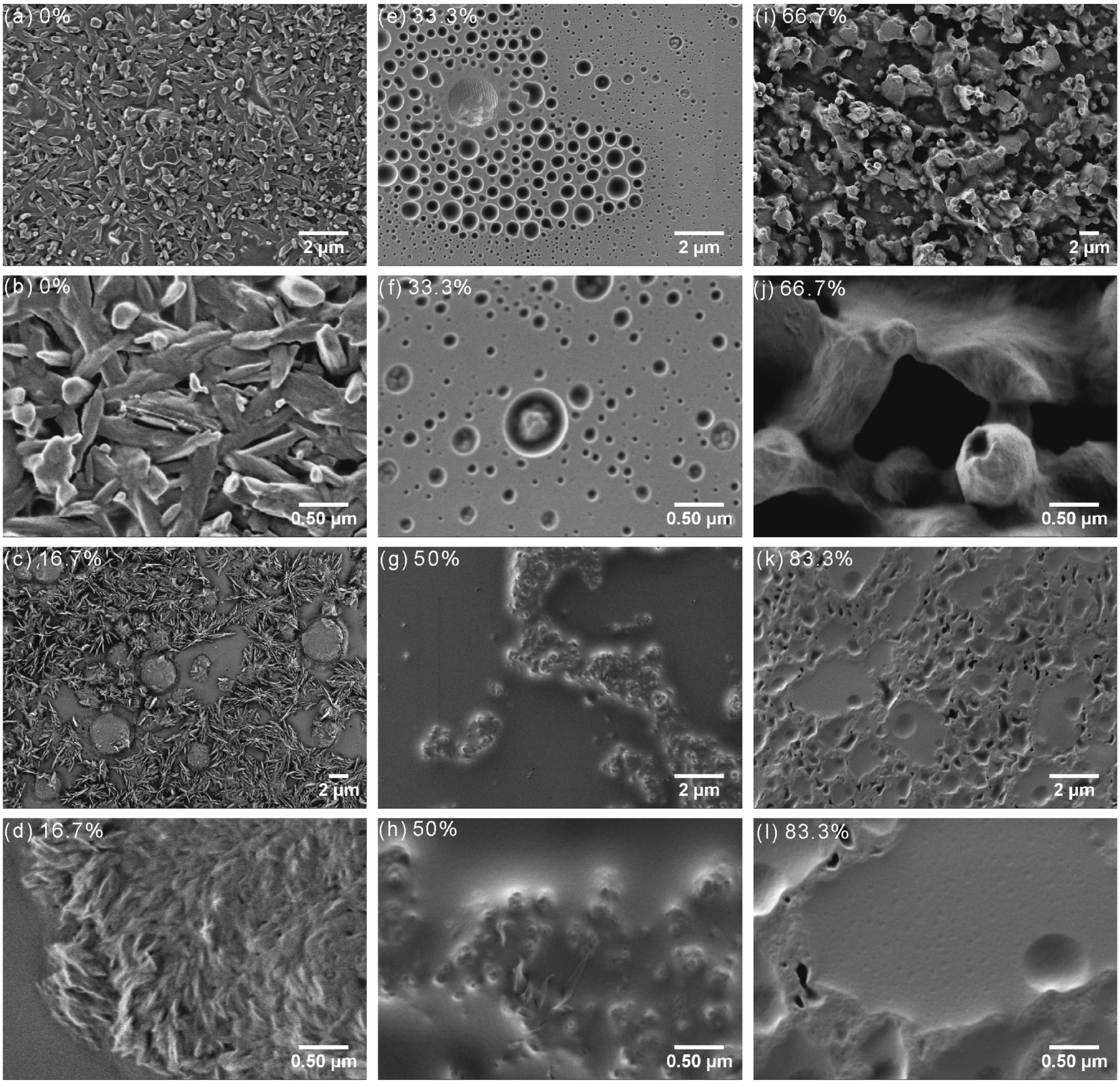
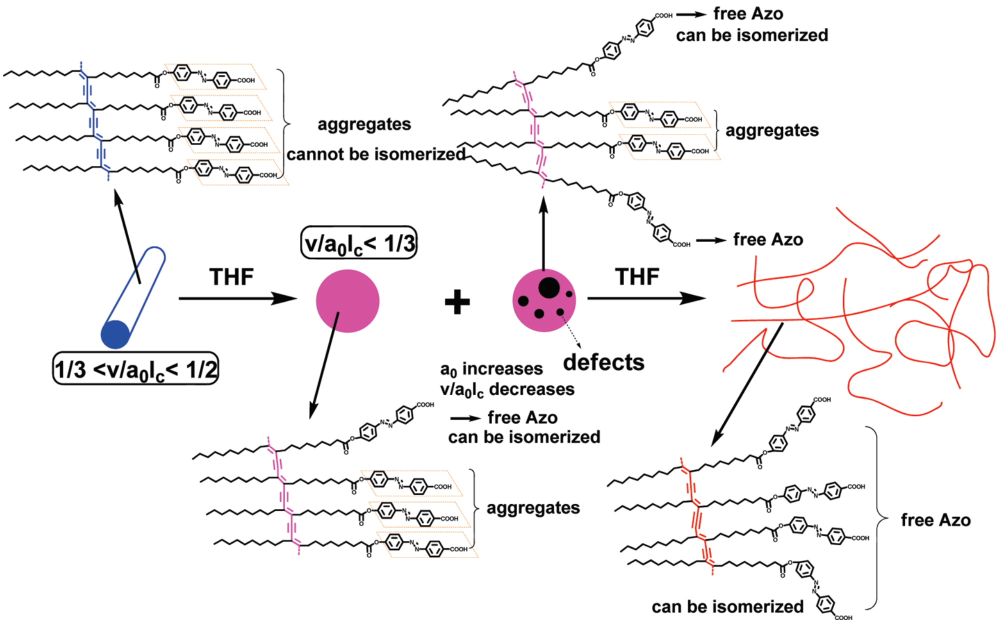


Figure 5. SEM images of polyAzoDA in different contents of THF: (a and b) without THF; (c and d) 16.7% THF; (e and f) 33.3% THF; (g and h) 50% THF; (i and j) 66.7% THF; (k and l) 83.3% THF.

Scheme 2. Schematic Model of the Morphological and Structural Changes of polyAzoDA Assemblies as the Content of THF Increases



When the content of THF increases to 33.3%, the polymer–solvent interactions must be considered, as we observed that the color of polyAzoDA changes and the $\pi-\pi^*$ transition band of azo chromophore narrows, indicating that polyAzoDA is partly swollen and the aggregation of azo chromophore is partly removed. When the azo chromophores change from aggregated states to freely mobile states, a_0 increases and v/a_0l_c decreases accordingly. The spherical shape of polyAzoDA in Figure 5, parts e and f, indicates that v/a_0l_c decreases to $<{}^1/_3$. We also observe that there are some holes and defects on some of the spheres, which we do not observe in the assemblies with lower THF contents. This result indicates that THF already starts to dissociate the assemblies of polyAzoDA at the content of 33.3%.

As shown in Figure 5g–l, at even higher THF contents (50%, 66.7% and 83.3%), the assemblies of polyAzoDA are dissociated by THF.

It is well-known that amphiphilic block copolymers also show solvent-induced morphological transitions.[27,28] The time scale of morphological transition of block copolymers is in the range of a few minutes determined by measuring the turbidity changes.[28] The morphological transitions of the assemblies of polyAzoDA are very quick, as we observe immediate color changes of the dispersion when THF is added.

3.3. Photoisomerization of the Azo Chromophore in polyAzoDA. In the polyAzoDA dispersion without organic solvent, the photoisomeriztion of azobenzene groups is hindered because of the strong aggregation.[13] We have shown above that the aggregation of azobenzene groups can be gradually eliminated by adding organic solvents. So, we expect that polyAzoDA would become photosensitive if the aggregation is not present anymore. To check this, we irradiated dispersions of polyAzoDA with different contents of ethanol and THF with UV light at 365 nm. The absorption spectra of these samples are recorded after different time intervals. The absorption spectra of polyAzoDA with different contents of ethanol during irradiation are shown in Figure 6 and the absorption spectra of polyAzoDA with different contents of THF during irradiation are shown in the Supporting Information.

As shown in Figure 6, photoisomerization of polyAzoDA does not take place using ethanol contents of 0%, 16.7% and 33.3%. If the contents of ethanol is increased to 50%, 66.7% and 83.3%, photoisomerization of polyAzoDA takes place, as we observe that the $\pi-\pi^*$ transition in the near UV range decreases gradually during irradiation. The isomerization rate and degree can be evaluated from the absorption spectra. Photoisomerization of the azobenzene groups is a first-order reaction which can be analyzed by the following kinetic equation:[15,16,29,30]

$$\ln[(A_\infty - A_t)/(A_\infty - A_0)] = -kt \tag{5}$$

where A_0, A_t, and A_∞ are the initial absorbance, absorbance at time t and absorbance at the photostationary state of azobenzene groups at $\lambda_{\max}$; k is the photoisomerization rate constant; t is the irradiation time.

The degree of photoisomerization R is estimated from the following equation:[15,29]

$$R = (A_0 - A_\infty)/A_0 \times 100\% \tag{6}$$

The kinetic process of photoisomerization of polyAzoDA in the solvent/water mixtures can be fitted well by these equations. The photoisomerization rate constant and degree of polyAzoDA with different contents of ethanol and THF are shown in Figure 7. The photoisomerization rate and degree increase as the contents of the organic solvents increase. As we know, without organic solvents, azo chromophores are in a strongly aggregated state and totally "frozen". As the content of the solvent increases, the aggregates of azo chromophores are gradually removed by the solvents and azo chromophores become photosensitive as elucidated in Scheme 2.

Figure 7 shows that photoisomerization of polyAzoDA begins to take place at concentration of 33.3% THF and 50% ethanol. The photoisomerization rate constants and degrees in THF/water are always larger than those in the same content of solvent in the ethanol/water system. These results indicate that the photoisomerization of polyAzoDA is easier in THF/water system than in ethanol/water system. The different photoisomerization behavior of polyAzoDA in the two solvent systems could be explained by azo chromophore-solvent interactions. If the aggregation of azo chromophores is removed by the organic solvents, the $\pi-\pi^*$ transition of azo chromophores narrows and the photoisomerization of

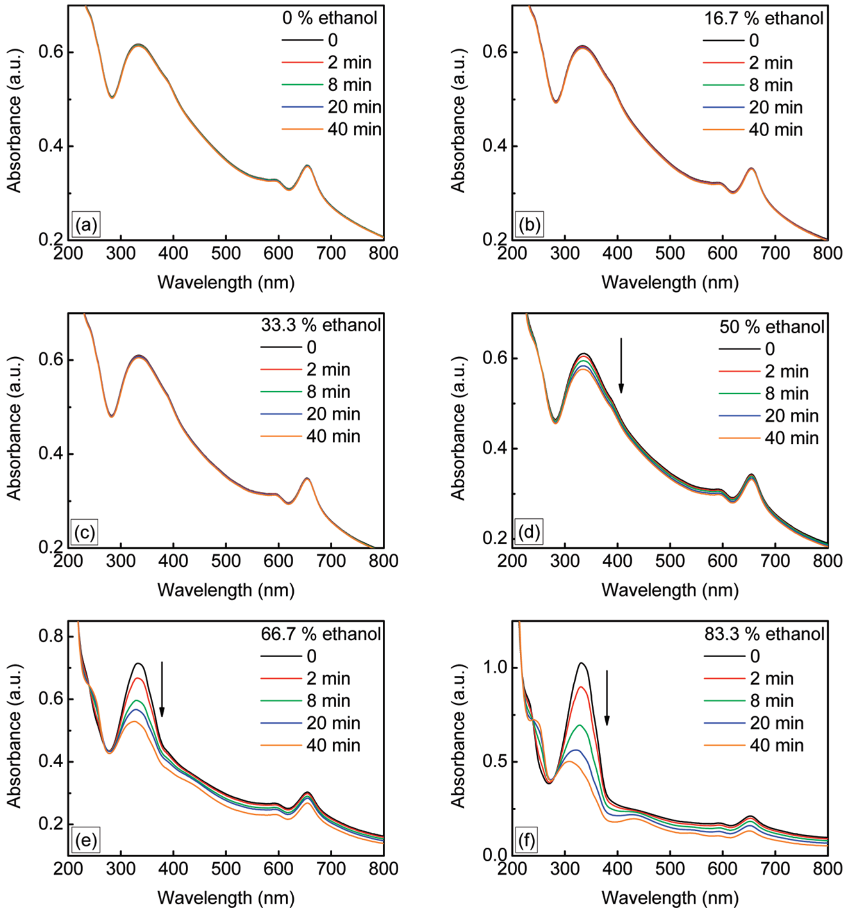


Figure 6. UV−vis absorption spectra of polyAzoDA with different contents of ethanol under the irradiation of UV light at 365 nm. The spectra were recorded after different irradiation times: (a) 0% ethanol; (b) 16.7% ethanol; (c) 33.3% ethanol; (d) 50% ethanol; (e) 66.7% ethanol and (f) 83.3% ethanol.

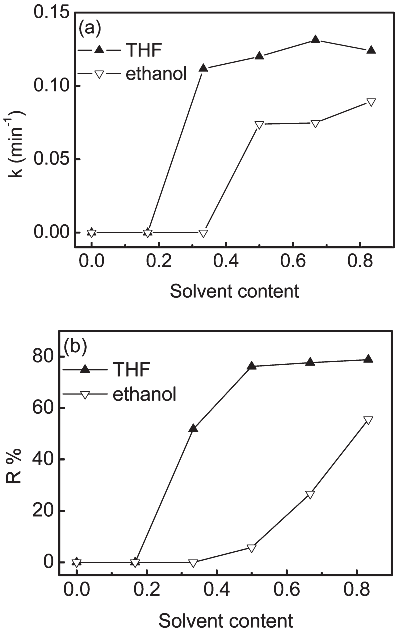


Figure 7. (a) Photoisomerization rate constant and (b) photoisomerization degree as a function of the solvent content.

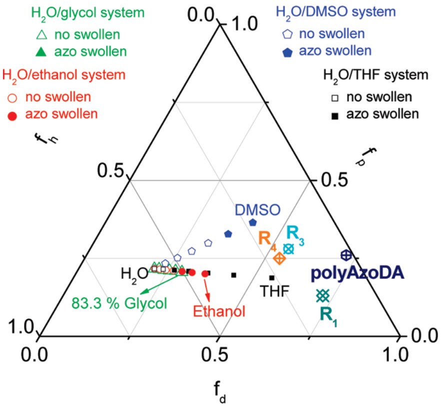


Figure 8. Teas plot of calculated solubility parameters of water-solvent mixtures, hydrophobic side chains (R_1), hydrophilic side chains (R_3), azo group (R_4) and polyAzoDA. The full and open symbols of the water-solvent mixtures represent aggregated state changes of azo chromophores. Full symbols: azo chromophores are swollen and H- and J-like aggregates are removed; open symbols: azo chormophores are not swollen and H- and J-like aggregates exist.

azo chromophores will not be hindered anymore. In Figure 8, a Teas plot according to the absorption spectra of Figure 3 is used to show the azo chromophore-solvent interactions. Azo chromophores begin to be swollen in 33.3% THF, 66.7% ethanol and 83.3% DMSO. We do not observe that azo chromophores are swollen in water/glycol mixtures in our experiment. By this approach, we know that the strength of the azo chromophore-solvent interaction should be in the following order: THF > ethanol > DMSO > glycol. So, compared with ethanol, THF has stronger ability to remove the aggregates of azo chromophores. We conclude that the photoisomerization of polyAzoDA is easiest in the THF/water system of all solvents studied, because the solubility parameters of the THF/water system are located closest to the position of polyAzoDA in the Teas plot.

3.4. Photoisomerization-Induced Structural Transitions of polyAzoDA. Interestingly, in polyAzoDA with 83.3% ethanol, the photoisomerization in the side chain induces a modification of the absorption features associated with the conjugated backbone. The enlarged UV−vis absorption spectra and the corresponding difference UV−vis absorption spectra of polyAzoDA with 83.3% ethanol at various irradiation times are shown in Figure 9. The absorption band around 650 nm decreases and the absorption band around 550 nm increases during UV irradiation. Indeed, the blue dispersion becomes purple after UV irradiation for 40 min, and this major color change can be related to a conformational transition of the PDA backbone. On the basis of previous results obtained with other PDAs, the decrease of the absorption band around 640 nm should be associated with the growth of a new absorption band around 550 nm.[2,11,12] Consequently, a novel dual photochromic behavior is found in polyAzoDA with 83.3% ethanol, where the trans−cis isomerization of azobenzene groups leads to a modification of the absorption features of the backbone to which they are attached. A schematic model for the dual photochromism is shown in Scheme 3. Photochromism of the PDA main chain of polyAzoDA cannot be caused by photochromism of PDA itself. If UV irradiation at 365 nm causes photochromism of PDA itself in polyAzoDA with 83.3% ethanol, it will also cause photochromism of PDA itself in polyAzoDA with lower contents of ethanol. So, UV irradiation of polyAzoDA with lower contents of ethanol (0%, 16.7%, 33.3%, 50% and 66.7%) can be considered as control experiments. Figure S5 shows these experimental results. Only polyAzoDA with 83.3% ethanol shows dual photochromism and polyAzoDA with lower contents of ethanol do not show blue-to-red color transition. So, dual photochromism of polyAzoDA with 83.3% ethanol must be caused by photoisomerization of azobenzene groups. Figure 6 and Figure 7 show that photoisomerization of azobenzene groups in polyAzoDA is strongly influenced by the content of ethanol. Only when the mobility of side chains is large enough can the conformational transition of the conjugated backbone take place.

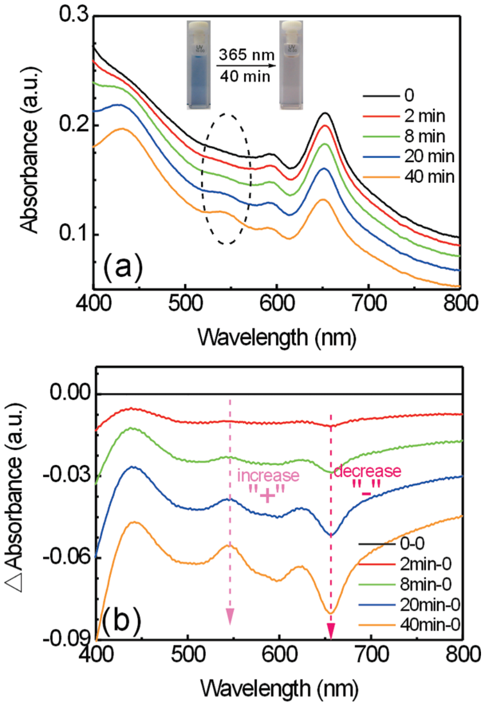
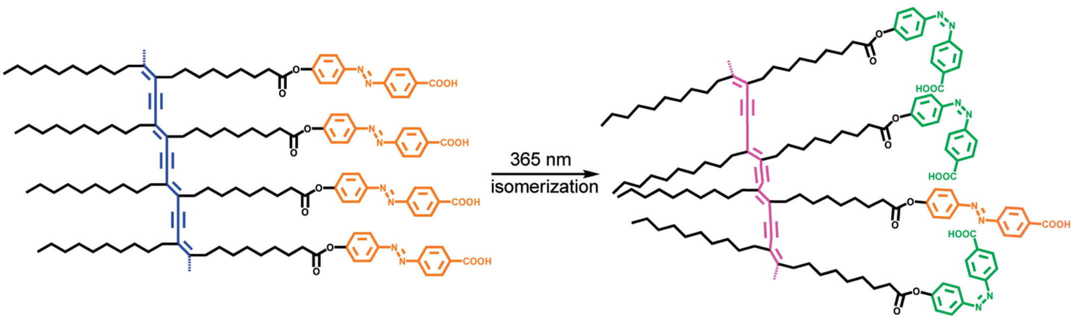


Figure 9. (a) UV−vis absorption spectra of polyAzoDA with 83.3% ethanol under the irradiation of UV light at 365 nm at different times. This figure is the enlargement of Figure 6f. The inset shows photographs of polyAzoDA with 83.3% ethanol before and after UV irradiation for 40 min. (b) UV−vis subtraction spectra of polyAzoDA with 83.3% ethanol under the irradiation of UV light at 365 nm at different time. The spectra are obtained by subtraction the absorption spectrum of polyAzoDA before UV irradiation from the original absorption spectra.

Leclerc et al. reported that the photoisomerization of azobenzene groups on the side chains changes the conformation of polythiophene backbone.[6,7] In their work, they found that there is an isosbestic point between the absorption of two distinct conformational structures of the backbone of polythiophene. Our result shown in Figure 9 is different from theirs, since there is no isosbestic point between the two absorption bands and the scattering tail in the absorption spectra decreases as the irradiation time increases. As discussed in sections 3.1 and 3.2, the decrease of light scattering at increasing THF content is an indication of solvent-induced morphological transition of polyAzoDA. We assume that the decrease of the scattering tail under UV irradiation shown in Figure 9 should also be an indication of a morphological transition in the assemblies.

To confirm if there is photoinduced morphological transition, the structures of polyAzoDA with 83.3% ethanol before and after UV irradiation for 40 min are observed by SEM. As shown in Figure 10, polyAzoDA forms micelle-like assemblies before UV irradiation. We observe a rough surface with holes but not particles after UV irradiation. This result indicates that photoinduced dissociation of the micelle-like assemblies happens in our samples. Recently, many groups reported their interesting observations on photoinduced morphological transitions of azo-containing assemblies.[31−35] Different from the work mentioned above,[31−35] polyAzoDA is a conjugated polymer and the azobenzene derivates used in the other work are nonconjugated polymers

Scheme 3. Schematic Model of the Dual Photochromism[a]



[a] Photoisomerization on the side chain induces conformational transition of the conjugated backbone.

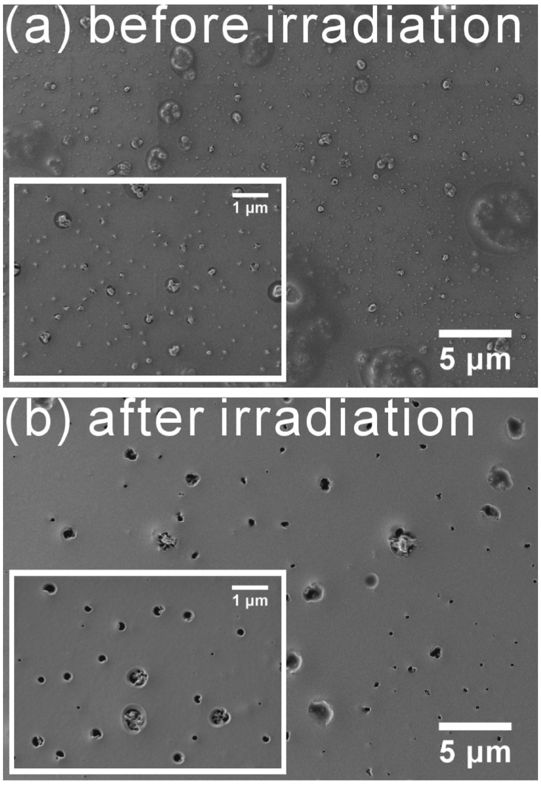


Figure 10. SEM images of polyAzoDA in 83.3% ethanol (a) before irradiation and (b) after UV irradiation for 40 min. Insets show the enlargement of the SEM images.

or small molecules. Compared with the nonconjugated polymers and small molecules, the conjugated polymer is more rigid due to the conjugated backbone. Furthermore, the $\pi-\pi$ interactions among the conjugated chains do not exist in the nonconjugated polymers and small molecules. So, the morphological transition should be more difficult to achieve in conjugated polymers. The results shown in Figure 10 indicate the movement of azobenzene groups in the process of photoisomerization is strong enough to induce the morphological transition of a rigid conjugated polymer.

4. Conclusion

The effects of solvents on the structure, morphology, and photophysical properties of an azo chromophore-functionalized polydiacetylene polyAzoDA have been explored. We use solubility parameters and Teas plots to study PDA−solvent interactions and explain the properties of polyAzoDA observed in different solvent environments. This method should not only be suitable for our system but also should be suitable for common polymers in different solvent environments. So, we believe using solvent parameters and Teas plots to study the interactions between solvents and functional polymers open up new avenues for the design of new stimuli-responsive polymers, sensors and molecular switches in special solvent environments. The novel dual photochromism and photoinduced morphological transition of polyAzoDA shows that the photoisomerization of azobenzene groups is strong enough to induce structural transitions of rigid CP systems. These results should be helpful to design new functional optoelectronic materials based on photoresponsive azobenzenes and CPs.

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Supporting Information Available: Figures showing UV−vis absorption spectra and chemical structures and tables giving calculations of the solubility parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

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