A Novel, Soluble Poly(diacetylene) Containing an Aromatic Substituent

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ABSTRACT: A series of diacetylenic monomers containing at least one aromatic substituent were synthesized. Since the aromatic side group is a rigid, pyrimidyl ring, it is necessary that the other side group has a high degree of flexibility to permit polymerization in the monomer single crystal. Among the five monomers synthesized, only 8-[[(butoxycarbonyl)methyl]urethanyl]-1-(5-pyrimidyl)octa-1,3-diyne (BPOD) monomer crystals turned into a polymer upon γ-irradiation with 68% monomer-to-polymer conversion. Poly(BPOD) is metallic red as polymerized and highly soluble in chloroform and undergoes a dramatic color transition from red (λ_{max} = 510 nm) to purple (λ_{max} = 599 nm) upon the addition of a nonsolvent such as hexane. This red-to-purple transition going from good to poor solvent is interpreted as a single-chain phenomenon. Aggregation may follow as the rigid chains interact with each other and crystallize. This aggregation could be prevented by increasing the side group–nonsolvent interaction by employing a nonsolvent which has high polarity and hydrogen-bonding capability.

Introduction

Poly(diacetylene) (PDA) single crystals can be obtained from monomeric single crystals by solid-state polymerization.[1] The polymerization is known to proceed by topochemical 1,4-addition and produces a fully conjugated backbone as shown in Figure 1. PDAs are considered to be potential candidates for photonic[2] and electronic[3,4] applications because of the presence of extensive π-electron delocalization along the backbone. It has been suggested that PDAs with aromatic substituents directly attached to the main backbone might be employed for enhancing and modulating these properties.[5] The number of π-electrons per repeating unit and the nature of π-delocalization might be increased through π-conjugation between the main backbone and side groups.[4,6-7] However, only a few such PDAs are polymerizable, and they are generally insoluble in common organic solvents.

It has been shown that longer, flexible side chains with the possibility of hydrogen bonding in PDAs promote the solubility of the polymers through the increased conformational entropy of the side groups as observed in the series of poly(*n*-BCMU) [$R_1 = R_2 = (CH_2)_nOCONHCH_2COO(CH_2)_3CH_3$].[8,9] High polymer conversion and good solubility of poly(4-BCMU) may be attributed to the high entropy of the side groups. Solvatochromic[10-16] and thermochromic[18,19] transitions in poly(4-BCMU) have been extensively investigated. Typically, poly(4-BCMU) forms yellow solutions (λ_{max} = 465 nm) in chloroform and shifts from yellow to red (λ_{max} = 545 nm) upon the addition of hexane. The origin of the color change has been a point of considerable debate. Patel and Miller[12] believed that the color transition was a result of the planar–nonplanar backbone conformational change which was caused by the disruption of the side-group hydrogen-bonded network. Lim et al.[10,11] claimed that the color change is due to a coil-to-rod conformational transition. Wegner et al.[13] and Hsu et al.[14] suggested that the solvatochromic shift was the consequence of aggregation of the wormlike coils present in the yellow solution. Recently, Nava et al.[15] and Rosenblatt and Rubner[16] concluded that the chromic behavior observed in poly(4-BCMU) solutions is neither purely a single-chain phenomenon nor just an aggregation effect but a combination of both. The complexity in understanding the origin of solvatochromic transitions in PDA solutions is partly due to the inability to isolate the effect of the energetics of side-group-related conformational changes from the energetics of the backbone conformational transitions and electron-delocalization effects.

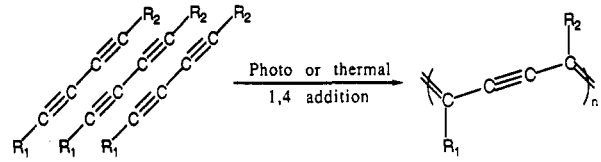

Figure 1. Topochemical solid-state polymerization of diacetylenes by 1,4-addition.

We report here a series of model diacetylene compounds containing a rigid, aromatic pyrimidyl side group directly attached to the diacetylene functionality as well as a polar, flexible side group (Scheme 1). In these diacetylenes the flexibility of one of the side groups is reduced compared to poly(4-BCMU), but the number of π-electrons per repeating unit is increased through possible π-conjugation between the main chain and one of the side groups. We propose to investigate these polymers as a model system for elucidation of the mechanisms responsible for chromism of soluble PDAs. We expect reasonably high monomer-to-polymer conversion and good solubility due to the presence of the same flexible side group as in 4-BCMU. Increased π-conjugation due to the aromatic side groups is also expected. Syntheses of these novel, soluble poly(diacetylenes), their monomer-to-polymer conversion via γ-irradiation, and the solvatochromic behavior are presented.

Experimental Section

(A) Synthesis of the Monomers. Synthetic routes of the diacetylenic monomers are shown in Scheme 1.

Chemicals. 5-Hexyn-1-ol was obtained from Fluka Chemicals, and butyl isocyanatoacetate was purchased from Eastman Kodak Co. Other chemicals were obtained from Aldrich Chemical Co. and were used as received unless otherwise mentioned.

Synthesis of 2-Methyl-4-(5-pyrimidyl)but-3-yn-2-ol. In a three-necked flask (500 mL) fitted with a N_2 inlet and an outlet,

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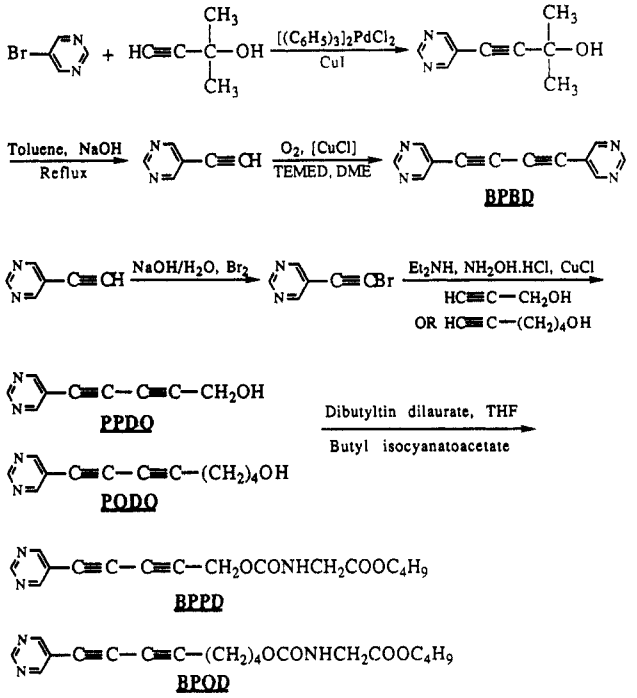
Scheme 1. Synthetic Route to Various Diacetylenic Monomers



5-bromopyrimidine (0.2 M) was dissolved in 300 mL of diethylamine. Bis(triphenylphosphine)palladium(II) dichloride (1 g) and 2-methyl-3-butyn-2-ol (0.3 M) were added, and the mixture was stirred for 5 min under N_2. A catalytic amount of CuI was added and stirred for 12 h. White solids, resulting from the salt formation of the reactants, started to form within a few minutes, and the amount is a good measure of the degree of reaction. After completion of the reaction, the reaction mixture was filtered, and the solvent was removed under vacuum. The solid residue was dissolved in ether, washed with H_2O, and dried over anhydrous $MgSO_4$. The solvent was evaporated under vacuum, and white crystals were obtained by recrystallization from toluene. Elem. Anal. Calcd for $C_9H_{10}N_2O$: C, 66.64; H, 6.21; N, 17.27; O, 9.86. Found: C, 66.36; H, 6.50; N, 17.43; O, 9.87.

Synthesis of Ethynylpyrimidine. In a round flask (500 mL), 2-methyl-4-(5-pyrimidyl)but-3-yn-2-ol (0.2 M) was dissolved in hot toluene (300 mL). Powdered NaOH (10 g) was added, and the mixture was refluxed for 3 h under stirring. The mixture was filtered, and the solvent was evaporated under vacuum. Occasionally, the reaction mixture showed a brown color. Stirring the mixture with a small amount of decolorizing agent (e.g., charcoal) helped remove the colored impurities. Pure ethynylpyrimidine was obtained by performing column chromatography on silica gel with an ethyl acetate and cyclohexane mixture followed by recrystallization in hexane. Elem. Anal. Calcd for $C_6H_4N_2$: C, 69.22; H, 3.87; N, 26.90. Found: C, 68.74; H, 4.15; N, 27.45.

Synthesis of 1-Bromo-2-(5-pyrimidyl)ethyne. Bromine (0.4 M) was added dropwise to NaOH/H_2O (1 M/150 mL) while stirring at 0–5 °C. A pale yellowish solution of NaOBr formed immediately. Ethynylpyrimidine in dioxane (0.1 M/50 mL) was added dropwise to the above mixture over 20 min at 10–20 °C. A white solid formed immediately. The reaction was monitored by TLC, and the reaction mixture, after 1 h, was poured into 200 mL of ice cold water with vigorous stirring. The filtered product was dried and recrystallized from methanol. Elem. Anal. Calcd for $C_6H_3N_2Br$: C, 39.38; H, 1.65; N, 15.31; Br, 43.66. Found: C, 39.46; H, 1.72; N, 15.32; Br, 43.22.

Synthesis of 1,4-Bis(5-pyrimidyl)buta-1,3-diyne (BPBD). In a three-necked flask (250 mL) fitted with a magnetic stirrer, and purged with O_2, ethynylpyrimidine (0.05 M) in dimethoxyethane (70 mL) was added. Freshly purified cuprous chloride (0.002 M) and *N,N,N',N'*-tetramethylethylenediamine (2 mL) were added. Oxygen was bubbled through the reaction mixture with continuous stirring. After 3 h, the solvent was removed, and the product was recrystallized twice from chloroform. Elem. Anal. Calcd for $C_{12}H_6N_4$: C, 69.90; H, 2.93; N, 27.17. Found: C, 69.73; H, 3.06; N, 27.94.

Synthesis of 1-(5-Pyrimidyl)penta-1,3-diyn-5-ol (PPDO). PPDO was prepared by the Chodkiewicz and Cadiot[20] coupling of ethynylpyrimidine and propargyl alcohol. A catalytic solution of CuCl, 70% aqueous ethylamine (10 mL), NH_2OH·HCl, and 50 mL of methanol was prepared in a three-necked flask (250 mL). The reaction was carried out in a N_2 atmosphere. Propargyl alcohol (0.07 M) was added in one portion under stirring. A yellow solution was formed. 1-Bromo-2-(5-pyrimidiyl)ethyne (0.05 M) was dissolved in methanol and added dropwise over a period of 2 h while maintaining the temperature between 30 and 35 °C. The reaction was continued for another 3 h. After completion of the reaction, a major part of the methanol was removed under vacuum. An aqueous solution of KCN and NH_4-Cl was then added under vigorous stirring. The product was isolated by extraction with ether, washing the extract with H_2O, drying over $MgSO_4$, and evaporation of the solvent. Column chromatography on silica gel was performed to separate the side product BPBD. Fine white crystals were obtained by performing recrystallization from toluene. Elem. Anal. Calcd for C_9H_6-N_2O: C, 68.35; H, 3.82; N, 17.71; O, 10.11. Found: C, 68.21; H, 3.96, N, 17.60; O, 10.22.

Synthesis of 1-(5-Pyrimidyl)octa-1,3-diyn-8-ol (PODO). A similar procedure to that described for BODO was used to synthesize PODO. 5-Hexyn-1-ol was used instead of propargyl alcohol. Elem. Anal. Calcd for $C_9H_{12}N_2O$: C, 71.98; H, 6.04; N, 13.98; O, 7.99. Found: C, 72.11; H, 5.99; N, 13.87; O, 8.12.

Synthesis of 5-[[(Butoxycarbonyl)methyl]urethanyl]-1-(5-pyrimidyl)penta-1,3-diyne (BPPD). To a solution of butyl isocyanatoacetate (0.03 M) and PPDO (0.025 M) in 50 mL of dry THF, 3-5 drops of dibutyltin dilaurate and 3–5 drops of triethylamine were added. The mixture was stirred for 2 h at room temperature. The solvent was evaporated, and the pure product was isolated by performing column chromatography on silica gel with ethyl acetate and cyclohexane eluent followed by recrystallization in hexane. Elem. Anal. Calcd for $C_{16}H_{17}N_3O_4$: C, 60.93; H, 5.40; N, 13.32; O, 20.29. Found: C, 60.66; H, 5.82; N, 13.41; O, 19.47.

Synthesis of 8-[[(Butoxycarbonyl)methyl]urethanyl]-1-(5-pyrimidyl)octa-1,3-diyne (BPOD). A similar procedure to that described for BPPD was employed to prepare BPOD. PODO was used instead of PPDO. Elem. Anal. Calcd for $C_{19}H_{23}N_3O_4$: C, 63.86; H, 6.49; N, 11.76; O, 17.90. Found: C, 63.32; H, 7.03; N, 11.55; O, 17.20.

Poly(4-BCMU) was prepared according to the method of Patel.[21]

(B) Solid-State Polymerization. Polymerization in the solid state of the monomers was carried out by ^{60}CO γ-ray irradiation with a dosage of 1 Mrad/h. The unreacted monomer was extracted with hot methanol/ethanol. The percentage polymer conversion was calculated by comparing the weight of the polymer before and after extraction.

(C) FT-Raman Measurements. The Raman spectra of the monomer, partial polymer, and extracted polymer were recorded at room temperature in the solid state by using a Perkin-Elmer 1760X FT-IR spectrometer with a Raman accessory in a 180° optical collection geometry. The excitation was achieved at 1.064-μm wavelength and 30 mW of laser power with a cw Nd:YAG laser.

(D) Molecular Weight Determination. Gel permeation chromatography (GPC) measurements were performed to determine the number- and weight-average molecular weights of the polymers. GPC measurements were carried out using a Waters Model 510 pump, Model 410 refractive index detector, and Model 730 module with 500–10^5-Å Ultrastyragel columns in series. Chloroform was used as the eluent at a flow rate of 1.0 mL/min. Sample concentrations of 0.5% (w/v) and injection volumes of 100 μL were used. Polystyrene standards with a low polydispersity (Aldrich) were used to generate a calibration curve.

(E) UV–Visible Spectroscopy. UV–visible spectra of the polymer solution were obtained on a Perkin-Elmer Lambda 9 UV/VIS/NIR spectrophotometer at room temperature. The solutions were obtained by first dissolving a known amount of polymer in chloroform. This stock solution was further diluted with chloroform and/or with the nonsolvent to obtain the desired

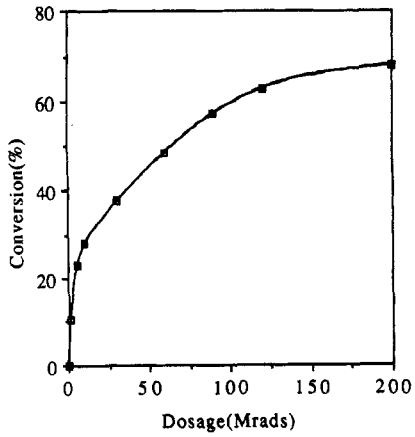


Figure 2. Plot of γ-irradiation dosage vs polymer conversion of BPOD.

concentration and solvent/nonsolvent ratios. All concentrations are stated as moles of polymer repeating units per liter.

Results and Discussion

(1) Solid-State Polymerization. Among the five diacetylenic monomers of this class synthesized in this study, only BPOD monomer crystals were converted into polymer upon γ-radiation. BPOD contains a longer alkyl spacer in the side group compared to the other monomers. A higher degree of side-group flexibility from one side group (R_1) was required to satisfy the polymerizable monomer packing conditions when the other side group (R_2) is the rigid, six-membered pyrimidyl ring. The polymer crystals appeared metallic red.

Figure 2 shows the polymer conversion of the BPOD vs γ-irradiation dosage. There was some spontaneous polymerization during the recrystallization and drying process of the monomer. Polymer conversion reached up to 68% with 200 Mrad of dosage. GPC measurements of the 200-Mrad irradiated sample showed the number- and weight-average molecular weights of 32 000 and 271 000, respectively. Surprisingly, the molecular weight of the 60-Mrad irradiated polymer was a little higher than that of the 200-Mrad sample, i.e., M_n = 42 000 and M_w = 330 000. It appears that the extended chains of the PDAs are partially scissioned into smaller fragments upon higher γ-irradiation.

Figure 3 shows the FT-Raman spectra of the monomer, partial polymer, monomer-free polymer of BPOD, and poly(4-BCMU). The BPOD monomer shows vibrational bands at 2245 and 2221 cm^{-1} (C≡C stretching) and 1570 cm^{-1} (C=C stretching of the aromatic ring). A weak peak from the monomer C≡C stretching (2245 cm^{-1}) and two strong peaks from the polymer backbone, i.e., 2100 cm^{-1} from C≡C stretching and 1466 cm^{-1} from C=C stretching, were observed in the Raman spectra of the partial polymer of BPOD. The Raman spectra of the monomer-free poly(BPOD) also showed two peaks at 2111 cm^{-1} from C≡C stretching and 1489 cm^{-1} from C=C stretching. A comparison of the Raman shifts of the partial polymer and monomer-free polymer clearly shows an increase in the disorder in the monomer-free polymer as evidenced by the increase in the C≡C and C=C stretching wavenumbers of the polymer backbone. Comparison of the FT-Raman spectra of poly(BPOD) and poly(4-BCMU) is made. The C≡C stretching vibrations for both of the polymers appear at 2111 cm^{-1}. On the other hand, poly(4-BCMU) shows the C=C stretching vibration at 1518 cm^{-1} as compared to that of poly(BPOD) at 1489 cm^{-1}. The lowering of the C=C stretching vibration in poly(BPOD) can be attributed to some degree of π-electron delocalization between the backbone double bonds and the π-conjugated aromatic (pyrimidyl) side groups. Studies on the crystal structures of the monomers and the polymers are in progress and will be published elsewhere.

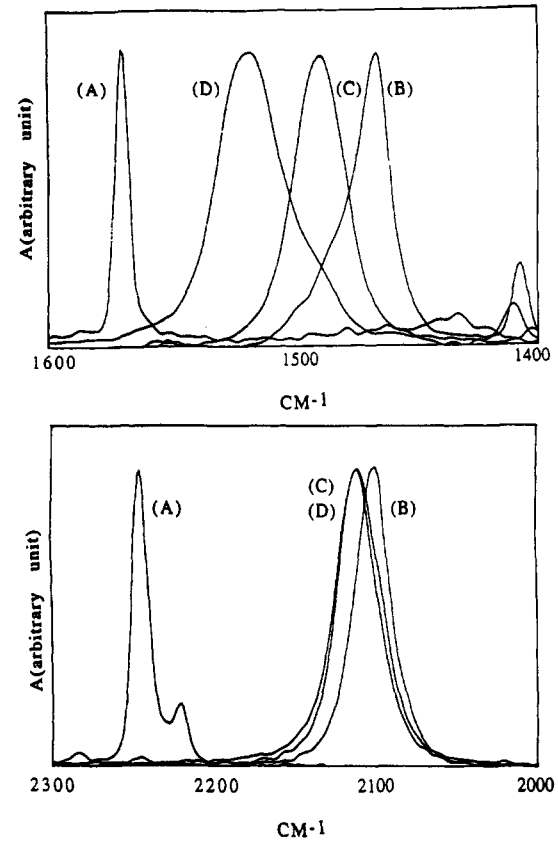


Figure 3. Principal Raman vibrational bands of BPOD (A) monomer, (B) partial polymer, (C) monomer-free polymer, and (D) poly(4-BCMU).

(2) Solvatochromic Behavior of Poly(BPOD). (A) Good Solutions. Poly(BPOD) is highly soluble in chloroform, less so in dichloromethane, and sparingly soluble in other organic solvents such as THF and DMF. Poly(4-BCMU), on the other hand, is soluble in THF and DMF as well as in chloroform. Dissolution of the poly(diacetylene)s is conjectured to arise from the conformational flexibility about the carbon–carbon single bonds in the polymer backbone. Further, the interaction between the side chains and the solvent molecules must be high enough to introduce such backbone carbon–carbon bond rotations. A decrease in flexibility of the side groups due to the introduction of the rigid, aromatic pyrimidyl group at one end is responsible for the lower solubility of poly(BPOD).

Poly(BPOD) forms a red solution in chloroform with the absorption maximum at 510 nm. The spectral profile of poly(BPOD) in chloroform solution does not change in the concentration range 6.00×10^{-7}–1.9×10^{-4} mol/L upon prolonged storage or on centrifugation. Filtration of the red polymer solutions through 0.2-μm filters does not result in any changes either in the spectral profile or in the absorbance. This indicates that the solutions are true polymer solutions with no significant interchain interactions.

An absorption maximum of 510 nm is unusual for good PDA solutions. The good solutions of all the reported soluble PDAs are yellow with the absorption maximum at about 470 nm. All these soluble PDAs contain long, flexible side groups. The absorption spectra of poly(4-BCMU) and poly(BPOD) in thermodynamically good solvents are shown in Figure 4I. Typically, good solutions of poly(4-

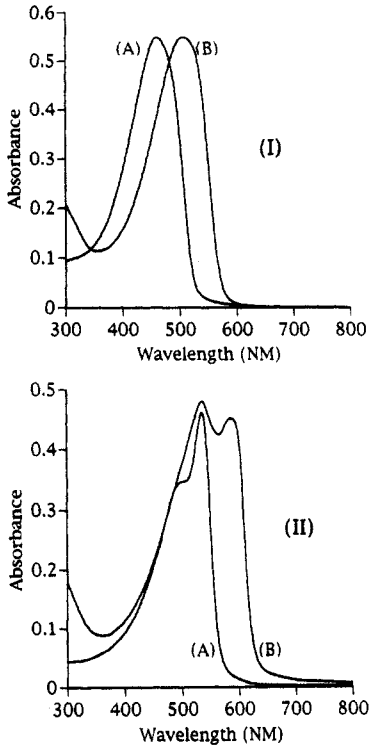


Figure 4. Absorption spectra of poly(4-BCMU) and poly(BPOD). (I) in chloroform; (II) in chloroform/hexane: (A) poly(4-BCMU); (B) poly(BPOD).

BCMU) in chloroform show the λ_{max} at 465 nm. The only structural difference in poly(BPOD) from that of poly(4-BCMU) is that the former has one of the flexible urethane side groups replaced by a rigid aromatic pyrimidyl group. The differences in the λ_{max} in the good solutions of poly(4-BCMU) (yellow) and poly(BPOD) (red) seem to arise from the presence of the π-conjugated pyrimidyl side groups next to the backbone. Two possibilities exist to explain this behavior: (i) the electronic interactions (π-electron delocalization) between the backbone and the side groups, leading to an increase in the λ_{max}; (ii) an increase in the effective delocalization length of the backbone due to the rigid side groups.

(B) Solvatochromism. Upon the addition of a poor solvent such as hexane, toluene, or acetonitrile to the red solution of poly(BPOD), a dramatic spontaneous color transition to purple (λ_{max} = 599 nm) takes place. The absorption spectra of poly(BPOD) and poly(4-BCMU) from solutions in thermodynamically poor solvent are shown in Figure 4II. The λ_{max}'s of poly(BPOD) and poly(4-BCMU) in a chloroform/hexane solution are 599 and 545 nm, respectively. As discussed earlier in the section on good solutions, this further proves that the aromatic side groups directly attached to the backbone can modify the electronic properties of PDAs.

The absorption spectra of poly(BPOD) in various chloroform/hexane mixtures are shown in Figure 5. The transition from red to purple occurs at around 6/4 (v/v), which is equivalent to 1/2.1 (M/M) and is consistently independent of the polymer concentration (10^{-4}–10^{-7} M). However, solvent mixtures with higher than 45% (v) hexane composition showed phase separation in which precipitation occurred subsequent to chromic transitions. The beginning of the precipitation point varied with the polymer concentration. Precipitation was also observed as the purple solution was left standing. Depending upon the composition, this occurred in a few seconds for the 20:80 (v/v) mixture and almost 40 h for the 45:55 (v/v) solution.

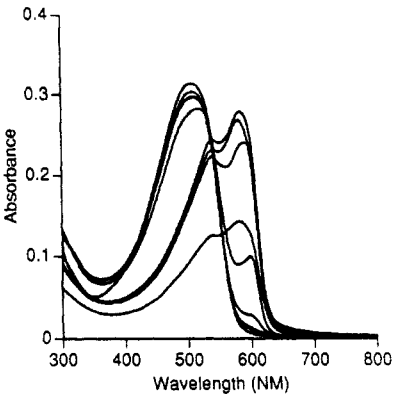


Figure 5. Absorption spectra of poly(BPOD) in various ratios of chloroform/hexane (v/v): 9/1 (top left), 8/2, 7/3, 6/4, 5/5, 4/6, 3/7, and 2/8 (bottom right). Concentration, 2.80×10^{-5} mol/L.

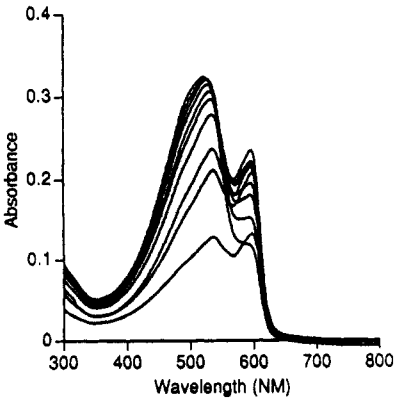


Figure 6. Absorption spectra of poly(BPOD) in 53/47 chloroform/hexane (v/v). 0 min (top left), 10 min, 1 h, 2 h, 3 h, 7 h, 21 h, 24 h, and 70 h (bottom right). Concentration, 2.80×10^{-5} mol/L.

From Figure 5, there is no evidence for the presence of an intermediate electronic species. There is an early onset of the 599-nm optical transition upon addition of the nonsolvent. At higher nonsolvent concentration, there is a complete transition of the electronic state to this new form. The induction period for precipitation varies with the history of the sample preparation as well as the polymer concentration and the nonsolvent fraction. As the polymer concentration and the nonsolvent fraction are increased and the rate of nonsolvent addition is faster, the precipitation is hastened.

Figure 6 shows the spectral changes of poly(BPOD) with time in 53/47 chloroform/hexane solution. The peak at 599 nm becomes sharper and more intense and the peak at the 525-nm spectral region gradually shifts to 534 nm as time elapsed. The intensity of the 599-nm peak starts to decrease after 21 h, and a blue polymer precipitates out of the solution after 70 h. The abrupt decrease in the overall absorption intensity (bottom right in Figure 6) is due to this precipitation.

The red-to-purple transition in poly(BPOD) solutions going from good to poor solvent may be due to an intramolecular conformational transition but not due to aggregation. In poly(4-BCMU) solutions, the chromic transition is believed to be caused by backbone conformational change from disordered (yellow) to ordered (red) structures. The structural ordering of the individual chains is accompanied with the formation of hydrogen bonding between the neighboring side groups. Rosenblatt and Rubner[16] suggest that the ordered polymer chains aggregate over a relatively short time scale to form small aggregates. Aggregation occurs as the rigid chains interact

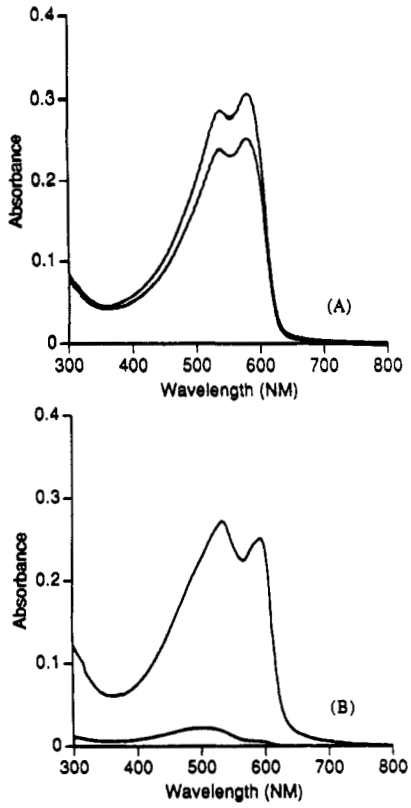


Figure 7. Absorption spectra of poly(BPOD) in (A) 5/5 chloroform/hexane (v/v) and (B) 1/9 chloroform/ethanol (v/v) before and after the filtration with a 1-μm PTFE filter. Spectra were taken 20 h after the sample preparation. Concentration 2.80×10^{-5} mol/L.

with each other and crystallize. Eventually, the aggregates fall out of the solution and precipitate. Similar backbone conformational changes may be responsible for the chromic transitions of the poly(BPOD) solutions.

The individual chains of poly(BPOD) have sufficient chain flexibility in chloroform, and a fully extended rigid rod conformation is adopted in the chloroform/hexane mixture. The extended chains start to aggregate since the interactions between the polymer chains now begin to dominate when they are in each others vicinity. Aggregation and subsequent precipitation after color transition may be prevented if the nonsolvent has the capability of holding the extended chain conformation and yet screening the interchain interaction, preventing subsequent crystallization.

Figure 7 shows the spectral changes of poly(BPOD) in chloroform/hexane and chloroform/ethanol mixtures before and after filtration with a 1-μm PTFE filter. Upon filtration, purple polymers were filtered out, and only a clear transparent solution was obtained in the case of chloroform/hexane solutions. On the contrary, poly(BPOD) in chloroform/ethanol mixtures showed some surprising results in several aspects. The spectral profiles were quite similar to those of the chloroform/hexane solutions but remained unchanged (except for a slight decrease in absorption intensity) after the filtration, and the solution was stable on standing for 2 months (to which time it is sitting in our lab) or centrifugation for 2 h at 10 000 rpm. The color transition occurred at much higher nonsolvent compositions, i.e., 28/72 (v/v), 1/12.7 (m/m), and the λ_{max} was at 585 nm, which is approximately 15 nm lower than in hexane solutions.

The resistance of the polymer chains in the purple solutions (chloroform/ethanol) of poly(BPOD) to aggregation indicates that the long-wavelength absorption

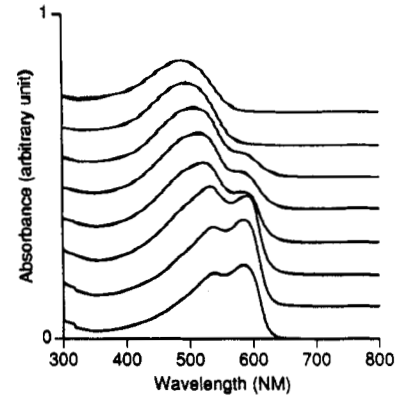


Figure 8. Effects of trifluoroacetic acid on the absorption spectra of poly(BPOD) in 28/72 chloroform/ethanol (v/v). From bottom to top: 0% (v/v), 5%, 10%, 20%, 30%, 50%, 60%, and 80%. Concentration, 2.80×10^{-5} mol/L.

maximum (585 nm) is an inherent property of individual ordered polymer chains. This confirms that the chromic transition is primarily a result of changes in the conformational ordering of the backbone. Aggregation is only a consequence of the chromic transition, and the time scale of aggregation depends on the environment.

Ethanol is a nonsolvent for the polymer and yet has a strong hydrogen-bonding potential with the side groups. There are several possibilities of hydrogen bonding in the chloroform/ethanol solution in addition to the intramolecular hydrogen bonding between the adjacent side groups of the polymer chains. They are between C=O in the ester group and OH and N= in the aromatic ring and OH. These hydrogen bonds may be strong enough to introduce an ethanol-rich solvent shell around the polymer chains. This will screen interchain Coulomb interactions and inhibit the interchain aggregation after the color transition. The small blue shift in the optical spectrum with respect to the chloroform/hexane solution may now be understood in terms of some loss of intramolecular hydrogen bonding. As ethanol competes for the formation of hydrogen bonds with the side groups, a few intramolecular hydrogen bonds may be broken, leading to some flexibility about the backbone single bonds.

Trifluoroacetic acid (TFA) is extremely effective in disrupting the hydrogen-bond network in these types of polymers. The effect of TFA on the chromic transitions in poly(4-BCMU) solution in chloroform/hexane was previously reported by Patel et al.[9] Figure 8 shows the effect of TFA on the optical spectra of poly(BPOD) in chloroform/ethanol solutions. An instantaneous blue shift from 599 to 483 nm was observed in chloroform/hexane solution upon the addition of a couple of drops of TFA (0.5% (v/v)) as was previously observed for poly(4-BCMU). This is a result of the breakage of the intramolecular hydrogen bonds, leading to rotational flexibility about the backbone single bonds. On the contrary, a much larger amount of TFA (60%) was required to observe the blue shift, and the shift was gradual in the case of the chloroform/ethanol solution. Similar results were observed for both ethanol and methanol. These observations were also confirmed for poly(4-BCMU) in chloroform/ethanol. This clearly indicated that the polymer single chains are tightly held by hydrogen bonding between the polymer and ethanol, and there is extensive hydrogen bonding unlike in chloroform/hexane solutions.

Conclusions

A novel, soluble poly(diacetylene), poly(8-[[(butoxycarbonyl)methyl]urethanyl]-1-(5-pyrimidyl)-octa-1,3-di-

yne) poly((BPOD)), containing aromatic substituents directly attached to the main backbone has been synthesized. The monomer crystals reach a high degree of polymer conversion (68%) upon γ-irradiation. The resultant polymer is highly soluble in chloroform (>0.05 mol/L). FT-Raman spectra of the polymer indicate that there is a considerable degree of π-electron interaction between the backbone and the aromatic side groups. Solutions of poly(BPOD) show dramatic color transitions from red (λ_{max} = 510 nm) to purple (λ_{max} = 599 nm) upon the addition of a nonsolvent. These are some of the longest wavelength absorptions for poly(diacetylene)s in solution. Comparison of the absorption spectra of the solutions of poly(BPOD) with those of poly(4-BCMU) indicates a substantial influence of the pyrimidyl groups on the optical characteristics of the PDAs and suggests the modulation of the optical properties. The red-to-purple transition going from good to poor solvent is not due to aggregation but is a pure, single-chain phenomenon. Aggregation may follow if the rigid chains are allowed to interact with each other and crystallize.

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