Cocrystallization and Copolymerization of Diacetylenes: Some Novel Observations

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ABSTRACT: The cocrystallization and copolymerization of two pairs of diacetylenes $R-C\equiv C-C\equiv C-R$, (1) 1BU [$R=-CH_2OCONHC_4H_9$] and 1EU [$R=-CH_2OCONHC_2H_5$], and (2) 2A [$R=-(CH_2)_2OH$] and 3A [$R=-(CH_2)_3OH$] was studied by differential scanning calorimetry and reflectance spectroscopy. Several novel features were observed. 1BU always crystallizes into a mixture of two phases, blue ($\lambda_{max}=585$ nm) and red ($\lambda_{max}=515$ nm). 1EU and 1BU cocrystallize to form solid solutions as evidenced by singlet endotherms or by different reflectance spectra. λ_{max} , the lowest energy optical transitions of partially polymerized cocrystallized mixtures, increases as the concentration of 1EU increases to about 90%. Mixtures of 2A and 3A form amorphous solid solutions. The amorphous solid solutions crystallize in the solid state before melting. DSC shows an exotherm followed by an endotherm during heating. Partially polymerized 3A changes from blue→red when touched by human hands. The color change is due to melting of unreacted monomer.

KEY WORDS Diacetylenes / Cocrystallization / Solid-State Copolymerization / Solid Solutions /

Monomers are typically gases or liquids. When monomers are solid, they are dissolved in suitable solvents for polymerization. Copolymerization of two or more monomers is usually carried out in a liquid medium containing the monomer mixture and a suitable catalyst system. The polymerization of monomers in the solid state requires that the reactive sites become adjacent to one another and that the bonding orbitals of the reacting atoms overlap. Copolymerization in the solid state is restricted to solid solutions only. In the absence of a solid solution, only homopolymers or block copolymers will result. The solid state copolymerization of both vinyl and heterocyclic monomers has been reported.¹ There are few reports of solid state copolymerization of diacetylenes.²⁻⁴

Diacetylenes, $R-C\equiv C-C\equiv C-R$, polymerize in the solid state upon thermal annealing or through exposure to high energy radiation,^{5,6}

Typically, the monomers are colorless. Partially polymerized diacetylenes are either blue, purple, or red; polydiacetylenes are metallic. Polydiacetylenes are highly colored because the π electron density is highly delocalized over the conjugated backbone. Since diacetylenes polymerize in the solid state one cannot use conventional polymerization catalysts. Polymerization of diacetylenes is initiated by radi-

cals,^{7,8} as for example, the diradical dimer, $\cdot\overset{\text{R}}{\text{C}}=\text{C}=\text{C}(\text{R})-\text{C}(\text{R})=\text{C}=\text{C}\cdot$. Radical initiators such as dicumylperoxide inhibit rather than initiate polymerization⁹ because first, they do not form a solid solution and second, the radicals do not become adjacent to the triple bonds. However, two isomorphous or chemically similar diacetylenes can

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cocrystallize to form a solid solution and the reactive sites can become adjacent.¹⁰ A solid solution can have a different melting point, reactivity, and color upon partial polymerization.

The polymerization of IPU ($R = -CH_2OCONH-$) by 1pCPU ($R = -CH_2OCONH-$ $-Cl$) is an excellent example of a diacetylene initiating polymerization of another.² If crystallized from acetone or tetrahydrofuran, IPU forms an inactive phase. This inactive phase does not polymerize upon thermal annealing or exposure to radiation. Thermal and radiation induced polymerization of IPU can be increased by several orders of magnitude² if it is cocrystallized with a few percent of 1pCPU.

If diacetylenes are truly cocrystallized, the mixture should have a single melting point. As IPU and 1pCPU decompose upon melting, it was not possible to determine the melting points of these cocrystallized diacetylenes. In this paper, we report the cocrystallization and copolymerization of two pairs of diacetylenes which do not decompose upon melting.

The two pairs are (1) 3,5-octadiyn-1,8-diol [$R = -(CH_2)_2OH$] and 4,6-decadiyn-1,10-diol [$R = -(CH_2)_3OH$], referred to hereafter as 2A and 3A respectively and (2) 2,4-hexadiyn-1,6-bis(*n*-butyl urethane), [$R = -CH_2OCONH(CH_2)_3CH_3$] and 2,4-hexadiyn-1,6-bis (ethyl urethane), [$R = -CH_2OCONHC_2H_5$], referred to hereafter as 1BU and 1EU respectively. Another reason for selecting the above pairs for the present study was that 2A and 3A are the precursors for urethane, carbonylate, sulfonate, carboxylic, and ether derivatives; and 1BU and 1EU are excellent sensitizers for acceleration of radiation induced crosslinking of polymers.¹¹ As diacetylenes often crystallize in more than one phase having different melting points, differential scanning calorimeter (DSC) data and visible spectra can be quite complicated.

EXPERIMENTAL

Synthesis

The Hays¹² and Glaser¹³ methods of oxidative coupling were used to synthesize 3,5-octadiyn-1,8-diol (2A) and 4,6-decadiyn-1,10-diol (3A). Both 2A and 3A were recrystallized from diethyl ether at $-20^\circ C$ and their structures were confirmed by IR and elemental analysis. 1BU and 1EU were prepared by reacting 2,4-hexadiyn-1,6-diol with *n*-butyl

isocyanate and ethyl isocyanate respectively, according to a procedure described elsewhere.¹¹

Cocrystallization

Fifty ml of 2% solutions containing different weight ratios of 2A and 3A were prepared in diethyl ether. Similarly, fifty ml of 2% solutions containing different weight ratios of 1BU and 1EU were prepared in acetone for reflectance spectroscopic studies; pieces of filter paper ($5 \times 7 \text{ cm}^2$) were dipped in each solution and these papers allowed to dry in air at room temperature (RT). For differential scanning calorimetry and for bulk polymerization the remainder of each solution was dried by rotary evaporator followed by vacuum drying. The four diacetylenes were polymerized by ^{60}Co γ -rays at RT. The diacetylenes coated on filter papers were polymerized thermally at RT.

Instrumental

Reflectance spectra of the thermally polymerized diacetylenes were recorded on a Perkin-Elmer UV-Visible Spectrophotometer Model 200 with a reflectance sphere described elsewhere.¹⁴ A DuPont 990 Differential Scanning Colorimeter (DSC) was used to determine melting points. About 5 mg of each sample crimped in an aluminum holder was heated at $10^\circ C \text{ min}^{-1}$ under an argon atmosphere.

RESULTS AND DISCUSSION

Differential Scanning Calorimetry

Figure 1 shows DSC scans for 1EU, 1BU, and their cocrystallized mixtures during initial heating, cooling, and reheating. A small endotherm for 1BU at $70^\circ C$ does not reappear upon reheating. This small endotherm is most probably due to the melting of a small fraction of an inactive phase. Except for this small endotherm, all the endotherms of 1BU, 1EU, and their cocrystallized mixtures obtained during initial heating and reheating were almost identical. The results indicate that, whether crystallized from acetone or from melt, both the diacetylenes and their mixtures crystallize into the same phases. Cocrystallized mixtures containing 20 and 80% 1EU have doublet endotherms. It can be assumed that 1EU and 1BU have homocrystallized, a phase separation. If the diacetylenes are indeed homocrystallized, there should be corresponding exotherms during crystallization. The crystalli-

Figure 1. DSC thermograms of 1EU, 1BU, and their cocrystallized mixtures during initial heating, cooling, and reheating.

zation temperatures of 1BU and 1EU were 61 and 67°C respectively. The crystallization exotherms for the mixtures are singlets at lower temperatures, *ca.* 47° and 56°C. The melting doublet endotherms of the cocrystallized mixtures do not correspond to the melting points of the pure diacetylenes. Since we found no evidence for phase separation, it is likely that both diacetylenes cocrystallized into two different solid solutions. Spectroscopic evidence supporting this conclusion is presented in *Spectroscopy* section.

Melting and crystallization temperatures for both the diacetylenes and their mixtures are plotted in Figure 2. The melting points of all the mixtures were

intermediate between those of the pure components while the crystallization temperatures showed a minimum at about 40% of 1EU.

DSC thermograms for 2A, 3A, and their cocrystallized mixtures during initial heating, cooling, and reheating are shown in Figure 3. The melting points of these diols are close. During crystallization, they display more than one exotherm, but upon reheating, they display one endotherm.

The cocrystallized mixtures exhibited novel behavior during heating and cooling. Though we made no quantitative measurements, the DSC thermograms of the mixtures showed that the heat of fusion and the heat of crystallization decreased as

Figure 2. Plots of melting and crystallization temperatures of 1EU, 1BU and their cocrystallized mixtures ($\square$, $\blacksquare$, and $\blacksquare$), and melting points of 2A and 3A and their cocrystallized mixtures ($\circ$), versus their concentration (w/w). A line is not drawn for the low temperature endotherms of 1EU, 1BU and their mixtures ($\blacksquare$).

the concentration of 2A increased up to 60%. At that concentration the enthalpy of the solid liquid state transition is almost zero. The mixture solidifies and liquefies at about -40°C . During heating from a low temperature, about -100°C , the mixtures containing 40 and 80% of 2A first displayed an exotherm followed by an endotherm. The mixtures are liquid at room temperature. Both the mixtures showed no exotherm during cooling. That is, they solidified into completely amorphous, solid solutions. During reheating, the mixtures first crystallized as evidenced by the exotherm and then the crystallized material melted, showing an endotherm at a higher temperature.

The size of the exotherm and the corresponding endotherm of the mixtures depends upon the heating rate. A slower heating rate (*ca.* $2.5^{\circ}\text{C min}^{-1}$) shows exotherms and endotherms larger than those obtained by a faster (*ca.* $20^{\circ}\text{C min}^{-1}$) heating rate. The absence of exotherms and endotherms during heating and cooling the 60% mixture of 2A suggests that the mixture solidified without crystallization. We believe that the formation of strong hydrogen bonds between the $-\text{OH}$ groups of 2A and 3A in the liquid state prevents crystallization of the mixtures.

Spectroscopy

1BU, 1EU, and their cocrystallized mixtures polymerized to give colored polymers, either upon thermal annealing or exposure to high energy radiation. The partially polymerized diacetylenes were either blue, purple, or red while the polydiacetylenes and the copolydiacetylenes obtained by 50 Mrads of ^{60}Co γ -rays were metallic green or copper colored. Figure 4 shows the reflectance spectra of partially polymerized 1BU, 1EU, and their cocrystallized mixtures. 1EU partially polymerized to a pink color while 1BU partially polymerized to a purple color. The reflectance spectra of partially polymerized 1BU suggest that it crystallized into two moderately active phases. One phase partially polymerized to a red color while the other to a blue color. The spectrum of purple colored partially polymerized 1BU in Figure 4 is crudely resolved into its two components, red ($\lambda_{\text{max}}=515\text{nm}$) and blue ($\lambda_{\text{max}}=585\text{nm}$).

An examination of the crystals under an optical microscope showed blue and red colored microcrystals and a small fraction of colorless crystals (the inactive phase). The colorless crystals melted just

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Figure 3. DSC scans of 2A, 3A and their mixtures during initial heating, cooling, and reheating.

before the blue and the red crystals. The blue and red crystals melted at the same temperature, *ca.* 75°C. Attempts were made to grow large, isolated single crystals of the blue and the red phase from different solvents, but we always obtained mixtures of both phase.

When crystallized from melt, 1BU also crystallizes into the same two phases. However, the ratio of the blue to the red phase varies with experimental conditions. For example, predominantly red crystals are obtained from hexane or heptane, while most of the crystals are blue when crystallized from acetone, tetrahydrofuran, or from melt. Figure 5 shows the reflectance spectra of partially polymerized 1BU crystals grown from heptane and from the melt. As can be seen from Figures 4 and 5, the intensity of the peaks at 515 and 585 nm varies with the experimental conditions.

Both the blue and the red phases have different thermal and radiation reactivities. The red phase

had a higher radiation reactivity than the blue one. The blue phase had a higher thermal reactivity than the red one. For example, when crystals grown from acetone were exposed to UV light, they appeared red because the red phase polymerized faster than the blue one. However, if the same crystals are thermally annealed, they appear blue because the blue phase polymerizes faster than the red one.

A partially polymerized diacetylene is a solid solution of unreacted monomer and polymer chains. Polymer chains in the blue colored ($\lambda_{\text{max}} = 585 \text{ nm}$) crystals of 1BU are either held planar or compressed by the adjacent unreacted monomer.¹⁵ When unreacted monomer is removed by extraction with a solvent such as acetone, the strain is released and the backbone becomes either slightly nonplanar or relaxed. As a result, the residual polymer chains appear red ($\lambda_{\text{max}} = 540 \text{ nm}$), a blue shift, on the other hand, polymer chains in the red crystals ($\lambda_{\text{max}} = 515 \text{ nm}$) are either relatively nonplanar or stretched

Figure 4. Reflectance Spectra of partially polymerized 1EU, 1BU, and their cocrystallized mixtures. R is the reflectivity and $-\log R$ is almost equivalent to the absorbance. The value of $-\log R$ at 700 nm was zero for all spectra. The spectrum of 1BU is crudely resolved into its two components, red and blue (see the text). The spectrum of 1EU is magnified ten times. Color and composition of diacetylenes is indicated on each spectrum. B represents 1BU and E represents 1EU. For example, B60, E40, represents a mixture containing 60% (by weight) 1BU and the rest 1EU. All compositions were polymerized at RT for two weeks before recording the spectra.

in order to maintain a solid solution.¹⁵ Upon extraction of the unreacted monomer, the backbone becomes either slightly planar or relaxes, resulting in a red shift. The residual polymer chains appear more red ($\lambda_{\max}=540$ nm). After extraction of the untreated monomer, the conformation of the polymer chains of blue and red crystals is identical (see broken spectra in Figure 5). The blue and the red

shifts of partially polymerized 1BU are very similar to those reported for 1mTU¹⁴ and are explained in ref 15.

The *n*-butyl urethane of 2,4-hexadiyn-1,6-diol is a novel example of a compound which crystallizes simultaneously into two different phases each having the same melting point. Each phase polymerizes to a different color. Each phase has different ther-

Figure 5. Reflectance spectra of partially polymerized 1BU crystallized from melt and heptane. The spectra after extraction of unreacted monomer with acetone are shown by broken lines.

mal and radiation reactivities. Diacetylenes are known to crystallize into more than one phase, and these phases are known to have different thermal and radiation reactivities.⁶ These different phases, however, are usually grown from different solvent systems. For example, 1*m*TU ($R = -CH_2OCONH-$

) crystallizes to a moderately reactive orange phase from acetone/hexane and to a highly reactive blue phase from *p*-dioxane/water. In contrast, 1BU crystallizes simultaneously to moderately reactive phases having different thermal and radiation reactivities. These phases can be differentiated by spectroscopy and by optical microscopy. Previously we mistook 1BU crystallized from hexane for an isolated red phase and that crystallized from acetone for an isolated blue phase.¹¹ X-ray diffraction studies are required to determine the molecular packing in the blue and the red phases of 1BU.

Since 1BU crystallizes into two moderately active phases, the reflectance spectra of partially polymerized cocrystallized mixtures (Figure 4) are complicated. Cocrystallized mixtures can contain more than one solid solution or homocrystallized phases. The melting endotherm of a cocrystallized mixture containing 80% 1BU is a doublet (Figure 1) indicating at least two solid solutions. The corresponding

reflectance spectrum (Figure 4) suggests that the mixture does have at least two, possibly three reactive phases. It is difficult to resolve the reflectance spectra of more than two reactive phases. The mixture containing 20% 1BU also has a doublet endotherm, but the corresponding reflectance spectrum shows that only one phase polymerizes to a blue color while the other is inactive. Another possibility, though less likely, is that both phases polymerize to the same blue color. The endotherm for the mixture containing 40% 1BU is a singlet, and the corresponding reflectance spectrum also shows a single phase. The reflectance spectrum of a mixture containing 60% 1BU indicates two reactive phases while the corresponding endotherm is a singlet.

Clearly, it is difficult to develop a relationship between the melting endotherms and the corresponding reflectance spectra of partially polymerized mixtures. However, it is interesting to note that cocrystallized diacetylenes do form solid solution. This is reflected by a continuous red shift in the reflectance spectra as the concentration of 1EU is increased to about 90%. Figure 6 shows a plot of $\lambda_{\max}$ for the lowest energy optical transition versus concentration of 1EU. The results suggest that the backbone of the copolymer becomes more planar as

Figure 6. Plot of $\lambda_{\max}$ (lowest energy optical transition) of partially polymerized compositions versus concentration of 1EU (weight-percent).

Figure 7. Reflectance spectra of partially polymerized 2A and 3A before (solid) and after (broken) extraction of unreacted monomer. 2A is about ten times more thermally reactive than 3A. 2A and 3A were allowed to polymerize at RT for 2 and 7 days respectively before the spectra were recorded.

the concentration of 1EU increases. 1EU partially polymerizes to a red color ($\lambda_{\max}=570$ nm). Cocrystallization of 1EU with about 10% 1BU not

only increases the rate of polymerization but also increases the planarity of the resultant backbone.

Figure 7 shows the reflectance spectra of partially

polymerized 2A and 3A before and after extraction of unreacted monomer. It was difficult to record the reflectance spectra of the partially polymerized cocrystallized mixtures of these diols because their melting points are below room temperature. The cocrystallized mixtures were polymerized by UV light at low temperatures. The mixture containing 80% 3A polymerizes to a blue color if irradiated at about -20°C , while the other mixtures do not. These amorphous mixtures polymerize only if they are allowed to crystallize in the solid state before UV irradiation. The mixture containing 60% 3A must be annealed at about 0°C for a few minutes in order to crystallize before it can be polymerized to a violet color. Likewise, the mixture containing 20% 3A requires annealing at about 20°C before it can be polymerized by UV light to a red color. If these mixtures are irradiated above their melting points, they do not polymerize. These partially polymerized mixtures turn red upon annealing at room temperature due to the melting (extraction) of unreacted monomers.

A mixtures containing 40% 3A does not polymerize at all even if it is annealed just below the visual melting point indicating that it remains glassy at all times.

Blue colored partially polymerized 3A turns red if touched by human hands. This color change is due to the melting of unreacted monomer at about body temperature (37°C); thus, partially polymerized 3A makes an ideal show-and-tell item for demonstrating the color change in partially polymerized diacetylenes upon extraction of unreacted monomer.

Attempts were made to grow large crystals of the diacetylenes and their cocrystallized mixtures for X-ray diffraction study. However, we were unsuccessful in growing single crystals large enough for such a study. The active phases of diacetylenes and their cocrystallized mixtures polymerize rapid-

ly upon exposure to X-rays. As a result we could not confirm the different phases of the cocrystallized mixtures.

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