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Synthesis and Polymerization of Diacetylenes Having Chromophoric Substituent Groups

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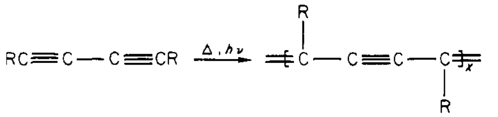
ABSTRACT: Synthesis and solid-state polymerization of diacetylenes, $RC{\equiv}C{-}C{\equiv}CR$, having chromophoric substituent groups are reported. The substituent groups are $(CH_2)_nOCONHC_6H_4N{=}NC_6H_5$ and $(CH_2)_nOSO_2C_6H_4N{=}NC_6H_5$, where $n = 1$–4. The diacetylenes are either light pink or yellow. The partially polymerized diacetylenes at about 2% polymer conversion appear gray, orange, or green, while at about 10% polymer conversion the color of the backbone dominates and they appear blue or red. **1AS**, where R = $CH_2OSO_2C_6H_4N{=}NC_6H_5$ polymerizes quantitatively either upon thermal annealing or upon exposure to γ radiation. The heat of polymerization, ΔH_p, and the activation energy of polymerization, ΔE_p, were determined by differential scanning calorimetry. The ΔH_p and the ΔE_p for **1AS** are 138 ± 6 and 94 ± 6 kJ/mol, respectively. The properties of **1AS** are compared with those of a well-characterized diacetylene, **1pTS**, where R = $CH_2OSO_2C_6H_4CH_3$.

Introduction

The principle of addition of colors is well-known.[1] One can obtain a number of different color shades, for example, yellow/yellowish green/green/blue, upon gradual addition of a blue solution into a yellow solution. For some applications[2] of diacetylenes, $RC{\equiv}C{-}C{\equiv}CR$, we needed more than one color transition. We have introduced such color transitions by synthesizing diacetylenes with chromophoric substituent groups.

Diacetylenes polymerize in the solid state either upon thermal annealing or upon exposure to high-energy radiation:[3-5]



$$RC{\equiv}C{-}C{\equiv}CR \xrightarrow{\Delta,\,h\nu} {=}\!\!\!\!\!\left[\overset{\overset{\large R}{|}}{C}{-}C{\equiv}C{-}\underset{\underset{\large R}{|}}{C}\right]_x\!\!\!\!{=}$$

The resultant polymers have fully conjugated backbones. Poly(diacetylenes) are highly colored because the π electrons are delocalized over long distances. Typically, the monomers are colorless solids while the partially polymerized diacetylenes are either blue or red. As the polymerization proceeds, the blue or red color intensifies. At high polymer yields (~10%), the intense blue or red color starts appearing metallic gold or metallic green in reflectance.

Synthesis and polymerization of a large number of diacetylenes with different functional substituent groups have been reported in the literature.[2-7] Unusual multiple-color transitions can arise upon the polymerization of diacetylenes having colored substituent groups. As diacetylenes polymerize to blue or red polymers, two primary colors, the best color to choose for the substituent group is yellow, the third primary color. Accordingly, we synthesized diacetylenes with yellow and light pink colored substituent groups, viz., $(CH_2)_nOCONHC_6H_4N{=}NC_6H_5$ and $(CH_2)_nOSO_2C_6H_4N{=}NC_6H_5$, where $n = 1$–4. In this paper, we report the synthesis and polymerization of these diacetylenes. Of the eight diacetylenes we synthesized, only **1AS** (R = $CH_2OSO_2C_6H_4N{=}NC_6H_5$) polymerizes quantitatively. The heat of polymerization and the activation energy of polymerization of **1AS** are determined by differential scanning calorimetry (DSC) and the properties are compared with those of a well-characterized diacetylene, **1pTS** (R = $CH_2OSO_2C_6H_4CH_3$).

Table I
Color of the Partially Polymerized Sulfonate-Substituted Diacetylenes, $RC{\equiv}C{-}C{\equiv}CR$, Where R Is $(CH_2)_nOSO_2C_6H_4N{=}NC_6H_5$

diacetylene	*n*	color of monomer	color of partially polymerized diacetylene 2% yield	5-10% yield
1AS	1	light pink	gray	blue
2AS	2	light pink	orange	red
3AS	3	light pink	orange	red
4AS	4	light pink	orange	red

Experimental Section

Synthesis. Monoacetylene monools, $HO(CH_2)_nC{\equiv}CH$, n = 1–4, were obtained from Farchan Research Laboratory. The corresponding diacetylene diols, $HO(CH_2)_nC{\equiv}CC{\equiv}C(CH_2)_nOH$, were prepared by Hay's method of oxidative coupling.[8]

A. Synthesis of 2,4-Hexadiynediyl 1,6-Bis(*p*-phenylazobenzenesulfonate) (1AS). To a three-necked 2-L round bottom flask fitted with an addition funnel and a stirrer were added 2.2 g (0.02 mol) of 2,4-hexadiyne-1,6-diol and 1 g (0.05 mol) of *p*-phenylazophenylsulfonyl chloride. Tetrahydrofuran (THF) (150 mL) was added to dissolve the mixture. The temperature of the solution was decreased to about 5 °C and 50 mL of cold (~5 °C) KOH solution (11.2 g in 150 mL) was added dropwise over 0.5 h. The reaction was allowed to proceed for 1 h, keeping the temperature at ~5 °C. The product was precipitated by adding cold water. The product was washed with cold water and methanol. The yield was almost quantitative. Anal. Calcd for $C_{30}H_{22}N_4O_6S_2$: C, 60.20; H, 3.68; N, 9.36; O, 16.05; S, 10.70. Found: C, 59.67; H, 3.8; N, 9.14; O, 14.63; S, 10.9.

The procedure described above was also used to prepare 3,5-octadiynediyl 1,8-bis(*p*-phenylazobenzenesulfonate), 4,6-decadiynediyl 1,10-bis(*p*-phenylazobenzenesulfonate), and 5,7-dodecadiynediyl 1,12-bis(*p*-phenylazobenzenesulfonate), hereafter referred to as **2AS**, **3AS**, and **4AS**, respectively (see Table I).

2AS: Anal. Calcd for $C_{32}H_{26}N_4O_6S_2$: C, 61.34; H, 4.15; N, 8.94; O, 15.33; S, 10.22. Found: C, 60.81; H, 4.18; N, 8.08; O, 15.40; S, 10.13.

3AS: Anal. Calcd for $C_{34}H_{30}N_4O_6S_2$: C, 62.38; H, 4.59; N, 8.56; O, 14.68; S, 9.78. Found: C, 61.48; H, 4.82; N, 8.41; O, 15.05; S, 0.02.

4AS: Anal. Calcd for $C_{36}H_{34}N_4O_6S_2$: C, 63.34; H, 4.98; N, 8.21; O, 14.07; S, 9.38. Found: C, 62.44; H, 5.22; N, 8.40; O, 13.92; S, 9.55.

The presence of the aryl-SO_2O functionality in the disulfonate-substituted diacetylenes was confirmed by IR analysis: asymmetric stretching at 1360 and 1375 cm^{-1}, symmetric stretching

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Table II
Color of the Partially Polymerized Urethane-Substituted Diacetylenes, $RC{\equiv}C{-}C{\equiv}CR$, Where R Is $(CH_2)_nOCONHC_6H_4N{=}NC_6H_5$

diacetylene	*n*	color of monomer	color of partially polymerized diacetylene 2% yield	color of partially polymerized diacetylene 5-10% yield
1AU	1	yellow	*a*	
2AU	2	yellow	orange	red
3AU	3	yellow	green	blue
4AU	4	yellow	*a*	

[a] 1AU and 4AU are almost inactive; they do not polymerize either upon thermal annealing or upon irradiation with γ rays.

at 1190 and 1170 cm^{-1}, and S–O–C stretching at 990 and 955 cm^{-1}.

B. Synthesis of 2,4-Hexadiyne-1,6-bis(*p*-phenylazophenylurethane) (1AU). To a 2-L round-bottom flask fitted with a thermometer, a stirrer, and an addition funnel were added 5.5 g (0.05 mol) of 2,4-hexadiyne-1,6-diol ($HOCH_2C{\equiv}CC{\equiv}CCH_2OH$), 300 mL of tetrahydrofuran (THF), 0.1 g of di-*tert*-butyltin di-2-hexanoate, and 2 mL of triethylamine (the catalysts). The resulting solution was stirred and 33.5 g (0.15 mol) of *p*-phenylazophenyl isocyanate ($C_6H_5N{=}NC_6H_4NCO$) dissolved in 200 mL of THF was added dropwise over 0.5 h. The reaction temperature was maintained at about 25 °C by a cold water bath. After 2 h, 1 L of hexane was added. The resulting precipitate was collected by filtration and dried under vacuum. The yield was quantitative. Anal. Calcd for $C_{32}H_{24}N_6O_4$: C, 69.06; H, 4.32; N, 15.1; O, 11.5. Found: C, 69.06; H, 4.50; N, 14.92; O, 11.36.

The procedure described above was used to synthesize 3,5-octadiyne-1,8-bis(*p*-phenylazophenylurethane), 4,6-decadiyne-1,10-bis(*p*-phenylazophenylurethane), and 5,7-dodecadiyne-1,12-bis(*p*-phenylazophenylurethane), hereafter referred to as **2AU**, **3AU**, and **4AU**, respectively (see Table II). All diacetylenes were purified by recrystallization from a suitable solvent system.

2AU: Anal. Calcd for $C_{34}H_{28}N_6O_4$: C, 69.86; H, 4.79; N, 14.38; O, 10.96. Found: C, 69.80; H, 5.12; N, 14.88; O, 11.92.

3AU: Anal. Calcd for $C_{36}H_{32}N_6O_4$: C, 70.59; H, 5.23; N, 13.72; O, 10.48. Found: C, 71.02; H, 5.45; N, 12.18; O, 11.02.

4AU: Anal. Calcd for $C_{38}H_{36}N_6O_4$: C, 71.25; H, 5.62; N, 13.12; O, 10.00. Found: C, 70.11; H, 5.89; N, 13.96; O, 10.04.

The presence of the urethane functionality (OCONH) was confirmed by IR analysis. Urethane bands were present in all diurethane-substituted diacetylenes: N–H stretching at 3330 cm^{-1}, amide I (COO) stretching at 1710 cm^{-1}, and amide II mixed vibrations of N–H in-plane blending and C–N stretching at 1545 cm^{-1}.

Polymerization. **1AS** was annealed at 80.5 °C for different periods of time. **1AS** was also polymerized with ^{60}Co γ rays at various dosages in air. Polymer conversions were determined gravimetrically by extracting the unreacted monomer with acetone.

Differential Scanning Calorimetry. A Perkin-Elmer DSC-2 instrument was used. The procedures used for determination of heat of polymerization have been described elsewhere.[9] Isothermal polymerization was carried out on ~10 mg of **1AS** at 110, 120, 125, 130, 135, and 140 °C. Heating rates of 2.5, 5, 10, and 20 °C/min were used for the programmed DSC.

Spectroscopy. The eight diacetylenes described in Tables I and II were coated on pieces of filter paper (2.5 × 7 cm^2) by diping them into about 1% solution followed by drying in air. Polymerization of the coated diacetylenes was carried out either upon thermal annealing or upon exposure to UV light.

The reflectance spectra of the diacetylenes before and after polymerization were recorded by a Perkin-Elmer UV-visible spectrophotometer Model 200, which is described elsewhere.[10]

Results and Discussion

Phenylazophenyl isocyanate is yellow and phenylazophenylsulfonyl chloride is light pink. As a result, the corresponding diacetylene diurethanes are yellow (see Table II) and the diacetylene disulfonates are light pink (see Table I). However, the monomers undergo color transitions as they polymerize. Diacetylenes, irrespective of the substituent group, polymerize to red or blue materials. As the polymer yield increases, the blue or red color intensifies. With the present chromophoric substituted groups, polymerization leads to a number of color hues because of a continuous increase in the intensity of the red or blue color. The partially polymerized diacetylenes at about 1–2% polymer yield acquire intermediate color hues, for example, yellow + blue = green, yellow + red = orange, or light pink + blue = gray. Between ~5 and 10% polymer yield, the red or blue color of the backbone dominates over the color of the substituent groups and the partially polymerized diacetylenes appear either dark red or blue. Above 10% polymer yield, they appear metallic (copper or gold) in reflectance.

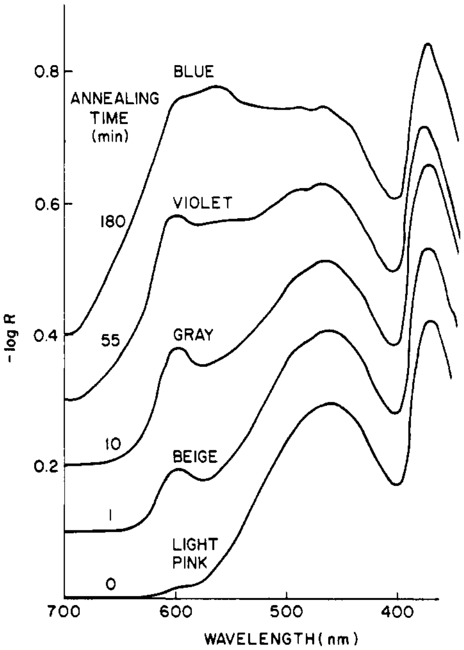

Figure 1. Reflectance spectra of **1AS** at various stages of polymerization at 90 °C. The annealing time and color of the partially polymerized diacetylene are indicated on each spectrum. The slight absorption at 600 nm for the unannealed sample is due to a slight polymerization during drying of the sample at room temperature. −log *R* is almost equivalent to absorbance. −log *R* at 700 nm was zero for each spectrum. The spectrum for the monomer was recorded in less than 1 min after coating on the paper.

Figure 1 displays reflectance spectra of **1AS** at different stages of polymerization at 90 (±2) °C. As can be seen from the figure, the intensity of the peaks at 460 and 370 nm remains unchanged during the polymerization, while a new peak appears at 595 nm and its intensity increases with increasing annealing time. Color hues at the different stages of polymerization are indicated on each spectrum. Figures 2 and 3 show reflectance spectra of monomeric and partially polymerized **3AU** and **3AS**, respectively. Partially polymerized **3AU** appears green because of addition of the blue color of the backbone to the yellow color of the substituent group, while partially polymerized **3AS** appears orange because the backbone has a red color while the substituent group has a yellow color. Colors of the other partially polymerized diacetylenes are listed in Tables I and II. Of the eight diacetylenes we synthesized, only **1AS** polymerizes quantitatively either upon thermal annealing or upon exposure to high-energy radiation. Hence, the rest of the discussion is focused on polymerization of **1AS**.

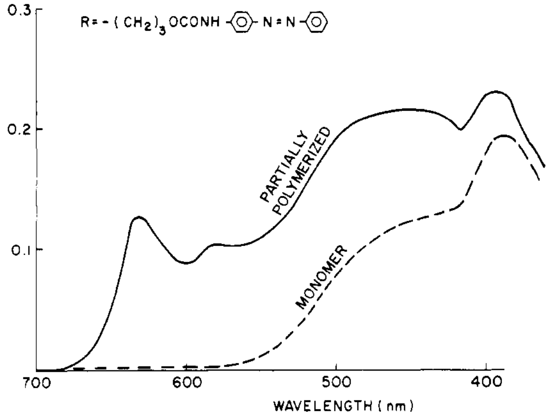

Figure 2. Reflectance spectra of **3AU**: (---) monomer; (—) partially polymerized by UV light. The spectra of the thermally polymerized **3AU** are identical with those polymerized by UV light. The spectrum of the partially polymerized **3AU** is expanded slightly for clarity.

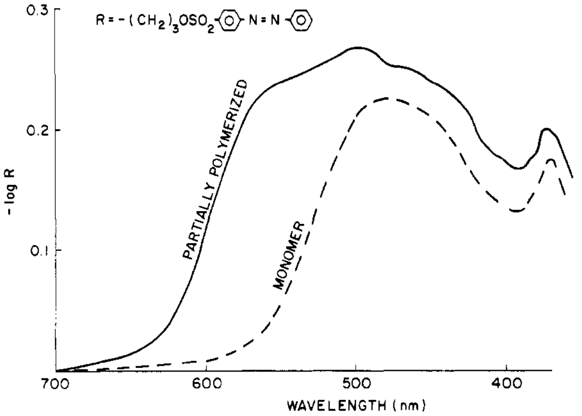

Figure 3. Reflectance spectra of **3AS**: (---) monomer; (—) partially polymerized by UV light. The spectra of the thermally polymerized **3AS** are identical with those polymerized by UV light. The spectrum of the partially polymerized **3AS** is expanded slightly for clarity.

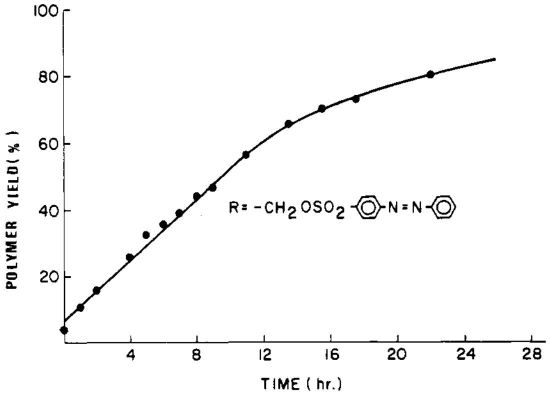

Figure 4. Plot of polymer conversion vs. annealing time (hours at 80.6 °C) for **1AS**. The polymer conversion in this figure and that in Figure 5 are not zero for the untreated sample because of rapid polymerization during crystallization and drying of the monomer (see text).

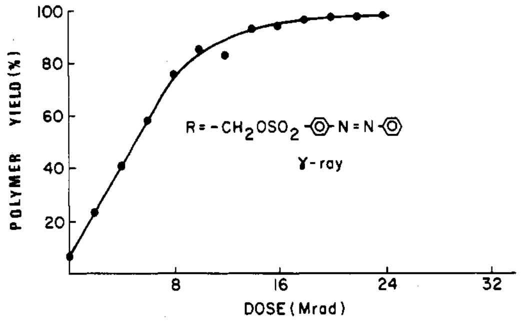

Figure 5. Plot of polymer conversion vs. γ-ray dose for **1AS**. The dose rate was 1 Mrd/h.

Table III
Comparison of Properties of 1AS with 1pTS

property	1AS	1pTS[a]
polymerization	fast initial reaction followed by a slow asymptotic polymerization	slow initial reaction followed by very fast autocatalytic polymerization (2, 12-15)
λ_{max},[b] nm	600	570 (12, 16)
$G(-m)_{initial}$	140	40 (11)
ΔE_p, kJ/mol	94 ± 6	94 ± 3 (9, 13-16)
ΔH_p, kJ/mol	138 ± 6	152 ± 4 (9, 14, 15)

[a] The numbers in the parentheses indicate the references. [b] At low polymer yield (<10%) only. 1pTS at high conversions has λ_{max} 615 nm.

Table IV
Time Required To Reach the Maximum Rate of Polymerization of 1AS[a]

temp, °C	t_{max}, min	temp, °C	t_{max}, min
110	32	130	6.2
120	13	135	4.4
125	9	140	3.2

[a] As assessed from the peak position in DSC.

Polymerization of **1AS** is so rapid upon thermal annealing that it was difficult to determine the melting point of the monomer. It polymerizes almost quantitatively if the heating rate is less than 20 °C/min. Figure 4 shows a plot of polymer yield vs. annealing time at 80.6 (±0.2) °C. Polymerization of **1AS** is nearly linear up to about 60% conversion followed by a slower asymptotic polymerization. Polymer yield is not zero for zero annealing time because the monomer undergoes about 6% polymerization during crystallization from the solvent and subsequent drying under vacuum at room temperature for 1 day.

1AS also polymerizes upon exposure to high-energy radiation, such as UV and γ radiation. Figure 5 presents a plot of polymer yield vs. γ-ray dose. The dode rate was 1 Mrd/h. Again the yield is not zero for the unirradiated sample because of thermal polymerization during crystallization and drying. The γ-ray polymerization behavior is similar to that occurring upon thermal annealing and is discussed further in the following section on thermal analysis. The initial rate of polymerization, as calculated from the initial slope of the plot in Figure 5, is 8.7%/Mrd. $G(-m)$, the number of monomers polymerized per 100 eV, is 140. $G(-m)$ for **1AS** was calculated from[11]

$$G(-m) = \frac{(6.02 \times 10^{23}) \times \%\ \text{yield}}{M_w \times 6.25 \times 10^{19} \times D}$$

where M_w is the molecular weight of the monomer and D is the dose in Mrd. $G(-m)$ of **1AS** is compared with that of **1pTS** in Table III. The higher $G(-m)$ for **1AS** shows that this compound initially polymerizes faster than **1pTS**. The $G(-m)$ values in Table III respresent initial values only.

Typical isothermal and programmed DSC scans for **1AS** are shown in Figure 6. The polymerization process is exothermic as expected. The heat of polymerization, ΔH_p,

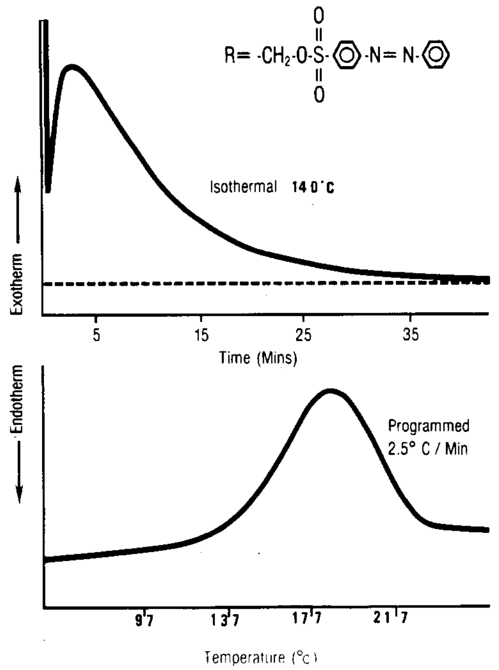

Figure 6. Programmed (2.5 °C/min) and isothermal (140 °C) polymerization of **1AS** by DSC.

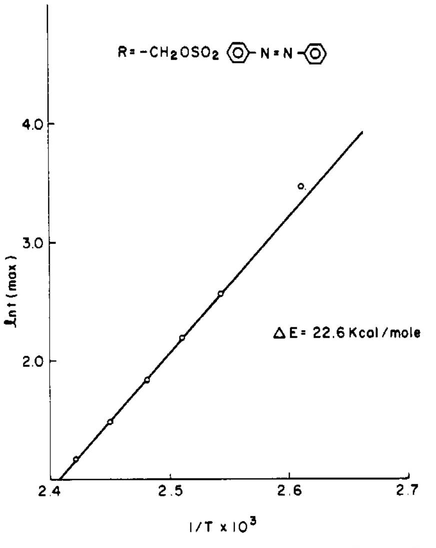

Figure 7. Arrhenius plot for the temperature dependence of t_{max} (time to the maximum polymerization rate) from Table IV.

was determined from the integral of (area under) these curves. The times required to achieve the maximum rate of polymerization, t_{max}, for **1AS** at different temperatures are given in Table IV. When corrected for the initial 6% polymerization during drying, ΔH_p for **1AS** is 138 ± 4 kJ/mol of monomer. The activation energy of polymerization, ΔE_p, for **1AS** was determined from the slope of the ln t_{max} vs. $1/T$ plot as shown in Figure 7. The activation energy of polymerization for **1AS** is 94 ± 3 kJ/mol of monomer. ΔH_p and ΔE_p for **1AS** are compared with **1pTS** in Table III.

As described earlier by Patel et al.,[9] isothermal DSC scans provide a fast and accurate method for determining polymer yield as a function of annealing time. Polymer yield at time t can be determined by taking a ratio of the area under the curve up to time t to that under the whole curve. Accordingly, we constructed a plot of polymer yield vs. t/t_{50}, where t_{50} is the time required for 50% polymerization from the 120 °C isothermal curve. The plot is shown in Figure 8. Also plotted in the figure are the gravimetric data on thermal and γ-ray polymerization from Figures 4 and 5. The agreement between the thermal (gravimetric and DSC) and the radiation polymerization is excellent.

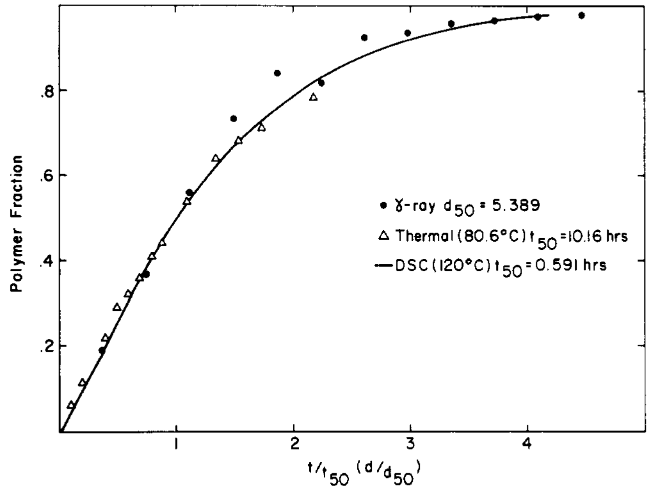

Figure 8. Polymer fraction vs. time obtained from the 120 °C DSC curve (solid line). The t_{50} normalization constant is the time required to reach 50% polymer. Polymer fraction vs. t/t_{50} obtained from the other isothermal DSC scans (110, 125, 130, and 140 °C) follow the same curve. Also plotted are the normalized data obtained by the gravimetric analysis from the isothermal polymerization at 80.6 °C (Figure 4) and γ-ray polymerization (Figure 5).

Table III compares the properties of **1pTS** and **1AS**. Both can be presented by a general formula, $YC_6H_4SO_2OCH_2C{\equiv}CC{\equiv}CCH_2OSO_2C_6H_4Y$. Y is CH_3 for **1pTS** and N = NC_6H_5 for **1AS**. Very few diacetylenes polymerize quantitatively upon thermal annealing; most require high dosages of high-energy radiation, such as γ rays. **1pTS** and **1AS** both polymerize quantitatively upon thermal annealing. **1pTS** displays an induction period of polymerization followed by a rapid autocatalytic polymerization, while **1AS** polymerizes almost linearly up to about 60% polymer conversion followed by a slow asymptotic polymerization. The sharpness between the induction period and the autocatalytic polymerization of **1pTS** decreases upon radiation polymerization (see Figure 5 of ref 12); however, the polymerization behavior of **1AS** upon thermal and γ-ray polymerization is identical (see Figure 8 of this paper). The initial rate of polymerization of **1AS** is higher than that of **1pTS** for both thermal and γ-ray polymerization. $G(-m)$ for both of the diacetylenes are given in Table III. **1pTS** partially polymerizes to a red-colored (λ_{max} 570 nm) polymer while **1AS** partially polymerizes to a blue-colored (λ_{max} 600 nm) polymer. The intermediate colors of partially polymerized **1AS** are due to the light pink-colored substituent groups. λ_{max} 600 nm suggests that the backbone of poly-**1AS** is either more planar or less strained than that of poly-**1pTS**. Very few diacetylene disulfonates polymerize to a blue color because there are no intramolecular hydrogen bonds between the adjacent side groups to stabilize the planarity of the backbone as is the case with a number of diacetylene diurethanes, especially those having three or four methylene groups adjacent to the backbone.

On the basis of the activation energy of polymerization and the heat of polymerization of **1pTS**, we have proposed a biradical dimer as the chain initiation species.[9] The radical species have recently been observed by Hori and Kispert by ESR.[17] As the activation energy and the heat of polymerization of **1As** are identical with the corresponding values for **1pTS**, we again propose a biradical dimer species as the chain initiator for **1AS**. It is likely that the solid-state polymerization of all diacetylenes is initiated by a biradical dimer species.

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Preparation and Characterization of H-Shaped Polystyrenes†

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ABSTRACT: A series of regular H-shaped polystyrenes ranging in molecular weight from 1 × 10^5 to 1.7 × 10^6 has been prepared. Their dilute-solution properties have been determined. They lie between those of regular three- and four-arm star polymers. The unperturbed radius of gyration is smaller by a factor g = 0.70 (g_{th} = 0.712) than that of the linear homologue. For the lower molecular weight H-polystyrenes a small Θ_{A_2} depression is observed. The ratios of the intrinsic viscosities of the H-polystyrenes and the linear polymers, g', are 0.80 and 0.73 in cyclohexane at the Θ temperature and in toluene, respectively. Small but significant deviations from the universal calibration relation log $[\eta]M \propto f(V_e)$ are observed in the exclusion chromatograms of the H-polymers.

Introduction

In order to study the effect of long-chain branching on the properties of polymers well-characterized branched polymers have to be available. For this reason regular star polymers have been prepared and studied.[1,2] Comb polymers consisting of a backbone to which a large number of branches are attached have also been prepared. Although the backbone and the branches are narrow-distribution polymers, the resulting comb polymers are not completely homogeneous in architecture and molecular weight because the placement of the branches along the backbone is by a random process.[3] An attempt has been made to obtain "regular" combs with equidistantly placed branches but the resulting samples were a mixture of comb polymers with an average number of branches.[4] We report now on the synthesis of regular H-shaped polystyrenes with two trifunctional branch points. The five segments that can be distinguished in the H-polymers have approximately equal molecular weights.

Experimental Section

Synthesis. The synthesis of the H-shaped polymers was performed in three steps, using anionic polymerization techniques in evacuated, *n*-BuLi-washed and rinsed vessels. The arms of the H-shaped polymers were prepared in benzene at room temperature, using *sec*-BuLi as the initiator. After the polymerization the living polymer was reacted with CH_3SiCl_3 according to

$$2(\underset{a_1}{\sim\sim\sim \mathrm{StLi}}) + \mathrm{CH_3SiCl_3} \rightarrow \underset{a_2}{(\sim\sim\sim \mathrm{St})_2(\mathrm{CH_3})\mathrm{SiCl}} + 2\mathrm{LiCl} \qquad (1)$$

A small excess of PStLi produced some three-arm star material. The polymer that will constitute the central bridge in (b), H-shaped polymer was prepared separately in a 50/50 mixture of benzene and THF at 0 °C with sodium naphthalenide as the initiator.[5] The molecular weight of this two-ended living polymer, NaSt∼∼∼StNa (b), was matched as closely as possible to that of one arm (a_1).

In the third step the bridge material (polymer b) was slowly added to the arm material (polymer a_2), allowing for complete reaction between successive additions, according to

$$2[\underset{a_2}{(\sim\sim\sim \mathrm{St})_2(\mathrm{CH_3})\mathrm{SiCl}}] + \mathrm{NaSt}\sim\underset{b}{\sim}\sim\mathrm{StNa} \rightarrow (\sim\sim\sim \mathrm{St})_2(\mathrm{CH_3})\mathrm{Si}(\mathrm{St}\sim\sim\sim\mathrm{St})\mathrm{Si}(\mathrm{CH_3})(\mathrm{St}\sim\sim\sim)_2 \qquad (2)$$

The second and third steps were executed consecutively and took about 3–4 h.

Presamples were removed from the reactor at various intermediate stages and terminated with $(CH_3)_2CHOH$. This allowed for the independent determination of the molecular weights of the arms (M_a), of the double arm (M_{a_2}), and of the bridge (M_b). It allowed also the monitoring of the course of reactions 1 and 2. The final product was submitted to repeated fractional precipitation. The H-polymer was recovered in the first fraction.

Analysis and Characterization. Polymers and presamples were routinely analyzed by size exclusion chromatography (GPC, Waters 301, equipped with five 4-ft columns of 10^6, 3 × 10^5, 10^5, 10^4, and 10^3 Å). Three-milligram samples were injected in 2 mL of solvent. The flow rate was 1.1 mL/min and the temperature 35 °C. Elution volumes (V_e) were reproducible to within 0.05 count. Either a linear polystyrene standard calibration technique was used to determine the molecular weight and distribution or the GPC was coupled with a low-angle laser light scattering instrument (LALLS, Chromatix KMX-6). THF was the eluting solvent. The dn/dc of polystyrene in THF was found to be 0.190_3 for 633-nm light at 25 °C. The composition of the crude reaction

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