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Thermoreversible Gelation of Regioregular Poly(3-hexylthiophene) in Xylene

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ABSTRACT: Regioregular poly(3-hexylthiophene) (P3HT) produces thermoreversible gel in xylene. The gel is brownish-red in color. SEM and TEM studies indicate the presence of fibrillar network. WAXS and electron diffraction pattern indicate the presence of P3HT crystallites in the gel. The gels exhibit a first-order phase transition when heated in DSC. A time-dependent UV−vis study indicates that gelation in this system is probably accompanied by two different processes, e.g., (1) coil-to-rod transformation and (2) aggregation of rods to form the crystallites producing the gel. The gelation rate (t_{gel}^{-1}) measured from the test tube tilting method is analyzed using the equation $t_{gel}^{-1} = f(C)\,f(T)$, where $f(c) = \phi^n$, ϕ being the reduced overlapping concentration and n is an exponent. The average "n" value determined is 0.52, which indicates that three-dimensional percolation is a suitable model for this gelation. The gelation rate is analyzed according to the Flory−Weaver theory of coil-to-helix transition, and the free energy of activation (ΔF) for the coil-to-rod transformation is found to be 23.7 kcal/mol. It is also analyzed using the theory of fibrillar crystallization in solution, and the free energy of formation of critical size crystalline nucleus (ΔG^*_{dil}) is found to be 37.5 kcal/mol. The conductivity of the dried P3HT gel becomes enhanced by ~10 times that of the cast film in the undoped state, but in the doped state there is an ~50-fold increase.

Introduction

Poly(3-hexylthiophene) (P3HT) is an important conducting polymer because of its solubility, processability, and environmental stability.[1] It possesses excellent electrical conductivity, electroluminescent property, and nonlinear optical activity.[2] It can be prepared in various ways; however, each way produces the polymer of different regioregularity (70−98%).[3−5] Conductivity of the sample depends on the amount of regioregularity present in the sample, and the regioregular samples have conductivity 3 orders of magnitude higher than the regioirregular samples under identical conditions.[5,6] In the higher regioregular samples (>91%) preferential orientation of the ordered domain with the 100 axis is normal to the plane of the film while for samples with low regioregularity it is preferentially oriented in the plane of the film.[7]

The structure of the regioregular poly(3-alkylthiophene) in solution is also different from that of the regioirregular poly(3-alkylthiophene). In the thermochromism and solvatochromism of nonregioregular P3HT in chloroform a single chain conformational change from coil to rod occurs.[8] The regioregular samples have more planar or rodlike structure, and it appears that the regioregular placement helps to drive a self-assembly in the solution.[9]

The electrical conductivity of the regioirregular P3HT indicates a variation of 2 orders of magnitude depending on the film preparation procedure.[10] The spin-coated film has conductance of 10^{-7} S/cm whereas the solvent-cast film has a conductance of 10^{-9} S/cm. The lower value of conductivity in the cast film has been attributed for the lower field effect mobility of the cast film. Also, the spectroscopic investigation indicates that the extent of conjugation is homogeneous in spin-coated film whereas it is inhomogeneous in the cast film.[10] Apart from the above two methods of film preparation, it can be prepared from the gel form by drying off the solvent without disturbing the network structure. Yet there is no report of conductivity of P3HT prepared from the gel form. In this report we want to determine whether there is any variation of conductivity of the dried gel than that in the film cast from the same solvent. For this purpose we have used regioregular P3HT, and it has been gelled in xylene.

The mechanism of thermoreversible gelation of polymers is the most poorly understood phenomenon since it may occur through various types of physical processes.[11−13] In crystalline polymers crystallites usually act as cross-linking junction, and a polymer chain passing through many such crystallites entraps the solvent to produce the gel.[14] Regioregular P3HT is semicrystalline in nature,[2] and similar to regioirregular samples it may also undergo coil-to-rod transformation in poor solvent.[8] Therefore, the thermoreversible gelation of this polymer may be a complicated process because the rodlike polymers may produce gel by many different mechanisms.[15] The gelation of rodlike polymers may occur by (I) microphase separation,[16] (II) entanglement formation,[12] (III) rod jamming,[17] (IV) glass transition,[18,19] etc. Russo and co-workers also showed that the gelation of the rodlike polymers is enthalpic in nature through interaction among the rods.[15] Thus, elucidation of gelation mechanism of P3HT is an interesting problem, and this report will focus on that. The gelation mechanism is now usually discussed from both the macroscopic and microscopic viewpoint; the former deals with the nature of connectedness (physical cross-linking) as a whole, and the latter sheds light in the molecular mechanism by which the physical connectedness occurs.[20,21] For this purpose we have measured the gelation rate, followed by DSC, UV−vis spectroscopy, SEM, TEM, and WAXS studies. From these results an attempt has been made to delineate the gelation mechanism of this important polymer. The conductivity of the dried gel and that of the film are also compared in both the doped and undoped state.

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Experimental Section

Samples. Regioregular poly(3-hexylthiophene) (P3HT) was purchased from Aldrich Chemical Co. As reported by the company, the samples were prepared by Rieke's method.[5] The sample contained some suspended impurities when dissolved in chloroform. They were filtered off through a sintered disk, and the solution was evaporated to dryness to obtain the samples in the film form. The reported molecular weight ($\overline{M}_w$) of the sample was 87 000. The head-to-tail (H−T) regioregularity of the sample was measured from ^{1}H NMR spectroscopy in a Bruker 300 MHz instrument. The H−T regioregularity was measured from the analysis of the protons of the α-carbon of the 3-substituted thiophene.[2,22] The resonance of H−H coupling occurs at 2.56 ppm, and that of the H−T coupling occurs at 2.79 ppm. From the integrated area of the peaks the percentage of H−T linkages was calculated to be 91.4 mol %. The solvent xylene was purchased from E. Merck, India, and was used as received. $CHCl_3$ (E. Merck, India) was also used as received.

Preparation of Gel and Its Characterization. The gels were prepared in two ways: for SEM, TEM, WAXS, and kinetic study the gels were prepared in glass tubes, and for thermal study the gels were prepared in Perkin-Elmer LVC capsules. The weighed amount of polymer and the solvent were taken in glass tubes, degassed by freeze−thaw technique, and were sealed in a vacuum (10^{-3} mmHg). They were made homogeneous at 150 °C and quickly gelled by quenching at 15 °C. For SEM study the gels were taken out of the tubes and dried at 35 °C for 3 days. They were then gold-coated, and their micrographs were recorded in a SEM apparatus (Hitachi S-415A). The TEM study was done by dropping a 0.3% (w/v) solution of P3HT in carbon-coated copper grid and then drying in a vacuum at 35 °C for 3 days. They were then observed directly in transmission electron microscope (Hitachi H-600). For WAXS study the gel was dried initially in a pool of air at room temperature (35 °C) and finally dried for 2 weeks in a vacuum at 35 °C. The scattering pattern was recorded in a Philips powder-diffraction apparatus (model PW1710). The gel was taken in a glass groove, and the diffractrogram was recorded using nickel-filtered Cu Kα radiation at the scanning rate of 1.5° 2θ/min.

Thermal Study. The thermal studies of the gels were done in a differential scanning calorimeter (DSC-7, Perkin-Elmer). The gels were prepared in LVC capsules by taking the polymer P3HT and xylene in appropriate amounts. They were then sealed in quick press and were heated in DSC at 120 °C for 10 min. They were then cooled to different isothermal temperatures (15−25 °C) and were kept there for 3 h. They are then heated from that temperature to 120 °C at the heating rate of 20°C/min. The peak temperature was taken as the gel melting temperature (T_{gm}). The equilibrium gel melting temperature (T^0_{gm}) was determined by plotting T_{gm} with gelation temperature (T_{gel}) and then extrapolating according to the Hoffman−Weeks procedure.[28] The equilibrium dissolution temperature (T^0_d) was measured by crystallizing the samples above 25 °C for 12 h and extrapolating similarly to get T^0_{gm}.

UV−Vis Spectroscopy. To understand the conformational characteristics of P3HT chain during gelation in xylene, UV−vis spectroscopy of the solution was done in a Hewlett-Packard UV−vis spectrophotometer (model 8453). Two different concentrations of P3HT in xylene were used, viz. 0.05% (w/v) and 4% (w/v). The solution was homogenized at 100 °C and was then transferred to a quartz cell (1 mm path length) at room temperature, and then it was kept at 10 °C through water circulation.

Kinetic Study. The kinetics of gelation was studied by the test tube tilting method.[20,21,24−28] Gels at different concentrations were made by taking 0.5 mL of xylene (density = 0.85 g/mL) and an appropriate amount of P3HT (5−60 mg) in glass tubes (8 mm i.d. and 1 mm thick). They were degassed by the freeze−thaw technique and were sealed under vacuum (10^{-3} mmHg). They were made homogeneous at 150 °C and were quickly transferred to a thermostatic bath set at a predetermined temperature. The gelation rate was measured by measuring the gelation time (t_{gel}) where no flow occurred after the tube was tilted. The error limit in the time measurement was ±5 s by a repeated trial-and-error procedure. The inverse of gelation time (t_{gel}^{-1}) was considered as the gelation rate.

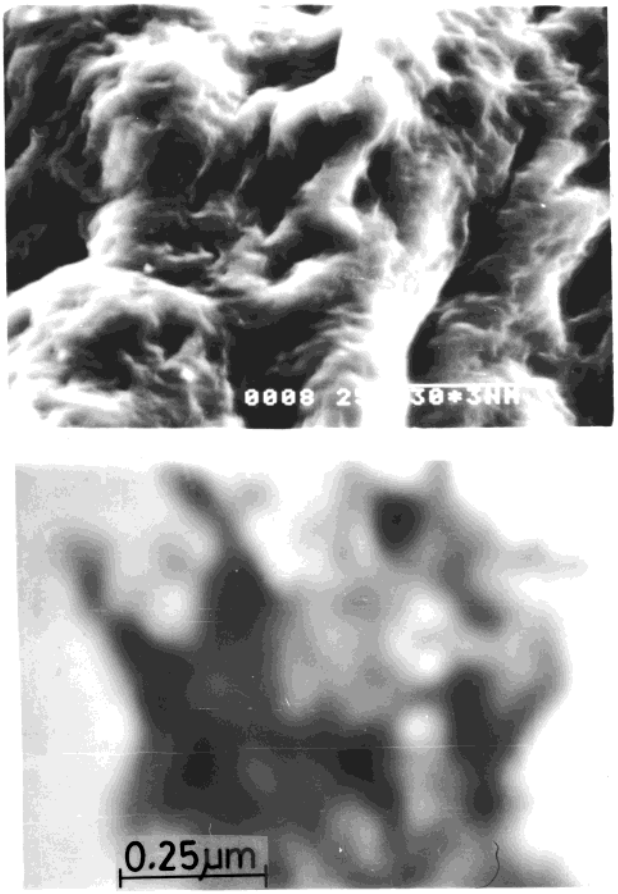

Figure 1. (a, top) SEM picture of 8% (w/v) P3HT−xylene (dried) gel. (b, bottom) TEM picture of dried P3HT gel in xylene (0.3% w/v).

Conductivity Measurement. The conductivity of the dried gel and that of the dried film cast from xylene were measured at room temperature (27°C) by the standard spring-loaded pressure−contact four-probe method[29] where the arrangement was such that the distances between the probes were same for all the experiments. The dried gel was prepared in a Teflon groove (1.3 cm diameter) by evaporating the solvent of the gel at 35 °C in a pool of air and finally in a vacuum at the same temperature. The P3HT film used in the conductivity measurement had also the same diameter as that of the gel. A constant current (I) from a constant direct current source electrometer (Keithley, model 617) was allowed to pass through two adjacent leads of the four probes, and the voltage (V) across the other two leads was measured using a multimeter (Keithley, model 2000). The conductivity (σ) was measured from the relation[29]

$$\sigma = \frac{\ln 2}{\Pi d}\,\frac{I}{V}$$

where d, the average thickness of the film/gel, was measured at four different positions using a screw gauge.

Result and Discussion

Morphology. The P3HT gel in xylene is brownish red in color. In Figure 1a the SEM picture of 8% P3HT dried gel is presented. From the figure it is apparent that fibrillar network morphology is present. This type of morphology is characteristics of thermoreversible gels

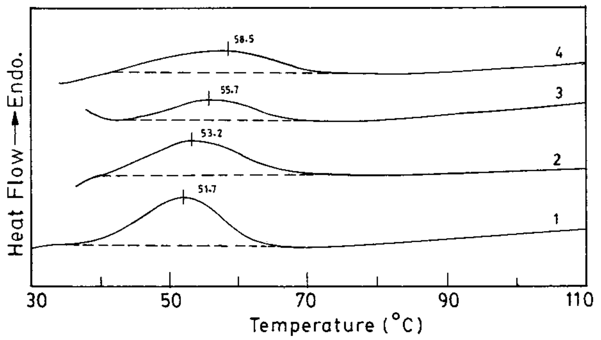

Figure 2. DSC thermograms of the gels prepared isothermally for 3 h (heating rate 20 °C/min) at (1) 15 °C, (2) 20 °C, (3) 22.5 °C, and (4) crystallized at 27 °C for 12 h.

of flexible polymers.[20,21,30] In Figure 1b the TEM picture of 0.3% P3HT in xylene is shown. In this figure also fibrillar network morphology is clearly seen. So from both the micrographs it may be inferred that the dried P3HT gels consist of fibrils which constitute the network structure. Of course, it is necessary to mention here that it has been assumed throughout the paper that P3HT gel in the undried state also has similar morphology. Another important criterion for thermoreversible gels is that they exhibit first-order phase transition during heating. In Figure 2 the thermograms of the gels prepared isothermally at different temperatures are shown. The gels exhibit an endothermic melting peak during heating. Thus, the presence of fibrillar network morphology and the presence of first-order phase transition indicates the formation of thermoreversible gels in this P3HT−xylene system.

Structure. To elucidate the structure of the gel, the WAXS pattern of the dried gel is obtained and is shown in Figure 3. The gels are dried at 35 °C, and since the gel melts above 52 °C, the network structure does not break during drying. Sharp crystalline peaks of the dried gels at $2\theta = 10.9°$, 16.4°, and 22.6° are observed, corresponding to *d* values of 8.11, 5.40, and 3.92 Å. These *d* values are the same with those of regioirregular P3HT crystals.[5,31] So, it may be surmised from these results that in the gel the fibrils are made from P3HT crystallites, or in other words the crystallites may act as cross-linking junctions in P3HT−xylene gels. To support this point, we have also performed electron diffraction experiment, and this is shown in the inset of Figure 3. In the figure diffraction rings are clearly seen, and this supports that the crystallites producing the fibrils are polycrystalline in nature. Therefore, from both the X-ray and electron diffraction experiments it may be surmised that P3HT gel in xylene is produced from the fibrillar crystallites.

Gelation Mechanism. a. UV−Vis Spectroscopic Study. P3HT being a polymer with conjugated double bonds has intense color in solution. The color changes during the sol-to-gel transformation from orange-red to reddish-brown. We want to follow the color change with time during the gelation process. Since the gelation occurs above the critical gelation concentration, the absorbance value exceeds the standard value of 4.0 for the instrument at lower wavelength (300−600 nm). Consequently for this region we choose lower concentration [0.05% (w/v)]. The solution was initially kept at 100 °C to make homogeneous and then transferred to a cell at room temperature (27 °C) and finally kept at 10 °C. The instrument is then scanned with a time interval of 1 min from 300 to 1000 nm and is shown in Figure 4a. It is apparent from Figure 4a that the $\Pi-\Pi^*$ transition peak shifts from 450 to 456 nm with time. Though no definite reason for this red shift is known, but in analogy with its spectral behavior in dimethyltetrahydrofuran it may be attributed to the conformational changes from the coil-to-rod (ordered conformer) transition.[8] During the transition the conjugation length increases; consequently, the electron becomes delocalized, and the red shift of the absorption band occurs. Thus, the spectrum indicates that P3HT in xylene at high temperature remains in coiled form, and probably a coil-to-rod

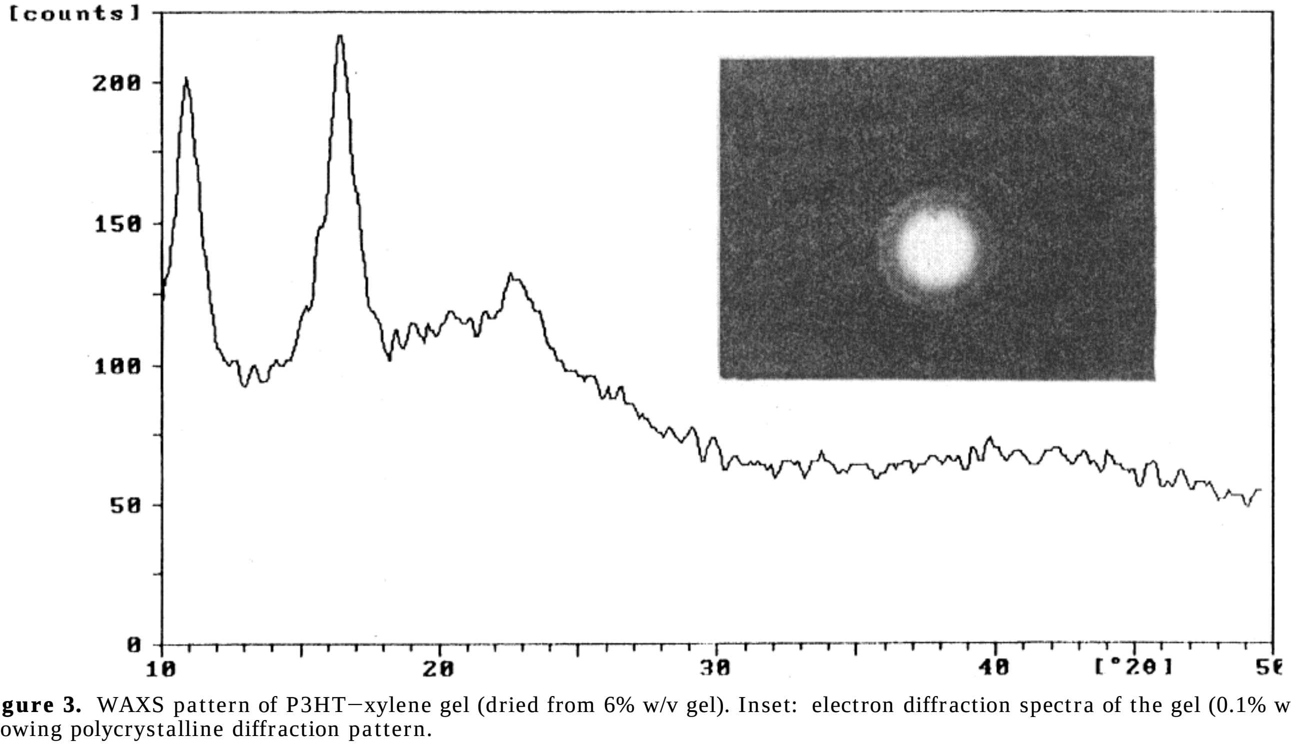

Figure 3. WAXS pattern of P3HT−xylene gel (dried from 6% w/v gel). Inset: electron diffraction spectra of the gel (0.1% w/v) showing polycrystalline diffraction pattern.

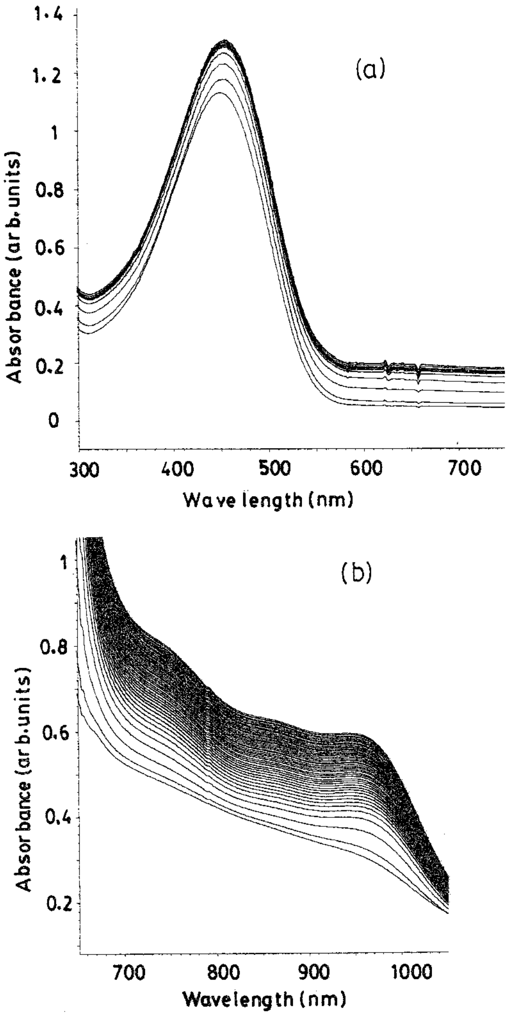

Figure 4. (a) UV–vis spectra of P3HT–xylene solution (0.05%) (w/v) for different times (1 min interval) at 10 °C (cooled from 100 °C). (b) UV–vis spectra for a P3HT–xylene sol (4% w/v) for different times (0.5 min interval) at 10 °C (cooled from 100 °C).

transition occurs with time for keeping the solution at 10 °C. However, such a transition alone does not produce a gel because higher concentration of polymer is required for gelation. The transitions due to vibronic coupling at 560 and 607 nm as observed in P3HT in methyltetrahydrofuran and dimethyltetrahydrofuran are not observed in this system.[8] Apart from the red shift, it is apparent from the figure that the absorbance value increases with increase in time. A probable reason is that there is a kinetics in the coil-to-rod formation process, and it takes some time to transform the coils into the equilibrium rod concentration.[8] At the present experimental condition it requires ~5 min in the leveling up of the absorbance value.

Figure 4b represents the UV–vis spectra for a sol (concentration 4 g/dL) at 10 °C into the cell. Because of the large absorbance, we are unable to get the spectra for the wavelength (300–650 nm); only the spectra from 650 to 1000 nm are shown for this gel sample. It is apparent from the figure that there is a blue shift of the peak from 953 to 946 nm with time during gelation. Also, two new shoulders at 745 and 865 nm are gradually growing during gelation. The reason for this behavior is not clear to us. The absorbance value increases with time, and it probably indicates that the aggregation part of the gelation process is also kinetically controlled. In Figure 5, absorbance vs time plots for both peaks at 450 and 950 nm are shown. With time, the absorbance in the coil-to-rod transformation (Figure 5a) levels up, but the absorbance for the gelation process does not level up completely (Figure 5b). From this study it may be surmised that there may be two processes for the gelation of P3HT: (1) coil-to-rod formation and (2) aggregation of rods, to produce the crystallites which produces the gel. So the gelation process of P3HT may be summarized as follows:

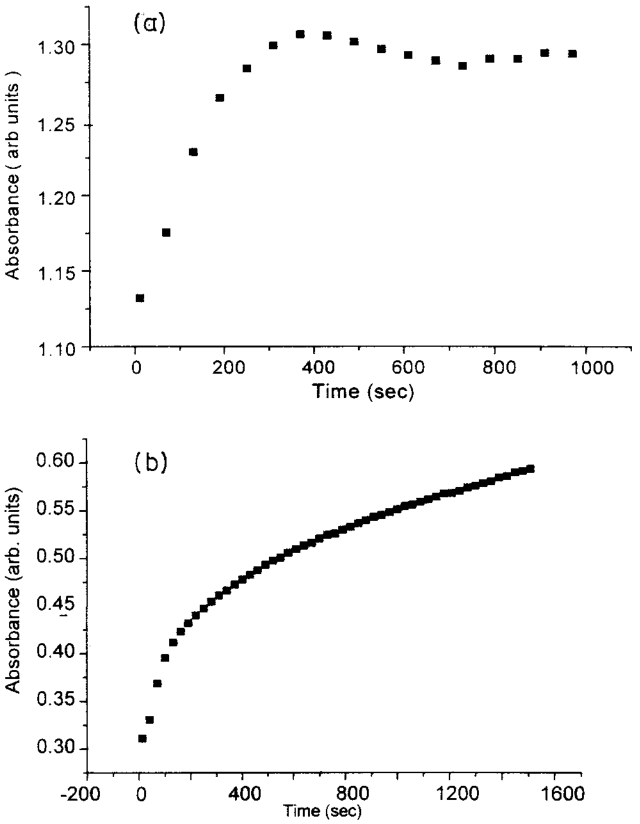

Figure 5. Absorbance vs time (min) plot for (a) P3HT–xylene solution (0.05%) at 450 nm and (b) P3HT–xylene sol (4% w/v) at 950 nm at 10 °C.

$$\text{coil} \rightarrow \text{rod} \rightarrow \text{crystallization (gelation)} \qquad (1)$$

Since the whole scheme cannot be analyzed for a concentration where gelation occurs by the spectroscopic method, so we have used the test tube tilting method to analyze both the processes, and it is discussed in the following section.

b. Gelation Rate. The gelation rate is an important tool to understand the gelation mechanism of polymers.[20,21,24–28] Both the macroscopic and microscopic mechanisms of gelation may be elucidated from the analysis of gelation rate (t_{gel}^{-1}) data. The t_{gel}^{-1} is usually expressed as a combination of two terms: the concentration function $f(C)$ and the temperature function $f(T)$.[20,21,26,28]

$$t_{gel}^{-1} \propto f(C)\, f(T) \qquad (2)$$

Analysis of the $f(C)$ yields the macroscopic mechanism and $f(T)$ yields the microscopic mechanism.[20,21] In Figure 6 the plot of gelation rate (t_{gel}^{-1}) with polymer concentration is shown for different gelation temperature (T_{gel}). At a particular T_{gel} the gelation rate increases in a

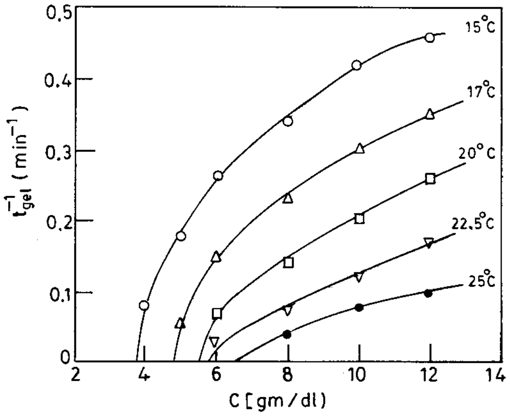

Figure 6. t_{gel}^{-1} vs concentration plot of the P3HT−xylene gel at indicated gelation temperatures.

Table 1. Exponent "*n*" Values from Least-Squares Slopes of log t_{gel}^{-1} vs log ϕ Plot of P3HT/Xylene Gel

temp (°C)	C^* (g/dL)	"*n*"
15	3.8	0.50
17.5	4.8	0.51
20	5.5	0.50
22.5	5.8	0.54
25	6.5	0.55
av		0.52
SD		0.02

nonlinear way with concentration, but at higher concentration it slowly levels up. The extrapolation of each curve to zero gelation rate yields the critical gelation concentration ($C^*_{t=\alpha}$) and is presented in Table 1.

c. The Concentration Function: Macroscopic Mechanism. At a particular temperature

$$t_{gel}^{-1} \propto f(C) \propto \Phi^n \tag{3}$$

where Φ is the reduced overlapping concentration[20,21,28] and is expressed as

$$\Phi = \frac{[C - C^*_{t=\alpha}(T)]}{C^*_{t=\alpha}(T)} \tag{4}$$

The *n* is an exponent, and its value can be calculated from the double-logarithmic plot of t_{gel}^{-1} vs ϕ and is shown in Figure 7. From the figure it is clear that the data points fit very well in straight lines. The "*n*" values are measured from the least-squares slopes of the plots and are also presented in Table 1. From the table it is clear that "*n*" values varies from 0.50 to 0.56 with an average value of 0.52. According to the percolation theory,[32,33] the gel fraction (*G*) is expressed as

$$G = (p - p_c)^\beta \tag{5}$$

where *p* is the conversion factor and p_c is its critical value and β is a critical exponent and has a value of 0.45 for three-dimensional lattice. In the approximation, that the theory of chemical reaction rate (i.e., rate ∝ fraction of molecules overcoming the energy barrier) is applicable to the physical gelation process,[28]

$$t_{gel}^{-1} \propto G \propto (p - p_c)^\beta \tag{6}$$

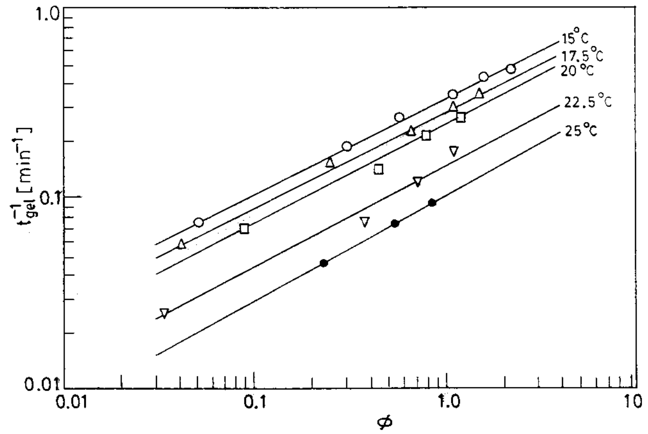

Figure 7. log t_{gel}^{-1} vs log ϕ plot of the P3HT−xylene gel for indicated temperatures.

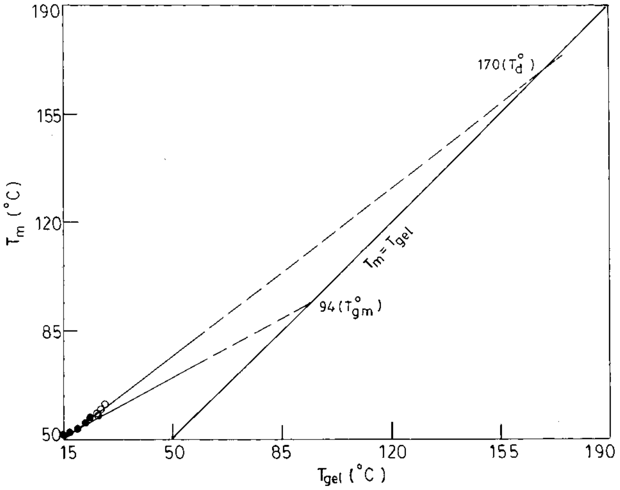

Figure 8. Hoffman−Weeks plot for 8% (w/v) P3HT gel in xylene: (●) for gelation at isothermal temperatures for 3 h and (○) for crystallization at different temperature for 12 h.

Comparing eqs 3 and 6 "*n*" may be equal to β (since $C < C^*$, no gelation occurs and if $P < P_c$, no percolation occurs). From Table 1 it is clear that "*n*" values vary from 0.50 to 0.55 with an average of 0.52. Therefore, the experimental "*n*" values are very close to the value of β (0.45). So it may be concluded that three-dimensional percolation is a suitable model for gelation of this comblike conducting polymer (P3HT) in xylene.

d. Microscopic Mechanism. From the UV−vis spectroscopy results of P3HT solution it has been proposed that gelation is a two-step process (eq 1), and each step has its own kinetics. Here, we shall discuss how both the rates of different process can be analyzed from the overall gelation rate data.[20,21,34] For this purpose we need to know both the equilibrium gel melting temperature (T_{gm}^0) and equilibrium dissolution temperature (T_d^0). In Figure 8 the Hoffman−Weeks plot for 8% (w/v) P3HT gel is shown. The melting point data at each T_{gel} are taken from Figure 2. Linear extrapolations of the plot yield two equilibrium melting points; the lower one is the T_{gm}^0 because at the lower *X*-axis temperatures (≤25 °C) gel can be produced isothermally. The higher one is the T_d^0 since at these higher *X*-axis temperature (≤25 °C) no gel is produced; rather, solution crystals are produced (cf. Figure 6). The T_{gm}^0 data will be used to understand the kinetics of rod formation from the gelation rate (t_{gel}^{-1}) data, and the

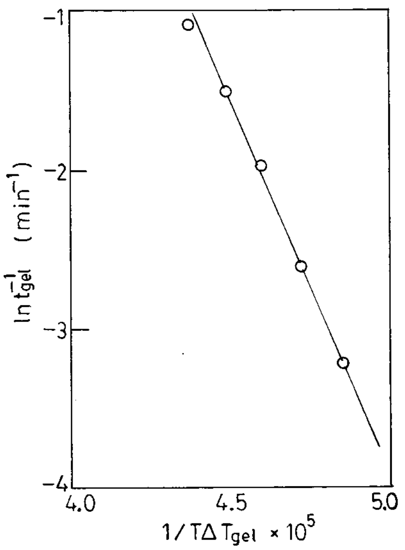

Figure 9. ln t_{gel}^{-1} vs $1/T\Delta T_{gel}$ plot for the P3HT−xylene gel (8% w/v).

T_d^0 data will be used to understand the kinetics of crystallization leading to gelation.[20,21]

e. Coil-to-Rod Transformation. Flory and Weaver[35] derived an expression for the rate constant (k) for coil-to-helix transition of a dilute aqueous collagen solution,

$$k = \text{const} \exp(-A/kT\Delta T) \qquad (7)$$

where $A = 2\sigma\Delta F/\Delta S$, σ is the surface energy of the new surface associated with the formation of helix, ΔF is the free energy of activation, and ΔS is the overall entropy change due to helix formation; ΔT is the undercooling. According to Rughoopath et al.,[8] a single chain coil-to-rod conformational transition is analogous to the coil-to-helix transition; so the Flory−Weaver theory can be applied in this coil-to-rod transformation. Since the measured gelation rate is accompanied by coil-to-rod transformation, "k" can be replaced by t_{gel}^{-1},[20,21,34]

$$t_{gel}^{-1} = \text{const} \exp(-A/kT\Delta T) \qquad (8)$$

where $\Delta T_{gel} = T_{gm}^0 - T$. Taking $T_{gm}^0 = 94$ °C, a plot has been made with t_{gel}^{-1} against $1/T\Delta T_{gel}$ and is shown in Figure 9. It is apparent from the figure that all the data points fit well in a straight line, indicating that coil-to-rod transition is the first step of the gelation process. This mechanism is similar to the gelation of poly(vinylidine fluoride) in glyceryl tributyrate[20] or in diesters[21,34] and *syn*-PMMA in toluene.[36] The former polymer transforms from coil to $TGT\bar{G}$ conformer while the latter one transforms from coil-to-helix structure prior to aggregation (gelation).

Now we would like to analyze the slope of the plot of Figure 9. From the measured least-squares slope of the plot "A" value was found to be 911.5 kcal/mol. From this "A" value the free energy of activation for the rod formation (ΔF) can be calculated if the lateral surface energy σ and the overall entropy change (ΔS) for the rod formation are known. According to a recent theory of Hoffman et al.,[37] ΔS can be equated to ($\Delta H_u^0/C_\alpha$) where ΔH_u^0 is the enthalpy change for melting of a perfect P3HT crystal and C_α is the chain characteristic ratio. Taking $\Delta H_u^0 = 3.8$ kcal/mol[38] and $C_\alpha = 9.36$,[40] ΔS is found to be 405 cal/(deg mol). The σ value of P3HT has been calculated from the relation[43]

$$\sigma = 0.1\Delta H_u^0 (ab)^{1/2} \qquad (9)$$

where "a" is the molecular width of the chain and "b" is the layer thickness. The a and b values may be taken from unit cell dimension of P3HT crystal obtained from wide-angle X-ray scattering studies.[31] Analysis of the unit cell structure clearly indicates that the molecular width of the chain "a" = 16.6 Å and the layer thickness b = 7.75 Å. Putting these values in eq 9, the σ value is found to be 12.1 ergs/cm^2 (7.8 kcal/mol). The σ value is almost identical to that of the other flexible chain polymers.[43] From the value of ΔS and σ, the activation energy for the coil-to-rod transformation is found to be 23.7 kcal/mol. The theoretical value of the maximum energy change for the rotation of poly(3-propylthiophene) (P3PT), with a change of dihedral angle from 0° to 90°, is ~15 kcal/mol.[44] In P3HT, due to the presence of the longer side chain, the energy barrier will be somewhat higher than that of P3PT. The experimental data, therefore, are approximately in accordance with the theoretical values.

f. Crystallization of the Rods. In the section we shall analyze the final step of scheme 1, i.e., crystallization of the rod to produce the gel. As evident from the SEM and TEM studies (Figures 1 and 2), the rods aggregate to produce fibrillar crystals. The growth rate of fibrils in the melt is given by[45,46]

$$G = G_0 \exp\left(-\frac{\Delta G_a}{kT}\right) \exp\left(-\frac{4\sigma^2 l T_m^0}{k\Delta H_u^0 T\Delta T}\right) \qquad (10)$$

where G_0 is constant, $\exp(-G_a/kT)$ is the transport factor, l is the length of the fibril, T_m^0 is the equilibrium melting point, and k is the Boltzmann constant. This expression can be extended for the growth of fibrillar crystals in solution.[21,47]

$$G = G^0 \exp\left[-\frac{G_a}{kT}\right] \exp\left[-\frac{4l\sigma^2 T_d^0}{kT\Delta H_u^0 \Delta T} + \frac{2\sigma^2 T_d^0}{a\Delta H_u^0 \Delta T} \ln \nu_2\right] \qquad (11)$$

where T_d^0 is equilibrium dissolution temperature, ν_2 is the volume fraction of polymer, and $\Delta T = T_d^0 - T$. Now, equating the gelation rate (t_{gel}^{-1}) with "G" of eq 11 and rearranging

$$\ln t_{gel}^{-1} - \left(\frac{2\sigma_s T_d^0}{a\Delta H_u^0 \Delta T}\right) \ln \nu_2 = A - \frac{4l\sigma_s^{\,2} T_d^0}{kT\Delta H_u^0 \Delta T} \qquad (12)$$

A plot of the left-hand side of the equation with $T_d^0/T\Delta T$ can be made and is shown in Figure 10. The straight-line nature of the plot supports that crystallization is the final step for the gelation in this system. In the calculation of ν_2, the density of P3HT has been taken as 1.11 g/cm^3 [48] and that of xylene 0.85 g/cm^3. The least-squares slope of this plot has been calculated, and from the slope of the plot the fibrillar length was calculated and is found to be 158 Å. This fibrillar length is about 10−15 times larger than that of the PVF$_2$ gels in diesters.[34] This seems to be reasonable because the P3HT chain is more rigid than the PVF$_2$ chain; the more

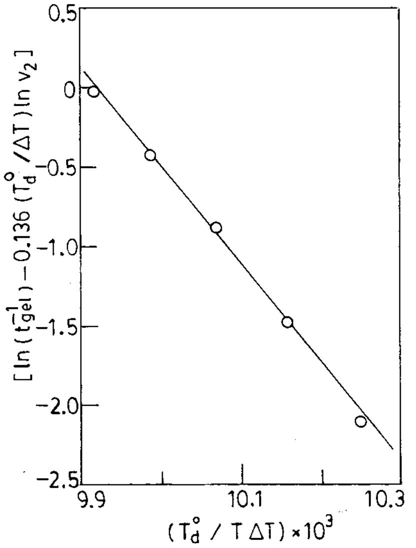

Figure 10. ln $t_{gel}^{-1} - (0.136T_d^0/\Delta T)$ ln ν_2 vs $T_d^0/T\Delta T$ plot for 8% (w/v) p3HT−xylene gel.

rigid the chain, the more is the tendency to crystallize in fibrillar form with longer fibrillar length.

Now we would like to compare the activation energy values for coil-to-rod transformation with that of the crystallization of rods. For this purpose the free energy for the formation of critical size nucleus has been calculated from the relation[21]

$$\Delta G^*_{dil} = \frac{4\sigma^2 l T_d^0}{\Delta H_u^0 \Delta T} - \frac{2\sigma^2 T T_d^0}{a \Delta H_u^0 \Delta T}\ln \nu_2 \qquad (13)$$

Using the values $\sigma = 12.1$ ergs/cm^2, $l = 158 \times 10^{-8}$ cm, $T_d^0 = 443$ K, $\Delta H_u^0 = 1.07 \times 10^9$ ergs/cm^3, $a = 16.6 \times 10^{-8}$ cm, $T = 293$ K, and $\nu_2 = 0.067$, the value of ΔG^*_{dil} was found to be 37.5 kcal/mol. The activation energy of the coil-to-rod transformation (23.7 kcal/mol) is lower than the activation energy of crystallite formation. Therefore, in this system crystallization is rather a difficult process than the coil-to-rod transformation. So gelation of P3HT in xylene obeys satisfactorily a two-step process of the coil-to-rod formation and crystallization, the latter being the rate-determining step.

Conductivity. The conductivity of dried P3HT gel prepared from 6% (w/v) P3HT in xylene was found to be 1.3×10^{-4} S/cm at 27 °C. However, the P3HT film cast from xylene [concentration 0.5% (w/v)] at 40 °C has a conductivity value of 2.0×10^{-5} S/cm measured at the same temperature. Therefore, the dried P3HT gel has a ~10 times higher conductivity than that of the film cast from the same solvent in the undoped state. When these films are doped for 24 h at 35 °C in iodine vapor, the dried gel has conductance of 15 S/cm whereas the film has conductance of 0.3 S/cm measured at the same temperature. So there is a ~50-fold increase in conductivity in the doped from of the dried gel than that of the film. Thus, it may be concluded that there is an increase in conductivity at least an order by magnitude due to the gel formation. This increase in conductivity may be due to interchain hopping[49] through the network which is produced during gelation.

Conclusions

In conclusion, it may be stated that P3HT produces thermoreversible gel in xylene. WAXS and electron diffraction experiments indicate the presence of crystallites in the gel. The gelation process may obey three-dimensional percolation model, and it may follow a two-step process of the coil-to-rod transformation and fibrillar crystallization, the latter being the rate-determining step. The conductivity of dried gel is ~10 times higher than that of the film cast from the same solvent.

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