

Influence of Alkyl Chain Length on the Gelation Mechanism of Thermoreversible Gels of Regioregular Poly(3-alkyl thiophenes) in Xylene

Sudip Malik, Arun K. Nandi

Polymer Science Unit, Indian Association for the Cultivation of Science, Jadavpur, Kolkata-32, West Bengal, India

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ABSTRACT: The gelation rates of poly(3-alkyl thiophenes) (P3AT) are strongly dependent on the pendent alkyl chain length. Poly(3-hexyl thiophene (P3HT) gels at higher isothermal temperatures than that of poly(3-dodecyl thiophene), (P3DDT). Gelation rate has been expressed as a combination of a temperature dependent function $f(T)$ and a concentration dependent function (φ^n); φ being the reduced overlapping concentration of P3AT. From the slope of double logarithmic plot of gelation rate and φ , n values are calculated to be 0.52 and 0.60 for P3HT and P3DDT, respectively. These values are close to the value of percolation exponent β (0.45) for three-dimensional lattice; so both the gels may approximately obey three dimensional percolation model. The $f(T)$ of gelation rate consists of two steps (i) coil-to-rod transformation followed by (ii) fibrillar crystallization. The coil-to-rod transition is accompanied by a red shift in the π - π^* transition band in UV-vis

spectra. Flory and Weaver theory is used to understand the coil-to-rod transformation process. The theory of fibrillar crystallization extended to dilute solution has been employed to understand the crystallization process. The results clearly indicate that the activation energy of conformational change (ΔF) is higher for P3DDT than that of P3HT. But the free energy change for the formation of critical size nucleus (ΔG_{dil}^*) is lower for P3DDT than that of P3HT. A comparison of ΔF and ΔG_{dil}^* values indicate conformational ordering is the rate-determining step for P3AT with dodecyl substituent whereas crystallization is the rate-determining step for P3AT with hexyl substituent. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 2528–2537, 2007

Key words: gelation; conformational analysis; conducting polymers; crystallization

INTRODUCTION

Poly(3-alkyl thiophenes) (P3ATs) have received great attention in the recent years because of its wide range of applications^{1–4} in electroactive devices, light emitting diodes, nonlinear optical devices, etc., and its enhanced physical properties such as solubility, processability, and environmental stability. Thanks to the synthetic polymer chemists^{5–12} whose tireless effort have led to synthesize highly regioregular P3ATs, and by using regioregular P3ATs one can tune the properties in the materials, e.g., the conductivity of regioregular samples is three order higher than that of regioirregular samples in which orientation of ordered domain is not normal to the plane of the film. In our earlier reports, we have established that regioregular P3ATs with different alkyl chain lengths (hexyl, octyl, and dodecyl) form thermoreversible gel in xylene,^{13,14} and the conductivity of the dried gels have one order higher than that of the cast film.¹⁴ It is reported that the polymer–solvent compound is liable

to produce gel during gelation of these systems¹⁵ and the solvent has strong influence on the gelation process as in poly(vinylidene fluoride)/solvent systems^{16,17} and polystyrene/solvent^{18,19} systems. Moreover, it is interesting to compare the gelation behavior with different alkyl chain length as in the melt crystals the side chain crystallinity has increased with increasing the side chain length.²⁰

The mechanism of thermoreversible gelation of polymers is not a completely understood phenomenon as it occurs through various types of physical processes.^{19,21} In crystalline polymers, crystallites usually act as cross-linking junctions and a polymer chain passing through many such crystallites entraps the solvent to produce the gel.²² Regioregular P3ATs are comb-like polymers and are semicrystalline in nature. Apart from the main chain, the side chain may influence the gelation process as it influences the crystallization process in the melt-cooled state.²⁰ We have reported the gelation mechanism of thermoreversible P3HT gel in xylene earlier.¹⁴ We proposed that gelation of P3ATs are two step processes: (A) coil-to-rod transformation and (B) crystallization of the rods and each step may depend on the alkyl chain length of P3AT. Thus elucidation of gelation mechanism of P3ATs with different alkyl chain

Correspondence to: (psuakn@mahendra.iacs.res.in).

length is an interesting problem and this report deals with the influence of alkyl chain length on the above processes.

The gelation mechanism is usually discussed from the macroscopic and microscopic view point, the former deals with the nature of the connectedness (physical crosslinking) as a whole and the latter sheds light on the molecular mechanism by which the physical connectedness occurs. As is customary the gelation rate is used to delineate the above two viewpoints along with other techniques. The gelation rate is generally expressed as a product of concentration function $f(C)$ and temperature function $f(T)$.^{13,14,16,23}

$$t_{\text{gel}}^{-1} \propto f(C)f(T) \quad (1)$$

where t_{gel}^{-1} is expressed as the gelation rate, t_{gel} being gelation time. When $f(T)$ is constant, the variation of the gelation rate with concentration yields the macroscopic mechanism of gelation, and the variation of the same with temperature at fixed $f(C)$ yields the microscopic mechanism of gelation.

Here we present the gelation mechanism of P3ATs mainly from the kinetic investigation of gelation process for regioregular poly(3-dodecyl thiophene) [P3DDT] and poly(3-hexyl thiophene) [P3HT] in xylene. An UV-vis study of the gelation process has also been used to understand the conformational changes of the polymer during gelation. The gelation mechanism of P3DDT will be elucidated first and then it will be compared with that of the P3HT-xylene gels reported earlier.¹⁴ Finally, the influence of alkyl chain length (e.g., hexyl and dodecyl) on the different gelation parameters of P3AT will be discussed thoroughly.

EXPERIMENTAL

Materials

Regioregular P3DDT and P3HT samples were purchased from Aldrich Chemicals and as reported by the company they were prepared by Rieke's method.¹² The sample was purified by dissolving in CHCl_3 , filtered off the suspended impurities, and then the solution was evaporated to dryness in a pool of air and finally it was dried in vacuum at 25°C for 5 days. The head-to tail regioregularity was measured from ¹H-NMR spectroscopy

copy²⁴ in a Bruker 300 MHz instrument and the regioregularity of P3DDT and P3HT was 88 and 91 mol %, respectively. Xylene was purchased from E. Merck, India, and was used as received. The characteristics of the materials are presented in Table I.

Preparation and characterization of gels

The gels were prepared in two different ways. For SEM investigations, the gels of different compositions were prepared in sealed glass tubes, and for thermal study, they were prepared in Perkin Elmer large volume capsules (LVC). In glass tubes, weighed amount of polymer and solvent were sealed in vacuum (10^{-3} mmHg) after degassing by freeze-thaw technique. They were made homogeneous at 150°C for 15 min and were gelled by quenching the tube at -20°C for 30 min. For SEM study, the gels were taken out of the tube by breaking the seal and they were dried at room temperature (25°C) in a pool of air and finally in vacuum at 25°C for 5 days. Care was taken that during the drying process the gel did not melt. They were gold coated and their micrographs were recorded in a SEM apparatus (Hitachi S-2300).

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 P3DDT and xylene in appropriate amount. They were then sealed in a quick press and were heated in DSC at 120°C for 15 min. They were then cooled to different isothermal gelation temperatures (-12°C to -2.5°C) and were kept there for 3 h. They were 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_{gm}^0) was determined by plotting T_{gm} with gelation temperature (T_{gel}) and then extrapolating according to the Hoffman-Weeks procedure.²⁵ The equilibrium dissolution temperature (T_d^0) was measured by crystallizing the samples above -2.5°C for 12 h and extrapolating similarly to get T_{gm}^0 .^{14,26,27} A 12-h time is required to produce the crystal and it does not produce gel as observed externally in the sealed tubes.

TABLE I
Characteristics of Polymers and Solvent Used in the Work

Characteristics	Poly(3-dodecyl thiophene) (P3DDT)	Poly(3-hexyl thiophene) (P3HT)	Xylene
Molecular weight (\bar{M}_w) $\times 10^4$	16.2	8.7	-
H-T regioregularity (± 2 mol %)	88	91	-
Melting point (°C)	~220	180	137 ^a
Density (g/mL)	1.07	1.11	0.85

^a Boiling point

UV-vis spectroscopy

To understand the conformational changes of P3HT chain during the gelation process, UV-vis spectroscopy of the solution was done at 5°C in a Hewlett-Packard UV-vis spectrophotometer (model 8453). 0.05% (w/v) P3DDT solution was homogenized at 100°C and was then transferred to a quartz cell (1 cm path length) placed in thermostatic water circulation at 5°C. The absorbance data were then recorded in every 13-s interval.

Kinetic study

The kinetics of gelation was studied by the test-tube tilting method.^{14,16,23,26-29} Gels at different concentrations were made by taking 0.5 mL xylene (density = 0.85 g/mL) and an appropriate amount of P3DDT (5–60 mg) in glass tubes (8 mm i.d. and 1 mm thick). They were degassed by 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 ± 10 s by repeated trial and error procedure. The inverse of gelation time (t_{gel}^{-1}) was considered as the gelation rate.

RESULTS AND DISCUSSIONS

Morphology and thermal behavior

A typical morphology of dried gel of P3DDT-xylene system is shown in Figure 1. Fibrillar network structures are clearly observed in the micrograph. Representative DSC thermograms of the 9% (w/w) P3DDT gel at different isothermal gelation temperatures are shown in Figure 2 for P3DDT/xylene gels. Thus, first-

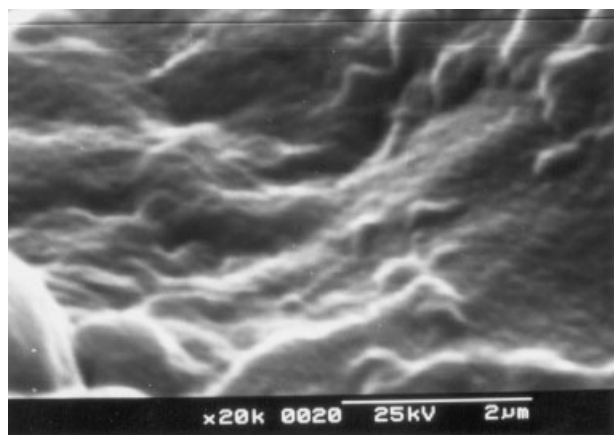


Figure 1 SEM picture of 12% (w/v) P3DDT/xylene (dried gel).

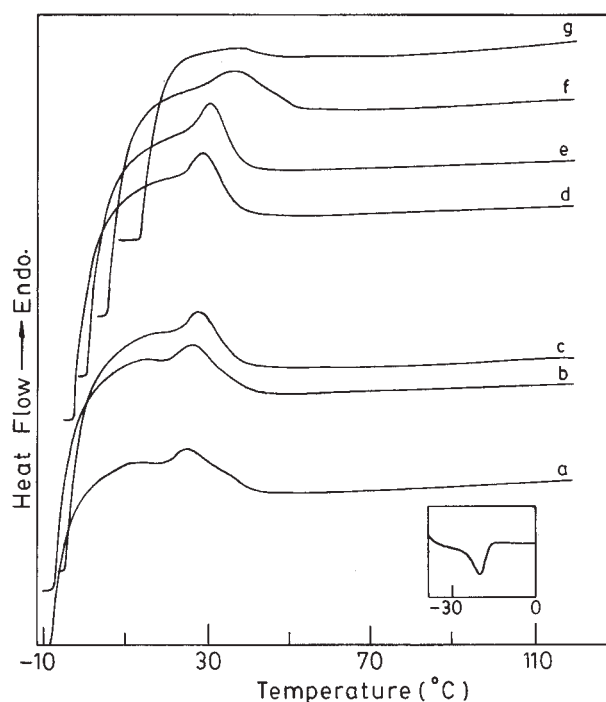


Figure 2 Representative DSC thermograms of the 9% (w/v) P3DDT gels prepared isothermally for 3 h (at the rate of 20°/min) at (a) -12°C , (b) -10°C , (c) -7.5°C , (d) -5°C , (e) -2.5°C , and the thermograms for the samples crystallized at (f) 2.5°C , (g) 7.5°C for 12 h. [Cooling thermogram from 120°C at the rate of $5^{\circ}/\text{min}$ is shown in inset.]

order phase transition is observed and it is true for the gels produced at different polymer concentrations. Also in the inset of the figure a representative cooling thermogram of this gel from the sol state at 120°C cooling at the rate of $5^{\circ}\text{C}/\text{min}$ is shown. Both the cooling isotherm and the heating isotherms clearly indicate the presence of reversible first-order phase transition in the system. Thus, the formation of fibrillar network structure and reversible first-order phase transformation conclude the formation of thermoreversible gel in P3DDT-xylene system^{19,30}, similar to the P3HT-xylene gels reported earlier.¹⁴

Gelation mechanism

UV-vis spectroscopy

During the sol to gel transition, P3DDT-xylene solution changes color from orange red to reddish brown. The color change during gelation is however difficult to follow because the critical gelation concentration required for gelation is very high where the absorbance value exceeds the standard value of 4.0 of the instrument at the wavelength 300–800 nm. Consequently, we chose lower concentration e.g., 0.05% (w/v) where the solution does not gel. The solution was homogenized at 100°C and then transferred to a cell kept at 5°C . The instrument was then scanned

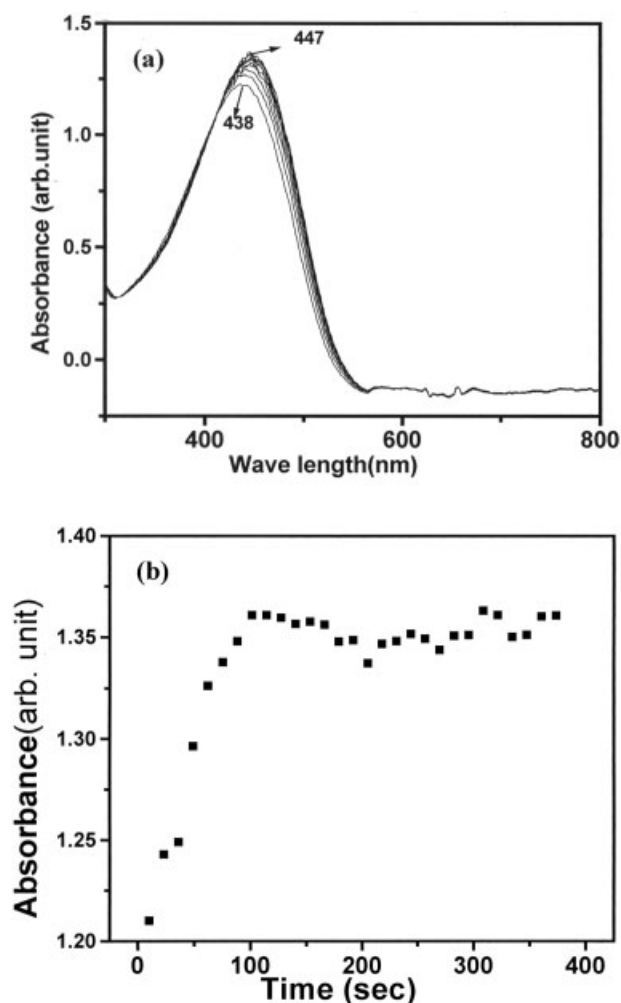


Figure 3 (a) UV-vis absorption spectra of P3DDT-xylene solution (0.05%) for different time interval (13 s) at 5°C, cooled from 100°C. (b) Absorbance versus time (s) plot for the UV-vis peak at 447 nm shown in (a).

from 300 to 800 nm with a time interval of 13 s. Figure 3(a) represents the spectra taken at different times and it is apparent from the figure that the absorbance peak shifts from 438 to 447 nm with time. The red shift may arise from the straightening of the P3DDT coils and this increases the conjugation length of the P3DDT chain causing the band gap to decrease. In the P3HT-xylene solution (0.05% w/v) similar red shift of π - π^* transition peak from 450 to 456 nm with time was observed at 10°C¹⁴ In analogy with P3HT solution in xylene and P3HT solution in dimethyl tetrahydrofuran the red shift may be attributed to the conformational transition from coil-to-rod structure (ordered conformer).^{14,31} This coil-to-rod transition is accompanied by an increase in conjugation length causing a red shift in the π - π^* transition of UV-vis spectra. Thus, these results suggest that P3DDT remains in coiled form in its xylene solution at high temperature and it changes into rod shape during cooling to 5°C. So it may be argued that the rod form of P3DDT is respon-

sible for the gelation process at high polymer concentration like the P3HT-xylene system.¹⁴ In Figure 3(b), the increase in absorbance value of the peak at 447 nm with time is shown. Initially, it rises abruptly and then levels up with time. This indicates that there is a kinetic process in the coil-to-rod transition and some time is required to reach the equilibrium rod concentration. Like the P3HT-xylene system we could not study the aggregation behavior of the P3DDT rods in xylene (8% concentration) by UV-vis spectroscopy. This is because the isothermal gelation process takes place below 0°C for this polymer and our instrument has limitation to work below 0°C due to frosting. Nonetheless we may extend the aggregation (crystallization) behavior of P3HT-xylene solution to the P3DDT-xylene solution as the final step of gelation. So the gelation process in this system may be surmised as:



As the whole scheme cannot be analyzed by spectroscopic method, we have used the test tube tilting method to analyze the above scheme by gelation rate measurement discussed below.

Gelation rate

The gelation rate versus composition plots of P3DDT-xylene system are shown in Figures 4 for different isothermal gelation temperatures (T_{gel}). In the inset of the figure the gelation rate versus composition plot of P3HT-xylene gel is compared. At a particular T_{gel} , the gelation rate increases in a nonlinear way with concentration but at a higher concentration it slowly levels up. At a fixed polymer concentration, the gelation rate gradually decreases with increase in temperature. The critical gelation concentration ($C_{t=\infty}^*$) obtained from the extrapolation of gelation rate versus composition plot to zero gelation rate is presented in Table II for P3DDT/xylene and P3HT/xylene systems. The $C_{t=\infty}^*$ values of P3DDT gels are higher than those of P3HT gels indicating P3HT chains can overlap more easily to produce gels than the P3DDT sample at similar kinetic condition for isothermal gelation temperatures. Usually critical gelation concentration depends on molecular weight, higher the molecular weight lower is the critical gelation concentration.^{32,33} In the P3HT and P3DDT samples as both have almost same regioregularity, so P3HT should exhibit higher $C_{t=\infty}^*$ value, but we observe a lower value than that of P3DDT sample. Probably due to the anchoring of heavier dodecyl group the main chain remains in coiled state more than that of P3HT main chain, lowering its dimension in the solution. As a result higher P3DDT concentration is required for overlapping of chains for the onset of gelation. Therefore, the gelation

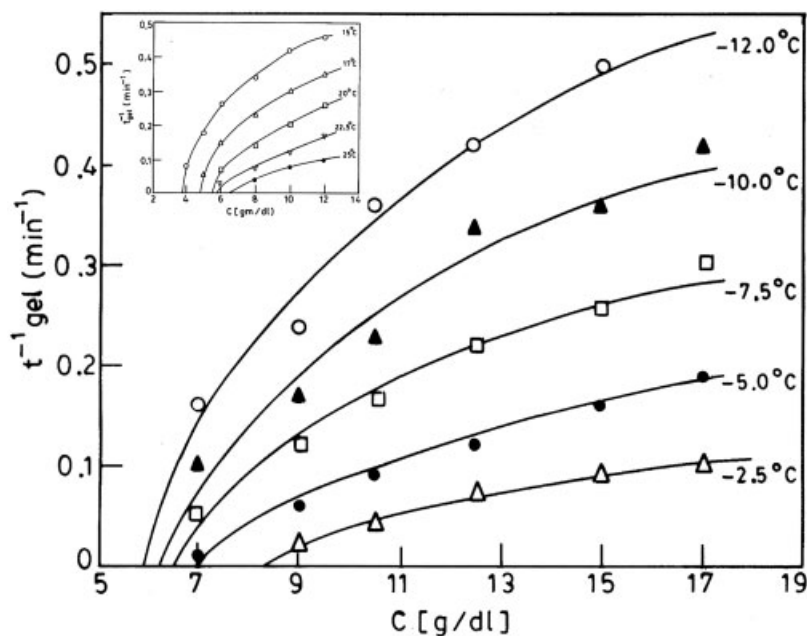


Figure 4 Plot of gelation rate (t_{gel}^{-1}) versus concentration of P3DDT/xylene gel at indicated isothermal gelation temperatures [Inset: gelation rate (t_{gel}^{-1}) versus concentration of P3HT/xylene gel¹⁴ for comparison].

tendency is lower for P3DDT and hence the isothermal gelation temperatures of P3HT are higher than that of P3DDT indicating gelation of P3HT is easier than P3DDT. These results clearly reveal that the gelation of P3AT with shorter pendent alkyl chain P3HT is easier than that of longer pendent alkyl chain P3DDT. Now we shall analyze gelation rate from the concentration and temperature function to understand the gelation mechanism clearly.

The concentration function: macroscopic mechanism

At a particular temperature, $f(T)$ is constant, so from eq. (1)

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

where Φ is the reduced overlapping concentration^{16,26,27} and is expressed as:

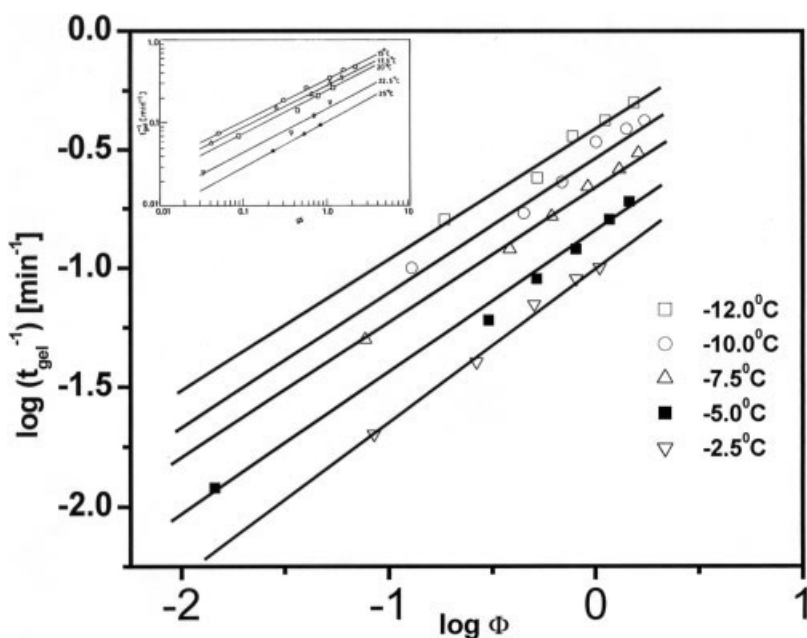


Figure 5 Plot of $\log t_{\text{gel}}^{-1}$ versus $\log \phi$ of P3DDT/xylene gel at indicated temperature [Inset: $\log t_{\text{gel}}^{-1}$ versus $\log \phi$ of P3HT/xylene gel¹⁴ for comparison].

TABLE II
Critical Gelation Concentration ($C_{t=\infty}^*$) and Exponent n
Values from Least Square Slopes of $\log t_{\text{gel}}^{-1}$ Versus \log
 ϕ plot of P3AT/Xylene Systems

Gelation temperature, T_{gel} (°C)	Critical gelation concentration ($C_{t=\infty}^*$, g/dL)	Exponent, n
P3DDT/Xylene		
-12.0	5.9	0.56
-10.0	6.2	0.58
-7.5	6.5	0.59
-5.0	6.9	0.59
-2.5	8.3	0.66
Av	-	0.60
SD	-	0.03
P3HT/Xylene ¹⁴		
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

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

where $C_{t=\alpha}^*(T)$ is the critical gelation concentration measured for infinite time of gelation at a particular temperature (T). The n is an exponent and its value can be calculated from the double logarithmic plot of t_{gel}^{-1} versus ϕ and is shown in Figure 5 for P3DDT-xylene system. For comparison, the same plots of P3HT-xylene system is also shown in the inset. Here the data points fit very well in straight lines at each temperature for both the systems. The n values are measured from the least square slopes of the plots and are presented in Table II. The n values vary from 0.56 to 0.66 with an average value of 0.60 for P3DDT-xylene system while for P3HT-xylene system the n values lies in the range 0.50 to 0.55. The average value of n is slightly lower for P3HT than that of P3DDT. This n can be correlated with the percolation theory for the gelation process. According to the percolation theory the gel fraction (G) is expressed as^{34,35}

$$G \propto (p - p_c)^\beta \quad (5)$$

where p and p_c stands for the conversion factor and its critical value required for gelation, respectively, and β is a critical exponent and it equals to 0.45 for percolation in three dimensional lattice. Within the approximation, that the theory of chemical reaction rate (i.e., rate \propto fraction of molecules overcoming the energy barrier) is applicable to physical gelation process, the gelation rate is, therefore, proportional to the gel fraction^{14,16,26,27} and so

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

Comparing eqs. (3) and (6) n may be equal to β because $C < C_{t=\alpha}^*$, no gelation takes place and if $P < P_c$, no percolation happens. The experimentally determined n values are approximately close to the theoretical value of β (0.45). So it may be surmised that within the experimental uncertainty three-dimensional percolation is an approximate model for the gelation of this comb-like conducting polymer (P3AT) in xylene and it is independent of the pendent alkyl chain length of P3AT.

Microscopic mechanism

Like gelation of P3HT in xylene¹⁴ it has been proposed earlier that gelation of P3DDT-xylene system is a two step process: (A) coil-to-rod transformation and (B) crystallization of the rods. Each step has its own kinetics. Here, we shall discuss how both the rates of different processes can be analyzed from the overall gelation rate data.^{14,17,26,27} To understand the above-mentioned processes, we need to measure both the equilibrium gel melting temperature (T_{gm}^0) and equilibrium dissolution temperature (T_d^0). In Figure 6 the Hoffman-Weeks plot²⁵ for 9% (w/v) P3DDT gel is shown, where the gel melting point data are plotted against isothermal gelation temperatures. This plot shows a break; below the break gelation occurs, and after the break, gelation does not occur even after 12 h of standing but solution crystals are produced. Linear extrapolation of the melting points at lower temperatures (i.e., below the break) produces the equilibrium gel melting temperature (T_{gm}^0). On the other hand, the extrapolation at higher temperature region (after the break) yields the equilibrium dissolution temperature (T_d^0). In P3DDT-xylene gels $T_{\text{gm}}^0 = 69^\circ\text{C}$ and $T_d^0 = 116^\circ\text{C}$ and both the values are much lower than those for P3HT-xylene gels ($T_{\text{gm}}^0 = 94^\circ\text{C}$ and $T_d^0 = 170^\circ\text{C}$, the Hoffman-Weeks plot for P3HT-xylene system is shown in the inset of the figure).¹⁴ So increasing the side chain length of P3AT a decrease in both T_{gm}^0 and T_d^0 values are observed. As gelation is a combination of conformational ordering and crystallization so the tendency of gelation is higher for P3HT than that for P3DDT as the driving force, i.e., the undercooling ($\Delta T = T_d^0 - T$ or $T_{\text{gm}}^0 - T$) is higher for P3HT at a particular temperature, T . Hence the isothermal gelation temperatures are lower for P3DDT than that of P3HT. The T_{gm}^0 data and the T_d^0 data will be used to understand the mechanism of coil-to-rod transformation and crystallization of rods leading to gelation^{14,26,27} respectively, from the gelation rate (t_{gel}^{-1}) data.

Coil-to-rod transformation

Assuming that the rate constant for coil-to-rod transition is analogous to the coil-to-helix transition of dilute aqueous collagen solution we applied the

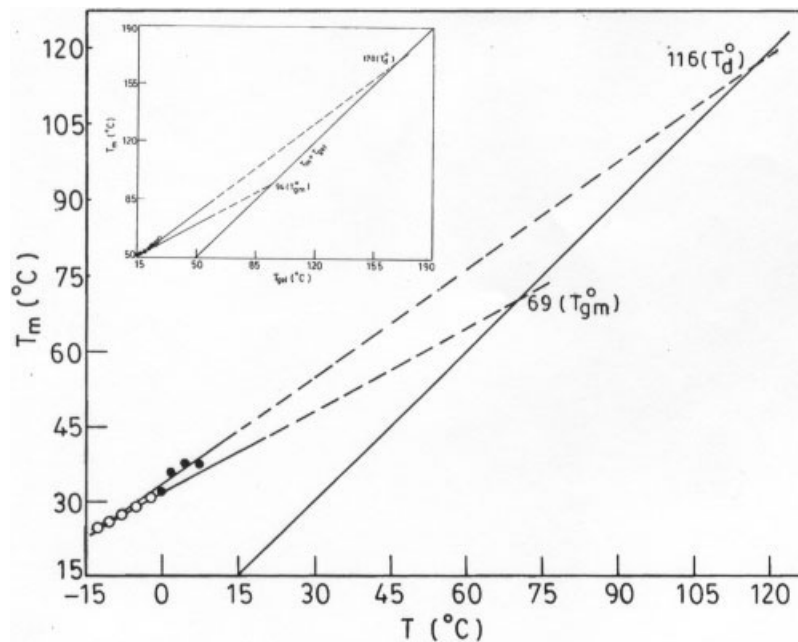


Figure 6 Hoffman-Weeks plot for 9% (w/v) P3DDT/xylene gel. (○) for gelation at isothermal temperatures for 3 h and (●) for crystallization at different temperature for 12 h; [Hoffman-Weeks plot for 8% (w/v) P3HT/xylene gel¹⁴ for comparison].

expression derived by Flory and Weaver for the variation of gelation rate constant with temperature.³⁶

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

where $A = \frac{2\sigma\Delta F}{\Delta S}$, σ is the surface energy of the new surface associated with the formation of rod, ΔF is the free energy of activation, and ΔS is the overall entropy change due to the rod formation, ΔT is the undercool-

ing. Since the measured gelation rate is accompanied by coil-to-rod transformation so k can be replaced by t_{gel}^{-1} ^{14,26,27}

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

where $\Delta T_{\text{gel}} = T_{\text{gm}}^0 - T$. Taking $T_{\text{gm}}^0 = 69^\circ\text{C}$ for P3DDT and $T_{\text{gm}}^0 = 94^\circ\text{C}$ for P3HT¹⁴ plots are made with $\ln t_{\text{gel}}^{-1}$ against $1/T\Delta T_{\text{gel}}$ and are shown in Figure 7. The straight line nature of the plots support that coil-to-rod transition is the first step of the gelation processes in both the systems. This mechanism is similar to the gelation of poly (vinylidene fluoride) (PVF₂) in glyceryl tributyrate or in diesters^{26,27} and syn-PMMA in toluene.³⁷ The former polymer transforms from coil to TGTG conformer while the later one transforms from coil-to-helix structure prior to aggregation (gelation).

From the measured least square slope of the Figure 7, A value was obtained 1086 kcal/mol for P3DDT-xylene gel, and this value is larger than that of P3HT-xylene gel (911.5 kcal/mol). The higher A value may be the cause of lower gelation rate of P3DDT gel than that in the later system, e.g., at 25°C , the P3DDT-xylene system does not form gel even standing for 15 days, whereas P3HT produces gel at the same temperature within 25 min. This A value is useful to calculate the free energy of activation for the coil-to-rod transformation (ΔF) if the values of lateral surface energy σ and the overall entropy change (ΔS) for the rod formation are known. According to Hoffman et al.,³⁸ $\Delta S = (\Delta H_u^0/C_\alpha)$ where ΔH_u^0 is the enthalpy change

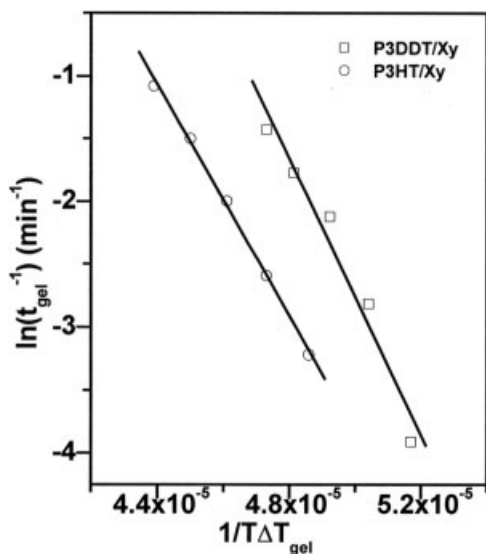


Figure 7 $\ln t_{\text{gel}}^{-1}$ versus $1/T\Delta T_{\text{gel}}$ plot for (9% w/v) P3DDT/xylene gel and (8% w/v) P3HT/xylene gel.

TABLE III
Gelation Parameters of P3ATs Obtained from Gelation Kinetics Study

Gelation parameters	P3DDT gel	P3HT gel ¹⁴
Equilibrium gel melting temperature (T_{gm}^0 , °C)	69	94
Equilibrium dissolution temperature (T_d^0 , °C)	116	170
Energy change of conformational transition (A , kcal/mol)	1086	911.5
Enthalpy of fusion (ΔH_u^0 , kcal/mol)	3.1	3.8
Chain characteristic ratio (C_∞)	5.88	9.36
Molecular width (a , Å)	26	16.6
Layer thickness (b , Å)	7.75	7.75
Entropy of conformational change (ΔS , kcal/deg/mol)	0.527	0.405
Surface energy (σ , kcal/mol)	7.6	7.8
Free energy of conformational change (ΔF , kcal/mol)	35	23.7
Fibrillar length (L , Å)	144	158
Free energy change for critical nucleus formation (ΔG_{del}^* , kcal/mol)	31.8	37.5

for melting of a perfect P3AT crystal²⁰ and C_∞ is the chain characteristic ratio.* The σ value of P3AT crystals has been calculated from the relation⁴³ $\sigma = 0.1 \times \Delta H_u^0(ab)^{1/2}$, 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 P3AT crystal obtained from the reports on wide angle X-ray scattering studies^{44,45} (Table III). Putting the values of ΔS and σ , the activation energy values for the coil-to-rod transformation (ΔF) is found to be 35 and 23.7 kcal/mol for P3DDT gel and P3HT gel, respectively. The volume fraction of polymer used in the measurements for P3HT and P3DDT are 0.067 and 0.07, respectively. So it may be considered that the difference in ΔF value is only due to the alkyl chain length difference. Thus with increase in side chain length, the free energy of activation of the conformational transition is increased. It is reported that the theoretical value of the maximum energy change for the rotation of poly (3-propyl thiophene) (P3PT), with a change of dihedral angle from 0° to 90°, is ~15 kcal/mol.⁴⁶ In P3DDT and P3HT, due to the presence of the longer side chain, the energy barrier would be somewhat higher than that of P3PT. The experimental data are, therefore, approximately in accordance with the theoretical prediction. The higher free energy of activation of the conformational transition (ΔF) for longer pendent alkyl chains may be attributed for the larger steric hindrance experienced by the P3AT main chain during bond rotation compared with that for shorter pendent alkyl chain.

* The C_∞ value of a polymer chain = \bar{r}_0^2/nl^2 , where \bar{r}_0^2 is the mean square unperturbed end to end distance, n is the number of segments and l is the length of the repeating unit. The \bar{r}_0^2/M value was measured from the molecular weight (\bar{M}_w) and intrinsic viscosity $[\eta]$ data of P3HT³⁹ and P3DDT³⁹ (present study) using BSF plot^{41,42} and was found to be 8.58×10^{-17} cm² and 3.58×10^{-17} cm² respectively. Taking $l = 3.9$ Å³⁹ the C_∞ values were found to 9.36 and 5.88 for P3HT and P3DDT, respectively.

Crystallization of the rods

Now, we shall analyze the crystallization of the rods to produce the gel. As evident from the SEM study (Fig. 1) the rods aggregate to produce fibrillar crystals. In our earlier works, we have reported that polymer-solvent compound formation that takes place in these systems, prevents any chain folding process and hence produces the fibrils.¹⁵ The growth rate of the crystals in the solution is given by the Lauritzen-Hoffmann expression^{43,47,48}

$$G = G_0 v_2 \exp\left(-\frac{\Delta G_a}{kT}\right) \exp\left(-\frac{\Delta G^*}{kT}\right) \quad (9)$$

where G_0 is pre-exponential factor, v_2 is the volume fraction of the crystalline polymer, and $\exp(-G_a/kT)$ is the transport factor. The last term is the nucleation term with ΔG^* is the free energy change for the formation of critical size nucleus. For the growth of fibrillar crystals in solution, this expression can be written as:^{27,48}

$$G = G^0 v_2 \exp\left[-\frac{G_a}{kT}\right] \exp\left[-\frac{4l\sigma^2 T_d^0}{kT\Delta H_u^0 \Delta T} + \frac{2\sigma T_d^0}{a\Delta H_u^0 \Delta T} \ln v_2\right] \quad (10)$$

where l is the length of the fibril and k is the Boltzmann constant. T_d^0 is equilibrium dissolution temperature and $\Delta T = T_d^0 - T$. Now, considering the gelation rate (t_{gel}^{-1}) equal to G of the eq. (10) and rearranging we may obtain the relation:

$$\ln t_{gel}^{-1} - \left(\frac{2\sigma_s T_d^0}{a\Delta H_u^0 \Delta T}\right) \ln v_2 = A - \frac{4l\sigma_s^2 T_d^0}{kT\Delta H_u^0 \Delta T} \quad (11)$$

A plot of left-hand-side (L.H.S.) of the equation 11 with $T_d^0/\Delta T$ is shown for the 9% (w/w) P3DDT-

xylene gel in Figure 8. The straight-line nature of the plot supports that crystallization is the final step for the gelation in these two systems. In the calculation of v_2 the density of P3DDT and P3HT has been taken as 1.07 and 1.11 g/cm^{3,44} and that of xylene 0.85 g/cm³. The least square slopes of these plots are calculated and from the slopes of the plots the fibrillar length for each system is calculated and is presented in Table III. The fibrillar length of P3DDT (14.4 nm) is lower than that of P3HT (15.8 nm) though the molecular weight of P3DDT is much higher than that of P3HT. Probably the heavier pendent dodecyl group induces the main chain to retain its coil form more than that in lighter hexyl group. These fibrillar lengths are about 10–15 times larger than that of the PVF₂ gels in diesters.^{27,49} This seems to be reasonable because the P3AT chains are more rigid than that of PVF₂ chain, the more rigid is the chain 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,²⁷

$$\Delta G_{\text{dil}}^* = \frac{4\sigma^2 l T_d^0}{\Delta H_u^0 \Delta T} - \frac{2\sigma k T T_d^0}{a \Delta H_u^0 \Delta T} \ln v_2 \quad (12)$$

Using the values $T = 293$ K, $v_2 = 0.07$ for P3DDT, $v_2 = 0.067$ for P3HT, the value of ΔG_{dil}^* is found to be 31.8 kcal/mol for P3DDT crystals and 37.5 kcal/mol for P3HT crystals, respectively. The activation energy value for crystallization of the rods is lower for P3DDT than that of P3HT indicating crystallization is easier for P3DDT than that of P3HT at similar thermo-

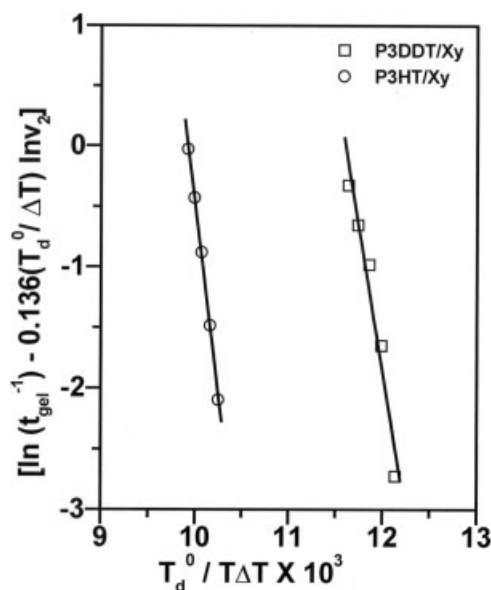


Figure 8 $\ln t_{\text{gel}}^{-1} - 0.136 T_d^0 / \Delta T \ln v_2$ versus $T_d^0 / T \Delta T$ plot for (9% w/v) P3DDT/xylene gel and (8% w/v) P3HT/xylene gel.

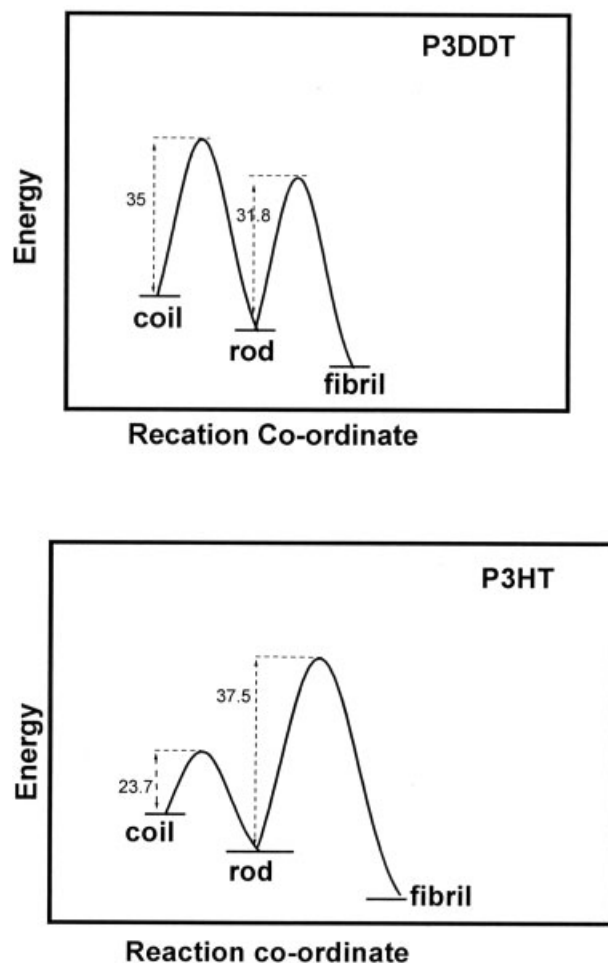


Figure 9 Schematic diagram of energetics of gelation processes of P3DDT and P3HT.

dynamic condition. This appears to be somewhat unusual because P3DDT has longer side chain length so it would be difficult to crystallize. But the ΔG_{dil}^* values indicate the opposite behavior. The probable explanation is the zipping effect of the side chains.²⁰ Owing to the longer side chain of P3DDT the side chain crystallize more easily than that in P3HT. This easier side chain crystallization would enforce the main chain to crystallize more easily. So due to the easier side chain crystallization feasibility the ΔG_{dil}^* is lower for P3DDT than that of P3HT.

In Figure 9, a schematic diagram is drawn to denote the activation energy values of both the processes for gelation in each system. The ΔG_{dil}^* of the P3DDT-xylene system is lower than its ΔF value (Table III). Consequently, here conformational ordering is the rate-determining step for the gelation process. This is in sharp contrast to P3HT gels where ΔG_{dil}^* has much higher value than its ΔF value. So in P3HT-xylene system crystallization is the rate-determining step for the gelation process. Thus, the gelation mechanism of P3AT changes significantly with increasing side chain length.

CONCLUSIONS

Morphology and the thermal investigations confirm the formation of thermoreversible gels in P3DDT xylene system. The isothermal gelation temperatures of P3DDT are much lower than those of P3HT in xylene at an identical concentration of the polymer. The gelation processes approximately obey three dimensional percolation model in both the systems indicating macroscopic mechanism do not change due to change in pendent alkyl chain length of P3AT. The microscopic mechanism of gelation follows a two step process of coil-to-rod transformation and fibrillar crystallization and their role changes with pendent alkyl chain length of P3AT. The fibrillar crystallization is the rate-determining step for the P3HT/xylene gel whereas coil-to-rod transformation is the rate-determining step for P3DDT/xylene gel.

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