Aggregation and Gelation of Fully Conjugated Rigid-Rod Polymers. Poly(2,5-dialkyl-1,4-phenyleneethynylene)s

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ABSTRACT: A series of π-conjugated rodlike polymers, poly(2,5-dialkyl *p*-phenyleneethynylene)s, PPE's, were synthesized with alkyl groups of *n*-butyl (**4a**), *n*-octyl (**4b**), *n*-tetradecyl (**4c**), 2-ethylhexyl (**4d**), and 2-cyclohexylethyl (**4e**). Polymers with linear alkyl side groups (**4a**, **4b**, and **4c**) formed gels in toluene solutions, but polymers with branched (**4d**) or bulky (**4e**) side groups did not. Copolymers also did not form gels. Gels of PPE-**4b** and **4c** show liquid crystalline structures at high concentrations. In the DSC cooling scans of toluene solutions, the primary processes of gelation are identified as distinct exotherms. In the case of PPE-**4c**, the primary exotherm was followed by secondary exotherms. Comparison of DSC scans of nascent and aged gels led to the conclusion that molecular arrangement in the aged gel continued beyond the initial process to result in more ordered microstructures. The fluorescence emission spectra of freshly prepared PPE-**4b** solutions showed two peaks at 425 and 450 nm over a wide range of concentrations, from 5×10^{-4} to 10 g/dL. Upon standing at 25 °C, the emission spectra of a 10 wt % PPE-**4b** solution did not change in the first 8 h. But a new peak at 500 nm emerged after 16 h. The location of the new broad peak is the same as that of solid-state emission due to aggregates/excimers. The intensity of the new peak then grew with time and reached a plateau value after 2 days, about the time needed for gelation by visual inspection.

Introduction

Electroluminescence devices utilizing π-conjugated polymers as emitting layers have become a subject of great interest since the first report of electroluminescence devices (ELDs) based on poly(phenylenevinylene) (PPV) in 1990.[1] Recently, the acetylene analogues of PPV, based on the phenylethynyl unit, poly(phenyleneethynylene)s (PPEs) received increasing attention, mainly due to their conjugated rigid-rod-like character and to their optical and electronic applications.[2−4]

Alkyl and alkoxy substituents improve the solubilities of PPE's in organic solvents, as demonstrated by Bunz[5,6] and West[7] among others,[8−10] thus facilitating the investigations of their properties in the solid and in the solution states. They have shown that the PPEs with linear alkyl or alkoxy substituents tend to aggregate in solutions. To increase our understanding of the aggregation/gelation phenomenon of this class of polymers, we have synthesized poly(2,5-dialkyl-*p*-phenyleneethynylene)s (Scheme 1) and report here a study of molecular aggregation in the sol and gel states of PPEs in toluene. This system was chosen for its typical behavior in a hydrocarbon solvent and for the convenient locations of the gelation temperatures. The work reveals the conditions for the aggregation prerequisite to gelation as well as the structure of the network responsible for the formation of the gel. Time-resolved, dynamic fluorescence analysis was used to study the kinetics of gelation after quenching the system from the sol state to room temperature. The fluorescence emission spectra did not change initially. With time, the fluorescence intensity at 425 nm decreased and the emission peaks shifted to longer wavelength, and eventually an opaque gel was formed.

Experimental Section

Materials. All chemicals used in this study were purchased from Aldrich Chemicals Co. Spectroscopic grade toluene was used for preparing polymer solutions.

Characterization. ^{1}H and ^{13}C NMR spectra were collected on a Bruker ACF 300 spectrometer with chloroform-*d* as solvent and tetramethylsilane (TMS) as the internal standard. Differential scanning calorimetry (DSC) was run on a DSC 2920 module in conjunction with the TA Instrument 5100 system. All melting temperature (T_m) and gelation temperature (T_{gel}) were obtained using DSC. The fluorescence spectra were collected by using Perkin-Elmer LS-50B luminescence spectrophotometer, where the solid-state emission was performed in the 30°/60° angle geometry. A polarized optical microscope (POM, Nikon Optihot) was employed to observe liquid crystal and morphological textures of the polymer sols and gels. A Krüss Processor Tensiometere (k122 program) was used for surface tension measurement with detection limit of ±0.01 mN/m.

Results and Discussion

Gel Formation. Gel formation was observed visually after the toluene solution was allowed to stand at room temperature for periods up to several weeks. The visual observations are compiled in Table 1. Polymers with linear alkyl groups (**4a**, **4b**, and **4c**) formed gels, whereas **4d**, **4e**, and copolymers, which have branched, bulky, or mixed side groups, did not. This indicates that the nature of the side chain has a dominant influence on gelation. It is worth emphasizing that (1) for the three gel-forming polymer solutions (**4a**−**c**) gelation occurred at concentrations as low as 2 wt %, although the gelation time at room temperature could be weeks, (2) gels made from **4c** were always turbid whereas polymer **4a** always formed transparent gels, and (3) polymer **4b** formed transparent gels at low concentrations but turbid gels at high concentrations. For the turbid gels, phase separation must have taken place during structural development.

Gelation Study by Differential Scanning Calorimetry (DSC). a. Gelation upon Cooling. Gelation of toluene solutions of PPE's was studied by DSC. The gels, placed in closed sample pans, were heated to 110 °C until they became fluid solutions and then cooled at

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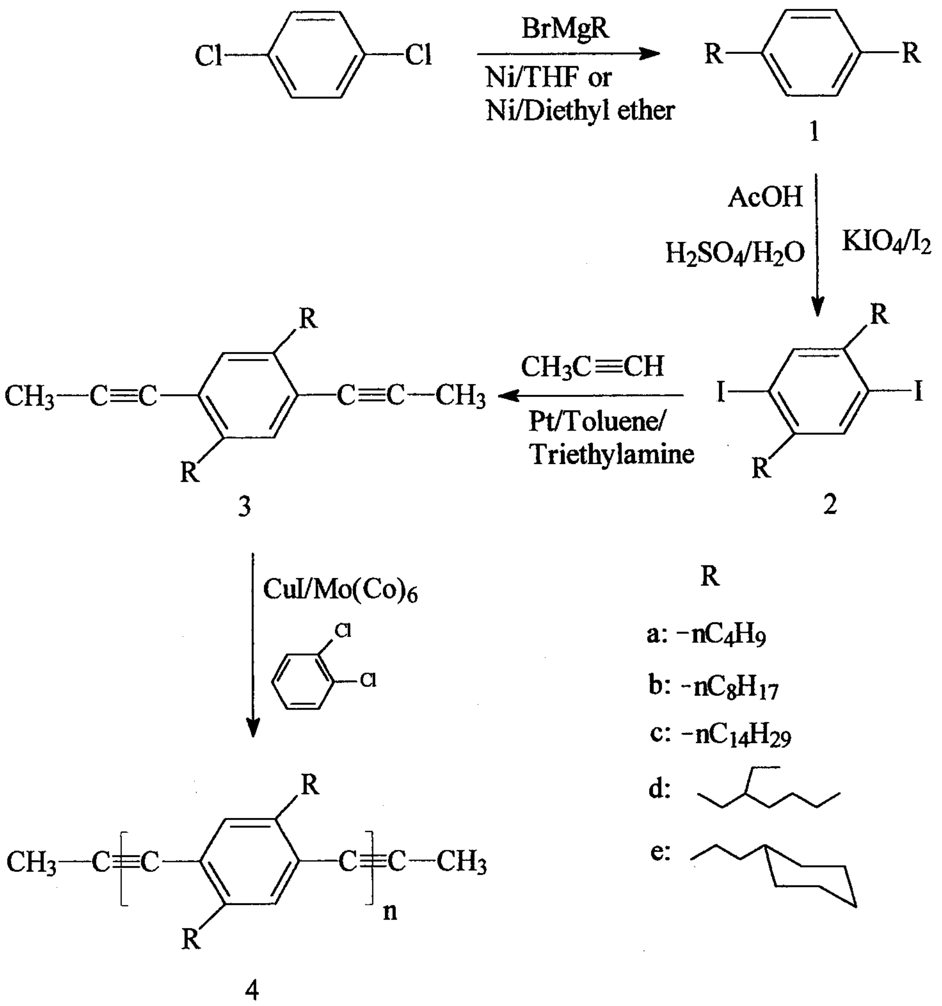
Scheme 1. Synthesis of PPEs



a rate of 5 °C/min to temperatures well below room temperature. Although the time scale of the cooling experiment is short and the scan does not always capture all the slow processes involved in gelation, the results still provide useful information. In Figure 1, DSC cooling traces of 10 wt % PPE solutions are shown for polymers **4a**, **4b**, and **4c**. For solution **4a**, a small but distinct exothermic event was seen at ~−41 °C (curve a) which was designated here as the gelation temperature, T_{gel}. The term gelation temperature used here is meant only to indicate the onset of a complex process. The discussion of the mechanism involved in this step will be deferred to the end of this paragraph. For solutions of polymers **4b** and **4c**, sharp exothermic peaks appeared at 8 and 19 °C, respectively, which were also designated as gelation temperatures (curves b and c). Clearly, the length of the alkyl side chain has an important bearing on T_{gel}. The primary process in gel formation in the PPE system is the assembly of rodlike chains into regular arrays akin to the structure in the solid state[11] but on a microscale. These microassemblies

Table 1. Gel Formation Properties of PPEs in Toluene at Room Temperature[a]

polymer	concn (wt %)	gelation	gelation time[e]	turbidity
4a	5	yes	12 h	clear
4b	2	yes	3 weeks	clear
4b	5	yes	1 week	clear
4b	10	yes	48 h	slightly cloudy
4b	20	yes	2 h	turbid
4c	5	yes	1 h	turbid
4d	5	no		
4e	dilute[d]	no		
4a-*co*-**4b**[b]	5	no		
4a-*co*-**4c**[c]	5	no		

[a] The gelation time is dependent on concentration that will be discussed in other sections. [b] The random copolymer of **4a** and **4b** in a molar ratio of 50/50. [c] The random copolymer of **4a** and **4c** in a molar ratio of 50/50. [d] Due to low solubility in toluene. [e] Measured by the inverted tube method.

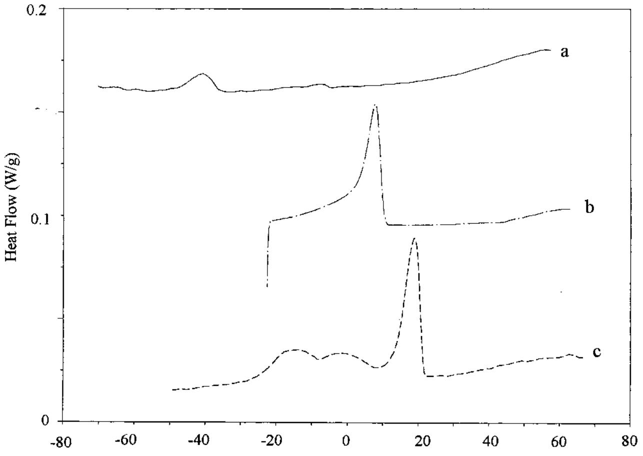


Figure 1. DSC cooling thermograms of 10 wt % PPE solutions in toluene: (a) **4a**, (b) **4b**, and (c) **4c**.

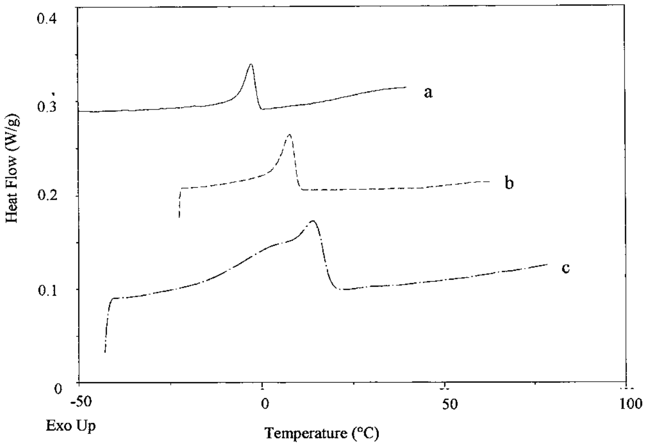


Figure 2. DSC cooling thermograms of **4b** in toluene: (a) 5 wt %, (b) 10 wt %, and (c) 20 wt %.

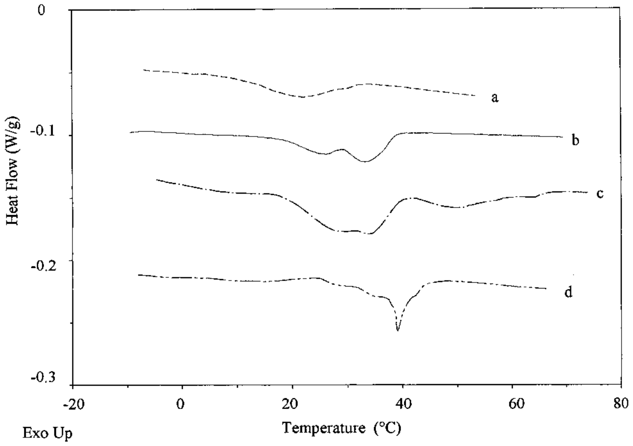


Figure 3. DSC heating scans of PPE4b gels in toluene: (a) 5 wt %, (b) 10 wt %, (c) 20 wt %, and (d) aged 10 wt %.

Table 2. Gel Formation Properties of PPEs in Toluene Measured by DSC Cooling Scan at 5 °C/min

polymer	concn (wt %)	gelation temp (°C)	enthalpy (J/g)
4a	10	−41	0.86
4b	10	8	5.33
4c	10	19, −1, −13	9.38[a]
4b	5	−3	3.52
4b	20	14, 4	9.41[a]

[a] Total enthalpy.

act as physical cross-links[12−16] in much the same way as aggregates of syndiotactic poly(methyl methacrylate) sequences in PMMA gels or isotactic polystyrene sequences in PS gels. Thus, it seems reasonable that long alkyl side chains, which promote the formation of ordered array structure in the solid state, also cause gelation to occur at a higher temperature.

Two additional exotherms are seen in Figure 1c at −1 and −13 °C, which are probably associated with secondary processes of structure development and network formation although there is no consensus in the literature[17−19] about the nature of the secondary processes. We hasten to add here that the absence of the secondary exotherm in the cooling curve b of Figure 2 does not mean that such processes are inoperative at room temperature over an extended period of time. The gelation of PPE-**4b** solutions was then studied at different concentrations. The DSC cooling scans of 5, 10, and 20 wt % solutions are shown in Figure 2. The gelation temperatures represented by the exothermic peaks increase with concentration from −3 to 8 and 14 °C (curves a, b, and c). The peak at 14 °C in curve c overlaps a broad exotherm ranging from about 5 to −20 °C, which is again thought to be associated with secondary processes in structure development. The gelation temperatures and the attendant enthalpy changes are listed in Table 2. As a point of reference, 5.33 J/g of polymer for PPE-**4b** equals 1.6 kJ/mol of repeating unit.

b. Nascent Gels. The nascent gels obtained from the cooling experiments were immediately heated in the sample pan. To study the gel melting processes, the DSC heating scans in Figure 3 for the PPE-**4b** nascent gels are shown for three concentrations, 5, 10, and 20 wt %. For the 20 wt % gel (Figure 3c), which is turbid, the thermogram shows two overlapping endotherms at 30 and 34 °C, respectively. The former is the counterpart of the secondary process in Figure 2c, and the latter, the counterpart of the primary process in the same curve. Shortly after the 34 °C event, there is another endotherm centered at 51 °C. Since the gel is turbid, i.e., phase-separated, and shows liquid crystalline structures, we surmise that the endotherm is related to transition in the liquid crystalline phase.

In the heating scan of the nascent PPE4b 10 wt % gel, two neighboring endotherms appear at 27 and 33 °C; these temperatures are very near the ones seen in the thermogram of the 20% gel and are therefore also assigned as counterparts to the secondary and the primary processes. The 10 wt % gel, however, exhibits only few isolated, small domains of liquid crystalline structure when examined by polarized optical microscopy. Consequently, the enthalpy associated with liquid crystalline transition is too small to be detected by DSC, and no endotherm at higher temperature is seen. For the 5 wt % gel, only one broad endotherm is seen at ∼5−35 °C which may actually encompass both the primary and the second processes.

c. Aged Gels. The full development of microstructure and network proceeds beyond the initial gelation process. Hence, the DSC heating scans of aged gels, such as the ones obtained by standing at room temperature for extended periods of time (Table 1), are not necessarily identical to the thermograms of the corresponding nascent gels. An example is given by curved d in Figure 3 for the 10 wt % PPE-**4b** gel after standing at room temperature for over a month. In comparing curves b and d in the figure, we see that the endotherm at 33 °C is much sharper in the aged sample. The secondary process now appears as shoulder(s) in curve d. the results may be construed as indication of ongoing process of molecular arrangement which leads to more ordered structures over a period of time.

Polarized Optical Microscopy (POM). After standing at room temperature for several hours to 3 weeks, depending on concentrations, PPE-**4b** solutions turned into gels. The minimum concentration for gelation was about 2 wt %. However, birefringence was observed only when the polymer concentration was above a certain critical value, about 10 wt % in toluene. Optical micrographs revealed nematic liquid crystalline structures (Figure 4a) in only few small domains, but the rest of the sample was isotropic (dark regions). Birefringence disappeared upon heating; in the meantime, solvent was evaporated slowly to increase the concentration for the next observation. After partial solvent evaporation, the

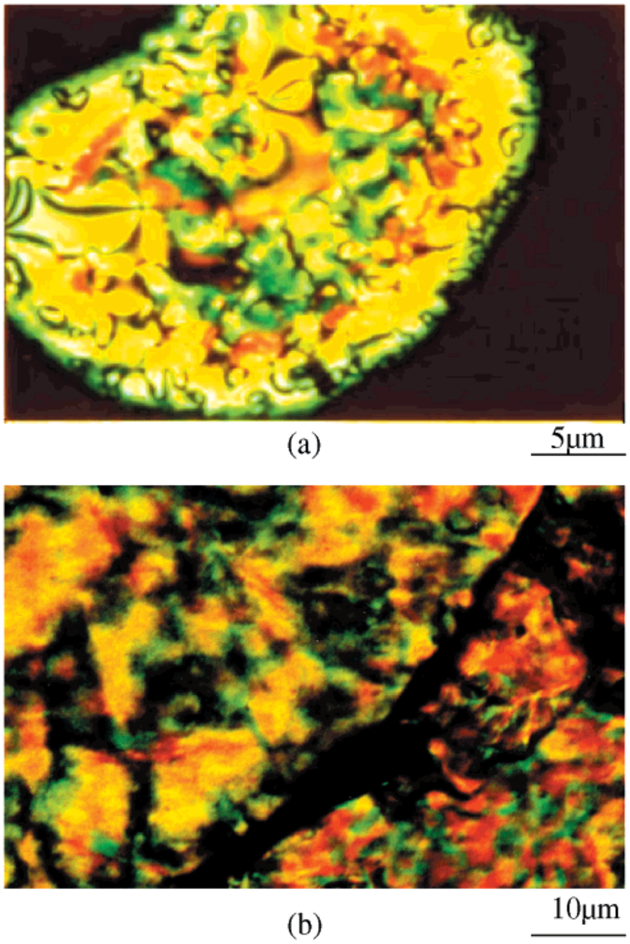


Figure 4. Polarized optical micrographs of PPE-**4b** in toluene at room temperature: (a) 10 wt % after 48 h and (b) 42 wt %.

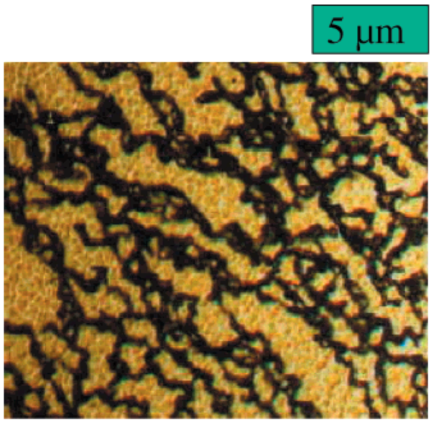


Figure 5. Optical micrographs of microgels prepared from 10 g/dL solutions (scale as indicated).

sample was cooled to room temperature, and the concentration was determined by weighing. At the sample concentration of about 42 wt %, birefringent domains filled nearly the whole sample, and nematic texture was clearly identified (Figure 4b). The same procedure was repeated to remove more solvent, but the texture remained almost unchanged except for some growth in the size of the domain. On the other hand, fibril structures were observed (Figure 5) when the sample was prepared by flashing off the solvent.

Photoluminescence Spectra. Photoluminescence spectroscopy is uniquely suitable to study molecular organization of highly conjugated polymers like the PPE's because the spectra is sensitive to the state of aggregation of the chromophores. In our experiments, a 1 mm sample cell in a front-face 30°/60° angle geometry was used for the measurement in order to minimize the self-filtering effects due to high optical densities or to sample turbidity. The photoluminescence spectra were found to be insensitive to the excitation wavelength in the range 330−400 nm. All emission spectra were obtained by excitation at the wavelength of the respective absorption maximum. The PPE-**4b** sample was studied more extensively than the other polymers, and the results are given below.

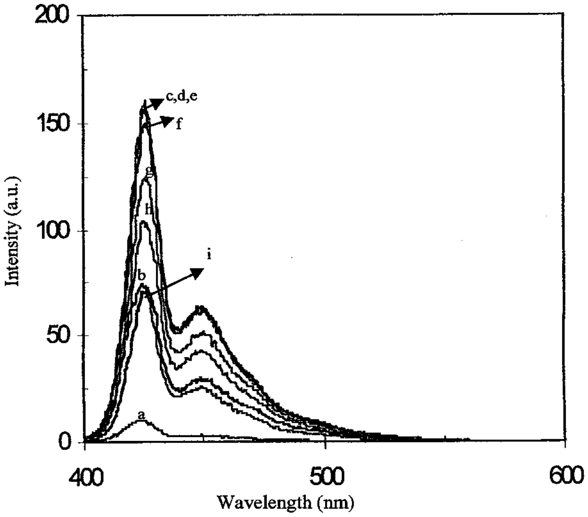


Figure 6. Fluorescence spectra of **4b** in toluene as a function of concentration: (a) 0.0005, (b) 0.005, (c) 0.05, (d) 0.1, (e) 0.3, (f) 0.5, (g) 3.0, (h) 5.0, and (i) 10.0 g/dL.

The PL spectra of PPE-**4b** (Figure 6) show resolved vibronic structures at 425 and 450 nm due to the coupling of the excitonic transitions to inter-ring bond stretching vibrations. But before we employed PL to study molecular aggregation in gel-forming solutions, the fluorescence emission spectra of freshly prepared toluene solutions of PPE-**4b** were acquired at 25 °C over a wide range of concentrations, from 5×10^{-4} to 10 g/dL (Figure 6). At low concentrations (curves a, b, and c), the emission intensity increased almost proportionally with concentration. In this concentration regime, the molecules act as individuals or isolated chains[20] independent from each other, and the emission intensity is the sum of the individual concentrations. From 0.05 to 0.3 g/dL, the emission intensities remained nearly constant (curves c, d, and e). At higher concentrations (curves f, g, h, and i), the emission intensity decreased as concentration increased. Once the solution concentration reaches ~0.05 g/dL and beyond, self-quenching and other factors increase the probability for energy losses and cause a decrease in fluorescence efficiency and emission intensity. Significantly, however, the intensity ratio of the two emission bands at 425 and 450 nm is almost invariant with concentration. This implies that all the emissions originate from the same category of species, that is, isolated chains.

Although the emission maxima are located at the same wavelengths in all freshly prepared PPE-**4b** solutions regardless of concentration, the PL spectra must change in the course of gelation since the state of molecular aggregation cannot remain the same. In using PL to probe microstructure development that leads to

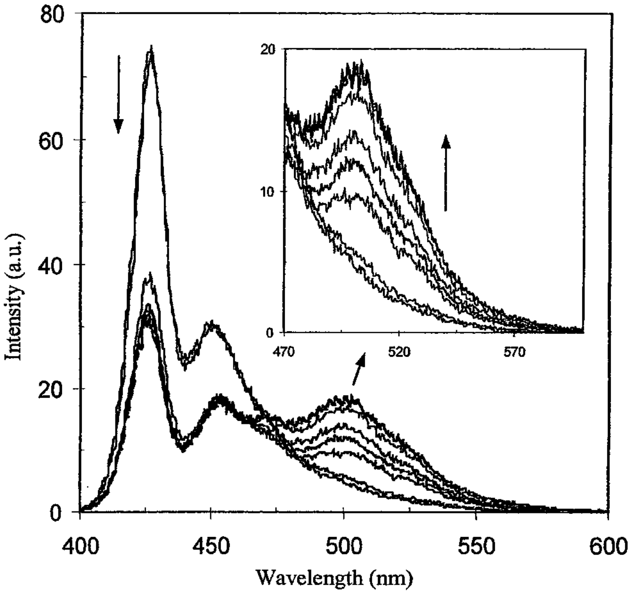


Figure 7. Fluorescence spectra of 10 wt % solution of **4b** in toluene as a function of time (follow the arrow direction from end to head): 0, 8, 16, 24, 32, 40, 48, 60, and 72 h, respectively.

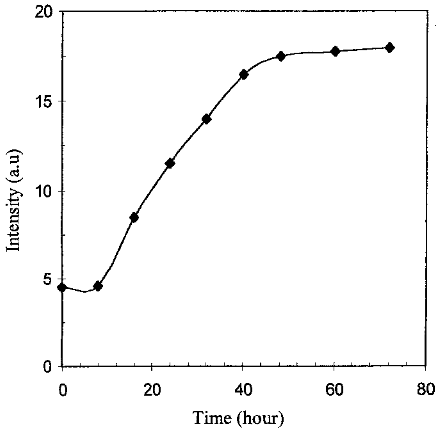


Figure 8. Intensity of the emission peak at 500 nm as a function of time.

gelation, the kinetics of emission of the 10 wt % PPE-**4b** toluene solution was monitored at 25 °C, and the results are presented in Figure 7. This particular concentration was chosen because the aged gel was birefringent and contained liquid crystalline domains. At short times (<8 h), the emission spectra remained the same. At 16 h, a new peak at 500 nm appeared, and the peak intensity increased gradually with time. Concomitantly, the intensities of the 425 and 450 nm peaks decreased at 16 h but then underwent no further change. Therefore, two different fluorescent species coexist after 16 h. The identities of the two species can be deduced from the following observations. First, the ratio of the intensities of the 425–450 nm peaks throughout the aging experiment is the same as in the freshly prepared solution and also the same as the value in dilute solutions. Second, the location of the featureless, broad peak at 500 nm is the same as that of solid-state emission due to aggregates/excimers. We therefore conclude that both isolated chains and excimers are present in the 10 wt % PPE-**4b** solution at long times. Figure 8 shows a plot of the peak intensity at 500 nm as a function of time. As can be seen, the intensity hardly changes in the first 8 h but increases steadily afterward until a plateau value is reached after 48 h, which is approximately the time needed for gelation according to visual observation. Thus, the full development of network of microaggregates is a slow and complex process.

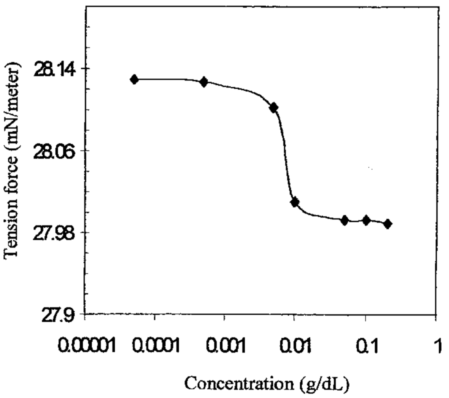


Figure 9. Surface tension force of PPE-**4b** as a function of concentration.

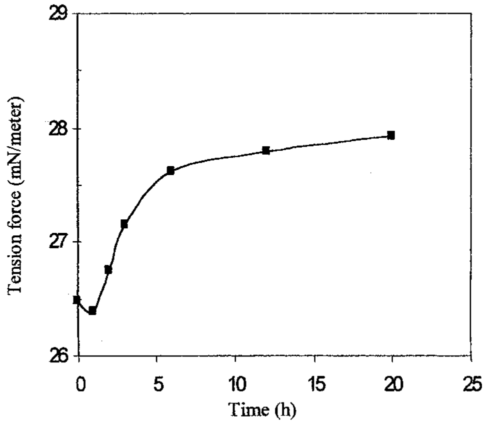


Figure 10. Surface tension force of 10 wt % PPE-**4b** in toluene as a function of time.

Surface Tension. The surface tensions of these PPE solutions were measured quickly in a short period of within 100 s and were found to be dependent on concentration (Figure 9). A sharp drop in the surface tension began at around 0.01 g/dL followed by another decrease between 0.1 and 10 g/dL. We have mentioned earlier that the PPE-**4b** 10 wt % gel is slightly cloudy. Therefore, phase separation must have taken place in the course of gelation. We surmise that one of the phases is solvent-rich, probably ~100% toluene. In search of a simple method to study this process, we tried surface tension measurements. A PPE-**4b** 10 wt % solution was quickly brought from the sol state to 25 °C and equilibrated at that temperature for 30 min. Surface tension measurements were conducted at various time intervals, and the results are given in Figure 10. There was an initial decrease in surface tension, but after 1 h the values started to increase and reach, after 40 h, 28.13 mN/m, near the value for toluene. Although the photoluminescence spectra in Figure 7 show no change in the first 8 h, the surface tension measurements suggest subtle processes of molecular organization already in progress. The final surface tension value is consistent with the notion of liquid–liquid phase separation.

If the above interpretation is correct, a gestation period at 25 °C precedes the appearance of excimers, which are composed of cofacially stacked chromophores a few angstroms (<5 Å) apart. This does not preclude the possibility of looser aggregates being formed during the gestation period. Nor is the scenario necessarily at odds with DSC cooling scans, since the gelation temperature in the cooling scan is 8 °C, at which the rate of aggregation may be quite different.

Conclusions

1. PPEs with linear side groups (**4a**, **4b**, and **4c**) formed gels in toluene solutions, but polymers with branched (**4d**), bulky (**4e**), or mixed side groups did not. Gels of PPE-**4b** and **4c** show liquid crystalline structures.

2. In the DSC cooling scans of toluene solutions, the primary processes of gelation were represented by distinct exotherms. For the PPE-**4c** 10% solution, the primary process was followed by secondary exotherms.

3. A comparison of the DSC heating scans of nascent and aged gels suggests that molecular arrangement in the aged gel is an ongoing event which goes beyond the initial primary process to result in more ordered microstructures.

4. The fluorescence emission spectra of freshly prepared PPE4b solutions, ranging in concentrations from 5×10^{-4} to 10 g/dL, showed two peaks at 425 and 450 nm. Upon standing at 25 °C, the emission spectra remained the same for the first 8 h, but a new peak appeared at 500 nm after 16 h. The intensity of the new peak increased steadily afterward until a plateau value was reached after 48 h, about the time required for gelation according to visual observation. The location of the new broad peak is the same as that of solid-state emission due to excimers.

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