Gel Formation via Physical Cross-Linking in the Soluble Conjugated Polymer, Poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene], in Solution by Addition of Alkanes

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Received January 11, 2008; Revised Manuscript Received June 22, 2008

ABSTRACT: In poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV) solution in 1,3-dichlorobenzene (DCB), an addition of nonsolvent alkane can lead to a formation of gel and a growth of the content of aggregates (with intersegmental $\pi-\pi$ interaction) on standing without stirring. Such a gel then becomes immobile after standing for about 13 h but mobile again after a vigor agitation. The viscosity of MEH-PPV solution in DCB is found to decrease with the addition of nonane until a minimum is reached at 30 vol % and then increase rapidly with further addition. Thus, we propose that the gel formation resulted from an occurrence of interchain physical cross-linking via interaction between neighboring alkoxy side chains with nonane as a bridge. The generated aggregates are found to be of "intrachain" because MEH-PPV chains tend to adopt a coil conformation in the presence of nonane as revealed by an initial drop of solution viscosity upon addition of nonane. Additions of other alkanes are investigated also, but a complete gelation can happen only as the linear chain length of alkanes is more than nine carbons.

Introduction

Conjugated polymer is one of the widely studied macromolecules recently because it possesses the characteristic of semiconductor and ease of solution processing.[1] Its application as emitting layer in polymer light-emitting diode (PLED) has been vastly reported due to that PLED is a potential candidate for next generation flat panel display.[2,3] In solution processing, sometimes a manipulation of solution viscosity is desired even to an extent of gelation.

Gel formation has been observed in nonconjugated comb-shaped polymers (for example, polyacrylates) when their solutions in alcohols or alkanes are cooled down to lower temperature (for example, poly(hexadecyl acrylate) in *n*-octyl alcohol at 24 °C).[4] The gel so generated is resulted from a formation of supermolecular networks in which crystalline intermolecular associates act as physical cross-linking sites. For polyacrylates, a presence of longer side chain or adding alcohols (or alkanes) with longer alkyl chain length can lead to an increased extent of gel formation. But, for the model conjugated polymer MEH-PPV,[5] a gel formation does not occur in its solutions in various alcohols (linear alkyl chain with carbon number from 1 to 4, 6, 8, 10, and 12) or alkanes (hexane and cyclohexane). These alcohols and alkanes are nonsolvents for MEH-PPV; only low-MW fractions can be dissolved. MEH-PPV in a homologous series of linear alcohols and solvent−nonsolvent systems has also been reported.[6] They prepared several percentage of hexanol/chloroform solutions, but there has no gelation been mentioned in their work. In addition, the gel formation of polyfluorenes has been reported in single solvent-based solution; for example, good solvent (1,2,4-trichlorobenzene)[7] and poor solvent (cyclohexane[8] and methylcyclohexane[9]) are used as the solvent. Low-molecular-weight organogels were also reported,[10] resulting from noncovalent interactions, such as hydrogen bonding, π-stacking, solvophobic effects, and donor−acceptor interactions. Reports on gel formation in solutions of MEH-PPV are scarce, except for MEH-PPV/polyethylene solution in xylene at 126 °C which could form a gel upon cooling[11] and MEH-PPV solution in toluene at room temperature, which is able to form a soft gel after long-term storage for several weeks.[12] Though the definition of soft gel is not given in ref 12, it can be taken as a gel with slight fluidity according to their description.

Here, we observed that a gel can form in MEH-PPV solution in 1,3-dichlorobenzene (1,3-DCB; designated as DCB for simplicity in this work) via an addition of alkanes such as nonane, which is attributed to an occurrence of interchain physical cross-linking by interaction between neighboring alkoxy side chains with alkane as a bridge. An immobile gel is generated as an appropriate amount of a linear alkane with a carbon number of nine or more is added. In addition, intrachain aggregates are found to form also during the gel formation due to an adoption of a contract coil conformation.

Experimental Section

Materials. MEH-PPV was synthesized by following the method proposed by Wudl and co-workers,[13] and the details were reported in our previous work.[14] The weight-averaged molecular weight (M_w) and polydispersity index of MEH-PPV are 379 000 Da and 1.55, respectively, as determined by gel permeation chromatography using polystyrenes as standards. 1,3-Dichlorobenzene (Tedia, >98%), nonane (TCI, >98%), hexane (Tedia, >99%), 3-methylpentane (Aldrich, >98%), and cyclohexane (Fisher Scientific, >98%) were directly used as purchased.

Instrumentation. *Ultraviolet−Visible (UV) Absorption, Photoluminescence (PL), and Photoluminescence Excitation (PLE) Spectroscopic Measurements.* The MEH-PPV solution used for measuring the optical spectra was prepared by first dissolving its powder in DCB under stirring with a concentration of 20 mg/mL and then pouring nonane into this solution to lower its concentration to 10 mg/mL so that the volume ratio of DCB to nonane is 1/1. UV−vis absorption spectra of the solutions were measured by a UV−vis−near-IR spectrometer (Perkin-Elmer, Lambda 19) with a cell of 1 mm path length quartz cuvette on standing without stirring for various periods of time: 0 min, 10 min, 30 min, 1 h, 4 h, 8 h, 13 h, 18 h, and 24 h. In the meantime, PL and PLE spectra of the solutions taken from the same batch as used for UV−vis measurements were also measured by a fluorescence spectrometer (FluoroMAX-3 from Jobin Yvon) with a cell of quartz cuvette (1 cm path length) on standing at the same time periods. The reason for choosing a 1 cm path cuvette is due to the PLE spectra measured

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10.1021/ma800076g CCC: $40.75

from a 0.1 cm cuvette would be similar to the UV−vis spectra, in which the peak at long wavelength (about 600 nm) is weak.[15]

Viscosity Measurements. The MEH-PPV solutions (0.5 mL, 10 mg/mL) in DCB/nonane with specific volume ratios were poored into a cylindrical sample container, which then was sealed by paraffin wax film to prevent DCB/nonane from evaporation during measurement. The solution viscosity was measured by a Brookfield DV-III+ rheometer at 27, 30, and 33 °C.

Results and Discussion

1. Gel and Aggregates Formation. The MEH-PPV solution (10 mg/mL in DCB/nonane at the volume ratio 1/1) becomes an “immobile gel” (defined as a gel without appreciable gravitational flow within a reasonable time period for eyes observation, a few hours for example) after standing without stirring at room temperature for 2 days, as shown in Figure 1a. Such gel formation is due to the addition of nonane, since the MEH-PPV solution in DCB with the same concentration (10 mg/mL) remains fluidic after standing without stirring for 2 days. However, a gelation does not occur as similar amount of the nonsolvent, such as methanol, is added into a MEH-PPV solution in the good solvent, chloroform.[5] We investigate the optical spectral changes during this gelation process as shown in Figure 1b in order to explore a possible occurrence of interchain and intrachain interactions. Obviously, the wavelength at the maximum intensity in the PL spectrum ($\lambda_{\max,\mathrm{PL}}$) shifts from 615 to 621 nm as the standing time increases from 0 to 13 h and remains unchanged afterward. In addition, the intensity of long-wavelength part (635−700 nm) increases with standing time but remains unchanged after 13 h. The fluidity of the solution becomes completely “immobile” after 13 h standing. In other words, the time required for the complete gelation can be taken as 13 h under standing without stirring. Because two peaks at 565 and 610 nm in the PL spectrum of MEH-PPV dilute solution (10^{-4} mg/mL in DCB, see inset (a) of Figure 1b) belong to 0−0 and 0−1 bands of isolated chain emissions of MEH-PPV, respectively,[15] it is straightforward to assign the PL emission peak at around 615 nm as the isolated chain emission (0−1 band) of MEH-PPV. However, the disappearance of isolated chain emission of the 0−0 band in Figure 1b means that the main peak (615 nm) actually originates from an emission of the interchain aggregates which form at higher solution concentration. For example, MEH-PPV solution in toluene with a concentration of 10^{-3} mg/mL shows a dominated emission band peaked at 598 nm contributing from interchain aggregates, which is very close to the 0−1 band of isolated chain emission, and the intensity of isolated chain emission of the 0−0 band (555 nm) appears only one-fifth of that of the aggregates.[16] Actually, the disappearance of isolated chain emission is due to the different measurement methods. We also performed the PL spectra of MEH-PPV solution (10 mg/mL in DCB) measurement by using front-face and side-face detections from a 0.1 cm cuvette, shown in Figure 1c. The PL spectra measured from a front-face detection shown a strong isolated chain emission at 569 and 610 nm, which can be assigned as the 0−0 and 0−1 bands of isolated chain emissions as the case of inset (a) in Figure 1b. The presence of strong 0−0 and 0−1 bands of isolated chain emission and weak aggregates emission means that the intensity of aggregates emission relative to isolated chain emission is highly dependent on different measurement methods. According to our previous work,[15] the front-face detection can be used to avoid self-absorption when the concentration higher than 10^{-2} mg/mL. However, for our case, the solution concentration (10 mg/mL) is very high, and the use of front-face detection still cannot avoid self-absorption, if the cuvette is as thick as 1 cm. It should be noted that the front-face detection from a 0.1 cm cuvette can avoid self-absorption and emphasize the emission of isolated chain.[17] However, the emission from aggregates at long-wavelength part would be weak, leading to an uncertainty in relative intensity at that part. Therefore, we have to use a 1.0 cm cuvette to perform PL spectra for investigation of generation of aggregates with time. Though, the growth of long-wavelength component might come from two origins: one is the generated aggregates (and its nature and formation will be described in more details in the next paragraph), and the other is excimers. From the observation that the intensity of the long-wavelength component (580−620 nm) in the UV−vis absorption spectra increases with standing time from 0 to 13 h and remains almost the same afterward (inset (b) of Figure 1b, in which the UV−vis spectra cover only 580−620 nm since below 580 nm the absorption spectra are over scale), it is clear that the ground-state emitting species (i.e., aggregates) form during the gel formation and contribute to the long-wavelength component in the PL spectra. A brief descrip-

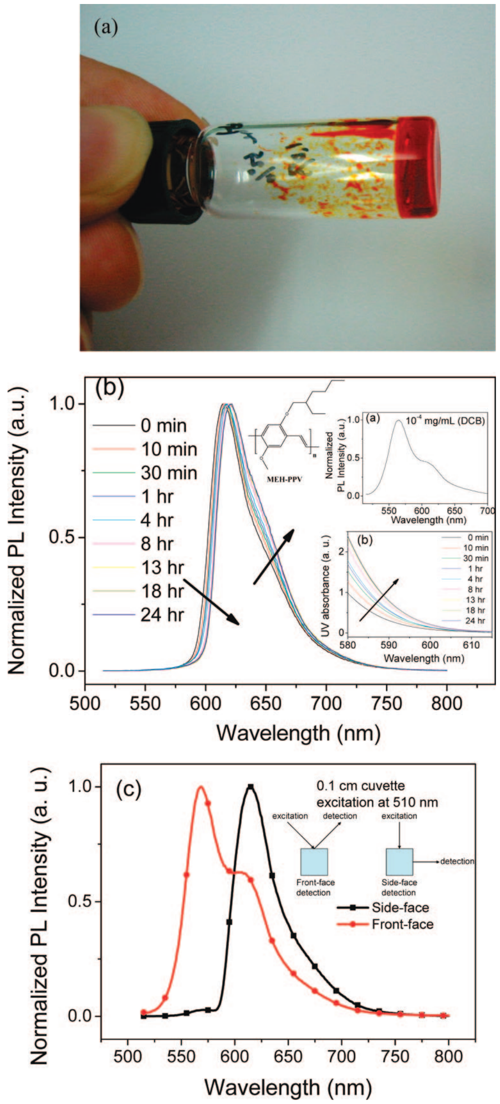

Figure 1. (a) The picture shows no gravitational flow of the gel formed in MEH-PPV solution (10 mg/mL, the volume ratio of DCB/nonane is 1/1) after standing for 2 days under room temperature without stirring. (b) PL spectra (excited at 510 nm) of MEH-PPV solution (10 mg/mL, the volume ratio of DCB/nonane is 1/1) after the standing times: 0 min, 10 min, 30 min, 1 h, 4 h, 8 h, 13 h, 18 h, and 24 h at room temperature without stirring. These PL spectra were normalized at their corresponding $\lambda_{\max}$. Inset (a) shows the PL spectrum (excited at 510 nm and normalized at 565 nm) of the MEH-PPV solution (in DCB) with a concentration of 10^{-4} mg/mL. Inset (b) illustrates the corresponding UV absorption spectra for different standing times. (c) PL spectra measurement of MEH-PPV solution (10 mg/mL in DCB) by using the front-face and side-face detections from a 0.1 cm cuvette.

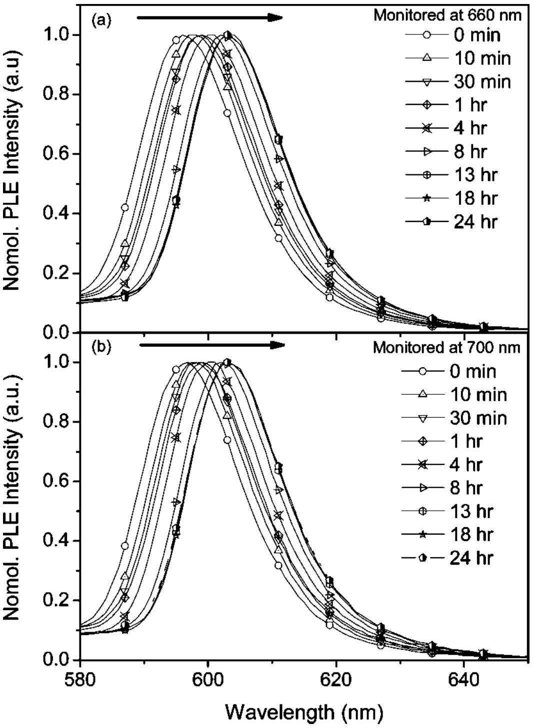

Figure 2. PLE spectra monitored at (a) 660 nm and (b) 700 nm from the MEH-PPV solution same as that used in Figure 1b. These PLE spectra were normalized at their corresponding $\lambda_{\max,\text{PLE}}$.

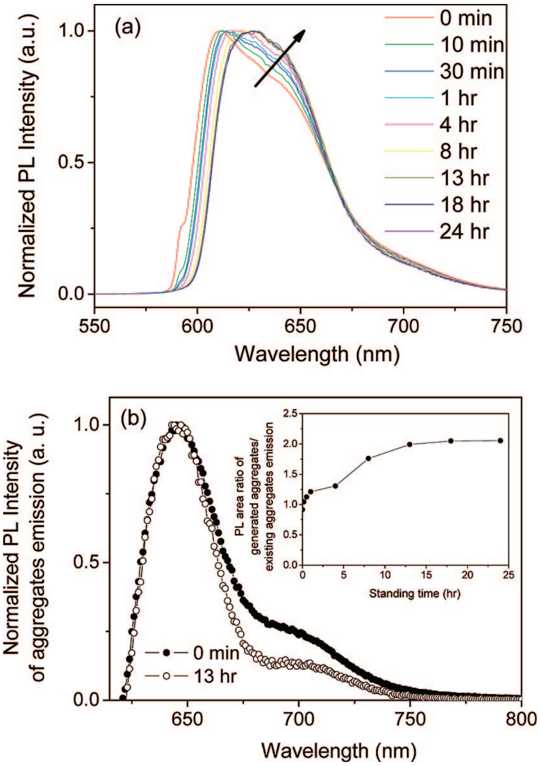

Figure 3. (a) PL spectra excited at 590 nm (normalized at their corresponding $\lambda_{\max}$) from the same MEHPPV solution as in Figure 1b. (b) Aggregates emission obtained by subtracting normalized PL spectrum excited at 510 nm (in Figure 1b) from that excited at 590 nm (a) at the standing times of 0 and 13 h. The inset in (b) shows the PL area ratio from the aggregates emission to the existing aggregates emission at the initial versus standing time.

tion on the characteristics and formation of the aggregates is given below.

Aggregates are ground-state emitting species formed by $\pi-\pi$ interaction between intersegments of same chain (intrachain aggregates) or neighboring chains (interchain aggregates).[18,19] The main characteristics of aggregates are that a presence of new absorption band and availability for direct excitation giving red-shifted and featureless emission spectrum relative to single chain emission.[18] For MEH-PPV, the formation of aggregates can be manipulated by a choice of good and poor solvents for interchain and intrachain aggregates formations, respectively,[5,18] change of solution concentration,[18] thermal annealing,[20,21] and extension of solution storage time.[11] Among these factors, effect of solvent power on aggregates formation is of particular interest since it explains the importance of chain conformation on optophysical (and even electrical) behaviors; a good solvent (for example, chloroform or chlorobenzene) allows a more extended MEH-PPV chains, but an addition of poor solvent (for example, alcohol) into the solution can lead to a coiling of main chain.[5,18]

Further support on the aggregates formation can be given by PLE spectral change of the MEH-PPV solution (same as that used in the PL measurements), as shown in Figure 2a. The excitation wavelength contributing to the PL emission intensity at 660 nm (the wavelength at the shoulder of the PLs in Figure 1b) apparently red shifts, and the peak position ($\lambda_{\max,\text{PLE}}$) changes from 596 to 603 nm as the standing time increases from 0 to 13 h, after which the PLE spectrum shows no appreciable change. At the monitored wavelength of PL emission 700 nm (the wavelength at the tail of the PLs in Figure 1b), the similar results are observed as for the case of 660 nm as shown in Figure 2b. Therefore, these PLE results further support that the new emitting species generated during the gelation period is aggregates, and its content increases with standing time and levels off at 13 h. The red shifts should not be resulted from an increase of conjugation length of MEH-PPV because the shapes of all the PLE spectra are featureless and an emission from single chain with increased conjugation length should involve a fine vibronic transition as reported in a study of solvatochromism of poly(3-hexylthiophene) in solvent/nonsolvent mixtures (for example, $CHCl_3$/methanol).[22]

Furthermore, the PL spectra (Figure 3a) of the same MEH-PPV solution (10 mg/mL in DCB/nonane at the volume ratio 1/1) excited by the light 590 nm (mainly for an excitation of aggregates) and collected at various standing times up to 24 h exhibit red shifts such that $\lambda_{\max,\text{PL}}$ shifts from 612 nm at the initial to 630 nm at 13 h and remains unchanged afterward. In order to investigate the growth of aggregates content quantitatively, we subtract the PL spectrum excited at 510 nm (Figure 1b) from that at 590 nm (Figure 3a) for the same specific gelation time.[18] The resulting aggregate emission spectra at the standing times, 0 and 13 h, are shown in Figure 3b, which are similar and both have a peak at 646 nm and a shoulder at around 700 nm, implying that the extent of $\pi-\pi$ interaction of the aggregates so formed does not increase with gelation time. We also calculate the PL area of the emission from the aggregates at each gelation time relative to that of the existing aggregates emission originally as shown in the inset of Figure 3b. As can be seen, the ratio increases rapidly at initial and then levels off at around the standing time 13 h, indicating that at which the gel formation is almost completed.

2. Physical Cross-Linking and Intrachain Aggregation during the Gelation. In order to explore the mechanism of gelation, variations of solution viscosity versus nonane content in the DCB/nonane solutions were measured at 27, 30, and 33 °C, as shown in Figure 4. The viscosity gradually decreases from 23.4 to 15 cP when nonane vol % increases from 0 to 30%, indicating that the gelation does not occur when nonane content is less than 30%. But, the viscosity then increases rapidly to 32 cP when nonane content reaches 40%. At the higher

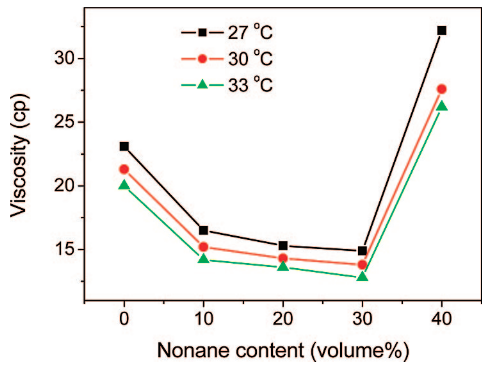

Figure 4. Viscosity versus nonane content measured at different temperatures for MEH-PPV solutions with a concentration of 10 mg/mL.

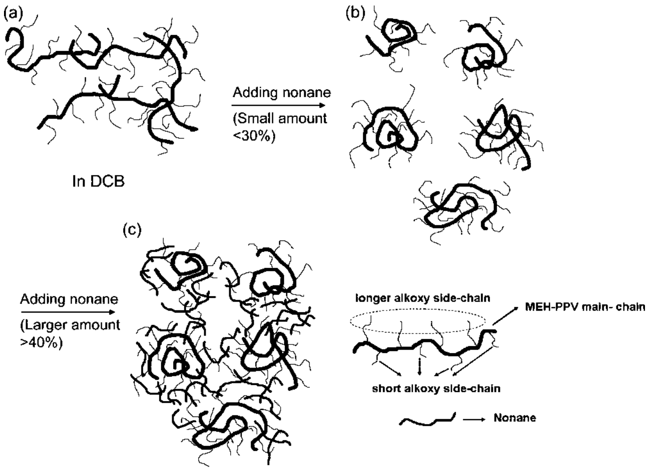

Figure 5. Schematic representation of physical cross-linking mechanism between MEH-PPV and nonane in solution.

temperatures, 30 and 33 °C, the trend of viscosity variations with nonane content is the same as that at 27 °C, while the level of viscosity decreases with increasing temperature.

The presence of viscosity minimum with nonane content can be explained as follows and depicted schematically in Figure 5. When MEH-PPV is dissolved in the good solvent, DCB, its main chains can adopt a more-extended conformation,[5,18] leading to a much higher extent of chain entanglement at the given concentration (step a) and thus the higher viscosity. As the nonane content increases up to 30%, MEH-PPV main chains prefer to adopt a more coil-like conformation owing to the poor solubility of MEH-PPV in nonane,[5] causing a viscosity lowering than in pure DCB (step b). Finally, as the nonane content increases to 40%, a dramatic increase in viscosity is observed. Such viscosity increase can not be resulted from a chain extension as chains are subject to a promoted poor solvent environment; a possible source is an occurrence of interchain connection via neighboring side chains with nonane molecules as bridges (step c). In other words, at this stage nonane actually serves as a physical cross-linking agent for connecting two neighboring side chains belonging to different coiled MEH-PPV chains.

In addition, the aggregates formed during the gelation as revealed in section 1 must be intrachain aggregates since the main chains adopt a coil-like conformation in the presence of nonane as discussed above. This situation resembles to that of MEHPPV dissolved in mixed chloroform/methanol due to the presence of the poor solvent, methanol.[5,23] On the other hand, the need of a time period to achieve the complete gelation (for example, 13 h for nonane as revealed in section 1) implies that the cross-linking formation is a kinetic process and requires considerable length of time to proceed. In other words, the presence of a nonane facilitates MEH-PPV to form a coil conformation and then create intrachain aggregates. In the meantime, the outstretched alkoxyl side chains of two neighboring polymer chains can interact with a nonane molecule to form a cross-linking site of the gel. In addition, the gel formation of poly(9,9-di-*n*-octyl-2,7-fluorene (PFO) solution is also observed. After standing time for 10 days, the PFO solution (10 mg/mL in DCB/nonane at the volume ratio 1/1), which has the same concentration and solvent composition as the MEH-PPV solution, becomes immobile completely as in the case of MEH-PPV solution. Since DCB and nonane are also good solvent and nonsolvent for PFO main chain and side chain, respectively, as for MEH-PPV, we can say that the proposed gelation process can also occur for other conjugated polymers with flexible side chains.

The gelation phenomenon could be useful in coating process for a fabrication of polymer electronic devices by tuning the content of nonane to achieve a desired viscosity without changing the concentration of polymer solution. During a rapid drying process, solution viscosity will be promoted due to gelation, which can prevent from a flow of the wet film. Yet, upon drying, a smooth film with uniform thickness can be expected since the low boiling point nonsolvent, alkane, will evaporate away much earlier than the high boiling point solvent, DCB.

3. Effect of Chain Length and Structure of Alkane on Gelation. In order to investigate structure parameters of alkanes that affect an occurrence of physical cross-linking, alkanes with different chain lengths and structures are added into MEH-PPV solutions in DCB to give resulting solutions with equal volume ratio of DCB/alkane at the MEH-PPV concentration of 10 mg/mL, and their effects on extent of gelation of the MEH-PPV solutions are examined. For the three linear-type alkanes including nonane, octane, and heptane, though gel formation is observed in all cases, only nonane can cause an immobile gel. For the latter two cases, the gel is termed “soft gel” even after standing for 1 month, which means the gel still remains slight fluidity. For the branch-type alkane, 3-methylpentane, the MEH-PPV solution also appears as a soft gel, but not an immobile gel. In the case of the ring-type alkane, cyclohexane (its longest linear dimension is equivalent to that of propane[24]), the solution remains “fluidity” as the original MEH-PPV solution in DCB. It is obvious that the linear chain length of the alkanes plays a dominant role in the occurrence of physical cross-linking because the longer linear chain length of alkanes results in the higher extent of gelation. A sufficient chain length of alkanes is essential for providing an adequate physical interaction and serving as a bridge between two neighboring alkane segments of alkoxy side chains. The effect of chain length and structure also serves as an additional support for that: the long alkane chain acts as a bridge for physical cross-linking.

Conclusions

The addition of nonane into MEH-PPV solution in DCB can result in a formation of intrachain aggregates accompanying with an occurrence of gelation. The presence of nonane, which is a good and poor solvent for MEH-PPV side and main chains, respectively, causes a conformation of MEH-PPV chains changing from a more extended conformation to a coil-like conformation, and the neighboring alkoxy side chains pointing outward tend to interact each other with nonane molecules as bridge to form physical cross-linking networks and subsequently become an immobile gel. A sufficient linear chain length of an alkane is essential for the physical cross-linking process to occur.

Acknowledgment. The authors thank the financial support from the Ministry of Education (Project No. 91E-FA04-2-4A) and from the National Science Council (Project No. 95-2752-E-007- 005 and 008-PAE).

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MA800076G