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Effect of Solvent on the Morphology and Microstructure of Light Emitting Organogels

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Summary: Self assembly of oligo(phenylene vinylene) based gelator is studied in three different solvents namely, trans-decahydronaphthalene (trans-decalin), benzene and benzyl alcohol. The morphology as well as the thermal properties are different for benzyl alcohol gel as compared to those gels in trans-decalin or benzene. X-ray diffraction studies indicate that in case of benzyl alcohol gel, the molecular organization is highly ordered with respect to the fibrils grown in other two solvents.

Keywords: lamellae; light emitting gel; self assembly; X-ray diffraction; π-π stacking

Introduction

The design and self-assembly of organic molecules to form functional superstructures is the main goal of supramolecular chemistry. Self-assembly of π-conjugated organic molecules in solution is a fundamental step to design ''bottom up'' optoelectronic devices.[1] In particular, molecular assemblies consisting of high degree of π-π stacking are of interest as the photo excited charge carriers can travel through it.[2–6] Therefore, to use the solution processing of such superstructures for device fabrication is of the utmost importance to understand how the self-assembly of these active molecules are influenced by the solvent used.

George et al. has reported a new class of Oligo (p-phenylene vinylene) (OPV) based amphiphile molecules which form highly anisotropic nanostructures in apolar solvents like hexane, dodecane etc. when their isotropic solution are quenched to room temperature or below, resulting in the gelation of the solvent medium.[7] The OPV gelators stacks onto one another by π-π non covalent interaction forces to produce fibrillar structures. The long pendent aliphatic chains build up a lamellar structure in one hand and in the other hand, several OPV molecules are also linked together by hydrogen bonding involving the hydroxymethyl end groups (see Scheme 1). Thus the fibrillar cross section is attributed to H-bonded supramolecular polymer chains laterally connected to each other by van der waals forces. Therefore, the preferential growth in either direction should determine the shape of these fibrillar crystals. In this contribution, we have made an attempt to explore the possible influences of solvent on the supramolecular organization of these light emitting gel fibrils. We have investigated the gelation behaviour in three solvents: benzene and a benzene derivative that can establish π-π interactions with the OPV namely, *benzyl alcohol*, which, in addition, mimics the terminal groups of the OPV molecule, and the two conformers of decahydronaphthalene (cis and *trans-decahydronaphthalene* designated as *cis*-decalin and *trans*-decalin in what follows), which does not contain any π electrons.

Experimental Part

Materials

The synthesis and properties of oligo (p-phenylene vinylene) gelator (OPVOH) is described in reference.[8] The basic

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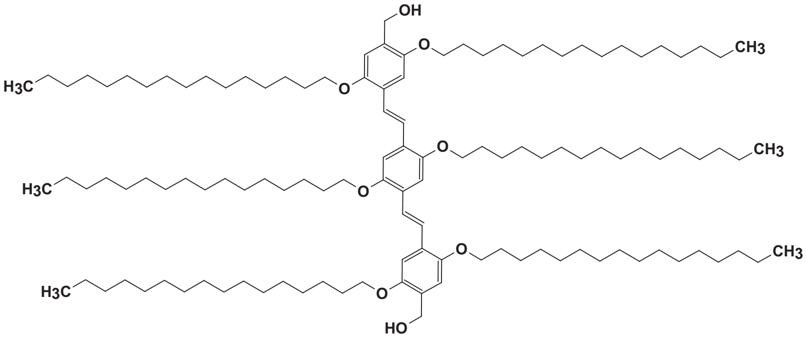

Scheme 1.

Chemical structure of OPVOH gelatorAll the solvents namely, benzene, benzyl alcohol and trans-decalin (of high purity grade) were purchased from Aldrich, and so were used without further purification.

chemical structure of the molecule used in this study is shown in Scheme 1 together with its designation.

Techniques

Differential Scanning Calorimetry

The gel formation and gel melting were investigated by means of the Diamond DSC from Perkin Elmer. Heating and cooling rates ranging from 2.5 °C/min to 20 °C/min were used. Homogeneous solutions were prepared by heating in hermetically closed test tube. Approximately 30 mg of these systems were transferred to ‘‘volatile stainless steel’’ sample pan (LVC pans) under their gel form. These pans were then hermetically sealed through an O-ring joint to prevent any solvent evaporation.

Optical Microscopy

Nomarsky phase contrast pictures were taken with a NIKON Optiphot-2 equipped with CCD camera. LUCIA^{TM} software, developed by Laboratory Imaging, was used for image processing and analysis. The samples were prepared by re-melting between glass-slides those gels obtained beforehand in a test-tube. Minimization of solvent evaporation was achieved by gluing the edge of the thin upper glass-slide with solvent-resistant epoxy resin. Fluorescence microscopy was done Nikon TE2000 Csi inverse microscope in fluorescence confocal mode.

Fluorescence Spectroscopy

Emission spectra were recorded on a SPEX-Fluorolog F112X spectrofluorimeter. Temperature dependent studies were carried out either in a or 0.1 cm quartz cuvette with a thermostat directly attached to the wall of the cuvette holder. Fluorescence spectra of optically diluted solutions were recorded at the excitation wavelengths of 380 nm. Fluorescence spectra of the gels were recorded using the front face geometry.

Atomic Force Microscopy

AFM experiments were carried out at room sample in air using a Nanoscope III instrument (Digital Instruments, Santa Barbara, CA). The image was taken by means of a silicon nitride cantilever (Scientec, France) having a spring constant of 25–50 N/m and a rotating frequency of 280–365 kHz. Films were prepared by deposition of a drop of hot, homogeneous solution onto a glass slide, and then the solvent was allowed to evaporate. The observation of the surface topography and phase images of the films was performed with a scanning rate varying from 1 to 2 Hz using tapping mode.

X-ray Diffraction

The X-ray experiments were performed on beamline BM-02 at the European Synchrotron Radiation Facility (ESRF), Grenoble, France. The experiments were carried out at a radiation energy of 15.8 KeV, which corresponds to a wavelength of $\lambda = 7.86 \times 10^{-2}$ nm. At the sample position the collimated beam was focused with a typical cross section of $0.1 \times 0.3\,mm^2$. The scattered photons were collected onto a two-dimensional CCD detector. The sample-to-detector distances was set at 0.16 m so as to access scattering vectors ranging from $q = 0.5\,nm^{-1}$ to $q = 10\,nm^{-1}$ (WAXS), with $q = (4\pi/\lambda)\, sin\theta/2$ and where λ and θ are the wavelength and the scattering angle, respectively (further information are available on http://www.esrf.fr).

The scattering intensities were corrected for the detector response, dark current, empty cell, sample transmission and sample thickness. A silver behenate sample was used for calibrating the q scale of the detector. Eventually, the intensity scattered $I_s\,(q)$ by the species of interest reads:

$$I_s(q) = I_{samples}(q) - [(1-\varphi) \times I_{sol}(q)] \quad (1)$$

where $I_{sol}\,(q)$ is the scattering by the solvent and φ is the volume fraction of the scattering species. Note that $I_{sol}\,(q)$ is the scattering by the solvent and by the glass container.

Gels were prepared beforehand in test tubes, and then transferred into well-calibrated, cylindrical thin-walled ($\approx$ 0.1 mm thick) glass tubes of 3 mm inner diameter. These tubes were finally sealed and the system was reheated in order to obtain homogeneous solutions and so apply the same thermal treatment as that used for the DSC experiments.

Results and Discussion

The isotropic solution of OPVOH in isomerically pure *cis*- or *trans*-decalin is blue emissive whereas the gel state is reached, when the temperature is decreased to 20 °C or below resulting in a green emissive self supported solid.

The gel state consists with green emitting microfibrils as illustrated in the fluorescence microscope image (Figure 1a); note that, the fluorescence is remarkably quenched (Figure 1b) and red shifted in the gel state which is indicative of the strong chromophoric aggregation definitely achieved through π-π stacking.[7] The hydroxymethyl end groups offer a cooperative effect to the self assembly process.

The structure of OPVOH self-assembly in both cis and trans decalins has been investigated in the wet state by X-ray diffraction measurements and the curves thus obtained suggest that the fibrillar cross section consists of lamellar structures produced by the hexadecyl aliphatic chains and they look similar for cis or trans decalin. Therefore, it is apparent that the solvent conformation does not influence the gel structure. The gel stability is also comparable in both isomeric solvents as the sol-gel transition temperatures are

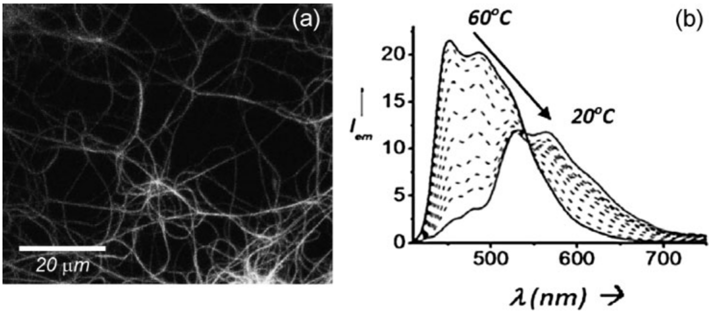

Figure 1.
(a) Fluorescence microscope image of OPVOH–trans decalin gel ($C_{OPV} = 0.004\,g/cm^3$) excited at wavelength 400 nm (b) Time resolved PL spectra of OPVOH solution in trans-decalin ($C_{OPV} = 0.0004\,g/cm^3$) upon cooling from 60 °C to 20 °C; $\lambda_{excitation} = 380$ nm.

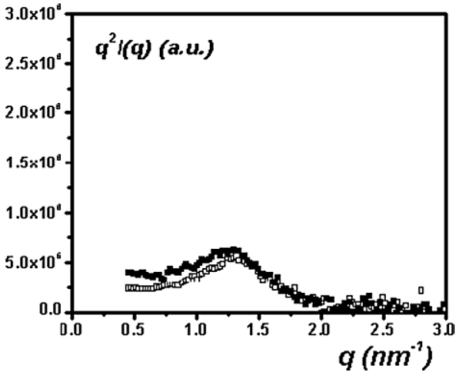

Figure 2.
WAXD patterns patterns showing the lamellar structures in OPVOH gels ($C_{OPV} = 0.004$ g/cm^3) in cis-decalin (□) and in trans-decalin (■).

quite close.[9] The value of the lamellar period namely 4.65 nm (corresponds to $q = 1.36$ nm^{-1}) refers to a totally extended C-16 bilayer structure.[8] An interdigited lamellar structure cannot be possible, as there is no room in between the two adjacent alkoxy chains of a gelator molecule to house another chain of a second molecule.

In what follows, we will compare the gelation habits of OPVOH molecules in trans decalin, benzene and in benzyl alcohol.

In Figure 3 the ''Temperature-Concentration'' phase diagram is shown for all the three binary systems in the concentration range between 0.002 to 0.025 gcm^{-3}. The observation that, for each binary solution, the gel melting temperature is higher than that of the gel formation temperature at any given concentration, suggesting a nucleation and growth mechanism. The benzyl alcohol gel has the highest gel melting and formation temperatures compared to the other two systems. In the inset, the gel melting and formation enthalpies are plotted for different binary systems as a function of concentration and it shows the same linear variation for all the systems.

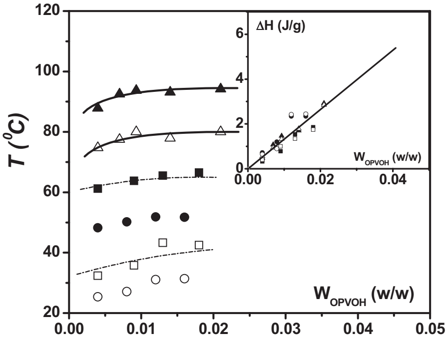

Figure 3.
Temperature-concentration phase diagram for OPVOH - benzyl alcohol. ▲ = gel melting Δ gel formation; OPVOH-trans decalin ■ gel melting □ gel formation; OPVOH - benzene • gel melting ○ gel formation. Inset: the corresponding enthalpies of gel melting and gel formation.

In Figure 4, the surface morphology of the gels in the same three solvents is compared. For the OPVOH-trans decalin gel and OPVOH-benzene gel, the fibrils look identical besides the fact that, in

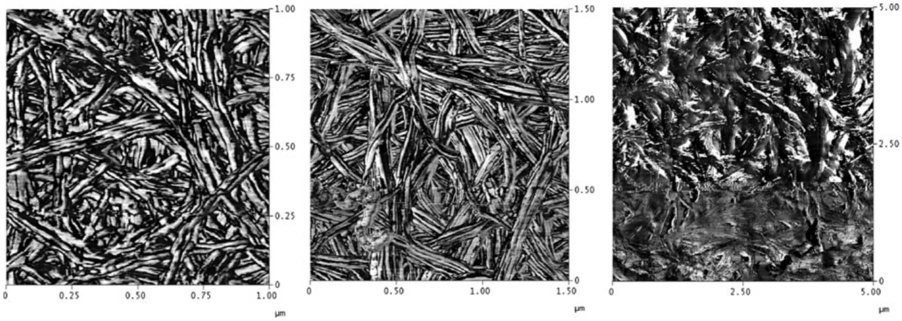

Figure 4.
Tapping mode AFM phase images of the dried OPVOH gels ($C_{OPV} = 0.004$ g/cm^3) in trans-decalin (left), benzene (middle) and in benzyl alcohol (right).

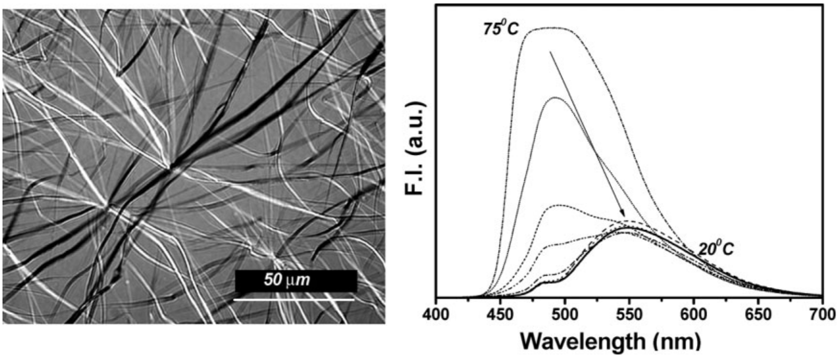

Figure 5.
Left: Optical micrograph of OPVOH-Benzyl alcohol ($C_{OPV} = 0.004\,g/cm^3$) gel; Right: time resolved PL spectra of OPVOH solution in benzyl alcohol ($C_{OPV} = 0.0004\,g/cm^3$) upon cooling from 75 °C to 20 °C; $\lambda_{excitation} = 380\,nm$.

benzene gel, they tend to form much aggregated structures which may be due to extremely fast evaporation of benzene as compared to decalin. The morphology of dried OPVOH-benzyl alcohol gel rather consists of bigger structures showing melted fibrillar aspects.

In contrast to the dried morphology, optical imaging of OPVOH-fibrils grown in benzyl alcohol in the gel state, gives a unique ‘‘web-like’ structures (Figure 5 left) made of supramolecular ribbons. They nucleate from definite points and grow straight. The SOL-GEL transition in benzyl alcohol is also associated with quenching of fluorescence with a red shift of 100 nm (Figure 5 right).

The fact that the OPVOH self-assembly produces a unique morphology in benzyl alcohol demands much attention on the supramolecular structure of these micro-objects. Figure 6 compares the X-ray diffraction patterns obtained from OPVOH gels in trans-decalin, benzene and in benzyl alcohol. As described earlier, the appearance of the Bragg's peaks suggests ordering of long alkyl pendent groups. In all the gel structures, the lamellar period measures nearly the same length (4.68 nm). But, unlike the other two cases, in benzyl alcohol the lamellae show preferential growth along the alkyl arms.

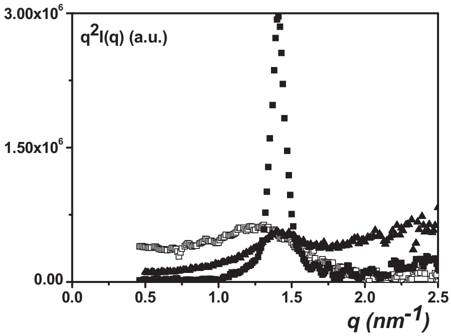

Figure 6.
WAXD patterns showing the lamellar structures in OPVOH gels ($C_{OPV} = 0.004\,g/cm^3$) in trans-decalin (□); benzene (▲) and in benzyl alcohol (■).

Figure 7b, illustrates the growth of fibrillar crystallites in nonpolar hydrocarbon solvents. The π-π stacking results in the faster growth along the long fibrillar axis. The long aliphatic side chains build up a lamellar structure and in the other hand, several OPV molecules lying in the same plane are also tethered via hydrogen bonding through their hydroxymethyl end groups. In case of OPVOH/benzyl alcohol gel system, OPVOH stacks may form a molecular compound[10] through specific interactions between end groups of the supramolecular building blocks and the solvent unlike the other two systems, thereby rendering the end group unavailable for the neighbouring gelator molecules. As a consequence, a privileged growth at the orthogonal direction

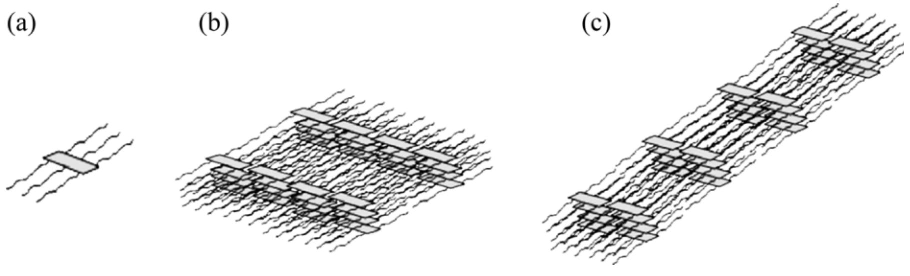

Figure 7.
(a) Schematic representation of OPVOH molecule (b) Lamellar structure inside trans-decalin or benzene gel fibrils (c) Lamellar structure inside benzyl alcohol gel fibrils.

(Figure 7c) that is along the alkyl chains resulted.

Moreover, Figure 8 presents the SAXS profile of OPVOH gels in *trans*-decalin and benzene. The peaks corresponding to the lamellae occur at virtually the same 'q' value'. Benzene is a better solvent for OPVOH than decalin and is able to interact with chromophoric part through π-π interaction. In the small '*q*' range the scattering profiles also differ in these two solvents, suggesting a difference in fibrillar cross section values in the bulk. For benzene gel, the scattering curve tends to go up at large 'q' range and this is probably attributed to the presence of some molecularly dissolved OPVOH molecules which again proves the higher affinity of gelator to benzene as compared to trans-decalin.

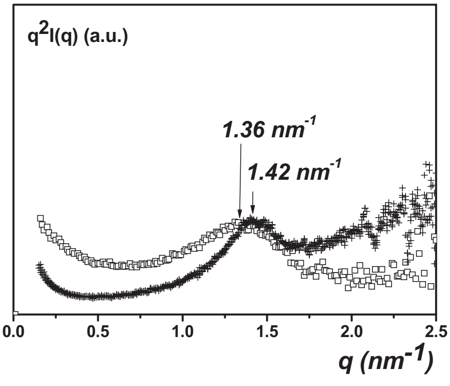

Figure 8.
SAXS patterns of OPVOH gels ($C_{OPV} = 0.004\ g/cm^3$) in trans-decalin (□) and in benzene (+).

Conclusion

In this contribution, we have shown that the non-covalent assembly of a oligo(phenylene vinylene) based gelator (OPVOH) is remarkably influenced by the solvent i.e., the gelation medium. OPVOH self-assembles in both non-polar (decalin and benzene) and polar solvents (benzyl alcohol). There is no noticeable effect of the solvent conformers of decalin on the structure of OPV gel. The gelation of OPVOH in benzyl alcohol proceeds via the formation of ribbon like fibril formation whereas, entangled cylindrical fibrils are seen for the gels in *trans*-decalin and benzene. X-ray diffraction reveals difference in growth patterns between benzyl alcohol gel and *trans*-decalin gel.

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