Solvent-Assisted Tyrosine-Based Dipeptide Forms Low-Molecular Weight Gel: Preparation and Its Potential Use in Dye Removal and Oil Spillage Separation from Water

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Supporting Information

ABSTRACT: Low-molecular weight gelators (supramolecular, or simply molecular gels) are highly important molecular frameworks because of their potential application in drug delivery, catalysis, pollutant removal, sensing materials, and so forth. Herein, a small dipeptide composed of N-(tert-butoxycarbonyl)pentafluoro-L-phenylalanine and O-benzyl-L-tyrosine methyl ester was synthesized, and its gelation ability was investigated in different solvent systems. It was found that the dipeptide was unable to form gel with a single solvent, but a mixture of solvent systems was found to be suitable for the gelation of this dipeptide. Interestingly, water was found to be essential for gelation with the polar protic solvent, and long-chain hydrocarbon units such as, petroleum ether, kerosene, and diesel, were important for gelation with aromatic solvents. The structural insights of these gels were characterized by field-emission scanning electronic microscopy, atomic force microscopy, Fourier transform infrared analysis, and X-ray diffraction studies, and their mechanical strengths were characterized by rheological experiments. Both of the gels obtained from these two solvent systems were thermoreversible in nature, and these translucent gels had potential application for the treatment of waste water. The gel obtained from dipeptides with methanol−water was used to remove toxic dyes (crystal violet, Eriochrome Black T, and rhodamine B) from water. Furthermore, the gel obtained from dipeptide with assistance from toluene−petroleum ether was used as a phase-selective gelator for oil-spill recovery.

INTRODUCTION

The peptide and amino acid-derived supramolecular gels are currently an important class of materials which have attracted significant interest because of their potential applications in advance material science, pharmaceutical preparation, drug delivery, oil-spill recovery, and as environmental pollutant-removing agents.1−14 Gels can be defined as soft materials in which solvent molecules self-assemble into one-dimensional structure that entrap and cross links to constitute a network.15−17 This has the ability to immobilize a particular solvent. In other words, gels are formed under suitable conditions where solvent molecules are trapped into a three-dimensional architecture.18−20 Most of the gels are polymeric materials and hyper-branched dendritic molecules. However, low-molecular weight gels or supramolecular gels are another fascinating class of materials because of their unique applications.21−23 These gelator molecules were formed via various noncovalent interactions such as-hydrogen bonds, van der Waals forces, π−π stacking, dipole−dipole, charge-transfer coordination interactions, and solvophobic effects.24−33 Among the abovementioned interactions, hydrogen bonding and/or π−π interactions are responsible for their gelatinous nature. In recent era, low-molecular weight gelators in organic and aqueous solvents were explored, having ample applications in nanomedicine, catalysis, light-harvesting, tissue engineering, sensing, templating, and nanoelectronics.21−23

With the development and industrialization of human civilization, there has been acute shortage of clean and hygienic water throughout the world.34,35 The degradation and contamination of water by harmful chemicals has made our natural resources (rivers, lakes, oceans, etc.) a great threat to us.34,36 Nowadays, water purification has become a matter of utmost importance in contemporary environmental research. The exclusive characteristics of supramolecular gels, that is, coordination interactions, and solvophobic effects.24−33 Among the abovementioned interactions, hydrogen bonding and/or π−π interactions are responsible for their gelatinous nature. In recent era, low-molecular weight gelators in organic and aqueous solvents were explored, having ample applications in nanomedicine, catalysis, light-harvesting, tissue engineering, sensing, templating, and nanoelectronics.21−23

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RESULTS AND DISCUSSION

In the present study, the gelation propensity of \textit{N}-(\textit{tert}-butoxycarbonyl)\textit{L}-phenylalanine-\textit{O}-benzyl-L-tyrosine was investigated for gelation of this dipeptide. For the formation of the gel, water was added to the methanolic solution of the dipeptide, a white-colored suspension appeared, and then keeping the solution without any disturbance formed a translucent gel within few seconds. The gelation test was carried out in a tube by tube inversion method (see Supporting Information). This gel is thermoreversible in nature which means heating the gel gives a clear solution and leaving it to stand (slow cooling) for few minutes gives a translucent gel. The minimum gelation concentration (MGC) of the dipeptide in the 50\% methanol–water system was 0.25\% w/v, and the calculated $T_{gel}$ of the corresponding MGC was found to be 72 °C. It was observed that gelation appeared immediately in the 50\% methanol–water system and with increasing methanol amount, less amount of gel formation was observed. Furthermore, this dipeptide also formed gel in assistance with DMF–water, DMSO–water, acetonitrile–water, and ethanol–water. Thereby, it can be concluded that water is essential for gelation due to water-assisted hydrogen bonding, and this was further confirmed from D$_2$O–exchange proton NMR study. In all cases, the gel was formed and stable for several weeks without any noticeable change under ambient conditions. Apart from the mixture of the polar protic solvent and water, this dipeptide is able to form the translucent gel in the mixture of aromatic solvents that is, toluene and nonpolar solvent like petroleum ether. The translucent gel formed by the dipeptide in accordance with the mixture of toluene and petroleum ether is thermoreversible in nature and stable for several weeks at ambient temperature. The MGC of the dipeptide in the (1:20) toluene–petroleum ether system was 0.2\% w/v, and $T_{gel}$ at this MGC was found to be 48 °C. The gel was also formed when benzene and xylene were used along with petroleum ether instead of toluene. The gel prepared from toluene and long-chain hydrocarbon (such as petroleum ether, kerosene and diesel) was prepared in the absence of water. Owing to the better gelation tendency of this dipeptide in the presence of 50\% methanol–water with 0.25\% w/v MGC, this gel has been further used in water purification by removing three different dyes. In addition, the gel from toluene–petroleum ether was found to act as a PSG which can selectively gelate the oil part in the oil–water mixture keeping the water part intact. This phase-selective gelation was again investigated using kerosene and diesel instead of petroleum ether (see Supporting Information).

Morphological Studies. FE-SEM Study. To gain a visual insight into the morphological study of this dipeptide, field-emission scanning electron microscopic experiment was carried out. All the xerogels prepared from their respective solvent system showed a highly cross-linked entangled structure at their MGC. An intertwined fibrillar network was observed in case of the methanol–water system (Figure 1a), where two or more fibers were linked to each other to obtain a thicker fiber and highly cross-linked, entangled sheets like structures were obtained in case of the toluene–petroleum ether solvent system (Figure 1b). Such entangled fibrillar network possibly encouraged the entrapment of large number of solvent molecules and also prevented the free movement of solvent molecules.

AFM Study. To understand the morphology of the self-assembled structure adapted by this dipeptide in its dilute solution, atomic force microscopic study was performed. For this reason, the dipeptide was dissolved separately in methanol and toluene and drop-cast on the mica film. The images were
recorded under the microscope after drying the sample. It was found that the widths of the fibers obtained from the dipeptide dissolved separately in methanol and toluene solution were 60–90 and 70–90 nm, respectively (Figure 2a,b). Therefore, it can be concluded that this dipeptide generates dispersed fibrils from dilute solution (5 μM). Moreover, the AFM images of this dipeptide were also in agreement with the cross-linked entangled structure, accounting for further aggregation of the discrete fibrils with the assistance of solvent molecules in the corresponding gel state. The morphology of the dipeptide in the mixture of solvents was also investigated, and it was found that the dipeptide also formed fibrils from dilute solution in its respective solvent system (see Supporting Information).

**NMR Study.** Deuterated (H/D) exchange proton NMR study of the dipeptide provided important insights into the hydrogen-bonding patterns of the two amide protons in the solution state. In the absence of D₂O, two doublet peaks appeared around δ 8.50 and 6.94 ppm for Hₐ and Hₜ, respectively because of two different chemical environments of two amine groups. The total 9 aromatic protons arose at δ 7.40 (2H), 7.34 (2H), 7.29–7.27 (1H), 7.08 (2H), and 6.87 (2H) ppm, respectively, for this dipeptide in the NMR spectrum (Figure 3a). After adding 10 μL of D₂O to a 10 mM dipeptide solution in DMSO-d₆, the intensity of the proton arose at δ 6.94 ppm for Hₜ being diminished rapidly (within 1 min) and shifted from 6.94 to 6.90 ppm as shown in (Figure 3b). This Hₜ proton may be involved in strong hydrogen bonding with DMSO. When D₂O was added, the interaction pattern of the hydrogen may be altered depending on its position and orientations. Because of this, the Hₜ proton shielded little bit. The intensity of the other proton appeared at δ 8.50 ppm for Hₐ being diminished rapidly (within 1 min) and shifted from 8.50 to 8.45 ppm as shown in (Figure 3c). From this NMR study, it can be concluded that both the protons Hₐ and Hₜ are solvent-exposed and participated in intermolecular H-bonding with another dipeptide molecules and the solvent molecules.

**FT-IR Analysis.** FT-IR spectroscopy study was performed to evaluate the molecular interactions that interplay to form gelation of the dipeptide in different solvent systems. For recording the FT-IR spectra of the dipeptide in its wet gel state; the gels were prepared in their respective solvent systems at their MGC, according the procedure given in the Results and Discussion part. The important FT-IR band positions are marked in the Figure 4, and assignment of these bands is placed in the Supporting Information (Table S1). The molecular interactions were influenced by the amide backbone configuration. The amide I, amide II, and amide III bands those were influenced by the geometry of the amide bond configuration and hydrogen-bonding pattern appeared at 1600–1690, 1480–1580 and 1230–1300 cm⁻¹, respectively. The amide I mode originated due to CO stretching vibration, and the amide II and amide III associated with the coupling of C–N stretching and N–H in-plane bending. In order to get the molecular interactions associated with the gelation of the dipeptide, we measured the FTIR spectra of the dipeptide in their solid and wet gel states (Figure 4). In the solid state of the dipeptide (Figure 4a), one sharp peak appeared at 1666 cm⁻¹ along with a hump at 1655 cm⁻¹, corresponding to the amide I vibrational mode of the carbamate carbonyl and the amide carbonyl, respectively. In the gel state of the dipeptide in the methanol–water solvent system (Figure 4b), the characteristics peak appeared at 1628, 1666, and 1740 cm⁻¹ with broadening nature compared to the solid state. This broadening of the amide peaks and the appearance of the peak at 1628 cm⁻¹ indicated that in the gel state, this dipeptide becomes hydrated through the water and methanol solvent system. The amide (–CONH) group may be involved in hydrogen bond formation with water. Thus, the associated water molecules contribute to the broadness at 1628 cm⁻¹. Similarly for the gel state of this dipeptide in toluene petroleum ether (Figure 4c), shifting of the amide peak from 1666 to 1658 cm⁻¹ along merged with the hump at 1655 cm⁻¹ was observed, suggesting strong hydrogen bonding in the gel state compared to the solid state.

**X-ray Diffraction Study.** To determine the solid-state molecular arrangement and packing of dipeptide (3) at the atomic level, powder X-ray diffraction (XRD) experiment was carried out in both gel state obtained from two different solvent systems and its solid state, as represented in Figure S.
Figure 3. H/D exchange experiment on the dipeptide (10 mM) in DMSO-d$_6$: (a) $^1$H NMR spectra of the dipeptide in the absence of D$_2$O, (b) $^1$H NMR spectra of the dipeptide after 1 min in the presence of 10 μL D$_2$O, (c) $^1$H NMR spectra of the dipeptide after 2 h in the presence of 10 μL D$_2$O, and (d) $^1$H NMR spectra of the dipeptide after 4 h in the presence of 10 μL D$_2$O.

Figure 4. FT-IR spectra of the dipeptide in the (a) solid state and (b) wet gel state prepared from the methanol–water (c) wet gel state prepared from the toluene–petroleum ether system.

Figure 5. (a) XRD patterns of the dipeptide in its solid state. (b) XRD patterns of the dipeptide in its xerogel state (toluene–petroleum ether system).
The xerogel form showed sharp reflections appeared in the 5–40° (2θ value) range and was therefore inferred to be crystalline in nature. Xerogel obtained from the dipeptide in the toluene–petroleum ether solvent system showed a peak (Figure 5b), corresponding to d-spacing 4.73 Å (2θ ≈ 18.7°) accompanied by the other peak at 9.71 Å (2θ ≈ 9.1°), which were indicative of a β-sheet-like arrangement of these gelator molecules. The peak at 4.73 Å represented the spacing between peptide chains within a β-sheet. Additionally, the peak at 9.71 Å was approximately doubled the β-sheet spacing. This may be due to either, the repeating unit of β-sheet type hydrogen bonding or the “side-chain” spacing between two interacting parallel sheets. Moreover, a peak at 2θ ≈ 26.29° (3.38 Å) was observed for the xerogel obtained from the toluene–petroleum ether solvent system, indicating the presence of π–π stacking interactions. In the case of the solid state, the broad peaks (Figure 5a) were due to the heavy scatterings, which represented semi-crystalline characteristics of the dipeptide. Despite the fact that the dipeptide partially lost its crystalline property in the dry state, the low intense peaks at 2θ ≈ 9.8° (9.01 Å), 18.2° (4.86 Å), and 25.3° (3.51 Å) were still present, which indicated the presence of β-sheet-like arrangement and π–π stacking interaction in the dry state, although these values are slightly shifted from the xerogel obtained from the toluene–petroleum ether solvent system. Further, few strong intense lines are also observed in the wet-gel state which may be due to pure phenylalanine or tyrosine as reported earlier. Unlike the sharp reflection in the toluene–petroleum ether solvent system, the XRD spectrum of the dipeptide in the methanol–water solvent system (see Supporting Information) showed broad peaks which indicated that the crystalline property of the dipeptide is less in this medium. It suggested that the xerogel state of the dipeptide significantly depended on the polarity of the environment. It showed peaks at 2θ ≈ 18.67° (4.74 Å) and 29.51° (3.02 Å), which may be due to β-sheet-like arrangement and π–π stacking interactions as obtained from the toluene–petroleum ether medium.

Rheological Experiment. Rheological experiments were carried out to find the mechanical strength of the gel. This experiment was important to gain information about the flow behavior and the rigidity of the gel. In a typical frequency, sweep experiment under a constant (0.1%) strain was performed to monitor the storage modulus (G'') and loss modulus (G′) as a function of applied angular frequency. It was found that for both gels, storage modulus (G′′) and loss modulus (G′) did not cross each other, and storage modulus (G′) is always greater than the loss modulus (G'') throughout the entire range of frequency for both solvent systems (Figure 6), which is in agreement with the fact that a soft solid-like gel-phase material was present.

Dye Adsorption Study. Toxic dyes are used by several industries for their various purposes and often the waste dyes are being dumped into river water. Nowadays, low-molecular weight gelators are used for the removal of these toxic dyes quite efficiently. The adsorption behavior of the gel obtained from the methanol–water mixture was investigated by adding aqueous solution of the dye to the gel. Surprisingly, three different dyes, crystal violet, Eriochrome Black T, and rhodamine B, were adsorbed rapidly over a period of time by this supramolecular adsorbent. The concentration of the dyes used was 0.01 mM. After 24 h, more than 90% of the dyes were adsorbed for crystal violet and Eriochrome Black T, and more than 80% dye was adsorbed for rhodamine B (Figure 7).

For rhodamine B, dye adsorption study was further investigated and found that 92% adsorption was done after 48 h (see Supporting Information). Adsorption of the dyes from aqueous solution was also examined by UV–vis spectroscopy, which showed that the dye was adsorbed by the gel leaving behind the clear water (Figure 8a–c). The morphological change of this gelator molecule after dye adsorption may be due to the hydrogen bonding and/or π–π stacking between the dye molecules and the gelator molecule.

Selective Organogelation. Low-molecular weight supramolecular gels offer a unique application through selective gelation of oil products having molecular weight larger than their own molecular weight. The phase-selective gelation from a given mixture of solvents becomes more challenging if water is used as one of the solvents. This property can be used as oil-spill remediation, so-called “bio-refinery design”. The insoluble behavior of the organogel in water and good gelation ability in

Figure 6. Frequency sweep experiment of the dipeptide at 0.1% constant strain: (a) methanol–water system and (b) toluene–petroleum ether system.

Figure 7. Photographic images of the gel obtained from the gelator dipeptide: (i) crystal violet (ii) Eriochrome Black T, and (iii) rhodamine B (a) before adsorption and (b) after adsorption.
many organic solvents make them suitable for selective gelation of the oil in oil−water mixture. In a typical procedure, 5 mg compound was added to the mixture of 1 mL of the toluene−pet-ether mixture (1:20) and 1 mL of water. The compound was then solubilized by heating in this two-phase and shaken vigorously to make it homogeneous. After cooling to room temperature, the organic layer was gelated, and the water layer remained intact in its liquid state (Figure 9). This procedure was further investigated for the toluene−kerosene and toluene−diesel system (see Supporting Information).

**CONCLUSIONS**

In conclusion, we developed a new low-molecular weight gelator peptide consisting of N-(tert-butoxycarbonyl)-pentafluoro-L-phenylalanine and O-benzyl-L-tyrosine, and its gelation ability had been investigated in different solvent systems. The mixture of the solvent system was found to be efficient for promoting the gelation of this dipeptide. Water is found to be essential along with polar protic solvent systems for gelation of this dipeptide. In addition, the long-chain hydrocarbon unit is found to be important in assistance with aromatic solvents for gelation of this dipeptide. Both of the gels prepared from these two solvent systems were thermoreversible and translucent in nature. These gelator molecules had the potential in water purification. The gel obtained from the methanol−water solvent system was used to remove three different toxic dyes (crystal violet, Eriochrome Black T, and rhodamine B) from aqueous solutions, and the gel prepared from the aromatic solvent and long-chain hydrocarbon was successfully employed as a PSG in oil-spill recovery.

**EXPERIMENTAL SECTION**

All chemicals were purchased from Sigma-Aldrich and used without further purification unless otherwise stated. Solvents were freshly distilled by the standard procedures prior to use. Column chromatography was performed on the silica gel (Merck, 60−120 mesh) with the required eluent. Finally, compounds were characterized by 1H NMR, 13C NMR, and mass spectrometry.

**Synthesis of the Dipeptide.** To a well-stirred solution of N-(tert-butoxycarbonyl)pentafluoro-L-phenylalanine (1, 1 g, 2.81 mmol) dissolved in N,N-dimethylformamide (15 mL), was added anhydrous hydroxybenzotriazole (HOBT; 455 mg,3.37 mmol) slowly followed by 1-ethyl-3,3-(dimethylamino)-propyl carbodiimide hydrochloride (EDC·HCl; 1 g,5.62 mmol) in cooled conditions under a nitrogen atmosphere. Then, stirring was continued for 10 min at ice-cooled conditions, and to this mixture triethylamine (TEA; 2 mL, 14.05 mmol) was added along with O-benzyl-L-tyrosine methyl ester (2, 900 mg, 2.81 mmol); subsequently, the reaction was further continued for 8 h at room temperature (monitoring via thin-layer chromatography). The reaction mixture was then concentrated to dryness and extracted with ethyl acetate from the aqueous layer. Evaporation of the solvent under reduced pressure produced the crude product, which was further purified by column chromatography over the silica gel (hexane/ethyl acetate) to afford the intermediate compound “3” as the white solid (yield = 80%) (Scheme 1).
multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet) were reported as follows: chemical shift, integration, and coupling constant (s) in hertz (Hz). All the experiments were performed at room temperature (25 °C).

**Atomic Force Microscope.** AFM images were obtained on Pico Plus 5500 AFM (Agilent Technologies, Inc., Santa Clara, CA, USA) with the piezo scanner range of 9 μm. The images (256 × 256 pixels) were captured with a scan size between 0.5 and 5 μm at the scan speed rate of 0.5 rpm. The images were processed through flattening via PicoView software (Molecular Imaging Inc., Ann Arbor, MI, USA). For this purpose, dipeptide solution incubated at room temperature for 24 h, and then the solution was applied to a mica foil, after drying the sample solution placed at the mica foil, and the specimen was observed through atomic force microscopy.

**FT-IR Spectroscopy.** The FT-IR spectra of the dipeptide were recorded on a PerkinElmer Spectrum Two spectrometer. For recording the FT-IR in wet-gel state, the gels were prepared in their respective solvents at their MGC. The spectra were scanned from 400 to 4000 cm\(^{-1}\) at 4 cm\(^{-1}\) resolution. Spectrum 10 software was used for data processing.

**Field-Emission Scanning Electron Microscopic Study.** Morphologies of the gel materials were investigated using field-emission scanning electron microscopy (FE-SEM). For FE-SEM study, dilute solutions of gel materials were dried, and platinum coating was carried out. Then, the micrographs were taken in an FE-SEM apparatus (JEOL Scanning Microscope-JSM-7600F). Another FE-SEM study of the gel after adsorption of the dye was performed in an FE-SEM apparatus Hitachi S-4800.

**UV–Vis Spectroscopy.** UV–vis absorption spectra were recorded using a JASCO V-630 spectrophotometer. A high-quality quartz cuvette was used for measuring the absorbance.

**Dye Adsorption.** The maximum amount of dye adsorption was monitored by adding 1 mL of dye (0.01 mM) to a sample tube together with 2 mg of compound (3). This solution was left for 24 h at rt to adsorb the dye. The final concentration of the dye in the solution was determined by UV–vis spectroscopy.

**Rheology Experiments.** The rheological measurement of the gel obtained from the toluene–petroleum ether solvent system was performed using a modular compact rheometer (Anton Parr, MCR 102, Austria). The instrument was equipped with an air compressor unit, which maintained the air pressure at 7 kg/cm\(^2\). A standard cone-plate geometry (CP-40, 40 mm outer diameter, angle 1°) was employed in the study. Frequency sweep (G, G” vs angular sweep) was measured in the oscillation mode. The data were analyzed using Rheoplus software (US 200, version 3.62). Another rheology experiment of the gel obtained from the methanol–water solvent system was performed in SDT Q Series Advanced Rheometer AR 2000.

**XRD Study.** XRD study of the xerogel was carried out by placing the sample on a glass plate. Experiments were carried out by using an X-ray diffractometer (Bruker AXS, model no. D8 Advance).

**Determination of Gel–Sol Transition Temperature (T\(_{\text{gel}}\)).** The gel-to-sol transition temperature (T\(_{\text{gel}}\)) was determined by placing the organogel containing inverted screw-capped glass vial into a thermostatted water bath and raising the temperature at a rate of 2 °C min\(^{-1}\). The T\(_{\text{gel}}\) was defined as the temperature (+0.5 °C) at which the gel melted and showed gravitational flow.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.9b01301.

\(^{1}\)H and \(^{13}\)C spectra, full IR spectra, XRD patterns of the xerogel in methanol–water solvent mixture, UV plot, and AFM images (PDF)

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**Notes**

The authors declare no competing financial interest.

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