

Adsorption of Anionic Dyes Using a Poly(styrene-*block*-4-vinylpyridine) Block Copolymer Organogel

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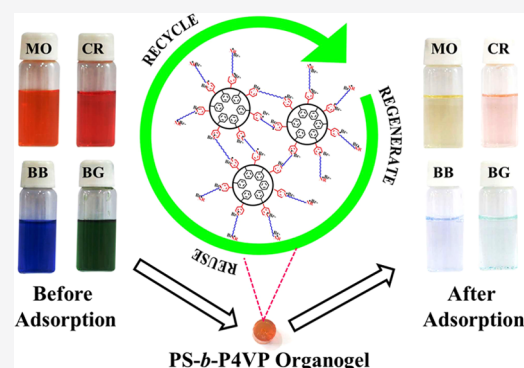
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ABSTRACT: An organogel was prepared by chemically cross-linking a poly(styrene-*block*-4-vinylpyridine) diblock copolymer using dibromododecane in dimethylformamide. Analysis of the prominent structure peak in small-angle X-ray scattering along with the results of light scattering and rheological profile suggests the bridging of the spherical micelles to one another to form an interconnected network after gelation. The use of this organogel as a selective adsorbent for removing anionic dyes from individual aqueous dye solutions and in a mixture of cationic and anionic dye solutions has shown more than 90% removal of the anionic dyes within 2 h. The regeneration and reusability studies showed that even after 20 cycles, the adsorption property of the organogel holds extremely well still beyond 90%. These results are indicative of the potential use of poly(styrene-*block*-4-vinylpyridine) organogel for the anionic ions removal in wastewater treatment.



INTRODUCTION

Contamination of water bodies by untreated textile effluents containing organic/inorganic dyes pose a severe threat to aquatic life and the dwellers, especially in developing countries relying on these water bodies. In particular, water contaminated with reactive textile dyes having azo groups are of significant concern as it can transform into carcinogenic aromatic amines.¹ Also, the dyeing of textiles demands a surplus amount of water. Thus, appropriate measures for textile effluent treatment and efficient water-recycling can significantly reduce the discharge of harmful dyes into the water bodies. Over the years, several effective treatment processes for dye removal, such as photo-degradation,^{2–5} bio-degradation,^{6–9} membrane-based filtration,^{10–13} adsorption,^{14–18} etc., have been reported. Among these methods, dye removal by adsorption is advantageous due to its relatively simple adsorption mechanism, removal efficiency, economic feasibility, and flexibility in the process involved. Persistent scientific efforts have been devoted to increasing the dye removal efficiency using various adsorbents based on polymers,^{19–22} gels,^{21,23–29} thin films,^{30–32} nanocomposites,^{17,18,33} clays,³⁴ etc. Given a myriad of adsorbents, selecting an effective adsorbent is quite challenging as concerns regarding their reusability, adsorption capacities, amount of adsorbent required, and dye removal rates are to be quizzed.

Due to the three-dimensional network and its associated porosity and high surface area, gels can quickly and effectively adsorb dye molecules. Reusability, selectivity, and recovery of the adsorbent are also crucial for large-scale deployment of the

treatment process. Gel-based adsorption thus will have promising applications in dye removal from wastewater for the reasons mentioned above. These adsorbents can remove both anionic and cationic dyes^{21,23} or can be specific to one particular ion.^{24–29} Most of the gel adsorbents investigated are based on hydrogels;^{26–29,35–38} there are also a few reports where microgels,¹ ionic liquid gels,^{25,39–42} metallogels,^{43,44} aerogels,⁴⁵ etc., are tested for dye adsorption. Of late, there has been a growing interest in the preparation of organogels, which are polymeric networks swollen in an organic solvent. Owing to their network structure and capability to trap small molecules, organogels have been utilized for adsorption of pollutants,⁴⁶ oil molecules,⁴⁷ and drug delivery;⁴⁸ however, their application in effluent treatment remains much unexplored.

Here, we report the preparation of an organogel from a quaternized poly(styrene-*block*-4-vinylpyridine) (PS-*b*-P4VP) diblock copolymer using 1,12-dibromododecane (DBD) as the cross-linker in *N,N*-dimethylformamide (DMF). Upon heating at 70 °C, the micelles of the PS-*b*-P4VP diblock copolymer are bridged together by DBD, which arrests the dynamics of the micelles and forms a gelled network, which we define here as

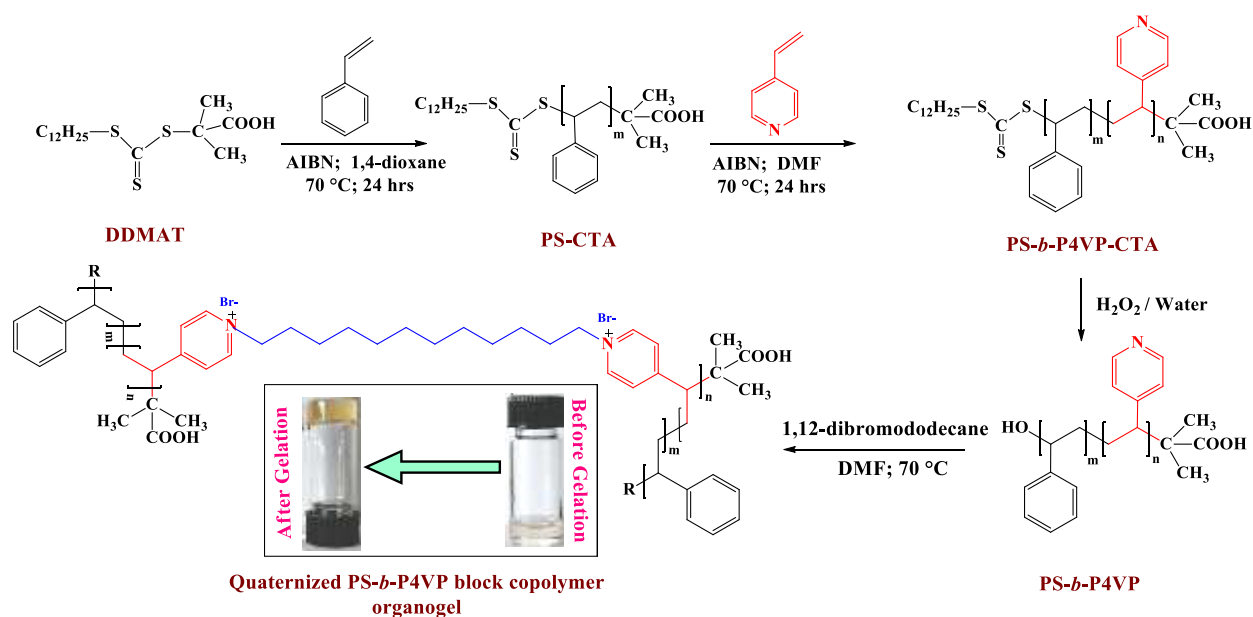
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Scheme 1. RAFT synthesis of PS-*b*-P4VP Diblock Copolymer and its Cross-Linking with DBD to form the Quaternized Organogel^a



^aThe inset shows the photograph of the 2 wt % PS-*b*-P4VP before and after gelation. Gelation is observed after 4 h heating the 2 wt % PS-*b*-P4VP with 0.8 wt % DBD at 70 °C.

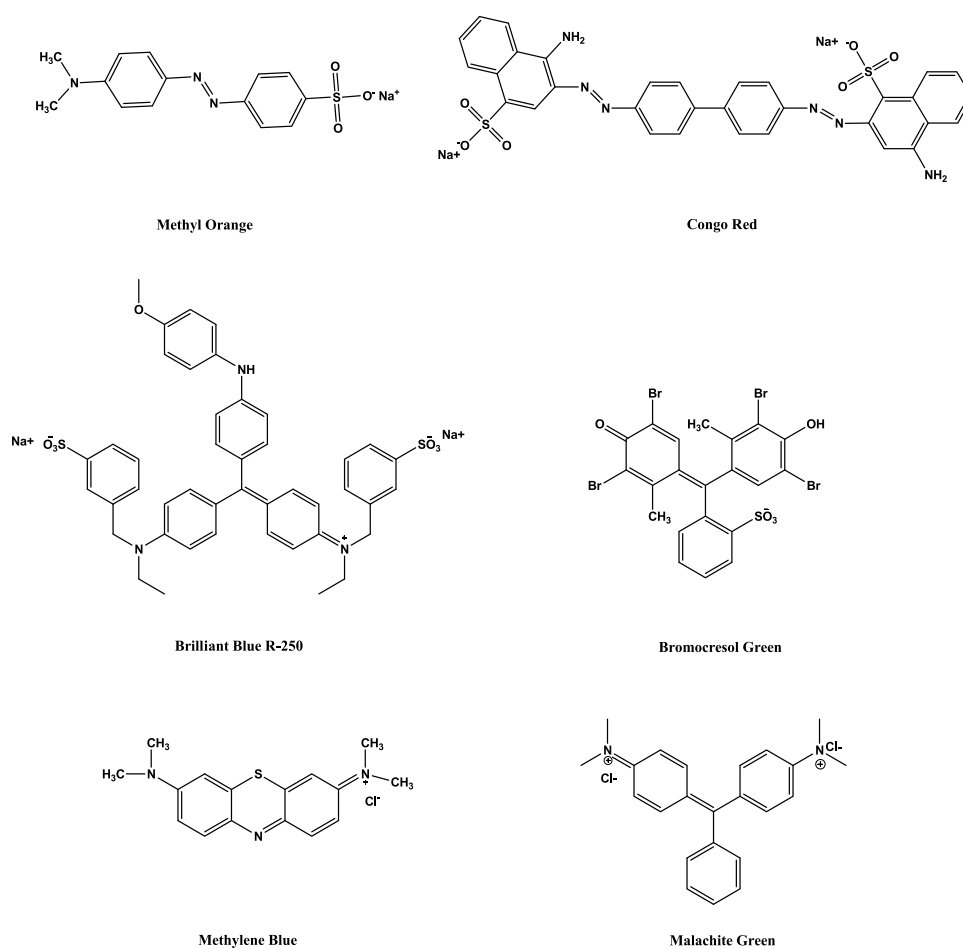


Figure 1. Molecular structure of the anionic and cationic dyes used in this study.

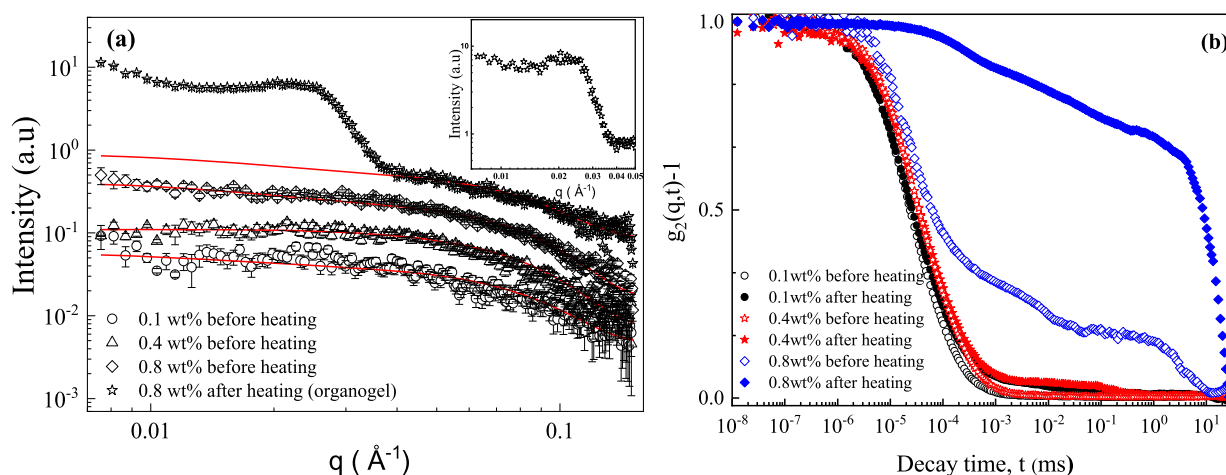


Figure 2. (a) SAXS profile of 2 wt % PS-*b*-P4VP for different concentrations of DBD. The individual scattering curves are shifted to improve their visibility (shift factors 1, 1, 2, and 6 along the *y*-direction). Symbols represent the experimental data, and lines are fits to eq 3. The inset shows the structure peak after decoupling the form factor from the SAXS profile, and (b) correlation functions, $g_2(q, t) - 1$, as a function of delay time at $q = 0.01926 \text{ nm}^{-1}$ for various percentage additions of DBD to the 2 wt % PS-*b*-P4VP block copolymer.

an organogel. There is no report on a PS-*b*-P4VP organogel or its related applications to the best of our knowledge. This organogel is anion-specific; we have validated its applicability as an adsorbent for anionic dyes by performing dye adsorption studies using four anionic organic dyes, two of which contain an azo group and the other two has a triphenylmethane backbone. Due to the pyridinium group's presence and the long-chain alkyl halide in the organogel, favorable molecular interaction occurs when these groups are in contact with the dye molecules. Interestingly, the organogel not only removes the dye but can be recycled, regenerated, and reused for more than 20 cycles without much deterioration in the dye removal efficiency.

EXPERIMENTAL SECTION

Materials and Characterizations. Styrene (Sigma-Aldrich, 99%) was washed and extracted three times with 5% sodium hydroxide to remove the inhibitor and dried over anhydrous Na_2SO_4 under vacuum. 4-Vinylpyridine (Sigma-Aldrich, 98%) was purified by passing through an alumina column to remove the inhibitor. Chain-transfer agent CTA, 2-(dodecylthiocarbonothioylthio)-2-methylpropionic acid (DDMAT, Sigma-Aldrich, 98%) and initiator 2,2'-azobis(2-methylpropionitrile) (AIBN, Sigma-Aldrich, 98%) were recrystallized from methanol before use. DBD (Sigma-Aldrich, 98%) was used as the cross-linker. All of the solvents and the dyes were used as received. Reversible addition–fragmentation chain transfer (RAFT) polymerization technique^{49–51} was followed to synthesize the block copolymer.

Synthesis of Poly(styrene-*block*-4-vinylpyridine) Diblock Copolymer (PS-*b*-P4VP). A two-step procedure was adopted for the synthesis of PS-*b*-P4VP by RAFT polymerization. First, PS-CTA was prepared. In a typical protocol, styrene/DDMAT/AIBN (325:6:1) was dissolved in 10 mL of 1,4-dioxane, and the reactants were taken in a Schlenk flask fitted with a stir bar. The flask was hermetically sealed, and the mixture was degassed at 0 °C for 30 min. Polymerization was carried out at 70 °C for 24 h. After polymerization, the reaction mixture was quenched by rapid cooling in an ice bath. Finally, the crude mixture was precipitated thrice into excess cold diethyl ether and dried under vacuum overnight. PS-CTA was recovered as a yellow powder.

In the second step, the PS-*b*-P4VP-CTA diblock copolymer was synthesized following the same protocol as that used for PS-CTA except that a different reagent ratio was utilized with PS-CTA as the precursor and DMF as the solvent. The ratio of 4-VP/PS-CTA/AIBN

was 300:100:1. After polymerization, the reaction mixture was quenched by rapid cooling in an ice bath. PS-*b*-P4VP-CTA was precipitated in cold hexane and dried under vacuum. The collected PS-*b*-P4VP-CTA powder had an orange color. The trithiocarbonate group (CTA) was removed from the polymer chain by treating it with hydrogen peroxide for 2 h, followed by thorough washing using cold water/hexane mixture. The resulting pale, whitish PS-*b*-P4VP powder was stored under vacuum.

Preparation of PS-*b*-P4VP Organogel. About 2 wt % diblock copolymer and 0.8 wt % DBD were dissolved in DMF and kept undisturbed at 70 °C for 4 h. The obtained PS-*b*-P4VP organogel was washed with cold diethyl ether to remove the unreacted chemicals.

The steps for synthesizing the PS-*b*-P4VP diblock copolymer and its subsequent cross-linking with DBD to form the organogel are given in Scheme 1. The inset in the scheme shows the photograph of the PS-*b*-P4VP block copolymer before and after gelation. It is also worth mentioning that leaving the diblock copolymer solution with 0.8 wt % DBD undisturbed for about two weeks resulted in gelation. However, heating at 70 °C was found to quicken the process of gelation.

The molecular weight of the polystyrene-CTA (PS-CTA) and poly(styrene-*b*-vinylpyridine) (PS-*b*-P4VP) diblock copolymer and their corresponding polydispersities were determined from advanced polymer chromatography (APC) (ACQUITY, Waters) using DMF as the eluent at a flow rate of 0.5 mL min^{−1}. The ¹H NMR analysis was performed on a JEOL 400 MHz spectrometer using CDCl_3 as the solvent. The block copolymer and the organogel were dissolved in the CDCl_3 solvent. The ¹H NMR spectra of the solutions in CDCl_3 were calibrated to tetramethylsilane as the internal standard (δH 0.00). Fourier transform infrared (FTIR) spectra of the block copolymer and the organogel were recorded on a Bruker spectrophotometer.

Small-angle X-ray scattering (SAXS) measurements were performed on a pinhole camera (Ganesha 300 XL, SAXSLAB, Denmark), covering a q range from 0.003 to 2.5 Å^{−1}. The block copolymer solutions were loaded in 1.3 mm diameter quartz glass capillaries (Hilgenberg), and a specially designed “cell” was used for loading the organogel; the organogel was sandwiched between two circular mica plates. The samples were measured at a temperature of 20 °C, which was controlled by an external recirculating water bath (Julabo, Seelbach, Germany). The scattering intensity was corrected to an absolute scale by calibrating against DMF. The scattered intensity profiles have been obtained by circular integration of the two-dimensional intensity profiles. Dynamic light scattering (DLS) was carried out using a three-dimensional (3D) LS spectrometer (LS Instruments AG, Fribourg, Switzerland) with a Cobolt DPSS laser light source (660 nm, 100 mW) in the 3D cross-correlation

configuration. For the nonergodic samples, the samples were rotated during the measurements to obtain the ensemble-averaged intensity correlation function.⁵² Oscillatory shear experiments were carried out at 25 °C using a stress-controlled MCR 301 rheometer (Physica, Anton Paar, Austria). A parallel plate geometry of 25 mm diameter was used for the measurements at a gap of 0.5 mm. Strain sweep experiments were carried out by varying the strain amplitude from 0.1 to 1000% at a frequency of 1 rad s⁻¹. Frequency dependencies of the storage (G') and loss (G'') moduli were determined by performing frequency sweep measurements on the samples from 0.1 to 100 rad s⁻¹. Dye adsorption studies have been carried out using a UV–vis–NIR spectrophotometer (JASCO V-670, Japan).

Dye Adsorption Experiments. Dye adsorption studies have been carried out using 2 wt % pellets of the organogel in various anionic dye solutions and in a mixture of anionic and cationic dyes as well. The molecular structure of the dyes is shown in Figure 1. The pellets of the organogel (weighing 20 mg) were obtained by cutting from the bulk of the organogel using a scalpel. Anionic dyes Congo red (CR), brilliant blue R-250 (BB), methyl orange (MO), bromocresol green (BG), and cationic methylene blue (MB) and malachite green (MG) were used for the study. The concentration of the dyes used in the experiments was 0.1 g L⁻¹. The time evolution of the UV–vis absorption spectrum was monitored after 15 min of contact of the dye solution with the organogel. The residual dye concentration was estimated from the quantitative analysis of UV–vis absorption. Regeneration experiments were carried out by immersing the dye-adsorbed organogel into 5 mL of ethanol. After 10 min, the organogel was recovered, and after drying, the reusability of the organogel was ratified by repeating the dye adsorption and subsequent dye removal (desorption) cycles.

The equilibrium adsorption capacity of the organogel is given by

$$Q_e = \frac{(C_0 - C_e)}{m} \times V \quad (1)$$

where C_0 and C_e are the initial and equilibrium dye concentrations, respectively, V is the volume of the dye solution, and m is the weight of the adsorbent.

RESULTS AND DISCUSSION

The molecular weights of PS-CTA and PS-*b*-P4VP were determined by APC analysis, $M_{n,APC}$, and the respective APC curves are given in Figure S1. The obtained values were then compared with the theoretically calculated value, $M_{n,th}$ using eq 2

$$M_{n,theor} = \frac{[M]_0}{[CTA]_0} \times M_m \times \text{conversion} + M_{CTA} \quad (2)$$

where M_m and M_{CTA} are the molecular weights of the monomer and the CTA and $[M]_0$ and $[CTA]_0$ are the initial concentrations of the monomer and the CTA, respectively. The obtained values of molecular weights are shown in Table 1. Using eq 2 and from the experimentally determined APC values, PS-CTA and PS-*b*-P4VP synthesized by RAFT polymerization proceed to 61.6 and 92% conversions, respectively.

Spectral Characterization. The chemical shifts for the PS-CTA (Figure S2i) occurs at $\delta = 0.8$ –2.1 ppm ($-\text{CH}_2-$) and $\delta = 6.3$ –7.3 ppm (s , $-\text{C}_6\text{H}_5$); in addition to the above chemical shifts, the PS-*b*-P4VP-CTA RAFT terminal (Figure S2ii) exhibited a shift at $\delta = 8.0$ –8.6 ppm (m , $-\text{CH}_2\text{CHC}_5\text{H}_4\text{N}$). The CTA end was removed from the block copolymer, and this was confirmed by the disappearance of the RAFT terminal at $\delta = 0.8$ –1.1 ppm (Figure S2iii). Bridging between the two pyridine groups of the block copolymer with DBD is confirmed by the δ at 4.2–4.5 ppm (Figure S2iv). The FTIR spectrum (Figure S3) exhibited the

Table 1. Estimate of the Molecular Weight of the PS-CTA and PS-*b*-P4VP Diblock Copolymer

label	$[M]_0/[CTA]_0/[I]_0$	conversion %	M_n (kg mol ⁻¹)		
			$M_{n,th}^a$	$M_{n,APC}^b$	$\bar{D}^c$
PS-CTA	325:6:1	61.6	20.6	12.6	1.06
PS- <i>b</i> -P4VP	300:100:1	92	65.9	60.9	1.32

^aTheoretical molecular weight determined by monomer conversion, according to eq 2. ^bMolecular weight determined by APC analysis. ^c $\bar{D}$ (M_w/M_n) values determined by APC analysis.

characteristic bands before and after gelation of PS-*b*-P4VP. The sample before gelation (Figure S3a) showed peaks at 1600–2000 cm⁻¹ corresponding to the aromatic C=C stretching; the peaks at 2950 and 3023 cm⁻¹ correspond to the C–H asymmetric aliphatic stretching and C–H asymmetric stretching of the aromatic ring, respectively. Upon gelation (organogel) (Figure S3b), the sample exhibited an asymmetric aliphatic C–H stretching peak at 2923 cm⁻¹ and a sharp aromatic symmetric stretching peak at 1644 cm⁻¹. Here, the conversion of pyridine to pyridinium ion is seen as a broad asymmetric N⁺–C stretching peak at 810–1145 cm⁻¹.

Scattering Analysis. To investigate the detailed spatial information on the PS-*b*-P4VP before and after gelation, SAXS measurements were performed. All of the measurements were carried out at 20 °C, and the resulting SAXS profile is shown in Figure 2a. The experimental data for 0.1, 0.4, and 0.8 wt % addition of DBD before gelation has been fitted with a polymer micelle model form factor,⁵³ $P_{pm}(q)$, with corrections accounted for the background

$$P_{pm}(q) = N^2\beta_s^2F_s(q) + N\beta_c^2F_c(q) + 2N^2\beta_s\beta_cS_{sc}(q) + N(N-1)\beta_c^2S_{cc}(q) \quad (3)$$

Here, N is the aggregation number of the micelle and $F_s(q)$ and $F_c(q)$ are self-correlation for the sphere with radius R_c and the Gaussian chain with a radius of gyration R_g , respectively. β_s and β_c are the total excess scattering lengths of a block in the spherical core and in the corona, respectively; s and c denote the spherical core and corona, respectively. S_{sc} defines the interference cross term between the spherical core and the chains, and S_{cc} defines the interference cross term between the chains in the corona. We used the SasView program, and the resulting fit lines are shown in Figure 2a (red lines). The core radius, R_c , of the particles determined from the fits using eq 3 is 2.7 nm for all three concentrations of DBD. However, slight decreases in the R_g values are noted upon increasing the DBD concentration, i.e., 7.8, 7.2, and 6.9 nm for 0.1, 0.4, and 0.8 wt % DBD. Upon heating the 0.8 wt % sample to 70 °C, the SAXS profile develops spatial correlations; see the black stars in Figure 2a. In this case, the scattering pattern, $I(q)$, is influenced both by the form factor, $P_{pm}(q)$, and the structure factor, $S_{pm}(q)$

$$I(q) \sim P_{pm}(q)S_{pm}(q) \quad (4)$$

The line going through the data points for the sample after heating is the form factor with the same parameters as those in the non-heated samples. This shows that the formed particles retain their shape and size also after heating. By dividing the intensity curve, $I(q)$, with $P_{pm}(q)$, only the structure factor is left, which gives information on the spatial structure in the system; see the inset in Figure 2a. From the peak maxima, the

average interparticle spacing is found to be 20 nm, which is almost twice the total radius of the spherical micelles, $R_{\text{tot}} = R_c + R_g$, formed before heating the sample. This indicates that the most probable distance between two micelles in the gel almost touches each other. In the micelles, the polystyrene chain forms the core, and the vinylpyridine groups form the corona.⁵⁴ Since there is no contraction in volume or any associated phase separation during the heating of the sample and its subsequent gelation, the system goes through a space-filling gelation mechanism. The heating of the sample results in the bridging of the outer P4VP chains of the spherical micelle and the long-chain DBD, assisting in reorientation of the randomly spaced spherical micelles. We believe that the structure of the organogel is an interconnected network of spherical micelles organized in a random percolated network structure, where the most probable distance between micelles is 20 nm. The electrostatic bridging of the micelles and the DBD chains are strong enough that the sample turns non-flowing and forms a rigid network. At this time, we have no proper model to fit the structure factor of the network formed in the sample. Attempts to fit the data with a Percus–Yevick approximation or an RMSA model yield an overestimation of the concentration. This, we believe, comes from the percolated network.

The light scattering experiments were performed at a constant temperature of 20 °C, between scattering angles of 30–150°. The intensity autocorrelation function $g_2(q, t) - 1$ for PS-*b*-P4VP as a function of DBD concentration is shown in Figure 2b. The intensity autocorrelation function $g_2(q, t) - 1$ for PS-*b*-P4VP with 0.1 and 0.4 wt % DBD before gelation shows a dominating single decay corresponding to a hydrodynamic radius of 9 nm. This corresponds well with the size of the total micelle radius, R_{tot} , determined with SAXS. After heating the 0.1 and 0.4 wt % DBD samples (no gelation), only a slight shift in the decay time and a small addition on the baseline can be seen. This means that the DBD concentration used in this sample is not sufficient to bridge the micelles to form a continuous network, but only a few aggregates are formed. These two samples do not show full dynamic arrests of the network fluctuation, reflecting the insufficient amount of DBD required to arrest the dynamics. However, the 0.8 wt % sample before gelation shows an apparent two-step decay and not fully relaxed $g_2(q, t) - 1$, i.e., the baseline at the large time does not decay to zero. This indicates that already before heating, a substantial amount of cross-linking occurs in the sample creating clusters, where the micelles are restricted to move. Upon heating this sample, $g_2(q, t) - 1$ exhibited a strong nonergodic behavior, where just a small proportion of the correlation function at fast time decays. This implies the complete arrest of the movement in the sample; the sample becomes non-flowing, where only the fast-local fluctuations can be monitored. This behavior correlates well with the SAXS results of the organogel, where we found a clear structural correlation for the 0.8 wt % DBD after heating but not in any of the other samples. The formation of spherical micelles with radii closely matching SAXS and DLS data is further confirmed by cryo-TEM imaging on the 0.1 wt % DBD added block copolymer after heating at 70 °C (Figure S4).

Rheological Properties of the Organogel. The rheological properties of the block copolymer in DMF with cross-linker DBD, before and after gelation, were characterized using dynamic oscillatory shear experiments. Figure 3a shows the variation of (G') and (G'') with frequency in the linear

viscoelastic limit for the PS-*b*-P4VP block copolymer in DMF with DBD, before and after heating at 70 °C. Before heating, the block copolymer–cross-linker mixture exhibits a typical behavior of a viscoelastic fluid. In the frequency range probed, G'' is higher than G' , indicating the viscous nature of the copolymer–cross-linker mixture. However, after heating, both G' and G'' are independent of frequency, with G' being an order of magnitude larger than G'' . This indicates the solid-like nature of the gels formed due to heating.

Insights into the large deformation behavior of the organogel were obtained by performing large amplitude oscillatory shear (LAOS) experiments. The variation of G' and G'' as a function of strain amplitude for the organogel with 2 wt % block copolymer and 0.8 wt % DBD is shown in Figure 3b. The organogel exhibits a plateau for G' and G'' , with G' an order of magnitude larger than G'' , at small strain amplitudes (<5%), up to the linear viscoelastic limit. At a strain amplitude of 10%, an overshoot is observed in G'' , which can be attributed to the breaking of the bridges formed between the cross-linker DBD and the block copolymer micelles. A similar observation was reported for poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide) (PEO–PPO–PEO) triblock copolymer solutions, where the close-packed micelles break into layers that can slide over each other.⁵⁵ We also noticed that, with a further increase in strain amplitude, a strain thinning regime is seen where both G' and G'' decreases. This could be attributed to the alignment of the micelles along the direction of shear, similar to that observed for block copolymer gels with micellar structures.^{55,56} The yield point is determined from the maximum of the stress curve⁵⁷ (blue stars), and the characteristic stress and strain values at the yield point are $\sigma_y = 500$ Pa and $\gamma_y = 13.3\%$, respectively. The onset of the liquid-like behavior from a solid-like behavior is the point at which $G' = G''$, and the corresponding stress and strain values are $\sigma_{\text{irr}} = 437$ Pa and $\gamma_{\text{irr}} = 23.7\%$.

The stability of the organogel at various solution environments such as pH, ionic strength, and temperature was evaluated. The mass change of the organogel as a function of time at three different pH levels (3, 7, and 9) and NaCl concentration was studied by placing the organogel in the respective solutions and allowed the organogel to rest in these solutions. The mass of the organogel was measured at regular intervals, and the obtained values are plotted in Figure S5a,b. Only a very slight increase in the organogel mass was observed (~4%), and thus, this organogel is found to be stable irrespective of the solution environment (pH, ionic strength). The stability of the organogel with temperature is studied by performing a temperature sweep using a rheometer at constant strain and frequency (Figure S5c). The G' and G'' remained constant throughout the temperature sweep, implying the stable nature of the organogel. Further, the organogel exhibited a self-sustainable nature,^{25,38,41} i.e., stood by itself without any support and retained the cylindrical shape after pulling it from the vial in which it was synthesized. Besides, the organogel also exhibited excellent load-bearing characteristics^{25,38} and could withstand metal weights of 5, 10, 20, and 50 g (Figure S6) placed on top of it.

Dye Adsorption Studies. The anionic dye adsorption potential of the PS-*b*-P4VP organogel was demonstrated using four types of anionic dyes. A pre-weighed 20 mg pellet of the organogel was added to a solution containing the anionic dyes, and the contact-time-dependent UV–vis absorption spectra were recorded (Figure 4). As can be seen from the spectra

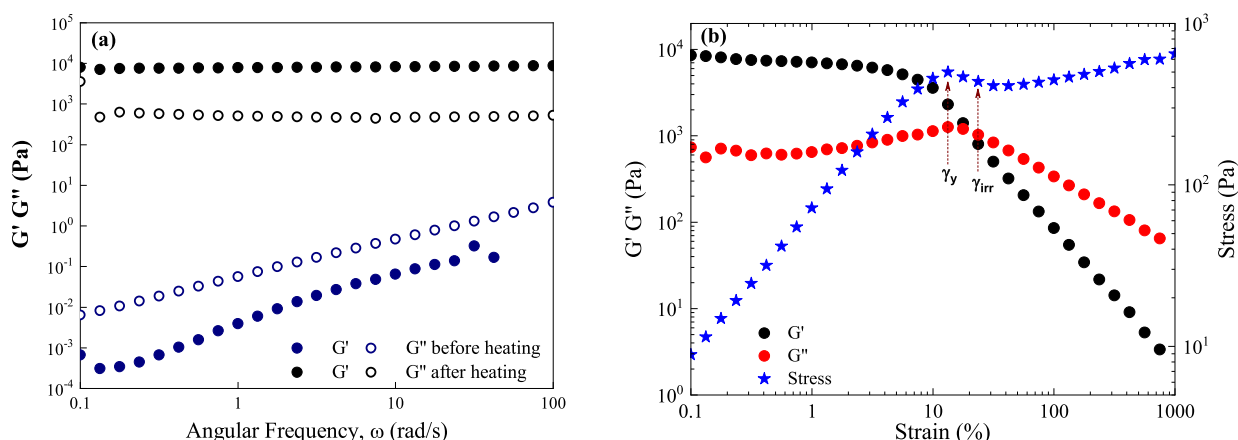


Figure 3. (a) Linear viscoelastic spectrum of the 2 wt % PS-*b*-P4VP block copolymer with 0.8 wt % DBD. G' (filled symbols) and G'' (open symbols) are presented as a function of angular frequency at a constant strain amplitude of 1%. Blue symbols correspond to measurements before heating, while black symbols are from measurements performed after heating (formation of the organogel). (b) Dynamic strain sweep at constant $\omega = 1 \text{ rad s}^{-1}$ to determine the linear viscoelastic range of the 2 wt % block copolymer with 0.8 wt % DBD (organogel). Arrows indicate the yield strain γ_y and the onset of liquid-like behavior, γ_{irr} .

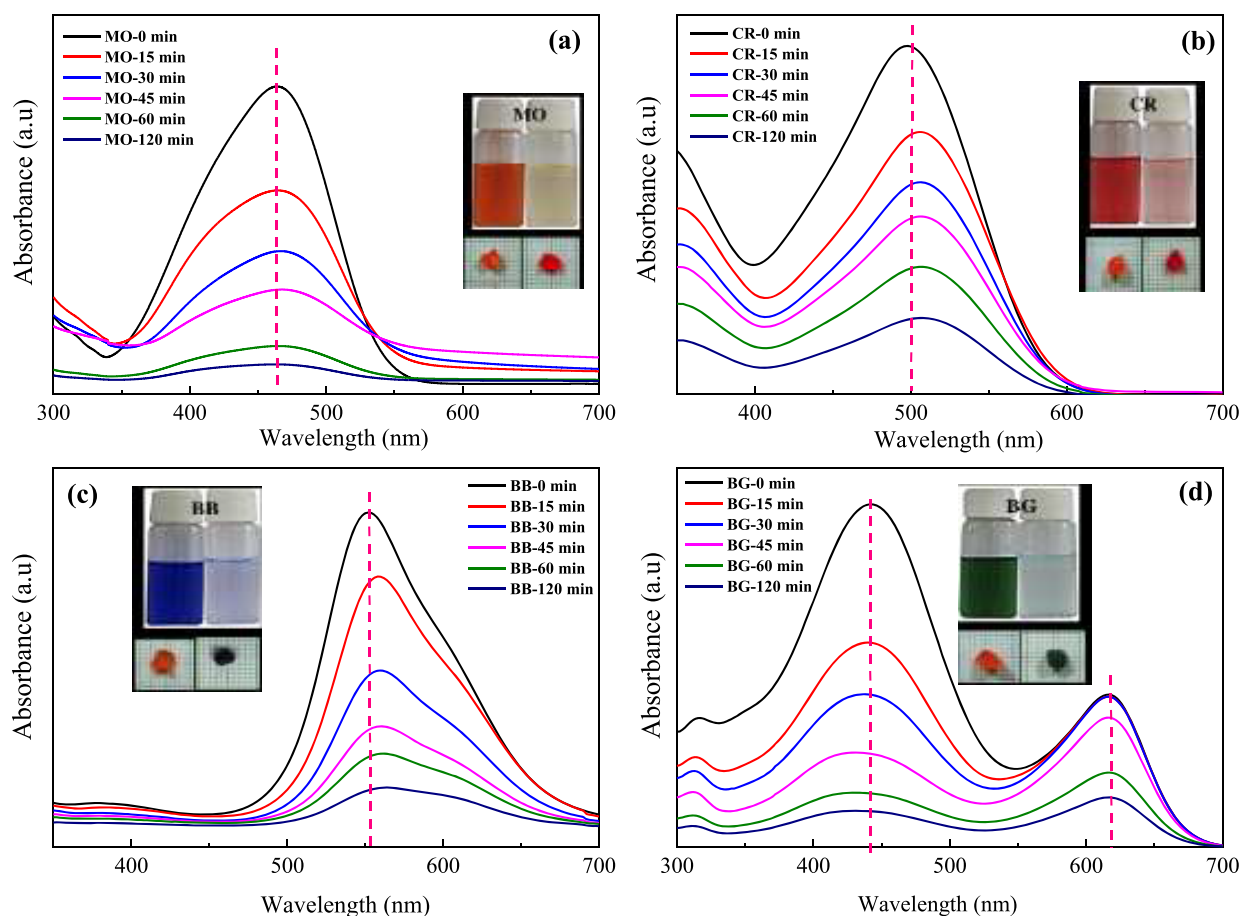


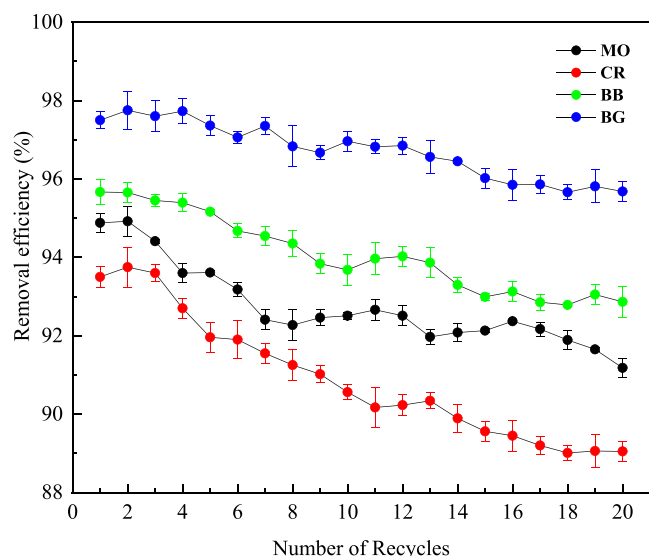
Figure 4. UV–visible spectral evolution with time of the various dye solutions in contact with the organogel: (a) methyl orange, (b) Congo red, (c) brilliant blue R-250, and (d) bromocresol green. Insets in the figure show the photographs of the various dye solutions before and after the removal of the dyes by the organogel (top row) and the color change of the organogel after 60 min of contact with the dye solution (bottom row).

(Figure 4a–d), there is a remarkable dye uptake by the organogel for all four anionic dyes. MO and BB had a single absorption maximum at 465 and 555 nm, whereas CR and BG exhibited two peaks: at 342, 500 nm and 437, 618 nm, respectively. An almost clear water-like solution is observed after 60 min of contact with the organogel. Generally, gel-

based selective adsorption occurs either via chemisorption or by electrostatic interaction between the reactive sites on the gel and the ionic groups on the dye molecules. In our study, the removal of the anionic dyes by the PS-*b*-P4VP organogel can be justified by the high electrostatic attraction between the pyridinium cations in the organogel and the anionic sulfonate

Table 2. Variation in pH of the Dye Solution before and after the Addition of the Organogel

dyes	pH of the dye solution	pH (after adding the organogel)	pH (after 120 min of adsorption)
MO	4.86	5.11	6.29
CR	5.71	6.02	6.73
BB	5.18	5.42	6.35
BG	3.85	4.36	6.12

**Figure 5.** Removal efficiency of the organogel for the anionic CR, MO, BB, and BG dyes as a function of the number of recycle times.

groups of MO, CR, BB, and BG. This adsorption behavior is in agreement with studies using an imidazolium-based supra-molecular gel adsorbent system, where dye adsorption for eosin yellow (EY) and MO proceeds via the electrostatic interaction between the positively charged imidazolium cation and the carboxylate/sulfonate anion group of the dye molecules.²⁴ No significant variation is noted in the ¹H NMR and FTIR spectra of the pure organogel and the organogel regenerated after dye adsorption (Figure S7).

Apart from the decrease in intensities with time, an additional red shift in the absorption maxima is noted for CR and BB. A similar red shift is noted during sonolysis of BB⁵⁸ and in the adsorption of CR using iron nanoparticles.⁵⁹ The red shift noticed for CR is attributed to the shift in pH to acidic conditions⁶⁰ during its degradation. We thus monitored the pH of the dye solution upon contact with the organogel and found that in our study; instead, the pH increases upon contact with the organogel (Table 2). This again corroborates the lowering of the acidic contribution from the sulfonate groups in the dye molecules upon contact with the organogel due to their electrostatic association with the N⁺ group of the organogel. Further, no detectable aggregation was observed in all four dye solutions during the dye adsorption. At this moment, we are unsure of what could have led to the red shift, but studies are being undertaken to understand the complexation behavior escalation due to the presence of NH₂ and OH groups in CR and BB, respectively, and the role of π - π stacking between dye molecules.

The photographs of the four dye solutions before and after adsorption by the organogel (top row) and the color change of the organogel after 60 min of contact with the dye solution (bottom row) are shown as insets in Figure 4. Importantly, we have used only a meager amount of the organogel (2 wt %) for the adsorption studies; upscaling the quantity of the organogel can significantly shorten the adsorption time.

The adsorption efficiency of the organogel calculated from eq 1 is found to be 600, 531, 570, and 580 mg g⁻¹ for the MO, CR, BB, and BG dyes, respectively (Figure S8). The dye adsorption behavior of the PS-*b*-P4VP organogel was evaluated using Langmuir (eq S1) and Freundlich isotherm (eq S2) models. The correlative fitted plots of Langmuir and Freundlich isotherms for the various dyes are shown in Figure S9a,b, respectively. The Langmuir isotherm model follows homogenous surface adsorption and the Freundlich isotherm model follows the heterogeneous surface with different types of surface adsorption. Here, we compared both models and obtained the best fit for the Freundlich isotherm, and thus, the adsorption proceeds via a heterogeneous process.

The absorption spectra as a function of dye (50, 100, 200, and 300 ppm for all of the dyes) and organogel (0.5, 1, 2, and 3

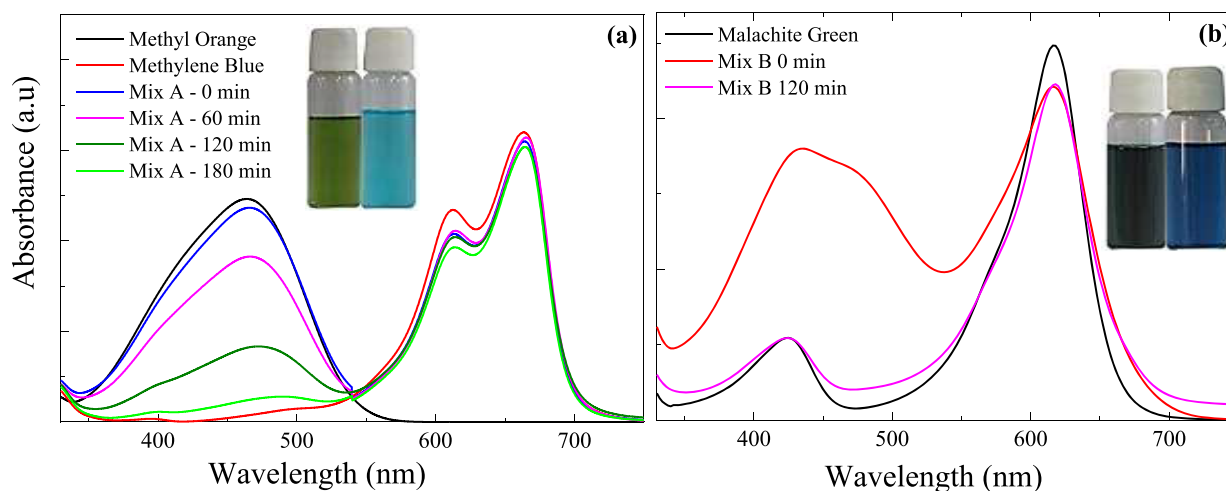
**Figure 6.** Time evolution of the UV-visible spectra for dye solutions in contact with the organogel: (a) mixture A containing methylene blue and methyl orange and (b) mixture with cationic dye malachite green and anionic dyes MO, CR, BB, and BG. Insets in the graphs show the color change of the dye solution before and after dye adsorption.

Table 3. % Removal Efficiency Reported by Various Research Groups for a Few Dyes Using Gel-Based Materials

type of gels	dyes	% dye removal
poly(<i>N</i> -isopropylacrylamide) microgels ¹ methacryloyloxyethyltrimethylammoniumchloride zwitterionic hydrogel ²¹	orange II	73.1
	acid red	95
	quinoline yellow	95
	methyl violet	10
	methylene blue	10
metal–organic gels ²³	Congo red	95
	rhodamine B	92
	methylene blue	85
	chrome azurol S	97
	methyl violet	94
	amido black 10B	67
	eosin yellow	80
	rhodamine B	95
	methylene blue	98
	methyl orange	35
imidazolium-based supramolecular gels ²⁴ supramolecular ionic liquid gels ²⁵ poly(acrylic acid)-based nanocomposites hydrogel ²⁶ lithocholic acid-based hydrogel ²⁶	amido black	96
	rhodamine 65G	35
	chrome azurol S	35
	DR 23	99
poly(epichlorohydrin-ethylenediamine) hydrogel ²⁸	AR1	99
	AO7	98
	AY36	99.8
	DB15	100
	eosin yellow	98
	brilliant green	99.3
	rhodamine B	
	direct red 80	~95
	reactive blue 4	
	methylene blue	97
folic acid–polyaniline hybrid hydrogel ²⁹ poly(acrylic acid)-kaolin hydrogel ³⁵ tripeptide-based hydrogels ³⁶	methyl orange	3
	malachite green	90
	methyl orange	90
	basic blue 41	97.4
alginate/polyaspartate hydrogel ³⁷	bromocresol green	41.5
	crystal violet	94.2
	Congo red	97.6
	methyl violet	95
	crystal violet	96
	rhodamine-6G	95
	methyl orange	95
	crystal violet	99
	malachite green	97
	rhodamine B	27
<i>N</i> ₂ , <i>N</i> ₆ -bis(3-(pyridin-2-yl)-1 <i>H</i> -pyrazol-5-yl)- pyridine-2,6-dicarboxamide-based metallogel ⁴⁴ terpyridine-based smart organic–inorganic hybrid gel ⁶²	uranine	4
	methyl orange	96
	Congo red	91
	brilliant blue R-250	86
poly(acrylic acid- <i>co</i> -hydroxyethyl methacrylate) interpenetrating network hydrogels ⁶³	bromocresol green	94
low-molecular-weight amphiphilic dipeptides ⁶⁴ phenylalanine-based low-molecular-weight gelator ⁶⁵		
glutamic acid-derived organogels ⁶⁶		
quaternized polystyrene- <i>b</i> -4-vinylpyridine organogel ^{this work}		

wt %) concentrations (Figures S10–S13) were also recorded. It is observed that as the concentration of the organogel increased, the dye removal efficiency also increased. It took about 90 min for the 0.5 and 1 wt % pellet of the organogel to show dye adsorption above 85%. For the 2 and 3 wt % organogel, more than 85% of the dye removal occurred within 30 min of contact time.

The dye removal efficiency (*R*, %) of the organogel was calculated using the following equation

$$R = 100 \times \frac{C_i - C_f}{C_i} \quad (5)$$

where *C_i* and *C_f* are the initial and final concentrations (mg L^{−1}) of the dye after adsorption. Quantitative analysis of the UV–vis spectra was performed by monitoring the main peak intensity and from eq 5. From the peak intensity, about 90% MO, 72% CR, 76% BB, and 89% BG were removed within 60 min of contact with the organogel (Figure 4a–d). Increasing the contact time to 120 min showed 98% MO, 90% CR, 88% BB, and 96% BG removal (Figure 4a–d).

Regeneration of the Adsorbent and Recycling Studies. Regeneration and reuse of the adsorbent are promising for the large-scale and cost-effective effluent treatment process. Also, the recovered dyes can be reused for the further dyeing process, and this will significantly reduce the continuous feed of dyes required for textile dyeing. This may also prohibit secondary contamination.⁶¹ To investigate the regeneration of the organogel, the dye absorbed mass was immersed in 5 mL of ethanol solution. After ensuring that no detectable dye remains on the gel (by recoding the UV–vis spectrum), the dye adsorption experiments were repeated. The regeneration and reuse studies were carried out for about 20 cycles on the four anionic dyes. Interestingly, the organogel retained its remarkable dye adsorption characteristics with removal efficiencies similar to the first use (Figure 5), weighing out the organogel as a promising adsorbent for anionic dyes. The organogel retained its original appearance with no visual deformation in shape.

Dye Specificity. For studies on dye specificity, a pre-weighed 20 mg pellet of the organogel was added to a solution containing a mixture of dyes, and the UV–vis spectra were recorded. Two different mixtures have been used in the study. Mixture A had anionic methyl orange and cationic methylene blue, and mixture B had four types of anionic dyes (MO, CR, BB, and BG) and one cationic dye (malachite green). The resulting UV–vis spectra with the progress of time are illustrated in Figure 6. For mixture A (Figure 6a), the broad but intense absorption maxima for MO exhibited signs of adsorption within 60 min of contact with the organogel, and at 180 min, the MO peak vanished; the absorption maxima of methylene blue remain almost unaltered during the adsorption process. In mixture B (Figure 6b), all of the anionic dyes were adsorbed, and the malachite green dye was recovered after 120 min of contact with the organogel (photograph in the inset). Here, we noticed that the activity of the organogel is almost similar to that noted for individual dye solutions. Irrespective of the difference and number of anions, the potential of N^+ to adsorb the anionic dyes is found to be superior. The anion specificity of the organogel aids in the separation of a mixture of cationic and anionic dyes; at the same time, the recovered dyes can be used for further applications.

CONCLUSIONS

This work describes the synthesis of an organogel of a poly(styrene-*block*-4-vinylpyridine) block copolymer using dibromododecane as the cross-linker. From 3D light-, small-angle X-ray scattering and rheological measurements, the cross-linking of the block copolymer into a gel is confirmed. Due to the presence of N^+ ions, the organogel acts as an adsorbent for anionic dyes and also exhibits anion selectivity in a mixture of cationic and anionic dyes, which is driven by electrostatic attraction between the positively charged gel and negatively charged dye molecules. This organogel is highly cost-effective as it can be recycled, reused, and regenerated with a very high throughput removal of anionic dyes within a short period—the performance of the organogel is expected to remain unaltered for long-term water treatment applications. The PS-*b*-P4VP organogel is high performing as compared with other reported gel-based adsorbents. In Table 3, we have shown the removal efficiency of several gel-based adsorbents. Comparing our work with the results summarized in Table 3, with a mere 2 wt % adsorbent used and much quicker times for dye removal, the organogel of PS-*b*-P4VP shows excellent

potential for applications in effluent water treatment. We strongly believe that the adsorption performance of the organogel will not deteriorate with time and remain unaltered for long-term effluent water treatment applications. Future work will address the use of this organogel as a filtration membrane for the removal of anions from salty water.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.langmuir.1c00288>.

APC spectra of the PS-CTA and PS-*b*-P4VP block copolymer; 1H NMR spectra of PS-CTA, PS-*b*-P4VP-CTA, PS-*b*-P4VP, and the organogel; FTIR spectra of PS-*b*-P4VP and the organogel; cryo-TEM image; stability of the organogel; load-bearing characteristics of the organogel; 1H NMR and FTIR spectra of the pure and regenerated organogel; equilibrium dye adsorption isotherms; Langmuir and Freundlich isotherm models; time evolution of UV spectra as a function of organogel and dye concentrations (PDF)

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Author Contributions

The manuscript was written through the contribution of all the authors. All authors have approved the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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