



Chemically crosslinked poly(N-isopropylacrylamide-*block*-4-vinylpyridine) organogel with myriad applications

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ABSTRACT

We report the synthesis of a poly(N-isopropylacrylamide-*block*-4-vinylpyridine) (PNIPAM-*b*-P4VP) block copolymer and its subsequent chemical crosslinking to form a quaternized organogel. Oscillatory shear measurements are indicative of a robust elastic network in the organogel, and the critical gel point is found to be 8 wt% block copolymer with 0.8 wt% crosslinker. Interestingly, the myriad applications of the organogel across domains, including anionic dye adsorption, heavy metal removal, and antibacterial activity, suggest a new paradigm for wastewater treatment.

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1. Introduction

Over the past few years, there have been significant developments in creating new and multi-functional soft materials based on polymeric gels such as the self-oscillating gels [1,2], lipophilic polyelectrolyte gels [3], color-changing gels [4,5], etc. Polymeric organogels capable of imbining organic solvent are used in drug delivery [6], dye removal [7], sensing devices [8], etc. Upon reaction with a suitable crosslinker, it is possible to convert block copolymers into organogels by making use of the van der Waals interactions [9], hydrogen bonding [10], dipole interactions [11], or π - π interactions [12,13].

In this contribution, we report the synthesis of a PNIPAM-*b*-P4VP diblock copolymer by reversible addition-fragmentation chain-transfer polymerization (RAFT) and its subsequent conversion to form a quaternized organogel by chemical crosslinking. This is the first report on the synthesis of this novel organogel and its related application. Oscillatory shear measurements suggest the gelation of the block copolymer at a composition of 8 wt% PNIPAM-*b*-P4VP with 0.8 wt% DBD. As the organogel has quaternary ammonium groups in its network, and due to its anion specific nature, the PNIPAM-*b*-P4VP organogel significantly removed anionic dyes and toxic heavy metals such as arsenic and chromium (arsenite and chromate anions). Also, the quaternary ammonium groups

with intrinsic positive charges are known to exhibit antibacterial activity [14], and this is confirmed by carrying out antibacterial studies on two bacterial species.

2. Methods and techniques

The PNIPAM-*b*-P4VP is synthesized using 2-(dodecylthiocarbonylthio)-2-methylpropanoic acid (DDMAT) as the RAFT agent and α , α' -azobisisobutyronitrile (AIBN) as the initiator. First, the poly(N-isopropylacrylamide)-chain transfer agent (PNIPAM-CTA) is synthesized by dissolving NIPAM, DDMAT, and AIBN in 1,4-dioxane in the ratio 325:6:1, followed by degassing the solution. The reaction is carried at 70 °C for 24 h under an inert atmosphere followed by precipitating the PNIPAM-CTA using cold diethyl ether. In the second step, the PNIPAM-*b*-P4VP diblock copolymer is synthesized by dissolving PNIPAM-CTA, 4-vinylpyridine, and AIBN in DMF in the ratio 300:100:1, polymerized and precipitated under conditions applied for PNIPAM-CTA. Next, the PNIPAM-*b*-P4VP is chemically crosslinked to DBD by dissolving it in DMF and heating it at 70 °C for 4 h. Fig. 1 shows the scheme for the organogel synthesis and the photographs of the block copolymer before and after gelation.

The molecular weight of the PNIPAM-CTA and PNIPAM-*b*-P4VP is determined from advanced polymer chromatography (APC) (ACQUITY, Waters) using DMF as the eluent at a flow rate of 0.25 mLmin⁻¹ and polymethylmethacrylate as the calibration standard. The ¹H NMR analysis is performed on a JEOL 400 MHz NMR

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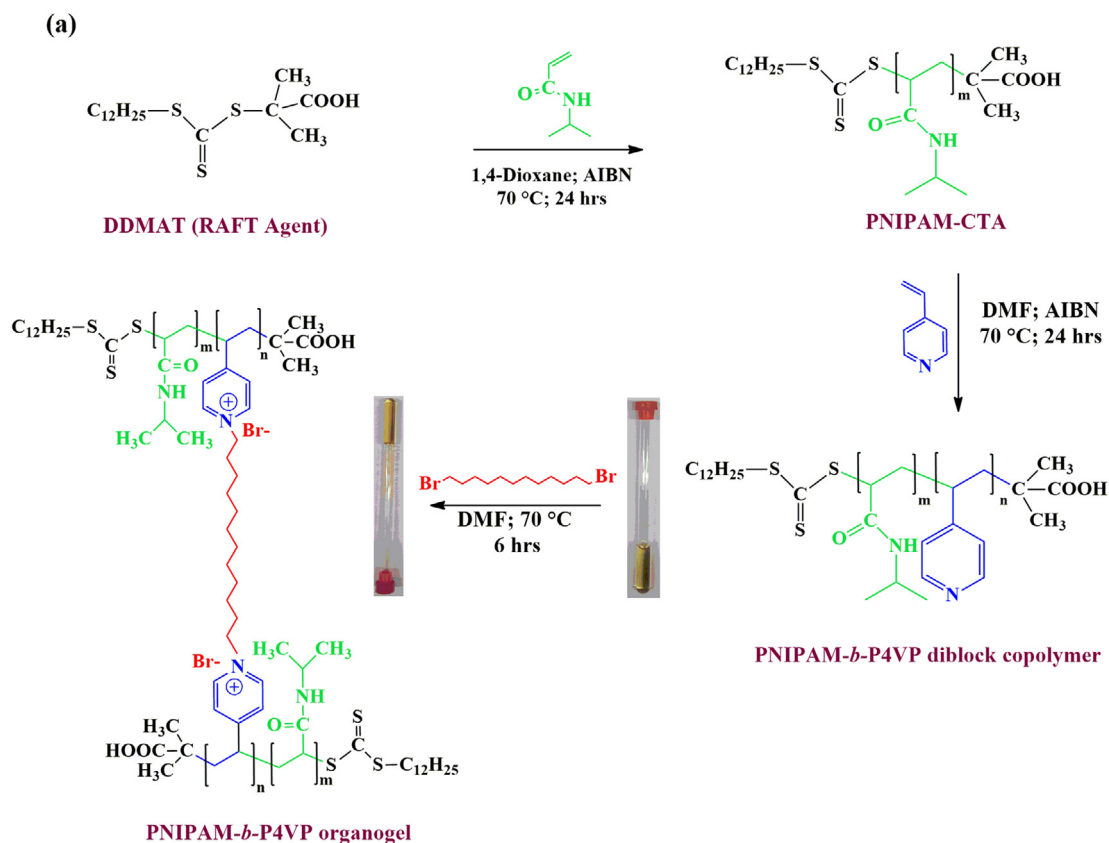


Fig. 1. Scheme for the organogel synthesis and photograph of the block copolymer before and after gelation.

spectrometer using CDCl_3 as the solvent. Fourier transform infrared (FTIR) spectra of the polymers are recorded on a Bruker spectrophotometer using the KBr pellet technique. Rheological measurements are carried out using a stress-controlled Physica rheometer MCR 301 (Anton Paar, Germany) in the parallel plate geometry. The storage modulus $G'(\omega)$ and loss modulus $G''(\omega)$ are determined from the amplitude strain and angular frequency sweep measurements in the range 0.1–1000% and 0.1–100 rad/s, respectively. Anionic dye adsorption is studied using a UV–Vis–NIR spectrophotometer (JASCO V-670, Japan). Arsenic and chromium content before and after 24 h of contact time with the organogel is measured using an inductively coupled plasma optical emission spectrometer (ICP-OES, Perkin Elmer Optima 5300 DV). Dye and heavy metal (arsenic, chromium) adsorption studies are carried out in aqueous solutions of the adsorbate with 2 wt% of the organogel. Antibacterial studies have been performed by the disc diffusion method on gram-positive (*Staphylococcus aureus*, *S. aureus*) and gram-negative (*Pseudomonas aeruginosa*, *P. aeruginosa*) bacteria.

3. Results and discussions

The PNIPAM-CTA (Fig. S1a, black lines) showed chemical shifts at 1.10–1.17 (m, $-\text{CH}_2-\text{CH}_3$), 1.70–2.50 (m, $-\text{CH}_2-\text{CH}-$), 3.18 ($-\text{CH}_2\text{S}$), 3.09 (m, $-\text{CH}(\text{CH}_3)_2$ and $-\text{CH}_2-\text{CH}-$ on the polymer's main chain), 6.50 (s, $-\text{NHCH}(\text{CH}_3)_2$). The PNIPAM-*b*-P4VP (Fig. S1a, red lines) showed additional chemical shifts at 1.08–1.37 (m, $-\text{CH}_2-\text{CH}_3$), 2.9–4.0 $-\text{CH}_2-\text{CH}-$ on the polymer's main chain), 6.35 (s, $-\text{NHCH}(\text{CH}_3)_2$), 7.9–8.2 (m, vinyl group). The chemical shift at 4.7 confirms the bridging of the pyridine groups of the block copolymer with DBD (Fig. S1a, blue lines). For the organogel, the peaks at 1085 and 565 cm^{-1} in the FTIR spectrum (Fig. S1b) corresponds to the

asymmetric and symmetric stretching of the quaternary ammonium ion. These peaks confirm the N^+-C bonding [15]. The theoretical molecular weight ($M_{n(\text{theory})}$) of the PNIPAM-CTA and PNIPAM-*b*-P4VP closely matches with the values experimentally determined from APC (Table S1).

The Winter-Chambon criterion is used to determine the gel point of the PNIPAM-*b*-P4VP copolymer/DBD crosslinker system [16]. The damping factor, $\tan\delta$, ($\tan\delta = G''/G'$) is plotted as a function of the polymer concentration for different angular frequencies (ω) (Fig. 2a). The convergence of the $\tan\delta$ is observed at a PNIPAM-*b*-P4VP concentration of 8 wt% when the crosslinker DBD is 0.8%, as shown in Fig. 2a. The evolution of the storage and loss moduli during the gel formation has been studied by time sweep measurements at 70 °C. A crossover from viscoelastic liquid-like to viscoelastic solid-like behavior is observed after 28 min for the 8 wt% PNIPAM-*b*-P4VP solution containing 0.8 wt% DBD, as shown in Fig. 2(b). Frequency sweep measurements show the linear viscoelastic behavior of PNIPAM-*b*-P4VP with various polymer–crosslinker ratios (Fig. 2c). A frequency-independent behavior of G' and G'' for the composition with 8 wt% PNIPAM-*b*-P4VP and 0.8 wt% DBD indicate the solid-like behavior of the organogel in the frequency range probed [17]. For other compositions, 4 and 6 wt%, the frequency-dependent nature of the G' and G'' indicate the absence of a volume spanning network in the sample or the existence of a weak gel network [18] (Fig. 2c). The results thus suggest that the critical concentration for the formation of the organogel requires 8 wt% of PNIPAM-*b*-P4VP with 0.8 wt% of the crosslinker DBD.

Dye adsorption studies have been carried out using 2 wt% pellet of the PNIPAM-*b*-P4VP organogel for the anionic dyes methyl orange (MO) and Congo red (CR). Fig. 3(a) and 3(b) shows the absorbance spectra of the PNIPAM-*b*-P4VP organogel towards MO and CR. Significant dye adsorption is noted with about 95% of

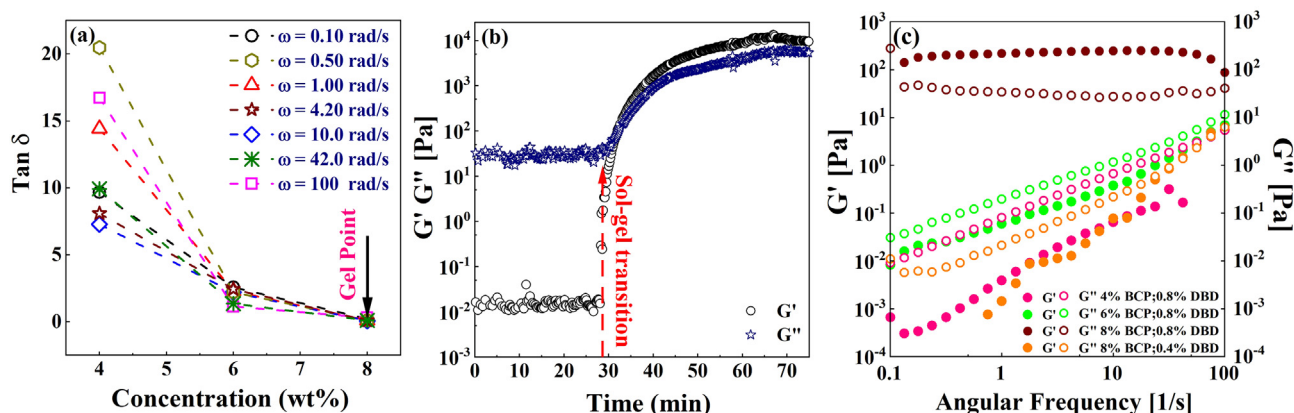


Fig. 2. (a) Variation of $\tan \delta$ as a function of PNIPAM-*b*-P4VP concentration at different ω , (b) time sweep measurement for 8 wt% PNIPAM-*b*-P4VP and 0.8 wt% DBD at 70 °C, and (c) angular frequency sweeps for different PNIPAM-*b*-P4VP and DBD concentrations at a shear strain of 1%.

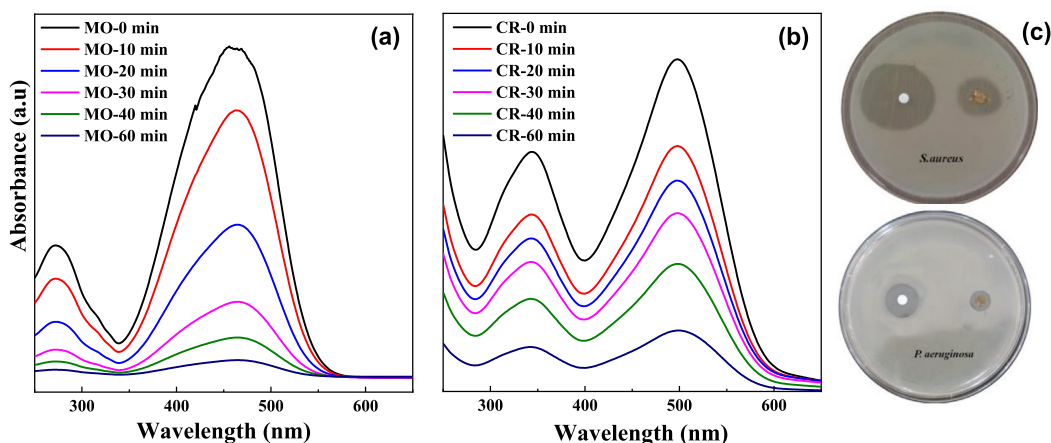


Fig. 3. UV-visible spectra of the dye solutions in contact with the organogel (a) methyl orange (b) Congo red, and (c) inhibition of the bacterial growth zone by the organogel against *S. aureus* and *P. aeruginosa*; chloramphenicol solution is used as the control. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

MO and 87% of CR removal after 60 min of contact with the organogel. The reusability of the organogel is tested by regenerating the organogel (by dissolving the adsorbed dye in 5 mL ethanol) and repeating the dye adsorption measurements (Fig. S2, recycling for 15 times). The experimental evaluation of As and Cr removal by the organogel from aqueous solutions containing sodium arsenite (AsNa_3O_3) and potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) has been carried out, and a very high adsorption is noted. The concentration of As and Cr decreased from 100 mg/L to 34.13 mg/L and 28.20 mg/L, respectively. This remarkable metal adsorption will be useful for water treatment in regions where arsenic levels in groundwater are very high and in the treatment of tannery effluent containing chromium. The antibacterial activity of the organogel is carried out by disk induction testing using chloramphenicol solution as the control. In Fig. 3(c) the zone formation for *S. aureus* and *P. aeruginosa* is observed, suggesting bactericidal properties of the organogel.

4. Conclusions

We report the synthesis and application of a novel PNIPAM-*b*-P4VP organogel, which exhibited superior dye, heavy metal adsorption, and bactericidal properties. This unique feature of a single gel material showing multiple application potential can be used for water treatment applications.

Author statement

S.S.P, R.S and J.B conceived the study and designed the experiments. S.S.P and R.K synthesized the polymer and carried out FTIR and NMR studies. S.S.P and C.S carried out dye and heavy metal adsorption studies. The manuscript is cowritten by J.B and S.S.P with inputs from all other co-authors.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.matlet.2020.127854>.

References

- [1] T. Masuda, T. Ueki, R. Tamate, K. Matsukawa, R. Yoshida, Chemomechanical motion of a self-oscillating gel in a protic ionic liquid, *Angew. Chem. - Int. Ed.* 57 (2018) 16693–16697.
- [2] M. Shintate, T. Inadomi, S. Yamamoto, Y. Kuboyama, Y. Ohsedo, T. Arimura, T. Nakazumi, Y. Hara, N. Miyamoto, Anisotropic self-oscillating reaction in liquid crystalline nanosheet hydrogels, *J. Phys. Chem. B.* 122 (2018) 2957–2961.
- [3] T. Ono, T. Sugimoto, S. Shinkai, K. Sada, Lipophilic polyelectrolyte gels as super-absorbent polymers for nonpolar organic solvents, *Nat. Mater.* 6 (2007) 429–433.
- [4] Y. Kang, J.J. Walish, T. Gorishnyy, E.L. Thomas, Broad-wavelength-range chemically tunable block-copolymer photonic gels, *Nat. Mater.* 6 (2007) 957–960.
- [5] H.S. Lim, J.H. Lee, J.J. Walish, E.L. Thomas, Dynamic swelling of tunable full-color block copolymer photonic gels via counterion exchange, *ACS Nano.* 6 (2012) 8933–8939.
- [6] A. Vintiloiu, J.C. Leroux, Organogels and their use in drug delivery - A review, *J. Control. Release.* 125 (2008) 179–192.
- [7] V. Bhalla, H. Singh, M. Kumar, S.K. Prasad, Triazole-modified triphenylene derivative: self-assembly and sensing applications, *Langmuir* 27 (2011) 15275–15281.
- [8] X. Cao, A. Gao, H. Lv, Y. Wu, X. Wang, Y. Fan, Light and acid dual-responsive organogel formation based on m-methyl red derivative, *Org. Biomol. Chem.* 11 (2013) 7931–7937.
- [9] M. Suzuki, Y. Nakajima, M. Yumoto, M. Kimura, H. Shirai, K. Hanabusa, Effects of hydrogen bonding and van der Waals interactions on organogelation using designed low-molecular-weight gelators and gel formation at room temperature, *Langmuir* 19 (2003) 8622–8624.
- [10] G. Ten Brinke, J. Ruokolainen, O. Ikkala, Supramolecular materials based on hydrogen-bonded polymers, *Adv. Polym. Sci.* 207 (2007) 113–177.
- [11] Z. Wei, J.H. Yang, J. Zhou, F. Xu, M. Zrínyi, P.H. Dussault, Y. Osada, Y.M. Chen, Self-healing gels based on constitutional dynamic chemistry and their potential applications, *Chem. Soc. Rev.* 43 (2014) 8114–8131.
- [12] S. Cheng, Y. Xue, Y. Lu, X. Li, J. Dong, Thermoresponsive pyrrolidone block copolymer organogels from 3D micellar networks, *ACS Omega.* 2 (2017) 105–112.
- [13] M.K. Gupta, J.R. Martin, T.A. Werfel, T. Shen, J.M. Page, C.L. Duvall, Cell protective, ABC triblock polymer-based thermoresponsive hydrogels with ROS-triggered degradation and drug release, *J. Am. Chem. Soc.* 136 (2014) 14896–14902.
- [14] Y. Yang, Z. Cai, Z. Huang, X. Tang, X. Zhang, Antimicrobial cationic polymers: from structural design to functional control, *Polym. J.* 50 (2018) 33–44.
- [15] M.A. Migahed, M.M. Shaban, A.A. Fadda, T.A. Ali, N.A. Negm, Synthesis of some quaternary ammonium gemini surfactants and evaluation of their performance as corrosion inhibitors for carbon steel in oil well formation water containing sulfide ions, *RSC Adv.* 5 (2015) 104480–104492.
- [16] M. Djabourov, K. Nishinari, S.B. Ross-Murphy, The Sol-Gel Transitions, *Physical Gels From Biological and Synthetic Polymers*, Cambridge University Press, 2013, pp. 64–96.
- [17] Y. Zhang, L. Tao, S. Li, Y. Wei, Synthesis of multiresponsive and dynamic chitosan-based hydrogels for controlled release of bioactive molecules, *Biomacromolecules* 12 (2011) 2894–2901.
- [18] S.S. Prasath, J. Brijitta, B.V.R. Tata, R.G. Joshi, K. Chennakesavulu, D.K. Gupta, Optical and rheological studies on weak gel-sol transition in aqueous solutions of poly(*N*-isopropylacrylamide)-block-polystyrene, *EXPRESS, Polymer Lett.* 11 (2017) 589–599.