

Thiol-Ene *Click* Synthesis of Adsorption Functionalized Poly(Ionic Liquid)s: Influence of the Mole Fraction of Pendant Enes

Wen Li

Ludong University

Aili Wang (✉ wang.aili@mail.scut.edu.cn)

Ludong University

Tingting Ye

Ludong University

Siqiang Li

Ludong University

Minghua Wang

Ludong University

Qijie Zhou

Ludong University

Tanghong Zheng

Ludong University

Research Article

Keywords: Poly(ionic liquid)s, The mole fraction of pendant enes, Adsorption

Posted Date: September 23rd, 2021

DOI: <https://doi.org/10.21203/rs.3.rs-898721/v1>

License: © ⓘ This work is licensed under a Creative Commons Attribution 4.0 International License.

[Read Full License](#)

Version of Record: A version of this preprint was published at Journal of Polymer Research on November 24th, 2021. See the published version at <https://doi.org/10.1007/s10965-021-02847-w>.

Abstract

Adsorption functionalized poly(ionic liquid)s could be thiol-ene click synthesized within surfactant-free ionic liquid microemulsions. However, the influence of the mole fraction of pendant enes on the as-prepared polymer is still unclear. Herein, the influence of the mole fraction of pendant enes on the molecular structure, surface morphology, thermostability and adsorption performance of poly(ionic liquid)s were investigated in detail. To characterize the as-prepared polymers, FTIR, NMR, TGA, DSC, SEM and UV-vis were used, and the adsorption isotherm/kinetics studies were carried out. The results show that the mole fraction of pendant enes had a significant difference on the characterization of poly(ionic liquid)s. The lower mole fraction of pendant enes donated lower T10% value, slower degradation rates and lower Tg, and the value of 0.30 was the boundary of forming structure with various beading sizes and structure with various irregularly shaped apertures. In addition, poly(ionic liquid)s with different mole fraction of pendant enes all showed excellent adsorption performance to DR, also indicate remarkable potential in the application of dyeing wastewater treatment.

1. Introduction

Ionic liquids are attractive solvents that can boost clean technology development¹⁻³. The derived poly(ionic liquid)s combine the characteristics of ionic liquids and traditional polymers, and hence show enormous advantages such as excellent designability, improved ionic conductivity, and mechanical durability⁴. Recently, in order to deal with the dyeing wastewater generated from industry, adsorption functionalized poly(ionic liquid)s attracted more and more attention⁵⁻⁷. Extensive efforts were continued carrying out to enhance the adsorption capacities of poly(ionic liquid)s towards different dyes⁸⁻⁹, for example, functionalizing poly(ionic liquid)s with graphene sheets or carbon nanosheets¹⁰, synthesizing poly(ionic liquid)s with enlarged specific surface area¹¹⁻¹², *etc.*

The common methods of preparing poly(ionic liquid)s include anion exchange and covalently crosslink¹³⁻¹⁵. Particularly, covalent crosslinking through the photoinduced thiol-ene click reaction is a typical method to transform poly(ionic liquid)s into porous forms¹⁶⁻¹⁷, and the particle size and morphology of as-prepared poly(ionic liquid)s significantly influence their adsorption performance toward dyeing wastewater. In 2017, Kloxin and coworkers prepared poly(ionic liquid)s via thiol-ene photopolymerization, and confirmed that the thiol-ene network charge and crosslink densities of poly(ionic liquid)s were controlled by varying the molar composition of the monomers in the formulation, specifically the ene-functionalized monomers¹⁸. These ene-functionalized monomers included ionic liquid monomer and cross-linking agent. When increasing the content of ionic monomer, the crosslink density decreased, and so as the rubbery elastic modulus.

Previously, we reported the poly(ionic liquid)s with controllable beading network structure which were in situ synthesized within surfactant-free ionic liquid microemulsions⁹. Interestingly, this network structure could be adjusted by altering the component proportion of the synthesis media, and donated a large pore

surface area to enhance the adsorption capacities of poly(ionic liquid)s toward nonionic dye disperse red (up to 1080 mg/g). These findings inspired us to further investigate the influencing factors of the poly(ionic liquid)s' structure and improve their overall performance. Nonetheless, the influence of the molar composition of the ene-functionalized monomers from ionic liquids (also known as mole fraction of pendant enes) on the adsorption performance of the final poly(ionic liquid)s is needed to be further investigated.

Herein, poly(ionic liquid)s with controllable pore size were synthesized through the *in situ* photoinitiated thiol-ene "click" reaction within surfactant-free ionic liquid microemulsions. These surfactant-free ionic liquid microemulsions are constructed using 1-allyl-3-methylimidazolium hexafluorophosphate (AMIMPF₆) and pentaerythritol tetrakis(3-mercaptopropionate) (PETMP) together as the polar phase, poly(ethylene glycol) diacrylate (PEGDA) and deionized water (H₂O) together as the nonpolar phase, *i*-propanol (*i*-PA) as the cosolvent. The influences of the mole fraction of pendant enes on the molecular structure, surface morphology, thermostability and adsorption performance for dyeing wastewater of the designed poly(ionic liquid)s were carried out in detail, with a constant thiol-to-ene ratio (1.10) maintained.

2. Experiments

2.1 Materials and chemicals

1-Allyl-3-methylimidazolium hexafluorophosphate (AMIMPF₆, > 99 wt%) was obtained from the Lanzhou Institute of Chemical Physics. Irgacure 184, disperse red (DR, > 99 wt%) and *i*-propanol (*i*-PA, > 99 wt%) were provided by Shanghai Titan Technology Ltd. Poly(ethylene glycol) diacrylate (PEGDA, Mn = 575) and pentaerythritol tetrakis (3-mercaptopropionate) (PETMP, > 95 wt%) were bought from Sigma Aldrich.

2.2 In situ synthesis of poly(ionic liquid)s within surfactant-free ionic liquid microemulsions

Firstly, the surfactant-free ionic liquid microemulsions were constructed following the procedure: (a) AMIMPF₆, PETMP, PEGDA and H₂O with the certain proportion were mixed at room temperature. (b) Under the same condition, co-solvent was dropped into the solution until the turbid solution becoming transparent.

Then, Irgacure 184 was added into to the obtained surfactant-free ionic liquid microemulsions to trigger the *in situ* thiol-ene "click" reaction under UV light. The final spongy polymers were obtained after washing and vacuum drying at 60°C for 24 hours, and named as poly-IL-0.45, poly-IL-0.35 and poly-IL-0.30. The general recipe is shown in Table 1.

Table 1
General recipe of the *in situ* synthesis of poly(ionic liquid)s within surfactant-free ionic liquid microemulsions

Sample	Mole fraction of pendant enes	$n_{(\text{AMIMPF}_6)}$ /mmol	$n_{(\text{PEGDA})}$ /mmol	$n_{(\text{PETMP})}$ /mmol	$n_{(\text{H}_2\text{O})}$ /mol	$n_{(i\text{-PA})}$ /mol	$n_{(184)}$ /mmol
poly-IL-0.45	0.45	4.515	2.752	2.316	0.142	0.159	0.191
poly-IL-0.35	0.35	3.500	3.250	2.307	0.140	0.170	0.195
poly-IL-0.30	0.30	3.017	3.544	2.273	0.140	0.170	0.196

2.3 Characterization of poly(ionic liquid)s

Fourier transform infrared spectroscopy (FTIR) of the as-prepared poly(ionic liquid)s were detected using Thermo Fisher Nicolet is50 FTIR spectrometer over the spectra range of 4000–400 cm^{-1} . The Morphology of poly(ionic liquid)s was investigated by scanning electron microscopy (SEM) SU8010, Hitachi. Nuclear magnetic resonance (NMR) data were collected by 500 MHz AVANCE Digital NMR spectrometer. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) using Netzsch STA449C F3 and Netzsch 204F1 calorimeter, respectively.

The adsorption capacities of poly-IL-0.45, poly-IL-0.35 and poly-IL-0.30 for disperse red (DR) were conducted by the following procedure: a certain amount of poly(ionic liquid) was placed in to a 100mL Erlenmeyer flask and 30 mL of 20 mg/L dye solutions was then added. The mixture was shaken in a thermostatic shaker for 8 h under the constant temperature of $25 \pm 1^\circ\text{C}$, then determined the concentration of DR via UV-vis absorption spectrum.

3. Results And Discussion

3.1 Molecular structures of poly(ionic liquid)s

Fig. 1 shows the FTIR spectrum of poly-IL-0.45, poly-IL-0.35, and poly-IL-0.30, respectively. It can be noticed that three poly(ionic liquid)s showed a similar FTIR spectrum, which illustrated that the mole fraction of pendant enes showed negligible influence on the molecular structure of poly(ionic liquid)s. Take the spectrum of poly-IL-0.35 for example, the absorption peak around 2883cm^{-1} was ascribed to the stretching vibration of C-H, the peak situated at 1728cm^{-1} were attributed to the stretching vibration of C=C from the PEDGA and ionic liquid, and the absorption peaks located at 838cm^{-1} was the characteristic adsorption peak of PF_6^- . Besides, no typical characteristic peak of S-H (about 2560cm^{-1}) was detected in the FTIR spectrum. These results indicated that then enes on AMIMPF_6 and PEGDA successfully reacted with the sulfydryl on PETMP. In addition, these poly(ionic liquid)s were also characterized using ^1H NMR

and ^{31}P NMR. As shown in the Fig.2., the ^1H NMR further confirmed the formation of the designed polymers. With the increasing of the mole fraction of pendant enes, the response of ^{31}P on NMR increased gradually (Fig.3), and this was mainly due to the increment of AMIMPF_6 dosage in the formulation.

3.2 Morphology of poly(ionic liquid)s

The surface morphology of poly(ionic liquid)s with different mole fraction of pendant enes (0.45/0.35/0.30) were shown in Fig. 4. In addition, poly(ionic liquid)s with mole fraction of pendant enes of 0.25, which was presented in our previous work was referred as comparison⁹. It can be noticed that the mole fraction of pendant enes had a significant difference on the morphology of each poly(ionic liquid), and when this value was under 0.30, porous poly(ionic liquid)s with various beading sizes could be formed. However, when the mole fraction of pendant enes was equal or greater than 0.30, only various irregularly shaped apertures showed on the surface of poly(ionic liquid)s, and with the decreasing value of the mole fraction of pendant enes in formulation, the average pore diameter diminished gradually. From the appearance photos, it can be detected that poly(ionic liquid)s which were more like white sponges were obtained with decreasing value of the mole fraction of pendant enes. These results indicated that the increasing amount of cross-linking agent (PEGDA) in the formulation of thiol-ene “click” reaction could reduce the interfacial tension of polymers, and hence made the poly(ionic liquid)s with various beading sizes easier to form.

3.3 Thermo-analysis of poly(ionic liquid)s

Figure 5. shows thermogravimetric analysis of poly-IL-0.45, poly-IL-0.35, poly-IL-0.30, and the thermogravimetric curve of neat AMIMPF_6 was presented for comparison. In the range of 0°C – 10°C , the as-prepared poly(ionic liquid)s showed a slight mass loss due to the evaporation of the absorbed water. From around 315°C , three poly(ionic liquid)s began the second stage of mass loss, and their maximum degradation rate all showed around 375°C , which was due to the decomposition of the ethyl group on poly(ionic liquid)s. However, these maximum degradation rates were all less than that of AMIMPF_6 , especially for poly-IL-0.30, and this result could be connected to the polymerization of PEGDA onto the polymers¹⁹.

It can be noticed that poly-IL-0.45 and poly-IL-0.35 showed a similar T10% (10 wt% loss temperature) values with neat AMIMPF_6 . However, the T10% value of poly-IL-0.30 was less than that of AMIMPF_6 , and it was closer to that of poly-IL-0.25 in our previous work⁹. Similar trends on decomposition rates of each poly(ionic liquid)s could also be observed. These results should be corresponded to the fact that the with the increment of the mole fraction of pendant enes, the average pore diameter of poly(ionic liquid)s decreased, which give the membrane a higher density. And this was in accordance with the results of morphological characterization.

Figure 6 shows that the glass transition temperature (T_g) of poly-IL-0.45, poly-IL-0.35 and poly-IL-0.30. With the increasing mole fraction of pendant enes from 0.30 to 0.45, the T_g of three poly(ionic liquid)s

showed a decrease from -12.8°C to -25.1°C . This result could be ascribed to a loss of flexibility of the polymeric chains with less cross-linking agent²⁰.

3.4 Adsorption performances of poly(ionic liquid)s

To investigate the adsorption performance of as-prepared poly(ionic liquid)s, nonionic dye of DR was selected as target adsorbates, and the effects of pH and C_0 of solution, dosage of adsorbent, and the contact time on the adsorption efficiency of poly-IL-0.45, poly-IL-35 and poly-IL-0.30 were shown in Fig. 7. It can be noticed that three samples all showed the highest adsorption efficiency for DR at pH of 5.5, and with the increment of adsorbent dosage, the removal efficiency increased gradually and tended to balance. The influence of C_0 on the adsorption behaviors of three poly(ionic liquid)s is provided as Fig. 7c. It can be detected that poly(ionic liquid) with a small mole fraction of pendant enes showed a high removal efficiency for DR. Commonly, the synergistic effect of the hydrogen bonding and the hydrophobic interaction played a critical role during the adsorption of poly(ionic liquid)s toward DR, and this synergistic effect could be enhanced by cross-linked structure, which was donated by decreasing the mole fraction of pendant enes²¹.

The experimental adsorption kinetic data and the linearly fitted plots of poly(ionic liquid)s toward DR in accordance with the pseudo-first- and the pseudo-second-order kinetic models, which were given in our reported literature, are presented in Fig. 8⁹, and the calculated fitting parameters are listed in Table 3. By contrast, we can see that the pseudo-second-order model could better describe the adsorption process of DR by poly-IL-0.45, poly-IL-35 and poly-IL-0.30 than the pseudo-first-order model, and that the mole fraction of pendant enes did not significantly change the valence forces between the molecule of DR and poly(ionic liquid)s. These results indicated that the chemical adsorption process was the main control step of the adsorption rate²².

Table 2
The kinetics parameters for DR adsorption onto different adsorbents

Sample	$Q_{e,exp}$ mg/g	Pseudo-first order			Pseudo-second order			
		$Q_{e,cal}$ mg/g	k_1	R^2	$Q_{e,cal}$ mg/g	$k_2 \times 10^4$	H mg/(g min)	R^2
Poly-IL-0.45	145.001	8.700	0.005	0.485	143.678	54.613	112.740	1.000
Poly-IL-0.35	145.017	7.543	0.004	0.408	143.472	67.473	138.889	1.000
Poly-IL-0.30	145.033	9.006	0.005	0.500	143.472	51.958	106.952	1.000

The adsorption isotherms of DR on poly(ionic liquid)s in accordance with Langmuir and the Freundlich adsorption isotherm models are presented in Fig. 8^{9,23}, and the fitting parameters are listed in Table 4. Results showed that the Freundlich adsorption isotherm models were more suitable in describing the adsorption of poly-IL-0.45, poly-IL-35 and poly-IL-0.30 toward DR than the Langmuir adsorption isotherm models, indicating a heterogeneous adsorbent surface during the adsorption. In addition, the values of n

were all more than 1 and followed the order: poly-IL-0.30 > poly-IL-35 > poly-IL-0.45, showing that the adsorption of DR onto poly-IL-0.45, poly-IL-35 and poly-IL-0.30 were all favorable, and this effect could be enhanced by decreasing the mole fraction of pendant enes²⁴.

Table 3
Adsorption isotherm parameters for DR adsorption onto different adsorbents

Sample	Langmuir isotherm			Freundlich isotherm		
	$Q_{m,cal}$	k_L	R^2	K_f	n	R^2
	mg/g	L/mg		L/g		
Poly-IL-10	8685.079	0.003	0.373	32.041	1.086	0.995
Poly-IL-15	5399.626	0.006	0.512	37.022	1.120	0.996
Poly-IL-20	4941.850	0.007	0.340	44.510	1.161	0.990

4. Conclusions

In this work, the influence of the mole fraction of pendant enes on the molecular structure, surface morphology, thermostability and adsorption performance of poly(ionic liquid)s were investigated in detail. These poly(ionic liquid)s were *in situ* thiol-ene “click” synthesized within surfactant-free ionic liquid microemulsions. FTIR and NMR results showed that typical poly(ionic liquid)s were successfully formed and the content of P on polymer increased gradually with the increasing of the mole fraction of pendant enes. SEM results indicated that the mole fraction of pendant enes had a significant difference on the surface morphology of poly(ionic liquid)s, and the value of 0.30 was the boundary of forming structure with various beading sizes and structure with various irregularly shaped apertures. Thermo-analysis of poly(ionic liquid)s showed that poly(ionic liquid)s with lower mole fraction of pendant enes presented lower T10% value, slower degradation rates and lower Tg. Typical nonionic dye DR was used as the target adsorbent, and poly(ionic liquid)s with different mole fraction of pendant enes all showed excellent adsorption performance to DR. In addition, kinetic studies and thermodynamic analysis proved that the adsorption of DR on poly(ionic liquid)s better followed the pseudo-second-order and Freundlich isotherm model, respectively.

5. Declarations

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

Acknowledgements

This research was supported by Natural Science Foundation of Shandong Province (ZR2020LFG003, ZR2019PB014), Research Fund Program of Guangdong Provincial Key Lab of Green Chemical Product Technology (GC201820), and School Scientific Research Foundation for Introduced Talent (LA2016001).

6. References

1. Freemantle, M., Designer solvents - Ionic liquids may boost clean technology development. *Chemical & Engineering News* **1998**,76 (13), 32-37.
2. Gordon, C. M.; Mccluskey, A., Ionic liquids: a convenient solvent for environmentally friendly allylation reactions with tetraallylstannane. *Chemical Communications* **1999**,(15), 1431-1432.
3. Wang, A. L.; Chen, L.; Zhang, J. X.; Sun, W. C.; Guo, P.; Ren, C. Y., Ionic liquid microemulsion-assisted synthesis and improved photocatalytic activity of ZnIn₂S₄. *Journal of Materials Science* **2017**,52 (5), 2413-2421.
4. Armand, M.; Endres, F.; Macfarlane, D. R.; Ohno, H.; Scrosati, B., Ionic-liquid materials for the electrochemical challenges of the future. *Nature Materials* **2009**,8 (8), 621.
5. Mu, B.; Wang, A., Adsorption of dyes onto palygorskite and its composites: A review. *Journal of Environmental Chemical Engineering* **2016**, S2213343716300367.
6. Zhang, Y.; Wan, J. Q., New development of the industrial wastewater pollution control. *Industrial Water Treatment* **2001**,1 (1), 9-12.
7. Poly(Ionic Liquid) Superabsorbent for Polar Organic Solvents. *Acs Appl Mater Interfaces* **2015**,7 (17), 8979.
8. Kazem; Majdzadeh-Ardakani; Elizabeth; A.; Lofgren; Saleh; A.; Jabarin, Novel preparation method for improving the dispersion of ionic liquid-modified montmorillonite in poly(ethylene terephthalate). *Polymer Composites* **2016**.
9. Aili Wang; Zilin Liu; Lu Xu; Nan Lou; Mengying Li; Liu, L., Controllable click synthesis of poly(ionic liquid)s by surfactant-free ionic liquid microemulsions for selective dyes reduction. *Reactive and Functional Polymers* **2020**,147, 104466.
10. Zhao, W.; Tang, Y.; Xi, J.; Kong, J., Functionalized graphene sheets with poly(ionic liquid)s and high adsorption capacity of anionic dyes. *Applied Surface Science* **2015**,326 (326), 276-284.
11. Wang, A.; Li, S.; Chen, H.; Liu, Y.; Peng, X., Construction of Novel Polymerizable Ionic Liquid Microemulsions and the In Situ Synthesis of Poly(Ionic Liquid) Adsorbents. *Nanomaterials* **2019**,9 (3).
12. Chen, Z.; Yang, L.; Dong, Y.; Fang, H.; Zhao, X.; Yin, J., Low-Temperature Interfacial Polymerization and Enhanced Electro-Responsive Characteristic of Poly(ionic liquid)s@polyaniline Core-shell Microspheres. *Macromolecular Rapid Communications* **2019**,40, 1800351-.
13. Qin, L.; Wang, B.; Zhang, Y.; Chen, L.; Gao, G., Anion exchange: a novel way of preparing hierarchical porous structure in poly(ionic liquid)s. *Chemical Communications* **2017**,53 (26).

14. Dani, A.; Täuber, K.; Zhang, W.; Schlaad, H.; Yuan, J., Stable covalently photo-cross-linked poly(ionic liquid) membrane with gradient pore size. **2018**.
15. Yuan, J. Y.; Mecerreyes, D.; Antonietti, M., Poly(ionic liquid)s: An update. *Progress in Polymer Science* **2013**,*38* (7), 1009-1036.
16. Tauber; Karoline; Schlaad; Helmut; Dani; Alessandro; Yuan; Jiayin; Zhang; Weiyi, Stable Covalently Photo-Crosslinked Poly(Ionic Liquid) Membrane with Gradient Pore Size. *Macromolecular rapid communications: Publishing the newsletters of the European Polymer Federation* **2017**.
17. Tuber, K.; Zimathies, A.; Yuan, J., Porous Membranes Built Up from Hydrophilic Poly(ionic liquid)s. *Macromolecular Rapid Communications* **2015**,*36*.
18. Yan; Yushan; S.; Tibbits; Andrew; C.; Kloxin; Christopher; J., Covalent Incorporation of Ionic Liquid into Ion-Conductive Networks via Thiol-Ene Photopolymerization. *Macromolecular Rapid Communications Publishing the Newsletters of the European Polymer Federation* **2017**.
19. PEGDA-based luminescent polymers prepared by frontal polymerization. *Journal of Polymer science Part A Polymer Chemistry* **2015**,*53* (24), 2890-2897.
20. González-Henríquez, C.; Pizarro, G.; Sarabia-Vallejos, M. A.; Terraza, C. A.; López-Cabañero, Z., In situ-preparation and characterization of silver-HEMA/PEGDA hydrogel matrix nanocomposites: Silver inclusion studies into hydrogel matrix. *Arabian Journal of Chemistry* **2014**, S1878535214002603.
21. Su, R. D.; Wang, F. D.; Ding, J. Z.; Li, Q.; Zhou, W. Z.; Liu, Y. Z.; Gao, B. Y.; Yue, Q. Y., Magnetic hydrogel derived from wheat straw cellulose/feather protein in ionic liquids as copper nanoparticles carrier for catalytic reduction. *Carbohydrate Polymers* **2019**,*220*, 202-210.
22. Gupta, V. K.; Pathania, D.; Agarwal, S.; Sharma, S., De-coloration of hazardous dye from water system using chemically modified Ficus carica adsorbent. *J. Mol. Liq.* **2012**,*174*, 86-94.
23. Wang, A.; Li, S.; Zhang, L.; Chen, H.; Li, Y.; Hu, L.; Peng, X., Ionic liquid microemulsion-mediated in situ thermosynthesis of poly(ionic liquid)s and their adsorption properties for Zn(II). *Polymer Engineering and Science* **2019**.
24. Zhang, P.; Niu, Y.; Qiao, W.; Xue, Z.; Bai, L.; Chen, H., Experimental and DFT investigation on the adsorption mechanism of silica gel supported sulfur-capped PAMAM dendrimers for Ag(I). *Journal of Molecular Liquids* **2018**, 390-398.

Figures

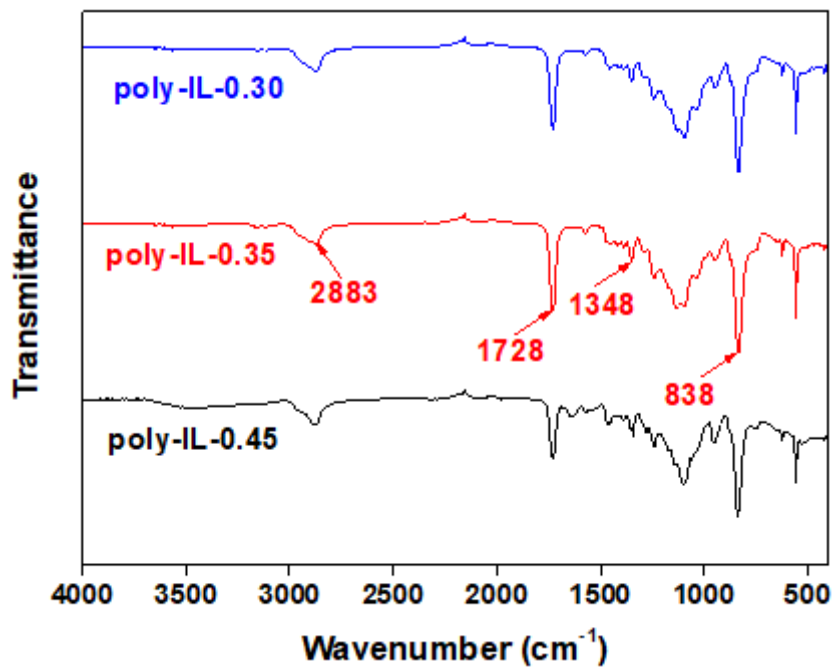


Figure 1

FTIR spectra of poly-IL-0.45, poly-IL-0.35, and poly-IL-0.30

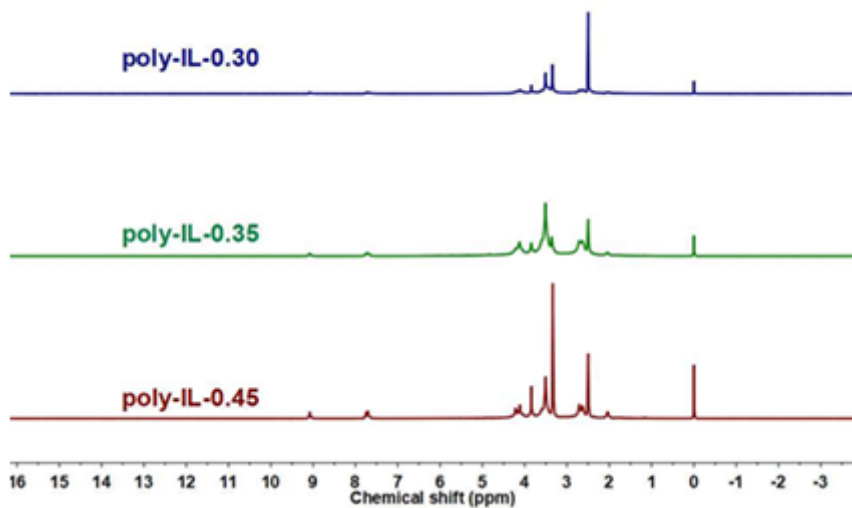


Figure 2

¹H NMR spectroscopy of poly-IL-0.45, poly-IL-0.35 and poly-IL-0.30

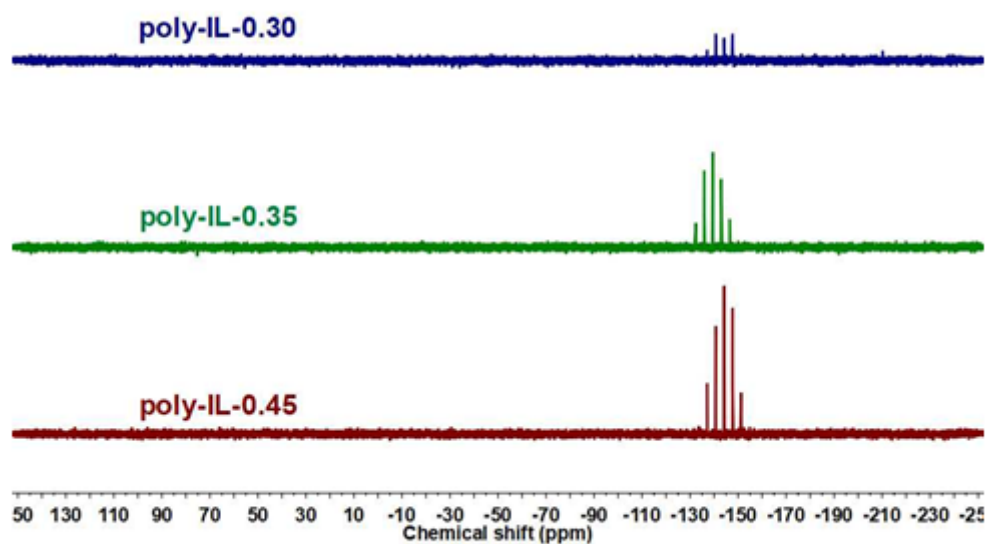


Figure 3

^{31}P NMR spectroscopy of poly-IL-0.45, poly-IL-0.35 and poly-IL-0.30

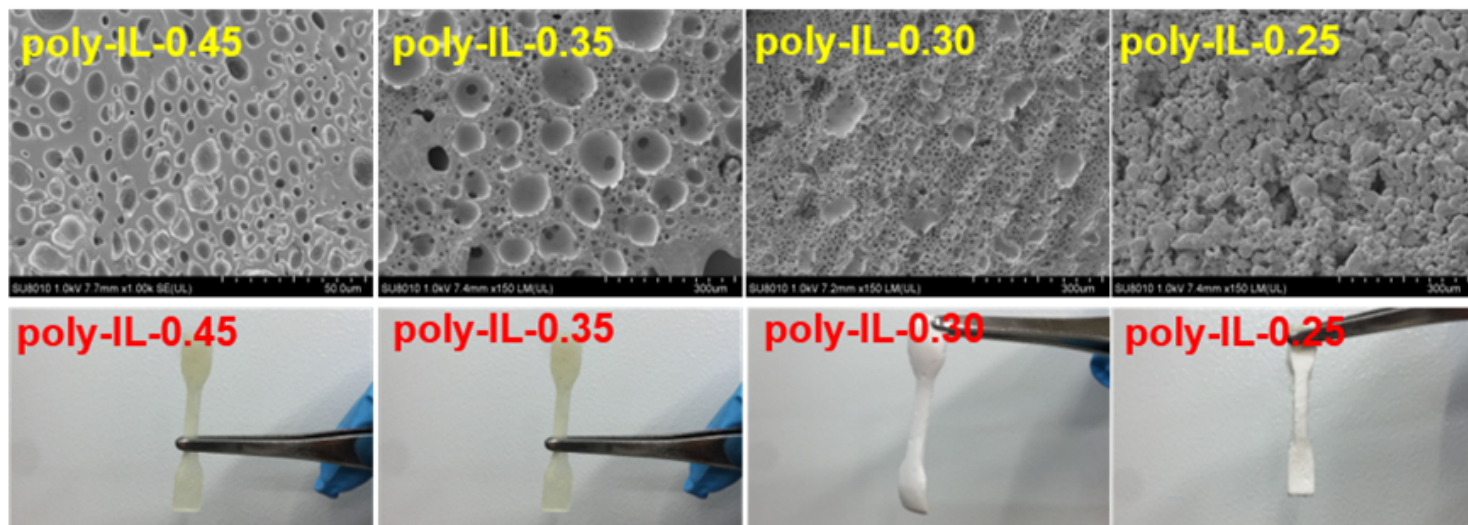


Figure 4

Surface morphology of poly-IL-0.45, poly-IL-0.35, poly-IL-0.30 and poly-0.259

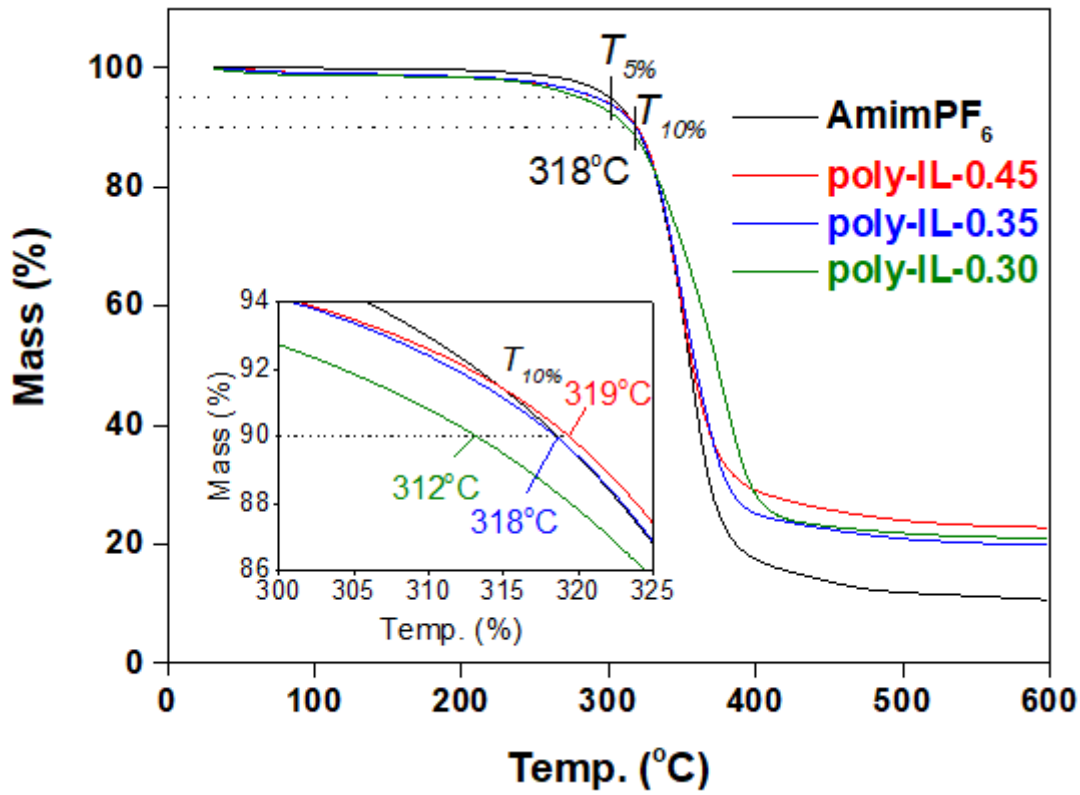


Figure 5

The thermogravimetric curves of poly-IL-0.45, poly-IL-0.35, poly-IL-0.30 and AMIMPF6.

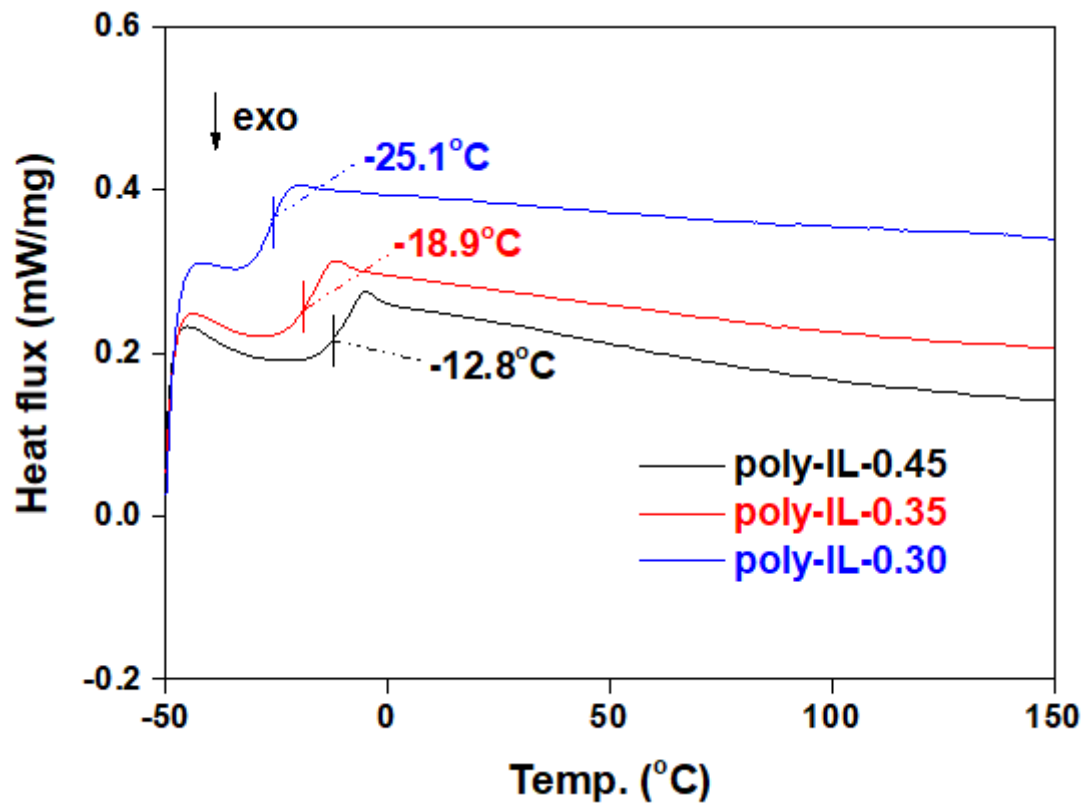


Figure 6

The DSC curves of poly-IL-0.45, poly-IL-35 and poly-IL-0.30

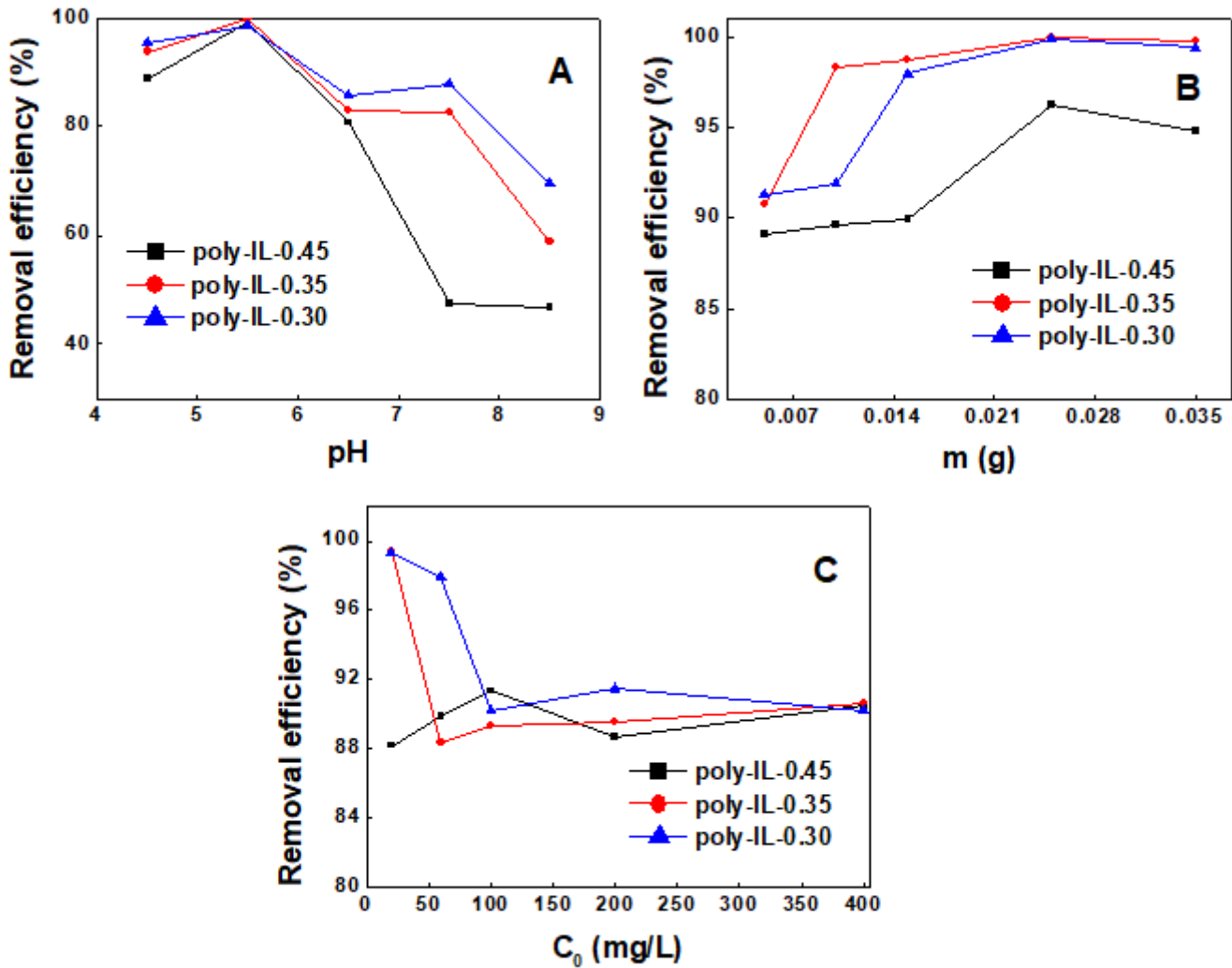


Figure 7

Effect of pH ($C_0=20\text{mg/L}$, $m=10\text{ mg}$, and $T=4\text{ h}$), adsorbent dosage ($C_0=20\text{mg/L}$, $\text{pH}=6.5$, and $T=4\text{ h}$) and C_0 ($m=0.035\text{g}$, $\text{pH}=6.5$, and $T=4\text{ h}$) on the removal efficiency of poly(ionic liquid)s toward DR

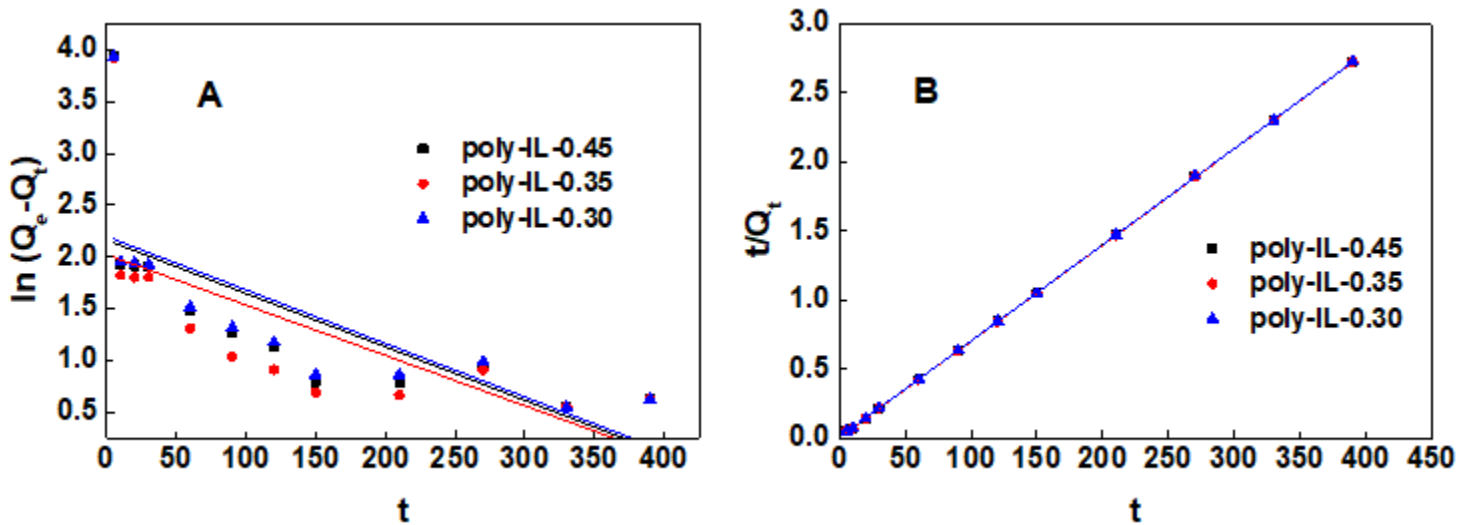


Figure 8

Pseudo-first-order kinetic model fitting (a) and pseudo-second-order kinetic model fitting (b) of the adsorption process for poly(ionic liquid)s toward DR

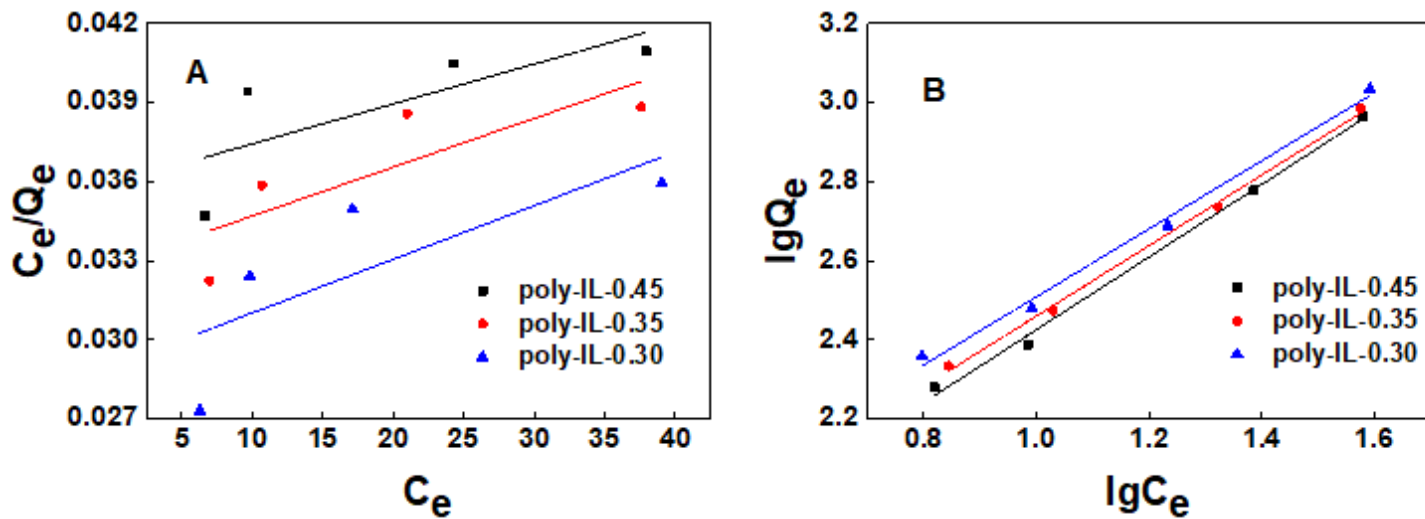


Figure 9

Langmuir (a) and Freundlich (b) adsorption isotherm for DR removal by poly(ionic liquid)s