

Synthesis and properties of lipophilic polyelectrolyte styrene/butyl methacrylate/stearyl methacrylate resin as absorbent materials for organic solvents and oils

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Abstract This article reported a novel type of lipophilic polyelectrolyte resin with high oil absorbency and mechanical properties, which was suitable to use, store, and recycle. A certain amount of weakly coordinating ions was introduced in a suitable network structure of copolymer resin of styrene/butyl methacrylate/stearyl methacrylate by chloromethylation reaction, quaternization reaction, and anion exchange reaction. The structure and particle morphology of resin were characterized by Fourier transform infrared spectrometry and scanning electron microscopy, respectively. Research on oil absorption test has revealed that lipophilic polyelectrolyte resin had higher oil absorbency, faster oil-adsorbing rate, and better reusability compared with non-ionic oil absorption resin. Meanwhile, the effect of the content of ionic groups on the oil absorbency of the lipophilic polyelectrolyte resin was also investigated. The results showed that the maximum of oil absorbency of the resin to the carbon tetrachloride was 37.86 g/g when the content of ionic groups was 4.54 wt%.

Keywords Lipophilic polyelectrolyte resin · Chloromethylation reaction · Ionic groups · Oil absorbency · Reusability

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Introduction

With the rapid development of the world oil industry, especially the growth of the off-shore oil industry and ocean oil transportation in recent years, oil spill is becoming a serious issue. It not only causes huge property losses but also seriously affects our living environment, such as the oil spill in the Gulf of Mexico in 2010 [1, 2]. In this case, oil absorption materials have caused people's broad attention [3–5].

Oil absorption resin is a kind of self-swelling oil absorption material with a three-dimensional network structure. Being different from traditional oil absorption materials, it has many advantages, such as high oil absorbency, good selective absorption of oil and water, and excellent oil retention [6–8]. It absorbs oil by van der Waals forces between the lipophilic group and the surrounding solvent. Therefore, the oil absorption resin has been interestingly researched.

Recently, some researchers have attempted to improve the oil absorbency by introducing the ionic groups into the oil absorption resin to prepare the lipophilic polyelectrolyte resin [9–14]. The lipophilic polyelectrolyte resin, being used as superabsorbent material for their high oil absorbency, is a new type of ionic polymer. Some polyelectrolyte resin could swell up to dozens of times of their dried size in some nonpolar organic solvents [15]. The high oil-absorbing abilities originate from excellent compatibility between the organic solvents and the polymer chains and the ionic pairs which bring osmotic pressure and electrostatic repulsion among the charged macromolecule chains [16, 17]. Compared with non-ionic oil absorption resin, it also possesses better oil retention and recyclability. Moreover, lipophilic polyelectrolyte resin has ionic groups which can ionize appropriately in the solvent. That is why it can improve the lipophilicity and permeability of some polar drugs. Hence, with the further development of ionic groups, the applications of lipophilic

polyelectrolyte resin are not only confined to oil spill but also extended to the medicine, biotechnology, and other aspects.

Some researchers have studied on lipophilic polyelectrolyte resin in recent years. T. Ono designed lipophilic polyelectrolyte gels (EG) as superabsorbent polymers with a high swelling degree in less polar or nonpolar organic solvents [18]. Zhou YB synthesized ionic resins modified by quaternary ammonium, which had great changes on electrostatic interactions and lipophilic properties after grafting [19]. However, the mechanism of lipophilic polyelectrolyte resin in organic solvents was still not clear. The way how ionic groups affected electrostatic interactions and lipophilic properties was also not researched in detail. Moreover, the gels had weak mechanical properties which were easy to collapse owing to aggregation of the ions in most organic solvents [18].

To solve these problems, a detailed and comprehensive study on the synthesis and properties of lipophilic polyelectrolyte resin was performed for the first time. Utilizing a series of copolymer resin of St/BMA/SMA (CRSBS) as supporting skeleton, a certain amount of weakly coordinating ions (triethylamine with long alkyl chains as a lipophilic cation and tetraphenylborate as a lipophilic anion) was introduced in CRSBS by chloromethylation reaction, quaternization reaction and anion exchange reaction. Besides, the morphologies, kinetics, reusability, as well as oil absorbency of the lipophilic polyelectrolyte resin were systematically investigated. More than that, the effect of content of ionic groups, which was an important mechanism on the absorbency of resin in different solvents, was also detailedly studied. These results were expected to achieve high oil-absorbing resin to meet the current needs for efficient oil absorption material in the market.

Experimental Section

Materials

The chemicals were styrene, butyl methacrylate, stearyl methacrylate, divinylbenzene, benzoyl peroxide, formaldehyde, phosphorus trichloride, anhydrous zinc chloride, 1,4-butanediol, 1,4-dioxane, triethylamine, acetone, ethyl acetate, and sodium tetraphenylborate. These chemicals were analytical reagents, and all of them were obtained from Tianjin Jiangtian Chemical Reagent Co., Ltd. (Tianjin, China).

Synthesis of lipophilic polyelectrolyte resin

The lipophilic polyelectrolyte resin showed in Scheme 1 was prepared by chloromethylation reaction, quaternization

reaction, and anion exchange reaction on the basis of non-ionic oil absorption resin. The non-ionic oil absorption resin, a ternary copolymerized long-chain polyacrylate with styrene (St), butyl methacrylate (BMA), and stearyl methacrylate (SMA) as the monomers, has already been prepared by suspension polymerization in advance according to ref [20].

(1) Chloromethylation reaction [21–25]

The resin of St/BMA/SMA (3.0 g) was first immersed in THF (80 mL) for 12 h in a three-necked flask equipped with a thermometer and stirrer. Then, the required amount of 1,4-bis(chloromethoxy)butane (BCMB, 10.0 mL) and Lewis acid catalyst (ZnCl_2 , 1.5 g) was fed into the flask, respectively. The whole reaction proceeded at room temperature for 6 h. The product was washed in turn by diluted hydrochloric acid, anhydrous ethanol, and deionized water. Finally, chloromethylated resin was obtained by drying under vacuum condition. The detailed preparation and characterization of BCMB can be found in the [supplementary information](#).

(2) Quaternization reaction

A certain amount of resin after chloromethylation and triethylamine (TETN, 15 mL) was fed into the flask. Acetone (35 mL) was added as the solvent. The reaction proceeded at 45 °C for 24 h under N_2 . The product was washed with ethyl acetate and then dried under vacuum at room temperature.

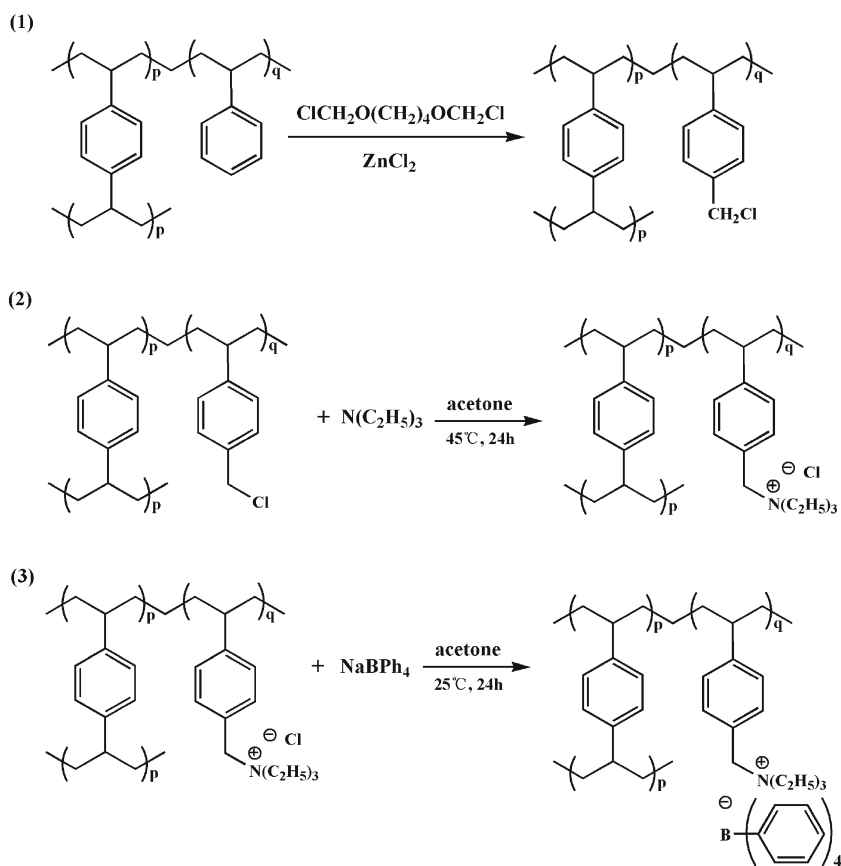
(3) Anion exchange reaction

The product of quaternization reaction was transferred to another three-necked flask, in which a certain amount of sodium tetraphenylborate (NaTPB, 3.0 g) and acetone (20 mL) was added. The mixture was stirred at room temperature for 24 h. The resulting products were rinsed several times with anhydrous ethanol and deionized water to eliminate the organic solvents.

Characterization

Fourier transform infrared (FTIR) spectrum was taken on a Bio-Rad FTS 135 FTIR (Bio-Rad, Hercules, USA) with a resolution of 4 cm^{-1} . Samples were powdered and mixed with KBr, processing into pellets. The scanning range was $4000\text{--}400 \text{ cm}^{-1}$. Morphology studies were performed with a PHILIPS XL 30 scanning electron microscopy (SEM, Philips, USA) with an acceleration voltage of 5 kV and samples were sputter coated with Au for 40 s before SEM measurement.

Scheme 1 Synthetic route of the lipophilic polyelectrolyte resin. ((1) chloromethylation reaction, (2) quaternization reaction, and (3) anion exchange reaction)



Oil absorption test

Oil absorbency

The oil absorbency (Q), specified as full oil absorbency, was determined by the weighing method. A quantity of dried resin (M_1) weighed beforehand was put into a filter bag and immersed in beaker with oil for 24 h at room temperature. Then, the filter bag with the resin was immediately taken out, drained for 1 min, and then the resin was reweighed (M_2). The oil absorbency was calculated according to the following equation:

$$Q = (M_2 - M_1) / M_1 \quad (1)$$

where M_1 and M_2 are the weights of resin before and after oil absorption, respectively.

The kinetics of oil absorption

The procedure was carried out every 0.5 h according to above steps.

Results and discussion

FTIR characterization

FTIR spectrum of non-ionic resin, chloromethylated resin, quaternized resin, and lipophilic polyelectrolyte resin (anion-exchanged resin) were illustrated in Fig. 1. The characteristic absorption peaks at 2917, 2845, 1721, 1505, 1450, 1100, and 757 cm^{-1} all appeared in (a), (b), (c), and (d). Peaks at 2917 and 2845 cm^{-1} were stretching vibration absorption peaks of $-\text{CH}_3$ and $-\text{CH}_2$. Peaks at 1721 and 1100 cm^{-1} were associated with $\text{C}=\text{O}$ bond and $\text{C}-\text{O}$ bond from ester group, separately. The absorption peaks at 1505 and 1450 cm^{-1} were obviously due to the stretching vibration of $\text{C}-\text{C}$ bond of benzene ring, while peak at 757 cm^{-1} was plane bending vibration of $\text{C}-\text{H}$ bond of benzene ring. Comparing (b) with (a), absorption peak at 697 cm^{-1} due to $\text{C}-\text{Cl}$ bond appeared, which showed the success of chloromethylation reaction. A peak at 1179 cm^{-1} which appeared in (c) corresponded to stretching vibration of $\text{C}-\text{N}$ bond and confirmed the introduction of triethylamine. The absorption peak of $\text{C}-\text{Cl}$ bond in (d) was decreased significantly, which indicated that chloride ion was exchanged successfully with tetraphenylborate in anion exchange reaction.

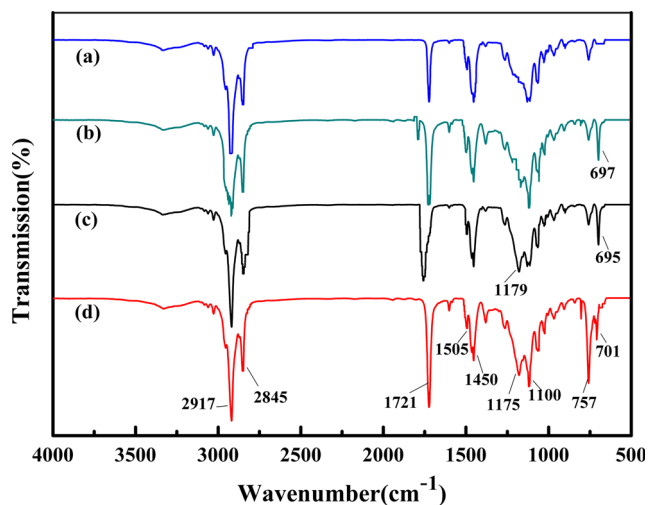


Fig. 1 FTIR spectra of (a) non-ionic resin, (b) chloromethylated resin, (c) quaternized resin, and (d) lipophilic polyelectrolyte resin (anion-exchange resin)

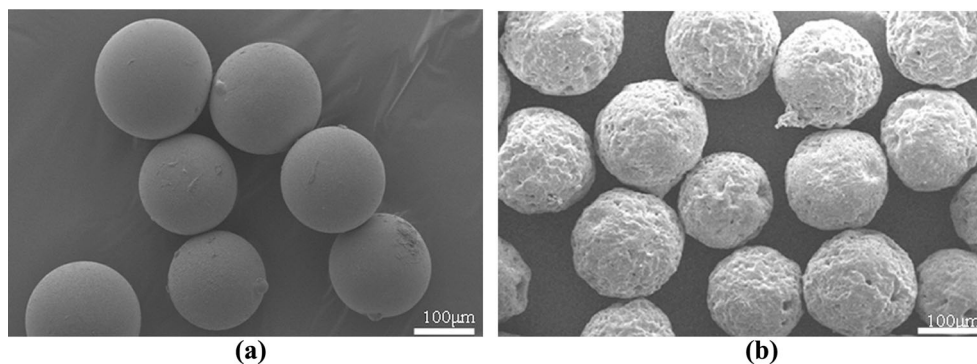
SEM characterization

SEM images of oil absorption resins were given in Fig. 2. The particle morphology of the lipophilic polyelectrolyte resin (b) presented rough and multiporous surface structure which was conducive to the absorption for the solvent while the surface of the non-ionic resin (a) was smooth. The reason for the phenomenon might be that the massive structure of tetraalkylammonium cation and tetraphenylborate anion changed the existing surface structure of the resin in ionization process. It might also be caused by the swelling-shrinkage behavior of resin during the ionization reaction. As a result, the introduction of the ionic groups increased the specific surface area of the lipophilic polyelectrolyte resin, which was beneficial to improve the oil absorbency of the resin.

Effect of the content of ionic groups on the oil absorbency

The content of ionic groups introduced into the resin was achieved by determining the content of chlorine in the final product after the chloromethylation reaction. The determination of chlorine content and effects of different reaction factors

Fig. 2 SEM microphotographs of **a** non-ionic resin and **b** lipophilic polyelectrolyte resin



on chlorine content were shown in [supplementary information](#).

Figure 3 showed the relationship between ionic content and oil absorbency. The oil absorbency increased with the increase of the content of ionic groups and then decreased, existing a peak value (37.86 g/g) when the content of ionic groups was 4.54 wt%. The lipophilic polyelectrolyte resin was formed by introducing weakly coordinating ionic groups on non-ionic resin. Being immersed into oil, weakly coordinating ionic groups delocalization brought an osmotic pressure inside and outside the network structure to promote the oil molecules into the resin network structure. Furthermore, mutual exclusion between ionic within the network would improve the stretch of network structure. Therefore, a certain content of ionic groups was beneficial to resin absorption of oil. When the content of ionic groups was too high, local aggregation of the ionic groups happened, leading the invalidity of mechanism of the electrostatic repulsion and osmotic pressure [15, 18]. Meanwhile, the new physical crosslinking points were formed, increasing the degree of crosslinking and compressed the network space volume, which led to the sharp decline in the oil absorbency of the resin [18].

Oil absorption properties of the lipophilic polyelectrolyte resin

The absorbency of the lipophilic polyelectrolyte resin in different solvents

The absorbency of the lipophilic polyelectrolyte resin in different oils (dimethylformamide (DMF), acetone (CP), xylene (XY), tetrahydrofuran (THF), dichloromethane (CH_2Cl_2), carbon tetrachloride (CCl_4), cyclohexane (CHX)) was illustrated in Fig. 4. It could be seen clearly from Fig. 4a that lipophilic polyelectrolyte resin had a high selectivity of oil. It had a high absorbency in less and nonpolar organic solvents, such as CH_2Cl_2 and CCl_4 , while a low absorbency in polar organic

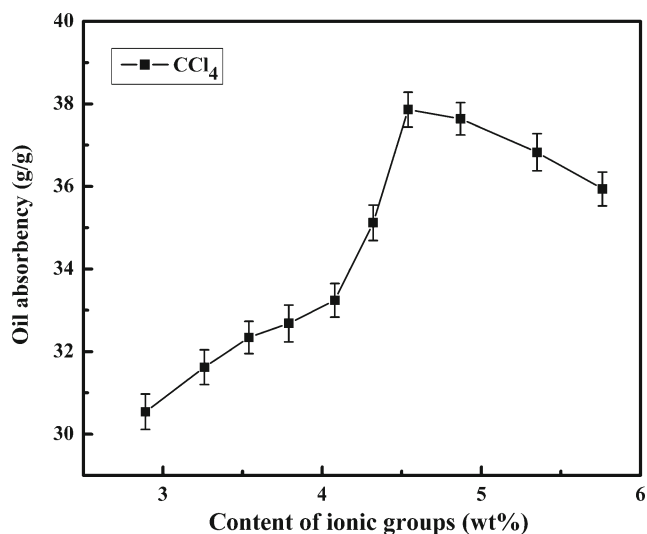


Fig. 3 The relationship between ionic content and oil absorbency. (The ionic content is 2.89, 3.34, 3.60, 3.81, 4.17, 4.42, 4.56, 4.88, 5.32, and 5.75 wt%, respectively)

solvents, such as DMF and CP. This phenomenon is due mainly to the compatibility of the resin network with the solvent and dissociation of the ion groups. Less and nonpolar solvents could promote the ion groups to be disassociated into free ions or loosely bound ion pairs, which enhances the swelling degree of resin. In the polar organic, however, the lipophilic polyelectrolyte resin had poor compatibility with them and did not allow penetration of the solvent molecules into the polymer networks, even though the ion groups would be easily dissociated [26]. It was evident that the oil absorbency of the lipophilic polyelectrolyte resin was higher than that of non-ionic resin. It also could be seen from Fig. 4b. This was because the oil absorbency of non-ionic resin was just due to its 3D networked structure and compatibility of the polymer chains with the solvents. On the contrary, the lipophilic polyelectrolyte resin, in addition to this, also originated from the dissociation of ionic groups.

The kinetics of oil absorption

It could be clearly observed from Fig. 5 that oil-absorbing rate of the resins was very fast at first and then reached a steady state. The maximum oil absorbency of the lipophilic polyelectrolyte resin (b–d) to CCl_4 was much higher than that of non-ionic resin (a). The time to reach the saturated oil absorbency of non-ionic resin also became shorter through ionization, and the time became gradually shorter with the increase of content of ionic groups. It was because the oil absorption of the lipophilic polyelectrolyte resin relied on the

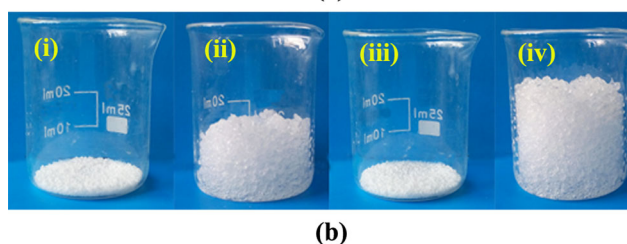
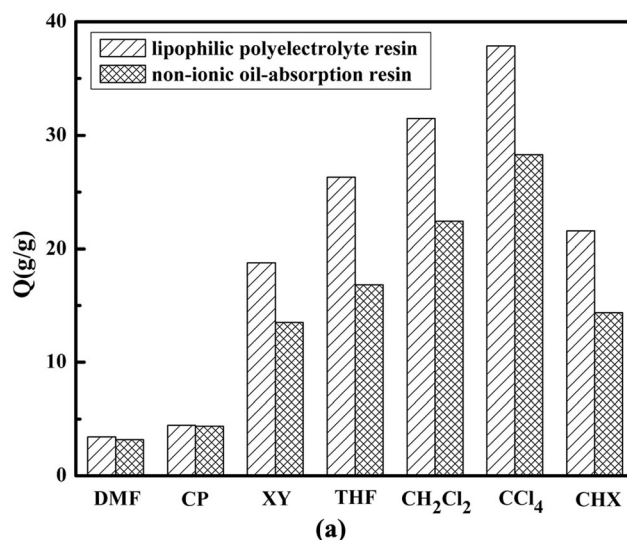


Fig. 4 **a** The absorbency of the lipophilic polyelectrolyte resin to different solvents and **b** their swelling behavior in CCl_4 ((i) dried non-ionic resin (1.0 g), (ii) non-ionic resin swollen in CCl_4 for 24 h, (iii) dried polyelectrolyte resin (1.0 g), and (iv) polyelectrolyte resin swollen in CCl_4 for 24 h)

compatibility and the impacts of electrostatic repulsion and osmotic brought by the ionic groups. Therefore, the oil absorbency and oil-absorbing rate of the lipophilic

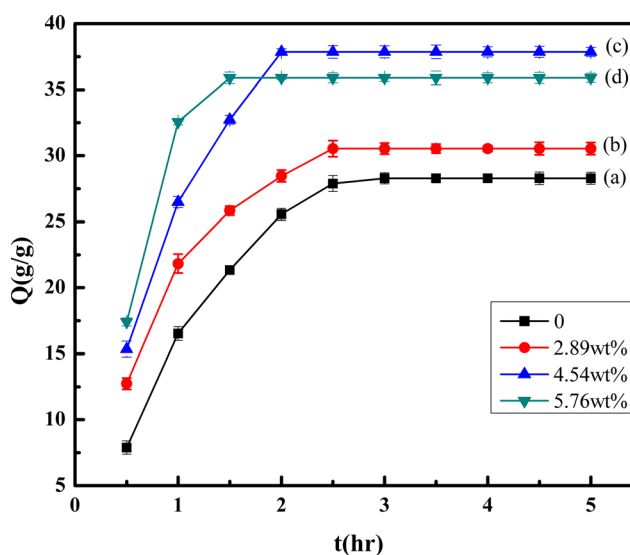


Fig. 5 The kinetics of the oil absorption of the resin with different ionic content

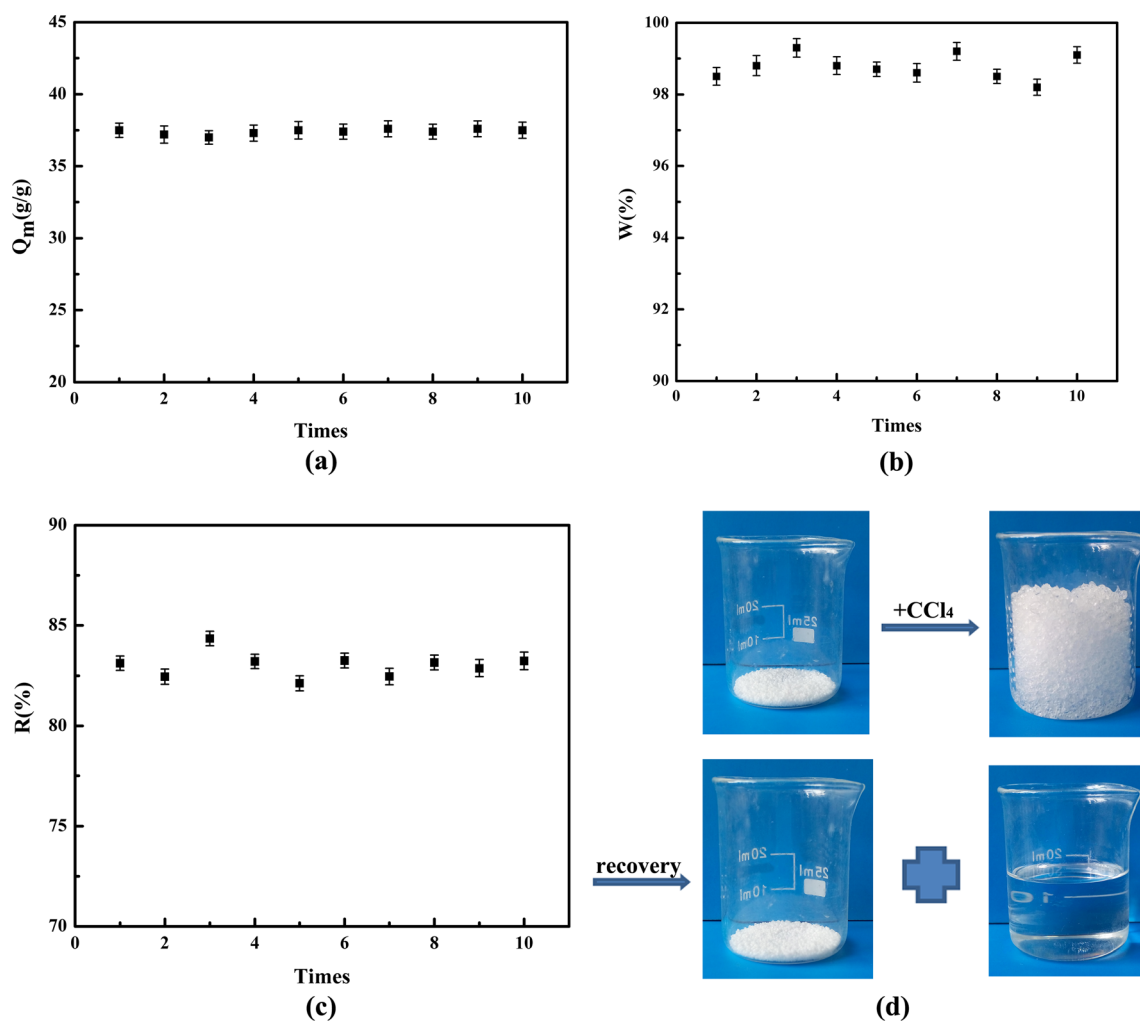


Fig. 6 Reusability of the lipophilic polyelectrolyte resin. (a) the absorbency of polyelectrolyte resin each cycle, (b) the recovery ratio of polyelectrolyte resin each cycle, (c) the recovery ratio of CCl_4 each cycle, and (d) the recovery process)

polyelectrolyte resin had been greatly improved, compared with non-ionic resin.

Reusability of the lipophilic polyelectrolyte resin

Figure 6 showed the reusability of the lipophilic polyelectrolyte resin. The detailed test procedure was shown in the [supplementary information](#). The oil absorbency of resin to CCl_4 kept about 37 g/g each time. The recovery ratio of the resin was over 98 % with less resin lost each time. The recovery ratio of CCl_4 reached more than 83 % each time. In addition, the process of reusability could also be seen from Fig. 6d. The results indicated that the lipophilic polyelectrolyte resin could be reused at least ten times. The high oil absorbency, the high recovery ratio of the resin, and the high recovery ratio of CCl_4 confirmed excellent reusability of the lipophilic polyelectrolyte resin.

Conclusion

In this study, the lipophilic polyelectrolyte resin with high oil absorbency and mechanical properties was successfully synthesized. Quaternary ammonium cations and tetraphenylborate anions were incorporated into the molecular structure of non-ionic resin. The effect of ionic content on the oil absorbency was also investigated. The oil absorbency of the lipophilic polyelectrolyte resin to CCl_4 was 37.86 g/g when the ionic content was 4.54 wt%, which was much higher than that of non-ionic oil absorption resin (CRSBS, 30.64 g/g). More importantly, it was found that the oil-adsorbing rate of lipophilic polyelectrolyte resin was faster than that of non-ionic resin. Furthermore, the lipophilic polyelectrolyte resin was reused at least ten times, and the results showed the resin had quite high oil absorbency, high recovery ratio of the resin, and high recovery ratio of CCl_4 , which was superior in terms of oily sewage treatment.

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