

Polyoxometalate and copolymer-functionalized ionic liquid catalyst for esterification*

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Abstract: A new room-temperature ionic liquid (RTIL) consisting of a polyoxometalate (POM) anion and tri-block copolymer (P123)-functionalized imidazolium cation was synthesized and utilized as a halogen-free catalyst for esterification. The catalytic system was a homogeneous solution at the beginning of the reaction, but an emulsion formed during the course of the reaction, and a progressive phase separation of the catalyst occurred at 0 °C over the course of 3 h. Dynamic light scattering (DLS), transmission electron microscopy (TEM), and Fourier transform/infrared spectroscopy (FT/IR) have been used to characterize the properties of the IL during the reaction. The new IL catalyst was found to be highly efficient in the esterification of various alcohols and can be recycled at least seven times.

Keywords: catalysis; emulsion; esterification; ionic liquids; phase separation; polyoxometalates.

INTRODUCTION

Polyoxometalates (POMs) represent a large series of anionic metal–oxygen clusters of early transition metals with discrete and molecularly defined structures. They exhibit a wide range of topologies and diverse physicochemical and electronic properties, and consequently stimulate many current research activities in broad fields of science such as catalysis and materials. They also have a very strong, approaching the super-acid region Brønsted acidity, and display fast reversible multi-electron redox transformations under mild conditions. These properties render POMs economically and environmentally attractive acid and redox catalysts in homogeneous as well as heterogeneous systems [1–5].

However, as a type of inorganic compound, POMs possess high crystal lattice energies and low solubility in nonpolar organic solvents, which largely restricted their applications in catalytic reactions in organic media. Fortunately, owing to the anionic nature of POMs, the synthesis of organic–inorganic hybrid POMs can be conveniently realized using a one-step exchange with cationic surfactants, leading to fine tuning of their properties such as acidity and solubility in various organic media. The resulting amphiphilic surfactant-encapsulated clusters (SECs) in which the cationic parts vary from water-soluble polymers, conductive polymers, dendrimer to block polymers showed great potential for the fabri-

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cation of POM-based materials and devices. In fact, the possibilities present for tuning phase behavior, phase structure, and even function of POMs by molecular design of the surfactant head group have been demonstrated in successful fabrications of a large number of assemblies of different morphology and functions from micelles, vesicles to liquid crystals, films, POM-based solid crystalline or even luminescent devices, etc. Many excellent reviews have covered these areas [6–10]. But as far as we know, there are only a few reports on the phase behavior of the liquid derivatives of POMs and their application in catalysis [11–13].

Compared with the advancement in fabrication of hybrid materials composed of cationic surfactant and POMs, the choices of the cations for coupling with POM anions applied in catalysis seem rather limited. The quaternary ammonium (e.g., tetrabutyl ammonium bromide), differing only in alkyl chain length, has been adopted in most of the catalytic systems. It has been noticed that this combination has already proved successful in a variety of catalytic reactions, such as selective oxidation of sulfur-containing compounds, alcohol oxidation, and epoxidation of olefins, etc. [3–5]. But we believe that given the potentially enormous number of cationic surfactants, it is certain that plenty of room still exists for expanding the exploration of the opportunities for introduction of novel functionalities and properties into the hybrid of POMs by varying cationic parts. One interesting example demonstrated by Giannelis's group is that the combination of a polyethylene oxide (PEG)-containing quaternary ammonium cation with a phosphotungstate Keggin anion, $[\text{PW}_{12}\text{O}_{40}]^{3-}$, successfully yielded a novel liquid derivative of bulky heteropoly acid, which showed unusually high conductivity [11]. Recently, imidazolium cation prevailing in the structures of ionic liquids (ILs) was also combined with heteropoly anion. This kind of hybrid material has shown many applications in the epoxidation of olefins and oxidation of the alcohols, and more are expected owing to the fact that the combinations of POM anions and IL cations are essentially countless [14–19]. In our previous reports, alkyl imidazole was quaternized with chlorinated PEG-300, producing a germinal room-temperature ionic liquid (RTIL) with chloride ions as anions, then $\{\text{PO}_4[\text{WO}(\text{O}_2)_2]_4\}^{3-}$ (venturello anions) was introduced by anion exchange [20]. This POM-based RTIL (POM-RTIL) was efficient in the epoxidation of olefins and proved to be recyclable. In addition, when PEG-2000-modified imidazolium cation was coupled with $[\text{HPW}_{12}\text{O}_{40}]^{2-}$, a strong emulsification between the POM-RTIL and substrates was observed during esterification of various alcohols with acetic acid, presumably influencing the reaction rate [21].

Esterification of alcohols by carboxylic acids is one of the most important reactions in organic synthesis. The importance stemmed from its utility in diverse fields both in the laboratory and in industry. For the preparation of esters, the major drawbacks of these common methods are the final neutralization of the homogeneous acid catalyst and the utilization of chlorinated solvents or halogen-containing catalysts, and, moreover, the removal of adsorbed products from the catalyst is quite difficult and requires a large excess of volatile organic solvents [22,23]. Based on our previous research [21], in this work, we introduced a block copolymer chain (Pluronic P123) into the germinal imidazolium cation of IL and employed this functionalized IL as a halogen-free catalyst for esterification. Then we attempted to clarify the following issues: firstly, how the more hydrophobic P123 chain instead of PEG chain changed the phase behavior of this catalytic system and second, how this change influenced the reaction rate in the esterification.

EXPERIMENTAL

Materials and methods

The manipulations involving air-sensitive materials were carried out using standard Schlenk line techniques under atmosphere of nitrogen. Alcohols, benzene, 1-butyl imidazole, and SOCl_2 were distilled before use. Pluronic P123 ($M_w = 5800$, $\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$) was purchased from Aldrich and used without further purification. All NMR spectra were recorded on a Bruker Avance 500 instrument (500 MHz ^1H , 200 MHz ^{31}P) using CDCl_3 as solvent. Gas chromatography (GC) and GC/MS were performed by GC

112A with flame ionization detector (FID) equipped with an HP-5 column (30 m, 0.25 mm i.d.). A Thermo Nicolet Nexus 670 was used for the FT/IR characterization. Transmission electron microscopic (TEM) and energy-dispersive spectrometric (EDS) characterization was conducted on Tecnai G2 20 S-TWIN. Dynamic light scattering (DLS) was performed on a Manern Zetasiler nano-zs instrument.

Catalyst preparation

Chlorination of P123

SOCl_2 (1.5 ml, 20 mmol) in benzene (10 ml) was added slowly during 0.5 h to a mixture of dried P123 (29 g, 5 mmol) and pyridine (0.8 ml, 10 mmol) in benzene (15 ml) at 25 °C. The mixture was refluxed for 8 h, then evaporated under reduced pressure. The solid residue was redissolved in benzene, and the mixture was filtered to remove any undissolved material. This procedure was repeated if necessary. The filtrate was evaporated to yield a chlorinated product. IR (cm^{-1}): 2970, 1973, 1639, 1455, 1373, 1347, 1297, 1110, 933, 747, 665 (C-Cl).

Preparation of P123-functionalized germinal imidazolium dichloride (PPO-Cl)

Chlorinated P123 (8.7 g, 1.5 mmol) and 1-butylimidazole (0.5 g, 4 mmol) were charged into a steel vessel, and then the reaction mixture was kept at 90 °C under 1.0 MPa nitrogen for 72 h with magnetically stirring. The product was dissolved in water and then washed thoroughly by diethyl ether. Then a slightly yellow viscous RTIL was obtained after the aqueous phase was evaporated under vacuum at 70 °C until no bubble was observed. ^1H NMR (500 MHz, CDCl_3) δ = 10.52 (s, 2H, CH), 7.73 (s, 2H, CH), 7.28 (s, 2H, CH), 4.66 (t, 4H, CH_2), 4.28 (t, 4H, CH_2), 3.30–3.80 (m, EO units), 1.88 (m, 4H, CH_2), 0.90–1.38 (m, CH_3 , CH_2).

Preparation of POM-based ionic liquid (PPO-PW₁₂)

The imidazolium dichloride (1.0 g, 0.16 mmol) in ethanol (1.0 ml) was slowly added to $\text{H}_3\text{PW}_{12}\text{O}_{40}$ (0.47 g, 0.16 mmol) in ethanol (1.0 ml) (POM/imidazolium dichloride molar ratio = 1:1) and then the mixture was stirred vigorously for 20 min. After the ethanol was removed, the product was dissolved in chloroform and was washed with distilled water (2 ml \times 4) until no chloride ions were detectable by silver nitrate test. Then organic solvent was removed to yield a viscous yellow liquid. IR (cm^{-1}): 2870, 1739, 1455, 1373, 1348, 1248, 1108, 1081, 978, 896, 819, 522. ^{31}P NMR (200 MHz, CDCl_3) δ = -15.4 ppm. Elementary analysis, found (Cal.): C, 40.9 (41.2); H, 7.56 (6.83); N, 0.58 (0.63), P, 0.37 (0.35), W, 25.3 (24.9).

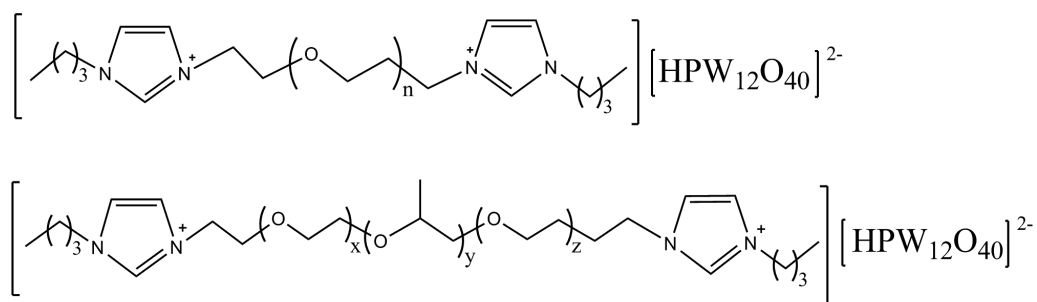
Typical procedure for esterification

IL catalyst (0.16 g, 0.017 mmol) was charged into a 25-ml schlenk glass flask with a magnetic stirrer and a reflux condenser, followed by adding lauryl alcohol (3.2 g, 17 mmol) and acetic acid (2.0 ml, 34 mmol) (IL:alcohol:acid = 0.001:1:2, molar ratio). Then the reaction was allowed to proceed for a required time at a certain temperature. After reaction, the reaction mixture stood still at 0 °C for 3 h. The clear upper layer was removed carefully and dissolved in cyclohexane. Then the catalyst was washed with cyclohexane three times. The cyclohexane layers were combined for GC and GC/MS analysis with the internal standard (octane) method. The IL catalyst was then dried under vacuum at 70 °C for the next run.

RESULTS AND DISCUSSION

In the previous study, we have already shown a novel emulsion between the substrates and POM-based RTIL (PEG-PW₁₂) during the whole course of the reaction, which was believed to facilitate the dispersion of the liquid catalyst into the substrates [21]. In this paper, we will report a new RTIL synthesized in a similar way using a more hydrophobic Pluronic P123 instead of hydrophilic PEG-2000 (see

Experimental section). The structures of the two POM-based RTILs are shown in Scheme 1. As shown in Fig. 1, the known characteristic bands 1080 cm^{-1} , 978 cm^{-1} , 896 cm^{-1} and 819 cm^{-1} resulted from the vibration of P–O, W=O, and W–O–W in POM anions [24]. The ^{31}P NMR (-15.4 ppm in CDCl_3) of PPO-PW₁₂ proved the presence and the integrity of the core clusters of Keggin-structure POM [25]. It implied the incorporation of copolymer chain-modified imidazolium into POM was accomplished by ion exchange of the surface protons of $\text{H}_3\text{PW}_{12}\text{O}_{40}$. It should be noted here that PPO-PW₁₂ and its parent IL (P123-Cl) were both liquid at room temperature (liquid even at $0\text{ }^\circ\text{C}$). This was different from PEG-PW₁₂ which gradually became semi-solid at room temperature. Besides, it has been observed that PPO-PW₁₂ was more hydrophobic than PEG-PW₁₂, which can be proved by that PPO-PW₁₂ can be well dissolved in ethyl acetate or lauryl alcohol at room temperature while PEG-PW₁₂ cannot. The change was expected to exert significant influence on reaction rates of esterification of hydrophobic alcohol with acid.



Scheme 1 The structure of PEG-PW₁₂ and PPO-PW₁₂ ILs.

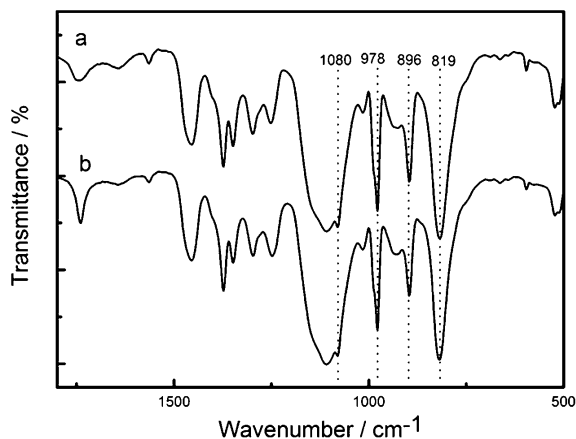


Fig. 1 IR spectra of the as-synthesized PPO-PW₁₂ IL (a) and after being recycled in the esterification reaction (b).

To investigate the possible difference of PPO-PW₁₂ and PEG-PW₁₂ in the catalytic performance, which may result from the difference of the cationic structures, both PPO-PW₁₂ and PEG-PW₁₂ were employed to catalyze the esterification of alcohols with acetic acid. The reaction rate between lauryl alcohol with acetic acid was shown in Fig. 2. It was clear that PPO-PW₁₂ turned out to be a more effective catalyst for this reaction, though the only structural difference of the two catalysts was the cationic part, not the catalytically active anion. Additionally, PPO-PW₁₂ also showed higher catalytic activity

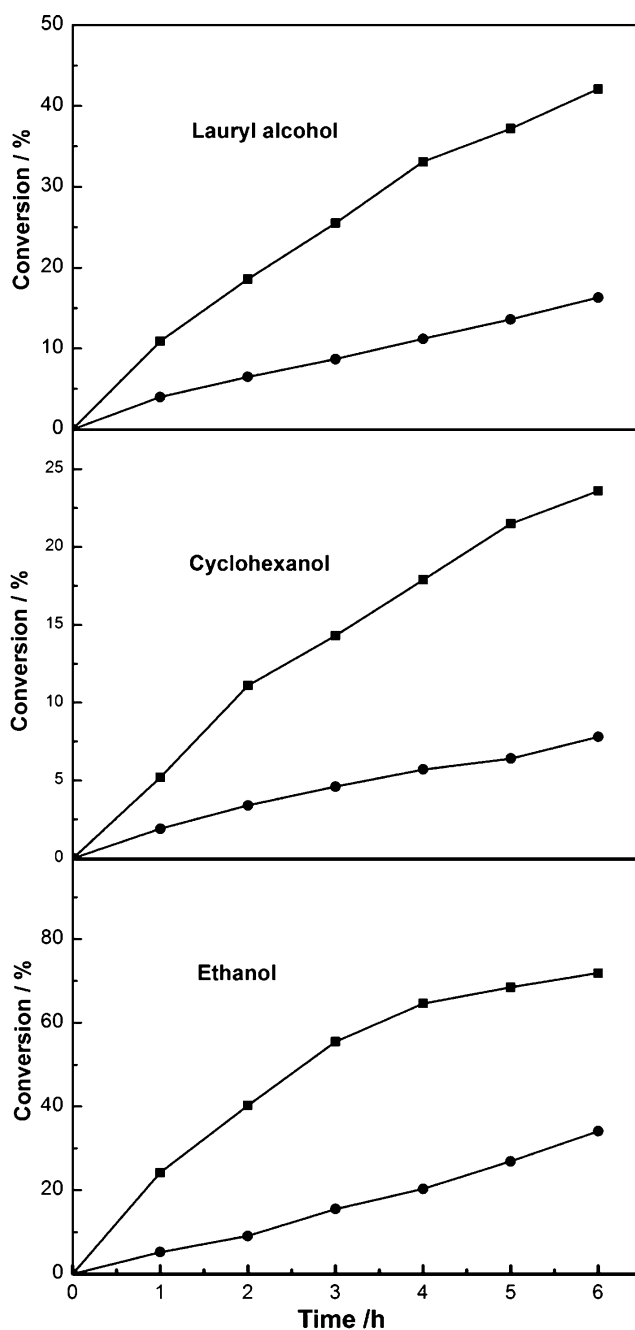


Fig. 2 Reaction conversion as a function of time for the esterification of alcohols with acetic acid catalyzed by PPO-PW₁₂ (■) and PEG-PW₁₂ (●). Reaction conditions: 0.017 mmol catalyst, 17 mmol alcohol, 34 mmol acetic acid, 60 °C.

when cyclohexanol and ethanol were used as substrates. On the basis of these results, it would be rational to conclude that the cations of the ILs did influence the activity of esterification considerably.

To gain an insight into the possible reason for the accelerated reaction rate by using PPO-PW₁₂ catalyst, phase behavior was examined in detail. It can be seen that after PPO-PW₁₂ was mixed with substrates (Fig. 3, left), a “homogeneous” solution was observed, which indicated the high solubility of the PPO-PW₁₂ in the mixed substrates. In contrast, an emulsion was immediately observed in the presence of PEG-PW₁₂ [21]. We believed that the difference in the solubility directly affected the dispersity of the IL catalyst, and accordingly the IL with high solubility in the substrate led to the enhanced catalytic activity. What was really interesting was that as the reaction proceeded for about 1 h, an emulsion was gradually observed in the presence of PPO-PW₁₂ (Fig. 3, middle). The formation of this emulsion can facilitate the separation of the catalyst because the emulsion was a thermodynamically less stable system in comparison with a homogeneous solution. In fact, after the reaction the reaction mixture only needed to stand still at 0 °C for 3 h to allow precipitating the catalyst quantitatively from the reaction system (Fig. 3, right). This was a quite attractive phase behavior from a point of view of saving input of energy of industrial process in which the separation of catalyst from products was not cost-effective generally.

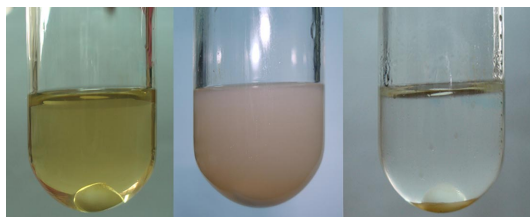


Fig. 3 Different stages of the esterification reaction between acetic acid and lauryl alcohol. left: PPO-PW₁₂ was well dissolved in mixture of lauryl alcohol and acetic acid before the reaction; middle: a strong emulsification happened during the reaction; right: the phase separation can lead to quantitative recovery of IL at the bottom of the flask at 0 °C for 3 h after the reaction.

The control experiments were conducted to find essential factors for the formation of the emulsion. The determination of solubility showed that the PPO-PW₁₂ IL in pure acetic acid formed an emulsion in any conditions, while a homogeneous solution in lauryl alcohol. Moreover, if the PPO-PW₁₂, acetic acid, and lauryl alcohol (molar ratio = 0.001:1:2) were mixed and stirred at room temperature even for one week, the mixture still kept transparent. When the mixture was stirred at 60 °C for 1 h, an emulsion was then observed, which indicated the reaction temperature was a very important factor for emulsification. The presence of acetic acid is equally necessary; no emulsion would be observed in the absence of acetic acid at any condition. When H₃PW₁₂O₄₀ was directly used as a catalyst under the same reaction condition, the emulsification was not seen throughout the reaction process. It should be noted that the solid catalyst was well dissolved in the mixture even after the reaction was completed and therefore very hard to be isolated although the heteropoly acid catalyst offered higher reaction rate than PPO-PW₁₂ catalyst (Fig. 2 vs. 4). These results strongly suggested that the constituents of the substrates, the temperature, and particularly the amphiphilic nature of the PPO-PW₁₂ are all necessary factors for this interesting phase behavior.

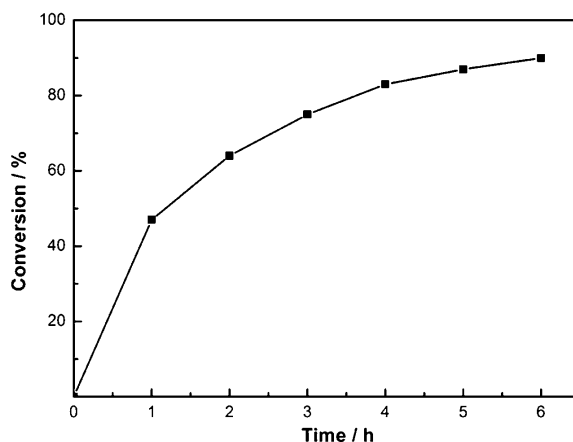


Fig. 4 Reaction conversion as a function of time for the esterification of lauryl alcohol with acetic acid catalyzed by $\text{H}_3\text{PW}_{12}\text{O}_{40}$. Reaction condition: 0.017 mmol $\text{H}_3\text{PW}_{12}\text{O}_{40}$, 17 mmol lauryl alcohol, 34 mmol acetic acid, 60 °C.

DLS is a strong tool to determine the size distribution of the colloidal particles. So the colloidal size of the IL (PPO-PW₁₂) in substrates was determined using this method. As shown in Fig. 5, after the catalyst was dissolved in lauryl alcohol, an average diameter of 376 nm was found at 25 °C (Fig. 5a). This value was obviously larger than the molecular size of the IL, which meant that the amphiphilic IL was dispersed in lauryl alcohol in the form of assembly of colloids other than individual molecules. A significant bigger size of 602 nm of these colloids was found when the IL is dispersed in the mixture of lauryl alcohol and acetic acid (Fig. 5b), indicating the crucial effect of acetic acid in the growth of the aggregates. After the reaction mixture was stirred at reaction conditions (60 °C) for 1 h, the average diameter became 1320 nm (Fig. 5c), corresponding to the observed emulsification. These results supported the conclusions as follows: the IL catalyst was dissolved in the reaction mixture under room temperature at first in the form of relatively small aggregates, when the reaction was started at elevated temperature, the sizes of the colloids became “bigger” gradually, and further formed drops of emulsion. And there was no doubt that the dispersity became worse along with the formation of larger colloidal particles.

In the next step, we characterized this emulsion by the methods of optical microscopy, TEM, and energy-dispersive X-ray (EDX). The results are shown in Fig. 6. As discussed above, the traditional hybrid catalysts composed of quaternary ammonium cations and POM anions were also found to assemble in emulsions and be potentially recoverable in a number of catalytic reactions [26–30]. However, there is a lack of characterization of the emulsion stabilized by a liquid derivative of POM. The optical picture showed a typical emulsion system in which the IL catalyst functions more like a surfactant. They arranged around a spherical liquid droplet (POM is not transparent due to its nature of metal oxide) where the reaction was supposed to proceed [29]. The analysis of the size distribution by counting 100 examples gave an average diameter of 1.38 μm (Fig. 6), which was in good agreement with the result obtained by DLS analysis (Fig. 5c). These spherical colloids with diameters around 1 μm were also observed in TEM, with their round shapes indicating the liquid nature of the material. The sizes of the colloids were actually smaller than that obtained in optical pictures possibly due to shrinkage of the emulsion drops under vacuum conditions. EDX at the nontransparent selected area clearly showed the presence of elements P, W, C and O, confirming those liquid drops are indeed composed of the PPO-PW₁₂.

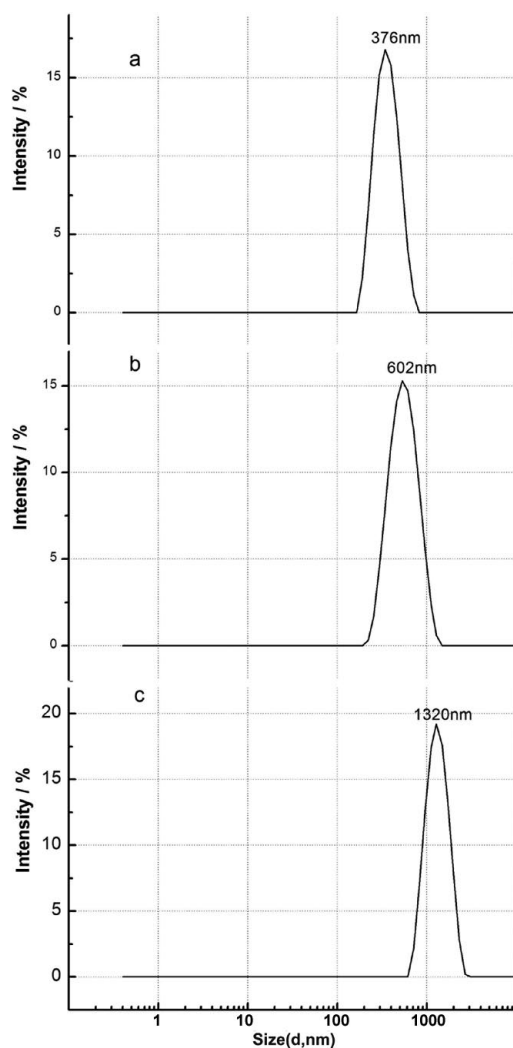


Fig. 5 DLS results of (a) PPO-PW₁₂ in lauryl alcohol at 25 °C; (b) PPO-PW₁₂ in the mixture of lauryl alcohol and acetic acid at 25 °C (the molar ratio of acetic acid to lauryl alcohol = 2); (c) The mixture in (b) was stirred at 60 °C for 1 h.

Summarizing the results above, we can see that the PPO-PW₁₂ IL can form bigger aggregates as the reaction proceeded and finally induced the formation of the emulsion, and accordingly facilitated the separation of the catalyst. It is also worth noting that neither copolymer P123 nor PPO-C1 IL formed emulsion under reaction conditions, so it was certain that the large POM head group in the PPO-PW₁₂ IL played a vital effect in this interesting phase behavior. Actually, the utility of the POMs functioning as head groups of the surfactants has been realized only very recently [31–33].

The ease with which the catalyst can be recycled is crucial to the utility of the interesting phase behavior. Thus, the recyclability of the liquid catalyst was conducted in a batch-type process. As can be seen in Fig. 7, no obvious loss of activity was seen even after seven consecutive uses in the esterification of lauryl alcohol, indicating the stability of the liquid catalyst, which was further proved by IR spectrum shown in Fig. 1. The spectrum of the catalyst after seven recycles contained all characteristic bands resulted from both the POM anion part and copolymer P123-modified imidazolium cation with

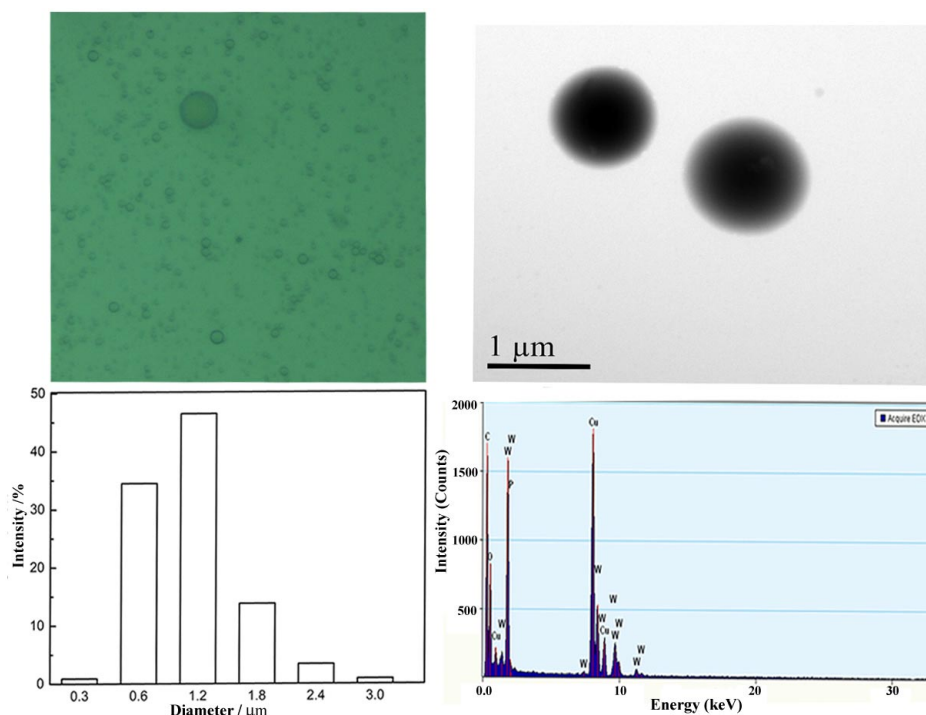


Fig. 6 Optical picture (upper left), TEM picture (upper right) of the emulsion system after reaction for 1 h. Histogram of diameter distribution was based on optical picture.

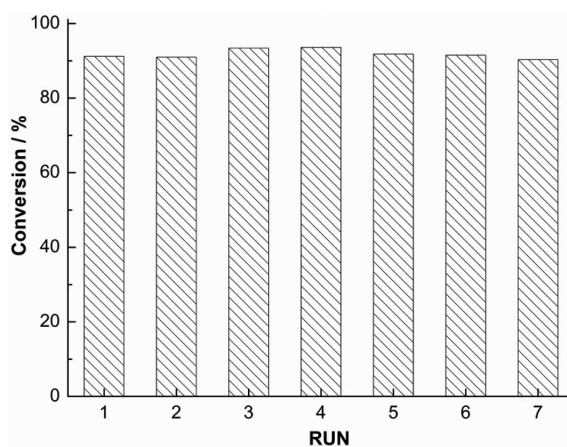


Fig. 7 Recycling of PPO-PW₁₂ in the esterification of lauryl alcohol with acetic acid. Reaction conditions: 0.017 mmol catalyst, 17 mmol alcohol, 34 mmol acetic acid, temperature 100 °C, time 8 h.

no detectable shift. After reaction, the amount of leaching W into the product was analyzed by inductively coupled plasma/atomic emission spectroscopy (ICP/AES). The result showed that only 12 ppm of W was lost into the product phase after three catalytic runs.

Different alcohols and acids were also employed as substrates to further demonstrate the utility of this liquid catalyst, and the results are shown in Table 1. Good to excellent conversions were achieved

for all selected alcohols with acetic acid (entries 1–6, Table 1). It should be noted here that after the catalyst was mixed with ethanol and 2 equiv acetic acid, emulsification was observed even at room temperature. Although emulsification was observed at the beginning of the reaction, the PPO-PW₁₂ catalyst still showed higher activity than PEG-PW₁₂ for the esterification of ethanol (Fig. 2). This can be explained from the phenomenon that PEG-PW₁₂ precipitated from the solution gradually with reaction going on, when the reaction was nearly completed, a large part of yellow liquid catalyst sunk to the bottom of the vessel as reported previously [21]. In contrast, no precipitate of PPO-PW₁₂ was observed during the whole reaction period. In other words, the emulsion formed by PPO-PW₁₂ was more stable than that by PEG-PW₁₂, which was favorable for keeping the high dispersity of catalyst in substrates, leading to the enhancement of the activity. Additionally, as shown in Table 1, excellent conversion was obtained by using other carboxylic acids (such as propionic acid and butanoic acid) and 1-butanol as reactants (entries 7 and 9, Table 1), while moderate conversion by using lauryl alcohol under same consideration (entries 8 and 10, Table 1). It should be worth noting that the unique phase behavior that the reaction mixture gradually changed from a transparent colloidal solution to an emulsion was also observed in the esterification of alcohols with propionic acid and butanoic acid.

Table 1 The esterification of different alcohols with acids catalyzed by PPO-PW₁₂^a.

Entry	Alcohols	Acid	Temperature (°C)	Time (h)	Conversion (%)
1	Ethanol	Acetic acid	80	4	95.5
2	1-Butanol	Acetic acid	80	4	94.7
3	1-Octanol	Acetic acid	80	6	93.3
4	Lauryl alcohol	Acetic acid	100	10	90.9
5	Cyclohexanol	Acetic acid	100	10	90.1
6	Benzyl alcohol	Acetic acid	80	6	91.4
7	1-Butanol	Propionic acid	100	10	93.7
8	Lauryl alcohol	Propionic acid	100	10	80.5
9	1-Butanol	Butanoic acid	100	10	93.1
10	Lauryl alcohol	Butanoic acid	100	10	70.6

^a0.017 mmol catalyst, 17 mmol alcohol, 34 mmol acid.

CONCLUSION

The novel IL has been prepared by the combination of copolymer P123 covalently linked imidazolium cations and POM anions. The hybrid IL catalyst was found to be highly efficient for the esterification of various alcohols with acetic acid. It was demonstrated that the IL formed nanostructural aggregates in substrates at the beginning of reaction, and grew bigger during the reaction process. Finally, a thermodynamically unstable emulsion was observed, and the catalyst can self-precipitate at the end of reaction. This is only supposed in the case where the catalyst is amphiphilic liquid since it is more flexible and tends to self-assembly in the chosen solvents. The adjustment of the cation structure had a favorable effect on the reaction rate. Given the multifunctionality and structural mobility of both cationic polymer and POMs, it is certain that much more attractive phase behaviors and catalytic applications of these liquid derivatives of POM remain to be identified.

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