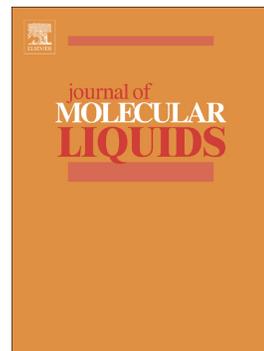


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# Novel bioactive imidazole-containing polymeric surfactants as petroleum-collecting and dispersing agents: Synthesis and surface-active properties

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## Abstract

Novel series of imidazole-containing polymers and polymeric surfactants have been synthesized *via* an efficient procedure. It included copolymerization of 1-vinylimidazole (VIM) with lauryl methacrylate (LMA) initiated by benzoyl peroxide and the <sup>1</sup>H NMR spectroscopic data was utilized to estimate the monomer reactivity ratio. Conversion of polymers to surfactants was achieved through quaternization of the imidazole nitrogen with dimethyl sulphate. Spectroscopic techniques were used to elucidate the chemical structures of all synthesized compounds. The surface-active properties of polymeric surfactants beside their activities against various microbes were investigated. In addition, petroleum-collecting and dispersing properties of surfactants in diluted and undiluted form in varying waters were evaluated.

**Keywords:** 1-Vinylimidazole; Lauryl methacrylate; Reactivity ratios; Polymeric surfactants; Petroleum-dispersing agents.

## 1. Introduction

Macromolecules, which include diazole moiety, have been proposed as carrying an active part of various electrolyte-containing enzymes [1-3]. A great

number of proteins, such as histamine and histidine, comprise of imidazole ring, which is partly attributable to their catalytic activity. Consequently, comprehensive research on the catalytic activity of imidazole monomers [4] and polymers [5] as well has been reported. Furthermore, homopolymers of 1-vinylimidazole and poly(*N*-vinylpyrrolidone)-co-poly(1-vinylimidazole) blocks have been used as new coating technology for separation of proteins [6].

The remarkable ability of polymeric surfactants to alter the indices of surfaces and interfaces make them so popular. Such synthesized compounds have become vital components in many formulations beside some industrial processes [7-13]. The properties of polymeric surfactants such as detergency, emulsification, and foaming may exhibit a great variation with the precise chemical characteristics. The characteristic and position of the water-loving groups together with the arrangement and number of the hydrophobic groups determined the surface-active properties of the molecule [14-16].

Fatty amphiphilic surfactants are commonly used for controlling the growth of bacterial strains in various media. These salts, with their quaternary nitrogen, exhibit a variety of pharmacological properties, which include germicidal, antibacterial and antifungal activities [17-19]. A series of cationic surfactants in which their nitrogen atoms were the heteroatoms in aromatic bases may be expected to improve the biological action [20-23]. Cationic surfactants, and more particularly the quaternary ammonium compounds, have the strongest effect against all round microorganisms. They have been used to diminish the growth of different bacterial strains [24, 25].

The main objective of the present work was to prepare and evaluate some novel polymeric compounds based surfactants as petroleum-collecting and petroleum-

dispersing chemicals in varying waters in various forms. In addition, their surface and antimicrobial properties were studied.

## 2. Materials and experimental techniques

### 2.1. Materials

1-Vinylimidazole (VIM), methacrylic acid and *N,N*-dicyclohexylcarbodiimide (DCC) were obtained from Sigma-Aldrich. Lauryl alcohol and benzoylperoxide (BP) were used as received from Sigma-Aldrich. Dimethyl sulphate (DMS), dichloromethane (DCM), dimethylformamide (DMF), tetrahydrofuran (THF), diethyl ether and methanol were purchased from Al-Nasr chemical company. FT-IR (ATR) spectra were recorded on Thermo-Scientific, Nicolet iS10 FT-IR spectrophotometer.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were measured in  $\text{CDCl}_3$  as solvent and tetramethylsilane (TMS) as internal standard on Varian Mercury operating at 300 MHz in Chemistry Department, Faculty of Science, Cairo University.

### 2.2. Experimental techniques

#### 2.2.1. Synthesis of lauryl methacrylate (LMA)

In an ice bath system, a solution of lauryl alcohol (10 mmol) in DCM was added drop wisely to a solution of DCC, (11 mmol) and methacrylic acid (10 mmol) in DCM (20 mL) within 10 minutes with continuous stirring. Stirring was continued for another 4 h at room temperature followed by filtration. The filtrate was concentrated under vacuum then the crude product was purified by column chromatography via silica gel as adsorbent (eluent: DCM) to afford lauryl methacrylate. Yield (86%); FT-IR ( $\nu$ ,  $\text{cm}^{-1}$ ): 2854–2925 (C-H aliphatic fatty chain), 1721 (C=O of ester group), and 1146 (C-O), (**Figure 1**).

<<Figure 1>>

### 2.2.2. Copolymerization of 1-vinylimidazole (VIM) and lauryl methacrylate (LMA)

Copolymerization of 1-vinylimidazole and lauryl methacrylate with different molar ratios was carried out in a four-necked kettle equipped with stirrer, reflux condenser, inlet system of inert gas and dropping funnel. In a water bath at 70-80°C, the polymerization kettle was placed. At first, dimethylformamide (DMF) and LMA were added to the kettle and heated to 70°C then, the initiator BP and VIM were charged drop by drop. The reaction mixture was stirred at 80°C. Copolymers were recovered by precipitation in methanol, filtered, refined and dried under vacuum. The yield of products **P2-P6** ranges from 80 to 90%.

**Figures 2a** and **3a** represent the FT-IR spectra of **P2** and **P4** copolymers, respectively. They reveal absorption bands at 2852–2952 for  $\nu$ C-H fatty aliphatic chain, 1721 for  $\nu$ C=O of ester, 1672 for  $\nu$ C=N, 1651 for  $\nu$ C=C, and 664  $\text{cm}^{-1}$  for  $\nu$ C-N.  $^1\text{H}$  NMR gave signals at  $\delta$  (ppm): 0.87(t, 3H, **CH<sub>3</sub>** of aliphatic chain), 1.25(m, 20H, **10CH<sub>2</sub>** of aliphatic fatty chain), 1.57(s, 3H, **CH<sub>3</sub>** of acrylate group), 1.92(t, 1H, N-**CH**), 2.14(d, 4H, **2CH<sub>2</sub>-CH**), 3.90(t, 2H, **CH<sub>2</sub>-O**), and 7.21-7.52(m, 3H, **CH** aromatic of imidazole ring) as shown in **Figures 2b** and **3b**.  $^{13}\text{C}$  NMR spectra for copolymer **P4** exhibited signals at  $\delta$  (ppm): 14.07(**CH<sub>3</sub>** of fatty chain), 22.60(**CH<sub>3</sub>-CH<sub>2</sub>**), 25.98(**CH<sub>3</sub>-C-C=O**), 29.17-29.60(9C, **9CH<sub>2</sub>** of fatty chain), 31.80(**CH<sub>2</sub>-C-C=O**), 36.45(**CH<sub>2</sub>-CH**), 44.32(**C-C=O**), 49.94(**CH-N**), 65.60(**CH<sub>2</sub>-O**), 118.28, 125.39, 137.81 (3C, **3CH** aromatic), and 173.37 (**C=O**), (**Figure 3c**).

<<Figure 2 & Figure 3>>

### 2.2.3. Quaternization of [VIM-co-LMA] copolymers

In a closed system, the polymeric surfactants were obtained by reacting the synthesized [**VIM-co-LMA**] copolymers with excess amount of DMS in the absence of solvent. The mixture was maintained at 80 °C for 72 h with stirring. The products

[PS2, PS3 & PS4] were afforded by recrystallization from diethyl ether several times to remove all unreacted substrates. The isolated yields of the products were 80-85%.

The structure of prepared polymeric surfactants were elucidated by FT-IR that showed strong absorption bands of the 1,3-dialkylimidazoliumcation [26] at 1465, 1253 and 1162  $\text{cm}^{-1}$ . The broad peak at 3443  $\text{cm}^{-1}$  is due to the absorbed water in the sample, showing the highly hygroscopic nature of target molecules as shown in **Figures 4a** and **4b**.

<<Figure 4>>

## 2.3. Measurements

### 2.3.1. Surface Tension and electrical conductivity

Values of surface tension of aqueous solutions of polymeric surfactants were recorded by Tensiometer-K6 processor (krüss company, Germany) using the ring method. Each sample was determined from the average of three times measurements and all measurements were recorded at 298°K. Before measurements, the surface tension value of the pure water was demonstrated in the range of  $72.0\pm 0.3$  mN/m. Also, the electrical conductivity of the obtained polymeric surfactant solutions was measured by conductivity meter (model Type AD3000; EC/TDS and Temperature meter) at 298 °K. The measurement values were done in triplicates for each solution at the same temperature.

### 2.3.2. Krafft point

The Krafft temperatures for the synthesized polymeric surfactants were measured by visual observations. The concentrations of surfactant solution were at least twice the CMC (critical micelle concentration) of the studied surfactants [27].

### **2.3.3. Foaming power**

After shaking 100 mL of 0.1% (wt/v) of the polymeric surfactant solution vigorously in a stoppered graduated 250 mL cylinder at room temperature, foam power of polymeric surfactants was measured [28]. Initially, the foam height (in cm) represent the foaming power, and the stability of foam was determined by the falling of height after 3 min.

### **2.3.4. Emulsifying stability**

A mixture of 10 mL (0.5%) of the surfactant solutions with 10 mL of paraffin oil at 303°K (room temperature) was shaken vigorously to measure the emulsion stability [29]. The strength of the polymeric surfactants to form a stable emulsion (emulsion stability) was expressed as the time needed to separate 9 mL of pure surfactant solution away from oil.

### **2.3.5. Petroleum-collecting and petroleum-dispersing capacities**

The study of collecting and dispersing activities towards petroleum thin films of the polymeric surfactants (in the pure state and in the form of 5 wt% aq. solution) has been carried out. The Red sea crude oil (density and kinematic viscosity at 20°C are 0.84 g/cm<sup>3</sup> and 0.13 cm<sup>2</sup>/s, respectively) from the oil fields in the South Sinai (Egypt) was used. The method in literature [30-32] was used for calculation.

### **2.3.6. Antimicrobial activity**

Evaluation of antimicrobial activities (*in vitro*) of prepared polymeric compounds was carried out against a range of microorganisms comprising bacteria and fungi.

### 2.3.6.1 Test organisms

The following microbial strains for testing purposes were obtained from the Botany Department, Faculty of Science, Benha University, Egypt: *Staphylococcus aureus* (Gram-positive), *Bacillus cereus* (Gram-negative), *Aspergillus niger*, and *Rhizopus oryzae*.

### 2.3.6.2 Hole-plate diffusion method

A hole-plate diffusion method [33] was used to estimate the ability of a drug to kill or inhibit the growth of living microorganisms. A suspension with 0.5 McFarland standard turbidity. Holes of 6 mm diameter were made on the Mueller-Hinton agar plate (8 mm thick) inoculated by flooding and filled with 200  $\mu$ L of compound aqueous solution (1 mg/mL). The plates containing the bacteria were incubated at 35-37°C for 24 h while those of fungi were incubated at 25-27 °C for 48 h. The inhibition zone around each hole was used to evaluate the activity against microbes. Standard antibacterial drug (*Tetracycline*) and antifungal one (*Amphotericin B*) were tested.

## 3. Results and discussion

### 3.1. Synthesis

The synthesis process of the polymeric surfactants is shown in **Figure 5**. The first step is an esterification reaction between lauryl alcohol and methacrylic acid to form lauryl methacrylate. The second one includes copolymerization of 1-vinylimidazole (VIM) with lauryl methacrylate (LMA) with different molar ratios to form polymeric compounds **P2-P6**. A simplified mechanism for the copolymerization involves initiation through phenyl radicals (generated from thermal decomposition of

benzoyl peroxide) followed by the chain propagation with the two monomers (VIM & LMA) and then termination of the formed chains (**Figure 6**).

<<Figure 5 & Figure 6>>

The copolymer composition was calculated *via* utilizing  $^1\text{H}$  NMR spectroscopic data. The method described in our previous work [34-36] was used in the present work for the quantitative analysis of these copolymers by  $^1\text{H}$  NMR spectroscopy. This method includes determining the resonance area that efficiently represents monomer component, subtracting any interferences and dividing that area by the number of protons per/monomer component giving that resonance, to obtain the relative moles of each component. The results are shown in (**Table 1**) and we found that monomer reactivity ratio for VIM-LMA copolymers are  $r_1 = 0.502$ ,  $r_2 = 5.084$  by Fineman–Ross (**Figure 7a**) and  $r_1 = 0.488$ ,  $r_2 = 4.992$  by Kelen–Tüdös (**Figure 7b**). The  $r_1r_2$  value for VIM-LMA equals 2.436, which indicates that the copolymer should have a random distribution of the monomer units. In addition, composition curve for copolymerization of VIM with LMA is shown in **Figure 8**.

<<Figure 7, Figure 8 & Table 1>>

The third step is a quaternization process of some synthesized polymeric compounds using DMS to form novel polymeric surfactants. In a word, these polymeric surfactants could be readily accessed in good yields under mild conditions, and the preparation/purification procedures were simplified in comparison to other polymeric surfactants reported previously. In addition, all synthesized compounds were confirmed from different spectroscopic techniques.

### ***3.2. Surface tension and micellization***

Surface tension is the most vital characteristic among the surface-active properties of a surfactant solution. The surface tension ( $\gamma$ ) values versus the

concentration of the obtained surfactant at 298 °K are shown in **Figure 9**. Such figure showed that the initial raise in the concentration leads to a sudden drop in the values of the surface tension of the surfactant solutions. However, a slow decrease in the surface tension took place at the break point, indicating the accumulation of surfactant molecules to form aggregates. The value of prepared polymeric surfactants concentration at the break point is shown as the CMC of the synthesized surfactants. The values of CMC recorded in **Table 2** for the synthesized compounds PS2, PS3 and PS4 are 0.015, 0.057 and 0.025%, respectively.

<<Figure 9 & Table 2>>

**Figure 10a-c** showed the relation between electrical conductivity of synthesized surfactants solution ( $k$ ) and concentration. In each plot, intersection at the point CMC has been obtained from two lines with different slopes. The CMC values calculated from electrical conductivity plots were recorded in **Table 2**. Finally, it was found that the values of CMC obtained from surface tension measurements are near to those obtained from electrical conductivity measurements.

<<Figure 10>>

### **3.3. Krafft point**

The Krafft points of surfactants can be used to evaluate their solubility. The lower the Krafft point of a surfactant, the better its solubility. From **Table 2**, it is noted that the obtained polymeric surfactant gave Krafft point values below 0 °C, this reveals the good solubility of these surfactants.

### **3.4. Emulsifying power**

The tendency of emulsification of the surfactants solution reflects its ability to locate at the boundaries between opposite phases. The increase in the elapsed time until separation of the desired quantity of aqueous layer, from the emulsified system,

refers to the stability of the formed emulsion and vice versa. The results in **Table 2** indicate that PS3 needs long time to separate a desired amount of water than the other synthesized compounds, so PS3 has high emulsion power than PS2 and PS4. Emulsion formation technology is very important in different applications, especially drug formulations, cosmetics and paints.

### ***3.5. Foaming properties***

The prepared polymeric surfactants exhibited relatively low foaming heights. As expected, the synthesized compounds solutions showed moderate foaming volumes ranging from 80 to 160 mL for PS2, PS3 and PS4 as shown in **Table 2**. The low-foaming tendency of surfactants is important in some applications such as dyeing auxiliaries in the modern textile industry and mechanical dishwashing agents.

### ***3.6. Petroleum-collecting and petroleum-dispersing properties***

Experiments were performed to investigate the effect of surfactants on the accumulation or dispersion of petroleum thin films. All results were recorded in **Table 3**, and it was noted that different forms (diluted/undiluted) of all furnished polymeric surfactants gave good petroleum-collecting and petroleum-dispersing action. PS2 exhibits very high petroleum-dispersing in both diluted and undiluted form, whereas  $K_d$  ranges from 91.30 to 97.50%,  $\tau = 55-166$  h (in distilled, fresh and sea waters).

#### **<<Table 3>>**

Interestingly, PS3 in undiluted form gave a good petroleum-collecting effect in all used waters and the values range from 30.11 to 33.50,  $\tau = 30-166$  h. Additionally, in distilled and fresh waters, diluted form of PS3 exhibited high petroleum-collecting properties, whereas  $K = 32.22$ ,  $\tau = 30-166$  h and  $K = 33.11$ ,  $\tau = 30-166$  h, respectively. However, in sea water, PS3 in diluted form gave high petroleum-

dispersing effect ( $K_d= 95.60\%$ ,  $\tau= 40-166$  h). By contrast, undiluted form of PS4 exhibited very good petroleum-collecting capacity in distilled water ( $K= 33.60$ ,  $\tau = 30-166$  h), but in fresh and sea waters gave very high petroleum-dispersing action, whereas  $K_d$  is  $97.60\%$ ,  $\tau = 30-166$  h. Also, in sea water, diluted form of PS4 exhibits very high petroleum-dispersing effect ( $K_d=97.60\%$ ,  $\tau = 20-166$  h).

By summarizing, all of the prepared polymeric surfactants gave good petroleum-dispersing and petroleum-collecting effects and it can be used as petroleum-dispersing and collecting agents. As well as we can see that the synthesized polymeric surfactants have better petroleum-dispersing and collecting properties comparing with the corresponding conventional surfactants studied before [37, 38].

### 3.7. Antimicrobial activity

The effectiveness of the synthesized polymeric surfactants against number of microorganisms was tested with the aim of obtaining specific derivatives that could be potent in chemistry, medicine or agriculture. Such compounds were screened for evaluation their potency against bacteria (*Staphylococcus aureus* and *Bacillus cereus*), and fungi (*Aspergillus niger* and *Rhizopus oryzae*). The obtained results, as diameter of inhibition zone (mm), were given in **Table 4**.

#### <<Table 4>>

Concerning the activity against Gram-positive bacteria (*Staphylococcus aureus*), all tested compounds showed excellent activities. On the other hand, compounds PS2 and PS3 showed good activities against Gram-negative bacteria (*Bacillus cereus*), while compound PS4 has no effect on this microbe. Concerning the data of antifungal activity, the three polymeric surfactants exhibited strong inhibition against *Aspergillus niger*, but they give negative results against the fungus *Rhizopus oryzae*.

#### 4. Conclusions

In this study, novel polymeric surfactants have been synthesized and characterized by FT-IR,  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra. The results of CMC values of synthesized surfactants were investigated *via* surface tension and electrical conductivity methods and the values are near to identical. In addition, the Krafft points of the synthesized polymeric surfactants are below  $0^\circ\text{C}$ , which indicate a good solubility of such compounds in aqueous media. The petroleum-collecting and petroleum-dispersing capacities of synthesized polymeric surfactants showed that all of them gave good petroleum-dispersing and petroleum-collecting effects and they can efficiently be used for this purpose. Compounds PS2 and PS3 exhibited good activities against Gram-negative bacteria (*Bacillus cereus*). Also, the data showed that the three polymeric surfactants exhibited strong inhibition against *Aspergillus niger*, but they gave negative results against the fungus *Rhizopus oryzae*.

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Figure 1:

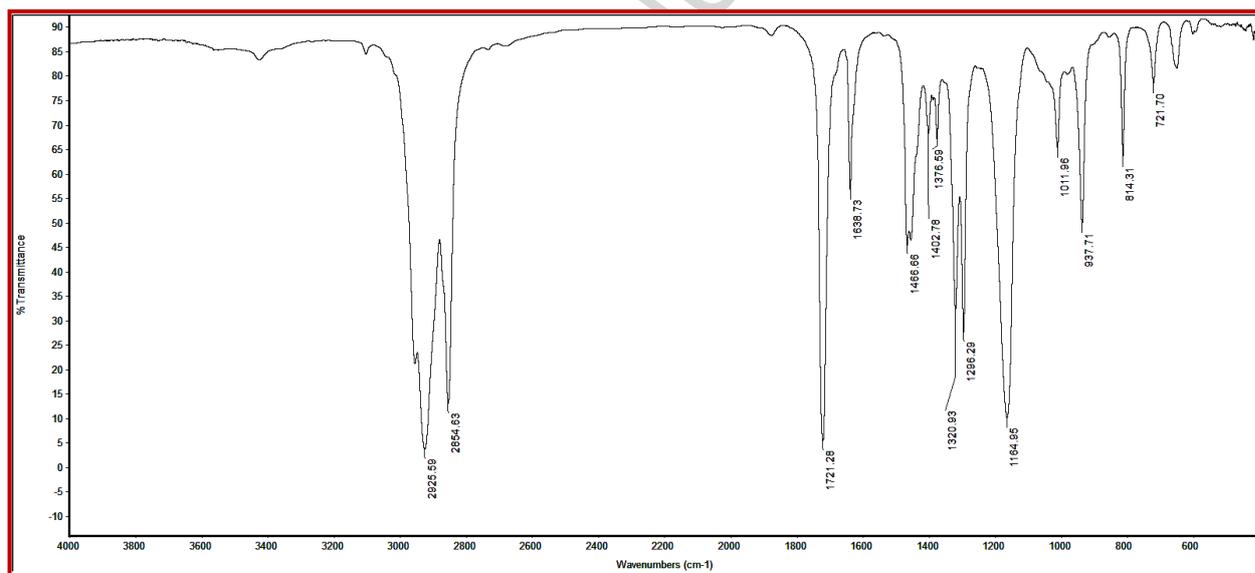


Figure 2:

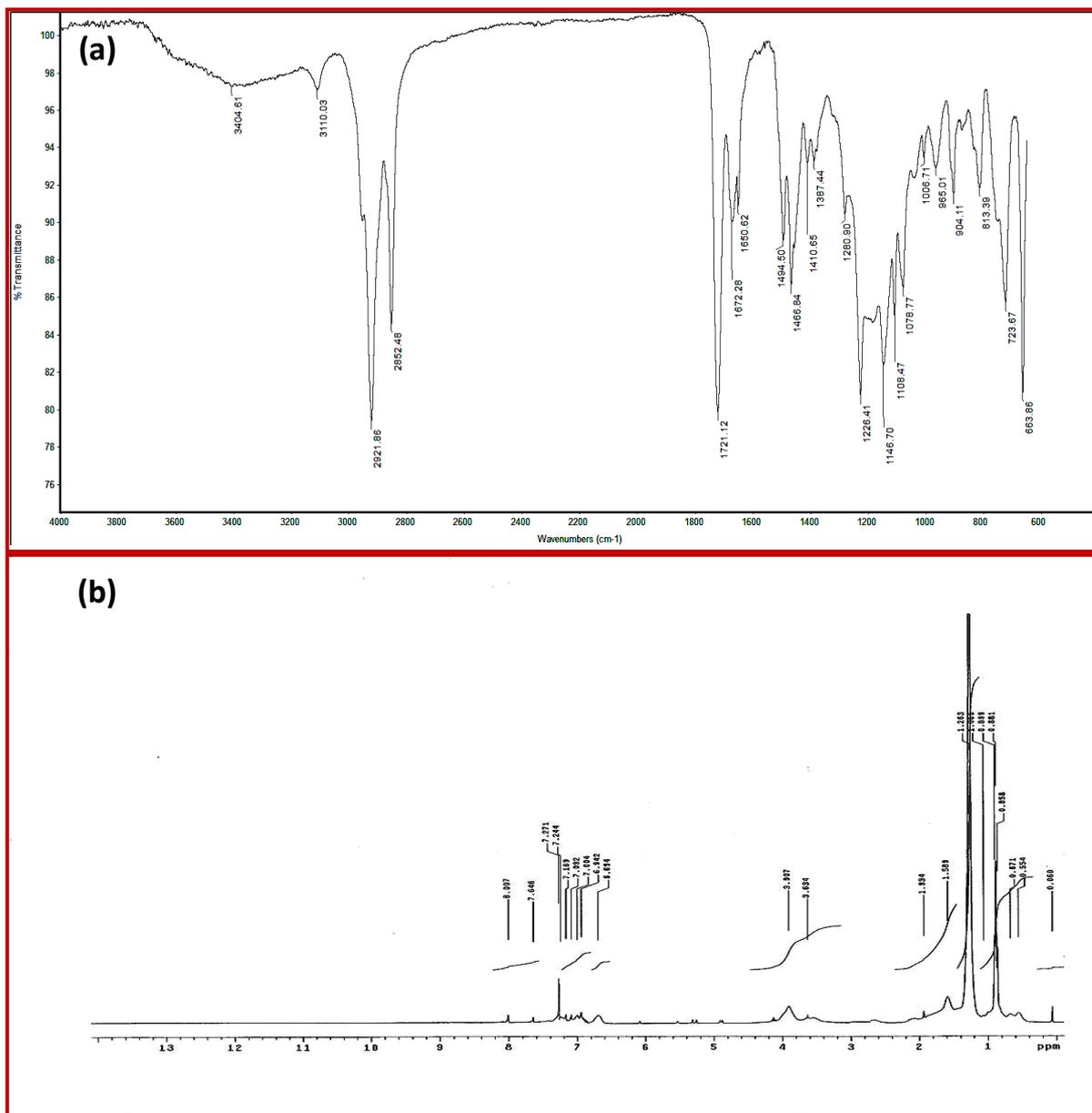


Figure 3:

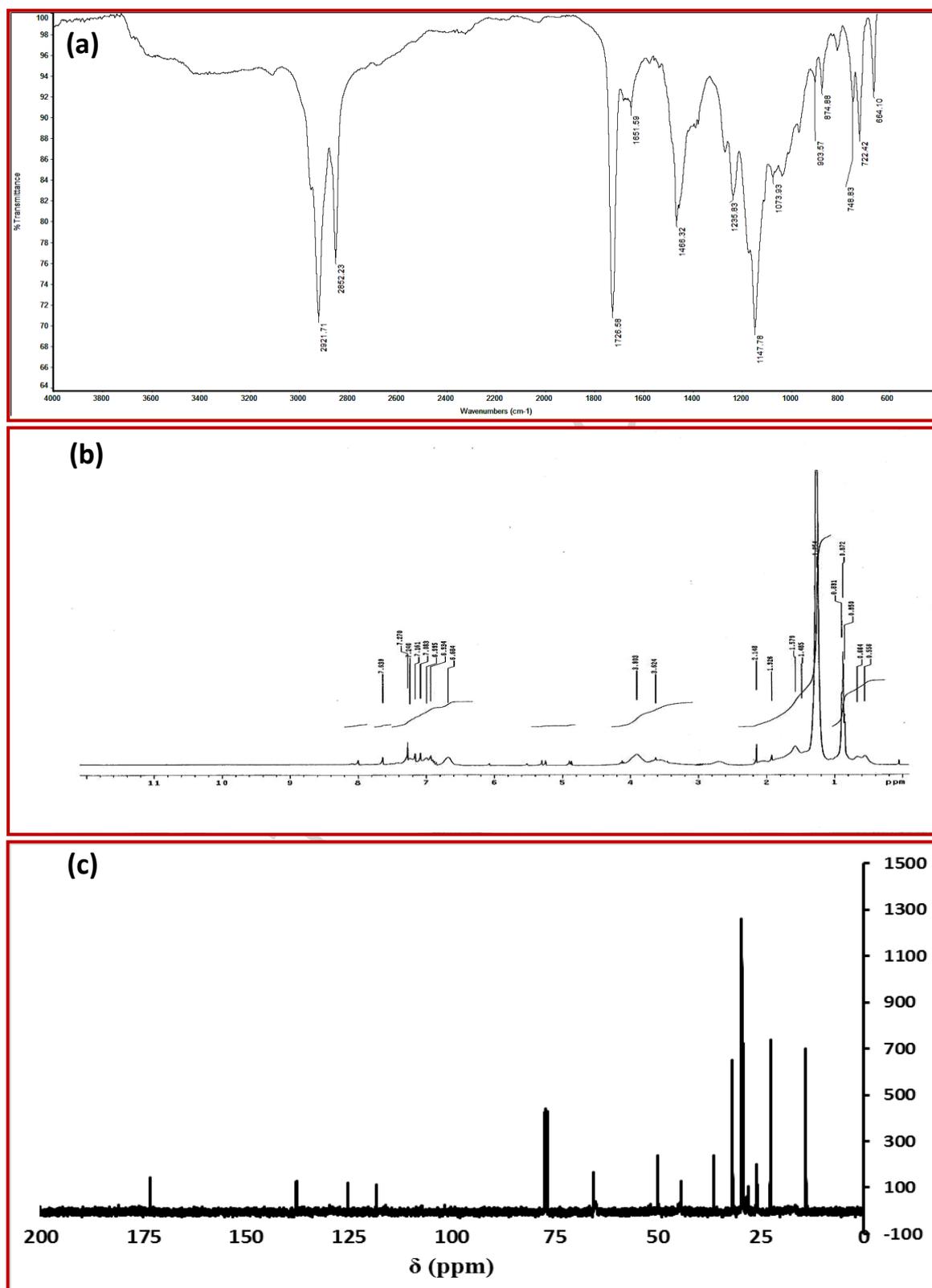


Figure 4:

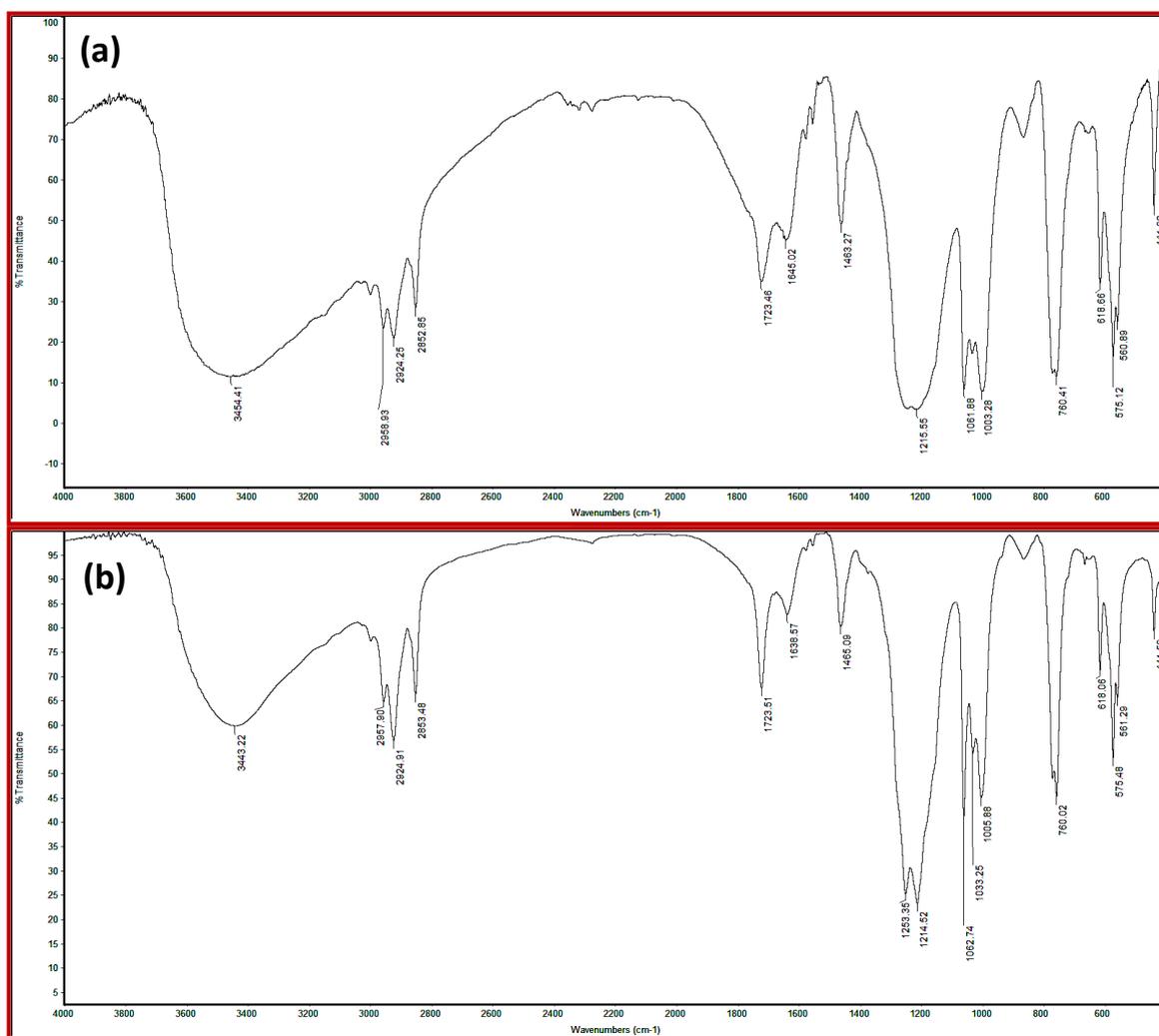


Figure 5:

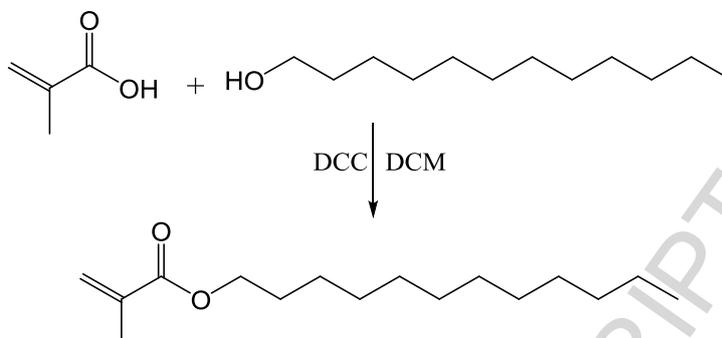
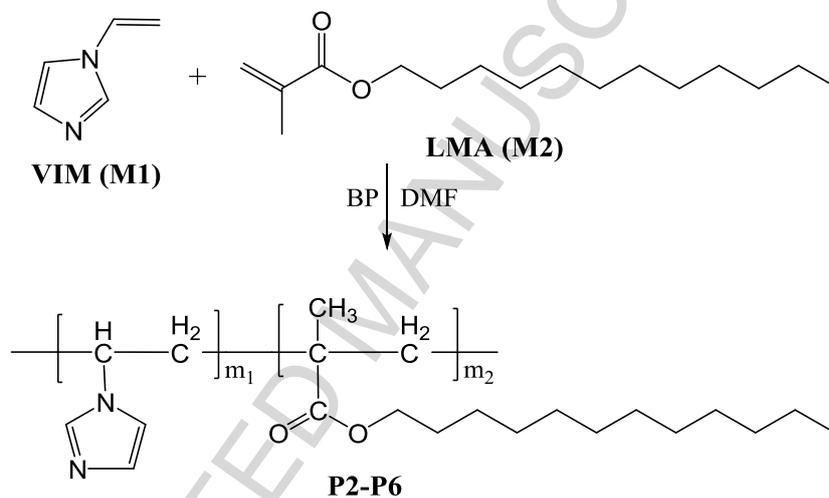
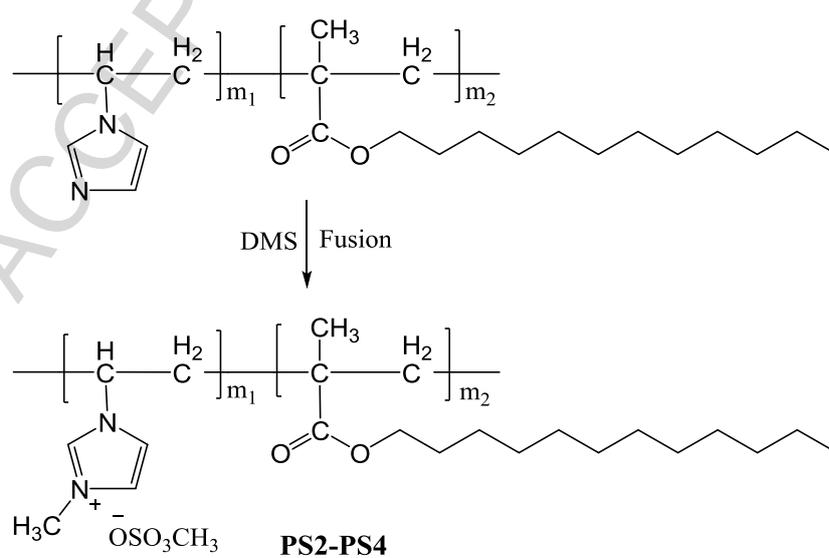
**Step 1: Synthesis of lauryl methacrylate (LMA)****Step 2: Copolymerization process****Step 3: Quaternization of synthesized polymers**

Figure 6:

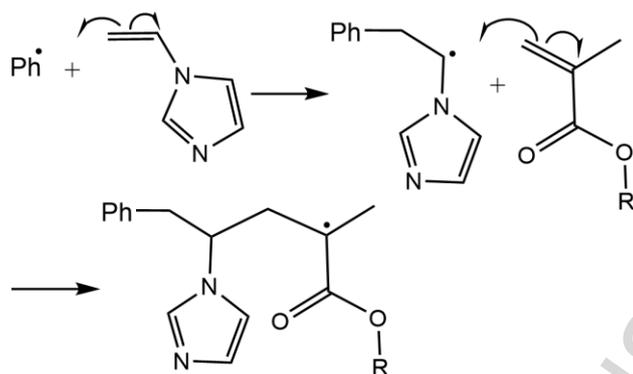
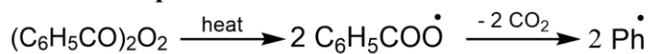
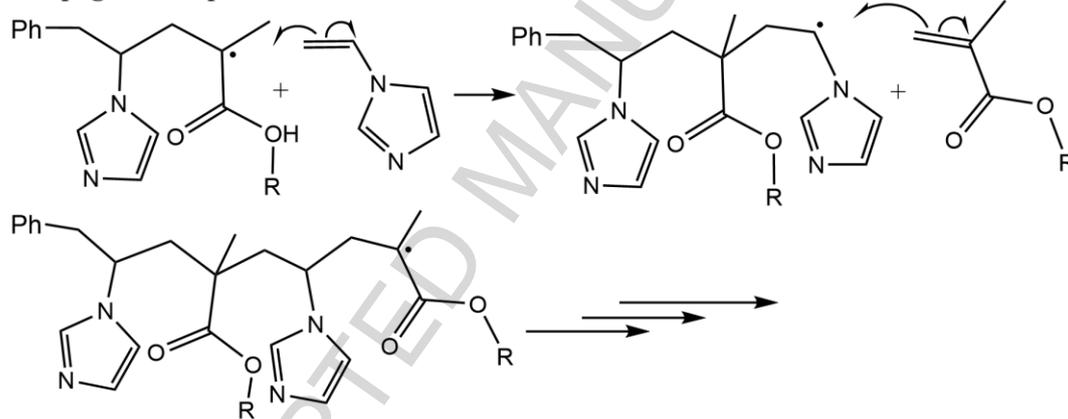
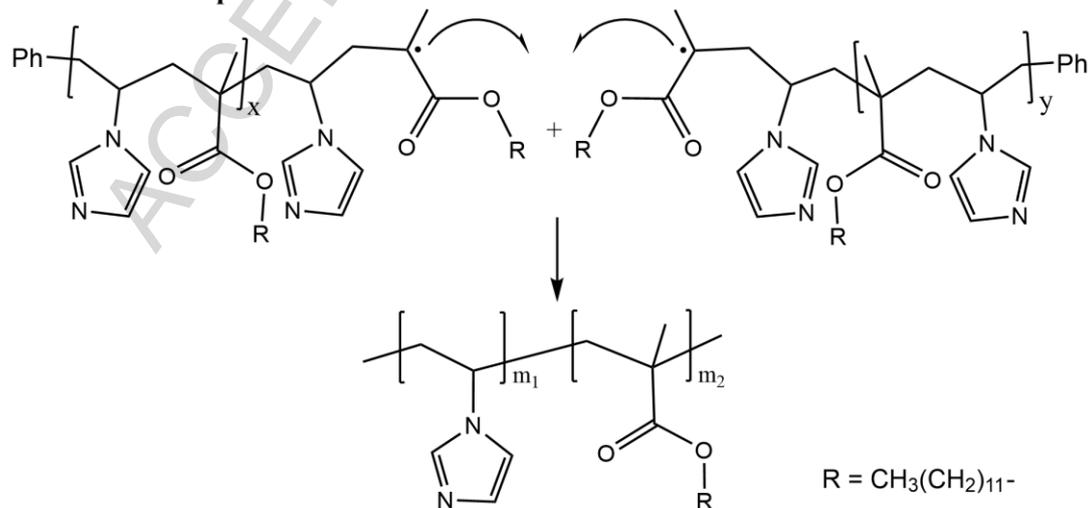
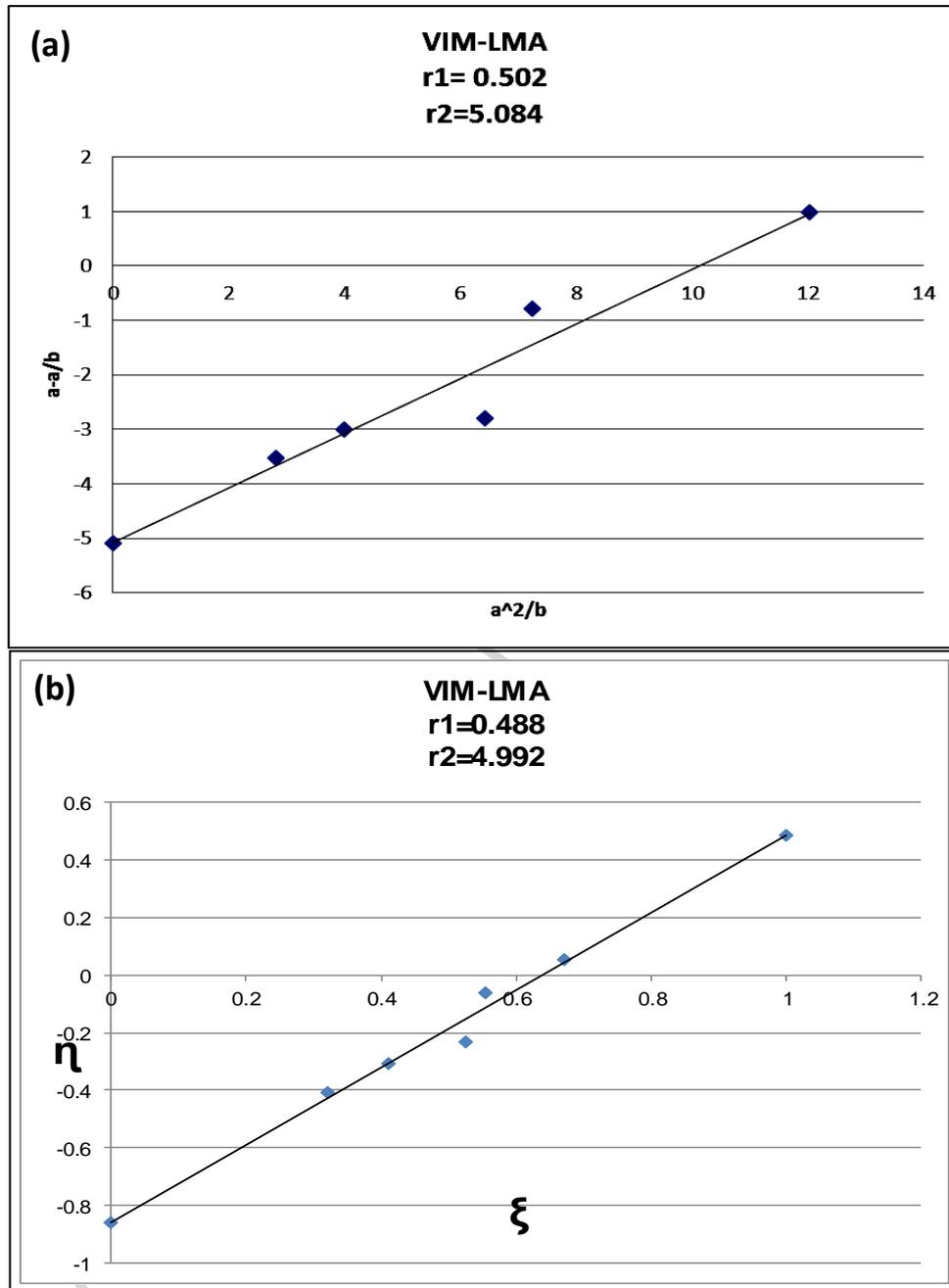
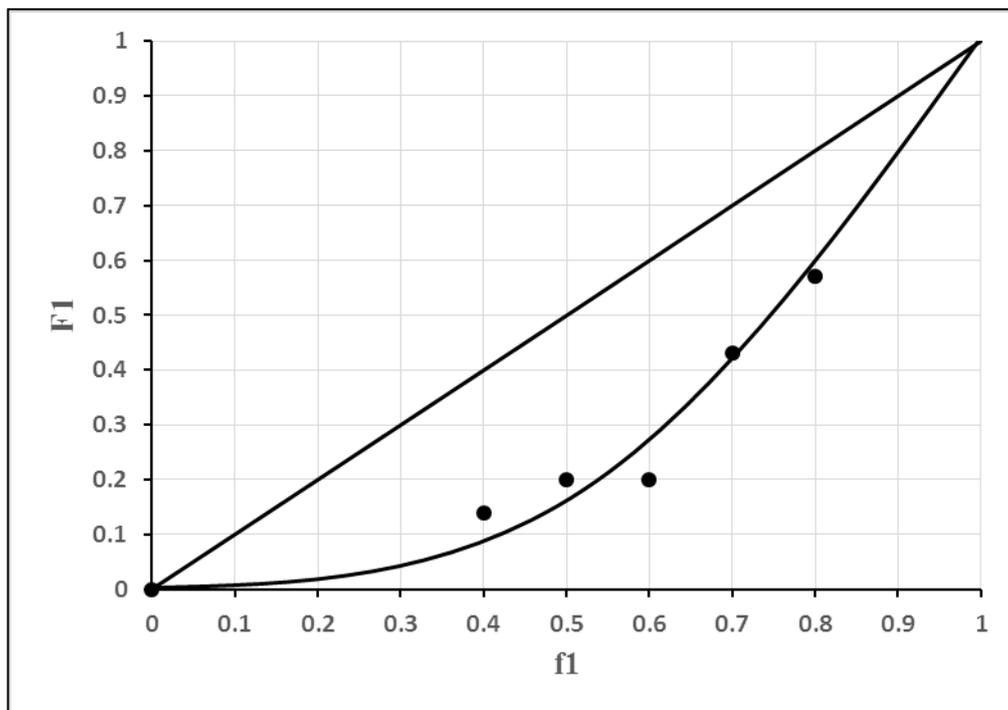
**i. Initiation step:****ii. Propagation step:****iii. Termination step:**

Figure 7:



where:  $\eta = a(b-1)/(\alpha b + a^2)$ ,  $\xi = a^2/(\alpha b + a^2)$  and  $\alpha = \frac{a_{\min} \cdot a_{\max}}{\dots}$

Figure 8:



ACCEPTED MANUSCRIPT

Figure 9:

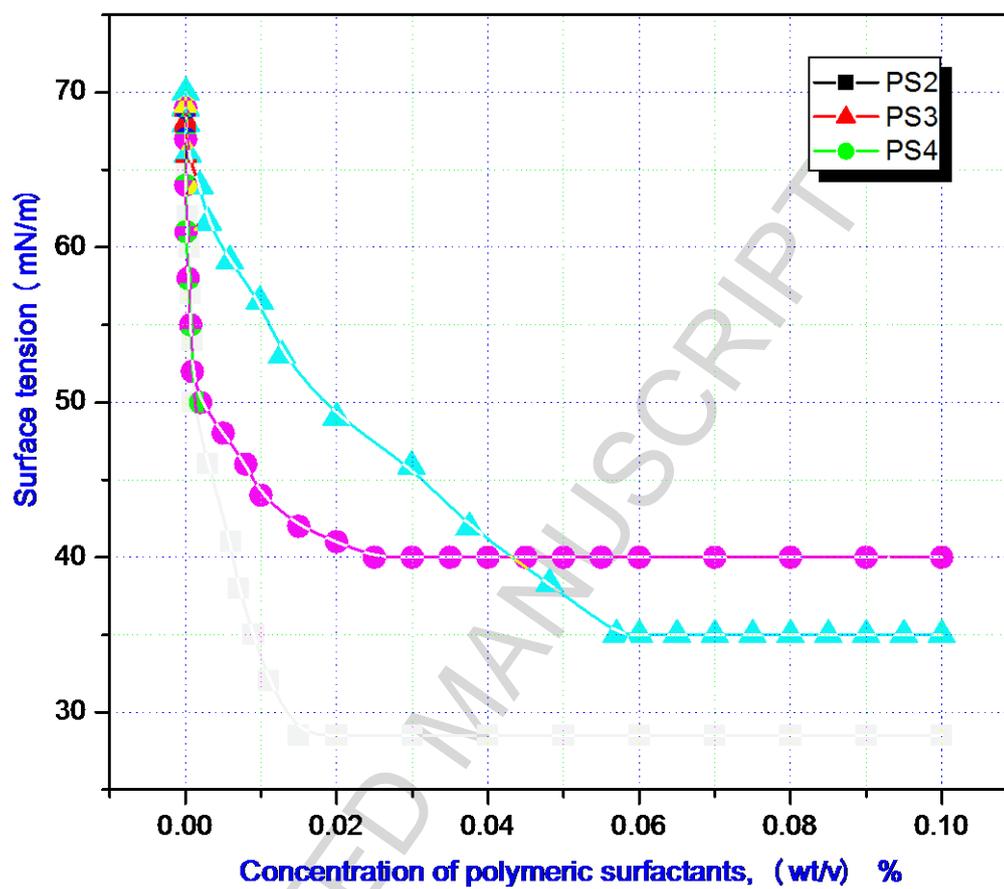
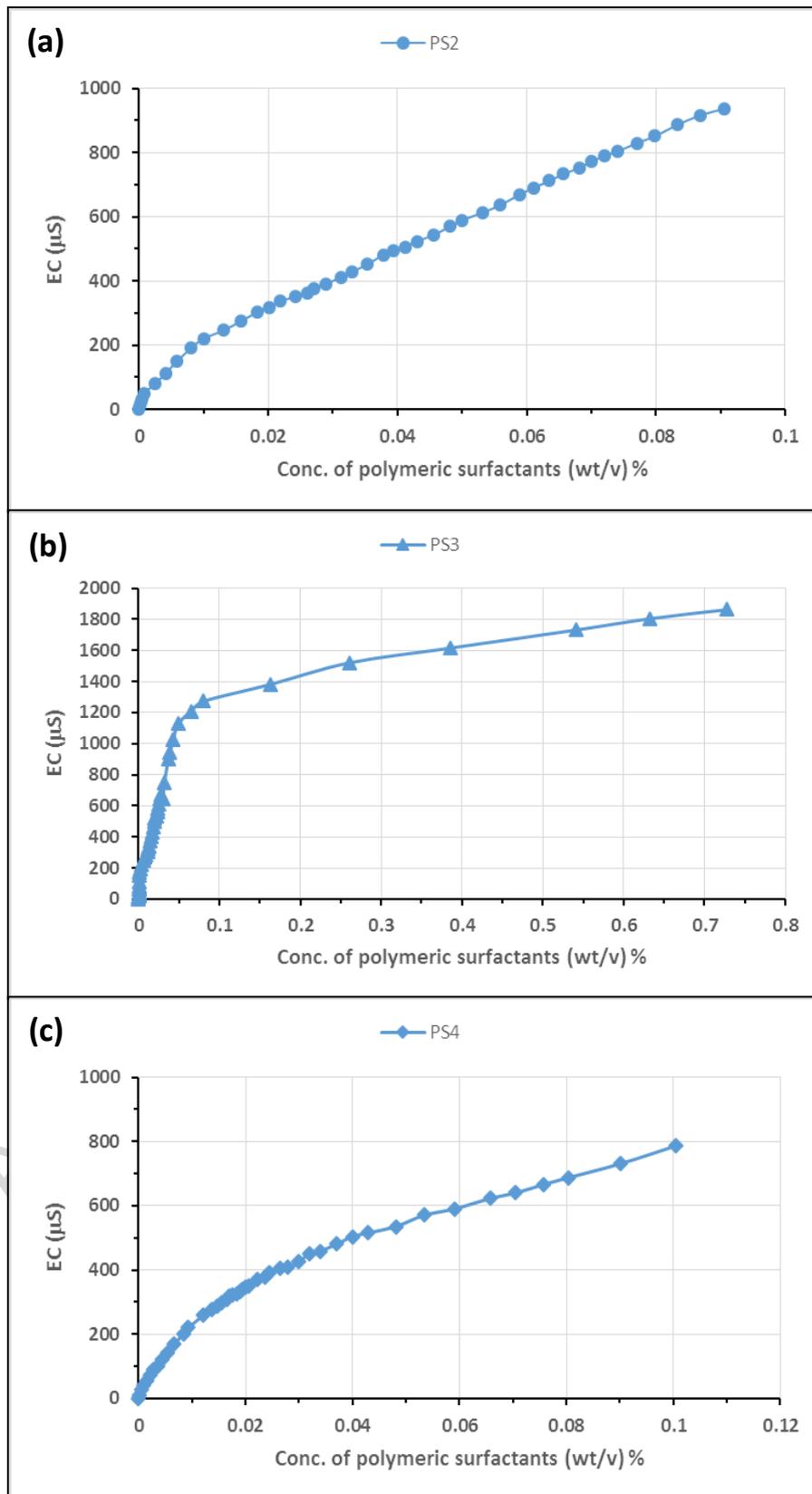


Figure 10:



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**LIST OF TABLES**

<b>No.</b>	<b>Caption</b>
<b>Table 1</b>	Analytical data for copolymerization of VIM with LMA with different ratios by using $^1\text{H}$ NMR.
<b>Table 2</b>	Surface-active properties of synthesized polymeric surfactants.
<b>Table 3</b>	Petroleum-collecting and petroleum-dispersing properties of some novel polymeric surfactants.
<b>Table 4</b>	Antimicrobial activity (in vitro) of the synthesized polymeric surfactants.

Table 1:

Compd. no.	Feed composition	Conversion weight	Copolymer composition
	a	(%)	b
P2	4.00	9.5	1.33
P3	2.33	8.8	0.75
P4	1.50	9.1	0.35
P5	1.00	7.11	0.25
P6	0.67	9.4	0.16

a M1/M2 in the feed composition

b M1/M2 in the copolymer composition

Table 2:

<b>Polymeric surfactant</b>	CMC <sup>a</sup> (wt/v), %	CMC <sup>b</sup> (wt/v), %	Emulsion power, min.	Foam height 0.1% (mL)	Krafft Point, °C
<b>PS2</b>	0.015	0.013	7	100	<0
<b>PS3</b>	0.057	0.064	37	160	<0
<b>PS4</b>	0.025	0.02	15	80	<0

CMC<sup>a</sup> values obtained from surface tension measurements.

CMC<sup>b</sup> values obtained from conductivity measurements.

Table 3:

Compd. no.	Undiluted product						5% wt. water solution					
	Distilled water		Fresh water		Sea water		Distilled water		Fresh water		Sea water	
	$\tau$ (h)	K ( $k_d$ )	$\tau$ (h)	K ( $k_d$ )	$\tau$ (h)	K ( $k_d$ )	$\tau$ (h)	K ( $k_d$ )	$\tau$ (h)	K ( $k_d$ )	$\tau$ (h)	K ( $k_d$ )
PS2	0-48	96.20	0-70	30.00	0-20	93.44	0-48	93.55	0-10	90.10	0-10	96.22
	60-166	97.11	100-166	95.10	30-166	95.10	55-166	97.50	20-166	91.30	15-166	97.50
PS3	0-55	28.70	0-20	21.12	0-20	22.00	0-20	30.11	0-30	30.50	0-30	93.30
	60-166	30.50	30-166	33.50	30-166	30.11	30-166	32.22	40-166	33.11	40-166	95.60
PS4	0-20	28.70	0-20	93.30	0-50	93.30	0-166	No effect	0-10	No effect	0-10	92.3
	30-166	33.60	30-166	97.60	60-166	97.60	----	----	20-166	10.33	20-166	97.60

Table 4:

Compd. no.	Inhibition zone diameter (mm)			
	Bacteria		Fungi	
	B. cereus	S. aureus	A. niger	R. oryzae
<b>PS2</b>	15	40	23	0
<b>PS3</b>	16	43	25	0
<b>PS4</b>	0	48	22	0
Tetracycline	32	28	NT <sup>c</sup>	NT
Amphotericin B	NT	NT	18	20

NT<sup>c</sup> = Not Tested

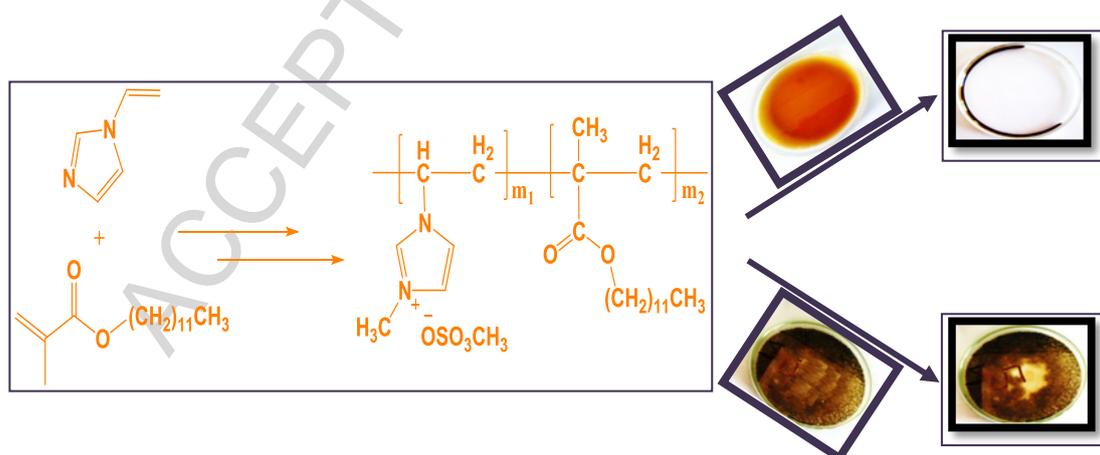
**Graphical abstract****Novel bioactive imidazole-containing polymeric surfactants as petroleum-collecting and dispersing agents: Synthesis and surface-active properties**

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### Highlights

- A novel series of copolymers/polymeric surfactants were synthesized through a facile procedure.
- Monomer reactivity ratio was evaluated by Fineman-Ross and Kelen-Tüdös *via*  $^1\text{H}$  NMR analysis.
- The prepared polymeric surfactants exhibited good surface properties and excellent petroleum-dispersing/collecting effects.
- Compounds PS2 and PS3 exhibited excellent activities against the Gram-negative bacteria (*Bacillus cereus*).