



Petroleum-dispersing and antimicrobial activity of newly synthesized polymeric surfactants tethering tetrachlorophthalimide moiety

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Abstract

The development of compounds with dual or multi-functions or activities is being paid attention in the scientific community. Herein, two series of phthalimide-containing copolymers were synthesized and structurally characterized and their potency against selected microbial strains was evaluated. Our study mainly focused on evaluating both the antimicrobial and surface activities of new corresponding polymeric cationic surfactants for removing petroleum thin films with their increased dispersing capacity. The synthesis process includes the formation of *N*-methacryloyloxytetrachlorophthalimide monomer, homopolymerization, and exchange reactions with various amino- and hydroxy-compounds for the synthesis of copolymers. Lastly, polymeric surfactants were obtained via the quaternization of some copolymers with dimethyl sulfate. Among the tested derivatives, compounds **5a**, **5b**, **6c**, **6d**, and **7b** showed higher activities than the standard drugs which reached 2.45-fold (44 mm against *A. niger*) in copolymer **5b**. Besides, the three polymeric surfactants displayed strong surface activity features including Krafft point, foaming, and emulsifying power. Moreover, polymeric surfactant **7b** exhibited strong dispersion behavior for petroleum in both undiluted form (K_d from 91.60 to 93.20%, $\tau = 30$ –96 h) and diluted form (K_d from 95.7 to 98.1%, $\tau = 5$ –96 h).

Keywords Copolymers · Polymeric surfactants · Antimicrobial activity · Petroleum-dispersing · Surface activity

Introduction

Phthalimide derivatives, especially *N*-hydroxytetrachlorophthalimides (NHTHPs), have been paid attention in recent years due to their wide range of valuable applications. Their synthetic procedures include condensation of substituted phthalic anhydrides with hydroxylamine in alkaline

conditions via either conventional or microwave-assisted reactions [1]. As applicable materials, NHTHPs in blend with 1,4-diamino-2,3-dichloroanthraquinone (DADCAQ) were used as catalysts to facilitate the aerobic oxidation of alkyl arenes [2].

In a novel one-step process, *N*-hydroxytetrachlorophthalimide (NHTCP) was utilized as a mediator for the electrochemical oxidation of allylic C–H bond on large scale. This operation exhibits high chemoselectivity, wide substrate extension, besides its effortlessness (Scheme 1) [3]. Catalytically, a donor–acceptor complex of *N*-acyloxyphthalimide and Hantzsch ester (HE) was used for the metal-free C(*sp*³)–H allylation via aryl carboxyl radicals in a regio- and chemoselective reaction [4].

For energy purposes and as an anolyte, *N*-methylphthalimide was employed for all-organic redox flow battery (AORFB) by electrochemical measurements in which 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) was used as catholyte [5].

In the polymers field, many studies for some homopolymers and copolymers which incorporate reactive phthalimide group were reported [6–11]. Decorating polyimides

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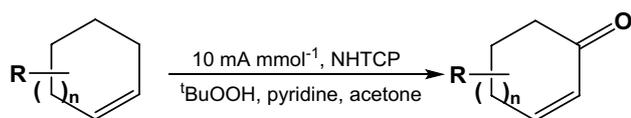
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Scheme 1 NHTCP-mediated scalable electrochemical allylic C–H oxidation

with some rigid phthalimide groups as chain-branch enhances their resistance for friction and heating stability without affecting their optical properties and solubility [12]. From this point of view, a high cell voltage (2.0 V) in a polymer-based AORFB system was constructed via introducing a phthalimide-loaded redox-active copolymer, a TEMPO-loaded polymer as cathode-active material and separator (a porous membrane) [13].

Physical combination of polymers and surfactants may lead to improvements in the thermal conductivity properties and performance of polymer-coated composites [14]. However, polymeric surfactants (PS, chemical hybrids of polymers and surfactants) combine the advantages of both components [15]. Some PS were developed to be used under harsh reservoir conditions through enhancing temperature stability, aqueous solubility, low adsorption, and foaming characteristics which make them suitable for reservoirs with elevated temperature and increased salinity [16], and other bio-based PS molecules have multiple pH-responsiveness [17]. Recent studies report their applications as efficient breakers for the asphaltic crude oil emulsion [18] or as petroleum thin-film removers from the water surface [19–28]. Besides, some alginates polymeric cationic surfactants exhibited good antimicrobial activities as well as high corrosion inhibition efficiency [29].

Dispersants are used to break up oil slicks during oil spill response efforts and limit floating oil from impacting sensitive ecosystems. There is a huge quantity of these chemicals annually at the water's surface and below the surface to combat oil. Their mechanism of action, the effect on marine animals, and other quality-determining features have been reported [30–34].

Herein, we report on the synthesis and characterization of tetrachlorophthalimide-incorporating copolymers and polymeric cationic surfactants. The current study focuses on the evaluation of antimicrobial activity for all prepared derivatives and the surface activity as well as the capacity in dispersing petroleum thin films for polymeric surfactants. Our work opens the doors for the development of polymeric materials, especially surfactants with excellent water solubility, for dual application as antimicrobials and surface-active agents.

Materials and experimental procedures

Materials

Tetrachlorophthalic anhydride, methacrylic acid, *N,N'*-dicyclohexylcarbodiimide (DCC), and benzoyl peroxide (BP) were supplied by Sigma-Aldrich (St. Louis, USA) and used without further purification. Hydroxylamine hydrochloride, *N,N*-dimethylethanolamine, *N,N*-dimethyl-1,3-propanediamine, 2-aminopyridine, 2-aminothiazole, salicylic acid, methyl 4-aminobenzoate, *p*-anisidine, phenol, benzyl alcohol, dimethyl sulfate (DMS), methylene chloride, methanol, dimethylformamide (DMF), and diethyl ether were provided by Al-Nasr chemical company (Cairo, Egypt). Infrared spectra were measured on a Thermo-Scientific Nicolet iS10 FTIR spectrometer. ¹H NMR spectra were generated on JNM-ECA II 500 MHz FT NMR JEOL system in DMSO-*d*₆ or CDCl₃ and tetramethylsilane (TMS) as an internal standard. Spectra of energy-dispersive X-ray (EDX) were measured using EDX JSM 5400, National Research Centre (Cairo, Egypt).

Experimental procedures

Synthesis of *N*-hydroxytetrachlorophthalimide (NHTCP, **2**)

A mixture of tetrachlorophthalic anhydride (2.86 g, 10 mmol) and hydroxylamine hydrochloride (1.39 g, 20 mmol, 2.0 equiv.) in pyridine (10 mL) was introduced into a round-bottom flask fixed within a reflux system. After refluxing for 4 h at 130 °C, the crude NHTCP was obtained by pouring the cold mixture on conc. HCl/crushed ice (pH = 2–3) followed by vacuum filtration. The product was recrystallized from ethanol to give 2.28 g (80%) of pure **2** with a melting point of 213–215 °C.

Synthesis of *N*-methacryloyloxytetrachlorophthalimide (NMATCP, **3**)

To a solution of NHTCP (**2**, 3.01 g, 10 mmol) in dry methylene chloride (30 mL), methacrylic acid (0.86 g, 10 mmol) was added and the mixture was cooled in ice-bath to (0–5 °C). As one portion, DCC (2.06 g, 1.0 equiv.) was added followed by stirring at room temperature for 20 h. The formed *N,N'*-dicyclohexylurea (DCU) was eliminated through filtration, and the filtrate was evaporated to dryness *in vacuo*. A mixture of benzene/methylene chloride (20/80) was used for purification of the solid residue via recrystallization to afford 2.10 g (70%), m. p. 142–144 °C. IR (ν, cm⁻¹): 2928 and 2852 (symm. &

asymm. C-H stretching of CH₂/CH₃), 1733 (C=O stretching of phthalimide moiety) and 1625 (olefinic C=C stretching). ¹H NMR (CDCl₃, δ, ppm): 2.11 (s, 3H, CH₃) and 5.97 (s, 1H, olefinic), 6.50 (s, 1H, olefinic) (Figure S1).

Synthesis of poly (*N*-methacryloyloxytetrachlorophthalimide) (**4**)

In a polymerization tube, a 10% solution of NMTCP in dioxane was treated efficiently with recrystallized benzoyl peroxide (1.0 mol%). The tube was flushed with nitrogen and placed for 6 h in a water bath at 65 °C. After cooling, the reaction mixture was portion wisely added to an excess of methanol, forming the crude polymer as yellow precipitate which was filtered. The homopolymer was dissolved in a little acetone and reprecipitated with petroleum ether to afford pure **4** with good yield (70%).

Exchange reactions of polymer **4** with amines: synthesis of copolymers **5a–5e**

The prepared homopolymer of *N*-methacryloyloxytetrachlorophthalimide (NMTCP) was subjected to react with amino compounds. The homopolymer was dissolved in DMF to form a 10% solution, and two equivalents of amine were added. The mixture was agitated for 6 h at 60 °C and then poured into diethyl ether. The copolymer was filtered, dissolved in DMF, and reprecipitated with diethyl ether.

Exchange reactions of polymer **4** with hydroxylated compounds: synthesis of copolymers **6a–6d**

As described above for amino compounds, the homopolymer **4** was reacted similarly with hydroxy-compounds. The reaction was catalyzed with two equivalents of triethylamine. The reaction was stopped after 6 h, and the products were purified as mentioned before. The chemical structures of the prepared copolymers are well characterized by ¹H NMR spectroscopy (Table 1 and Figures S3–S9).

Quaternization of copolymers: synthesis of polymeric surfactants **7a–7c**

The polymeric surfactants were obtained by heating copolymers **5a**, **5c**, or **6a** with excess DMS under free-solvent conditions. The reaction was preserved at 95 °C for 48 h with continuous stirring. The products **7a–7c** were washed several times with diethyl ether, and the isolated yields were 80–85%.

Table 1 ¹H NMR spectral data with exchange yield percent for copolymers **5b–5e** and **6b–6d**

Compd. No.	Segment	Chemical shift δ (ppm)	Yield %
5b	CH ₃ , CH ₂ ,	2.71, 2.86,	14
	C ₅ H ₄ N,	6.51–7.84,	
	NH	11.02	
5c	CH ₃ , CH ₂ ,	2.71, 2.86,	97.5
	C ₃ H ₂ NS,	6.98–7.93,	
	NH	11.92	
5d	CH ₃ , CH ₂ ,	3.60, 3.70,	54
	OCH ₃ ,	3.81,	
	C ₆ H ₄ ,	6.49–8.50,	
	NH	10.82	
5e	CH ₃ , CH ₂ ,	2.74, 2.90,	27
	CH ₃ O,	3.73,	
	C ₆ H ₄ ,	6.55–8.16,	
	NH	11.11	
6b	CH ₃ , CH ₂ ,	1.20, 3.09,	99.9
	C ₆ H ₄ ,	6.78–7.76,	
	COOH	10.19	
6c	CH ₃ , CH ₂ ,	1.17, 3.04,	25
	C ₆ H ₅	6.45–7.51	
6d	CH ₃ , CH ₂ ,	1.12, 2.89,	95
	CH ₂ O,	3.69,	
	C ₆ H ₅	7.34–7.37	

Table 2 EDX spectroscopy data showing elemental composition for the copolymers **5a** and **6a**

Element	Atomic %		Net Int.	
	5a	6a	5a	6a
C	65.37	63.81	73.77	12.32
O	27.95	24.37	23.68	14.52
Cl	6.68	11.82	2.55	139.89

Measurements

Critical micelle concentration

(a) Surface tension

Tensiometer-K6 processor (KrÜss. GmbH, Germany) was used to evaluate the surface tension of the target polymeric surfactants' solutions. Each measured sample was repeated for three times at 298°K and determined from the average of them, whereas the surface tension value of demineralized water was adjusted to 72.0 mN/m at 298°K and the uncertainty did not override ±0.1 mN/m.

(b) Electrical conductivity

The electrical conductivity values for surfactant solutions were determined at 298°K via “model Type AD3000; EC/TDS and Temperature meter” (Shanghai, China). The recorded values were repeated three times for all prepared solutions.

Krafft point

Via visual observations, the Krafft points for the three surfactants' solutions were determined. The concentrations of solutions were at least two equivalents than the CMC of the investigated surfactants.

Foaming power

In a 250-mL graduated cylinder, 100 mL of the surfactant solution (0.1% (wt./v)) was added. The cylinder was stoppered and shaken vigorously at room temperature for 20 s. The initial foam height represents the foaming ability, while the foam stability was estimated by recording the time required to reduce the foam to half of its initial value [35]. A minimum of four replicate determinations was introduced for each sample solution.

Emulsifying stability

The stability of the emulsion was determined via shaking vigorously a mixture of 10 mL (0.1% w/v) of the sample solution with 10 mL of paraffinic oil at 298°K for 10 s. The required time for separating surfactant solution (8 mL) from the emulsification system at a steady-state was represented as the emulsion stability [35]. Four replicates of the experiment were performed.

Petroleum-dispersing evaluation

The petro-dispersing capacities of the polymeric surfactants (in both pure state and 5 wt% aq. solution) have been determined on the surface of three water of various mineralization degrees via the Red sea crude oil from the oil fields in the South Sinai (Egypt). For this purpose, both un-thinned polymeric surfactant and its 5% wt. aqueous solution were utilized. The studies were done according to the known procedure [27].

Antimicrobial activity

All synthesized polymeric compounds were evaluated as antimicrobial agents (in vitro) against various microbes comprising bacteria and fungi. The tested microbial pathogens include two bacterial strains (*Staphylococcus aureus*

and *Escherichia coli*) and two fungal strains (*Aspergillus niger* and *Rhizopus oryzae*).

Two highly common antimicrobial agents, Tetracycline and Amphotericin B, were used to serve as positive controls. The effect of polymeric compounds on living microorganisms, whether to kill or inhibit their growth, was measured through the agar disk diffusion technique [36]. Filter paper disks of 6 mm diameter were immersed in the solution of the tested compound (1.0 mg/mL) and placed on the surface of the agar. Agar plates were previously inoculated with a standard inoculum size of microorganisms. The Petri dishes with bacterial strains were taken to incubate for 24 h at 35–37 °C, while those of fungal strains were incubated for 48 h at 25–27 °C. The zones of growth inhibition were measured which represent the antimicrobial activities of compounds.

Results and discussion

Synthesis

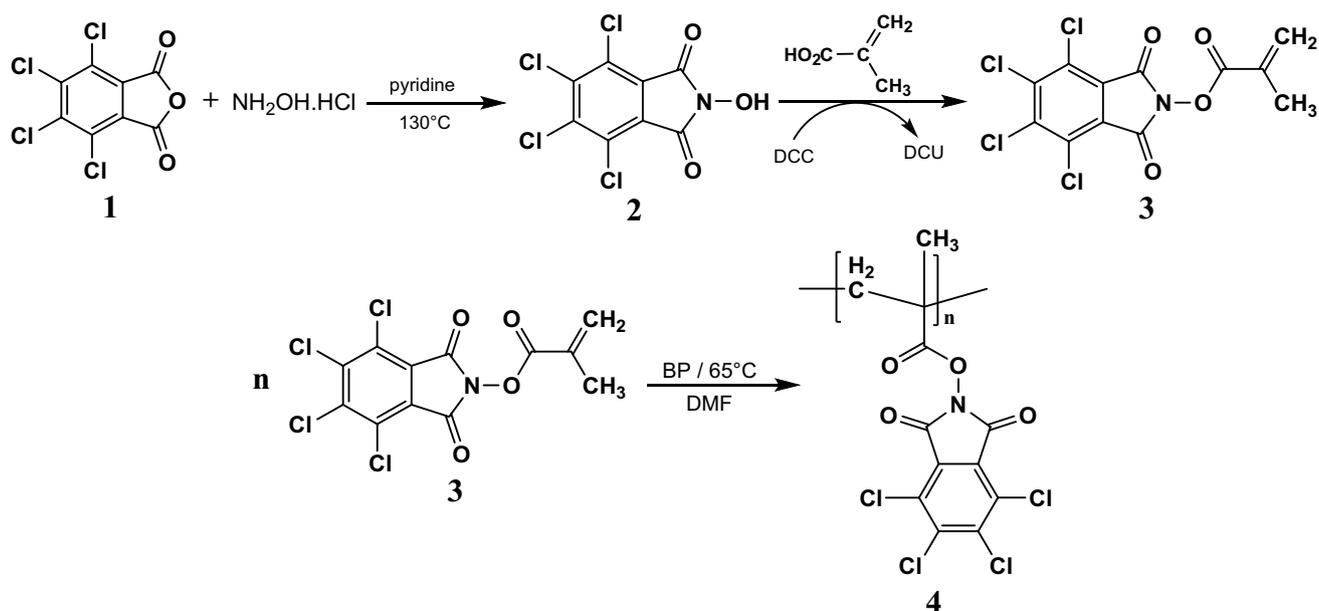
The main homopolymer, poly *N*-methacryloyloxytetrachlorophthalimide (**4**), was synthesized by a three-step reaction. Firstly, the hydroxylamine nitrogen replaced the cyclic ester oxygen of tetrachlorophthalic anhydride (**1**) via condensation. Then, the hydroxyl group of product **2** was subjected to form an ester with methacrylic acid and the reaction was catalyzed by DCC. Thirdly, the monomer **3** was polymerized in DMF using BP for the initiation (Scheme 2).

The first series of copolymers (**5a–5e**) was synthesized via exchanging the reactive tetrachlorophthalimidoxyl (TCPO) group in the polymer **4** with different amino compounds. Thus, it was subjected to react with *N,N*-dimethyl-1,3-diaminopropane, 2-aminopyridine, 2-aminothiazole, *p*-anisidine, and methyl 4-aminobenzoate (Scheme 3).

The second copolymers' series (**6a–6d**) was synthesized through the displacement of the TCPO group under Et₃N-catalyzed reaction with some hydroxyl group-containing compounds, namely *N,N*-dimethylethanolamine, salicylic acid, phenol and benzyl alcohol (Scheme 4).

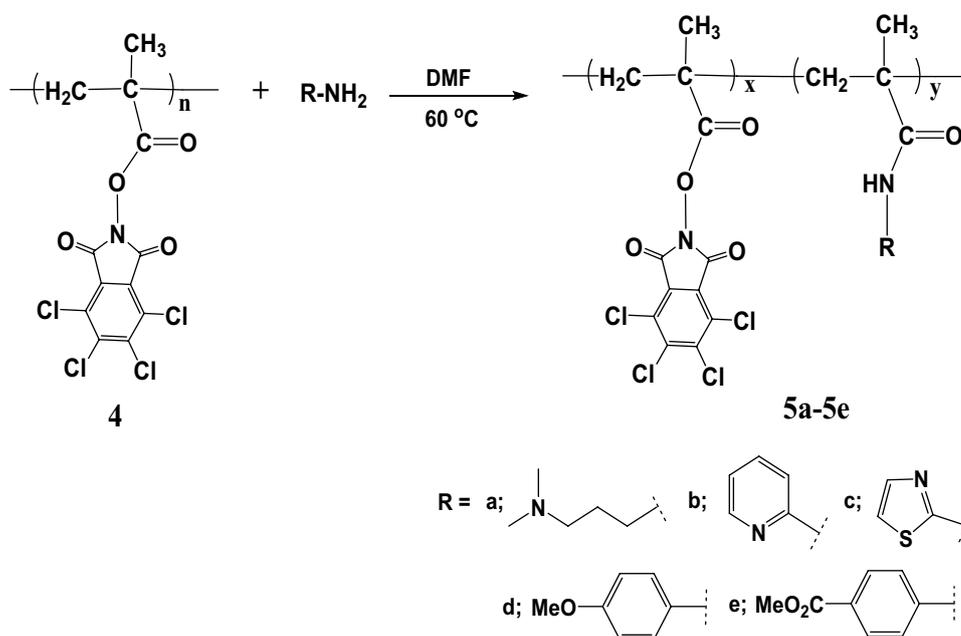
Both EDX spectra (Table 2 and Figure S2) and ¹H NMR spectra (Table 1 and Figures S3–S9) were utilized to calculate the yields of the exchange reactions. The yield of the copolymer **5a** is 98%, while that of copolymer **6a** is 90%.

Copolymers **5a**, **5c**, and **6a** in which their structures incorporate tertiary nitrogen atoms were quaternized with dimethyl sulfate (DMS) under solvent-free conditions to give polymeric cationic surfactants **7a–7c** according to Scheme 5, which represents the quaternization process and the preparation of polymeric surfactants.



Scheme 2 Synthetic route for poly(*N*-methacryloyloxytetrachlorophthalimide)

Scheme 3 Synthesis of copolymers **5a–5e** via exchange reactions of **4** with various primary amines



Surface tension and micellization

The studying of surface activity of these polymeric surfactants was to evaluate their possible applications in different industrial fields. Whereas the increase in amphiphile concentration leads to these properties corrupt progressively from ideality and at the concentration, the molecules monomers will be aggregated to form micelles; an abrupt change is noted. So, values of CMC of synthesized polymeric surfactants have been gotten graphically by

drawing the surface tension (γ) of obtained solutions of targeted surfactants versus their concentrations (wt/v) at 25 °C as shown in Fig. 1.

Also, from Fig. 2, the CMC values of the quaternary exchangeable polymers were calculated from the values of electrical conductivity versus the concentration (wt/v) of the obtained compounds at 25 °C. Collectively, the CMC values, determined via both from surface tension and electrical conductivity measurements, seemed identical.

Scheme 4 Synthesis of copolymers **6a–6d** via exchange reactions of **4** with various hydroxylated compounds

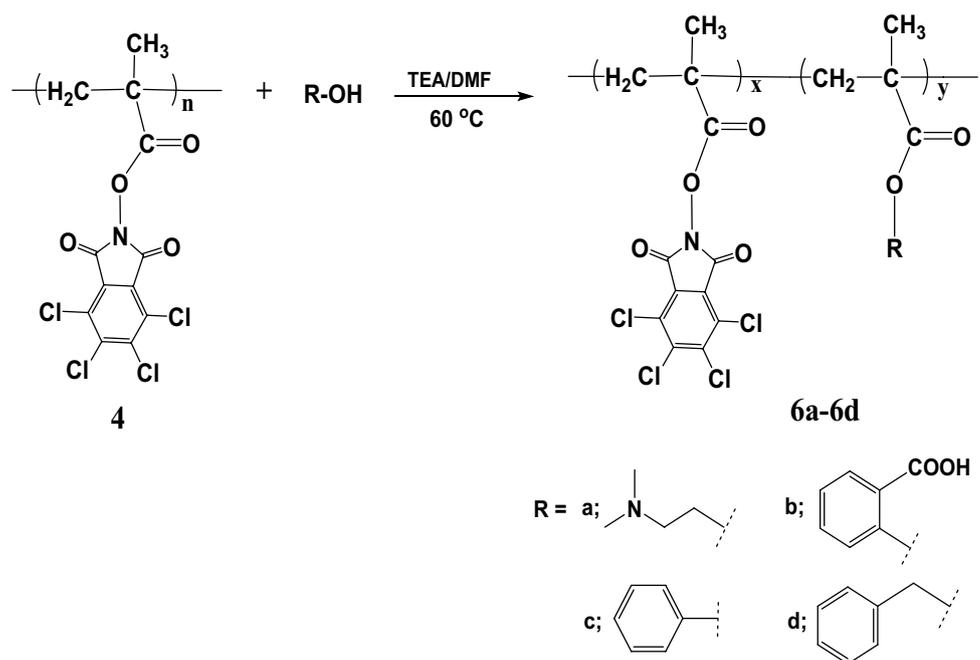


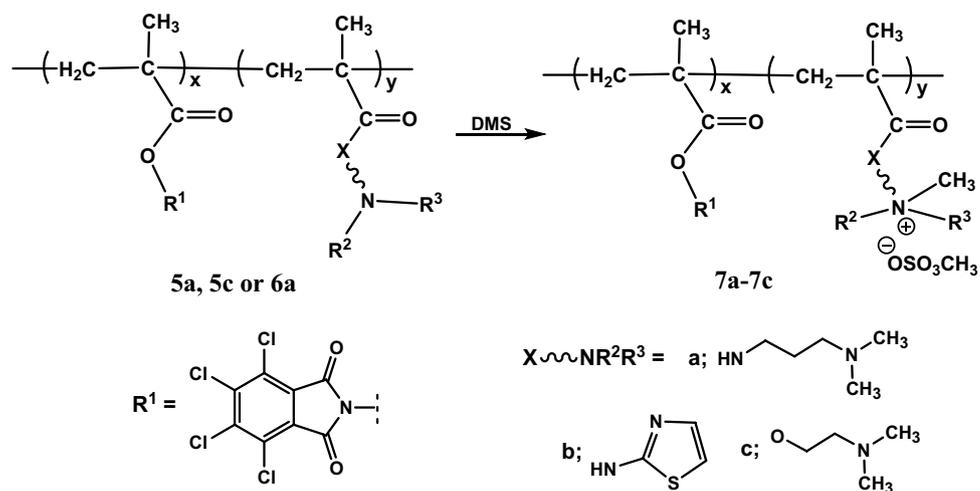
Table 3 Surface activity parameters for the synthesized polymeric surfactants

Compd. no.	CMC ^a (wt/v)	CMC ^b (wt/v)	Emulsion power (min)	Foaming properties		Krafft point (°C)
				Foaming ability (mL)	Foam stability (t _{1/2} ; min)	
7a	0.038	0.037	10 ± 2.2	70 ± 4.5	120 ± 3.3	< 0
7b	0.120	0.110	25 ± 3.1	90 ± 3.0	135 ± 4.1	< 0
7c	0.039	0.040	40 ± 3.2	110 ± 5.5	155 ± 4.8	< 0

^aCMC values obtained from surface tension measurements

^bCMC values obtained from conductivity measurements

Scheme 5 Synthesis of polymeric cationic surfactants **7a–7c**



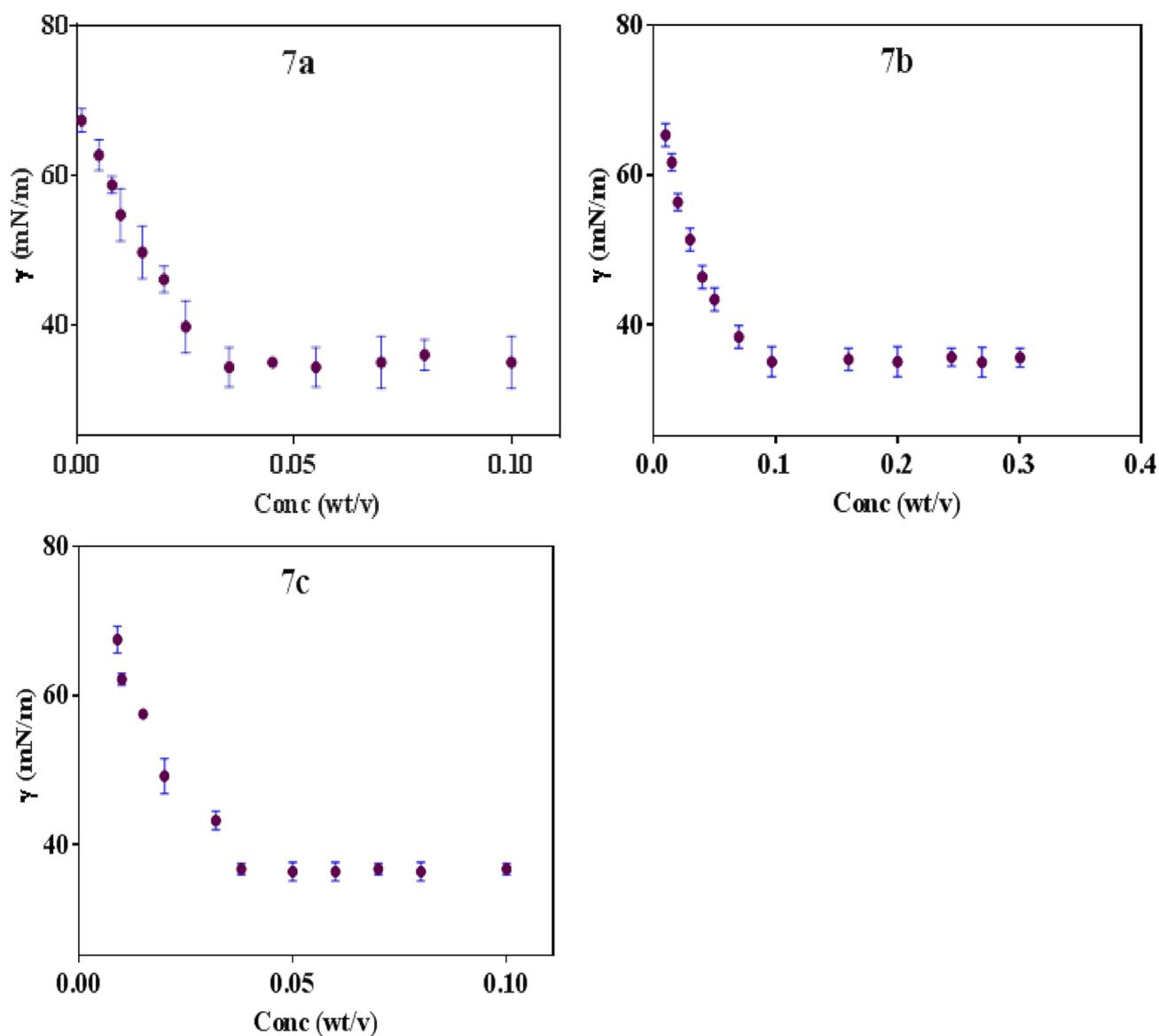


Fig. 1 Variation of the surface tension with the concentration of polymeric surfactant (wt/v) in water at 298°K

Krafft point

The solubility of cationic surfactants can be assessed through the quantification of Krafft point values. The lower the value of the Krafft point of the prepared cationic polymer, the better its solubility. The data in Table 3 showed that all furnished polymeric surfactants exhibited Krafft point values lower than 0 °C, and this indicates that these surfactants have good water solubility.

Emulsifying power

Emulsifying power measures the surfactant tendency to form both types of emulsion and reflects the capacity of

surfactant molecules to be situated at the interface between different phases. Thusly, the more molecules adsorbed at the interface, the more impressive the emulsifying agent.

In our study, the time needed for separating 8 mL of water from the emulsion system (0.1% surfactant solution wt and paraffin oil 10 mL) was set as the emulsification efficiency. The ability of the surfactant particles to keep the oil globule apart from each other for a longer period is responsible for the high stability of the hydrophobic emulsion. The results depicted in Table 3 confirmed that the synthesized surfactants can form effective emulsions with oil and therefore can be utilized for the preparation of stable emulsions.

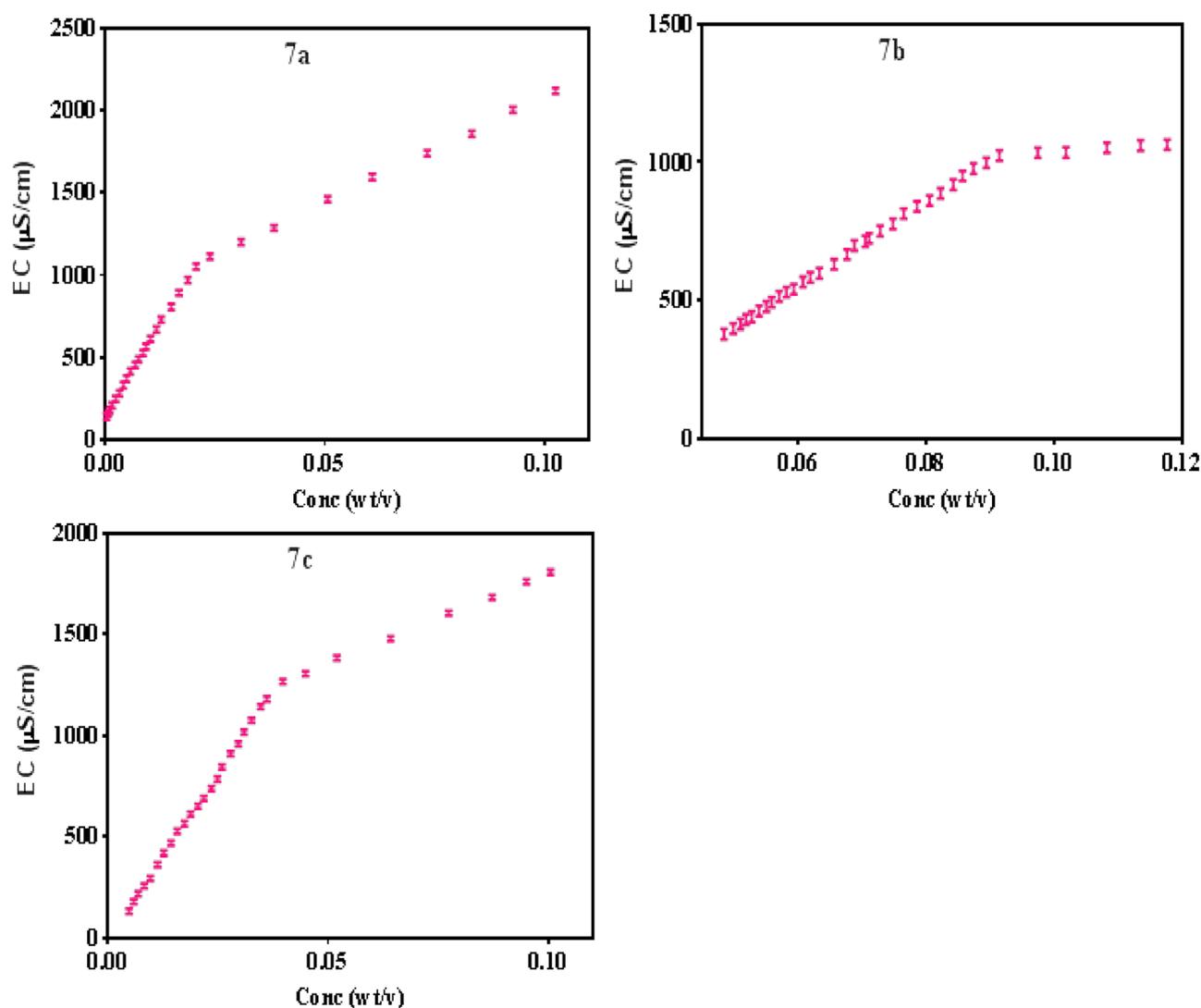


Fig. 2 Variation of concentration of polymeric surfactant (wt/v) with electrical conductivity (EC, $\mu\text{S}/\text{cm}$) at 298°K

Foaming properties

Foaming indices are utilized to judge the commercial applicability of novel synthesized surfactants. Such indices were recorded for three polymeric surfactants to comprehend the versatility of the shaped monolayer of fluid surfactant solution in the foam. The foam properties data (Table 3) showed that all surfactants exhibited good foaming properties. Compound **7c** displayed high foamability and strong foam stability.

Petroleum-dispersing properties

The results of the study of petroleum-dispersing effects of generated polymeric surfactants are recorded in Table 4. It can be noticed that compound **7b** gave high

petroleum-dispersing action in un-thinned surfactant, whereas K_d ranges from 91.60 to 93.20%, $\tau = 30\text{--}96$ h. (in freshwater). Also, it exhibited a strong petroleum-dispersing effect in 5% wt. aqueous solution, whereas K_d ranges from 95.7 to 98.1%, $\tau = 5\text{--}96$ h. (in the three water of various mineralization degrees). Moreover, compound **7a** exhibited low petroleum-collecting in both diluted and undiluted forms, whereas K ranges from 1.29 to 6.36, $\tau = 0\text{--}96$ h, in all used waters. Finally, compound **7c** was unstable to enhance petro-dispersing properties.

Antimicrobial activity

Polymeric materials with strong microbial growth inhibition effect possess a vital role in many applications. When sensitive types of equipment such as dental tools, health-care

Table 4 Petroleum-collecting/dispersing properties of the synthesized polymeric surfactants **7a–7c**

Compd. no.	Undiluted product						5% wt. water solution					
	Distilled water		Fresh water		Sea water		Distilled water		Fresh water		Sea water	
	τ (h)	K (k_d)	τ (h)	K (k_d)	τ (h)	K (k_d)	τ (h)	K (k_d)	τ (h)	K (k_d)	τ (h)	K (k_d)
7a	0	1.69	0	1.29	0–2	1.29	0–2	1.29	0–2	1.29	0–2	1.69
	30	3.91	20	2.84	5–20	3.91	30	4.27	30	2.30	20	2.64
	60–96	5.17	25–96	4.70	30–60	3.30	48	5.73	40–60	5.17	40–96	3.30
	–	–	–	–	70–96	8.1	–	–	70–96	6.36	–	–
7b	0–2	3.45	0–2	4.10	0–2	5.40	0–2	2.90	0–2	4.30	0–2	2.00
	2–55	NC ^a	30–60	91.6%	5–20	NC	5–20	NC	20–30	95.7%	5–30	97.8%
	60–96	NC	60–96	93.2%	30–96	NC	30–96	NC	40–96	96.1%	40–96	98.0%
7c	0–96	NE ^b	0–96	NE	96	NE	0–96	NE	0–96	NE	0–96	NE

^aNC=No Change; ^bNE=No Effect

Table 5 Antimicrobial activity (in vitro) of the synthesized polymeric materials

Compd. No.	Inhibition zone diameter (IZD, mm)			
	Bacteria		Fungi	
	<i>E. coli</i>	<i>S. aureus</i>	<i>A. niger</i>	<i>R. oryzae</i>
5a	11.3	17.3	24.3	0.0
5b	Nil	23.0	44.0	0.0
5c	29.0	24.6	9.6	0.0
5d	18.3	22.0	9.3	0.0
5e	Nil	17.6	18.3	0.0
6a	20.0	25.3	5.6	0.0
6b	Nil	24.3	21.0	0.0
6c	Nil	19.3	28.6	0.0
6d	Nil	26.0	34.6	0.0
7a	Nil	20.6	24.0	0.0
7b	20.0	30.3	21.0	0.0
7c	11.6	27.3	17.0	0.0
Tetracycline	32.0	28.0	NT ^a	NT
Amphotericin B	NT	NT	18.0	20.0

^aNT=Not Tested

products, water purification systems, or medical devices are contaminated by microbes, serious issues will be developed. To avoid microbial contamination, it is better to develop candidates with strong activity against microbes.

Antimicrobial activity of copolymers

The synthesized copolymers, with their bioactive tetrachlorophthalimide group, were screened for the effectiveness to control or inhibit the growth of bacterial species as well as fungal species.

The results presented in Table 5 indicate that the tested compounds have strong antimicrobial activities with

comparable values to the reference agents. By focusing on the inhibition zones for *E. coli*, only four compounds exhibited activity with a range between 11.3 and 29 mm compared to 32 mm for Tetracycline. However, for *S. aureus*, the values range from 17.3 to 26 mm compared to 28 mm for Tetracycline. Interestingly, five compounds (**5a**, **5b**, **5e**, **6c**, and **6d**) displayed high potency (> 18 mm) against *A. niger* with inhibition zone values higher than the reference drug Amphotericin B. On the other hand, all compounds do not affect the fungus *R. oryzae*.

Antimicrobial activity of polymeric surfactants

By the same technique, the antimicrobial activity for the synthesized polymeric surfactants **7a–7c** was evaluated toward various microbes. The values of the inhibition zone diameters ranged between 11.6 and 30.3 mm (Table 5), which are considered high values compared with the reference used. All tested compounds exhibited good activity against the Gram-positive bacterium *S. aureus* and the fungus *A. niger*. Like copolymers, the three polymeric surfactants gave negative results against *R. oryzae*.

Conclusions

In all scientific issues, identifying compounds with dual or multi-functions is of great importance. One major way for such development is the use of conjugate chemistry. The current work describes a facile route for the synthesis of new copolymers tethering tetrachlorophthalimide moiety. Some of the copolymers with tertiary nitrogen atom were converted into the corresponding polymeric surfactants via quaternization with dimethyl sulfate. Also, the antimicrobial activities for all polymeric materials and surface properties including petroleum-collecting/dispersing capacities for

surfactants have been evaluated. Compound **5b** with TCPO/pyridine conjugate displayed the highest activity against *A. niger* with a value of about 2.45-fold higher than that of the Amphotericin B. Moreover, polymeric surfactant **7b** exhibited very strong petroleum dispersibility in both diluted and undiluted forms.

Compliance with ethical standards

Conflict of interest None declared.

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