



Synthesis and Evaluation of New Cationic Polymeric Surfactant Based on N-phthalimidomethyl methacrylate

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Abstract

In our previous work *N*-phthalimidomethyl methacrylate (*NPMMA*) monomer was prepared through the reaction of *N*-hydroxymethyl phthalimide with methacrylic acid in the presence of *N,N*-dicyclohexylcarbodiimide (*DCCI*) as a condensing agent. Then a new series of copolymers containing imidazole have been synthesized through the reaction of *NPMMA* monomer with 1-vinylimidazole (*VIM*) in the presence of benzoyl peroxide as initiator. The copolymer composition was determined by ¹H NMR spectroscopy and the values of monomer reactivity ratio ($r_1 = 0.756$, $r_2 = 1.033$, and $r_1 r_2 = 0.781$) were calculated through Fineman Ross and Kelen-Tüdös methods. Conversion of copolymers to surfactants was achieved through quaternization of the imidazole nitrogen with dimethyl sulphate. The chemical structure of the produced monomer, copolymers, co-polymeric surfactants was confirmed by spectroscopic tools. The surface properties included surface tension, foaming power, emulsion stability, critical micelle concentration (*CMC*) have been measured in aqueous medium by traditional procedures. Also the different air/ water interface parameters including effectiveness (π_{cmc}), efficiency (P_{c20}), maximum surface excess (Γ_{max}) and minimum surface area (A_{min}) were also recorded. Moreover, the biodegradability for these cationic surfactants has been investigated and their D % was ranged from 67 to 100 %.

Keywords: *N*-phthalimidomethyl methacrylate monomer; 1-vinylimidazole; copolymerization reaction; monomer reactivity ratios; surface properties.

1. Introduction

The cyclic imides especially phthalimide and its derivatives are an essential ingredient of many natural products and designed pharmaceutical molecules due to their broad range of applications as insecticidal agents, immunomodulatory, analgesics, anticonvulsants, herbicidal and anti-inflammatories [1-5]. Many activated polymers containing phthalimide group have been used as macromolecular drugs [6-9]. Polymers and macro cyclic compounds with reactive functional groups are always required for applications such as sensors, actuators, corrosion inhibitors, drug and gene delivery and some medical applications. This is due to the lone pair of electron on heteroatom of its structure [10,11]. Copolymerization is a very useful way to develop new compounds which are important class in polymer science since they enable a wide range of features and functions that different from those of the homopolymers [11-17]. Recently, the copolymers involving *N*-vinylimidazole (*VIM*) and its derivatives

showed unparalleled features such as ion exchange and complexing formation, catalytic, biological, physiological activities, and heat resistance. These copolymers are used as carrier agents for protein separations, for an active moiety of electrolytic enzymes, for the preparation of strong anion exchange membranes and new steric stabilizers for polyaniline colloids [18,22]. Monomer reactivity ratios are very important parameters for the demonstration of copolymer structure (copolymer composition, and monomer sequence distribution) which help for the prediction of copolymer properties and the correlation between structure and properties. [23-29]. Hundreds of years ago, many of methods have been developed to determine and predict the (r) parameters. ¹HNMR spectroscopy has been assured to be one of the most important and efficient techniques for studying the polymer structure and the copolymer composition. On-line ¹HNMR kinetic experiments have been successfully used for the kinetic study of free radical homo- and

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copolymerization [29-32]. Surfactants are being one of the most usage and powerful class of materials used in the chemical industry [33,34]. Polymeric surfactants may be used as an alternative to classical surfactants in many applications including detergents, coatings, inks, pharmaceuticals, personal care products, and advanced materials such as Nano-composites [35,36]. Polymerizable surfactants have reactive functionalities that can exist in the hydrophobic tail or the polar head group [37,38]. Our study is aimed to synthesis a new series of copolymers containing imidazole by the solution polymerization and determination of monomer reactivity ratios (r_1 , r_2) by Fineman Ross and Kelen-Tüdös methods through ^1H NMR spectroscopy. Then synthesis a new series of biodegradable co-polymeric surfactants that have wide range industrial applications and environmental friend.

2. Materials and Methods

A. Materials

N-hydroxymethyl phthalimide (*NHMPH*), 1-vinylimidazole (*VIM*), methacrylic acid, *N,N* dicyclohexylcarbodiimide (*DCCI*) and benzoyl peroxide (*Bz₂O*) were obtained from Sigma-Aldrich chemical company. Dimethyl sulphate (*DMS*), methylene chloride (*CH₂Cl₂*), dimethyl formamide (*DMF*), diethyl ether, methanol and chloroform were purchased from Al-Nasr chemical company.

B. Methods:

1- Synthesis of *N*-phthalimidomethyl methacrylate (*NPMMA*) monomer:

NPMMA monomer was prepared through addition of *N,N*-dicyclohexylcarbodiimide (*DCCI*) 20.6 g (0.1 mol) in one portion to a well-stirred cooled solution (-5 °C) of methacrylic acid 8.6 g (0.1 mol) and *N*-hydroxymethyl phthalimide 17.7 g (0.1 mol) in 100 ml of dry methylene chloride, the reaction mixture was stirred for 6 hrs [39,40]. Filtration of the mixture to remove the precipitated dicyclohexyl urea, then the filtrate evaporated to dryness in vacuo. The *NPMMA* monomer was recrystallized from benzene/petroleum ether mixture (20:80) to give purified white solids crystals (yield 90%, melting point 121-122 °C).

2- Copolymerization reactions:

The copolymer of *NPMMA* with *VIM* was obtained by the solution polymerization method in the presence of the free radical initiator *BzO₂* in a concentration of 1 mol/100 mol monomers. So, the pre-determined amounts of the comonomers were

placed in glass tubes, and diluted with *DMF*. The tubes were flushed with oxygen-free nitrogen for 10 minutes, capped and thermostated at 60 °C for 6 hrs depending on the comonomer pairs and composition [22,41]. The conversion were kept low (7-10%) and all copolymers were purified by reprecipitation from methanol, washed several times, dried and weighed.

3- Preparation of co-polymeric surfactants:

The polymeric surfactants (*Co-PS*)¹⁻⁵ were obtained after the reaction of the synthesized polymers with excess amount of dimethyl sulphate (*DMS*) in the absence of solvent [22]. The mixture was standing at 80 °C for 96 hrs in a closed system. The products were recrystallized using diethyl ether several times to remove all unreacted substrates and to yield was 85% brown viscous oily.

4- Surface properties

a- Surface and Interfacial tension

Surface and interfacial tension measurements were obtained Tensiometer K6 Krüss, Germany, (Du Nouy tensiometer with Platinum-Iridium ring) in Egyptian Petroleum Research Institute (*EPR*). [42,43]. Interfacial tension was measured for surfactant-oil system at 25 °C with a 0.1 % surfactant solution. The value, at which the ring was separated at the interfacial surface between the two layers, was measured as interfacial tension [44,45].

b- Krafft point (T_{kp}):

The Krafft temperature for co-polymeric surfactants was determined by heating the surfactant solution until a clear solution was obtained. All the surfactants solution concentrations were 0.2 wt. % (at least twice the *CMC* of studied Gemini surfactant) [40,46].

c- Foaming power:

Foam power of polymeric surfactants was measured at room temperature after shaking 100 mL of 0.1% (wt./v) of the polymeric surfactant solution in a 500 mL graduated cylinder. Initially, the foam height (in mm) represents the foaming power, and the stability of foam was determined by the falling of height after time [40,47].

d- Emulsification stability:

10 mL (0.1 wt. %) of each of the different surfactant solutions was placed in a 100 mL cylinder and then 10 mL of the paraffin oil was added. The cylinder was shaken vigorously for 10 min and then allowed to settle. The time required to separate 9 mL

of pure surfactant solution was recorded and was taken as an indication of the emulsification power of each surfactant [40,48].

e- Critical micelle concentration (CMC):

A freshly prepared aqueous solution of the synthesized cationic co-polymeric surfactants in distilled water was prepared with a different molar concentration at 25°C to determine the CMC values of these surfactants by surface tension techniques [49,50].

f- Effectiveness (π_{cmc}):

The surface tension (γ_{cmc}) values at the CMC were used to calculate the surface pressure (effectiveness) values, from the following equation:

$$\pi_{cmc} = \gamma_0 - \gamma_{cmc} \quad (1)$$

Where γ_0 and γ_{cmc} are the surface tensions of pure water and surface tension at CMC, respectively [50,51].

g- Maximum surface excess (Γ_{max}):

The maximum surface excess concentration (Γ_{max}) is defined as the effectiveness of adsorption at interface. Γ_{max} was calculated from the slope of the straight line in the surface tension plot ($\delta \gamma / \delta \log c$) below CMC, using the appropriate form of Gibbs adsorption equation [52,53].

$$\Gamma_{max} = -(\delta \gamma / \delta \log c) T / 2.303 n RT \quad (2)$$

Where Γ_{max} is the maximum surface excess concentration of surfactant ions, $n=2$ in case of conventional surfactants and $n=3$ in case of gemini surfactants, R is the gas constant, T is the absolute temperature, ($\delta \gamma / \delta \log c$) is the slope of the γ vs. $-\log$ concentration plot at room temperature.

h- Minimum surface area (A_{min}):

The average minimum surface area (A_{min} ; in square angstrom) occupied by each molecule adsorbed at the interface is given by:

$$A_{min} = 10^{16} / N_A \cdot \Gamma_{max} \quad (3)$$

Where N_A is the Avogadro's number ($N_A = 6.02214076 \times 10^{23} \text{ mol}^{-1}$) and Γ_{max} (mol m^{-2}) is the maximum surface excess of adsorbed surfactant molecules at the interface [53,54].

i- Efficiency (PC_{20}):

Efficiency (PC_{20}) is determined by the concentration (mol/l) of the surfactant solution capable of suppressing the surface tension by 20 mN/m. The efficiency has been determined by extrapolating from $\gamma = 52$ to the linear portion before CMC of the γ versus $-\log$ conc plot at 25°C [51,55].

j- Biodegradability:

The biodegradability was carried out by the Die-away test in the River Nile water of the surfactant using a surface tension method [56,57]. From the surface tension measurements, the percentage of biodegradation (D%) was calculated as follows:

$$D\% = (\gamma_t - \gamma_0) / (\gamma_{bt} - \gamma_0) * 100 \quad (4)$$

where γ_0 is the surface tension at zero time, γ_t ; the surface tension at time t , γ_{bt} ; the surface tension of blank experiment at time t (without samples).

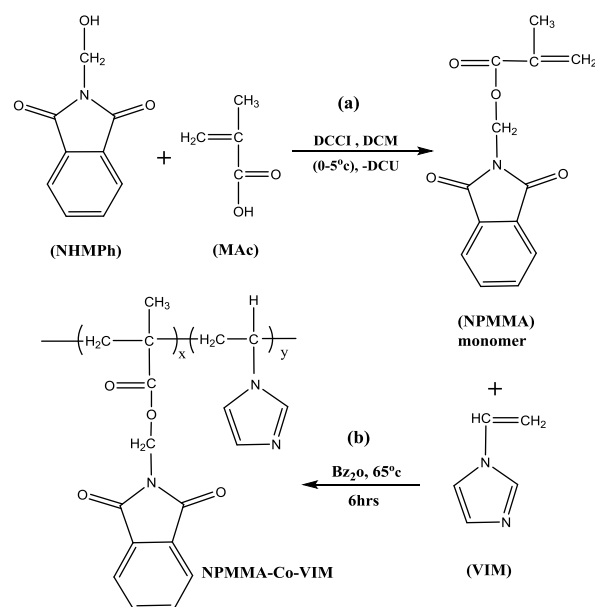
5- Spectral analysis:

^1H NMR spectra were recorded on a Varian Gemini 500 MHz spectrophotometer, Mansoura University. The chemical shifts (δ) are given down field relative to tetramethylsilane (TMS) as the internal standard.

IR spectra were recorded (KBr) on a Pye-Unicam Sp-883 Perkin Elmer spectrophotometer.

Result and discussion

In the present investigation; *N*-phthalimidomethyl methacrylate (NPMMA) monomer was prepared by the reaction of *N*-hydroxymethyl phthalimide (NHMPH) with methacrylic acid (MAc) in the presence of the condensing agent *N,N*-dicyclohexyl carbodiimide (DCCI), also, the copolymerization reaction of (NPMMA) with 1-vinylimidazole (VIM) was studied according to the previous method and they can be represented as in (Scheme 1).



Scheme 1: a: Synthesis of *N*-phthalimidomethyl methacrylate (NPMMA) monomer, b: Synthesis of copolymer (NPMMA-Co-VIM).

The solubility of monomer and copolymers was tested in several solvents in a cold condition. They were white crystalline solids, easily soluble in *DMF*, tetrahydrofuran, dimethylsulfoxide, chloroform, and dichloromethane (monomer only), but insoluble in methanol, ethanol, water, toluene, n-hexane, petroleum ether, and diethyl ether. The structure of the monomer was confirmed by IR and ^1H NMR spectroscopy (Fig 1) as following:

The IR spectrum of *NPMMA* shows a band at 3065 cm^{-1} (aromatic *C-H* stretching), 3100 cm^{-1} (olefinic *C-H*), 2931 and 2856 cm^{-1} (symmetrical and asymmetrical *C-H* stretching due to CH_2 and CH_3), 1714 cm^{-1} ($\text{C}=\text{O}$ of ester group), 1783 and 1651 cm^{-1} due to coupling band, 1627 cm^{-1} (olefinic $\text{C}=\text{C}$). ^1H NMR (ppm): 7.301-7.928 (aromatic protons), 5.582 and 6.100 (*2H*) [olefinic protons], broad singlet at 4.2 (CH_2) of ester and 1.329 (*3H*) [Methyl].

IR spectroscopy of copolymers (Fig 2) that shows a band at 3050 cm^{-1} due to the aromatic ν *C-H* stretching, a band at 2933 and 2857 cm^{-1} due to (CH_2, CH_3), a strong band around 1736 - 1783 cm^{-1} characteristic to ν $\text{C}=\text{O}$ of ester and ν $\text{C}=\text{O}$ of coupling band of phthalimide group, bands at 975 and 1134 cm^{-1} due to ν *C-O-C* bending, bands at 1626 and 1544 cm^{-1} characteristic to ν $\text{C}=\text{C}$ and ν $\text{C}=\text{N}$ of imidazole.

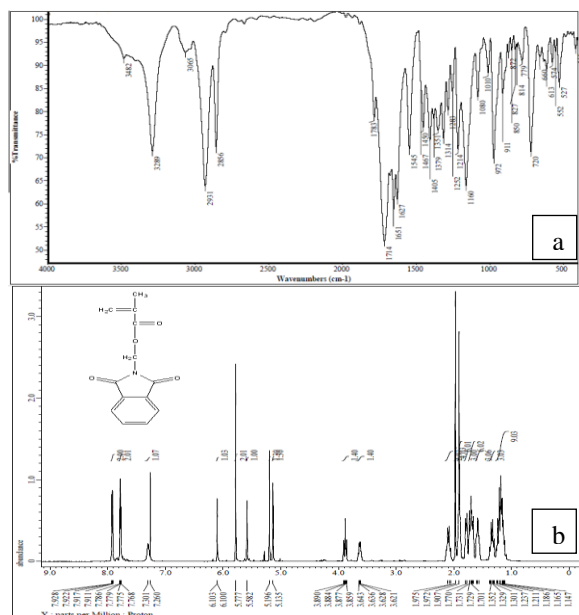


Fig (1): a: IR and b: ^1H NMR spectra of *NPMMA* monomer.

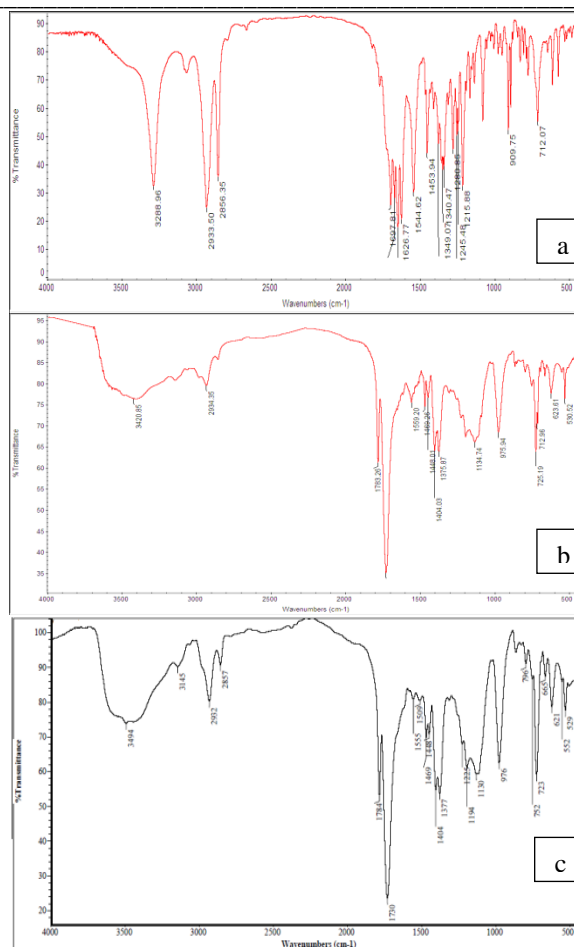
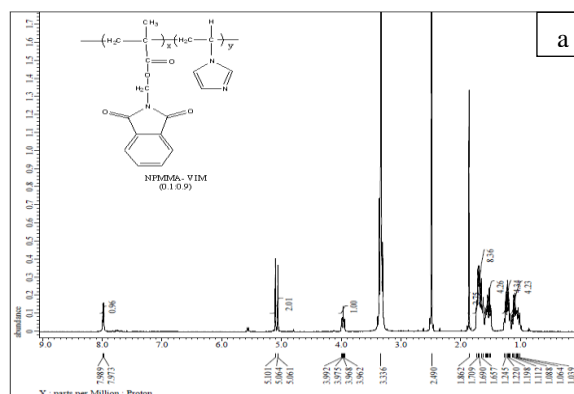


Fig (2): IR spectra of Copolymers; a: (0.2:0.8), b: (0.5:0.5) and c: (0.6:0.4).

The copolymer composition was determined by ^1H NMR spectral analysis which is one of the most Spectroscopic methods that offers simple and rapid evaluation of copolymer composition compared to the other techniques [58,59]. Typical ^1H NMR spectra for the samples of copolymer system of *NPMMA-VIM* are found in (Fig 3).



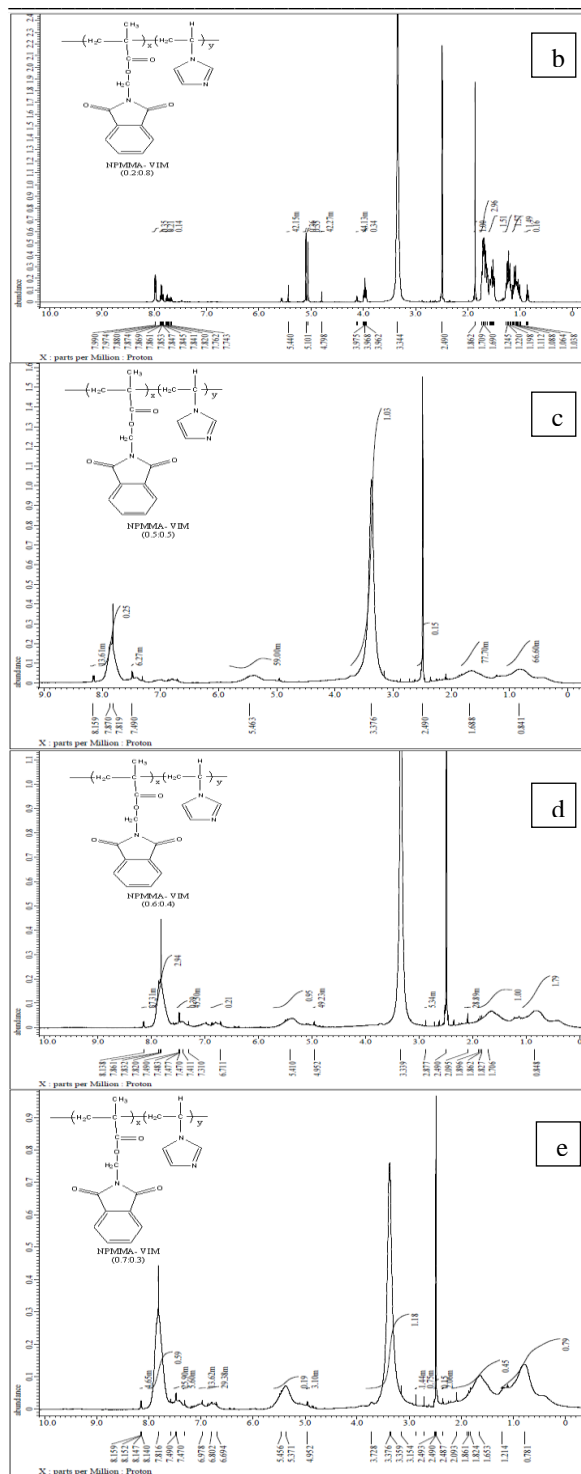


Fig (3): ¹H NMR spectra of Copolymers; a: (0.1:0.9) b: (0.2:0.8), c: (0.5:0.5), d: (0.6:0.4) and e: (0.7:0.3).

From the values of feed and copolymer compositions in (Table 1), the monomer reactivity ratios (r_1, r_2) of the copolymer were determined by Fineman Ross [60,61] and Kelen-Tüdös [62,63] methods (Figs 4,5). The values of r_1 and r_2 from the

Kelen-Tüdös and Fineman-Ross methods are in (Table 2). The $r_1 r_2$ value for the system (0.781) indicates that the copolymer should have a random distribution of the monomer units with a tendency toward alternation. (Fig 6) shows the composition curve calculated on the bases of the determined monomer reactivity ratios and it is found that *NPMMA-Co-VIM* system gave no azeotropic composition.

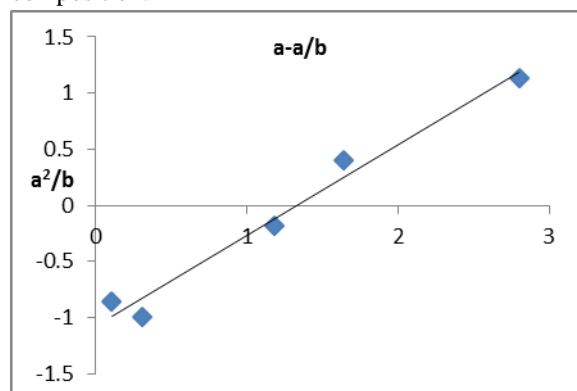


Fig (4): Fineman-Ross plot for copolymer system.

Where $[a - (a/b) = r_1(a/b) - r_2]$

$a = [M_1 / M_2]$ the molar ratio of monomer feed, and $b = m_1 / m_2$ the molar ratio of the copolymer.

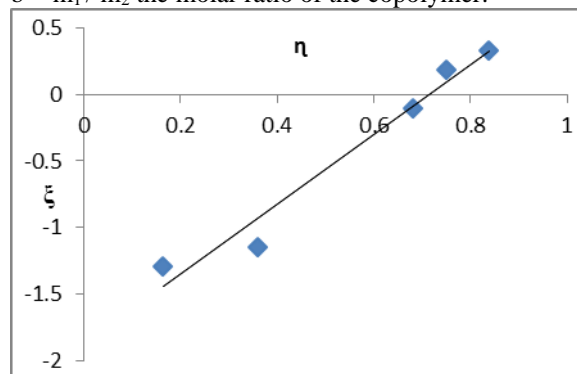


Fig (5): Kelen-Tüdös plot for copolymer system.

Where: $\eta = (r_1 + r_2 / \alpha) \xi - (r_2 / \alpha)$,

$\xi = a^2 / (\alpha b + a^2)$ and $\alpha = a_{min} * a_{max} / \sqrt{b_{min} * b_{max}}$

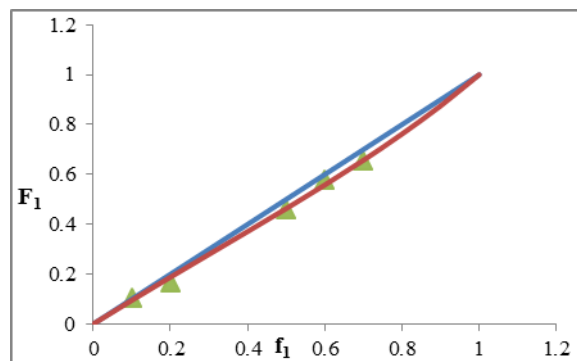


Fig (6): Composition curve for copolymerization of *NPMMA* with *VIM*.

Line represents calculated value and (Δ) represents experimental values, f_1 = mole fraction of M_1 in the feed, F_1 = mole fraction of M_1 in the copolymer.

Table (1): Copolymerization of NPMMA + 1-vinylimidazole (VIM).

Initial monomer composition		Conversion %	Copolymer composition		Fieman-Ross method		Kelen-Tudos method	
a*	f_1^0		b*	F_1^0	a-a / b	a^2/ b	η	ξ
0.1111	0.1	3.790	0.115	0.103	-0.855	0.107	0.163	-1.298
0.250	0.2	9.79	0.202	0.168	-0.987	0.309	0.360	-1.148
1.000	0.5	14.7	0.848	0.459	-0.179	1.179	0.682	-0.104
1.500	0.6	44.4	1.369	0.578	0.405	1.642	0.749	0.185
2.333	0.7	39	1.915	0.657	1.117	2.835	0.837	0.330

(a*) Molar ratio : M_1/M_2 in feed composition and (f_1^0) Mole fraction of M_1 in feed composition.

(b*) m_1/m_2 in copolymer composition and (F_1^0) Mole fraction of m_1 in copolymer composition.

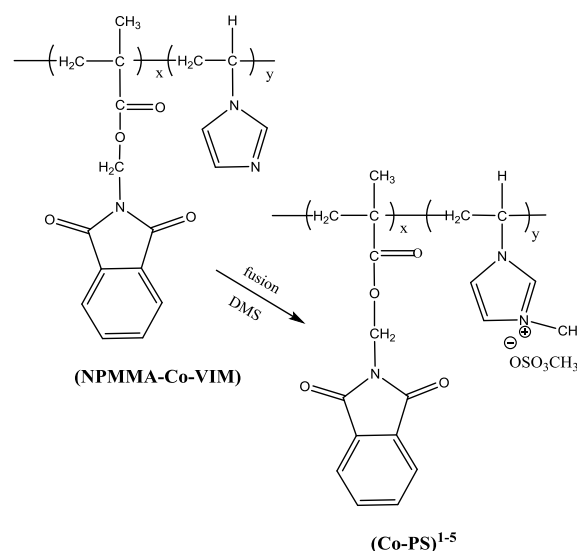
Table. (2): Monomer reactivity ratios for Copolymerization of NPMMA + 1-vinylimidazole (VIM).

M_1-M_2	Fieman-ross method		Kelen-tudos method			
	r_1	r_2	r_1	r_2	α	$r_1 r_2$
NPMMA-VIM	0.789 ± 0.0157	1.059 ± 0.0246	0.756 ± 0.0815	1.033 ± 0.0959	0.551	0.781

Preparation of co-polymeric surfactants:

Co-polymeric surfactants were obtained by the reaction of the produced (NPMMA-Co-VIM) polymers with excess amount of DMS in the absence of solvent. The mixture was maintained in a closed system at 80 °C for 96 hrs.

The structure of the produced co-polymeric surfactant was investigated by IR spectra (fig 7) that show band around 2500 cm^{-1} due to N^+ of quaternary salt, broad band at 3470 cm^{-1} due to the absorbed water in the sample that shows the highly hygroscopic nature of the produced polymer, band at 1720 cm^{-1} characteristic to $\nu C=O$ of ester and around $1643\text{-}1768\text{ cm}^{-1}$ characteristic to $\nu C=O$ of coupling band of phthalimide group, bands at 1643 and 1550 cm^{-1} characteristic to $\nu C=C$ and $\nu C=N$ of imidazole, 1212 and 1310 cm^{-1} characteristic to SO and SO_2 .



Scheme 2: Synthesis of Co-polymeric surfactants ($(Co-PS)^{1-5}$) from copolymer (NPMMA-Co-VIM).

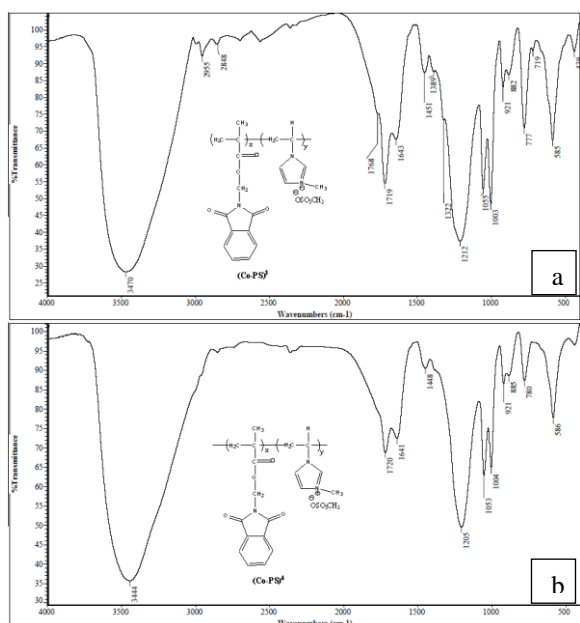


Fig (7): IR spectrum of co-polymeric surfactant (Co-PS)^{3,4}

Surface properties of the prepared co-polymeric surfactants

Surface tension and interfacial tension:

Surface tension is a characteristic property for liquids. This phenomenon appeared from the attraction force between the molecules at the surface. The surface tension value of the used distilled water at 25 °C was 72.4 mN/m. The relation between surface tension of the co-polymeric surfactant solutions (γ) and -logarithm of concentrations (-log conc) found in (Fig 8), the data of Surface and interfacial tension is showed in (Table 3).

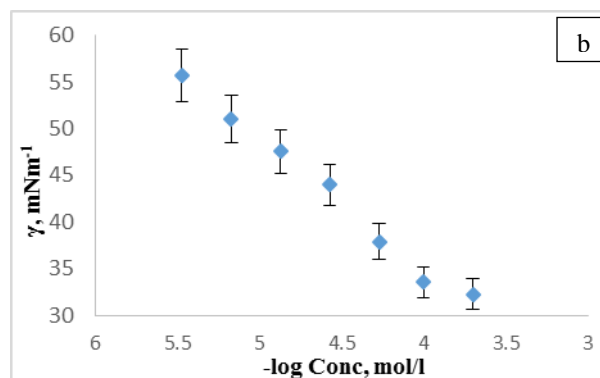
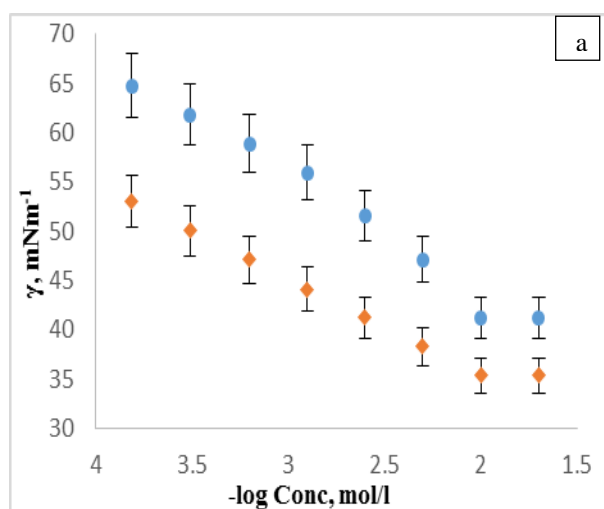


Fig (8): Variation of the surface tension with -logarithm of concentrations a: for (Co-PS)^{3,5} and b: for (Co-PS)⁴ in water at 25 °C.

Krafft point (T_{kp}):

All of the produced co-polymeric surfactants gave Krafft point values below 0 °C, this indicates to the good solubility of these surfactants and gives it the ability to be used at low temperatures.

Foaming power:

The foaming power of surfactants is an important phenomenon while it determines in which types of applications it can be used in. From the obtained data of foam height, it showed that all surfactants have good foaming properties. Co-polymeric surfactant (Co-PS)⁵ is the most stable one and recorded the higher foam height and (Co-PS)¹ is less stable and recorded the lower foam height (Fig 9). By increasing the hydrophobic part of the prepared surfactants; a corresponding increase in the foam stability and foam height is occurring. Decreasing the hydrophilic part of the prepared surfactants causes a decrease in the foam stability and lead to decrease in foam height.

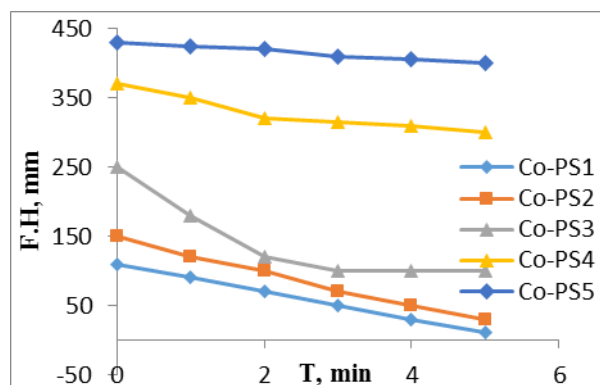


Fig (9): Foam stability of the co-polymeric surfactants (Co-PS)¹⁻⁵.

Emulsification stability:

Increasing the time required for separation of the desired amount of pure water (9 mL) from the emulsified system formed between surfactant solution (0.1 % wt) and paraffin oil (10 mL: 10 mL) indicates the stability of the formed emulsion, and vice versa [39]. From the data in (Table 3, Fig 10); polymeric surfactant (*Co-PS*)⁵ was the most stable compound, (*Co-PS*)^{1,2} were the less stable, so that these surfactants cannot be used as long-term emulsion stabilizers.

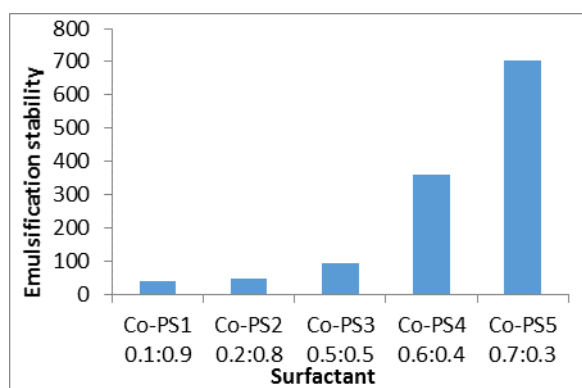


Fig (10): Emulsification stability of the co-polymeric surfactants (*Co-PS*)¹⁻⁵.

Critical micelle concentration (CMC):

The critical micelle concentration is defined as the concentration of the surfactant at which no further decrease in the surface tension could be obtained upon further increase of the surfactant concentration. The surface tension value at the respective CMC is called (γ_{cmc}). The intersection has been obtained from the two lines with different slopes is the CMC point in each plot. The CMC values were recorded in (Table 3).

Compounds (*Co-PS*)^{1,2} are highly hydrophilic, more miscible with H₂O and give characteristic of hydrophilic only.

Effectiveness (π_{cmc}):

The surface tension (γ) values at the CMC are used to calculate values of the surface pressure effectiveness as mentioned before.

$$\pi_{cmc} = \gamma_0 - \gamma_{cmc}$$

The effectiveness of adsorption is an important factor for foaming, wetting and emulsification, and its values are considered to be a good variable in

comparing between two surfactants in the same series. From values of π_{cmc} listed in Table (4), it was observed that the most effective surfactant is (*Co-PS*)⁴ that gives the maximum reduction of the surface tension at its CMC value along the prepared surfactants series.

Maximum surface excess (Γ_{max}):

The number of surfactant molecules located in unit area at the air/water interface is showed by the maximum surface excess of the surfactant solution. Values of Γ_{max} represented in Table (4) showed that, increasing the hydrophobic character of the prepared compounds causes a decrease in their Γ_{max} values.

Minimum surface area (A_{min}):

Table (4) shows that increasing the hydrophobic chain length as well as the spacer length along the studied surfactants (*Co-PS*)³⁻⁵ leads to an increase in A_{min} values.

Efficiency (Pc_{20}):

The larger the value of Pc_{20} , the most efficiently the surfactant is adsorbed at the interface and the more efficiently it reduces surface or interfacial tension. Results of Pc_{20} listed in (Table 4) showed that (*Co-PS*)³ was found to be the most efficient surfactants structure for detergency.

Biodegradability:

The biodegradation ratio of some synthesized cationic surfactants after the 15th day of exposure to microorganisms in the river water using die-away tests is showed in (Table 4, Fig 11). These results reflected that the biodegradation % of the prepared cationic surfactant solutions increases with increasing the time and length of the hydrophobic chain. (*Co-PS*)³ recorded higher degree of degradation than the other prepared co-polymeric surfactants, (*Co-PS*)⁵ recorded the lower one.

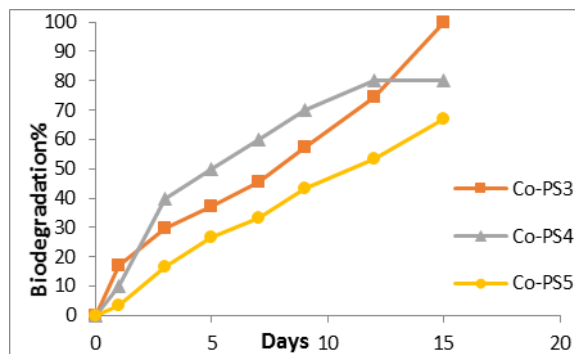


Fig (11): Variation of biodegradation % of the co-polymeric surfactants (*Co-PS*)³⁻⁵ with days.

Table (3): surface properties of the prepared co-polymeric surfactants.

Co-polymeric surfactant	Surface Tension	Interfacial Tension	Krafft Point °C	Foam height 0.1% (mm)	Emulsion stability (sec)	CMC (mol/l)
(Co-PS) ¹ _(0.1:0.9)	-	-	<0	110	41	-
(Co-PS) ² _(0.2:0.8)	-	-	<0	150	49	-
(Co-PS) ³ _(0.5:0.5)	41.2	5.2	<0	250	94	0.001
(Co-PS) ⁴ _(0.6:0.4)	32.28	6.5	<0	370	360	0.0001
(Co-PS) ⁵ _(0.7:0.3)	35.32	3.2	<0	430	703	0.001

Table (4): Surface parameters of the prepared co-polymeric surfactants (S³⁻⁵) at 25 °C.

Surfactants	Monomer ratios	γ_{cmc} (mN/m)	π_{cmc} (mN/m)	$\Gamma_{max} \times 10^{-10}$ (mol/cm ²)	A _{min} (nm ²)	Pc ₂₀	Biodegradability (%) after 15 days
(Co-PS) ³	0.5:0.5	41.2	22.87	5.27	0.315	6.61x10 ⁻³	100
(Co-PS) ⁴	0.6:0.4	33.6	38.89	4.60	0.361	5.012x10 ⁻⁶	80
(Co-PS) ⁵	0.7:0.3	35.3	32.38	3.40	0.488	7.08x10 ⁻⁴	66.7

Conclusion

The conclusion of this work can be drawn in the following points:

- New polymeric surfactants were obtained from the copolymer series (Co-PS)¹⁻⁵ of N-phthalimidomethyl methacrylate (NPMMA) monomer with 1-vinylimidazole.
- These prepared co-polymeric surfactants gave a good surface activity that found to be increase with increase the hydrophobic character along the surfactants series.
- The biodegradation% of these co-polymeric surfactants ranged from 67 to 100 %, so they can be classified as biodegradable and environmentally friendly surfactants.

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