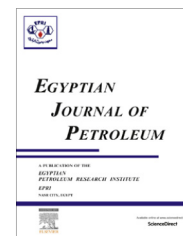




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FULL LENGTH ARTICLE

Preparation of some thermal stable polymers based on diesters of polyethylene and polypropylene oxides macro monomers to use as surfactants at high temperature and pressure



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Abstract Based on polyethylene (PE) and polypropylene (PP) oxides, six macromonomers were prepared through two steps. The first step was esterification of the PE and PP oxides, with oleic acid to give the corresponding monoesters. The second was the diesterification of the prepared monoesters with methacrylic acid to give the corresponding diesters. The prepared macromonomers (diesters) were polymerized to obtain six polymers. The chemical structure of the prepared mono- and diesters and polymers was justified by IR, NMR, GPC and TGA. The obtained results confirmed that the prepared polymers have a high thermal stability and can be used in high pressure and temperature during the drainage of the water from water-in-oil emulsions. The surface active and thermodynamics parameters of these polymers in non-aqueous solution were also investigated and it was found that, these materials have high thermal stability which leads to the possibility to be used under severe reservoir conditions as surfactants.

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1. Introduction

Polymeric surfactants, which contain hydrophilic poly (ethylene oxide) (PEO) or hydrophobic poly(propylene oxide)

(PPO) are commercially available and widely used [1,2]. These macromolecular surface-active agents can form normal micelles, reverse micelles, monolayers, star-like structures, and liquid crystals in aqueous and non-aqueous solutions [3–9]. Variation of the molecular characteristics (PPO or PEO composition ratio, molecular weight) of the polymer during the synthesis allows the production of molecules with optimum properties that meet the specific requirements of different

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Table 1 Name and abbreviation of synthesized materials according to Figs. 1 and 2.

Name	M.wt.	HLB	Alkylene oxide		
			e.o. unit	p.o. unit	
Polyethylene oxide (M.wt. 430)	EG1	430	20	7.98	0.0
Polyethylene oxide (M.wt. 650)	EG2	650	20	13.86	0.0
Polyethylene oxide (M.wt. 1100)	EG3	1100	20	21.81	0.0
Polyethylene oxide (M.wt. 400) monooleate	EO1	694	11.9	7.98	0.0
Polyethylene oxide (M.wt. 600) monooleate	EO2	914	13.8	13.86	0.0
Polyethylene oxide (M.wt. 1000) monooleate	EO3	1364	15.9	21.81	0.0
Polyethylene oxide (M.wt. 400) oleate methacrylate diester	EM1	762	10.3	7.98	0.0
Polyethylene oxide (M.wt. 600) oleate methacrylate diester	EM2	982	12.5	13.86	0.0
Polyethylene oxide (M.wt. 1000) oleate methacrylate diester	EM3	1432	14.9	21.81	0.0
MacroPolyethylene oxide (M.wt. 400) oleate methacrylate diester	ED1	4943	1.7	7.98	0.0
MacroPolyethylene oxide (M.wt. 600) oleate methacrylate diester	ED2	7231	1.8	13.86	0.0
MacroPolyethylene oxide (M.wt. 1000) oleate methacrylate diester	ED3	12,088	1.9	21.81	0.0
Polypropylene oxide (M.wt. 425)	PG1	425	0	0.0	9.39
Polypropylene oxide (M.wt. 725)	PG2	725	0	0.0	14.38
Polypropylene oxide (M.wt. 1130)	PG3	1130	0	0.0	24.61
Polypropylene oxide (M.wt. 425) monooleate	PO1	689	0	0.0	9.39
Polypropylene oxide (M.wt. 725) monooleate	PO2	989	0	0.0	14.38
Polypropylene oxide (M.wt. 1000) monooleate	PO3	1394	0	0.0	24.61
Polypropylene oxide (M.wt. 425) oleate methacrylate diester	PM1	757	0	0.0	9.39
Polypropylene oxide (M.wt. 725) oleate methacrylate diester	PM2	1057	0	0.0	14.38
Polypropylene oxide (M.wt. 1000) oleate methacrylate diester	PM3	1462	0	0.0	24.61
MacroPolypropylene oxide (M.wt. 425) oleate methacrylate diester	PD1	5964	0	0.0	9.39
MacroPolypropylene oxide (M.wt. 725) oleate methacrylate diester	PD2	7362	0	0.0	14.38
MacroPolypropylene oxide (M.wt. 1000) oleate methacrylate diester	PD3	14,450	0	0.0	24.61

industrial applications in detergency, dispersion stabilization, foaming, lubrication, demulsification, foods and food emulsions, pharmaceuticals, cosmetics, and agricultural applications of pesticides and herbicides. Additional uses include cutting oils, detergents, dry cleaning fluids, miscellaneous specialized applications, etc.

Several aspects of the structural and dynamic properties of micelles of these polymers have been investigated by a variety of experimental methods including FT-IR spectroscopy [10,11], ¹H-NMR spectroscopy [12,13], thermal gravimetric analysis and gel permeation chromatography (TGA) [14,15]. Surface properties and aggregation behaviors of aqueous solutions based on these polymers, including the surface tension, critical micelle concentration, and aggregation conformation, often play a central role in determining and controlling polymer performance in many practical applications [16].

Recently, the polyethylene oxides or polypropylene oxides have become useful in manufacturing surfactants in different fields, due to their low toxicity, low cost, chemical stability, and water solubility. The lower molecular weight liquids are useful solvents; and the higher molecular weight solids, having a waxy appearance and various melting ranges are ideally suited for many applications in the surfactant industry [17–19].

The main purpose of this work is to synthesise some polymers based on polyethylene oxide and polypropylene oxide (with different molecular weights) and confirm their chemical structures. The thermal stability and surface active properties of these polymers were investigated.

2. Materials and methods

Ethylene oxide, propylene oxide, oleic acid and methacrylic acid were purchased from Aldrich while xylene (b.p. 137 °C),

p-toluene sulfonic acid, petroleum ether (b.p. 42–62 °C) and isopropanol were supplied by Bio.Chem, Egypt. All materials were used as received without further purification.

2.1. Preparation of poly ethylene and poly propylene oxides

A high-pressure stainless steel autoclave (Parr model 4530, USA) of 1 L capacity, 400 psi maximum pressure, and high temperatures was utilized through ethoxylation and propoxylation reactions. The autoclave is equipped with a magnetic drive stirrer, an electric heating mantle with a thermocouple inserted in the reactor body, a cooling coil, a pressure gauge, and a drain valve. Both reaction mixtures were heated to 160 °C with continuous stirring while passing a stream of nitrogen gas through the system for 10 min to flush out air. The nitrogen stream was then replaced by ethylene or propylene oxide individually at different ratios. Generally, as a result of the introduction of ethylene or propylene oxide, the pressure was substantially increased as indicated by the pressure gauge, until it reached a maximum value. The pressure drop indicates ethylene or propylene oxide consumption [20].

The reaction completion was established when the pressure reached its minimum value. At this stage, heating was stopped and the contents were cooled gradually to ambient temperature by means of the cooling coil connected to the reactor carrying cold water.

The ethoxylation process was carried out through anionic addition polymerization. Polyethylene oxide was produced by the interaction of ethylene oxide with ethylene oxide [21]. The reaction was catalyzed by 0.3 wt.% catalyst, sodium metal to prepare low-molecular-weight polyethylene oxide with a low polydispersity (narrow molecular weight distribution). The polymer chain length depends on the ratio of ethylene oxide

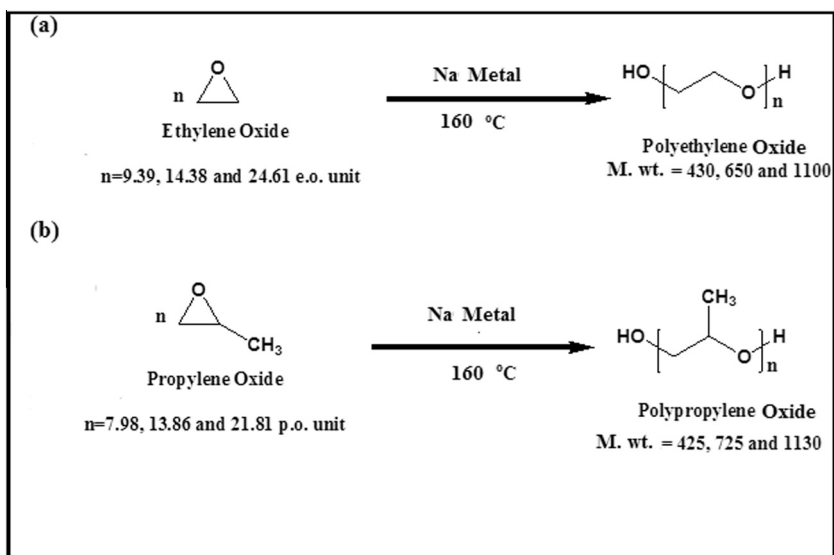


Figure 1 (a) Preparation scheme of polyethylene oxide. (b) Preparation scheme of polypropylene oxide.

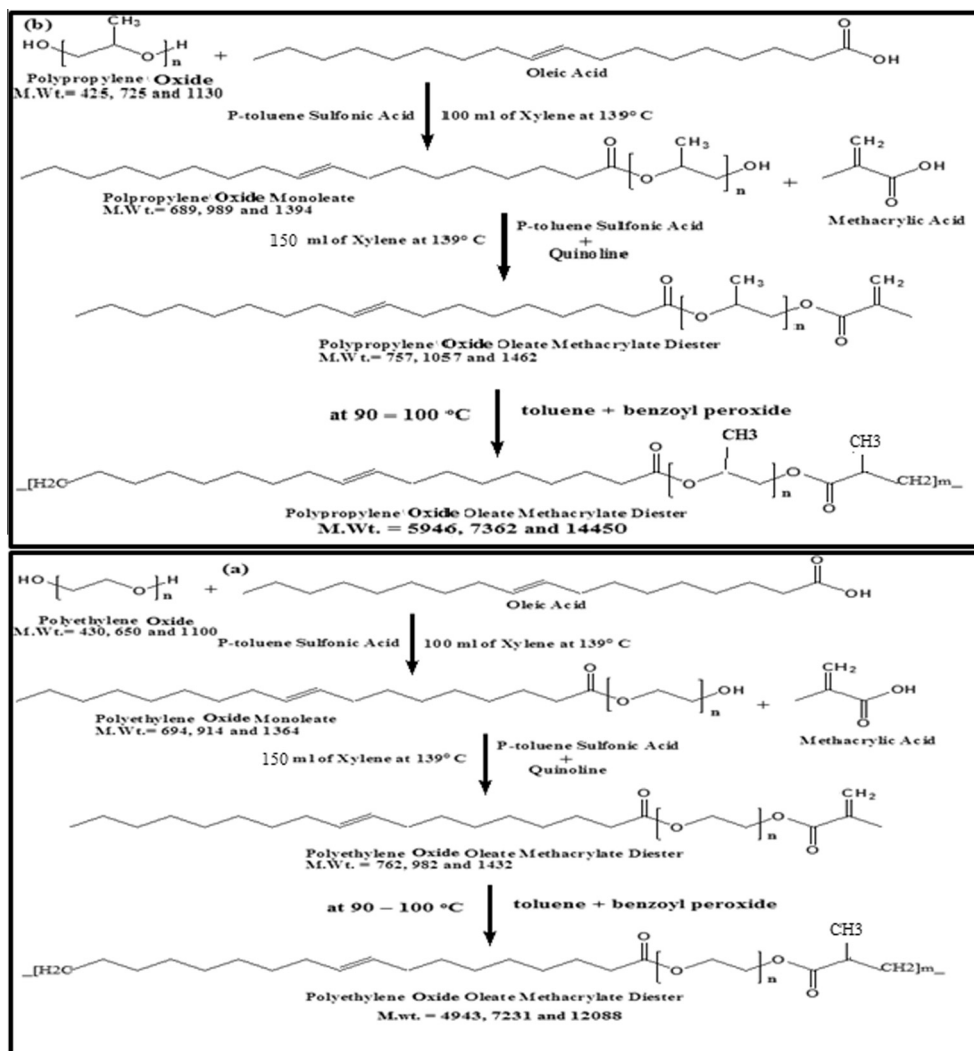


Figure 2 (a) Preparation scheme of mono and diesters of polyethylene oxide. (b) Preparation scheme of mono and diester of polypropylene oxide.

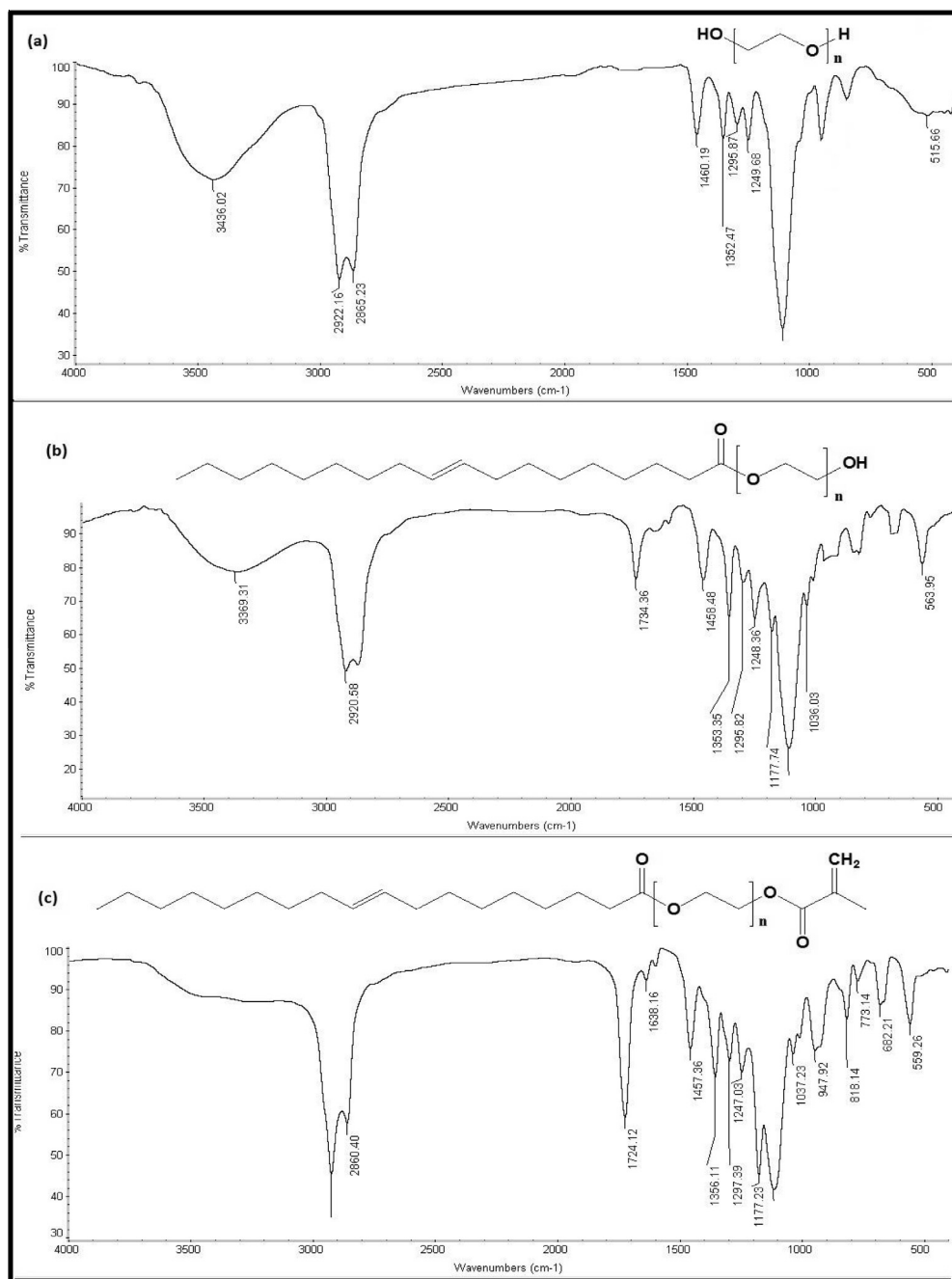


Figure 3 Shows FT-IR spectrum for (a) polyethylene oxide 400 (b) polyethylene oxide monooleate (c) polyethylene oxide oleate methacrylate diester.

(e.o. about ≈ 9.39 , 14.38 and 24.61 unit to get polymer with molecular weight about ≈ 430 , 650 and 1100 respectively) as shown in (Table 1) and scheme of preparation (Fig. 1).

The propoxylation process was carried out by ring-opening polymerization of propylene oxide, polypropylene oxide was produced by the additional polymerization of propylene oxide units at 160 °C in the presence of sodium metal (0.3 wt.%) as catalyst [22]. The molecular weight of the prepared polymers depends on the added number of propylene oxide units (p.o. about ≈ 7.98 , 13.86 and 21.81 units) to get polymers with

molecular weights (about ≈ 425 , 725 and 1130 respectively) as shown in Table 1.

2.2. Preparation of poly ethylene and poly propylene oxides mono oleate

The esterification took place in a 250 ml round-bottom flask with continuous stirring. Water was continuously removed from the reactor, in order to favorably shift the equilibrium. In a typical synthesis, the reaction was carried out at 140 °C

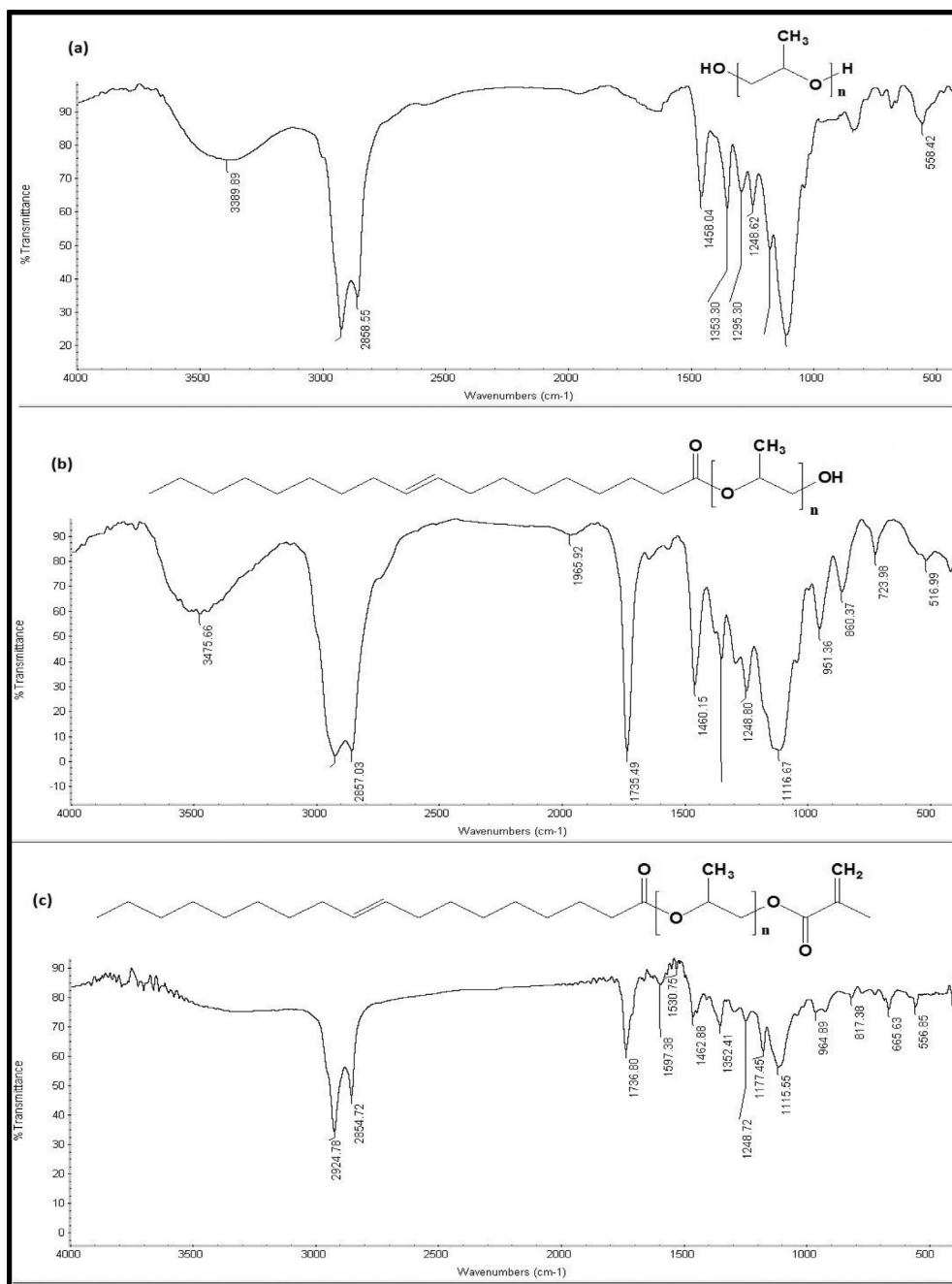


Figure 4 Shows FT-IR spectrum for (a) polypropylene oxide 725 (b) polypropylene oxide monooleate (c) polypropylene oxide oleate methacrylate diester.

for 12 h or until 1.8 ml of water was collected as a by-product of the reaction. The molar ratio of poly ethylene oxide (PEO) [M.wt. = 430, 650, 1100] or poly propylene oxide (PPO) [M.wt. = 425, 725, 1130] to oleic acid 1:1 was dissolved in 150 ml xylene in the presence of p-toluene sulfonic acid as a dehydrating agent then the oleic acid was added to the reaction drop by drop [23–25]. Excess was removed and the sample was washed by isopropanol and super saturated NaCl solution in a separated funnel and the purified product was dried at 60 °C. The yield was 97% and their abbreviations are PEOMO and PPOMO as shown in Table 1 and Fig. 2.

2.3. Preparation of poly ethylene and poly propylene oxides oleate methacrylates diesters

0.1 M of poly ethylene oxide mono oleate or poly propylene oxide mono oleate was dissolved in 150 ml xylene in the presence of p-toluene sulfonic acid as a dehydrating agent and hydroquinone as a polymerization inhibitor at 140 °C till 1.8 ml of water was collected as a by-product of the reaction then 0.1 M of methacrylic acid was added step by step to the reaction [25–28]. The prepared diesters and their abbreviations are illustrated in Table 1 and Fig. 2. The purification for the

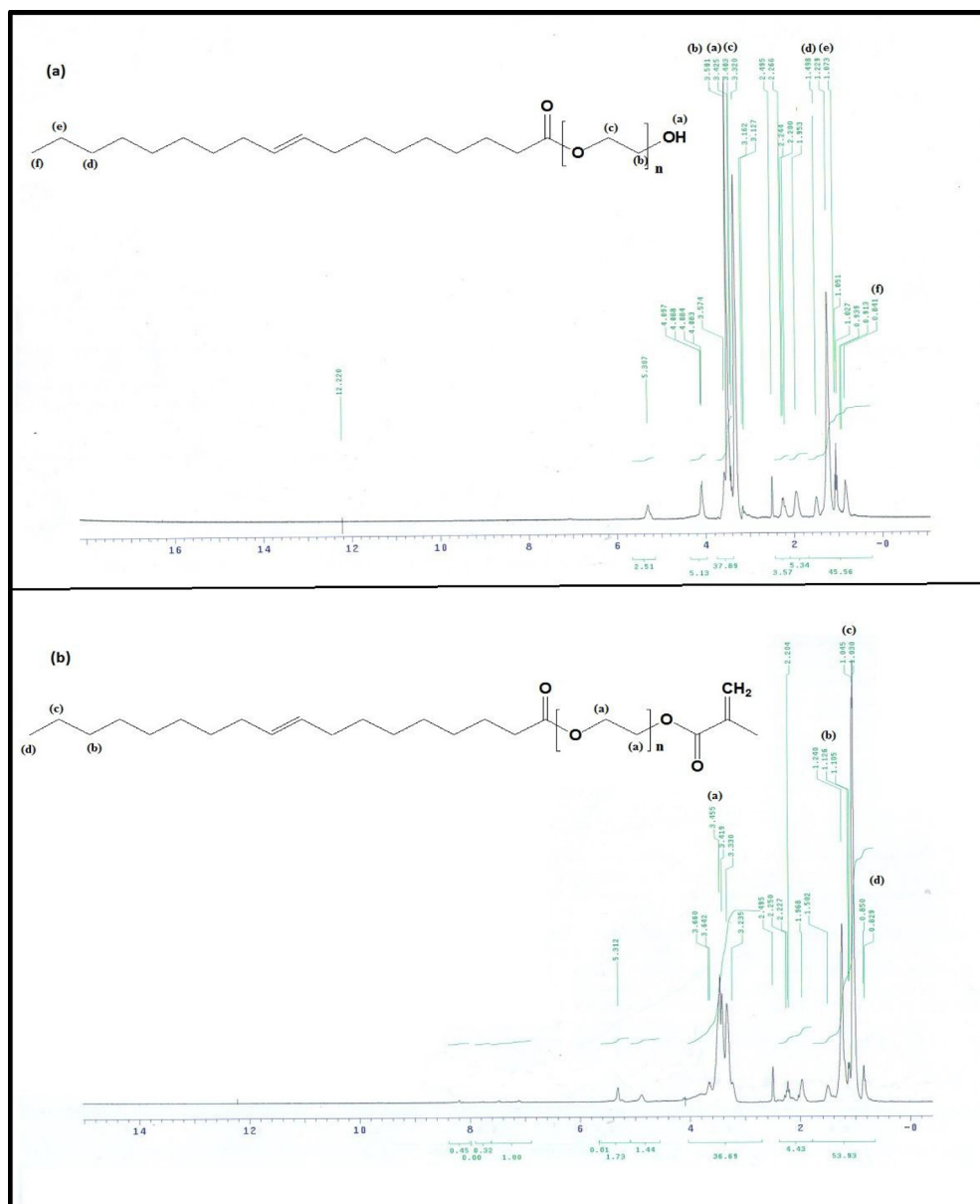


Figure 5 ^1H NMR analysis for (a) polyethylene oxide monooleate (EO1), (b) polyethylene oxide oleate methacrylate diester (EM1).

diesters was carried out by the addition of isopropanol and super saturated NaCl solution at 90°C , by shaking and the separation of the product should be obtained in 96% after the solvent was distilled off.

2.4. Preparation of macropoly ethylene and propylene oxides oleate methacrylate

5.0 g of polyethylene oxide oleate methacrylate or polypropylene oxide oleate methacrylate was dissolved in 15 ml of toluene as a solvent in the presence of 0.1% wt. of benzoyl peroxide as an initiator at $90\text{--}100^\circ\text{C}$ for 6 h. The product was precipitated and washed by methanol. The yield was 80%.

2.5. Materials characterization

The Nicolet IS-10 Fourier Transform Infrared (FTIR) spectrometer was used to examine the structure of the polymer. The samples were recorded by making pellets with potassium bromide (E-Merck, IR Grade). The FTIR analysis was carried out in the range of $4000\text{--}550\text{ cm}^{-1}$ with a scanning resolution of 2 cm^{-1} . The ^1H NMR spectra of the polymers were recorded using Bruker DPX 300 MHz spectrometer at room temperature, tetramethylsilane (TMS) was the internal standard. It was recorded in CDCl_3 solution. The molecular weight of several polymer samples was measured by GPC using Water 2410 Refractive Index Detector and Ultrahydrogel Column. The sample was dissolved at 40°C in THF for 24 h to achieve

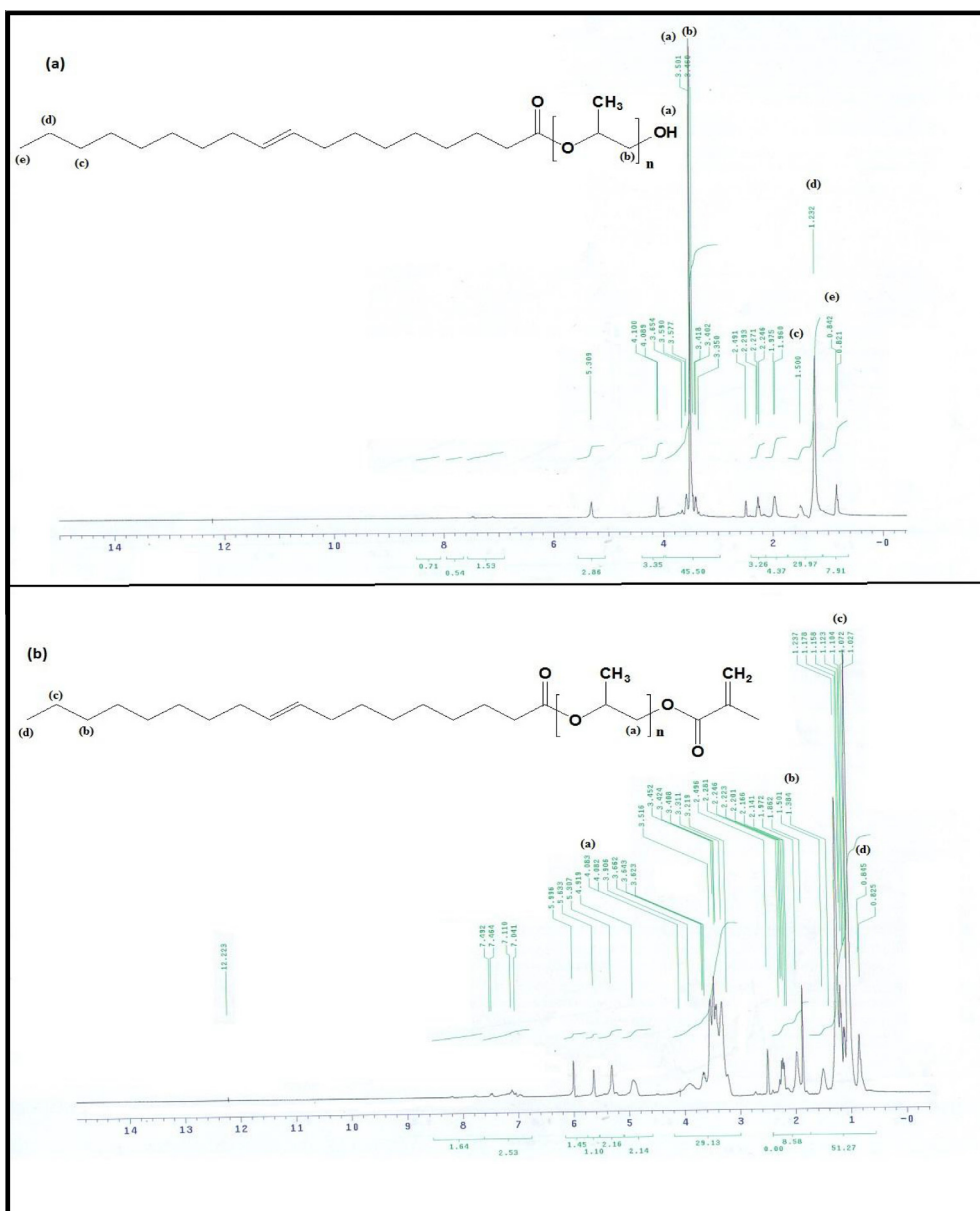


Figure 6 ^1H NMR analysis for (a) polypropylene oxide monooleate (PO1), (b) polypropylene oxide oleate methacrylate diester (PM1).

equilibrium and injected into the system. The injection volume was $100\ \mu\text{l}$ and the operation time was 55 min for each sample.

The thermogravimetric analysis (TGA) technically was used primarily to determine the thermal properties of the prepared polymers (SDT Q600 V20.5 Build 15). The technique can analyze materials that exhibit either mass loss due to decomposition, oxidation or loss of volatiles (such as moisture).

2.6. Surface tension measurements (γ)

The surface tension measurements were obtained using DeNoüy Tensiometer (Kruss-K6 type) and applying a platinum ring technique. A freshly prepared solution of the synthesized nonionic surfactants in xylene was prepared with a different molar concentration range of 1×10^{-1} – $10\ \text{mol/l}$ at different temperatures 25 and $60\ ^\circ\text{C}$. The ring was washed twice after

each reading first by ethanol and then xylene. The apparent surface tension was measured five times for each sample within a 2 min interval between each reading.

2.7. Hydrophile lipophile balance “HLB”

The surfactant was characterized by hydrophilic–lipophile balance (HLB) values. The HLB scale varies from 0 to 20. A high HLB value refers to a hydrophilic or water-soluble surfactant. The HLB of the prepared demulsifiers were calculated according to the following equation:

$$\text{HLB} = 20 \left[\frac{\text{MH}}{\text{MH} + \text{ML}} \right]$$

where MH is the formula weight of the hydrophilic portion of the molecules and ML is the formula weight of the lipophile (hydrophobic) portion of the molecule.

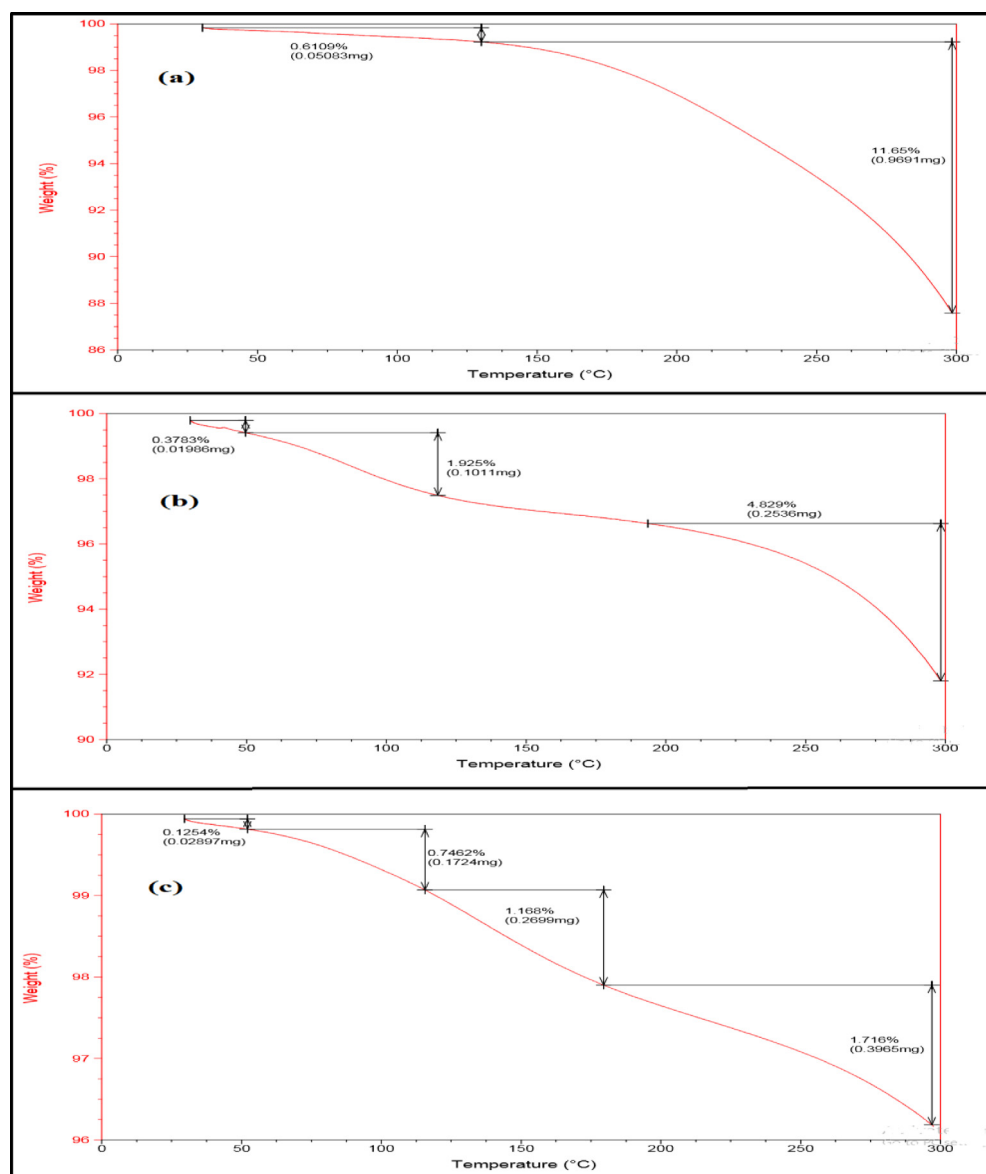


Figure 7 TGA analysis for (a) polyethylene oxide (M.wt. 430) oleate (EO1) (b) polyethylene oxide (M.wt. 430) oleate methacrylate diester (EM1) (c) macroPolyethylene oxide (M.wt. 430) oleate methacrylate diester (ED1).

3. Results and discussion

3.1. Data and explanation

The characterization of the prepared products was carried out using FTIR-spectrometer. The FT-IR spectrum for the purified (dried), EG1, EO1 and EM1 samples are shown in Fig. 3(a, b and c). The spectra show that; absorption peaks observed at 1253 cm^{-1} which are assigned etheral group (C—O—C) and the stretching band at $3300\text{--}3400\text{ cm}^{-1}$ for OH group which appears only in case of EG1 and EO1 only and disappeared in the diester in EM1 that, the diester have been successfully formed. The main evidence to prove that the monoesters and diesters have been successfully formed is the appearance of the absorption peaks at $800\text{--}900\text{ cm}^{-1}$ which

Table 2 Parameters of molecular weight by GPC analysis for poly ethylene and poly propylene oxides.

Demulsifier	M_w	M_n	M_p	M_z	M_{z+1}	Poly dispersity index
ED1	4943	4151	5222	4936	5412	1.129
ED2	7231	5512	9102	11,920	15,739	1.47
ED3	12,088	9671	11,406	22,813	31,939	1.35
PD1	5964	4552	5112	6222	7342	1.31
PD2	7362	6364	10,135	12,810	16,928	1.16
PD3	14,450	9764	11,633	23,267	32,574	1.48

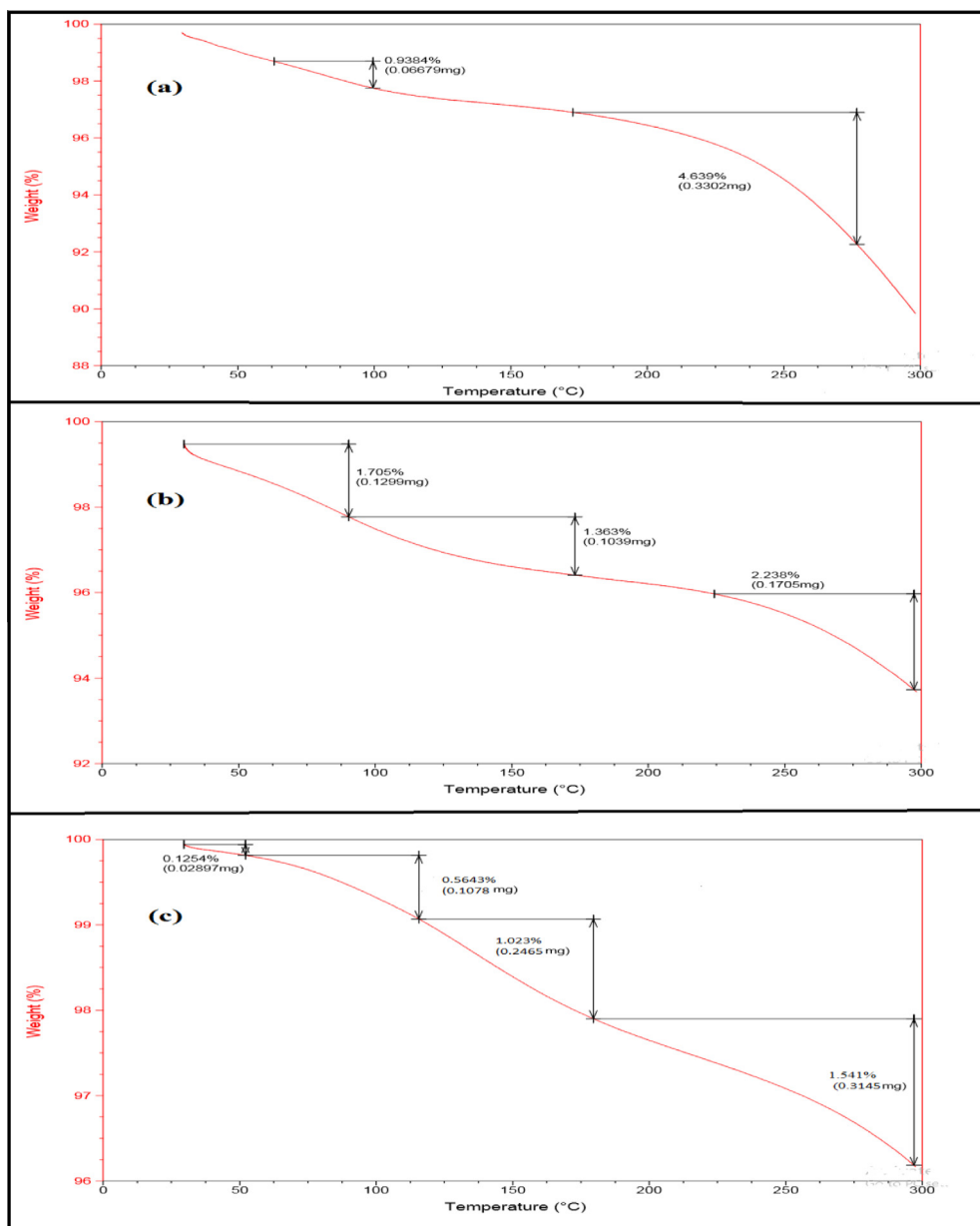


Figure 8 TGA analysis for (a) polypropylene oxide (M.wt. 425) oleate (PO1) (b) polypropylene oxide (M.wt. 425) oleate methacrylate diester (PM1) (c) macroPolypropylene oxide (M.wt. 425) oleate methacrylate diester (PD1).

are assigned as C—H bonding due to C=CH₂ group, the stretching vibration band of C=C at 1600–1650 cm⁻¹ and the stretching band of C=O at 1600–1700 cm⁻¹. All these peaks appeared due to ester formation.

Fig. 4(a)–(c) shows the FTIR spectra for PG1, PO1 and PM1. The chemical structure of PG is quite similar to that of EG. So the FT-IR spectrum for the PG2 and its esters is much similar to EG1 and its esters.

Also the H¹NMR analysis was used to elucidate the chemical structures as shown in Figs. 5 and 6 representing EO1 and EM1 where (CH₂—O—CO—) 4.0–4.1 δ (*t*) (peak c), (—CH₂—CH₂—CH₃) 1.3 δ (*m*) (peak d), (—CH₂—CH₃) 1.09 δ (*m*) (peak e), (—CH₃) 0.8–0.9 δ (*t*) (peak f). While in the case of PEGMO-4 appears a sharp and clear splitting for (—OH)

3.5–3.6 δ (*s*) (peak a), (—CH₂—OH) 3.3–3.49 δ (*t*) (peak b). it is the same as in Fig. 6 which presents PO1 and PM1.

The GPC trend for ED1, ED2 and ED3 exhibits strong peaks around 50, 44 and 45 min respectively, which correspond to a molecular weight (M_w) of 4687, 6325 and 13,110 g/mol, and their poly dispersity indexes were 1.129, 1.47 and 1.35 respectively.

The PD1, PD2 and PD3 in Table 2 exhibit strong peaks which correspond to a molecular weight (M_w); 5964, 7362 and 14,450 g/mol respectively and their poly dispersity indexes were 1.31, 1.16 and 1.48. These results may be prove that the sweet polymerization was obtained during the preparation process.

Fig. 7 shows the TGA results generated on (a) polyethylene oxide oleate (EO1) (M.wt. 430) (b) polyethylene oxide oleate

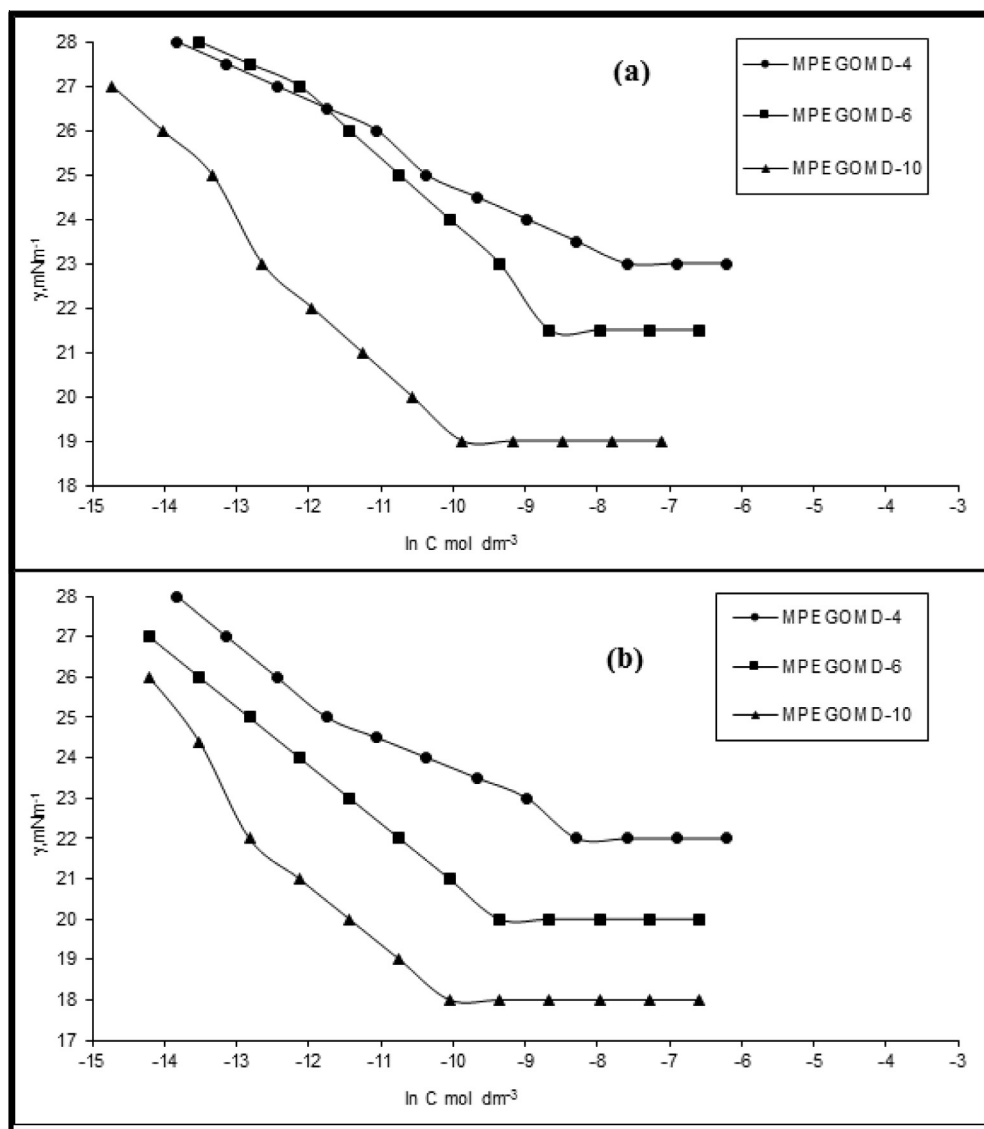


Figure 9 $\gamma - \ln C$ isotherm for ED1, ED2, ED3 at different temperatures (a) 25 °C (b) 60 °C.

methacrylate diester (EM1) (M.wt. 430) and (c) macro polyethylene oxide oleate methacrylate diester (ED1) (M.wt. 430). On the first stage, weight losses related to the physically adsorbed and fractional hydrogen-bonded water, which could not be removed completely by drying. The percent of weight loss at near 140 °C. The polyethylene oxide oleate (EO1) (M.wt. 430) undergoes thermal degradation beginning at 200 °C and with a total mass loss of 20.0%. There is an amount of inert remaining (80%). While Polyethylene oxide oleate methacrylate diester (EM1) (M.wt. 430) undergoes thermal degradation at 250 °C with a total loss of 10% and the remaining weight is 90%. The most stable one was macro polyethylene oxide oleate methacrylate diester (EM1) (M.wt. 430) which degraded by 4% at 300 °C and the remaining mass amount was 96%.

The TGA data in (Fig. 8) for (a) polypropylene oxide oleate (PO1) (M.wt. 425) (b) polypropylene oxides oleate methacrylate diester (PM1) (M.wt. 425) (c) macropolypropylene oxides oleate methacrylate diester (PD1) (M.wt. 425).

Fig. 8 shows that the thermal stability was ranked as; macropolypropylene oxide oleate methacrylate diester (PD1) (M.wt. 425) then polypropylene oxide oleate methacrylate diester (PM1) (M.wt. 425) and finally polypropylene oxide oleate (PO1) (M.wt. 425) and their total loss was 4%, 8% and 18% respectively at 250 °C.

3.2. Surface tension parameters

Micelles of surfactants are formed in bulk non-aqueous solution above a given concentration for each surfactant and this concentration is known as the critical micelle concentration (CMC). The CMC of the investigated individual surfactants at 25 and 60 °C was determined by plotting the surface tension (γ) versus logarithm surfactant concentration ($-\ln C$), as shown in Figs. 9 and 10 for ED1, ED2, ED3, PD1, PD2 and PD3 and the surface tension parameters were calculated and recorded in Table 3. It is evident that the general trend is a continuous decrease in CMC with the increase in the number of

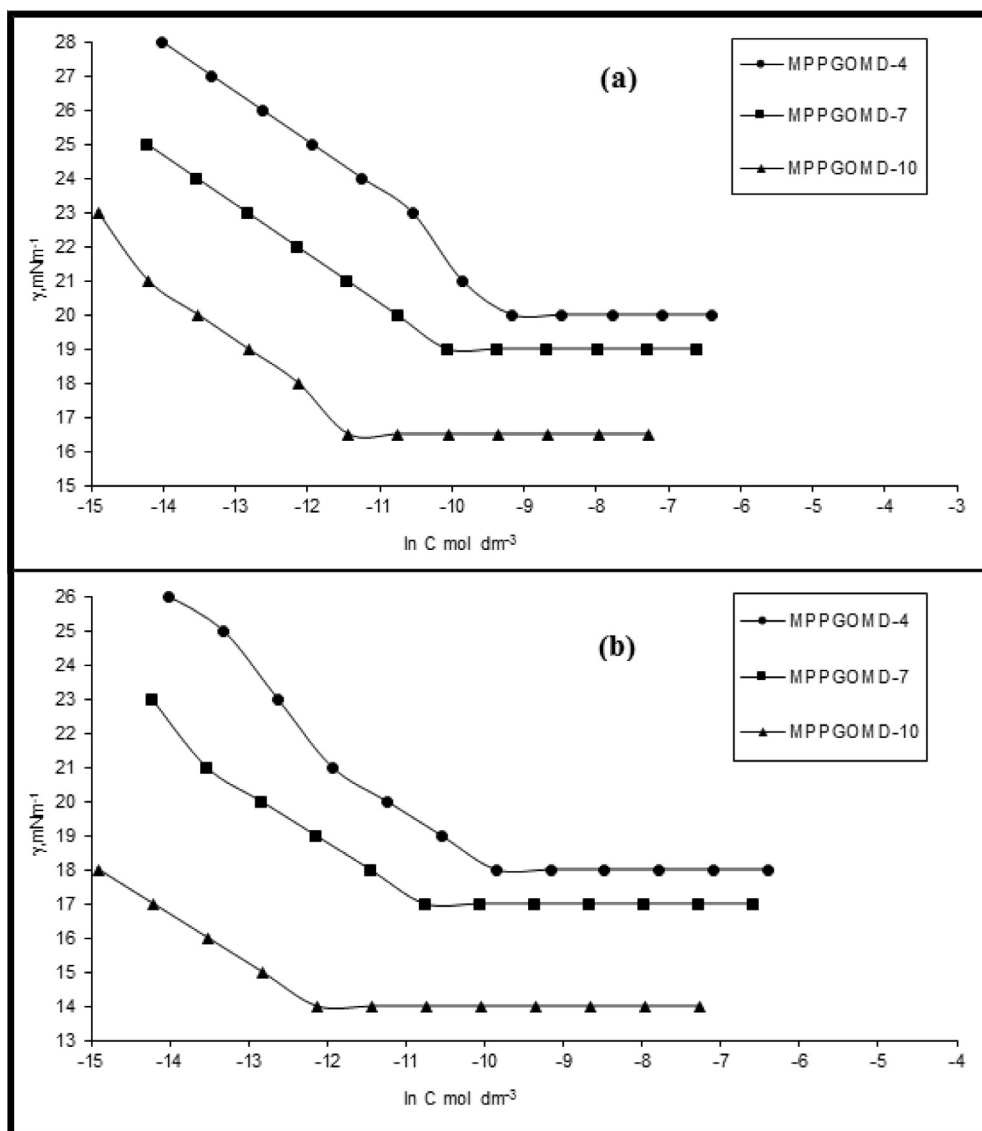


Figure 10 γ – $\ln C$ isotherm for PD1, PD2, PD3 at different temperatures (a) 25 °C (b) 60 °C.

Table 3 Surface active and thermodynamic parameters of ED1, ED2, ED3, PD1, PD2, and PD3 at different temperatures.

Demulsifier	Temp.	CMC (mol/dm)	γ (mN/m)	Γ (mol/m)	A_{\min}	Π_{CM} (mN/m)	ΔG_{mic} (kJ/mol)	ΔG_{Ads} (kJ/mol)
ED1	25 °C	5.11×10^{-4}	23	4.9×10^{-4}	571.8	5	-19.09	-20.81
	60 °C	1.27×10^{-4}	22	4.1×10^{-4}	402.16	6	-22.59	-24.04
ED2	25 °C	1.73×10^{-4}	21.5	4.37×10^{-4}	379.6	6.5	-21.81	-23.30
	60 °C	8.70×10^{-5}	20	3.92×10^{-4}	423.33	8	-23.55	-25.59
ED3	25 °C	5.22×10^{-5}	19	4.45×10^{-4}	373.4	9	-24.83	-26.86
	60 °C	2.59×10^{-5}	18	3.91×10^{-4}	424.19	10	-26.6	-29.15
PD1	25 °C	1.05×10^{-4}	20	4.64×10^{-4}	357.5	8	-24.93	-26.39
	60 °C	5.27×10^{-5}	18	4.1×10^{-4}	402.2	10	-27.37	-29.20
PD2	25 °C	4.28×10^{-5}	19	3.49×10^{-4}	475.28	9	-28.06	-29.70
	60 °C	2.12×10^{-5}	17	2.7×10^{-4}	609.7	11	-31.28	-33.29
PD3	25 °C	1.09×10^{-5}	16.5	3.05×10^{-4}	543.18	11.5	-32.69	-34.79
	60 °C	5.45×10^{-6}	14	1.8×10^{-4}	921.3	14	-38.43	-40.99

ethyleneoxide units and hydrophilic lyophilic balance (HLB) for the prepared surfactant. This behavior may be due to a coiling of the polyethylene oxide chains attributed to decrease in the solubility of the ethoxylated surfactants. An increase in the temperature from 25 to 60 °C leads to a decrease in the CMC for the ethoxylated and propoxylated surfactants.

Table 3 indicates that the CMC decreases with the rise in temperature. The values of Γ and A_{\min} are calculated and listed in Table 3:

$$\Gamma = -10[1/RT][d\gamma/d\ln C] \quad (1)$$

where (Γ_{\max}) is called surface excess concentration of surfactant (mol/cm), R is the gas constant ($R = 8.314 \text{ J/mol K}$), T is the temperature in K, γ is the surface or interfacial tension (mN/m) and C is the concentration of surfactant (mol).

$$A_{\min} = 10^{16}/[\Gamma_{\max} \cdot N] \quad (2)$$

where, A_{\min} is the surface area per molecule of solvent in square nanometers (nm), and N is Avogadro's number.

In Table 3 it is evident that, the A_{\min} is not related to the number of ethylene oxide and propylene oxide units. However, it is evident that A_{\min} increases with an increase in the temperature, this is probably due to the increase of thermal motion. This may be attributed to the increase of the hydrophilic units in the compound which leads to an increase of the surface area occupied by the surfactant molecules. The effectiveness of surface tension reduction $\Pi_{\text{CMC}} (= \gamma_o - \gamma_{\text{CMC}}$, where γ_o is the surface tension of solvent without surfactant and γ_{CMC} is the surface tension of the solvent with surfactant at CMC) was measured at CMC [16]. The propoxylated and ethoxylated compounds exhibited great surface tension reduction and this behavior is shown from the data of Π_{CMC} in Table 3. The Π_{CMC} continuously increases with the rise in temperature. The result of thermodynamic parameters of micellization expressed by the standard Gibbs-free energy, ΔG_{mic} , (micellization) and ΔG_{ad} (adsorption), of the surfactant is listed in Table 3:

$$\Delta G_{\text{min}} = R T \ln \text{CMC} \quad (3)$$

where, R is the gas constant, T , absolute temperature, and α is the fraction of counter ions bound by the micelle in case of ionic surfactants ($\alpha = 0$ for nonionic surfactant).

The thermodynamic free energy of adsorption ΔG was calculated from the following equation:

$$\Delta G_{\text{ad}} = \Delta G_{\text{mic}} - [0.6022 \times \Pi \times A] \quad (4)$$

Since ($\Delta G < 0$) means that the micellization is a spontaneous process, the ΔG_{mic} negative values are greater than ΔG_{Ads} , indicating that the surfactant preferred to adsorb on the interface than to form micelle in the bulk of solvent. Since the adsorption on the interface is associated with a decrease in the free energy of the system there is a direct relationship between the efficiency of surfactants and the values of ΔG_{ad} . The obtained results giving us a good opportunity for future work to evaluate these polymers in the field of water separation from water in oil emulsion at severe conditions.

4. Conclusion

Polymeric surfactants have been prepared from a macro monomer diester, their chemical structures have been confirmed and

justified by $^1\text{H-NMR}$, IR and the molecular weights for polymer were determined by GPC.

The thermal gravimetric analysis (TGA) was performed to study the thermal stability of the prepared polymers and it was found that, these materials have high thermal stability which leads to the possibility to be used under severe reservoir conditions as surfactants.

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