SURFACE ACTIVITY OF AMPHIPHILIC 2-ACRYLAMIDO-2-METHYLPROPANE SULFONIC ACID - CO-N-ISOPROPYL ACRYLAMIDE NANOPARTICLES IN AQUEOUS AND NON-AQUEOUS MEDIA

By

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Points of interest

1. Amphiphilic nanoparticles are target of the future.

2. Aim of the Work

3- Scheme of the Work

4- Characterization of the nanoparticles

5- Surface Properties of the nanoparticles

6- Conclusions and Recommendation.

Emulsion Stabilizers

- The majority of studies on emulsion, foam, miniemulsion and dispersion polymerisation systems have been limited to systems containing water and an oil.

- The scarcity of information regarding non-aqueous and non-oil containing emulsions is unfortunate because many unique and useful properties may be found among such systems.

- Non-aqueous emulsions may have potential applications in painting, pharmaceutical or cosmetic areas.

- The major challenge for preparing stable non-aqueous emulsions was to find a suitable stabiliser which is selectively soluble in either of the immiscible oil phases.

Design of special stabilisers

- Mostly high concentration (20-30 %) of molecular weight amphiphilic block copolymers of poly(isoprene)-block-poly(methyl methacrylate), for each couple of oils which was considered as a drawback for this approach.

- Recently, solid particles alone have been used as emulsifiers for aqueous emulsions.

L-I. Atanase, G. Riess, Polym. Int. 2011, 60, 1563–1573

Amphiphilic nanoparticles are target of the future.

- It is used to control particle size,
- Excellent surface properties
- Protecting drugs from degradation,

targeting to site of action and reduction toxicity or side effects,

- They help to increase the stability of drugs/proteins and possess useful controlled release properties.

Even though the emulsifying properties of these solid particles have been recognized for more than a century, it is only recently that the precise role of the solid particles has begun to be elucidated in surfactant-free systems.

Aim of the work

It is expected that the solid particles based on poly(N-isopropylacrylamide) (PNIPAM) will be a promising candidate as an emulsifier for nonaqueous emulsions.

It is widely recognized that amphiphilic block copolymers consisting of a PNIPAM segment and a hydrophobic segment can form a core–shell micellar structure.

This article aims to prepare nanogel on the basis crosslinked N-isopropylacrylamide NIPAm and 2-acrylamido-2-methylpropane sulfonic acid (AMPS) copolymers using modified technique based on nonaqueous emulsion polymerization in the presence of a modified reactive surfactant.

The surface adsorption state and surface adsorbed layer of the amphiphilic nanogels were also discussed.

Challenges

The present work is the first report to discuss the ability of nanogels to reduce the surface and interfacial tensions (IFTs) of organic solvents to unprecedented values..

Moreover, we extended the current work to use the synthesized nanogels as stabilizers to prepare crosslinked AMPS/styrene (St) copolymers on the basis of nonaqueous emulsion polymerization technique.

We introduce here novel kinetically stable microgel-stabilised non-aqueous oil-in-oil (o/o) emulsions.

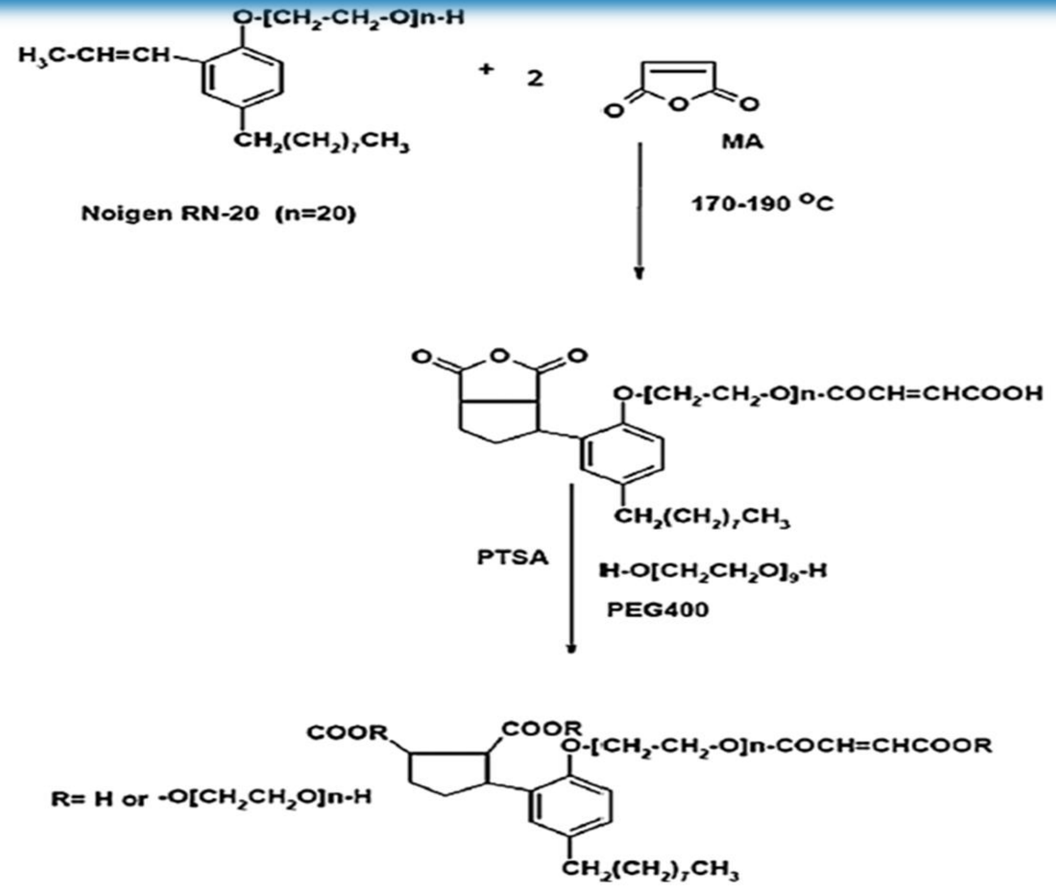
Scheme of the work

- **A new bifunctional reactive surfactant was first prepared by reacting polyoxyethylene 4-nonyl -2-propylene-phenol nonionic reactive surfactant (Noigen RN20) with maleic anhydride followed by esterification with poly (ethylene) glycol***

- ***Ayman M. Atta, Amro K.F. Dyab and Hamad A. Al-Lohedan, J. Surfact. Deterg., 2013, 16, 343.***
- ***Ayman M Atta, POLYMER INTERNATIONAL, Article first published online : 24 MAY 2013, DOI: 10.1002/pi.4537***

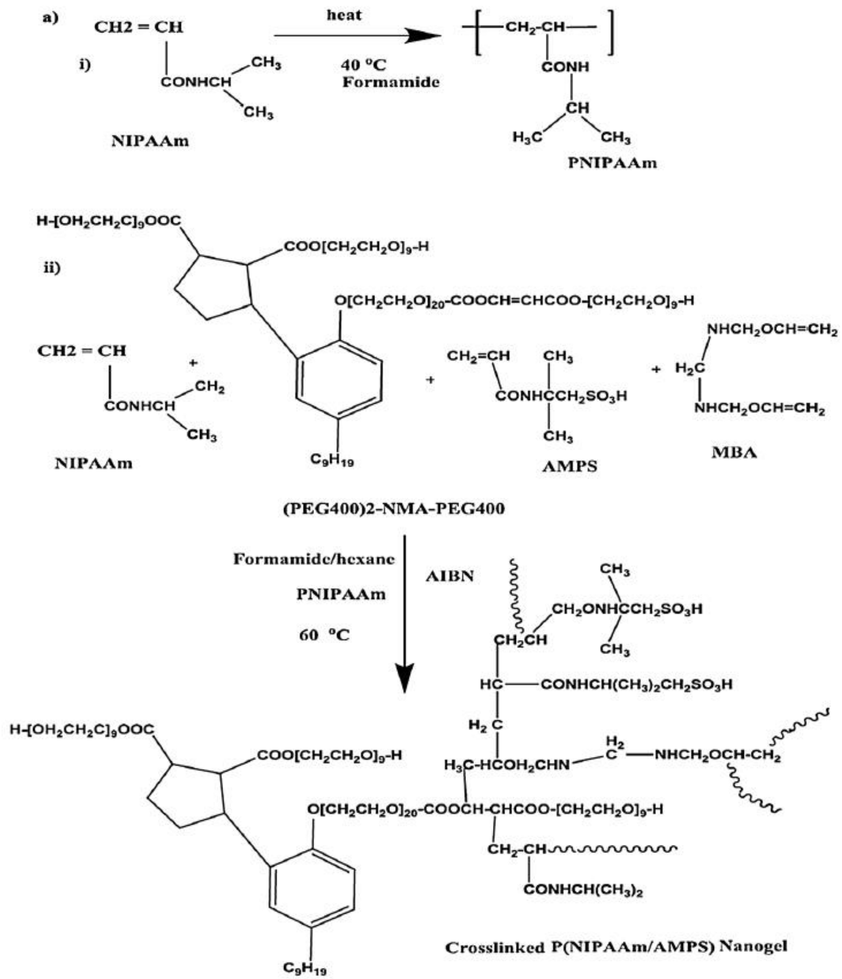
The amphiphilic microgel particles were synthesised in organic solvents with varying degree of mole percentage of the NIPAM and AMPS monomers (90:10, 95:5 and 98:2 mole %).

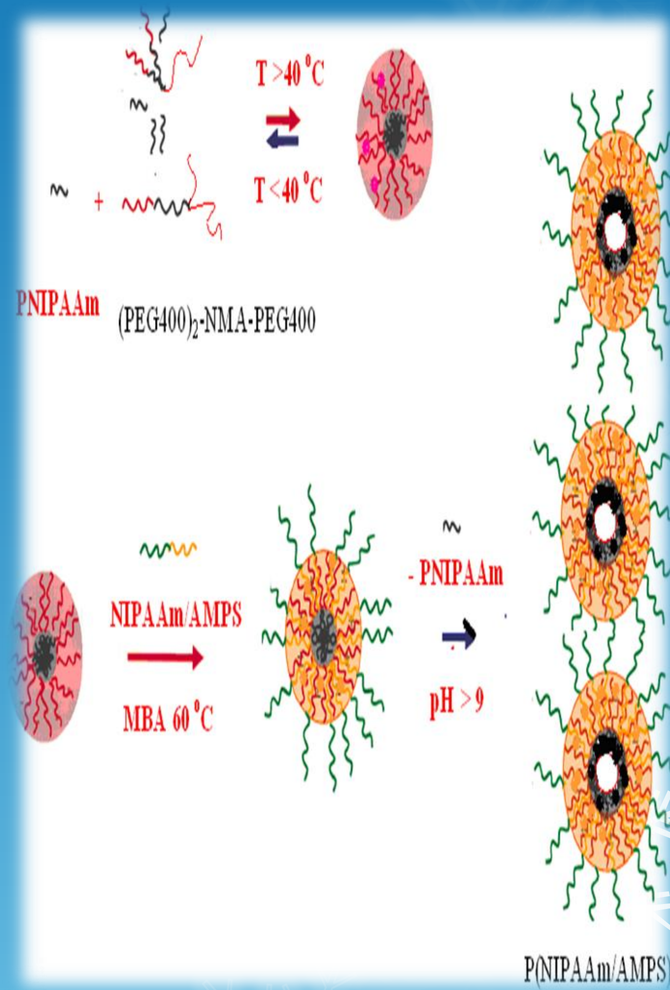
Scheme of synthesis bifunctional reactive surfactant



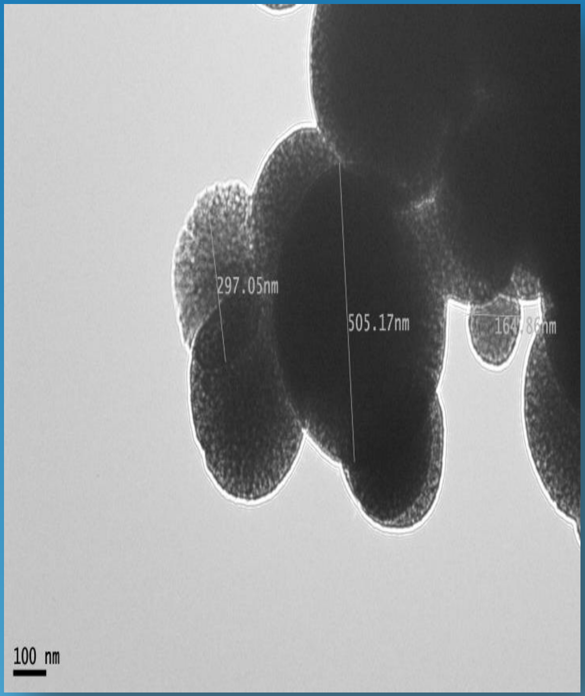
Scheme 1. Synthesis of NMA20- (PEG 400)$_3$.

Scheme of synthesis nanogel

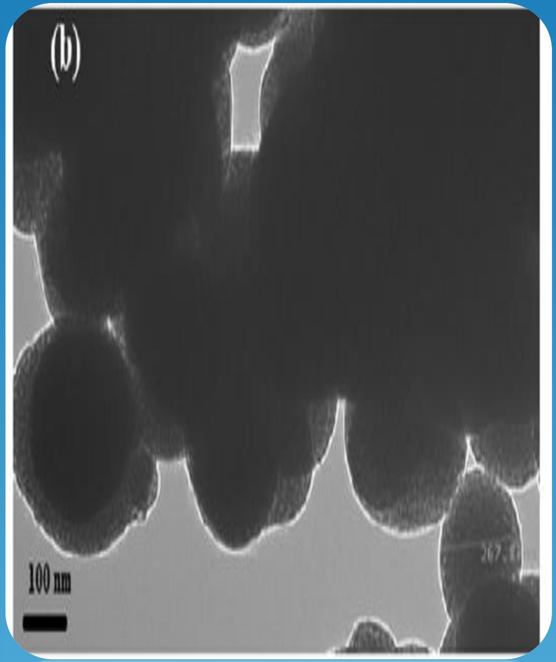




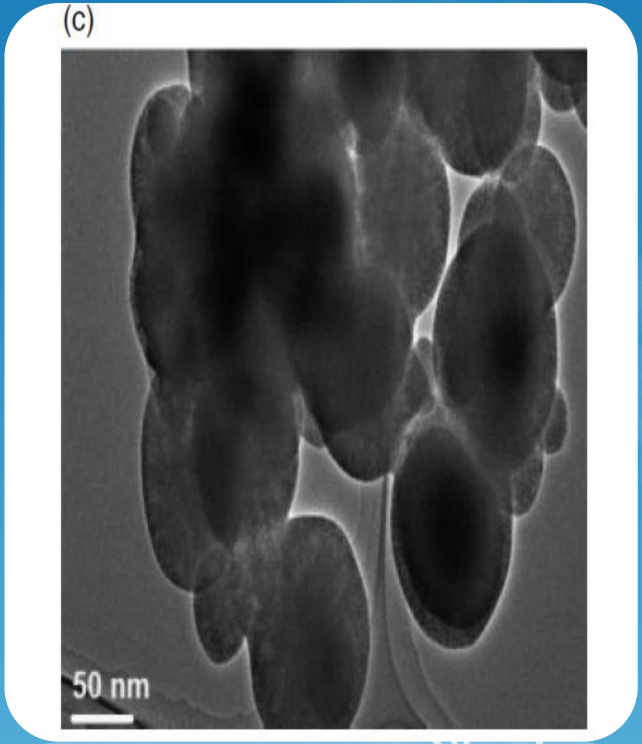
TEM image (NIPAM/AMPS) microgels



90:10 mole %
(NIPAM/AMPS)
microgels

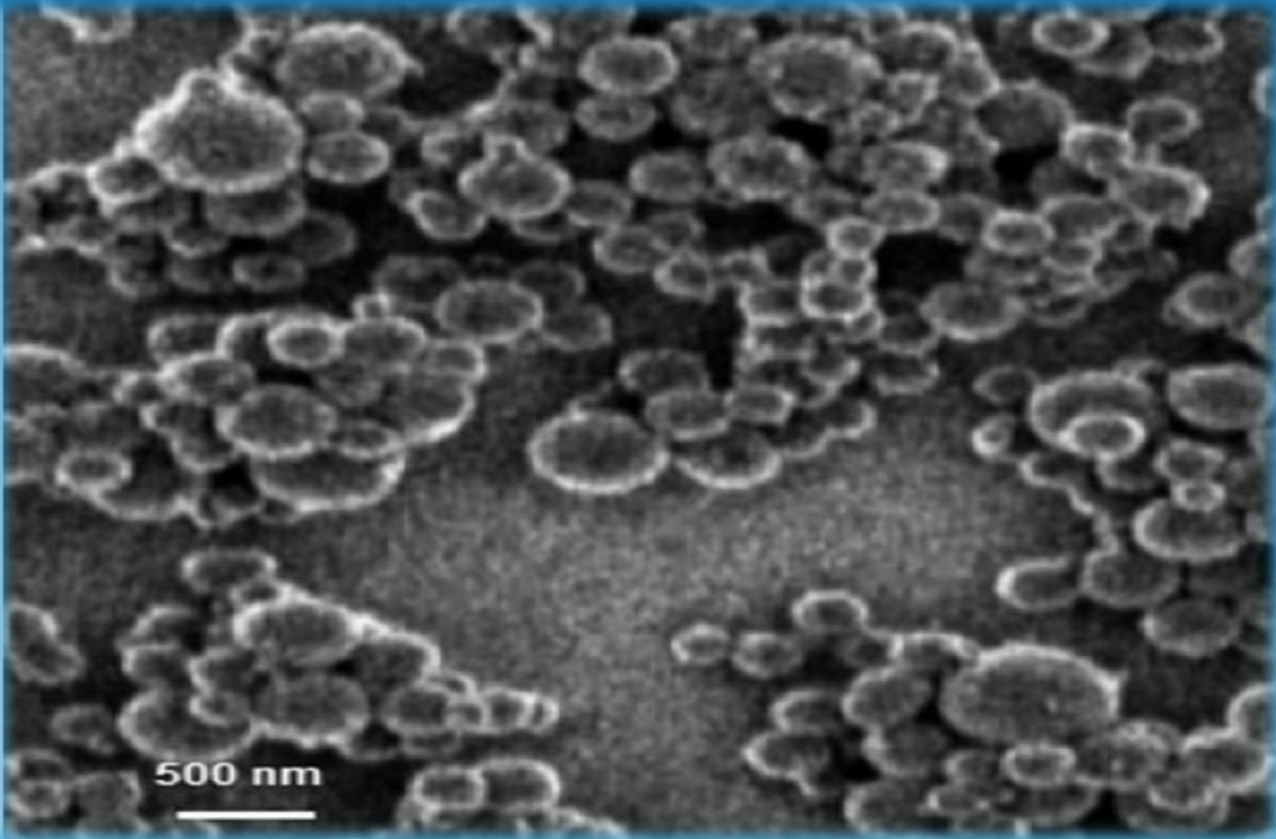


95:5 mole %
(NIPAM/AMPS)
microgels



98 : 2 mole %
(NIPAM/AMPS)
Nanogels

SEM image (NIPAM/AMPS) microgels



90:10 mole % (NIPAM/AMPS) microgels

Surface tension of (NIPAM/AMPS) in water

Table 2. Surface properties of NIPAm/AMPS nanogels at various temperatures

NIPAm/AMPS (mol%)	Temperature (°C)	cac (mol L^{-1})	γ_{cac} (mN m^{-1})	γ (mN m^{-1})	$(-\partial\gamma/\partial \ln c)$	Γ_{max} (x 10^{10} mol cm^{-2})	A_{min} (nm^2 per molecule)
90/10	298	0.012	37.2	35.0	4.03	1.62	0.102
	313	0.007	35.8	33.1	4.58	1.68	0.096
95/5	298	0.009	34.2	28.0	5.03	2.03	0.082
	313	0.005	32.8	36.1	5.46	2.07	0.080
98/2	298	0.006	30.1	43.1	5.8	2.26	0.069
	313	0.003	33.4	35.4	5.4	2.18	0.076

Surface tension of (NIPAM/AMPS) in water

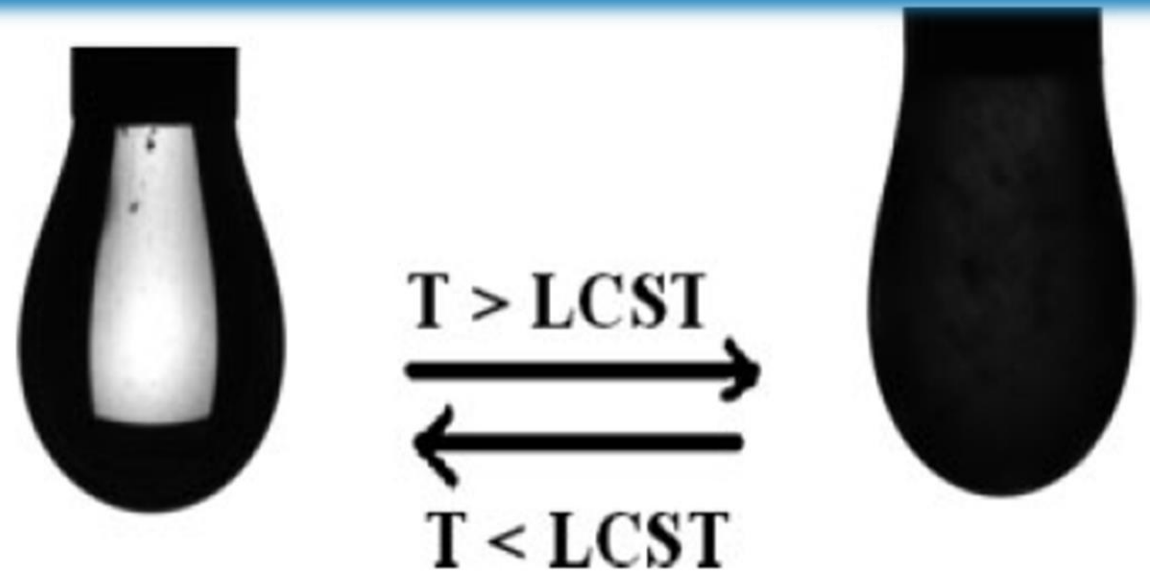


Figure 7. Effect of temperature on drop opacity of (0.175 mol L^{-1}) NIPAm/AMPS (98/2 mol%) nanogel.

Surface tension of (NIPAM/AMPS) in formamide

Table 1. Surface properties of the NMA20-(PEG400)$_3$-P(NIPAm/AMPS) nanogels in formamide at different temperatures

Designation NIPAm/AMPS	Temperature °C)	cac mol/L	γ_{cac} mN/m	$(-\partial\gamma/\partial \ln c)$	$\Gamma_{max} \times 10^{10}$ mol/cm^2	A_{min} nm^2/molecule
90/10	25	0.14	33.2	2.9	1.16	0.143
	35	0.10	36.1	4.1	1.59	0.104
	45	0.08	38.8	4.6	1.73	0.096
95/5	25	0.10	31.2	5.1	2.05	0.082
	35	0.08	33.5	5.4	2.18	0.076
	45	0.04	35.8	5.8	2.26	0.069
98/2	25	0.08	38.1	4.6	1.85	0.096
	35	0.03	39.4	4.2	1.64	0.101
	45	0.01	40.7	3.9	1.48	0.112

cac, critical aggregation concentrations; NIPAm/AMPS, N-isopropylacrylamide/2-acrylamido-2-methylpropane sulfonic acid.

Surface tension of (NIPAM/AMPS) in formamide

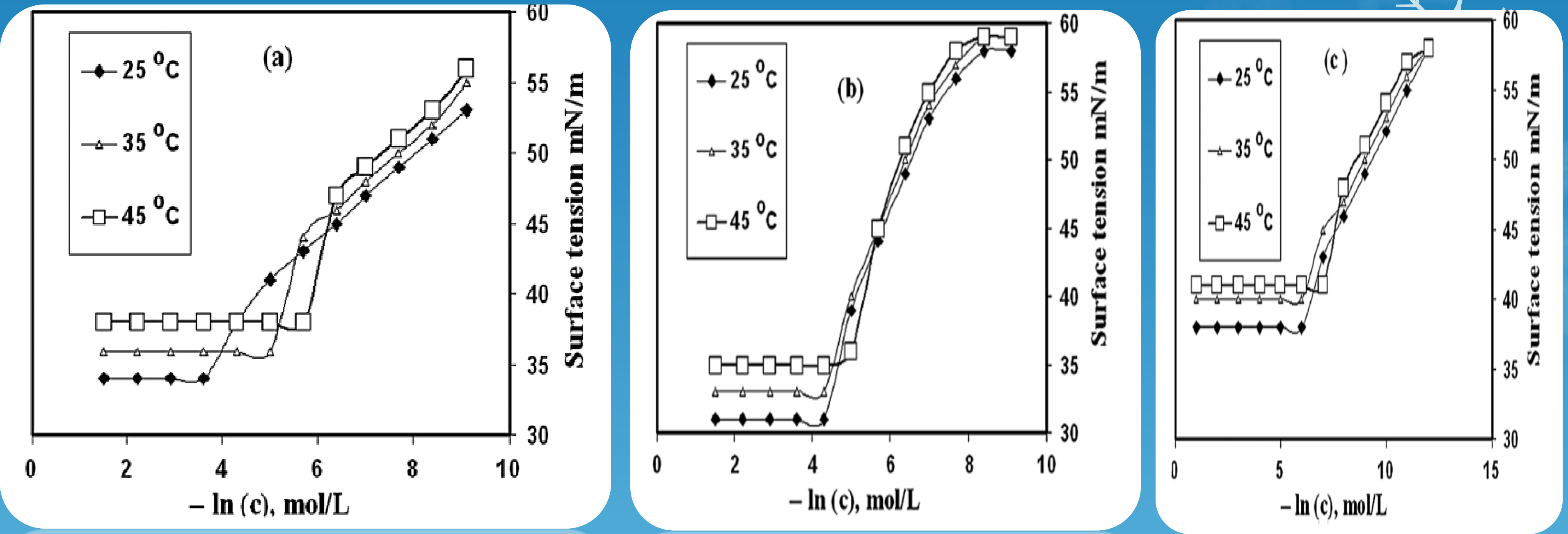
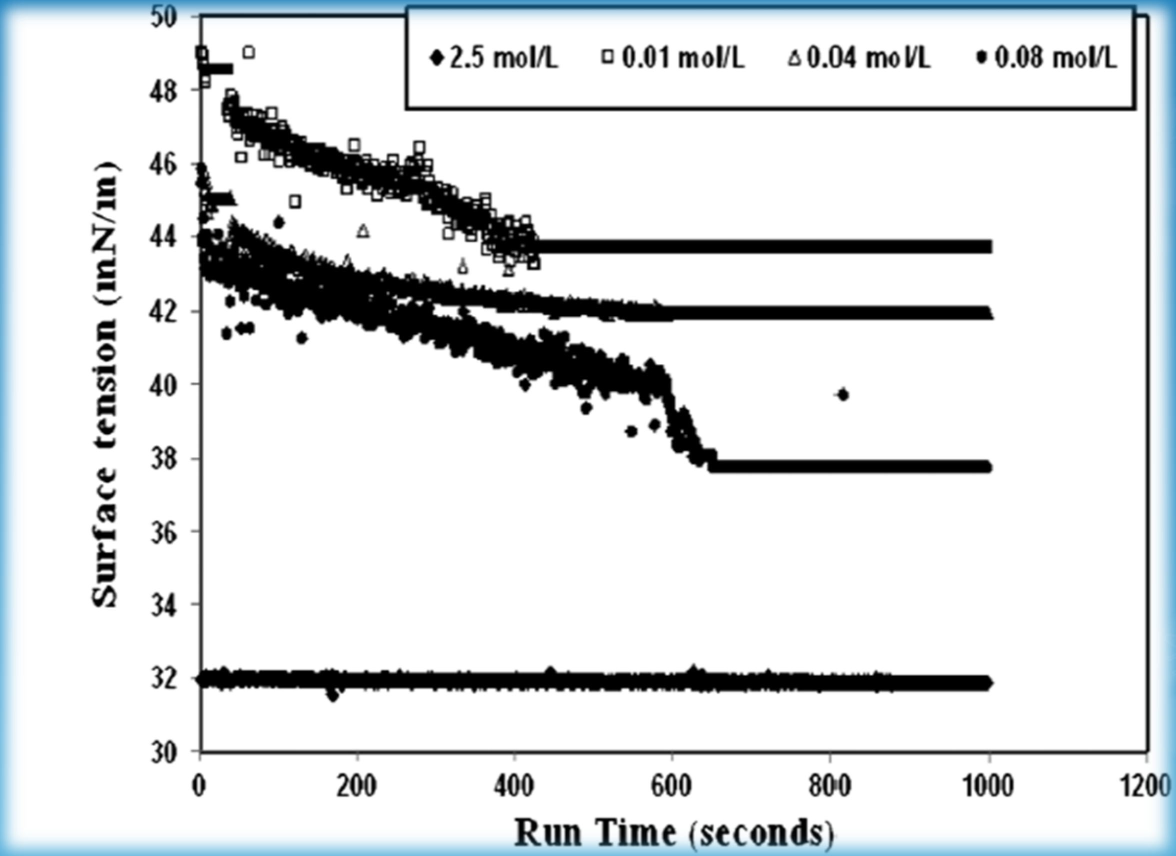


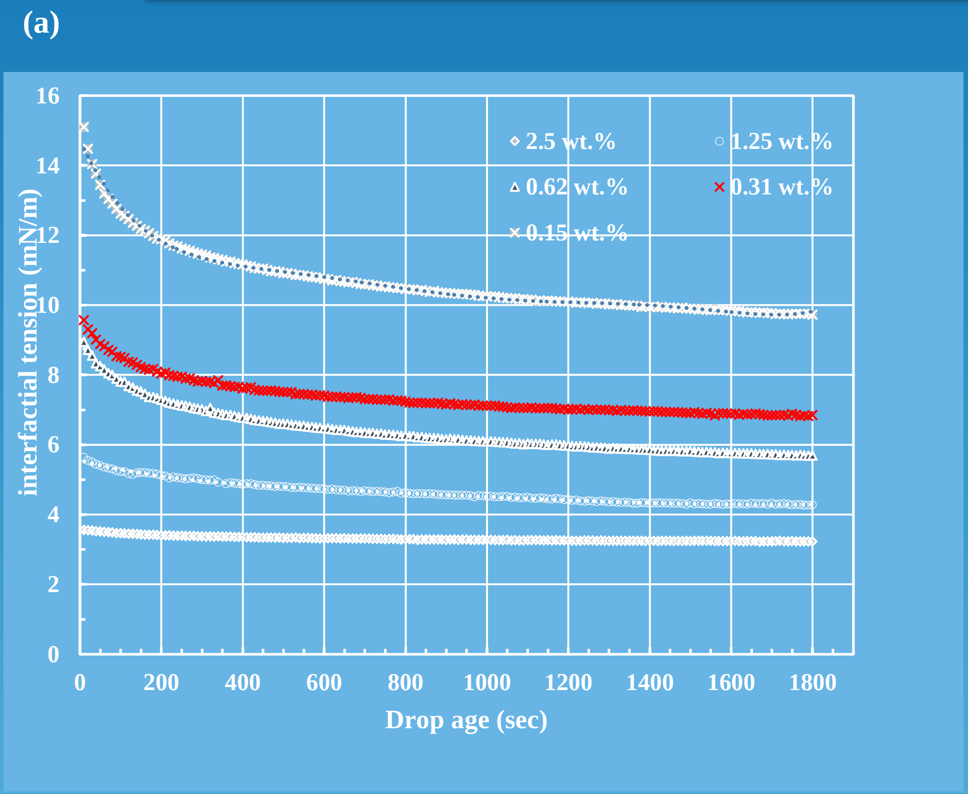
Figure 4. Adsorption isothems of NMA20-(PEG400)3-P(NIPAm/2-acrylamido-2-methylpropane sulfonic acid) (a)90/10, (b) 95/5, and (c) 98/2 mol% nanogels at different temperatures.

Surface tension of (NIPAM/AMPS) in formamide



90:10 mole % (NIPAM/AMPS) microgels

Interfacial tension (IFT)



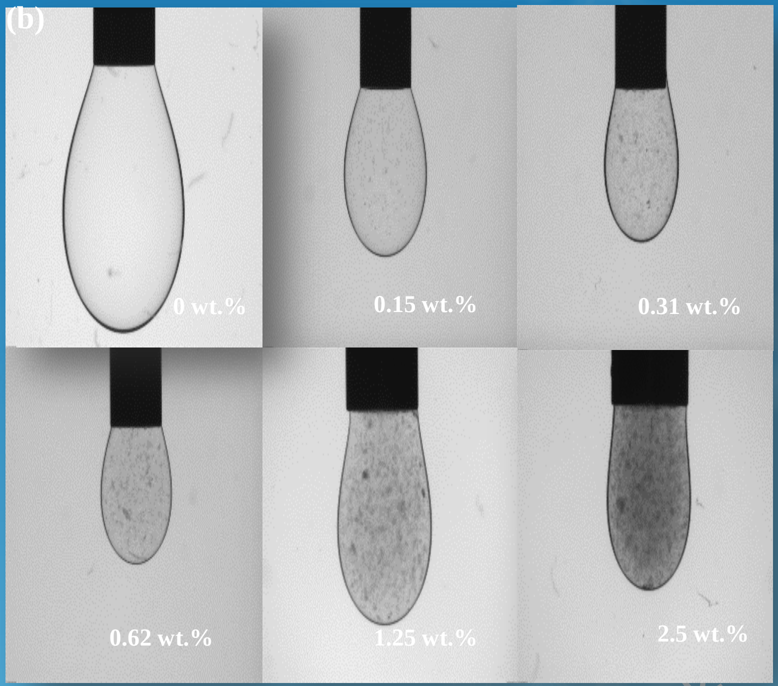
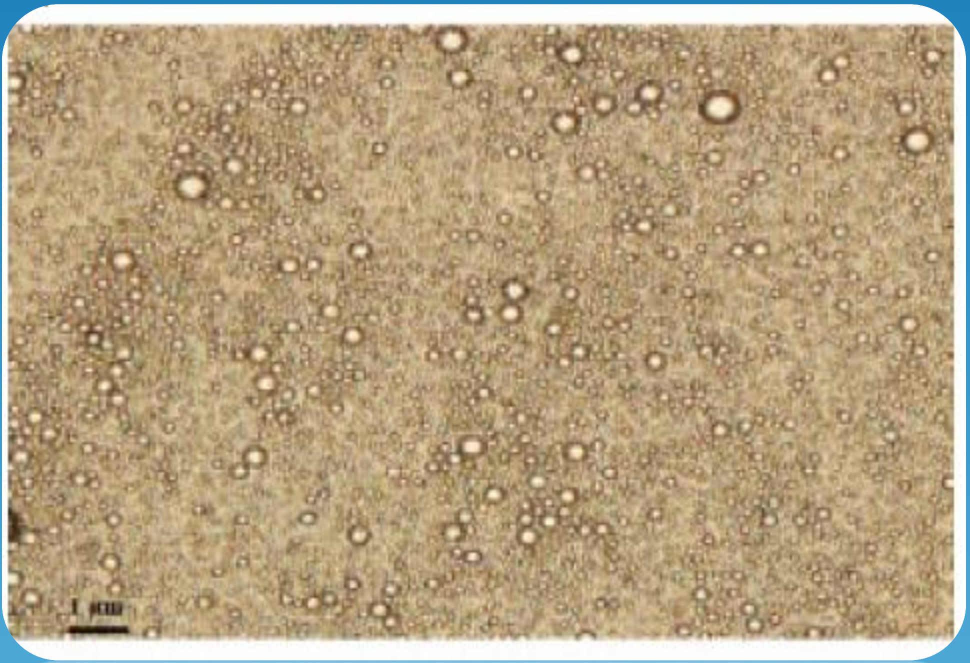


Fig. (a) Dynamic interfacial tension of 90/10 (NIPAM/AMPS) microgels at formamide-paraffin oil interface. (b) Evolution of pendant drop profile and interfacial coverage of a formamide drop in paraffin oil as a function of microgel concentrations in formamide as in (a) in (wt.% given) after equilibrium.

Emulsion stability between water and styrene

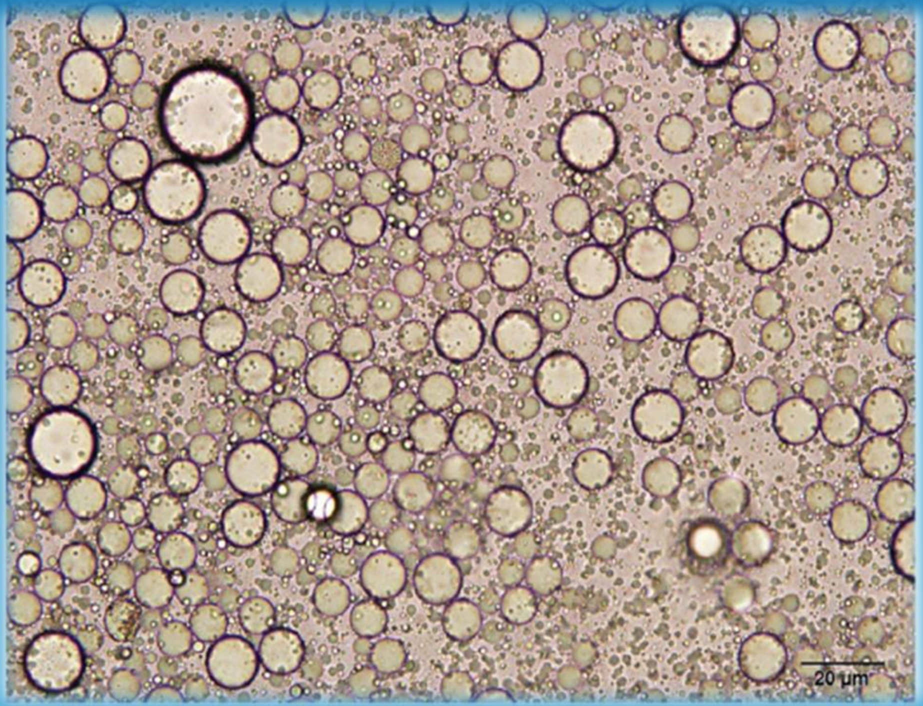


Optical microscope image 90:10 mole % (NIPAM/AMPS) microgels

Table 3. Interfacial tension (IFT) and equilibrium time for NIPAm/AMPS nanogels at 298 K

NIPAm/AMPS (mol%)	Concentration (mol L^{-1})	IFT (mN m^{-1})	Time (min)
90/10	0.160	3.8	10
	0.080	4.5	15
	0.040	4.8	18
	0.004	5.1	20
95/5	0.160	1.2	5
	0.080	1.8	8
	0.040	2.1	10
	0.004	2.8	12
98/2	0.160	2.5	7
	0.080	2.9	10
	0.040	3.2	12
	0.004	3.6	15

Emulsion stability between formamide and styrene



Optical microscope image 95:5 mole % (NIPAM/AMPS) microgels

Table 2. Interfacial tension characteristics and equilibrium time of the NMA20-$(PEG400)_3$ P(NIPAm/AMPS)nanogels at 25°C

Designation NIPAm/AMPS	Concentration (mol/L)	IFT mN/m	Time (minute)
90/10	0.160	0.98	10
	0.080	1.1	15
	0.040	1.2	18
	0.004	1.3	20
95/5	0.160	0.12	5
	0.080	0.18	8
	0.040	0.21	10
	0.004	0.25	12
98/2	0.160	1.54	7
	0.08	1.97	10
	0.040	2.23	12
	0.004	3.8	15

IFT, interfacial tension; NIPAm/AMPS, N-isopropylacrylamide/2-acrylamido-2-methylpropane sulfonic acid.

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Emulsion stability between formamide and Paraffin oil

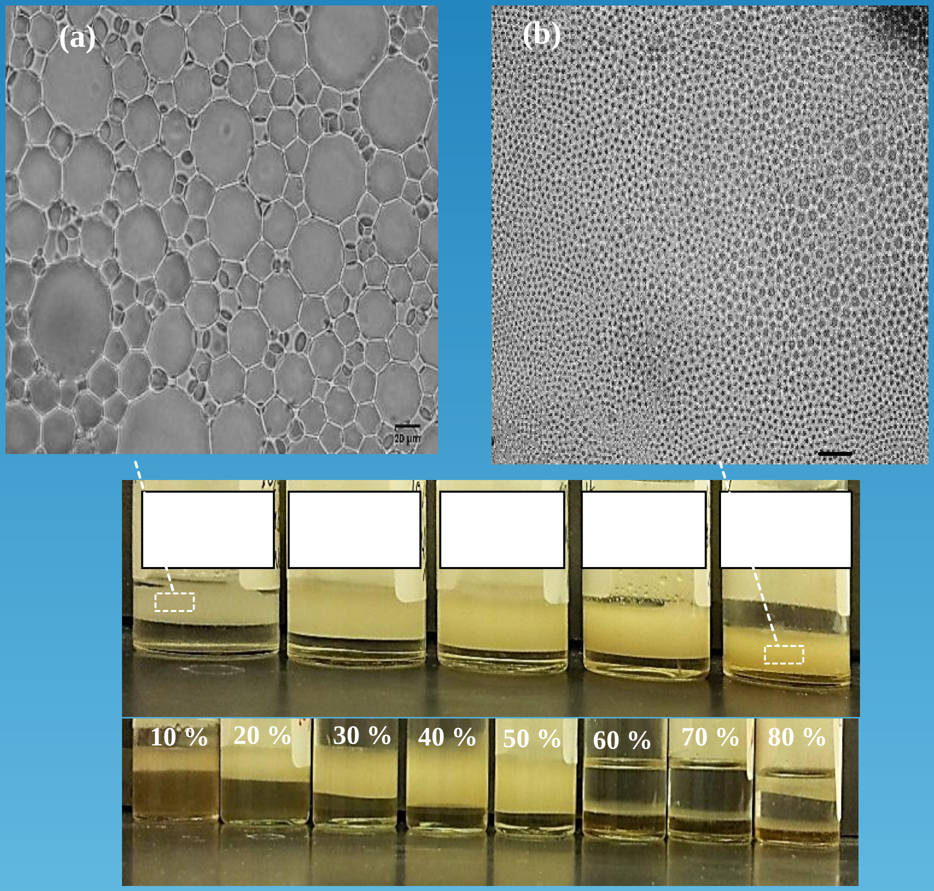
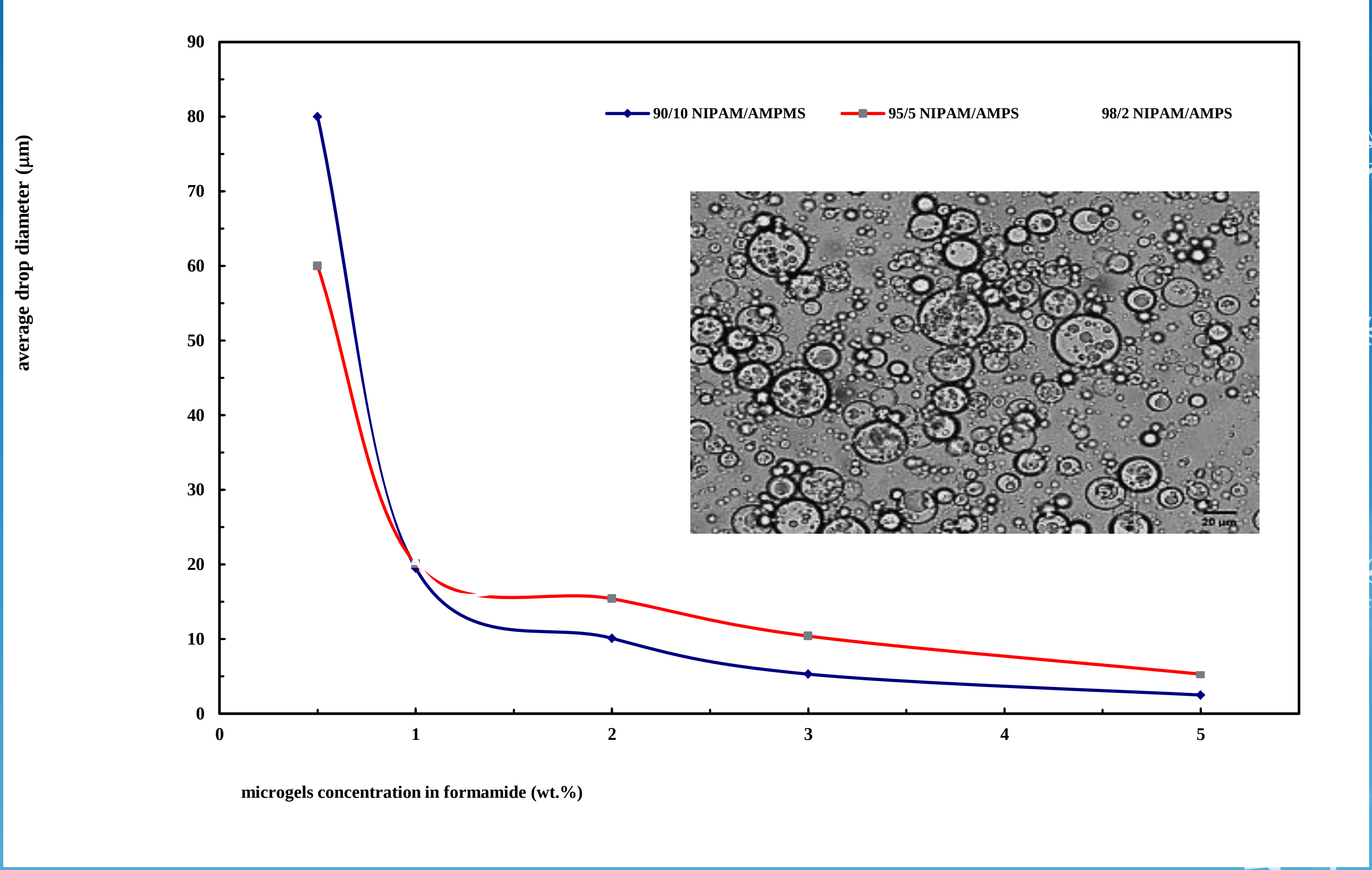


Fig.3 (a-c) optical and digital images for paraffin oil-in-formamide (o/o) emulsions as a function of 90/10 (NIPAM/AMPS) microgel concentrations in formamide (in wt.% given). (d) Digital images of the same emulsions as a function of formamide volume fraction (f_{fa}) at fixed microgel concentration of 2 wt.% in formamide



Evolution of sizes of paraffin oil drops in paraffin oil-in-formamide emulsions as a function of microgel concentrations in formamide using different molar ratio of NIPAM/AMPS.

conclusions

1. we have prepared poly(NIPAM-*co*-AMPS) microgels functionalised with nonionic polymerisable surfactant in non-aqueous media at different monomers molar ratio.
2. These particles showed an obvious core–shell structure with a black core and surrounding shadows, indicating that the nanogels might have an inhomogeneous crosslink density.
3. The data of surface activity of nanogels in FA indicated that (95/5mol%) has uniform network and smaller particle size, which are able to adsorb at interface, and has the ability to reduce the surface tension more than NIPAm/AMPS (90/10mol%) nanogels.

conclusions

4. The data of surface activity indicated the surface tension increased with increasing the temperature for NMA20-(PEG400)3-P(NIPAm/AMPS) (90/10mol%), (95/5mol%), and (98/2mol%). The NMA20-(PEG400)3-P(NIPAm/AMPS) (95/5mol%) achieved unprecedented value for the reduction of interfactial tension between FA and St.

5. Using these novel soft and porous microgels, we are able to prepare storage stable non-aqueous emulsions for the first time which show excellent stability against temperature up to 80 C unlike water based emulsions.

6. These microgel particles greatly reduced both surface and interfacial tensions of both aqueous and non aqueous solvents.

Acknowledgment

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