

NOVEL ONE POT SYNTHESIS OF N-ALKYL ACRYLAMIDE POLYMERS AS MINERAL SCALE INHIBITORS IN WATER COOLING SYSTEM: PART-I

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ABSTRACT: Novel one pot synthesis of low molecular weight n-alkyl acrylamide homopolymers by solution polymerization have shown usefulness as an efficient scale inhibitor. Solution polymerization of n-alkyl acrylamide monomer with BPO (7.5 mol %) as an initiator resulted in 85 – 90 % polymer yield. Synthesized n-alkyl acrylamide homopolymers were characterized by using different spectral analysis such as FT-IR, NMR and GPC. The molecular weight of synthesized homopolymers was found to be in range of 1000 – 4500 with polydispersity between 1.0 and 3.0. Spectral data confirms the successful homopolymerization of n-alkyl acrylamide. It also shows that the homopolymers are having a linear structure in which monomers are randomly attached.

KEYWORDS: Novel Homopolymers; Low Molecular Weight, Spectral Analysis; Characterization.

1. INTRODUCTION

During various industrial processes like desalination, reverse osmosis, and water cooling the scale formation or scaling is occurring predominantly. Scales are a prevalent problem in water treatment industry and are unique due to the complexity of its mechanism. These deposits have different mechanical properties depending upon different operational conditions and are termed accordingly. Hard scale, soft scale, powdered scale or sludge scales are terms describing their bond with the adhering surfaces. Scales once formed are very difficult to remove, hence its formation can cause severe technical problems and great economic impact.

During the past two decades, new generation of scale inhibitors have emerged commercially, in which the active ingredients are mostly proprietary mixtures of various molecular weight polycarboxylate, polyphosphate and polyphosphonate. But polyphosphonate experience hydrolytic reaction and self-degradation which results in formation sludge of phosphate at temperature of over 90 °C. Furthermore, the conversion of polyphosphonates to orthophosphate, which is a nutrient for algae and are hazardous when released in environment. The polymerization reaction of many polymers is multi steps synthesis with low yield. But polymers containing amide or amine functional group have been found to be very effective in controlling CaSO₄ and CaCO₃ scale formation. [1-10].

The main objective of this research is to develop such synthetic methods which are cost effective and single step process, giving eco-friendly and efficient scale inhibitors. The ideal molecular weight of the compound to show good scaling inhibition should be in the range of 500 – 6000 [11]. Hence, keeping this factor in mind we have synthesized low molecular weight n – alkyl acrylamide homopolymers with Mw in the range of 500 – 5000 by solution polymerization.

2. EXPERIMENTAL

a) Materials

n – propyl amine (Sigma, 98 %), n – butyl amine (Fluka, 99%), n – hexyl amine (Merck, 98%), acryloyl chloride (Fluka, 96 %) and barium hydroxide (Sigma, 98%) were used as received without any further purification. Benzoyl peroxide (BPO) (Fluka, 97 %) was recrystallized from reagent grade methanol before use. Tetrahydrofuran (Sigma – Aldrich, 99.9%) for spectroscopic analysis was of analytical grade and used as such without further purification.

b) Instruments

A 500 ml zipperclave stirred laboratory reactor from autoclave engineers was used for n – alkyl acrylamide homopolymer synthesis. It could ideally work at a pressure of 2200 psi (151 bar) and temperature 450 °F (232

°C). Molecular weight of n-alkyl acrylamide homopolymers were carried out in waters GPC using three columns styragel HR 0.5, HR 5, and HR 4 (range from 0 to 400000 dalton). Polystyrene was used as a standard for molecular weight analysis. ¹H-NMR spectra and ¹³C-NMR spectra were obtained using a Bruker AM400 NMR spectrometer. Fourier – transform infrared spectroscopy were recorded with Perkin Elmer 16 – PC FT-IR spectrometer using KBr discs.

c) Polymer Synthesis

Low molecular weight n-alkyl acrylamide Homopolymers were synthesized in two steps. Firstly n-alkyl acrylamide monomers were synthesized followed by homopolymerization in o-xylene solvent at 150 °C.

i. General Monomer Synthesis

Substituted n-alkyl amines (n – hexyl amine / n – butyl amine / n – propyl amine) and barium hydroxide (1%) were placed in the flask and stirred until the temperature equilibrated. Acryloyl chloride was added dropwise till the mixture in the reaction vessel becomes thick. The resulting solution was whitish-yellow. The resulting material was recrystallized and stored at 0 °C. Similarly, three monomers were prepared.

- n – Propyl acrylamide monomer (AAP)

After synthesis, this compound was separated by extraction with water and CHCl₃ mixture (1:3) ratio, respectively. An 85% yield was obtained after purification. C₆H₁₁NO: Calculated C 63.68, H 9.8, N 12.38; Found C 62.68, H 10.00, N 12.17.

- n – Butyl acrylamide monomer (AAB)

An 88% yield of light yellow-colored oily compound was obtained after recrystallization with CHCl₃. C₇H₁₃NO: Calculated C 66.10, H 10.30, N 11.01; Found C 66.01, H 10.53, N 11.59.

- n – Hexyl acrylamide monomer (AAH)

A light yellow-colored oily compound was separated after recrystallization with CHCl₃ with a yield of 89%. C₉H₁₇NO: Calculated C 69.63, H 11.04, N 9.02; Found C 69.01, H 11.10, N 9.17.

ii. Homopolymerization of n-Alkyl Acrylamide

n-Hexyl acrylamide homopolymer (AAH), n – Propyl acrylamide homopolymer (AAP) and n – butyl acrylamide homopolymer (AAB) were synthesized by using 0.02 moles of monomer in 100 ml of o-xylene. BPO was used as an initiator at a concentration of 7.5 mole % with respect to the monomer, and reaction mixture was allowed to reach 140 °C temperature. After 10 hours the reaction was stopped, and the synthesized polymer was recrystallized by using appropriate solvent before conducting further spectral analysis and characterization.

3. RESULTS AND DISCUSSION

In order to develop effective scale and corrosion inhibitors for industrial purpose it is necessary that it should be of low molecular weight in range of 500 -5000. Molecular weight of n-alkyl acrylamide determined by GPC is illustrated in Table-1, which is in range of 1000-4500. Structural characterization of three n-alkyl acrylamide homopolymers by ¹H-NMR and ¹³C- NMR spectra have been discussed in detail. The FT-IR spectra of homopolymers shows the adsorption bands for respective functional group present in the synthesized homopolymers.

a) Reaction Mechanism for N – Alkyl Acrylamide Homopolymers (N – AAA) Synthesis

The reaction scheme shown in Fig. 1 can be divided in two parts. Part one is monomer synthesis followed by homo-polymerization. In part one, acryloyl chloride is allowed to react with n – substituted amine (n-butylamine, n-hexylamine, and n-propylamine) in the presence of barium hydroxide, results in n-alkyl acrylamide monomer with the evolution of HCl gas. In second step of homopolymerization, n-alkyl acrylamide monomers are allowed to react in the presence of an initiator BPO, which results in the formation of n – AAA homopolymers. The –R group in homopolymer can be attributed to propyl, butyl, or hexyl amine.

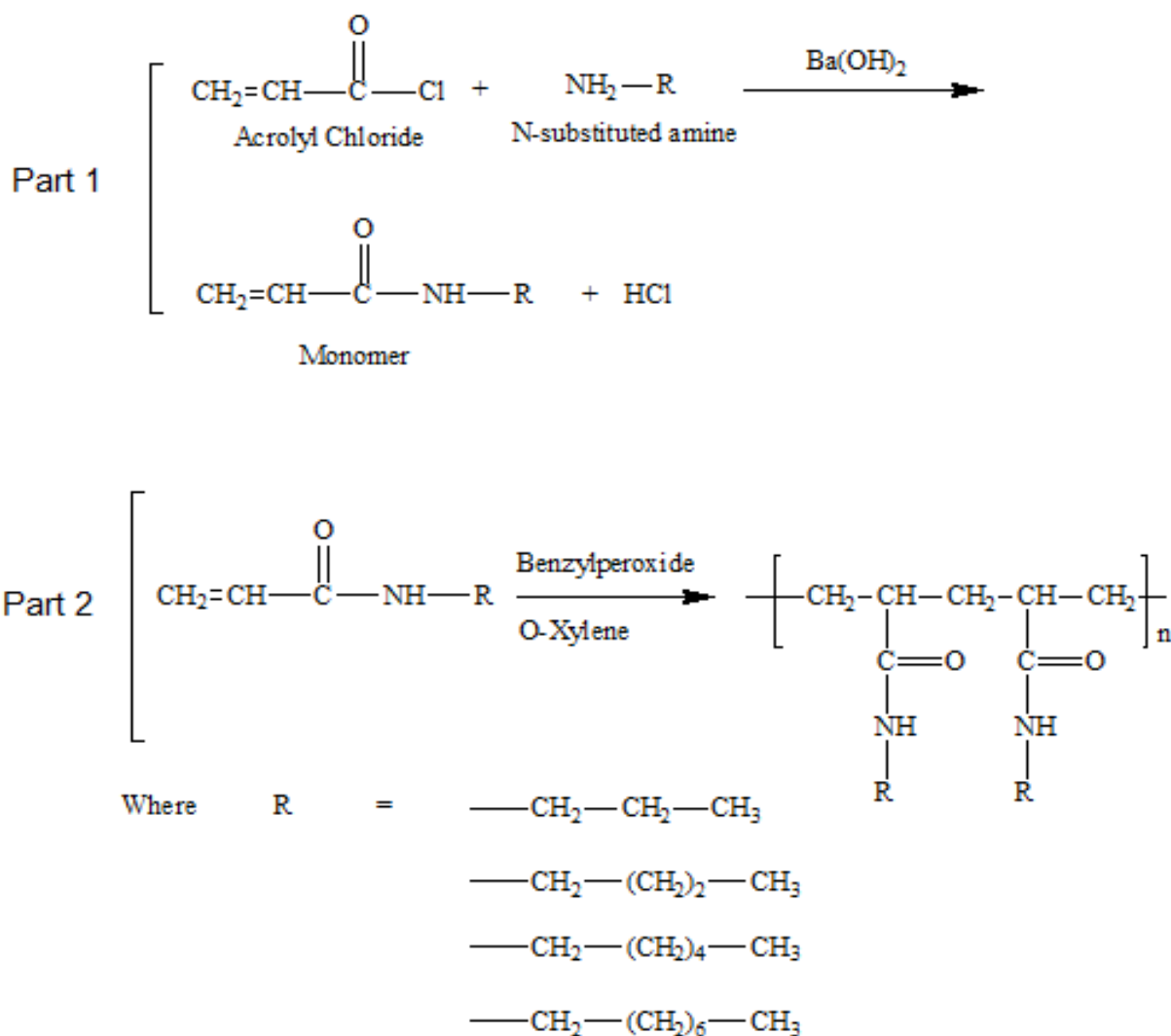


Figure – 1: reaction scheme for n – alkyl acrylamide homopolymers synthesis.

b) Polymer Characterization

Characterization of n-AAA homopolymers was done by nuclear magnetic resonance (¹H – NMR and ¹³C – NMR) and Fourier – transform infrared spectroscopy (FT – IR).

In the proton NMR spectras of n-AAA homopolymers the protons were indexed from “a to i” starting from the benzene ring of BPO radical as given in Fig. 2. Peaks in the region of 0.5 – 1.5 ppm can be assigned to aliphatic protons [H_i – H_h] of the attached hexyl amine group. Peaks between 2 – 4 ppm can be attributed to methylene proton [H_g] near the amide group and methane proton [H_e]. The methylene proton [H_b] near the BPO radical shows peaks in the range of 4 – 5 ppm. At last –NH proton [H_f] show peak near 8 ppm [12-13].

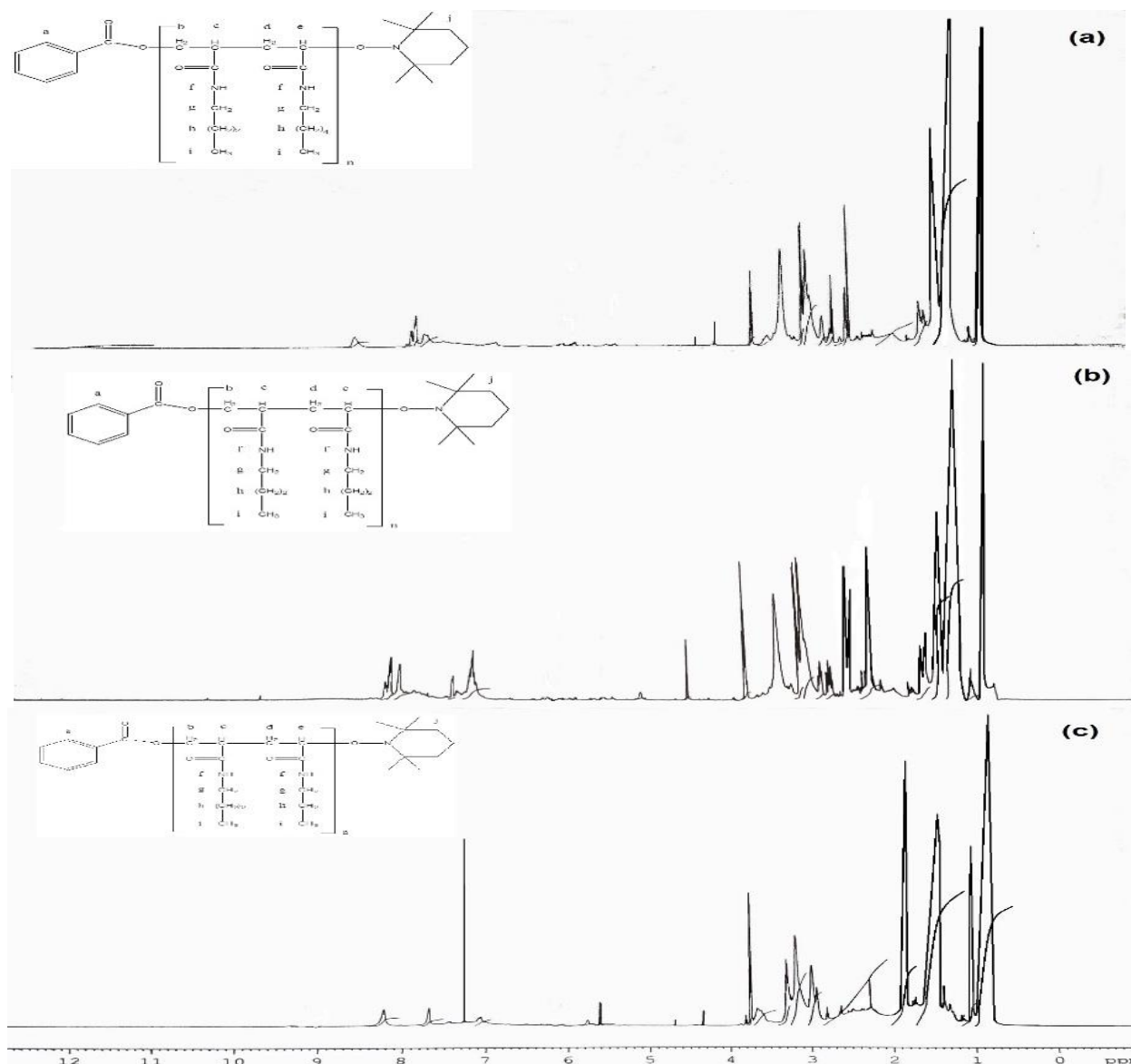


Figure -2 : ^1H – NMR spectroscopy for n – alkyl acrylamide homopolymers, (a) n – hexyl acrylamide (b) n – butyl acrylamide (c) n – propyl acrylamide

In ^{13}C – NMR spectra of n-AAA homopolymers different peaks are divided into 3 different groups (I, II, and III) as shown in Fig. 3. The first group (I) peaks range from 15 to 50 ppm, the second group (II) peaks lie between 120 – 132 ppm and the final (III) third group peaks extend from 160 – 180 ppm. In the first group the methylene and methyl group of alkyl unit and due to the alkoxyamine group it shows a peak at 13.5 – 50 ppm. The peaks at 50 – 60 ppm are assigned to the CH_2 group which is attached to BPO radical. The benzene ring of BPO shows peaks in the range of 125 – 140 ppm. The carbonyls in the amide group and BPO radical give peaks between 165 – 175 ppm [12-13].

The FT – IR spectrum of n – AAA homopolymers show an absorption band between $3288 - 3072 \text{ cm}^{-1}$ due to $-\text{NH}$ stretching vibration which can be observed in Fig. 4(a, b, c). Two absorption bands are observed between $2955 - 2926 \text{ cm}^{-1}$ due to aliphatic (C – H) stretching. Absorptions bands due to the carbonyl group are observed between $1555 - 1650 \text{ cm}^{-1}$ [14].

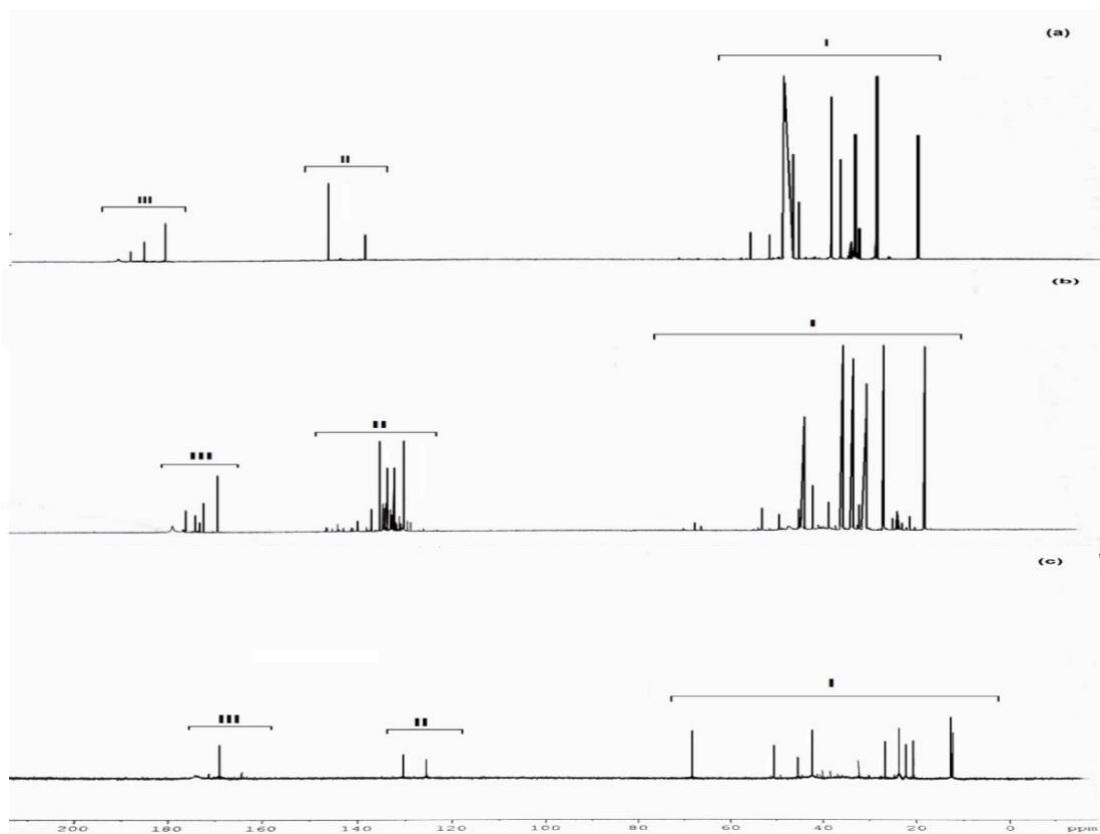


Figure – 3: ¹³C – NMR spectroscopy for n – alkyl acrylamide homopolymers, (a) n – hexyl acrylamide (b) n – butyl acrylamide (c) n – propyl acrylamide

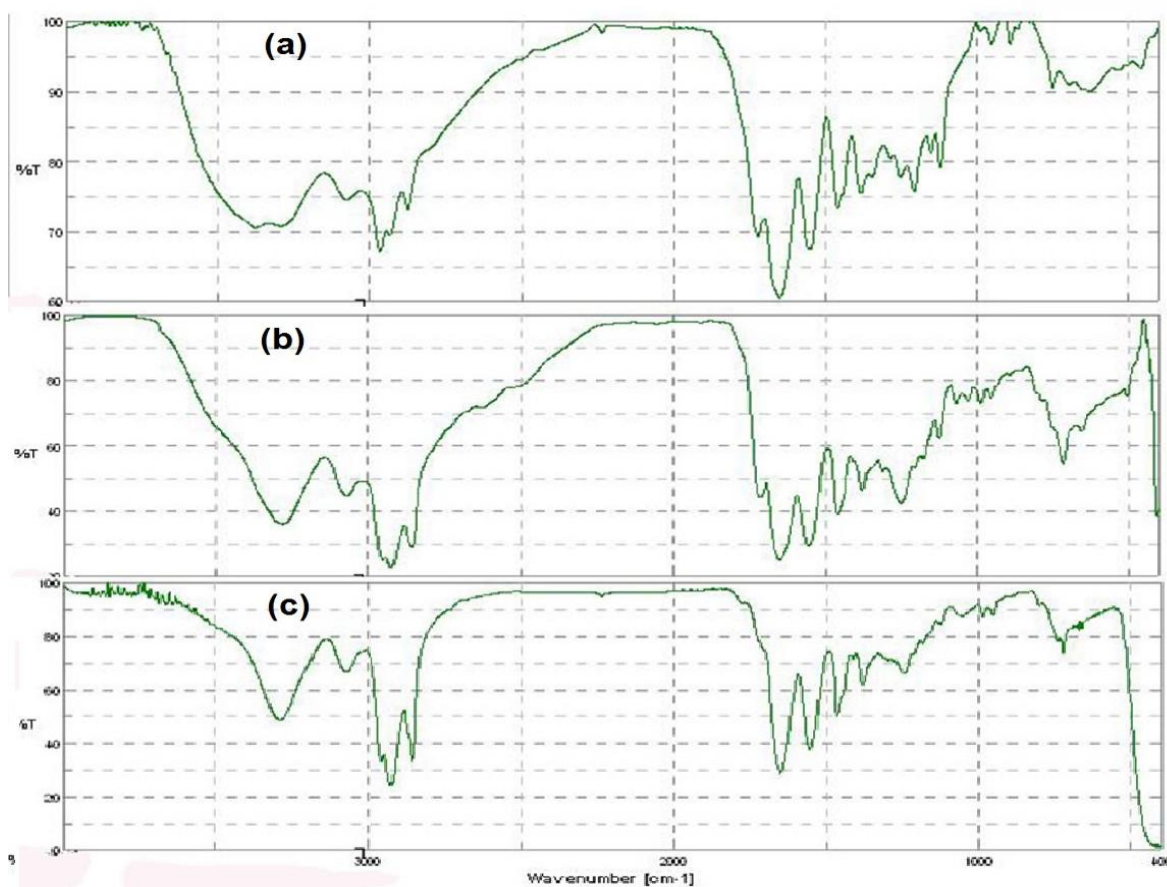


Figure – 4: FT – IR spectroscopy for n – alkyl acrylamide homopolymers, (a) n – hexyl acrylamide (b) n – butyl acrylamide (c) n – propyl acrylamide

4. MOLECULAR WEIGHT DETERMINATION AND CONVERSION

This work aims to synthesize such homopolymers which are efficient in scale and corrosion inhibition. It has been shown in previous studies that the low molecular weight compounds are good scale and corrosion inhibitor [14] preferably between 500 – 5000.

Table 1 shows the reaction condition and conversion degree of homopolymers of n – AAA. The molecular weight so obtained was in the range of 1000 – 4500 and the highest yield (89 %) was obtained by n – hexyl acrylamide with 1.5 polydispersity (M_w/M_n). The molecular weight achieved after such conversion is 4253. The compound lost during the purification and recrystallization process can be the reason for the lower yield of AAP and AAB homopolymers [15].

Table 1 reaction conditions and results of homopolymerization of n – alkyl acrylamide monomers in o-xylene at 150 °C.

S. NO	Polymers	Monomers (Mole %)	Initiator (Mole %)	Mw ^a	M _w /M _n	Conversion %
1.	n – Hexyl Acrylamide	0.02	BPO ^b (7.5)	4253	1.5	89
2.	n – Butyl Acrylamide	0.02	BPO (7.5)	3965	1.32	88
3.	n – Propyl Acrylamide	0.02	BPO (7.5)	1072	1.82	85

Mw^a = molecular weight, BPO^b = Benzoyl peroxide;

5. CONCLUSION

The present research work is focused on synthesis and characterization of the homopolymers for their utility as efficient corrosion and scale inhibitors. The main objective of this research is to synthesize eco-friendly, cost-effective homopolymers with enhanced scale and corrosion inhibition performance which is requisite in the final endeavor to utilize in industry. The conversion range or yield so obtained for n – AAA homopolymers was in between 80 to 89 %. Results obtained from GPC shows molecular weight of n-alkyl acrylamide is in range of 1000-4500 which comes under desired range. ¹³C-NMR, ¹H-NMR and FT – IR spectra of the compounds show that the homopolymers are having a linear structure in which monomers are randomly attached.

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