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Free Radical Solution Copolymerization of n-Octylacrylamide and Maleic Anhydride in a Non Polar Solvent; Synthesis and Characterization of a Difunctional Copolymer

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Summary

A novel difunctional random copolymer of maleic anhydride (MA) and n-octyl-acrylamide (acrylamide-n-octyl, AAO) with both anhydride and acrylamide moieties was synthesized. The copolymer had a molecular weight by SEC of between 950 and 1900 and a polydispersity of between 1.0 and 4.0. The performance of initiators azo-isobutyronitrile (AIBN) and benzoyl peroxide (BPO) at varying concentrations in solvent o-xylene were compared at four different initial MA:AAO ratios (7:3, 5:5, 6:4 and 4:6). The molecular weight of the synthesized copolymers at 7.5 mol % initiator concentration increased proportionally with the conversion at a 5:5 monomer ratio, whereas copolymerization at other initiator concentration and monomer ratios revealed a non-linear behavior. Characterization of monomer and copolymer on the basis of ^{1}H-NMR and ^{13}C-NMR is also reported.

Introduction

Polymers containing carboxylic acid and/or amide functional groups have been employed in a wide range of applications as corrosion inhibitors [1, 2], dispersants for particulate matter [3, 4], inhibitors of mineral scale formation and deposition [5-11] and in the field of medicine [12-15]. Several investigators have examined polymers based on either maleic or the acrylamide product for use as anti-corrosion and anti-scaling agents [16-20].

The synthesis and characterization of maleic anhydride copolymers have been reported by several authors [21-27]. Lee and Huang reported the synthesis of maleic anhydride and acrylamide copolymers in the solvents benzene, dioxane and methyl ethyl ketone using AIBN as initiator. The copolymers so prepared were further imidized using maleic anhydride moiety to give polysulfobetaines and corresponding cationic polymers that are usually used in industries concerned with textiles, charged dispersing agents, protective colloids and other related materials [28].

The preparation of alternating copolymers of straight chain α-olefins and maleic anhydride has been reported by Davis and his coworkers [29]. A similar study of the copolymerization of higher α -olefins and maleic anhydride by a dilatometric method has also been undertaken by Tanchuk *et al.*[30]. It was shown that the reaction occurs by a radical mechanism with the formation of an alternating copolymer. The maximum copolymerization rate and yield of copolymer anhydrides were attained when the reaction was carried out in a dichloroethane medium at a temperature of 343-353 K in 6-8 hours in the presence of benzoyl peroxide as the initiator.

Tsiourvas and Paleos have reported the reaction of maleic anhydride with amines and alcohols [31]. Veron and his coworkers prepared alternate N-vinyl pyrrolidone-maleic anhydride copolymers by radical solution polymerization in dioxane with various maleic anhydride contents in the monomer feed [13].

Erceg et al reported the copolymerization of maleic anhydride with chlorinated styrenes in toluene at 65°C. It was shown that copolymers prepared under different monomer-to-monomer ratios in the feed have an alternating composition [32]. High molecular weight alternating polymers of caprolactone and maleic anhydride have been synthesized by Ramaswamy et al. [33]. The polymerization reaction was carried out in bulk under a nitrogen atmosphere. Stannous octate and 2, 2’-azoisobutyronitrile were used as catalyst and initiator respectively.

Synthesis and swelling behavior of cross-linked copolymers of neutralized maleic anhydride have been reported by You et al. [34]. These novel copolymers based on maleic anhydride, acrylamide, hydroxyethyl methacrylate and N, N’-methylene bisacrylamide were prepared by inverse-suspension polymerization, having an alternate composition.

Although, a vast literature is available on the synthesis and characterization of both maleic anhydride copolymers and n-alkylacrylamide copolymers, there are few studies on the copolymerization of n-octylacrylamide (AAO) with maleic anhydride (MA). This work was an attempt to investigate the copolymerization of MA and AAO in detail, since precise control of polymer properties and process productivity is one of the key issues in designing or optimizing the free radical copolymerization process.

The foregoing discussion shows that MA usually copolymerizes by the formation of a charge transfer complex, resulting in alternate copolymers. The polymerization process as described herein provides for the first time random copolymers by free radical copolymerization of AAO with MA.

The present work was carried out with the following objectives: (i) characterization of monomer and copolymers of MA and AAO that generate a series of low molecular weight difunctional copolymers, (ii) to demonstrate the effect of different initiators on the copolymerization process so as to obtain a concentration/yield of polymer effect and (iii) to determine the effect of varying monomer ratios and initiator concentration on the molecular weight of the copolymers.

Experimental

Materials

Maleic anhydride (Sigma, 99%) was recrystallized from reagent grade benzene and dried under vacuum at room temperature. n-Octyl amine (98%) and acrolyl chloride (96%) were purchased from Aldrich and used without further purification. BPO (Sigma-Aldrich, 97%) and AIBN (Sigma-Aldrich, 97%) were crystallized from reagent grade methanol prior to use. Solvents used for the spectroscopic measurements were of spectral grade (Sigma-Aldrich) and were used as received.

Instrumental Measurements

Molecular weight measurements of the monomers and copolymers were carried out by high temperature size exclusion chromatography (SEC). The chromatograph was a Waters 150C ALC/GPC system equipped with three styragel HR 5µm columns of 50, 10^3, 10^4 A°, respectively, and a differential refractometer detector. The permeation solvent was THF. The concentration was in the range 4-6 mg/l and the injection volume was 200 µl. A polystyrene calibration was used for SEC analysis.
^{1}H-NMR spectra and ^{13}C-NMR spectra were obtained using a Bruker AM 400 NMR spectrometer. The samples were dissolved in $CDCl_3$ or acetone-d_6 and the shifts were referenced to tetramethylsilane.

Copolymerization of MA

Monomer Synthesis:
A 200 ml round bottom flask equipped with a glass stir bar was placed in an ice bath. n-Octyl amine and barium hydroxide (1%) were placed in the flask and stirred until the temperature equilibrated. Acrolyl chloride was added drop wise to the flask containing the n-octyl amine while continuously stirring. The mixture in the reaction vessel thickened after about 7 minutes indicating the formation of the monomer.
The reaction mixture was then heated gradually up to 85°C, until hydrogen chloride was eliminated. The resulting solution was whitish-yellow and turbid. Doubly deionized water was added to the vessel with vigorous stirring to separate the monomer. The procedure was repeated several times to eliminate excess reactants. The resulting material was dried by placing it in a 40°C oven. The waxy white colored final product was then stored at 0°C.

Copolymerization:
Copolymerization of MA with AAO was conducted with the objective of characterizing the reaction and to generate a series of low molecular weight co-polymers of varying composition. The reaction was conducted at four different concentrations. The samples were labeled as: MA / 30 AAO, MA / 50 AAO, MA / 60 AAO and MA / 40 AAO indicating 70:30, 50:50, 40:60 and 60:40 mol % of MA:AAO, respectively. A dry N_2 inert gas atmosphere was maintained throughout all experiments. Two different initiators azo-isobutyronitrile (AIBN) and benzoyl peroxide (BPO), were used in the copolymerization study. The concentration of initiators (5, 7.5, 10 and 12 mol % of monomers) was varied to select and optimize their performance. The reaction temperature was maintained at the reflux temperature of o-xylene. The progress of the reaction was followed by measuring the disappearance of the monomer, which was conducted by taking out a small sample of reaction mixture every hour and determining its monomer content by LC and increase in molecular weight of the polymer by gel permeation chromatography.

A typical polymerization was carried out as follows. MA dissolved in 200ml of o-xylene was stirred and heated to reflux under a N_2 atmosphere until the temperature reached 70°C. AAO and initiator dissolved in 50 ml of solvent were added over a period of five minutes. Refluxing was continued for a further 9 hours and the polymer was allowed to separate from the solution. Excess solvent was distilled off and the oily layer obtained was recrystallized in benzene to give the copolymer product.

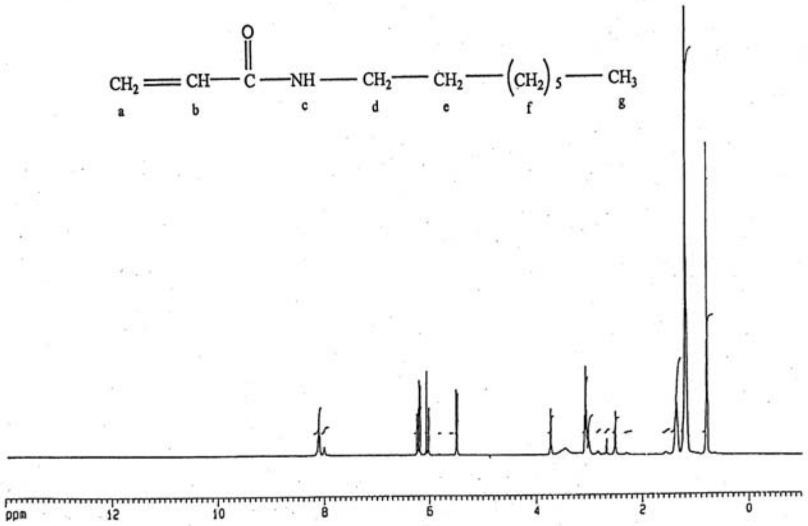

Figure 1. ^{1}H NMR spectra of n-octylacrylamide.

Results and Discussion

Monomer Characterization:

In the ^{1}H-NMR spectra of AAO, protons were indexed starting from the acrylamido function. Signals between 0.8 and 1.4 ppm due to methyl and methylene protons from [H_e - H_g] as shown in Figure 1. Peak at 3.0 – 3.1 ppm can be attributed to the methylene proton [H_d] close to the amide group. The protons [H_a and H_b] give a multiplet in the region 5.49 to 5.51 and 6.1 to 6.2 ppm. The small peak observed in the region of 6.0 ppm is due to the –NH proton.

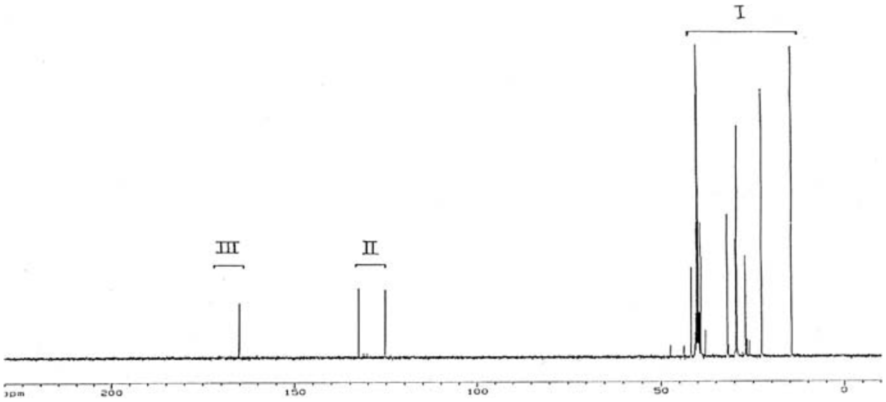

Figure 2. ^{13}C-NMR spectra of n-octylacrylamide.

Figure 2 shows the ^{13}C-NMR spectrum of AAO. The peaks were distributed among three groups: the first group (I), from 14 – 40 ppm; the second group (II) from 125 - 132 ppm; and an isolated peak (III) at 167 ppm. The peaks located at 14 – 40 ppm correspond to methyl and methylene groups of the aliphatic octyl unit. Peaks located between 125 – 132 ppm can be attributed to a vinyl group and the isolated peak at 167 ppm is due to the carbonyl of the amide group [35].

Copolymer Characterization:

The series of n-octylacrylamide-maleic anhydride copolymers prepared by the free radical mechanism were analyzed by ^{1}H-NMR and ^{13}C-NMR spectroscopy to determine the copolymer composition and to examine the polymer microstructure, specifically that of the end groups. The ^{1}H-NMR spectra of the copolymer containing MA and AAO in the ratio 5:5 initiated by BPO (7.5 mol %) is shown in Figure 3.

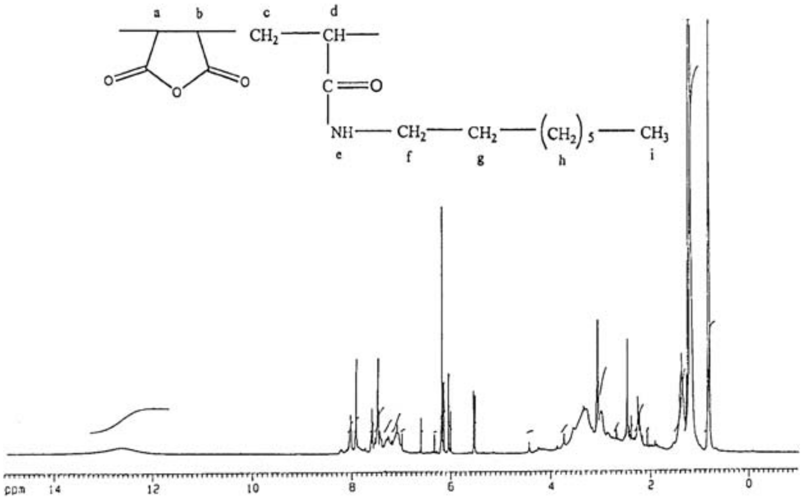

Figure 3. ^{1}H-NMR spectra of n-octylacrylamide- maleic anhydride copolymer.

Protons were indexed starting from the MA function. Signals between 0.8 and 1.4 ppm can be attributed to aliphatic protons $[H_g – H_i]$ of AAO. The peak at 3.39 ppm corresponds to a methylene proton $[H_f]$. Methylene and methene protons of the maleic anhydride unit $[H_a – H_b]$ give rise to a complex pattern in the 3.0 – 3.85 ppm range. Peaks between 1.5 and 2.2 ppm can be attributed to methylene and methene protons $[H_c – H_d]$. The presences of these peaks confirm the formation of a copolymer with the structure shown in Figure 3. The peak at 7.9 ppm can be assigned to an –NH proton $[H_e]$. Finally, a small signal in the vinylic region (5.5 ppm) can be attributed to the –CH= protons of AAO units.

The low molecular weight of the copolymer readily enables end-group analysis by ^{1}H-NMR and ^{13}C-NMR spectroscopy to be undertaken. Peaks due to aromatic protons of the benzoyloxy group for initiator BPO were observed between 7.4 and 7.6 ppm. The small peak at 7.96 ppm may be assigned to ortho protons of benzoyloxy units attached to the minor co-monomer maleic anhydride. The ratio of MA units to AAO units in the copolymer is 1:2. Comparison of the integrated area of the peak at 1.24 ppm in Figure 4 arising from the aliphatic protons of the octylacrylamide unit indicates that in the

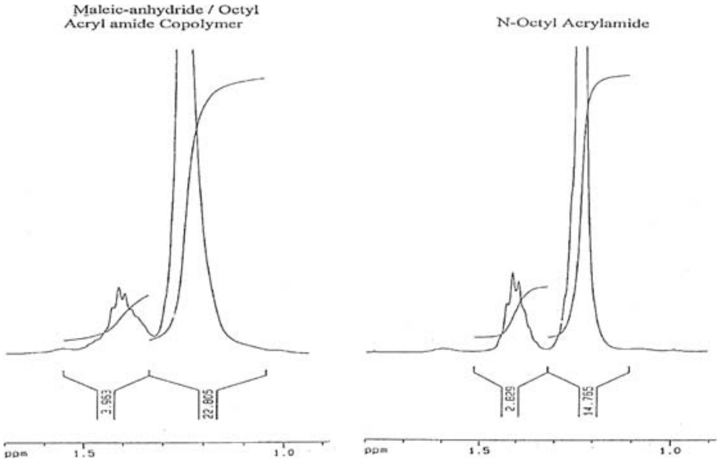

Figure 4. Comparison between ^{1}H-NMR spectra of n-octylacrylamide-maleic anhydride copolymer and octylacrylamide monomer.

copolymer spectra the peak area is approximately twice that of the monomer area. This clearly shows that the incorporation of AAO monomer in the copolymer is greater than that of MA. This is further supported by considering the magnitude of the reactivity ratios of $r_{MA} = 0.85$ and $r_{AAO} = 1.05$ calculated by a linearization method [36], which shows that AAO has a greater tendency to homopolymerize. It is assumed that an oligomer of AAO (DP=2 or 3) was formed, which further reacts with an MA unit to form a random copolymer of n-octylacrylamide- maleic anhydride.

A ^{13}C-NMR spectrum of the copolymer is shown in Figure 5. Peaks in the spectra are divided into five groups: The first group (I) from 14 – 40 ppm, second group (II) from 125 – 130 ppm, third (III) from 131 – 135 ppm and the fourth (VI) group from 165 – 167 ppm. The final group (V) extends from 173 – 175 ppm. The first group (14 – 40 ppm) is attributed to methylene and methyl groups of the AAO unit. The peak located in the range 125 – 130 ppm corresponds to the vinyl group of the AAO unit, while that situated at 131 – 135 ppm can be attributed to MA (Cα of the carbonyl in both cases). The carbonyl in the MA and amide groups gives peaks in the

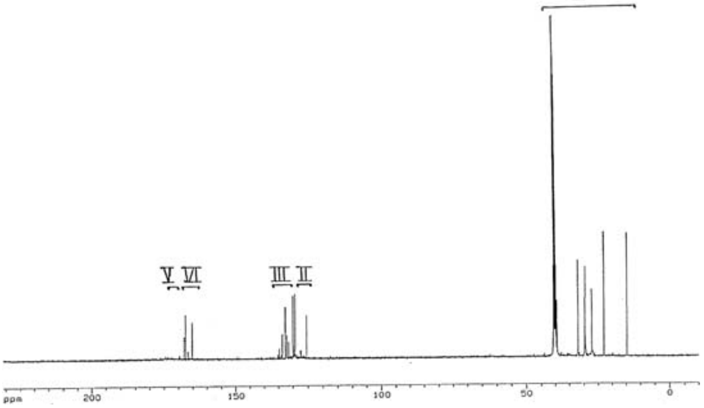

Figure 5. ^{13}C-NMR spectra of octylacrylamide- maleic anhydride copolymer.

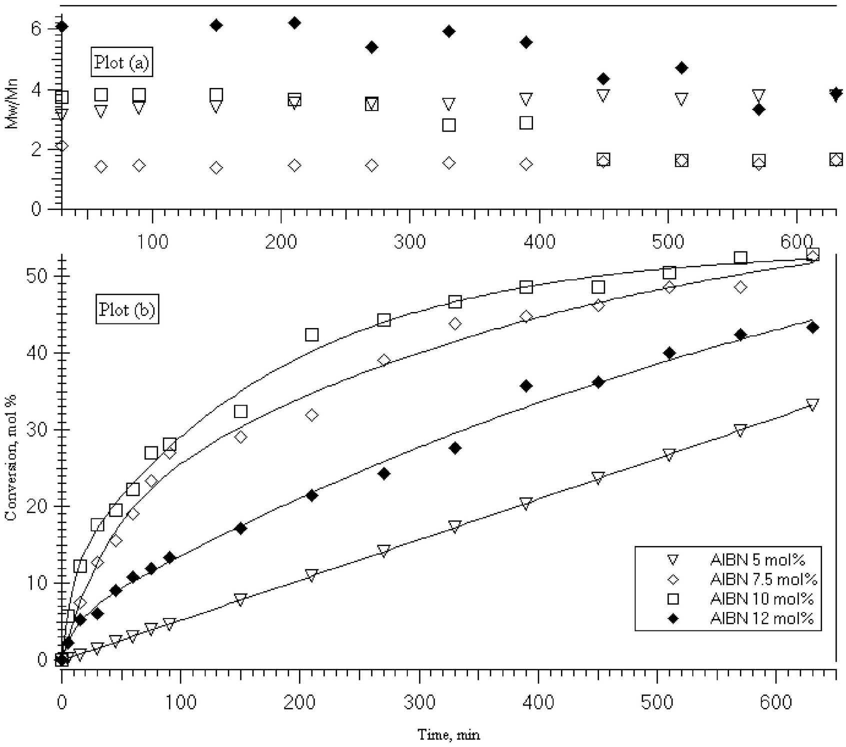

Figure 6. Plots showing (a) Polydispersity and (b) Monomer conversion with time in the copolymerization of MA and AAO at different AIBN concentrations in o-xylene at 5:5 monomer ratio.

Table 1. Conditions and Results for the Radical Copolymerization of MA and AAO in O-Xylene.

Run	Composition of Monomer Mixture (Mol %)		Initiator	Initiator Composition (Mol%)	Conversion %	Mw/Mn	Mn[c]
	MA	AAO					
1	70	30	BPO[a]	7.5	49	3.89	1152
2	60	40	BPO	7.5	43.5	3.47	1345
3	50	50	BPO	7.5	52.5	1.89	1759
4	40	60	BPO	7.5	37.56	3.87	935
5	70	30	AIBN[b]	7.5	43.5	1.36	1658
6	60	40	AIBN	7.5	53.3	1.66	1646
7	50	50	AIBN	7.5	53	1.61	1890
8	40	60	AIBN	7.5	17	3.62	1469
9	50	50	BPO	5	40.2	1.63	1545
10	50	50	BPO	10	62	3.4	1364
11	50	50	BPO	12	50	3.1	1135
12	50	50	AIBN	5	33.25	3.78	1562
13	50	50	AIBN	10	53	1.67	1725
14	50	50	AIBN	12	43.5	3.86	1267

[a]BPO = Bezoyl peroxide; [b]AIBN = Azoisobutyronitrile; [c]Molecular weight obtained from SEC

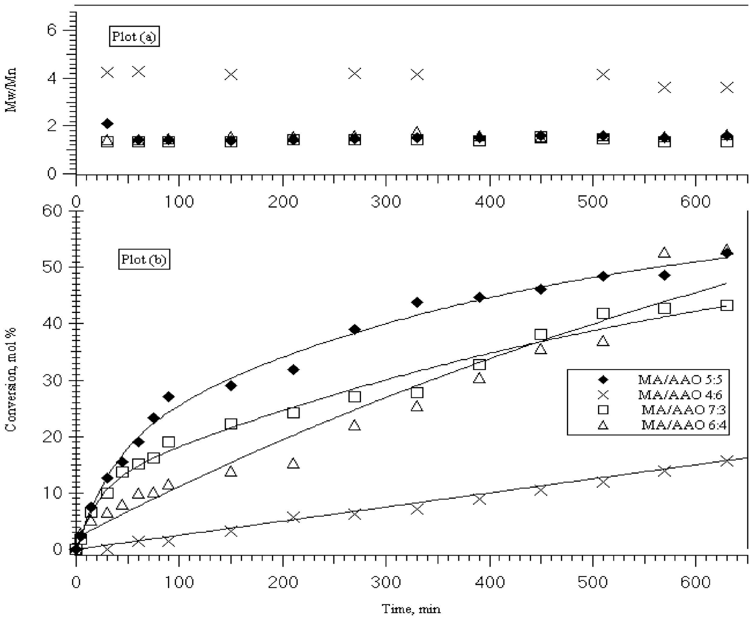

Figure 7. Plots showing (a) Polydispersity and (b) Monomer conversion with time in the copolymerization of AAO and MA in o-xylene for different monomer ratios in AIBN (7.5 mol %)

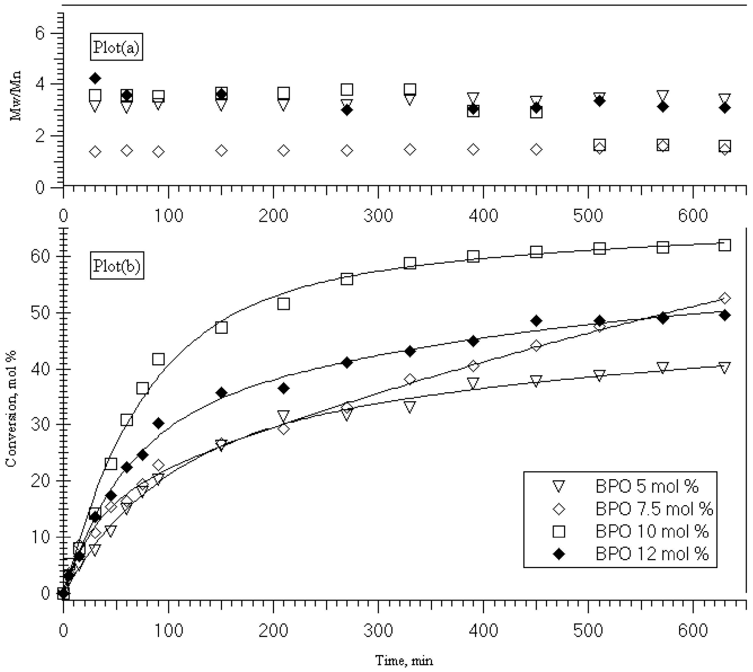

Figure 8. Plots showing (a) Polydispersity and (b) Monomer conversion with time in the copolymerization of MA and AAO at different BPO concentrations in o-xylene at 5:5 monomer ratio

165 – 169 ppm range. Finally the peaks at 173 – 175 ppm are due to carbonyls of succinic anhydride. The presence of these peaks further confirms the formation of copolymer.

It should be observed that the very low molecular weight of the particular sample analyzed leads to a relative enhancement of the effect of the end groups. Those due to initiator and/or termination of radical polymerization should certainly play an important role. Not only can the vinyl and aliphatic alkane signals (peaks of group II and III) be explained in this way; the peaks at 7.4 – 7.9 ppm and 2.5 ppm (in ^{1}H-NMR) can also be attributed to the end group. Termination by dismutation can lead to saturated (succinic type) or unsaturated (maleic- or fumaric- type) end groups [37]. Supplementary effects can be due to the possible transformation of some anhydride functions into carboxylic acid functions with water contamination during the preparation or in deuterated DMSO. All these possibilities agree with the proposed attribution of the observed peaks.

Molecular Weight Determination:

The main focus of this work was to select the optimum initiator concentration and monomer ratio so as to design a new model for the radical copolymerization of MA and AAO. The experimental results showed that the polymerization reaction depended on several factors such as reaction time, initiator concentration, monomer composition, type of solvent and temperature. An increase of time and temperature, however, had an enhancing effect on the polymer yield. Copolymerization of MA and

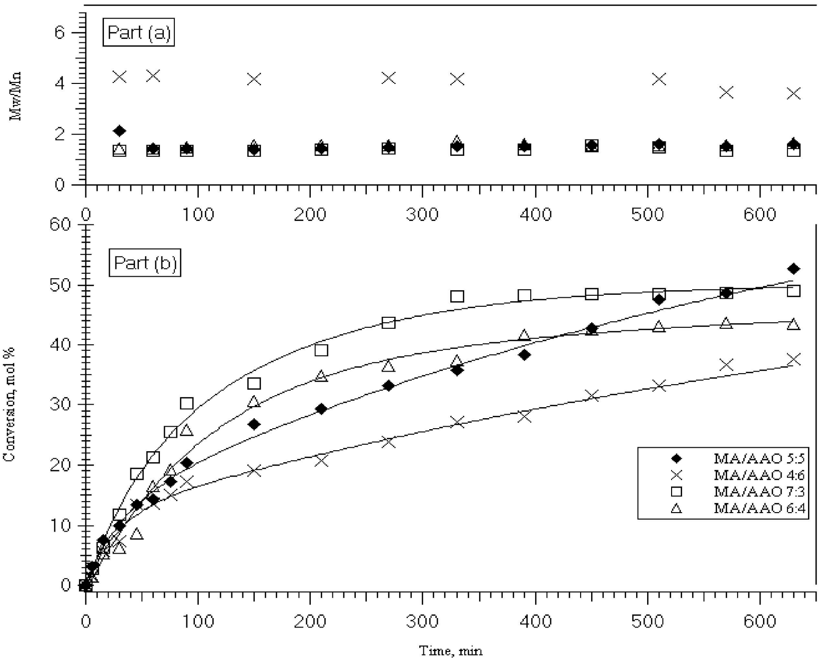

Figure 9. Plots showing (a) Polydispersity and (b) Monomer conversion with time in the copolymerization of AAO and MA in o-xylene for different monomer ratios in BPO (7.5 mol %)

AAO was carried out in four different solvents: 2-butanone, THF, toluene and o-xylene. Copolymerization in 2-butanone and THF yielded a dark oily substance, which was difficult to purify. The product obtained in toluene was a light brown solid with a very low molecular weight. MA and AAO copolymerized most effectively in o-xylene. The results of the experiment conducted at different monomer compositions and varying initiator concentrations are given in the Table-1.

Figures 6-9 (Plots-a) compare the molecular weight distributions as a function of time. The best-controlled reaction was observed in AIBN at 7.5 mol % concentration and varying monomer ratios (Mw/Mn ≈ 1.5). Copolymerization with BPO at 7.5 mol % concentration revealed similar results with polydispersities between 1.3 and 1.4. When concentrations of AIBN and BPO above or below 7.5 mol % were used, all the copolymers isolated exhibited Mw/Mn > 1.5 over the whole range of conversion, indicating uncontrolled bimolecular termination. The faster polymerization and almost constant Mn are consistent with this.

Figures 6-9 (Plots-b) illustrate conversion-time plots for the copolymerization of maleic anhydride and n-octylacrylamide. Comparison of these plots at varying monomer concentrations indicates a better performance with both AIBN and BPO at a MA/AAO 5:5 monomer ratio. There was a good conversion and the molecular weight was in the range of 1750-1900. A glance at the results for different AIBN and BPO concentrations clearly indicates that 7.5 mol % is the optimum.

The molecular weight and conversion data for these samples, which are shown in Figures 10 – 13, further support this observation. The molecular weight obtained at 7.5 mol % concentration increased linearly with conversion for both AIBN and BPO.

However, the rest of the data showed completely different characteristics. The molecular weight increased sharply up to 20% conversion, after which Mn, approached a constant value. This is characteristic of a fast and uncontrolled bimolecular termination and Mw/Mn > 1.5 irrespective of conversion.

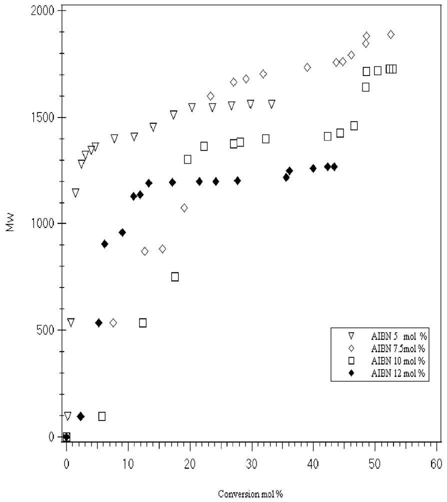

Figure 10. Dependence of molecular weight on monomer conversion in the copolymerization of AAO with MA at different AIBN concentrations in o-xylene at 5:5 monomer ratio.

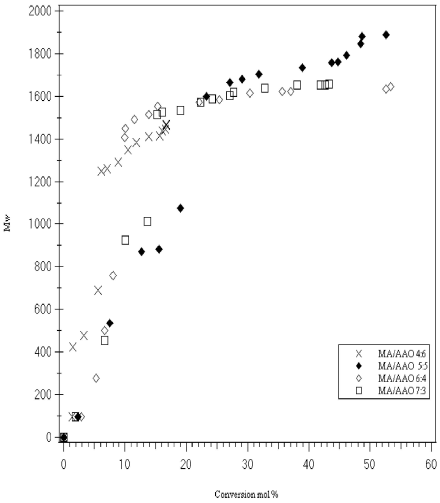

Figure 11. Dependence of molecular weight on monomer conversion at different monomer ratios using AIBN (7.5 mol %) in o-xylene.

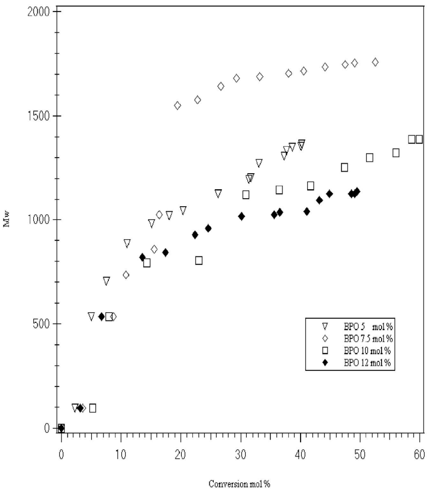

Figure 12. Dependence of molecular weight on monomer conversion in the copolymerization of AAO with MA at different BPO concentrations in o-xylene at 5:5 monomer ratio.

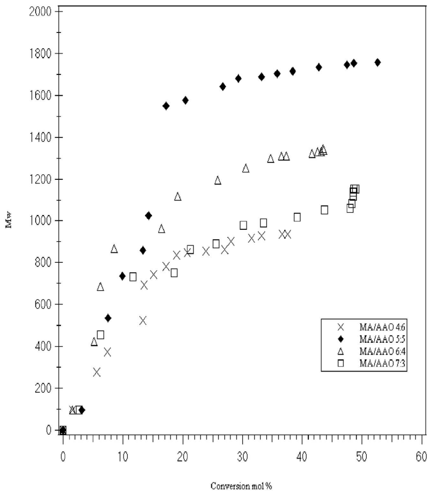

Figure 13. Dependence of molecular weight on monomer conversion at different monomer ratios using BPO (7.5 mol %) in o-xylene.

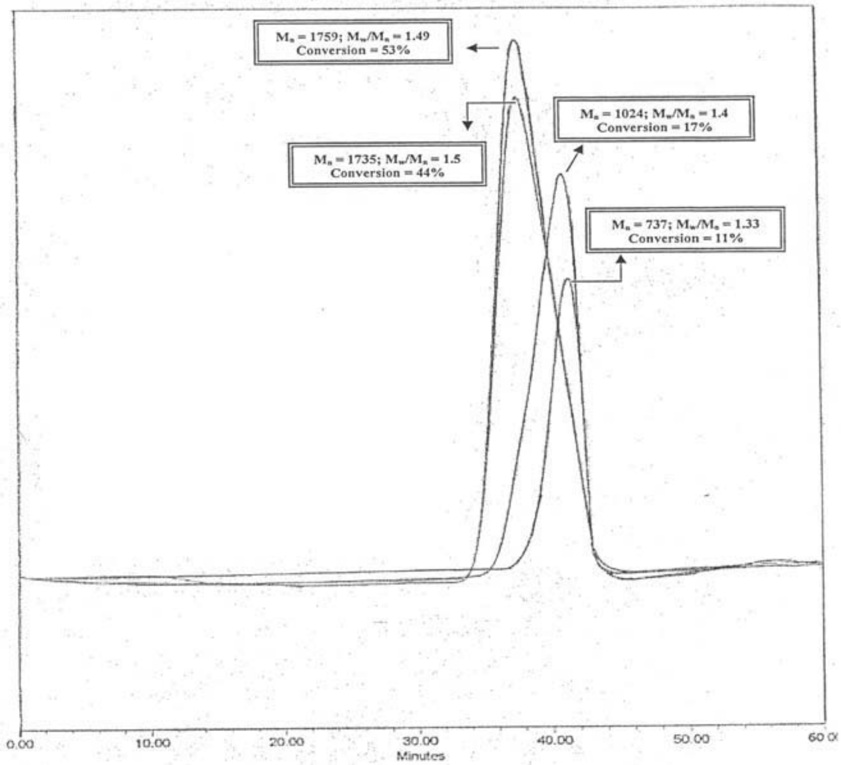

Figure 14. SEC chromatogram of n-octylacrylamide - maleic anhydride copolymer in o-xylene at AIBN concentration of 7.5 mol % and 5:5 monomer ratio.

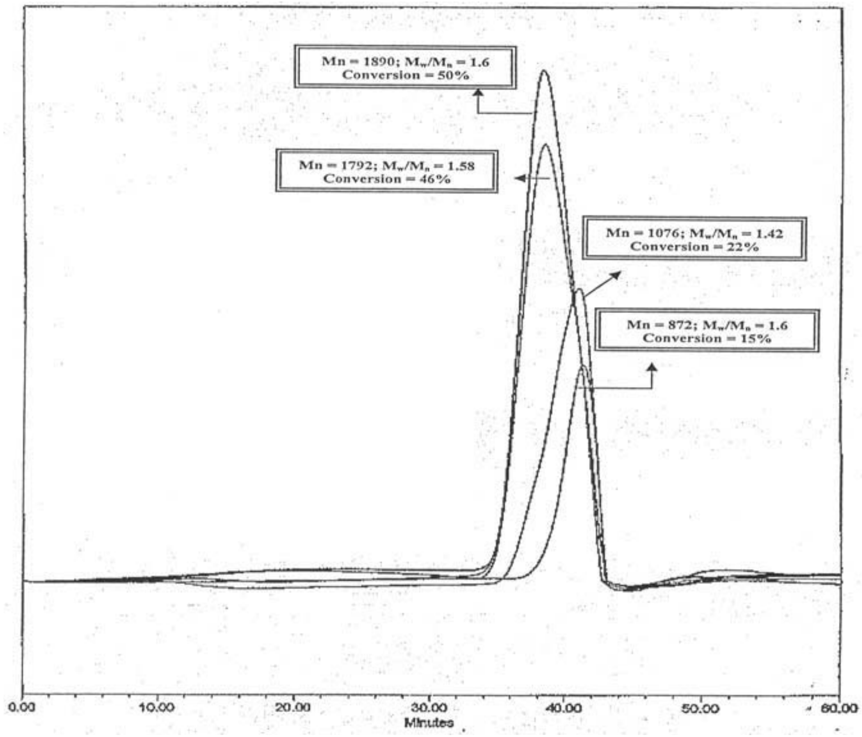

Figure 15. SEC chromatogram of n-octylacrylamide - maleic anhydride copolymer in o-xylene at BPO concentration of 7.5 mol % and 5:5 monomer ratio.

Figures 14 and 15 shows SEC chromatograms for AIBN and BPO at a 7.5 mol % concentration and a 5:5 monomer ratio. It can be observed that the molecular weight and conversion both increased with time whilst PDI remained narrow, indicating controlled polymerization.

Conclusion

Random difunctional copolymers of MA/AAO have been prepared by a free radical mechanism. They had a low molecular weight, in the range 950 – 1900, and a polydispersity of 1 – 4. ^{1}H-NMR and ^{13}C-NMR spectra showed that, compared to MA, AAO is largely incorporated into the copolymer in a random sequence. Comparison of both initiators clearly indicates that AIBN attained a higher molecular weight than BPO at 7.5 mol % concentration. The observed increase of molecular weight with time formed a kinetic relationship curve between the extent of reaction and the molecular weight of the polymer.

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