Methyl Acrylate/1-Octene Copolymers: Lewis Acid-Mediated Polymerization

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ABSTRACT: Copolymerization of methyl acrylate (MA) with 1-octene (1-Oct) was conducted in the presence of free radical initiator, 2,2′-azobis(2-methylpropionitrile) (AIBN) using heterogeneous Lewis acid, acidic alumina. The polymers obtained were transparent and highly viscous liquids. The copolymer composition calculated from ^{1}H NMR showed alkene incorporation in the range of 10–61%. The monomodal nature of chromatographic curves corresponding to the molecular weight distribution in gel permeation chromatography (GPC) further confirmed that the polymers obtained are true copolymers. The number–average molecular weights (M_n) of the copolymers were in the range of 1.1×10^4–1.6×10^4 with polydispersity index of 1.75–2.29. The effects of varying the acidic alumina amount, time of polymerization, and monomer infeed on the incorporation of 1-Oct in the polymer chain were studied. Increased 1-Oct infeed led to its higher inclusion in the copolymer chain as elucidated by NMR. DEPT-135 NMR spectral analysis was used to explicate the nature of arrangement of monomer sequences in the copolymer chain. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 111: 87–93, 2009

Key words: copolymerization; functionalization of polymers; gel permeation chromatography (GPC); Lewis acid-mediated polymerization; 1-octene; acidic alumina

INTRODUCTION

Designing of novel polymeric material is a challenging yet exciting task.[1] The novelty in these materials lies in conceptualization and in the feasibility of their formation. The properties and hence the related applications are major ruled by the molecular structure that includes topology, composition, and functionality.[2,3] Apart from this, the molecular weight and molecular weight distribution of the polymers are also an important factor in polymer applications.[4]

The main focus for synthesizing such type of polymeric material in innovative and technically demanding applications is through post reactor techniques.[5–7] Hence, global efforts are focused on improvements in design principles, new processing techniques, and in the determination of the influence of the processing conditions on material characteristics. Therefore, there is a need for developing such types of polymerization techniques that are reactor based, i.e., formation of polymeric material through direct polymerization. There is a requirement for striking a right equilibrium with the past knowledge bank we have with new accomplishments that keep the advancements in this area.

Polyolefins are the most extensively used commodity polymers. Synthetic procedure for making functional olefins have been one of the major areas of interest of polymer chemist for that requires a unique technique that can copolymerize two different categories of monomers.[8] This area of enduring industrial importance has been explored by different scientific approach such as free radical polymerization,[9] Lewis acid-mediated polymerization,[10,11] palladium-based polymerization,[12–15] and of lately, controlled radical polymerization.[16–20]

Copolymerization of acrylates with olefins through free radical polymerization route results in the formation of copolymers having very less incorporation of olefins. The large difference in the reactivity ratios of the two monomers is the reason behind this observation. The tendency of the acrylate monomer to homopolymerize becomes high due to the more reactive nature of the acrylate and its corresponding radical. This problem is dealt in Lewis acid-mediated polymerization that utilizes the ability of electron-deficient component (Lewis acid) to coordinate with the electron rich functionality, the oxygen of the carbonyl group of acrylic monomer, as well as its radical species. This in turn increases the likelihood of the olefin electron-rich double bond to attack or to be attacked by the electron-deficient acrylic double bond as well as the radical leading to
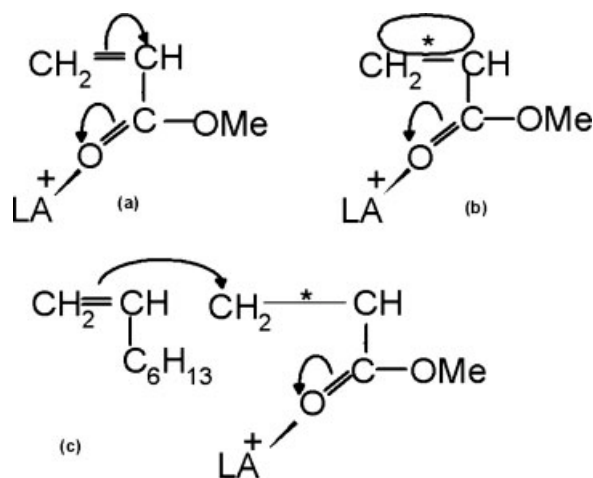
Scheme 1 Coordination of Lewis Acid with (a) methyl acrylate (b) methyl acrylate radical and (c) attack of 1-octene to coordinated methyl acrylate.

increase in percentage conversion as well as olefin incorporation. (Scheme 1)

Taking advantage of such type of coordination effect, Sen and coworkers have reported polymerization of α-olefins such as ethene, propene, 1-hexene, 1-decene, and norbornene with methyl acrylate (MA) and methyl methacrylate. Different Lewis acid such as AlCl₃,[17] Sc(Otf)₃,[10] and lately, heterogeneous acidic alumina[11] were used for copolymerization with ethene, and the polymers obtain were nearly alternating in nature with maximum alkene incorporation of 48%. In case of acidic alumina, copolymerization with 1-hexene has led to maximum alkene incorporation of 35%. The variation of Lewis acid to acrylate ratio was studied on polymerization kinetics in terms of percentage acrylate conversion and olefin incorporation in mole percentage and characterization through gel permeation chromatography (GPC) and NMR.[10,17]

Logothetis and McKenna[21–23] in late 1970s reported the alternating copolymers of ethylene and propylene with ethyl acrylate synthesized using free radical polymerization in the presence of boron trifluoride as the Lewis acid in dichloromethane under mild conditions. With four- to fivefold excess of alkene, alternating copolymers are obtained, which were characterized in terms of inherent viscosity, copolymer composition from ¹H NMR, and percentage conversion. Substantiation of the alternating characteristics of the copolymers having maximum alkene incorporation of 50% was done from ¹³C{¹H} NMR, IR Spectroscopy, viscosity relationship, and glass transition temperatures.

This article is the first report on the synthesis of MA and 1-octene (1-Oct) copolymers using AIBN under the presence of acidic alumina as Lewis acid with alkene incorporation in the range of 10–61%.

The polymers obtained were transparent highly viscous liquids. The polymers were monomodal in nature with molecular weight distribution in range of 1.75–2.29. NMR spectral analysis provides information on the arrangement of monomer units in the copolymer chain.

EXPERIMENTAL

Materials

1-Octene (1-Oct, 98%), methyl acrylate (MA, 99%), and aluminum oxide (activated, acidic, Brockmann I, standard grade, ∼ 150 mesh, pH = 4.5 ± 0.5 in aqueous solution) were received from Aldrich (Mumbai, India). MA was distilled and kept at 5°C before use. 2,2′-Azobis(2-methylpropionitrile) (AIBN, 98%, Acros) was recrystallized from ethanol before use.

Polymerization procedures

All the polymerizations were carried out under nitrogen atmosphere. In a typical procedure, 10 mL chlorobenzene was added to a round-bottom flask, followed by desired amount of acidic alumina and AIBN as given in Table I. 1-Oct and MA were then added in required mole ratio (as shown in Table I) into the flask under nitrogen. The reaction mixture was then heated to 70°C and stirred. After the required polymerization time, the mixture was cooled and filtered under nitrogen for removing acidic alumina. The polymers obtained by precipitating in large excess of methanol were dried under vacuum at 60°C till constant weight.

Polymer characterization

Percentage polymer conversion was measured gravimetrically. Molecular weights and molecular weight distributions were determined by size exclusion chromatography (SEC) with Perkin–Elmer Series 200 instrument (Columns: Waters Styragel HR 3 and 4,

TABLE I
Variation in the Reaction Parameters for the Copolymerization of Methyl Acrylate (MA) with 1-Octene (1-Oct) Using AIBN[a] in the Presence of Acidic Alumina[b] at 70°C

No.	Parameters
1[c]	MA/Alumina = 4 : 1, 2 : 1, 1 : 1
2[d]	MA/1-Oct = 4 : 1, 2 : 1, 1 : 1,
	0.5 : 1, 0.25 : 1, 0.1 : 1, 0.05 : 1, 0.02 : 1
3[e]	Reaction time = 16 h, 4 h

[a] 0.03 g in all experiments; PhCl, 10 mL.
[b] 1 : 2 (mole ratio) to MA for entries 2 and 3.
[c] Conditions: MA, 0.07 mol; 1-Oct, 0.14 mol; 4 h.
[d] Conditions: MA, 0.07 mol; 4 h.
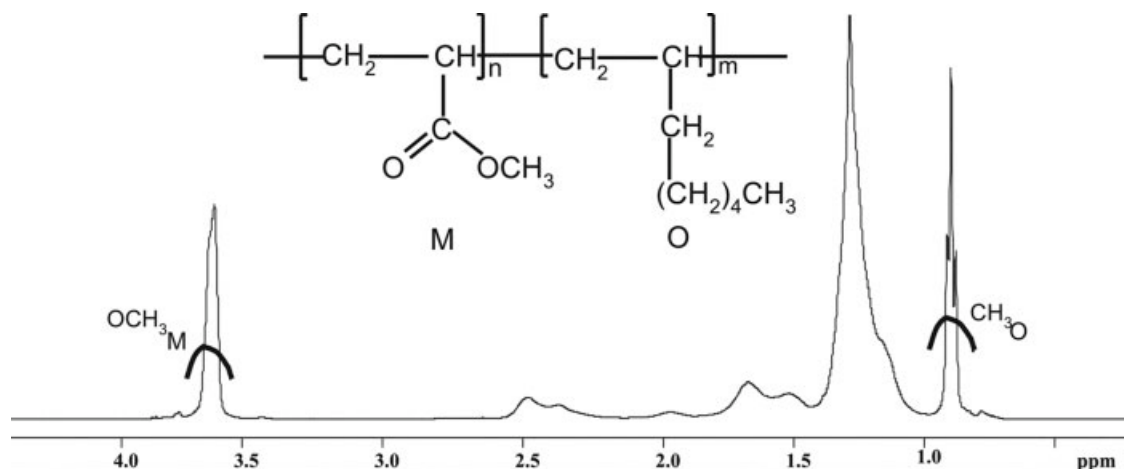[e] Conditions: MA, 0.07 mol; 1-Oct, 0.14 mol.

Figure 1 ^{1}H NMR of MA/1-Oct copolymer having $F_{1-Oct} = 0.49$ in CDCl$_3$ at 30°C synthesized in presence of acidic alumina using AIBN.

7.8 × 300 mm, 5 μm particle size) equipped with Perkin–Elmer Series 200 pump and Perkin–Elmer Series 200a refractive index detector in 1,2,4-trichlorobenzene at flow rate of 0.5 mL/min at 35°C. The system was calibrated with polystyrene standards. All the spectra were recorded on a Bruker Avance-400 spectrometer in CDCl$_3$ at frequencies of 400 and 100 MHz for ^{1}H and ^{13}C, respectively, at 45°C. A delay time of 10 s was given for recording ^{1}H NMR spectra, whereas for ^{13}C{^{1}H} NMR spectra, a 2 s delay time was given and 5000 scans were accumulated. DEPT-90, 135 spectra were recorded using standard pulse sequence with J modulation time of 3.7 ms ($J_{CH} = 135$ Hz) with a delay time of 2 s. The signal intensities of the spectra peak were measured from the integrated areas calculated with electronic integrator. NMR measurements were made on 10% (w/v) polymer solutions.

Copolymer composition

For calculating the mole fraction of 1-Oct in the copolymer (F_{1-oct}),[24,25] the relative areas of the intensities of the proton resonance of the CH$_3$ of the 1-Oct unit (I_{CH3}) and the —OCH$_3$ of the MA (I_{OCH3}) unit in the ^{1}H NMR (Fig. 1) were used. The formula used is as follows:

$$F_{1-Oct} = \frac{I_{CH_3}/3}{I_{OCH_3}/3 + I_{CH_3}/3}$$

RESULTS AND DISCUSSION

Copolymerization of MA with 1-Oct was studied under the reaction conditions as summarized in Table I. All the variations stated were performed to evaluate their effect on the copolymer composition,

total percentage conversion, and molecular weights. At constant [MA]/[1-Oct] ratio, polymerizations were conducted for 4 h at 70°C for three different [MA]/[Alumina] ratios. Similarly, at constant [MA]/[Alumina] ratio of 2 and [MA]/[1-Oct] ratio of 0.5, copolymerizations were performed for 4 and 16 h. [MA]/[1-Oct] ratio variations were conducted at 70°C for 4 h having [MA]/[Alumina] ratio of 2.

As the coordination of acidic alumina with the acrylate unit will increase the probability of attack of 1-Oct, the effect of adding acidic alumina in different mole percent with respect to MA on incorporation of 1-Oct in the copolymer was examined (Fig. 2). In all the cases, F_{1-Oct} remained almost constant with decreasing acidic alumina amount but the molecular weight of the polymers decreased. Clearly, the results indicate that in radically initiated copolymerization of MA with 1-Oct, adjusting the amount of acidic alumina has a diminutive role in getting the desired copolymer composition. Consequently, we need to look in for other parameters for here the maximum 1-Oct content in copolymer is 23%.
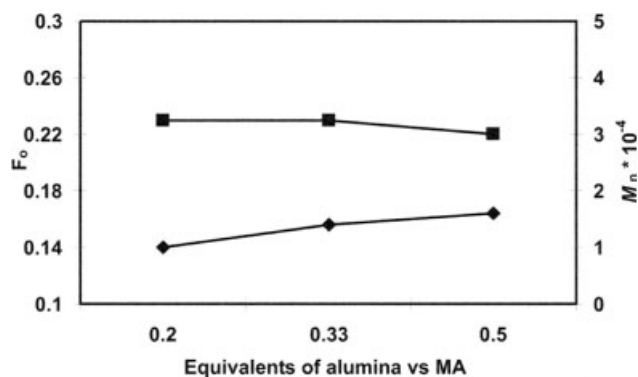

Figure 2 Variation of amount of acidic alumina on F_{1-Oct} and M_n for MA/1-Oct copolymers synthesized in presence of acidic alumina using AIBN.

TABLE II
Copolymerization of Methyl Acrylate (MA) with 1-Octene (1-Oct) Using AIBN[a] in
the Presence of Acidic Alumina[b] at 70°C

No.	[MA]/[1-Oct]	[MA]/[Alumina]	Time (h)	% Conv.	$F_{1\text{-Oct}}$	M_n ($\times 10^{-4}$)	PDI
1	0.5 : 1	4 : 1	4	23	0.23	1.0	2.01
2	0.5 : 1	2 : 1	4	22	0.23	1.4	2.06
3	0.5 : 1	1 : 1	4	20	0.22	1.6	2.03
4	0.5 : 1	2 : 1	16	21	0.25	1.5	2.11
5	4 : 1	2 : 1	4	26	0.08	1.4	2.29
6	2 : 1	2 : 1	4	24	0.10	1.2	2.23
7	1 : 1	2 : 1	4	27	0.14	1.3	2.03
8	0.2 : 1	2 : 1	4	23	0.30	1.4	1.98
9	0.1 : 1	2 : 1	4	21	0.34	1.2	1.73
10	0.05 : 1	2 : 1	4	19	0.49	1.5	1.78
11	0.02 : 1	2 : 1	4	20	0.61	1.3	1.75

[a] 0.03 g in all experiments; PhCl, 10 mL.
[b] 1 : 2 (mole ratio) to MA.

Luo and Sen [11] have also reported that for MA/1-hexene copolymerization, decreasing the acidic alumina amount with respect to MA, the alkene inclusion in copolymer remains almost constant but the molecular weights showed not trend.

The change in polymerization time, i.e., increasing from 4 to 16 h was studied to have an insight on its effect on the percentage alkene incorporation in the copolymer and on total percentage conversion. When the polymerization time of 16 h was kept for MA/1-Oct copolymerization (entries 2 and 4; Table I), it was found that the mole fraction of 1-Oct in copolymer is virtually comparable to the polymer synthesized by copolymerizing MA/1-Oct at 4 h. The total percentage conversion as well as the molecular weights were almost the same. The above-mentioned results suggest that the polymerizations are completed in the first 4 h, which has also been reported for MA/1-hexene and MA/1-decene copolymerization.[11]

Polymerizations having variation in the comonomer infeed molar ratio at constant [MA]/[Alumina] ratio of 2 : 1 were carried out for 4 h to understand the effect on copolymer composition. The results of the above study in terms of $F_{1\text{-Oct}}$ (Table II) showed that with increase in the fraction of 1-Oct in the comonomer infeed ($f_{1\text{-Oct}}$), $F_{1\text{-Oct}}$ in the copolymer increases although there is a slight decrease observed in the percentage conversion. This trend is very evidently depicted in Figure 3, where maximum incorporation of 1-Oct in the copolymers is 61% having total percentage conversion of 20%.

Molecular weights of the copolymers (Table II) are in the range of 1.1×10^4–1.6×10^4 and a decrease in PDI with increasing the comonomer infeed molar ratio. This trend indicates that the probability of 1-Oct (double bond) to attack the MA radical becomes predominant when compared with the probability of 1-Oct to act as chain transfer agent because of the coordination of MA with acidic alumina.

Figure 4 shows the completely assigned $^{13}C\{^1H\}$ NMR of MA/1-Oct copolymer having $F_{1\text{-Oct}}$ as 0.49. The assignments have been done in comparison with the $^{13}C\{^1H\}$ NMR spectrum of the corresponding homopolymers, DEPT-135 (methylene carbon appears in negative phase whereas methyl and methine carbon are in positive phase), and DEPT-90 (only methine carbon signals are observed).[24–26] The carbonyl carbon resonance of MA unit is assigned to the region around 175.9 ppm. The $-OC^{12}H_3$ carbon of the MA unit appears around 51.65 ppm, whereas C^8H_3 and C^7H_2 carbons of the 1-Oct unit appear as singlet around 14.03 and 22.51, respectively, directing to their insensitivity toward composition as well as configuration sequences. The spectral region around 25.41–42.10 ppm is quite complex because of the overlapping of the resonance signals of the backbone methylene and methine carbons of both MA and 1-Oct unit and the side chain methylene carbons (C^3, C^4, C^5, C^6) of 1-Oct unit.
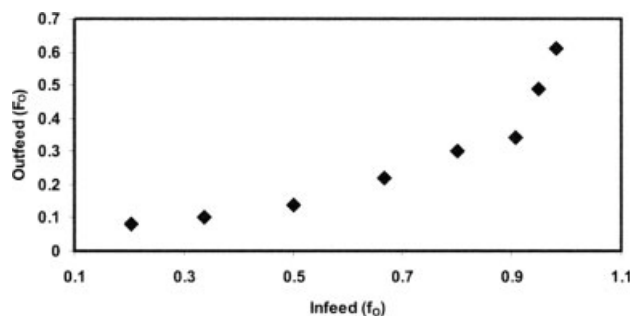

Figure 3 Variation of copolymer composition ($F_{1\text{-Oct}}$) with monomer infeed ($f_{1\text{-Oct}}$) for MA/1Oct copolymers synthesized in presence of acidic alumina using AIBN.
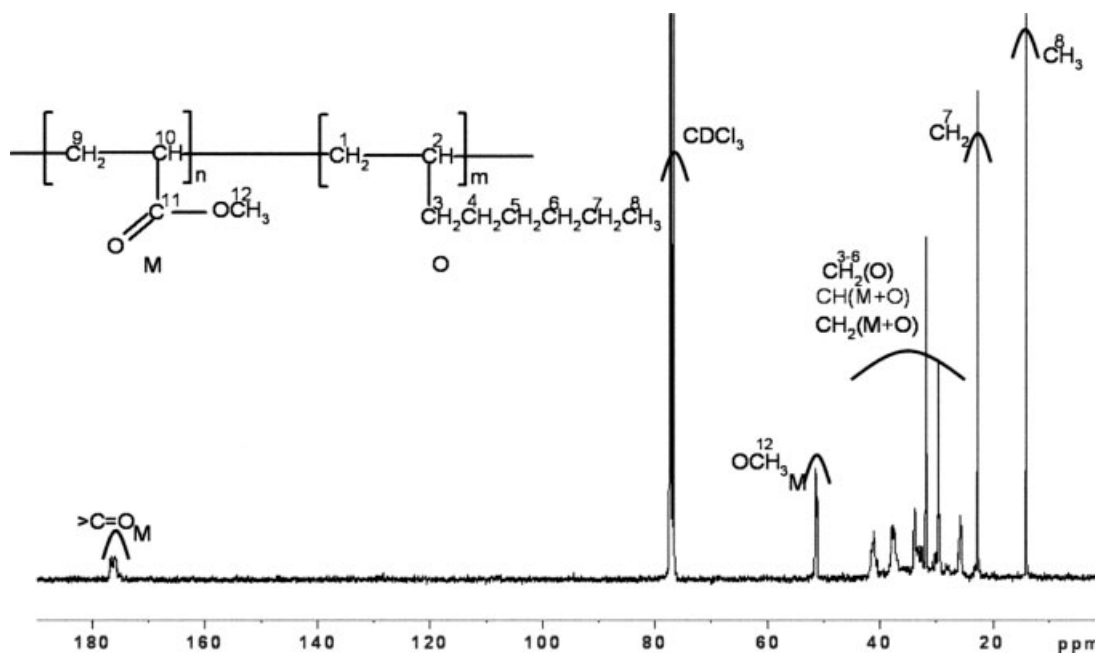
Figure 4 $^{13}C\{^1H\}$ NMR spectrum of MA/1-Oct copolymer having $F_{1\text{-Oct}} = 0.49$ in CDCl$_3$ at 30°C synthesized in presence of acidic alumina using AIBN.

To resolve these overlapping resonances, DEPT-135 along with DEPT-90 spectral analysis (Fig. 5) has been carried out. The spectral region between 25.41–26.01 and 28.75–29.95 ppm has been assigned to

C^{4}H$_2$ and C^{5}H$_2$ carbons of the 1-Oct unit, respectively, while the region of 33.49–38.89 ppm belongs to the C^{1}H$_2$, C^{3}H$_2$, and C^{9}H$_2$ of 1-Oct and MA, respectively. All the above regions are broad
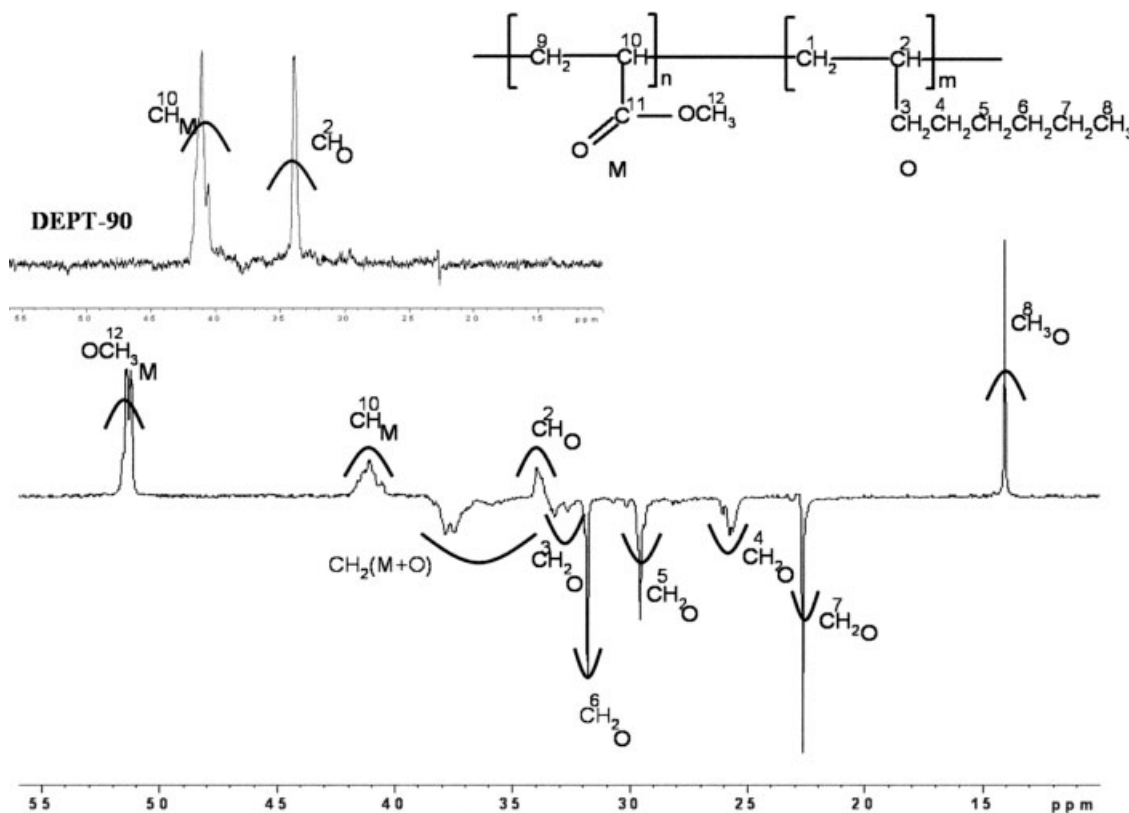

Figure 5 DEPT-135 NMR spectrum of MA/1-Oct copolymers having $F_{1\text{-Oct}} = 0.49$ synthesized in presence of acidic alumina using AIBN in CDCl$_3$ at 30°C
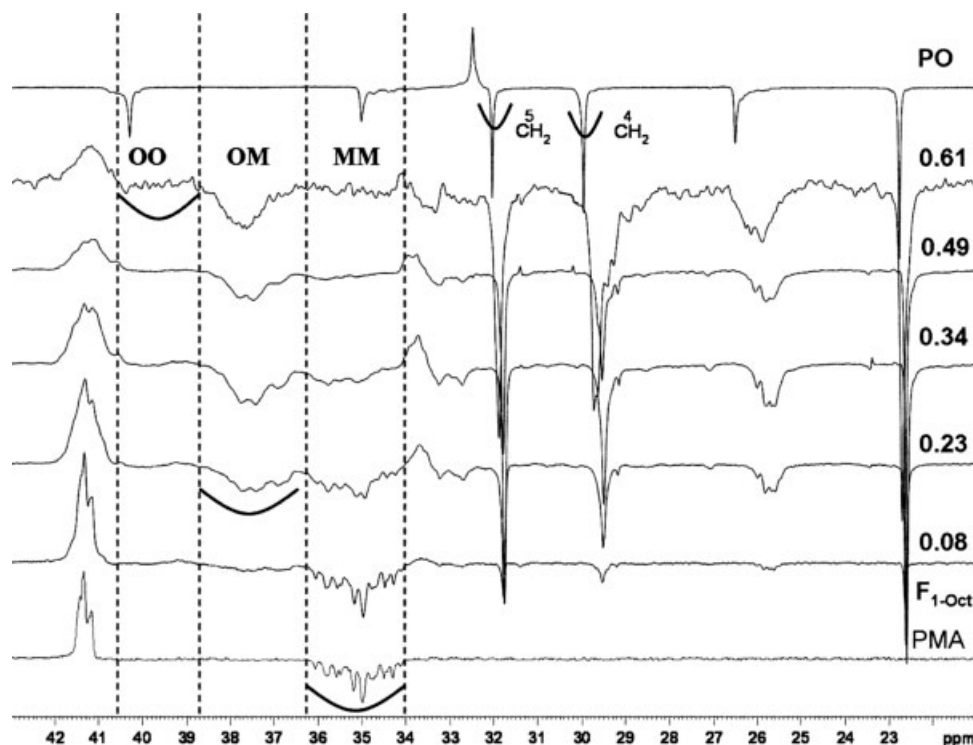
Figure 6 Expanded DEPT-135 NMR spectra of MA/1-Oct copolymers showing resonance pattern from 22.04 to 42.57 ppm with increasing $F_{1\text{-Oct}}$ in CDCl$_3$ at 30°C synthesized in presence of acidic alumina using AIBN.

indicative of their sensitivity toward configuration as well compositions sequences. The methine carbons ($C^2H_{1\text{-Oct}}$ and $C^{10}H_{MA}$) were assigned with the help of DEPT-90 (insert in Fig. 5) because it was overlapping with the C^1H_2 and C^3H_2 carbons resonance region.

A comparison of the spectral region from 22.04 to 42.57 ppm in DEPT-135 for MA/1-Oct copolymers with increasing F_O in their chains is shown in Figure 6. It is observed that with increase in the 1-Oct content in the copolymer, the intensities of the peak corresponding to C^4H_2 and C^5H_2 of 1-Oct unit increases. These carbon nuclei are configurational sensitive, as the resonance patterns for each methylene carbon remain identical in spite of the composition variation, which means that these carbons are configurational sensitive rather than compositional. Considering the region from 32.01 to 41.03 ppm, with increase in 1-Oct content in the copolymer, the resonances not only show change in intensity but also in splitting indicating their sensitivity toward configuration as well as composition.

Another interesting feature that is observed was shifting of the resonance peaks belonging to the backbone methine ($^2CH_{1\text{-Oct}}$) and methylene ($^1CH_2$) carbons of 1-Oct unit in the copolymer (Fig. 6). In the homopolymer, poly(1-octene) (PO),[26] the resonance peak for methine carbon comes around 32.51 ppm, which in copolymer is coming at 33.99 ppm having a downfield shift of $\sim$ 1.5 ppm. For the backbone methylene carbon of 1-Oct in the copolymer, the resonance peak that comes around 40.12 ppm in the homopolymer has shifted upfield to 36.0 to 38.0 ppm. This might be due to the spatial vicinity of carbonyl carbon of MA unit to the methine and methylene carbon of 1-Oct.

The resonance pattern in the spectral region (Fig. 6) from 33.51 to 39.76 ppm belonging to the backbone methylene carbons of the MA and 1-Oct unit can be divided into three regions. The region around 34.0–36.21 ppm can be assigned to MM dyad,[24] whereas region from 36.11 to 38.36 ppm belongs to OM dyad. The OO dyad[27] can be assigned to the region from 38.40 to 40.21 ppm. The variation in the intensity of the resonance peaks with varying copolymer composition clearly indicates that as the 1-Oct content in the copolymer increases, the intensity of MM dyad decreases whereas that of OM dyad increases. This feature supports the assumption that as the amount of 1-Oct in the comonomer infeed is increased, it prefers to copolymerize rather than act as chain transfer agent. The reason behind this feature is because there is a competition between the double bond of both MA and 1-Oct units to attack the MA radical. But, as MA is now coordinated with acidic alumina, its reactivity decreases leading to higher probability of double bond of 1-Oct to attack and hence formation of OM dyad.

When the 1-Oct content is at the lower side in the comonomer infeed, the MM dyad sequences

predominate due to the higher probability of MA radical to attack MA as its amount is higher. But, once the optimum 1-Oct concentration is achieved, the alternate monomer sequences in the form of OM dyad become predominant in the polymer chain.

Acidic alumina-mediated copolymerization of MA and 1-Oct in the presence AIBN at 70°C for 4 h resulted in copolymers having predominantly alternative sequences (OM dyad) as depicted by NMR studies. The incorporation of 1-Oct into the polymer chain increased as the infeed of 1-Oct was increased. 1-Oct content in copolymer was found to be 0.61, specifically at MA/1-Oct of 0.02. MA/acidic alumina ratio was found to control the total percentage conversion during copolymerization but independent for alkene incorporation.

CONCLUSIONS

Lewis acid-mediated copolymerization of MA with 1-Oct using heterogeneous acidic alumina leads to the formation of alkene-rich copolymers with maximum alkene incorporation of 61%. The variation of amount of acidic alumina and the polymerization time does not play a role in obtaining the desired copolymer composition. Increasing the 1-Oct content in the infeed increased its incorporation in the copolymer leading to formation of alkene-rich copolymers. DEPT-135 NMR gave an effective insight into the copolymer nature.

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