ORIGINAL PAPER

Synthesis of acrylate-1-hexene based functional polyolefin using activators regenerated by electron transfer atom transfer radical polymerization (ARGET ATRP)

Hiren M Bhajiwala and Virendrakumar Gupta[*]

Reliance Research Development Group, Reliance Industries Ltd., Reliance Corporate Park, Ghansoli, Navi Mumbai, Maharashtra – 400701, India

ABSTRACT

The copolymerization of methyl acrylate (MA) and glycidyl methacrylate (GMA) with 1-hexene was carried out using activator regenerator by electron transfer atom transfer radical polymerization (ARGET ATRP) employing $Cu(0)/CuBr_2$ as a catalyst, pentamethyl diethylenetriamine (PMDETA) as a ligand, and ethyl 2-bromoisopropionate (EBriP) as the initiator, all at a reaction temperature of 70°C. This process resulted in the production of viscous and transparent copolymers, namely poly (methyl acrylate-*co*-1-hexene) or PMH and poly (glycidyl methacrylate-*co*-1-hexene) or PGMH. For the MA/1-Hex copolymer, conversion rates ranged from a maximum of 31 wt.% to a minimum of 12 wt.%, while the GMA/1-hexene copolymer exhibited conversion rates ranging from a maximum of 42 wt.% to a minimum of 12 wt.%. It was observed that increasing the amount of 1-hexene during the synthesis led to a higher incorporation of 1-hexene content in both the MA and GMA polymer backbones, with a maximum of 15 wt.% and 18 wt.% of 1-hexene being incorporated into PMH and PGMH, respectively. The incorporation of 1-hexene was confirmed through Nuclear Magnetic Resonance (NMR) studies, including ^{1}H, ^{13}C, and DEPT 135 studies. Additionally, the copolymer PMH and PGMH exhibited monomodal molecular weight distribution curves when evaluated using the size exclusion chromatography (SEC) high-performance liquid chromatography (HPLC) technique, with polydispersity values in the range of 1.19-1.37 and 1.07-1.11, respectively. These findings indicate that the copolymerization process was well-controlled and followed a radical polymerization mechanism. **Polyolefins J (2023) 10: 235-242**

Keywords: ARGET ATRP; methyl acrylate; glycidyl methacrylate; 1-hexene; control radical polymerization (CRP).

INTRODUCTION

Polyolefins are widely embraced as commodity polymers due to their cost-effectiveness and well-balanced chemical and physical properties, rendering them the most preferred choice for various applications in modern life [1-3]. However, a significant drawback of polyolefins is their lack of functional groups, which hinders their utilization in domains such as adhesion, dyeability, and printability. This limitation can be overcome by the incorporation of functional monomers in the olefin backbone to produce functional polyolefins. Consequently, the pursuit of functional polyolefins has emerged as an important area for academic and industrial communities [4-8]. Crafting specialty materials that incorporate polar and nonpolar monomers remains a challenging task [9].

Copolymerization of polar monomers with non-polar alkenes remains an interesting area as the combination of the polar-nonpolar monomer can greatly enhance the polymer properties [10-12]. Typically, polar and non-polar monomers necessitate distinct catalyst systems

[*]Corresponding Author - E-mail: Virendrakumar.Gupta@ril.com

and reaction conditions for polymerization. Polar monomers typically polymerize readily through a free-radical mechanism [13-14], whereas non-polar monomers often require Ziegler-Natta or metallocene-type catalysts or harsh conditions for free-radical polymerization [15].

Over the past decade, various living-controlled polymerization methods, such as Atom Transfer Radical Polymerization (ATRP), Nitroxide Mediated Polymerization (NMP), and Reversible Addition Transfer Polymerization (RAFT), have experienced rapid development. This growth is driven by the demand for diverse polymer architectures tailored for specialized applications. Among these techniques, ATRP stands out as a popular method for achieving living (or controlled) radical polymerization. In copper-mediated ATRP, the carbon-halogen bond within an alkyl halide (RX) is reversibly cleaved by a Cu(I)X/ligand system. This cleavage generates a radical (R•) and Cu(II)X$_2$/ligand complex, which acts as a deactivator. The resulting radical can either reversibly deactivate, engage with a monomer, or undergo an irreversible termination step in the polymerization process [16-17]. ATRP is now a well-established living polymerization technique that provides not only control over polymer architecture and composition but also over molecular weights [7, 18].

Nowadays, the innovative concept of ARGET ATRP has allowed polymerizations to be conducted with very less quantities (at ppm level) of catalysts making it more attractive for commercial acceptance [19-21]. Sen et al. conducted a comprehensive investigation into copper-mediated controlled copolymerization. They explored the combination of methyl acrylate with 1-alkene using the ATRP technique [22-24]. Klumperman et al studied the copolymerization of acrylate with 1-octene using a CuBr catalyst system with various ligands like 4,4'-di(5-nonyl)-2,2'bipyridine (dNbpy) and PMDETA [25-26]. Matyjaszewski and his team reported a controlled copolymerization involving *n*-butyl acrylate and nonpolar 1-alkene, employing the ARGET ATRP method. Notably, ARGET ATRP demonstrated its efficiency by requiring significantly less catalyst than conventional ATRP [27]. This technique employed Cu (0) as a reducing agent during the polymerization of acrylates with 1-alkene, effectively reducing Cu (II) to Cu(I) in the course of the reaction [28, 29].

It is desirable to study the ARGET ATRP technique for 1-alkene and different polar monomers. We have studied 1-hexene and methyl acrylate/glycidyl methacrylate systems for synthesis and polymer characterization study. Such a system is studied to a lesser extent as mostly 1-octene and acrylates (methyl or butyl acrylate)-based systems are studied by ARGET ATRP. In this study, we reported control polymerization of MA and GMA with 1-hexene using ARGET ATRP at different monomer molar ratios and different catalyst concentrations using Cu (0) as the reducing agent with CuBr$_2$/PMDETA as the catalyst system and EBriP as initiator. [1]H nuclear magnetic resonance (NMR) spectroscopy was utilized to monitor the individual monomer conversion. The incorporation of 1-alkene was also characterized through ^{13}C and DEPT 135 (Distortion less Enhancement by Polarization Transfer) techniques.

EXPERIMENTAL

Materials

Methyl acrylate (MA, 99%), glycidyl methacrylates (GMA, 99%,) 1-hexene (98%), ethyl 2-bromoisopropionate (EBriP, 99%), copper (II) bromide (CuBr$_2$, 99 %), and copper powder [Cu (0), 99 %], were purchased from Sigma Aldrich and used for synthesis. LR grade pentamethyl diethylenetriamine (PMDETA) was purchased from Fluka and used as a ligand. MA and GMA were distilled for removing the stabilizer, both were stored at lower temperatures before being used for testing.

Polymerization procedure

Polymerizations were carried out either under bulk condition in a nitrogen atmosphere for MA/1-hexene or in toluene media for GMA/1-hexene polymerization, as GMA under bulk condition gives a solid polymer, which is difficult to solubilize into any solvent, probably due to very high rate of reaction in bulk conditions. A calculated amount of MA or GMA, 1-hexene, Cu (0) powder, CuBr$_2$, and PMDETA was added in a 100 ml two-neck flask, and then the mixture was stirred for 10 minutes thoroughly followed by the addition of EBriP initiator. The flask was immersed in a thermostatic oil bath and the reaction temperature was maintained at 70°C. The reaction mixture was cooled after the desired polymerization time and diluted with chloroform, followed by subsequently passing through a neutral alumina column to remove the catalyst. Further, the solution was concentrated, and the polymer was precipitated in excess of methanol. The synthesized polymer was dried in a vacuum oven at 60°C till a constant weight was obtained to ascertain the removal of excess solvent.

Characterization of poly (methyl acrylate-*co*-1-hexene) PMH and poly (glycidyl methacrylate-*co*-1-hexene) PGMH

The total percentage conversion was measured gravimetrically. The incorporation of non-polar species into the polar backbone was quantified through proton resonance of $-CH_3$ of 1-hexene and $-OCH_3$ of methyl acrylate unit in ^{1}H NMR [30-32]. The molecular weight of the PMH and PGMH copolymer was determined by Size Exclusion Chromatography (SEC) using a Perkin-Elmer Series 200 instrument (columns: Waters Styragel HR 3, 7.8×300 mm, 5-micron particle size) equipped with Perkin–Elmer Series 200 pump and refractive index detector system at a flow rate of 0.5 ml/min at 35°C. The system was calibrated with polystyrene standards.

All the NMR spectra of PMH and PGMH were recorded on a Bruker Advance-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 10s was given for recording ^{1}H NMR spectra. For $^{13}C\{^1H\}$ NMR spectra, a 2s delay time was given and 5000 scans were accumulated. By using DEPT-90, 135 spectra were recorded using a standard pulse sequence with a J modulation time of 3.7 ms (JCH ¼ 135 Hz) with a delay time of 2s. Signal intensities of spectra peak were measured from the integrated areas calculated with an electronic integrator. NMR measurements were made on 10% weight/volume (% w/v) polymer solutions.

RESULTS AND DISCUSSION

Synthesis of copolymer of MA/1-hexene and GMA/1-hexene by ARGET ATRP

The impact of monomer concentration on conversion and molecular weight characteristics was investigated by varying the quantity of MA/1-hexene, with mole ratios of 0.5:1.0, 1.0:1.0, and 2.0:1.0, as detailed in Table 1. The molar ratio of $CuBr_2$: PMDETA: Cu(0): EBriP was maintained at 0.004:0.02:0.1:1, and the polymerization reaction was conducted at 70°C for 24 hours. The results demonstrated that an increase in the amount of MA led to a decrease in the incorporation of 1-hexene, reducing it from 15 wt.% to 5.0 wt.%. The level of 1-hexene incorporation was determined through ^{1}H NMR, following the method described in previous literature [30-32]. Monomer-to-copolymer conversion (%Conv.) was found to be higher when the MA quantity was increased (Experiment #3) compared to situations with equal or lower MA-to-1-hexene ratios. The conversions for experiments #1, #2, and #3 ranged from 12% to 31% wt.%, which aligns with findings by Matyjaszewski et al., where butyl acrylate/1-octene exhibited 11.8% and 21.7% wt.% conversion after 21 and 33 hours, respectively. Similarly, in the synthesis of the GMA/1-Hex copolymer (PGMH) (Experiments #4 and #5), conversions of 12% and 42% wt.% were observed, along with 18% and 16% wt.% incorporation of 1-hexene, as detailed in Table 1.

A molecular weight analysis of PMH revealed a polydispersity index (PDI) ranging from 1.19 to 1.37. This range indicates that the polymerization process is controlled and exhibits living polymerization characteristics. The weighted average molecular weight (M_w) of the synthesized polymer fell within the range of 2.83×10^4 to 3.67×10^4. That indicated that a higher quantity of 1-hexene in Experiment #1 led to a lower M_w. This can be attributed to the reduced probability of MA propagation due to the higher availability of 1-hexene in the reaction mixture compared to MA. In contrast, PGMA exhibited a higher molecular weight and a narrower PDI

Table 1. Study on effect of monomer ratio on conversion and molecular weight for copolymerization of MA with 1-hexene using ARGET ATRP[a].

Expt #	Acrylate : 1-hexene (mole basis)	% Conv (Wt.%)	F_{1-Hex}[d]	M_w[e] ×10^-4	PDI (M_w/M_n)
1[b]	0.5:1.0	12	15.0	2.83	1.19
2[b]	1.0:1.0	21	12.0	3.74	1.23
3[b]	2.0:1.0	31	5.0	3.67	1.37
4[c]	1.0:1.0	12	18	1.25	1.11
5[c]	2.0:1.0	42	16	1.28	1.07

Experimental condition:
[a]$CuBr_2$:PMDETA:Cu(0):EBriP = 0.004 :0.02 : 0.1: 1 in all experiments; Temp -70°C, Reaction time – 24 hrs.; [b]MA: 1-hexene (mole basis), MA = 2.25 ml, 0.025 mole (expt #1); 4.5 ml, 0.05 mole (expt #2); 7.75 ml, 0.1 mole (expt #3); 1-hexene = 6.5 ml, 0.05 mole (expt #1 to 3); [c]GMA : 1-hexene(mole basis), GMA = 6.2 ml, 0.05 mole (expt # 4), 12.4 ml, 0.1 mole (expt # 5), 1-hexene = 6.5 ml, 0.05 mole (expt #4 to 5), $CuBr_2$ = 0.45 mg, 0.2×10^{-2} mmol; Cu(0) = 3.1 mg, 0.05 mmol; EbriP = 90.5 mg, 0.5 mmol; PMDETA = 1.73 mg, 0.01 mmol; [d]Determined by ^{1}H NMR, [e]Determined by GPC.

Table 2. Study on effect of CuBr$_2$ concentration on conversion and molecular weight for copolymerization of MA with 1-hexene using ARGET ATRP[a].

Exp[b] #	CuBr$_2$ (Mole basis)	% Conv (Wt %)	F$_{1-Hex}$[c]	M$_w$[d] x10^{-4}	PDI (M$_w$/M$_n$)
2	0.004	21	12.0	3.74	1.23
6	0.002	19	7.2	2.51	1.32

Experimenal condition:
[a]MA : 1-Hexene : PMDETA : Cu(0): EbriP = 100:100:0.02:0.1:1; Temp -70°C, Reaction time = 24 hrs.; [b] Quantity of MA, 1-hexene, PMDETA, Cu(0) are same as Table 1; CuBr$_2$ = 0.45 mg, 0.2 × 10^{-2} mmol (expt #2), 0.23 mg, 0.1 × 10^{-2} mmol (expt #4); [c] determined by ^{1}H NMR; [d] determined by GPC.

compared to PMA. This difference can be attributed to the cyclic structure and pendant group of glycidyl methacrylate, which may create steric hindrance, limiting the access of the monomer to the active Cu site. This limitation leads to lower molecular weight in the case of PGMA compared to the linear structure of the pendant group in MA. Furthermore, the impact of changing the concentration of the transition metal catalyst (CuBr$_2$/EBriP molar concentration of 0.004 and 0.002) was examined while maintaining a fixed molar ratio of MA:1-hexene:PMDETA:Cu(0):EBriP at 1.0:1.0:0.02:0.1:1. The results indicated that an increase in catalyst concentration resulted in slightly higher conversion and molecular weight, along with increased 1-hexene incorporation, as shown in Table 2. Importantly, the polydispersity was narrower at higher catalyst quantities, highlighting the controlled nature of the polymerization process. This suggests that an optimal catalyst quantity is crucial for achieving controlled polymerization. The reaction schematic illustrating the MA/1-Hexene polymerization process is depicted in Scheme 1.

A kinetic investigation of the polymerization process was carried out with a composition of MA:1-hexene: CuBr$_2$: PMDETA: Cu(0):EBriP at a ratio of 2.0:1.0:0.004:0.02:0.1:1. This study involved monitoring the conversion at three-hour intervals for a total duration of 24 hours during the synthesis of PMH, as detailed in Table 3. The conversion of the monomer was determined through gravimetric analysis, based on the initial monomer weight. The maximum observed conversion reached 31 wt.% after 24 hours, with a nearly linear increase in M$_w$ during the initial 12 hours. Figure 2 illustrates that the polydispersity index (PDI) remained within the range of 1.2 to 1.4. This trend clearly suggests that employing Cu (0) at the parts per million (ppm) level in the copolymerization of methyl acrylate and 1-hexene results in a nearly constant concentration of growing species. The consistently low PDI indicates a preference for adding monomer units to the growing polymer chain during the activation cycle, favoring the forward reaction over the formation of dormant chain ends. During the first 12 hours, the conversion rate was relatively rapid, reaching 26 wt.% conversion. Subsequently, the conversion rate slowed, with an additional 5 wt.% conversion achieved (increasing from 26 wt.% to 31 wt.%), as indicated in Table 3. In Figure 1, the variation of ln([M0]/[M]) versus polymerization time exhibits a slight curvature near the end, indicating a decrease in the number of growing radicals at that stage.

The copolymerization of methyl acrylate with

Table 3. Polymerization kinetics study of MA with 1-hexene using ARGET ATRP[a].

| Time (hrs.)	% Conv. (wt %)	M$_w$[b]x10^{-4}	PDI (M$_w$/M$_n$)
3	6	1.43	1.29
6	18	2.01	1.36
9	21	2.49	1.19
12	26	3.11	1.30
18	27	3.21	1.32
24	31	3.67	1.37

Experimental condition:
[a] MA : 1-Hexene : CuBr$_2$: PMDETA : Cu(0) : EBriP = 200 : 100 : 0.004 :0.02 : 0.1 : 1 in all experiments; Temp -70°C, Reaction time – 24 hrs.; MA = 7.75 ml , 0.1 mole ; 1-hexene = 6.5 ml, 0.05 mole ; CuBr$_2$ = 0.45 mg, 0.2 × 10^{-2} mmol; Cu(0) = 3.1 mg, 0.05 mmol; EBriP = 90.5 mg, 0.5 mmol; PMDETA = 1.73 mg, 0.01 mmol; [b] determined by GPC.

Figure 1. Polymerization kinetics of MA with 1-hexene, reaction condition= MA :1-Hexene: CuBr$_2$: PMDETA: Cu (0) : EBriP = 200 : 100 : 0.004 : 0.02 : 0.1 : 1; reaction temperature = 70°C.
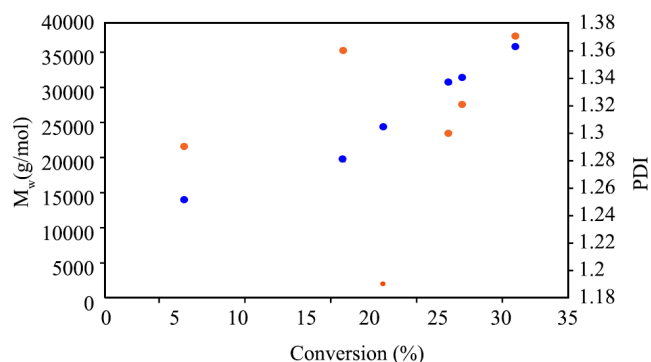
Figure 2. Polymerization kinetics of MA with 1-hexene, reaction condition= MA :1-Hexene: CuBr$_2$: PMDETA: Cu (0): EBriP = 200 : 100 : 0.004 : 0.02 : 0.1 : 1 reaction temperature = 70°C, Molecular weight and polydispersity dependence on total monomer conversion.

Figure 3. ^{1}H NMR of MA/1-hexene copolymer having F1-Hex = 0.15 (Expt #1) in CDCl$_3$ at 30°C synthesized by ARGET ATRP.

1-hexene that is conducted with a reduced concentration of copper catalyst in the presence of Cu (0) powder is a well-controlled reaction. This approach, involving a limited presence of Cu (II) species, helped to minimize the formation of dormant polymer chains. Thus, it promoted the addition of monomers to the growing polymer chains, enabling more propagation and ultimately achieving a total conversion of 31% with a narrow PDI. In the later stages of the polymerization, a decline in the number of active radicals was observed, as indicated by the slight curvature in the kinetic plot. This observation indirectly suggests the high reactivity of methyl acrylate monomers, which had a greater tendency to incorporate into the polymer chain compared to 1-octene. Hence, at the end of polymerization, higher concentration of 1-octene in the reaction mixture led to an increased termination reaction. The size exclusion chromatography (SEC) data shown in Figure 10 confirms a monomodal distribution of the resulting polymers.

NMR studies of poly(methyl acrylate-*co*-1-hexene) and poly (glycidyl methacrylate-*co*-1-hexene)

The NMR analysis of PMH derived from Experiment #1, with a molecular weight (M$_w$) of 2.83 × 10^4 and a polydispersity index (PDI) of 1.19, is illustrated in Figure 3. The spectra clearly indicate separate signals for the -OCH$_3$ group of MA and the -CH$_3$ group of 1-hexene, which were utilized for the quantification of 1-hexene content. Within the spectrum, multiple peaks were observed in the range of 1.61-2.31 ppm, corresponding to the -CH$_2$ and -CH groups of both MA and 1-hexene. Additionally, another resonance signal appeared at 4.13 ppm, situated near the methoxy group of MA. This signal was attributed to the -CHBr
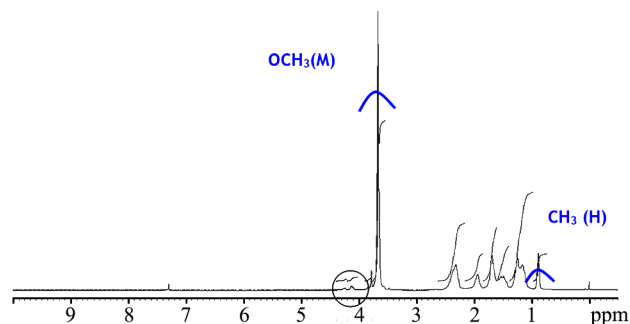
group at the end of the polymer chain [29].

The ^{13}C NMR analysis unveiled specific carbon resonances: the carbonyl carbon of MA was detected in the region around 175.9 ppm. Meanwhile, the carbon signals for the -C^{6}H$_3$ and -C^{5}H$_2$ groups of the 1-hexene unit were observed at 14.3 and 23.0 ppm, respectively. Additionally, the -OC^{4}H$_3$ and -C^{2}H carbons of the MA unit appeared at 51.8 and 41.4 ppm, respectively. However, the spectral region spanning from 37.5 to 28.0 ppm presented a complex profile due to signal overlap. This overlap resulted from the signals of the -C^{6}H group of 1-hexene, the -C^{5,7,8} H$_2$ groups of 1-hexene, and the -C^{1}H$_2$ group of MA, as depicted in Figure 4.

Detail peak identification of methyl, methylene, and methine carbon signals was carried out by DEPT 135 which showed that methylene carbon signals a negative phase, while methyl and methine carbon signals a positive phase [30-31]. DEPT 135 indicated that –C^{9}H$_2$, –C^{7}H$_2$, –C^{6}H have been assigned to 1-hexene, whereas region between 33.6-37.5 ppm assigned to
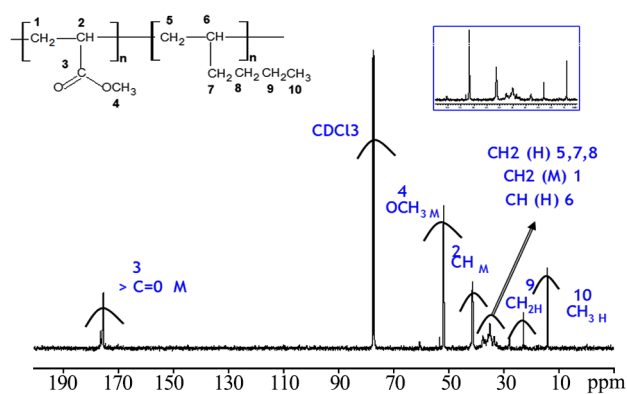
Figure 4. ^{13}C NMR spectra of MA/1-hexene copolymer having F1-Hex = 0.15 (Expt #1) in CDCl$_3$ at 30°C synthesized by ARGET ATRP.
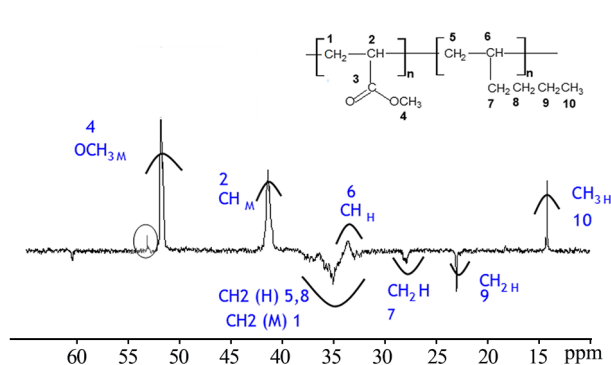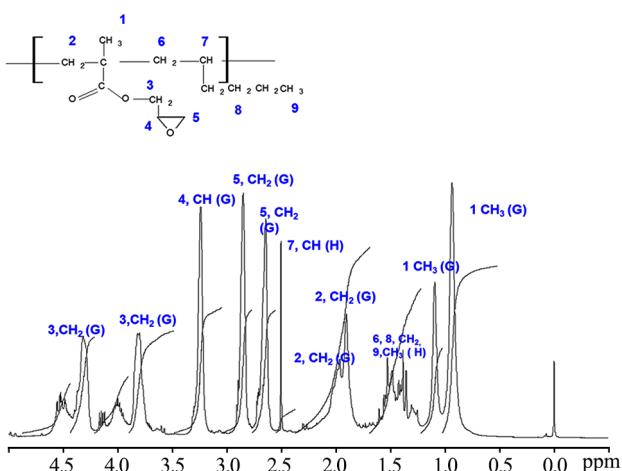
Figure 5. DEPT-135 NMR of MA/1-hexene copolymer having F1-Hex = 0.15 (Expt #1) at 30°C synthesized by ARGET ATRP.
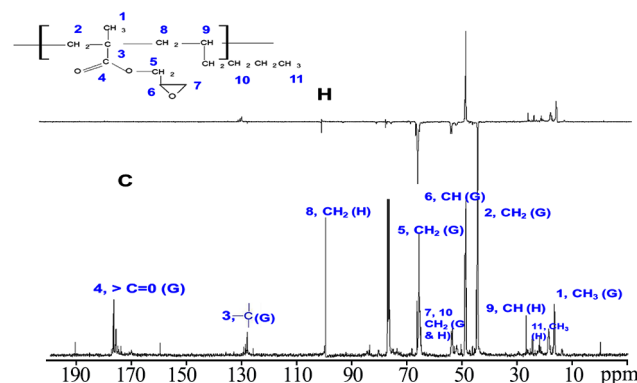

Figure 7. ^{13}C & DEPT 135 NMR spectra of GMA/1-hexene copolymer having F1-Hex = 0.18 (Expt #4) in CDCl$_3$ at 30°C synthesized by ARGET ATRP.

–C^{5,8}H$_2$ of 1-hexene and –C^{1}H$_2$ of MA. One smaller signal at 52.6 ppm was observed in the positive phase which represents –CHBr (Figure 5). NMR study thus confirmed the formation of the random nature of MA/1-hexene copolymer.

NMR study of PGMH from Experiment # 4 having M$_w$ 1.25 × 10^{-5} and PDI of 1.11 is depicted in Figure 5. Spectra indicated that the –CH signal of GMA and the -CH signal of 1-hexene were clearly separated which was used for the calculation of incorporation of 1-hexene. The multiple peaks observed between 1.2-1.8 ppm were due to –CH$_2$ and –CH$_3$ of 1-hexene.
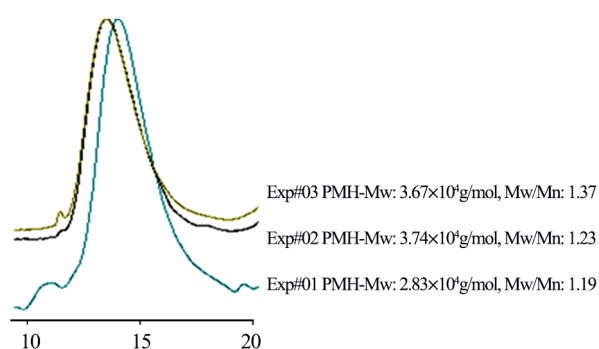
^{13}C NMR study of copolymer revealed that carbonyl carbon resonance of GMA assigned to the region around 175.9 ppm. The -C^{1}H$_3$ of GMA and -C^{11}H$_3$ carbon of the 1-hexene unit appeared at 16 and 18.5 ppm, respectively, whereas -C^{2,5}H$_2$ of GMA appeared at 44.7, 65.4 ppm, respectively, and –C^{8}H$_2$ of 1-hexene appeared at 100.0 ppm. -C^{6}H carbon of GMA appeared


Figure 8. SEC traces of PMH synthesized using ARGET ATRP

at 48.8 ppm and -C^{9}H carbon of 1-hexane appeared at 26.8 ppm. The spectral region of 48 to 55 ppm was found to be quite a complex region because of the overlapping signals of -C^{7,10}H$_2$ of GMA and 1-hexene (Figure 6). Detail peak identification of methyl, methylene, and methine carbon signals was carried out by DEPT 135 which showed that methylene carbon signals a negative phase, while methyl and methine carbon signals a positive phase (Figure 7). NMR study thus confirmed the formation of the random nature of GMA/1-hexene copolymer.

Figure 6. ^{1}H NMR of GMA/1-hexene copolymer having F1-Hex = 0.18 (Expt #4) in CDCl$_3$ at 30°C synthesized by ARGET ATRP.
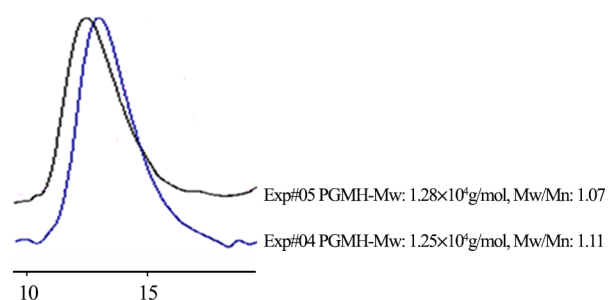
Figure 9. SEC traces of PGMH synthesized using ARGET ATRP.
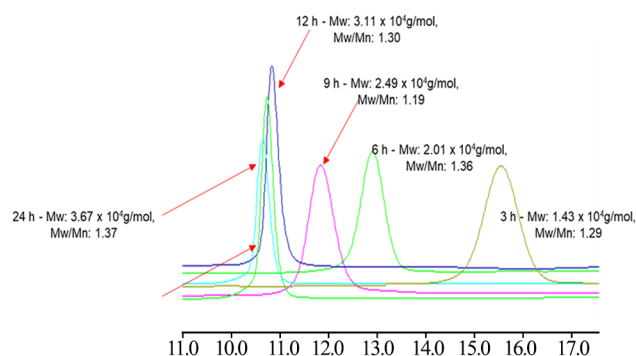
Figure 10. SEC traces of PMH molecular weight and molecular weight distribution at different times (MA :1-Hexene: CuBr$_2$: PMDETA: Cu (0) : EBriP = 200 : 100 : 0.004 : 0.02 : 0.1 : 1 reaction temperature = 70°C).

CONCLUSION

A comprehensive investigation of ARGET ATRP was conducted for both MA with 1-hexene and GMA with 1-hexene. In the case of PMH, the polymer exhibited a maximum 15 wt.% incorporation of 1-hexene into the MA backbone, whereas PGMH showed an 18% incorporation of 1-hexene into the GMA backbone. These copolymers were synthesized using EBriP as the initiator, PMDETA as the ligand, and CuBr$_2$/Cu(0) as the catalyst system. As the content of 1-hexene increased during synthesis, it resulted in higher levels of 1-hexene incorporation for PMH. All the synthesized PMH and PGMH polymers displayed narrow molecular weight distributions, indicating a controlled radical polymerization process. An increase in the catalyst quantity led to a higher weight average molecular weight while retaining a narrow molecular weight distribution for the copolymer. The ^{13}C and DEPT135 NMR analysis of the polymer confirmed the incorporation of 1-hexene into the MA backbone.

CONFLICTS OF INTEREST

The authors declare that they have no conflicts of interest.

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