

Synthesis and Characterization of Sustainable Co-polymers Using a Series of Methacrylate Monomers and β -myrcene

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ABSTRACT

This paper describes the synthesis and characterization of sustainable polymers using β -myrcene monomer as a terpene compound. These polymers were synthesized using an environmentally benign emulsion copolymerization method, three monomers were used: isodecyl methacrylate, isobutyl methacrylate, and cyclohexyl methacrylate, each of which was polymerized separately with β -myrcene monomer. All these polymers can be vulcanized latex, which can be used to make semi-synthetic rubber. Ammonium persulfate was used as an initiator, sodium dodecyl sulfate SDS as an emulsion, and sodium bicarbonate as a pH regulator to synthesis the copolymers in a 50/50 ratio. Fourier transform infrared (FTIR), proton nuclear magnetic resonance ($^1\text{H-NMR}$) and carbon-13 nuclear magnetic resonance ($^{13}\text{CNMR}$) spectroscopy were used to characterize the synthesized copolymers, the spectra results indicated that their signals correspond to the chemical formula of the copolymer. The glass transition temperature means that the polymer is rubbery in nature, and the glass transition temperature values are similar to those of homogeneous methacrylate polymers, it was discovered that the length of the side chain of methacrylate monomers affects the polymerization reaction, and the optimum conditions for this reaction are 60°C for 20 hours.

Keywords: β -myrcene, Cyclohexyl methacrylate, Emulsion polymerization, Isodecyl methacrylate, Isobutyl methacrylate, Rubber.

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INTRODUCTION

Recently, macromolecular science and technology have concentrated on the need for sustainable development and a reduction in our dependence on petroleum-based goods; as a result, research has primarily focused on substituting renewable raw materials for fossil raw materials to provide a better quality of life and a cleaner climate.¹⁻⁴ With the emergence of bio-based polymers, bio-based elastomers from natural reservoirs have gotten much attention.⁵ After being subjected to stress, elastomers have a high degree of extensibility, up to several hundred percent, and can return to their original shape and structure.⁶ Elastomers have a wide range of applications, and play a significant role in automobiles, safety, and everyday life. Terpenes have sparked much interest in recent research on the many natural and sustainable elastomeric materials derived from renewable biomass or agricultural waste.⁷⁻⁹ Terpenes are a common class of natural compounds found in turpentine, citrus, and pine oils, and they could readily be converted into platform chemicals utilizing existing petrochemical methods.^{10,11} Furthermore, Amyris has created a novel industrial biotechnological manufacturing pathway that promises large-scale terpene supply by fermentation of plant sugars and cellulose waste.^{12,13} β -myrcene, which

features a conjugated double bond, has recently been used to make a variety of macromolecular compounds. Pyrolysis of α -pinene, one of the major components in turpentine, can provide substantial amounts of β -myrcene.¹⁴ Recently, the manufacture of myrcene using metabolic engineering of *Escherichia coli*.¹⁵ Emulsion polymerization is a green chemical technique widely utilized to make various polymeric materials.¹⁶ Although this is a preferred manufacturing procedure, there have been a limited number of research publications published in recent years that use this technology to prepare sustainable polymers.¹⁷ Copolymers based on methacrylate derivatives are a type of functional polymer that could be used in various applications.^{18,19} Until far, no study has focused on the green polymerization of biobased copolymers of β -myrcene and certain methacrylate derivatives. The major goal of this study is to create a bio-based elastomer. As a result, β -myrcene was chosen as the major monomer since it provides the polymer with rubbery qualities.

MATERIAL AND METHODS

Material

β -myrcene was purchased from Sigma-Aldrich used without further purification, Isodecyl methacrylate, Isobutyl

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methacrylate, and cyclohexyl methacrylate. They were bought from Sigma-Aldrich and purified through a standard alumina column to remove the inhibitor. Sodium bicarbonate, Sodium dodecyl sulfate, and Ammonium persulfate were purchased from Sigma and used as received. Solvents were bought from G.C.C.

Synthesis of a Series of Copolymers

In a 25 mL dry round bottom flask containing few drops of deionized water, (0.042 g) of sodium dodecyl sulfate (SDS) as emulsifier was dissolved with (0.025 g) of sodium bicarbonate as a buffer, and then complete the volume to 4.20 mL. The mixture was stirred for 20 minutes, then (1-mL, 0.83 gm) of β -myrcene was added over 10 minutes, followed by the addition of (0.95 mL, 0.83 gm) one of the methacrylate monomers. The reaction mixture was kept for 30 minutes without stirring, to form an inert blanket. The flask was sealed with a rubber stopper and then injected with nitrogen. The temperature was then set to 60°C, then an aqueous solution of ammonium persulfate was added as a thermal radical initiator. After 20 hours copolymers precipitated as a coagulated mass, which was forcefully agitated several times with ethanol, then washed with deionized water and dried at 40°C for 10 hours, and the amounts of the polymerization materials reported in Table 1.

The three copolymers were synthesized according to the quantities/volumes, and route of reaction is shown in Scheme 1 to 3.

Appearance that resulting product was a small soft latex piece for the three polymers in which is (myrcene-co-isodecyl methacrylate), poly(myrcene-co-isobutyl methacrylate), poly(myrcene-co-cyclohexyl methacrylate), and their colors were roughly between yellow and light yellow as shown in Figure 1.

Measurements

The FTIR spectra were recorded as ATR using Bruker-Tensor 27 spectrometer. $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra were recorded using Bruker-300 MHz spectrometer and Deuterated chloroform as a solvent. Thermogravimetric analysis performed using SDT Q600-Simultaneous TGA/DSC within 40 to 600°C, 20°C/min range.

RESULTS AND DISCUSSION

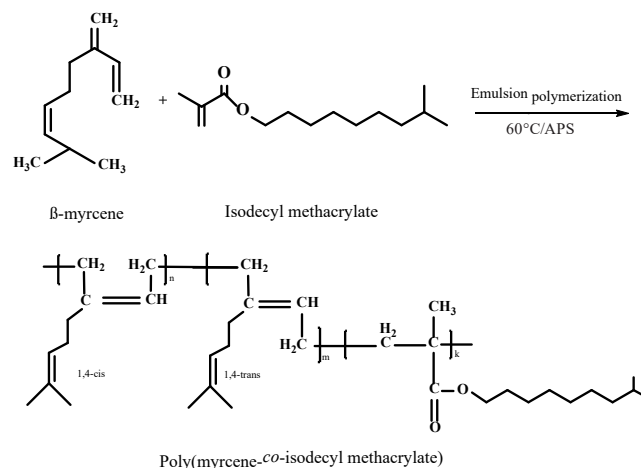
Three methacrylate monomers (Isodecyl methacrylate IDMA, Isobutyl methacrylate IBMA, and Cyclohexyl methacrylate

CHMA) and β -myrcene were polymerized via emulsion polymerization at 60°C for 20 hours using persulfate as an initiator. It has been observed that the side chain of methacrylate monomers has a significant role in polymerization reaction.^{20,21} Therefore, polymerization process showed that the rate of the polymerization reaction is in order of following:



The side chain has been found to have an important role in polymerization. This effect fluctuated between cyclic and linear hydrocarbons, as well as their linked with the ester group. As a result, the apparent rate constant (K_{app}) for each polymerization process was used to determine the conversion of monomers to polymers. Figure 2.

Myrcene with IDMA, IBMA, and CHMA monomers was polymerized by emulsion copolymerization, SDS was used as a surfactant, and NaHCO_3 was utilized as a buffer. It is known that emulsion copolymerization is affected by a variety of factors, including polarity, solubility, and emulsion stability, in addition to side groups of methacrylate monomers. Micelles are formed when SDS molecules aggregate together, and monomers are absorbed simultaneously within these micelles. Interval I begin by adding an aqueous ammonium persulfate solution to the reaction system, which causes free



Scheme 1: Schematic for the copolymerization of myrcene and isodecyl methacrylate

Table 1: Recipe amounts for emulsion copolymerization reactions

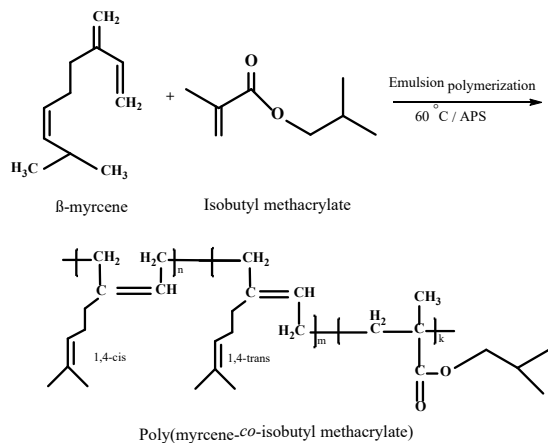
Materials	Amount (g)	Volume mL	Density g/cm ³	Molecular weight g/mol
β -Myrcene	0.8300	1.00	0.7940	136.23
Isodecyl methacrylate	0.8300	0.95	0.0878	226.33
Isobutyl methacrylate	0.8300	0.90	0.8860	142.20
Cyclohexyl methacrylate	0.8300	0.86	0.9640	168.23
Sodium dodecyl sulfate	0.0420	0.042	1.0100	288.38
Sodium bicarbonate	0.0250	0.011 + 4.20DI	2.200	84.01
Ammonium persulfate	0.0060	0.003	1.9800	228.20
Deionized water	-	4.20	1.0000	18.015

radicals to scatter in the aqueous medium, polymerizing monomer molecules. The residual free radicals continued to form oligomeric radicals (relatively insoluble in the aqueous medium), which enter the micelles to propagate and finally transform into particle nuclei. The formation of latex particles is determined by the consumption of monomers by free radicals inside micelles. Hence the reaction between polymeric radicals and monomer molecules continues in interval 2. The monomer

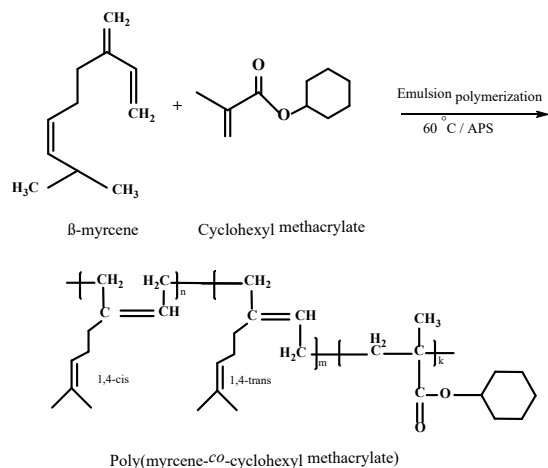
concentration continues to fall at this point, and disappear the monomer droplets, the leftover free radicals may react with other free radicals or with two radicals in the particle to terminate the reaction (Figure 3).²²

Impact of Temperature and Time on Polymerization Reaction

The optimum conditions for polymerization reaction of β -Myrcene with IDMA, IBMA, and CHMA monomers were



Scheme 2: Schematic for the copolymerization of myrcene and isobutyl methacrylate



Scheme 3: Schematic for the copolymerization of myrcene and cyclohexyl methacrylate



Figure 1: Photographs of the three copolymers synthesized by emulsion polymerization

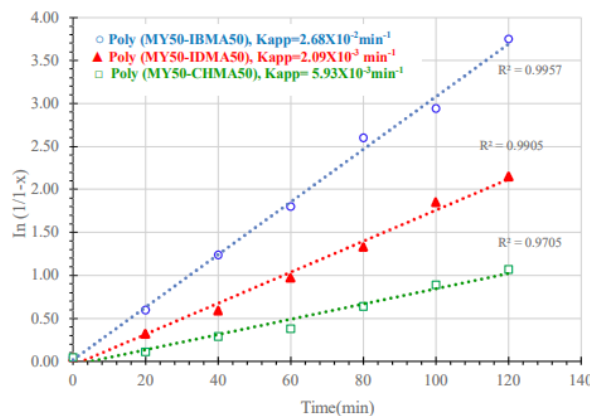


Figure 2: Apparent rate constant (K_{app}) and conversion percent (X) for each emulsion copolymerization

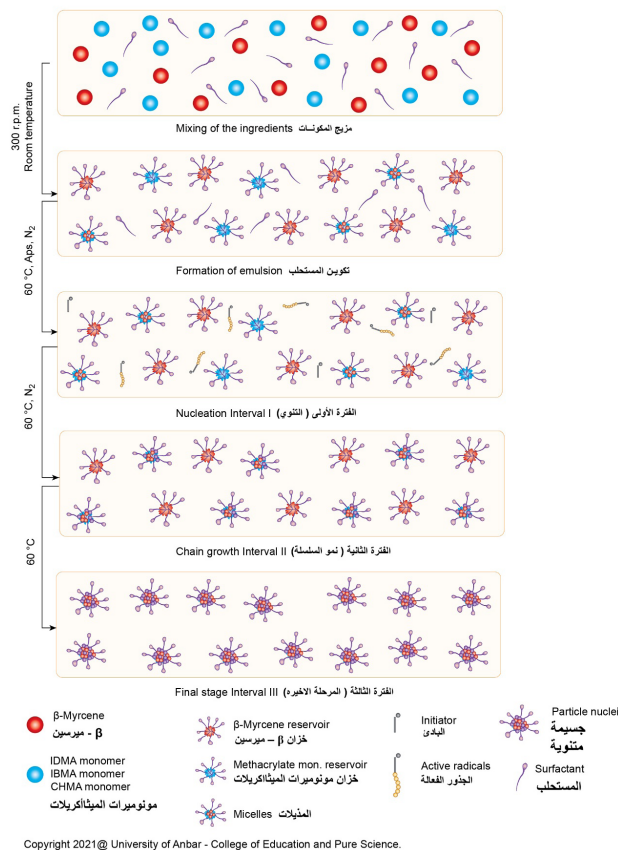


Figure 3: Emulsion copolymerization mechanism at different intervals of β -myrcene and the methacrylate derivatives

determined individually by measuring the temperature, as it increased by 5°C within temperature range 50–70°C during 20 hours (Figure 4).

According to the data, the yield percent increases until it reaches 60°C, thereafter it begins to decline, the drop in yield is due to decopolymerization, which is caused by side chains causing heat breakdown of bonds in the polymer chain. The polymerization time was calculated using the mass weight of the polymer, Figure 5.

Figure 5 shows that the yield increases with time until it reaches 24 hours at 60°C, with 20 hours being the optimum duration, after which the yield decreases due to polymer decomposition and oligomers formation.

The Copolymers' Solubility and Swelling Behavior

The theoretical solubility parameter was estimated using the Hoftzyer and van Krevelen technique in accordance with the group contribution principle, and the solubility and swelling values of the polymers were assessed using certain aprotic polar solvents, Table 2.

Despite that the side chains of the polymers were different, they all exhibited a good solubility in CHCl_3 at room temperature, hence CHCl_3 was utilized as a solvent in spectroscopic analysis. The solubility parameter values for polymers are very comparable, and they show solubility in common solvents (THF, CHCl_3 , and Toluene). However, the polymers swell and become insoluble in mitogen-activated

protein kinase kinase (MEK) and dimethylsulfoxide (DMSO) due to the difference inside chains of polymers.

Thermal Analysis of the Synthesized Copolymers

Simultaneous differential scanning calorimetry (DSC) and Thermogravimetric analysis (TGA) experiments were used to assess the thermal behavior (glass transition temperatures T_g) of poly(MY_{50} -IDMA $_{50}$), (MY_{50} -IBMA $_{50}$) and (MY_{50} -CHMA $_{50}$). The T_g for polymers was found to be 127.01, 116.25, and 117.50°C. This is thought to be attributable to the type of side chains.^{24,25} DSC thermal analysis were performed within the range (Figure 6). Figure S1 and S2 in the supporting information, DSC for poly(MY_{50} -IDMA $_{50}$) showed T_g at 127.01, which implies a modest decrease in polymer chain elasticity and an increase in hardness. There is exothermic band at 300°C attributable to crystallization temperature (T_c). In comparison (melting temperature) T_m was observed at 389.57°C as broad absorption band, lastly (decomposition temperature) T_d at 550°C, data are given in Table 3.

Copolymer Characterization

The FT-IR for synthesized copolymers were recorded using an ATR sampling technique in a Bruker-Tensor 25 machine within a spectral range of 4000 to 500 cm^{-1} . The stretching vibration band of C=O ester at 1720 cm^{-1} in the spectra (Figure 7) of poly (MY-IDMA) suggests that the methacrylate moiety was successfully synthesized into the copolymer structure, the

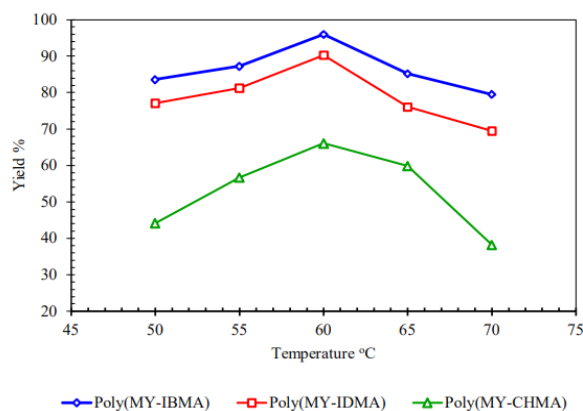


Figure 4: Temperature dependence of poly(MY_{50} -IBMA $_{50}$), (MY_{50} -IDMA $_{50}$) and (MY_{50} -CHMA $_{50}$) synthesis

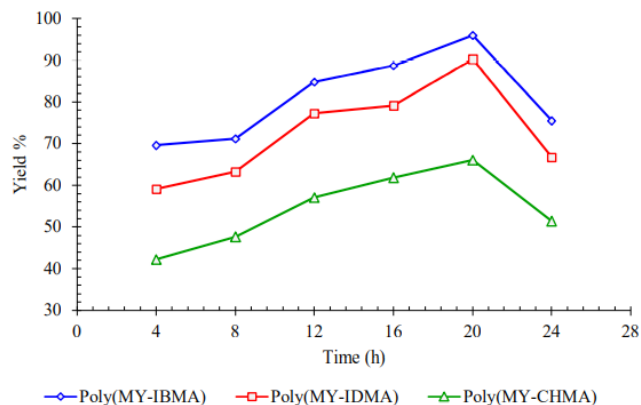


Figure 5: Time dependence of poly(MY_{50} -IBMA $_{50}$), (MY_{50} -IDMA $_{50}$) and (MY_{50} -CHMA $_{50}$) synthesis

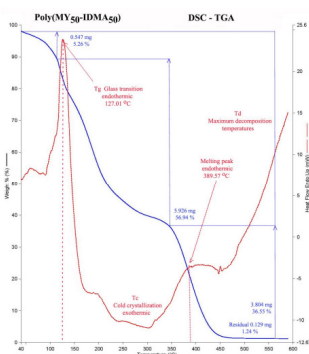
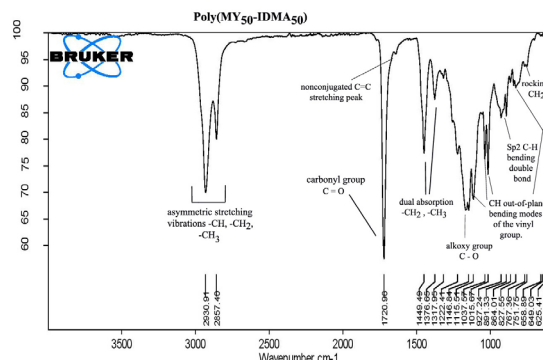
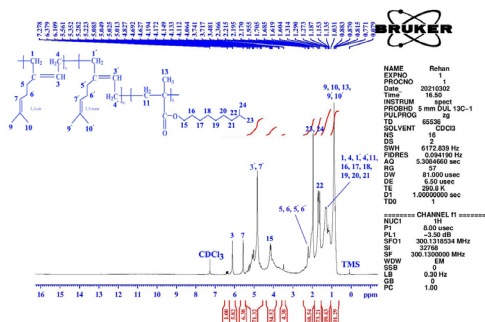
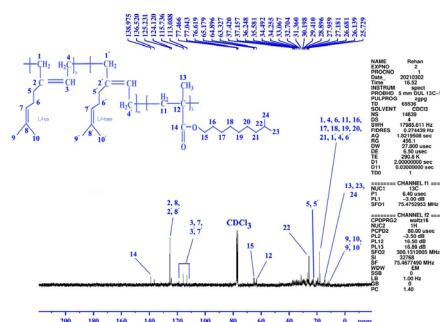
Table 2: Estimation of the produced copolymers solubility behavior and theoretical parameters (see Appendix A, B, and C in the supporting information)

Copolymer (theoretical solubility parameter, $\text{MPa}^{1/2}$)	Solvents (solubility parameter, $\text{MPa}^{1/2}$)				
	Toluene (18.2)	THF (18.6)	CHCl_3 (19.0)	MEK (19.0)	DMSO (29.7)
(MY_{50} -IDMA $_{50}$) (17.2-17.8)	+	+	+	S,-	-
(MY_{50} -IBMA $_{50}$) (16.8-21.5)	+	+	+	S, +	S
(MY_{50} -CHMA $_{50}$) (18.3-18.6)	+	+	+	S, +	-

+: completely soluble, ±: partially soluble, -: insoluble, s: swells but not soluble Values are calculated by the Hoftzyer and Van Krevelen methods, as well as the Small methods, and values were taken from reference [23]

Table 3: Thermal analysis data for synthesized copolymers

Sample	T_g ($^{\circ}\text{C}$)	Transition temperature ($^{\circ}\text{C}$)			Weight loss at transition (%)	Residual weight (%) at $\sim 577^{\circ}\text{C}$
		T_c	T_m	T_d		
poly(MY ₅₀ -IDMA ₅₀)	127.01	300.00	389.57	550.00	98	1.24
poly(MY ₅₀ -IBMA ₅₀)	116.25	180.00	302.50	576.25	98	1.98
poly(MY ₅₀ -CHMA ₅₀)	117.50	175.00	372.50	575.20	97	2.69


Figure 6: TGA, DSC thermogram of poly (MY₅₀-IDMA₅₀)

Figure 7: FT-IR Spectrum for synthesized Poly (MY-IDMA)

Figure 8: ¹H-NMR Spectrum for synthesized Poly (MY₅₀-IDMA₅₀)

Figure 9: ¹³C NMR Spectrum for synthesized Poly (MY50-IDMA50)

stretching absorption bands for aliphatic C-H for myrcene and methacrylate moieties were observed within a range 2800 to 2900 cm^{-1} , the band at 1146 cm^{-1} attributable for C-O for side chain, while a band at 751 cm^{-1} assigned to rocking for CH_2 .

The FTIR spectrum of poly (MY-IBMA) (Figure S3 in the supporting information) showed the stretching vibration for C=O at 1725 cm^{-1} , $\nu\text{C-H}_{\text{aliphatic}}$ within the range 2800–2900 cm^{-1} , 1148 cm^{-1} ascribe to $\nu\text{C-O}$. Out of plane bending C-H for vinyl moiety was observed 933–1109 cm^{-1} , while rocking vibration for CH_2 observed at 750 cm^{-1} .

While FT-IR spectrum of poly (MY-CHMA) (Figure S4 in the supporting information) showed the stretching vibration for C=O at 1719 cm^{-1} , $\nu\text{C-H}_{\text{aliphatic}}$ within the range 2800–900 cm^{-1} , 1165 cm^{-1} ascribe to $\nu\text{C-O}$. Bending of C-H was observed within the range 1294–1455 cm^{-1} and disappearance of bending out of plane C-H for vinyl.

NMR spectroscopy was used to determine the structures of myrcene/methacrylate copolymers, and the following is a discussion of the ¹H-NMR chemical shift values of the synthesized copolymers:

Poly(MY₅₀-IDMA₅₀): ¹H-NMR (300 MHz, CDCl_3 , δ , ppm): 6.11(1H), 5.56 (1H), 4.83 (2H), 4.15 (2H), 2.22 (8H) 1.96 (6H), 1.71(1H), 1.60(22H), 0.88(15H). (Figure 8)

Poly(MY₅₀-IDMA₅₀) spectrum showed proton signals of the vinyl group at 6.11, 5.56, 4.83 ppm, O- CH_2 signal for isodecyl group observed at 4.15 ppm, methylene group for myrcene signaling at 2.22 ppm, and two methyl groups for isodecyl signaling at 1.96 ppm. While $-\text{CH}(\text{CH}_3)_2$ for isodecyl appeared at 1.71 ppm, C1 and C4 signals for myrcene appeared at 1.60 ppm, signal at 0.88 ppm attributable for two methyl groups for myrcene moiety $-\text{CH}(\text{CH}_3)_2$.

Poly(MY₅₀-IBMA₅₀): ¹H NMR (300 MHz, CDCl_3 , δ , ppm): 6.38- 6.35 (2H), 6.31-5.56 (2H), 3.95 (2H), 3.91 (1H), 2.00 (8H), 1.71 (9H), 1.69(8H), 0.98-0.96(14H).

Poly(MY₅₀-IBMA₅₀) spectrum showed protons signals of the vinyl groups =CH- for myrcene and isopropylidene were observed at 5.56, 6.31, 6.35, 6.38 ppm, O- CH_2 signal for isobutyl group observed at 3.95 ppm, methylene group for myrcene signaling at 2.00 and 1.69 ppm for myrcene and at 0.98 ppm for IBMA, and methyl groups $-\text{CH}(\text{CH}_3)_2$ for isobutyl and myrcene signaling at 1.71 and 0.96 ppm

Poly(MY₅₀-CHMA₅₀): ¹H NMR (300 MHz, CDCl₃, δ , ppm): 6.09-5.53 (4H), 4.77 (1H), 1.94 (16H), 1.83 (2H), 1.68 (10H), 1.42 (12H), 1.26(3H).

Poly (MY₅₀-CHMA₅₀) spectrum showed protons signals of the vinyl group for myrcene were observed within the range 5.53 to 6.09 ppm, O-CH signal for cyclohexyl group observed at 4.77 ppm, methylene group for myrcene signaling at 1.68 ppm, and two methyl groups -CH(CH₃)₂ for myrcene signaling at 1.26 and 1.42 ppm.

Furthermore, ¹³C NMR was used to determine the copolymer structures, the chemical shift values for produced polymers were discussed as the following

Poly(MY₅₀-IDMA₅₀): ¹³C NMR (300 MHz, CDCl₃, δ , ppm): 138.97 (1C), 125.23 (4C), 115.73-113.08 (4C), 64.89 (1C), 63.32 (1C), 26.13(1C), 25.27(2C), 19.64 (13C), 14.41(3C), 11.47 (4C).

¹³C NMR spectrum for Poly(MY₅₀-IDMA₅₀) spectrum in Figure 9 shows the carbon signal for carbonyl group (O=C) was observed at 138.97 ppm for IDMA unit, the olefinic carbon atom =C= (C2 and C8) for the myrcene unit was recorded at 125.23 ppm, vinyl carbon atom C3 and C7 were observed at 113.08 and 115.73 ppm, carbon signal for -OCH₂ group which confirms copolymerization for MY and IDMA was recorded at 64.89 ppm. the signal for quaternary carbon (for IDMA moiety) was located at ppm 63.32, while the signals for methylene carbon atom for MY and IDMA moiety were found at 25.72 and 19.64 ppm. Finally, methyl group (CH₃) carbon signals were recorded at 14.41 and 11.47 ppm.

Poly(MY₅₀-IBMA₅₀): ¹³C NMR (300 MHz, CDCl₃, δ , ppm): 177.90 (1C), 138.97 (2C), 124.72-124.12 (2C), 118.79 (2C), 115.72- 113.08(2C), 70.45(1C), 58.48(1C), 37.85 (1C), 34.86 (2C), 29.71- 23.98(7C), 19.13(3C), 17.68(4C).

¹³C NMR spectrum for Poly(MY₅₀-IBMA₅₀) spectrum (Figure S7) shows the carbon signal for carbonyl group (O=C) was observed at 177.90 ppm for IBMA unit, the olefinic carbon atom =C= (C2 and C8) for the myrcene unit was recorded within the range 124.12–138.97 ppm, vinyl carbon atom C3 and C7 were observed at 113.08, 115.72 and 118.79 ppm, carbon signal for -OCH₂ group which confirms copolymerization for MY and IBMA was recorded at 70.45 ppm. the signal for quaternary carbon (for IBMA moiety) was located at ppm 58.48, while the signals for methylene carbon atom for MY and IBMA moiety were found within the range 23.98 to 34.71 ppm, Finally, methyl group (CH₃) carbon signals were recorded within the range 17.68 to 19.13 ppm.

Poly(MY₅₀-CHMA₅₀): ¹³C NMR (300 MHz, CDCl₃, δ , ppm): 177.21 (1C), 124.67 (4C), 119.34 (4C), 71.81 (1C), 40.33 (1C), 37.85(2C), 37.43(2C), 34.82 (3C), 25.44 (7C), 23.43(3C), 19.12(1C).

¹³C NMR spectrum for Poly(MY₅₀-CHMA₅₀) spectrum (Figure S8 in the supporting information) shows the carbon signal for carbonyl group (O=C) was observed at 177.21 ppm for CHMA unit. The olefinic carbon atom =C= (C2 and C8) for the myrcene unit was recorded within the range 124.67 ppm, vinyl carbon atom C3 and C7 were observed at 119.34 ppm, carbon signal for -OCH₂ group which confirms copolymerization for MY and CHMA was recorded at 71.81 ppm. The signal for

quaternary carbon (for MY moiety) was located at ppm 40.33, while the signals for methylene carbon atom for MY moiety were found within 37.85 ppm, Finally, methyl group (CH₃) carbon signals were recorded at 23.44 and 19.12 ppm.

CONCLUSIONS

The polymers poly(myrcene-co-isodecyl methacrylate), poly(myrcene-co-isobutyl methacrylate), and poly(myrcene-co-cyclohexyl methacrylate)] were synthesized utilizing β -myrcene and methacrylate monomers under optimum conditions of 60°C for 20 hours. NMR and FT IR confirmed their structures. Although side chains of polymers have diverse structures, they have good thermal stability. The study demonstrate that the polymerization rate decreased when the side chain length and the presence of aromatic rings were increased the, the T_g of the polymers (myrcene-cyclohexyl and isobutyl methacrylate) was within (116–117), which is similar to the T_g of methacrylate homopolymers, which is 105. The solubility behavior of copolymers in organic solvents was investigated, and according to solubility parameters, it was discovered that toluene and chloroform are suitable solubilities for latex.

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