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Preparation and identification of green polymers towards the production of sustainable latex from β -myrcene and some methacrylate monomers

Fouad M. Hussein

Department of Chemistry, College of Education for Pure Sciences,
University of Anbar, Al-Ramadi, Iraq

Ali S. Ismail

Department of Chemistry, College of Education for Pure Sciences,
University of Anbar, Al-Ramadi, Iraq
Corresponding author email: esp.ali.sami@uoanbar.edu.iq

Abstract---Sustainable polymers have enough potential to overcome petroleum materials and not completely rely on them for the presence of renewable raw materials, as well as the possibility of developing polymerization methods for renewable raw materials to have these materials recyclability, biodegradability and being a non-toxic material. This has been the focus of recent years. Solvent-free emulsion copolymerization of β -myrcene, a naturally occurring monoterpene monomer, the co-monomers that were used with β -myrcene, tetrahydrofurfuryl methacrylate, *iso*-bornyl methacrylate, and *tert*-butyl methacrylate, and each methacrylate monomer was polymerized separately with β -myrcene monomer, β -myrcene –methacrylate monomer (MY/MA) copolymers of different compositions were synthesized under nitrogen atmosphere at 60 °C, using copolymers composition 50/50 comonomer reactivity ratios, and has been added sodium dodecyl sulfate as emulsifier, and ammonium persulfate as initiator. $^1\text{H-NMR}$, $^{13}\text{CNMR}$ and FTIR spectroscopy were used to confirm the chemical structure and composition. It was found that the copolymerization reaction of each copolymer is influenced with the form of the methacrylate(s) side chain. Furthermore, the thermal properties of copolymers were characterized by DSC and TGA, where the value T_g indicate that random composition copolymers, due to the difference in crystallization of each side chain. The current study would thus

expedite in synthesizing myrcene-based elastomers as new route for sustainable material.

Keywords---emulsion copolymerization, myrcene, tetrahydrofurfuryl methacrylate, *iso*-bornyl methacrylate, *tert*-butyl methacrylate.

Introduction

In order to use green chemistry principles for the purpose of developing and modernizing chemical products and processes, with the intent to reduce and dispose of its waste, its production of toxic chemicals and its energy consumption during manufacturing (Joseph, 2014). This requires staying away from traditional petrochemical, fossil oils-based polymer materials, like isoprene, butadiene and styrene, and during the past years, due to the emergence of many environmental problems (Noppalit et al., 2019; Grune et al., 2019). Working papers were issued from many conferences, including improving awareness of environmental protection, there is a growing demand to replace petroleum-based materials with biomaterials based on renewable resources (Lei et al., 2018). This requires the extraction of small particles directly from natural resources, for example vegetable(pant) oils and terpenes. Their polymerization has been studied and exploited α -pinene, ocimene, limonene and myrcene are typical representatives of such monomers (Gandini, 2008). The first research on the polymerization of β -myrcene dating back to history 1960; in this paper, the authors examined the potentially of polymerizing β -myrcene by free radical, cationic, anionic, and coordinative mechanisms. Currently, information is beginning to unfold about the molecular structure, molecular weight, and microstructures, and polydispersity of this polymer. Being non-existent in the domain of monomers and polymerization although it has a double bond a conjugated system and is close to isoprene and butadiene. In particular, β -myrcene (7-methyl-3-methylene-1,6-octadiene) is monoterpene, which is extracted from plant oils (hops, cannabis, houttuynia, bay, verbenas) or by pyrolysis of β -pinene (Beher & Johnen 2009; Marvel & Hwa 1960; Hulnik et al., 2018). The direct free radical homogenesis polymerization of these monomers was not felicitous at that time, but their copolymerization with chemical-based monomers (e.g. styrene, methacrylates) typically yielded a low combination of the bio-sourced monomers. Nevertheless, some examples were promising, such as the copolymerization of myrcene with methacrylates and/or styrene (Noppalit et al., 2020; Holmberg et al., 2014; Sarkar & Bhowmick 2017; Trumbo, 2018).

Sarkar and Bhowmick (Sarkar & Bhowmick 2017) have reported the fabrication of terpene based sustainable butyl, lauryl and stearyl methacrylate polymers by an environmentally benign emulsion polymerization method. It was found that the copolymerization with MY rendered the synthesized copolymers as completely amorphous material, add to it length monomer of methacrylate side chain was found to have a profound effect on the polymerization reaction, and with increase inside chain length, the kinetic rate of the copolymerization slowed down to a significant extent, also indicate that the glass transition temperature indicates rubbery nature of the synthesized copolymers. More importantly, it was found

that there is residual unsaturation from the terpene moiety could act as an additional crosslinking site. And that the noticeable changes appeared when changing glass transition temperature value was found to be maximum in the case of MY-BM series and minimum for MY-SM series. Although the pristine poly (stearyl methacrylate) displayed side chain crystallization behavior. More recently, (Sahu et al., 2018) utilized design of a molecular architecture via a green route for improved silica reinforced nanocomposite using glycidyl methacrylate GMA with monomer of myrcene MY, it was found that the copolymer with 90 wt % β -myrcene and 10 wt % of GMA, poly (MY₉₀-GMA₁₀) was considered for detailed structural characterization study. The emulsion polymerized (MY-co-GMA) polymer can be a solution to improve the performances of silica tire tread composite and have a great potential in the tire industry.

The major goal of this study is to create a bio-based elastomer. As a result, β -myrcene was chosen as the major monomer and inferred that this facile, benign, and inexpensive technology could also be translated for the synthesis of other terpene-based methacrylate polymers provides the polymer with rubbery qualities.

Materials and Methods

Material

β -myrcene (technical grade), the monomers- tetrahydrofurfuryl methacrylate ($\geq 97\%$), *iso*-bornyl methacrylate (technical grade), *tert*-butyl methacrylate ($\geq 98\%$), Sodium bicarbonate NaHCO₃ ($\geq 99.7\%$) as a buffer, Sodium dodecyl sulfate C₁₂H₂₅O₄SNa ($\geq 98.5\%$) as an emulsifier, and Ammonium persulfate N₂H₈S₂O₈ ($\geq 98\%$) as an initiator, and basic alumina Al₂O₃ (Brockmann, Type I, 150 mesh) as an inhibitor for removal monomethyl ether hydroquinone from methacrylate monomers were acquired from Sigma-Aldrich. Methanol (99%), tetrahydrofuran ($\geq 99\%$), toluene (99.8%), dimethyl sulfoxide (99.9%), and methyl ethyl ketone (99.5%) were obtained from Gainland Chemical Co. and used as received.

Copolymerization of β myrcene with Monomers of Methacrylate

First stage, it was dissolved a weight of (0.125 g) of the emulsifier is sodium dodecyl sulfate (SDS), with (0.075 g) of sodium bicarbonate as a buffer in a few drops of deionized water and then complete the volume to (12.50) mL, as shown in Table 1, and mixed well in a 25 mL dry round bottom flask and then put the mixture on magnetic stirring for 20 min.

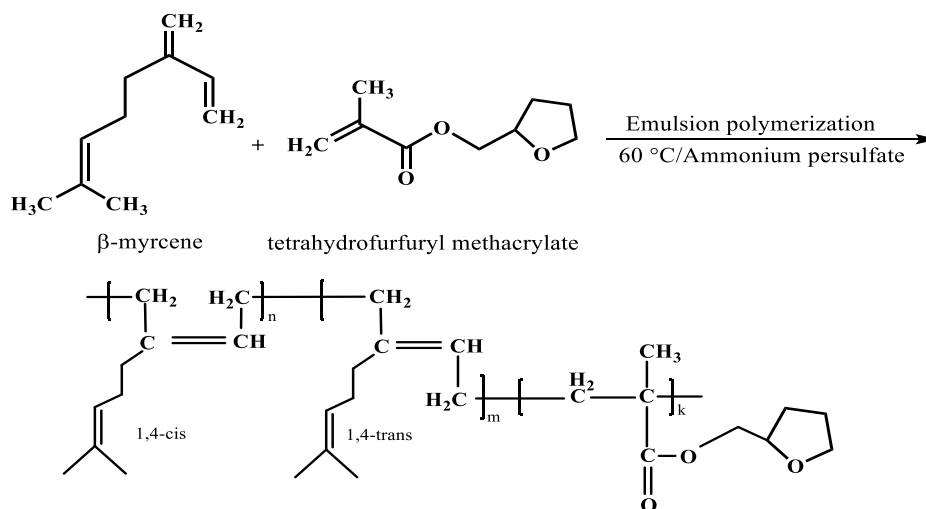
Second stage, this was followed by the addition (2.50 g, 3.17 mL) of myrcene to the reaction flask slowly over a period of 10 minutes, followed by the addition of the first monomer, tetrahydrofurfuryl methacrylate (2.50 g, 2.40 mL) and so on for the remaining monomers. To stabilize the polymerization system, the reaction mixture was left for 20 minutes, followed by closing the orifice of the flask tightly with a rubber stopper and then a teflon paper cover, and then followed by injecting the flask with nitrogen gas.

Third stage, the temperature of the Mantle-hot plate was set at (60 °C), followed by injection of the ammonium persulfate thermal initiator by syringe in the form of droplets of aqueous solution and successively. The polymerization reaction was continued for 20 hours, after this time, the first copolymer, poly (MY₅₀-co-THFMA₅₀) was precipitated in the form of latex curd. Then the curds were washed with ethanol for several times. Then the latex curd was washed in deionized water and dried at 30 °C for 24 hours.

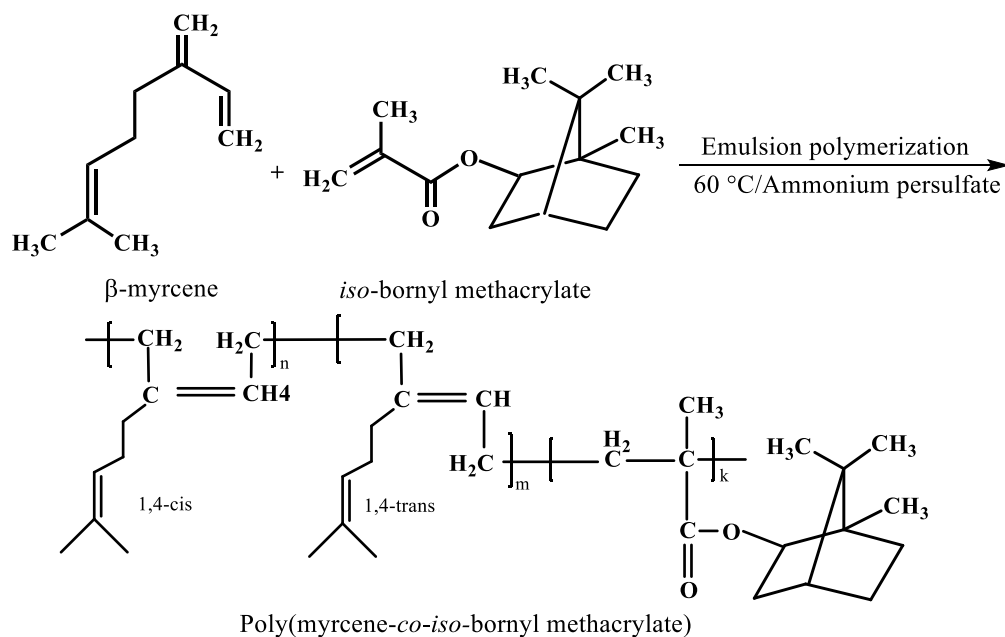
Table 1
Experimental conditions for MY-MA polymerizations for 20 h initiated by ammonium persulfate

Materials	Amount (g)	Volume mL	Density g/cm ³	Molecular weight g/mol
β-Myrcene	2.5000	3.170	0.7940	136.23
Tetrahydrofurfuryl methacrylate	2.5000	2.400	1.0440	170.21
iso-bornyl methacrylate	2.5000	2.540	0.9830	222.32
tert-butyl methacrylate	2.5000	2.850	0.8750	142.20
Sodium dodecyl sulfate	0.1250	0.130	1.0100	288.38
Sodium bicarbonate	0.0750	0.035	2.2000	84.01
Ammonium persulfate	0.0175	0.009	1.9800	228.20
Deionized water	-	12.500	1.0000	18.015

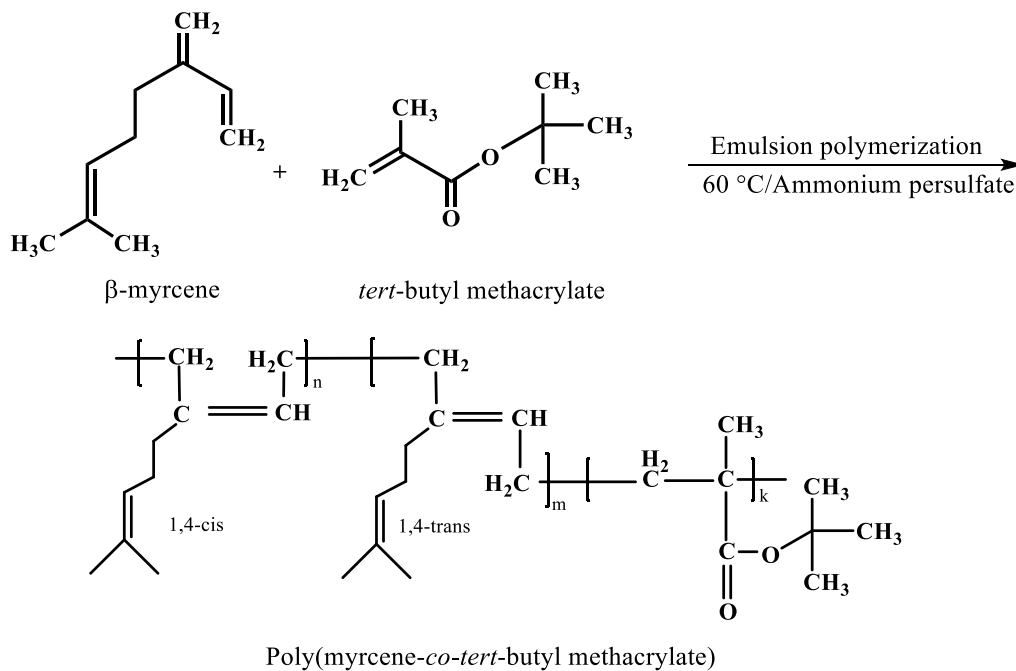
Synthetic route for preparation the copolymers carried out according to the experimental conditions for MY-MA polymerizations, and the reaction route is shown in Schemes 1, 2 and 3.



Scheme 1. Synthetic route for preparation poly (myrcene-co-tetrahydrofurfuryl methacrylate)



Scheme 2. Synthetic route for preparation poly (myrcene-*co*-iso-bornyl methacrylate)



Scheme 3. Synthetic route for preparation poly (myrcene-*co*-tert-butyl methacrylate)

The resulting product from the copolymerization reaction is a soft latex belonging to the three copolymers (MY-co-THFMA), (MY-co-*iso*BMA) and (MY-co-*t*BMA) and its appearance was between white and light brown colors as shown in Figure 1.

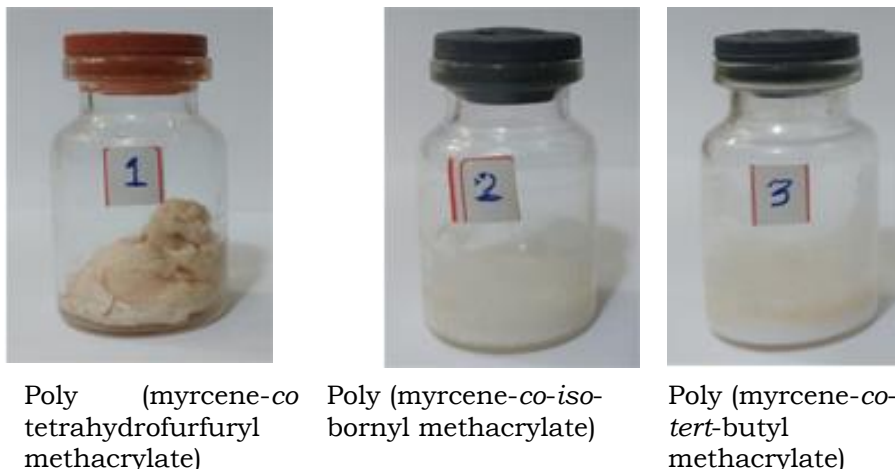


Figure 1. Appearance of copolymers resulting from emulsion polymerization

Measurements

Conversions of monomers were determined by gravimetry, to obtain information on the molecular structure of copolymers based on the mass of dried polymer. ^1H and ^{13}C NMR spectra were obtained by using a Bruker 300 MHz spectrometer. Differential Scanning Calorimetry (DSC) and thermal gravimetric analysis (TGA) was used to determine the copolymers T_g , and thermal stability. The FTIR spectra of the copolymers were performed with Bruker- Tensor 27 spectrometer.

Results and Discussion

To stabilize and choose optimal conditions for the reactions of the emulsion copolymerization of β -myrcene with methacrylate monomers having different structures in their side chains, which are tetrahydrofurfuryl, *iso*-bornyl and *t*-butyl, with the initiator ammonium persulfate, and sodium dodecyl sulfate as anionic emulsifier is also used in emulsion polymerization, sodium bicarbonate as a buffer and stabilizer of the pH of the reaction mixture, with the use of deionized water deionized water as a dispersion medium to ensure complete dissociation of the initiator molecules. According to the emulsion polymerization mechanism, after thermal decomposition of the initiator, the anionic sulfate radical is added with a few monomer units, to become insoluble in water enough, and then enters the swelled micelles of the monomer to form particles, which will continue further for the polymerization reaction. In *t*-butyl monomer, it has the smallest alkyl side chain and is therefore relatively hydrophilic. Therefore, the presence of *t*-butyl methacrylate widely distributed in the aqueous phase and will lead to the formation of surface-active radicals, which would enter the swollen micelles of the

monomer in a way faster to form particle nuclei. Thus, the decrease in the hydrophilic nature will hinder the formation of "particle nuclei", including *iso*-bornyl, which has a side chain containing the ring filled with methylene groups, and the number of carbon atoms for the ring and branching is up to 10 atoms, and under these conditions, the polymerization rate of the polymer is the lowest (Coote et al., 1998; Heuts et al., 1999). However, the monomer of tetrahydrofurfuryl has fewer methylene groups in the side chain that includes the methylene group with the tetrahydrofuran (THF) ring, but it is better in polymerization rate than *iso*-bornyl. In the polymerization process, the apparent rate constant (K_{app}) was used to determine the conversion of monomers into copolymers. Figure 2. In our study, we found the rate of the polymerization reaction in the following order:

$$t\text{-BMA} > \text{THFMA} > \textit{iso}\text{-BMA}$$

The copolymerization stages include three intervals until reaching the latex polymer chains as shown in Figure 3, which are the nucleation interval, chain growth and the formation of latex particles (Saleh & Ismail 2020).

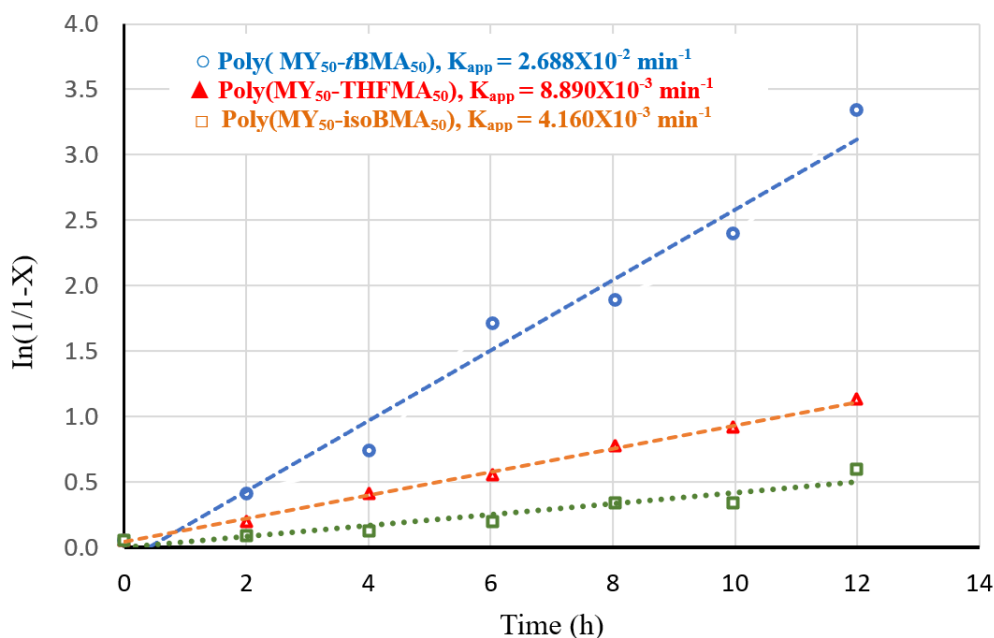
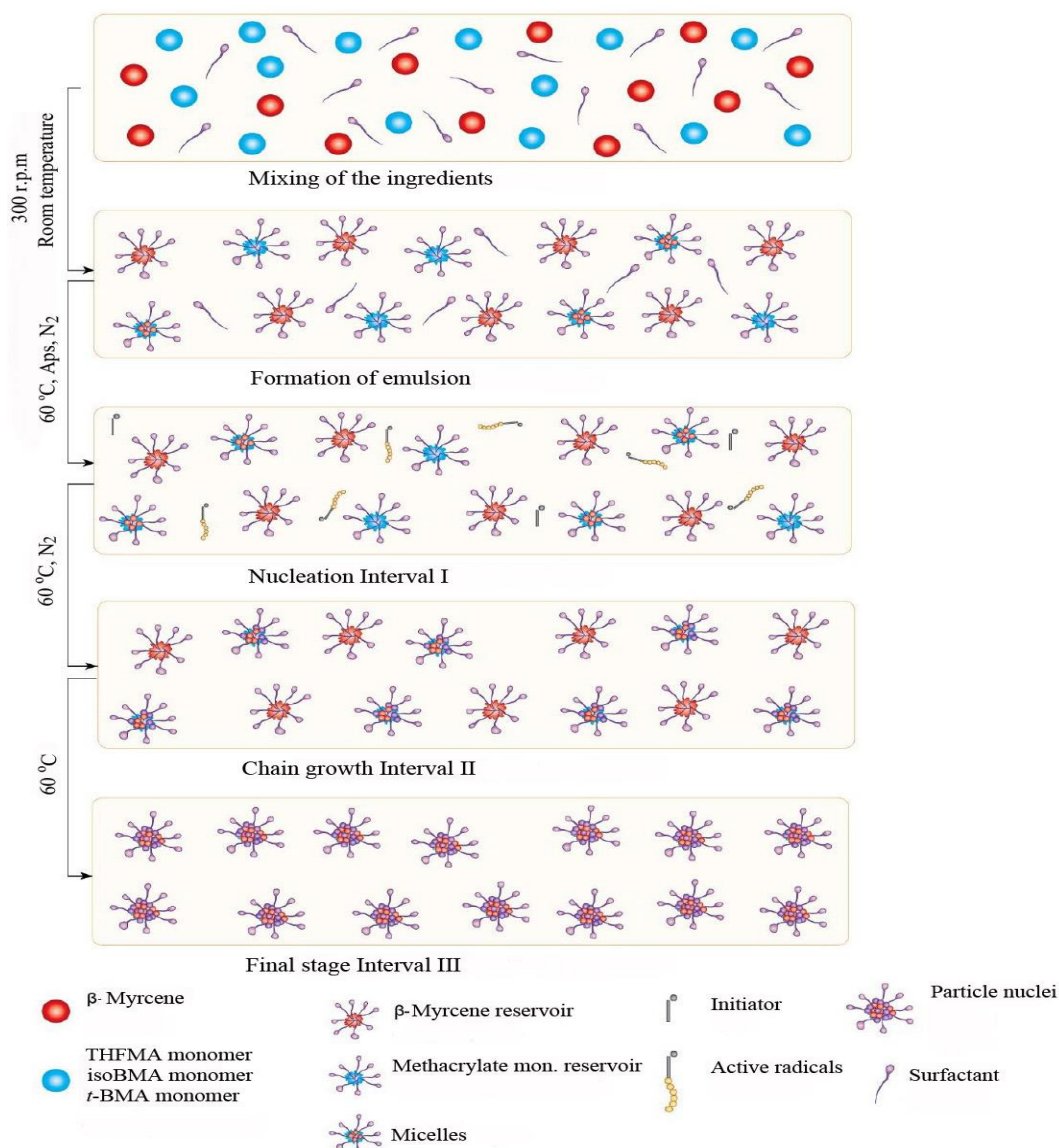


Figure 2. Calculate the apparent rate constant (K_{app}) through conversions of monomers were determined by gravimetry



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Figure 3. The nucleation, chain growth and the formation of latex particles intervals in emulsion polymerization mechanism

Influence of Temperature and Time During the Polymerization Reaction

The influences of temperature and time on the preparation of methacrylate monomers with myrcene monomer, and both separately, was studied. Five different temperatures were set, starting from 40 °C to 80 °C, and then the polymerization reaction time was fixed to 20 hours, where the lowest and highest were chosen temperature to ensure complete initiator decomposition. Figure 4

shows that the percentage of the polymerization product of the copolymers begins to increase with increasing temperature, until it reaches a temperature of 60 °C, and after this temperature there is no increase in the percentage of the copolymer product. This can be attributed to the fact that at a temperature of 60 °C the rate of diffusion of the reaction increases and the completion of polymerization of the monomers in the reaction vessel. After this temperature, thermal decomposition of the polymer chains predominates, and reducing the percentage of polymerization product.

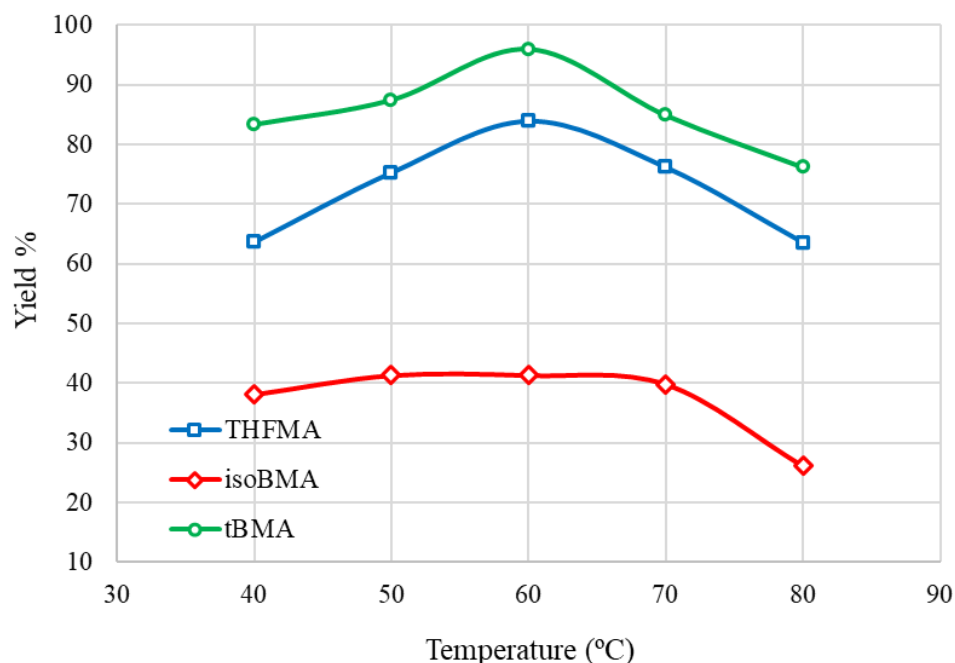


Figure 4. Temperature dependence of poly (MY₅₀-THFMA₅₀), (MY₅₀-iso-MA₅₀) and (MY₅₀-tert-BMA₅₀) synthesis

Figure 5. When following up on the Influence of time on the polymerization reaction, it was found that the percentage of the product increases with the time of the polymerization reaction up to 20 hours, and it is believed that prolonging the time more than 20 hours will lead to the cleavage of the polymeric chains and turn them into chains with specific repeating units (oligomers), and through the cumulative study of the dependence of temperature and time (Wang et al., 2012).

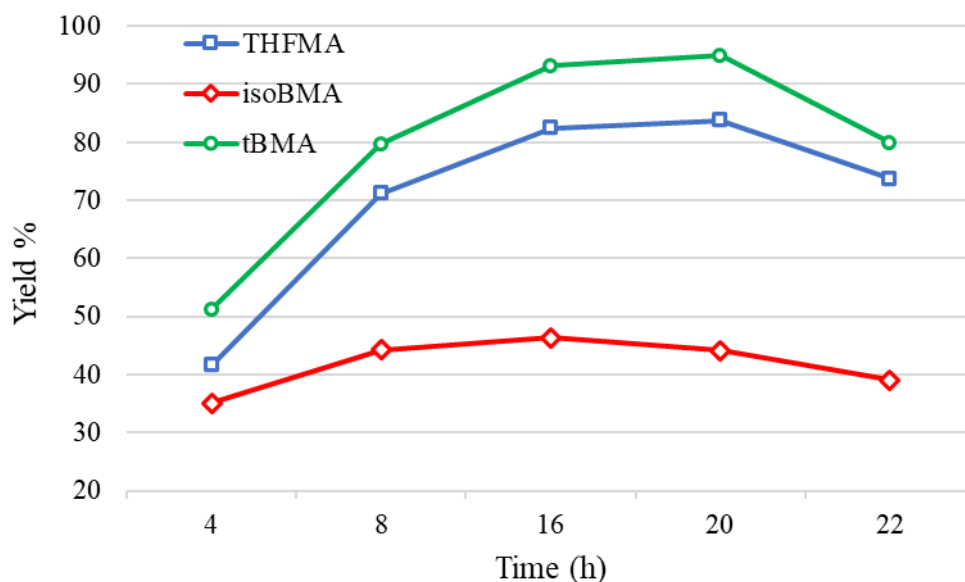


Figure 5. Time dependence of poly (MY₅₀-THFMA₅₀), (MY₅₀-*iso*-MA₅₀) and (MY₅₀-*tert*-BMA₅₀) synthesis

Solubility and Swelling of Copolymers

The solubility and swelling behavior of copolymers were tested in common organic solvents at 25 °C, and the theoretical solubility parameter was calculated according to the group contribution methods (detailed in Appendix a, b and c in supplementary information) the theoretical solubility parameter was calculated by (Hoftyzer - van Krevelen) method, as well as the Small methods, and values were taken from reference (Krevelen, & Nijenhuis 2009), as shown in Table 2, CHCl₃, THF and toluene had good solubility characteristics in these solvents.

Table 2
Solubility parameters for common solvents for myrcene-methacrylate copolymers

Copolymer (theoretical solubility parameter, MPa ^{1/2})	Solvents (solubility parameter, MPa ^{1/2})				
	CHCl ₃ (19.0)	THF (18.6)	Toluene (18.2)	DMSO (29.7)	MEK (19.0)
(MY ₅₀ -THFMA ₅₀) (16.6-17.7)	completely soluble	completely soluble	completely soluble	partially soluble, swells but not soluble	insoluble
(MY ₅₀ - <i>iso</i> -BMA ₅₀) (15.2-16.5)	completely soluble	completely soluble	completely soluble	partially soluble	insoluble
(MY ₅₀ - <i>t</i> -BMA ₅₀) (16.0-18.6)	completely soluble	completely soluble	completely soluble	partially soluble	partially soluble

Glass Transition and Decomposition Temperatures of the Synthesized Copolymers

Glass transition and decomposition temperatures of poly (MY₅₀-THFMA₅₀), (MY₅₀- *iso*-BMA₅₀) and (MY₅₀- *t*-BMA₅₀), it was used to evaluate the nature of the copolymers, which has been illustrated in the thermograms (Figure 6 and 7). (Figure S1, S2, S3 and S4 in the supplementary information for second and third copolymers), and it was found the (glass transition temperatures T_g) of copolymers at 75, 66, and 54 °C. DSC for poly (MY₅₀-THFMA₅₀) showed T_g at 75 °C, it is believed that the differential calorimetry analysis of the copolymer has undergone the double steps of crystallization (T_c) and melting (T_m) as well as the degradation (T_d) stage, with only one stage. The reason for the merging of the phases is due to the presence of the monomer of myrcene, which is a natural organic material (NOM), and the presence of the heterogeneous ring in the side chain of the methacrylate monomer, that is, the crystallization process of the copolymer occurred in one stage with the phase of melting and decomposition at a temperature of 499 °C, and then the rapid copolymer degradation begins, and this is explained by TGA, when the mass of the sample lost its weight, and the remaining weight was 0.0846 mg of heterogeneous copolymer with a percentage of 3.79% (Young & Leboeuf 2000).

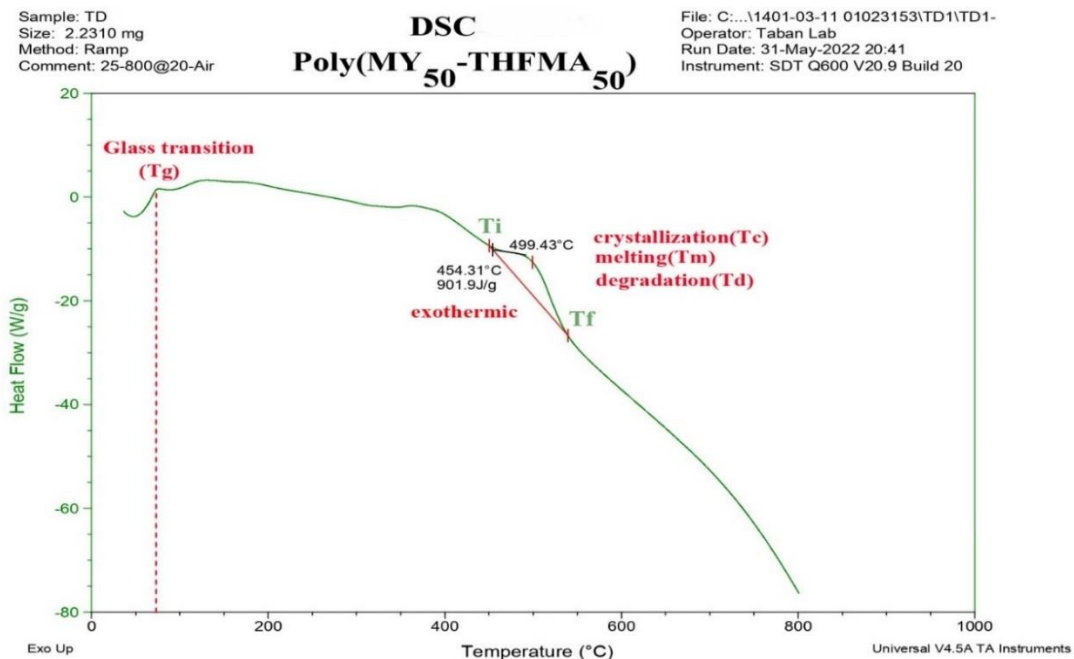


Figure 6. DSC thermogram of poly (MY₅₀-THFMA₅₀)

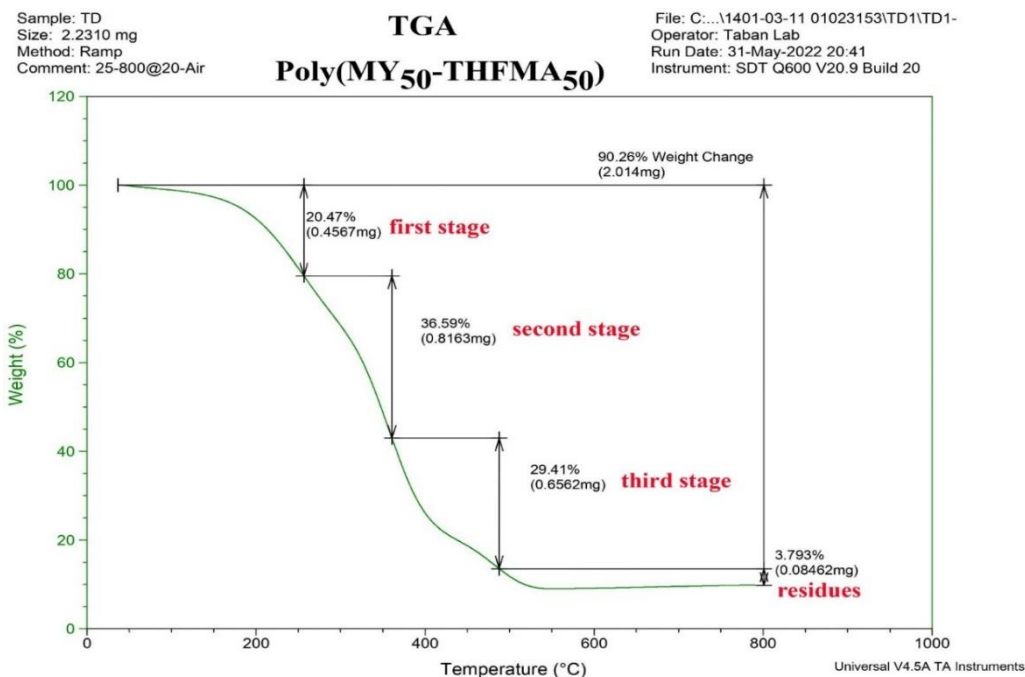


Figure 7. TGA thermogram of poly (MY₅₀-THFMA₅₀)

DSC analysis plot for the poly (MY₅₀-*iso*-BMA₅₀) copolymer that was analyzed under the same temperature range and heating rate of the copolymer, and the observed glass transition was 66°C (taken from the middle of the slope). It differs somewhat from the glass transition of Poly (MY₅₀-THFMA₅₀) with a slight change in the slope of the curve. Where it was noted that the peak of exothermic heat expulsion at 112 °C. Regarding the third copolymer poly (MY₅₀-*t*-BMA₅₀). the glass transition T_g that was observed was 54 °C, and since this copolymer contains an alkyl (*tert*-butyl) side chain, the change in T_g is minimal, and the alkyl side chain is expected to dominate the thermal transitions in the copolymers (Mojumdar et al., 2009). It was noted that the peak of the exothermic heat was at 114 °C, which is the cold crystallization (T_c) stage. followed by a peak at 499 °C which includes polymer melting (T_m), a coupling with the degradation (T_d) stage, with only one stage, for the same reason mentioned in the previous two polymers, but the difference in this copolymer, is the presence of *tert*-butyl group instead of rings.

FT-IR Spectroscopy

The synthesized copolymers were characterized by FT-IR spectroscopy to determine of the characteristic group frequencies. Figure 8 for poly (MY₅₀-THFBMA₅₀) focuses on four regions of the FT-IR absorption spectra of the prepared copolymer. The first is the 1716 cm⁻¹ region assigned to C=O ester and suggests to presence of methacrylate moiety, and this indicates that the preparation of the copolymer has been completed, the peaks at 2877 to 2953 cm⁻¹ in second region assigned to stretching vibrations of C–

H bonds for myrcene and methacrylate moieties. The third is the 1159 cm^{-1} region assigned to C-O for side chain, finally the peak in rocking vibration region at 650 cm^{-1} for the methylene group.

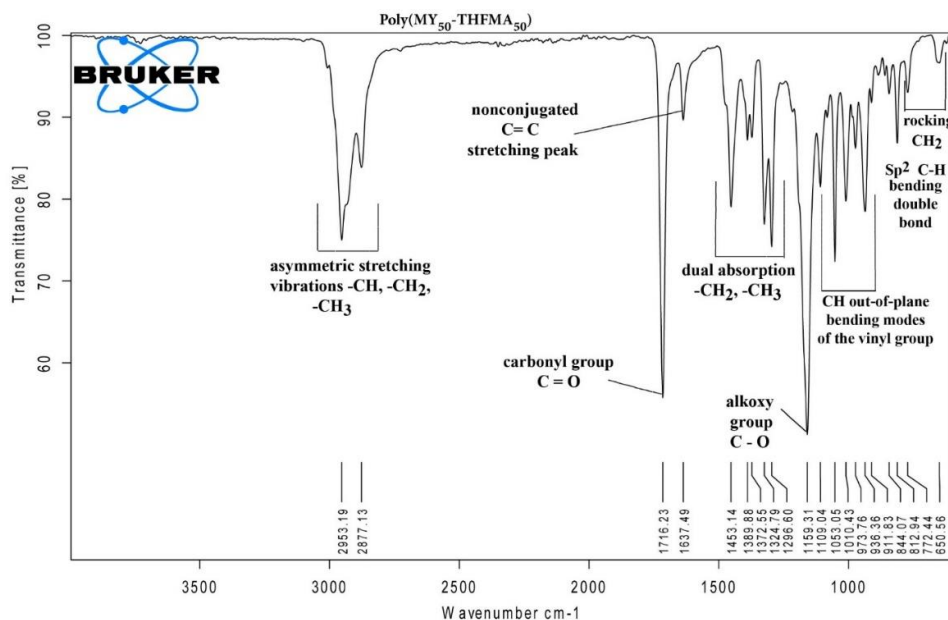


Figure 8. FT-IR Spectrum for synthesized Poly (MY₅₀-THFMA₅₀)

As for poly (MY₅₀-*iso*-MA₅₀) (Figure S5 in the supplementary information) focuses on five regions of the FT-IR absorption spectra of the prepared copolymer. The first is the 1724 cm^{-1} region assigned to C=O ester, the peaks at 2873 to 2930 cm^{-1} in second region assigned to stretching vibrations of C-H bonds, the third is the 1150 cm^{-1} region assigned to C-O for side chain, and it was out of plane bending C-H for vinyl moiety assigned to $990\text{--}1079\text{ cm}^{-1}$, finally the peak in rocking vibration region at 748 cm^{-1} for the methylene group.

While for poly (MY- *t*-BMA) (Figure S6 in the supplementary information) focuses on five regions of the FT-IR absorption spectra of the prepared copolymer. The first is the 1719 cm^{-1} region assigned to C=O ester, the peaks at 2856 to 2968 cm^{-1} in second region assigned to stretching vibrations of C-H bonds, the third is the 1143 cm^{-1} region assigned to C-O, finally the appearance of C-H bending in the range of $1366\text{--}1447\text{ cm}^{-1}$. The spectral signals are clearly mapped to the various magnetically different protons and carbons. In a copolymer (MY₅₀-THFMA₅₀) the chemical shift values of the peaks for this copolymer in the ^1H and ^{13}C NMR spectra are listed below.

Poly (MY₅₀-THFMA₅₀): ^1H NMR (300 MHz, CDCl₃, δ , ppm): 7.19(4H), 6.37(2H), 3.60 (1H), 3.35 (6H), 3.27 (12H), 2.83 (16H), 2.66(2H), 2.53(3H). (Figure 9)

Poly (MY₅₀-THFMA₅₀): ^{13}C NMR (300 MHz, CDCl₃, δ , ppm): 166.87 (1C), 136.85 (4C), 124.39 (4C), 81.16 (1C), 77.44-76.59 (2C), 46.90(1C),

38.83(1C), 33.70 (1C), 27.02(2H), 26.51(2H), 20.07(5C), 19.87(4C), 11.44(1C). (Figure 10)

^1H -NMR spectra showed a narrow intense peak in 7.19 ppm is assigned to the protons of the vinyl group and isopropylidene group for myrcene, O-CH₂ signal for tetrahydrofurfuryl group observed at 6.37 ppm, spectrum also showed the signals of the protons of the heterogeneous ring of THF in carbon a at 3.60 ppm, followed by the peak of other protons of the same ring in carbon b, c and d positions in 3.35 ppm, and showed proton signal methyl group for myrcene at 3.27 ppm, in the same unit of myrcene, protons were observed for methylene group at 2.83 ppm, while observed methylene group for tetrahydrofurfuryl at 2.66 ppm, finally protons of methyl group for tetrahydrofurfuryl were observed at 2.53 ppm.

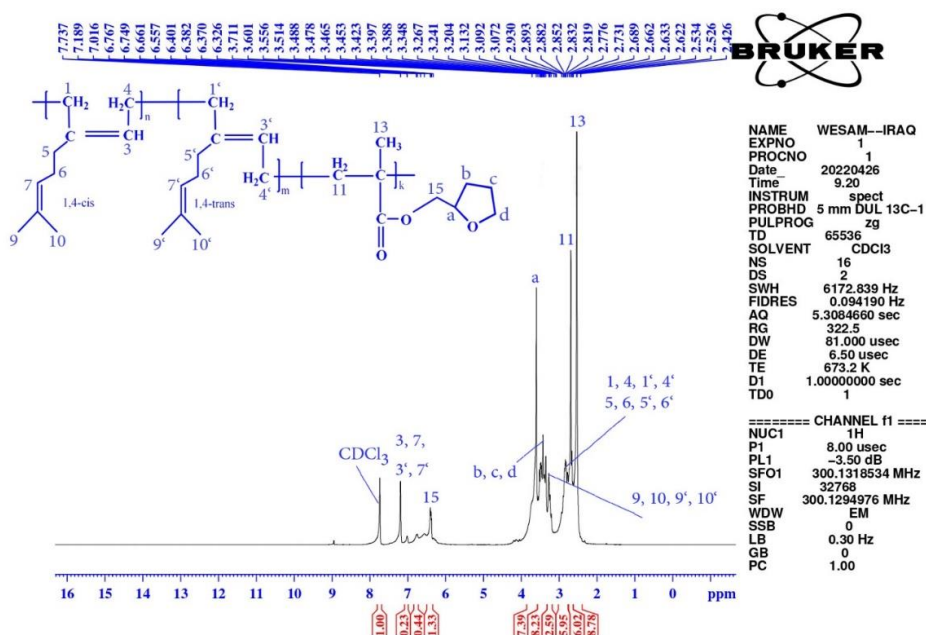


Figure 9. ^1H -NMR spectra of copolymer (MY₅₀-THFMA₅₀) in CDCl_3

In the ^{13}C NMR spectra for the same copolymer in Figure 10 shows the peak at $\delta = 166.87$ ppm correspond to the group (O=C) for THFMA monomer. The characteristic signal for olefinic carbon atom =C= (at atoms C₂ and C₈) appear at $\delta = 136.85$ ppm for myrcene monomer, while the peak at $\delta = 124.39$ ppm correspond to the vinyl carbon atom (at atoms C₃ and C₇). The signature peak at $\delta = 81.16$ ppm is attributed to the -OCH₂ group for THFMA monomer, as for the signals for methylene carbon atom for myrcene and methylene carbon atom for heterocyclic ring of THFMA moiety were found at 77.44, 76.59, 38.83, 33.70, 27.02, 26.51 and 20.07 ppm, and interfere with the signal of quaternary carbon that belongs to moiety of THFMA monomer. Student spectra were recorded from $\delta = 11.44$ –19.87 ppm for methyl group (CH₃) carbon.

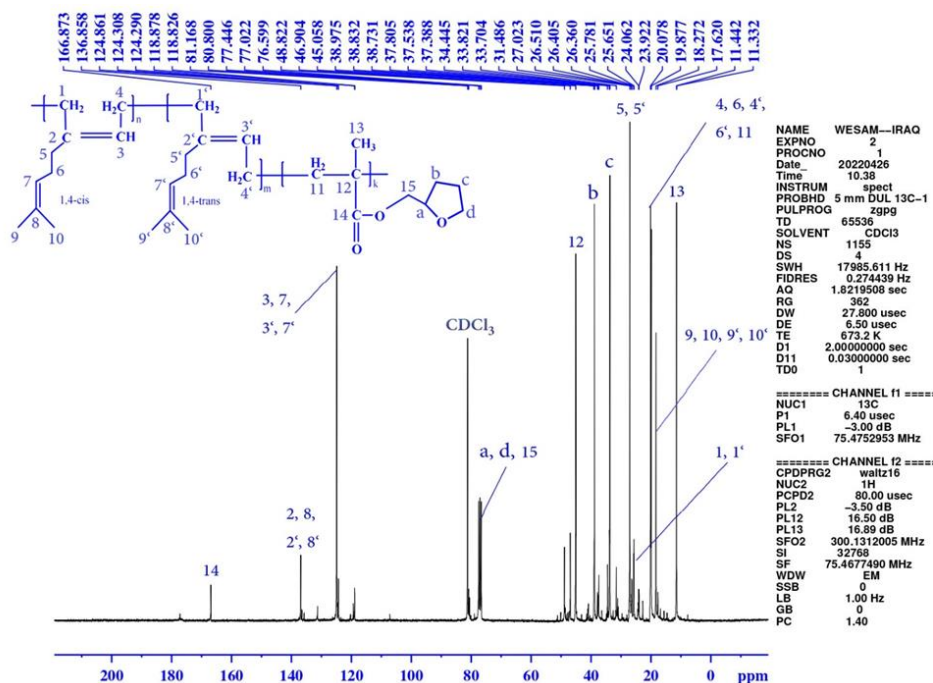


Figure 10. ^{13}C -NMR spectra of copolymer ($\text{MY}_{50}\text{-THFMA}_{50}$) in CDCl_3

Poly ($\text{MY}_{50}\text{-isoBMA}_{50}$): ^1H NMR (300 MHz, CDCl_3 , δ , ppm): 5.36(4H), 5.10 (1H), 4.13 (1H), 3.88 (6H), 1.95 (16H), 1.65 (12H), 1.28(2H), 1.22 (3H), 0.86 (9H). (Figure S7 in the supplementary information).

Poly ($\text{MY}_{50}\text{-isoBMA}_{50}$): ^{13}C NMR (300 MHz, CDCl_3 , δ , ppm): 169.84 (1C), 124.26 (8C), 68.34 (2C), 66.99 (3C), 45.12 (3C), 28.36(10C), 25.66 (7C). (Figure S8 in the supplementary information).

In a copolymer ($\text{MY}_{50}\text{-iso-BMA}_{50}$) ^1H -NMR spectra, which signals are no different from the previous copolymer, where showed a narrow intense peak in $\delta=5.36$ ppm is assigned to the protons of the of the vinyl group for myrcene and isopropylidene, and O-CH signal for isobutyl group observed at $\delta=5.10$ ppm, immediately followed by the signal of a proton group $=\text{CH}$ whose chemical shift values for bornyl ring is about $\delta=4.13$ ppm, it also shows protons of methylene groups for bornyl ring signaling at $\delta=3.88$ ppm and $\delta=1.95$ ppm for myrcene monomer and at $\delta=0.98$ ppm for *iso*-BMA, and methyl groups for myrcene signaling at $\delta=1.62$ ppm. then it comes back and shows protons of methylene group for bornyl ring signaling at $\delta=1.28$ ppm, finally protons of methyl group for bornyl ring were observed at $\delta=1.22$ and $\delta=0.86$ ppm.

In the ^{13}C NMR spectra for the same copolymer in Figure S12 shows the peak at $\delta=169.84$ ppm correspond to the group ($\text{O}=\text{C}$) for *iso*-BMA monomer. The characteristic signal for olefinic carbon atom $=\text{C}=($ at atoms C_2 , C_3 , C_7 and C_8) appear at $\delta=124.26$ ppm for myrcene monomer, while the peak at $\delta=68.34$ ppm correspond to $-\text{OCH}$ and $=\text{CH}$ groups for *iso*-BMA monomer. The signature peak at $\delta=66.99$ ppm is attributed to quaternary carbon (for *iso*-BMA moiety), as for the signals for methylene

carbon atom for myrcene and methylene carbon atom for *iso*-BMA moiety were found at 45.12 ppm, 28.36 ppm, and the carbon atoms methyl groups for the same ring attached together with their, Finally, student spectra were recorded at δ =25.66 ppm for methyl group (CH₃) carbon for myrcene and *iso*-BMA monomers .

Poly (MY₅₀-*t*BMA₅₀): ¹H NMR (300 MHz, CDCl₃, δ , ppm): 4.87 (4H), 2.04 (16H), 1.96 (12H), 1.44 (9H), 1.27 (3H), 1.12 (3H). (Figure S9 in the supplementary information).

Poly (MY₅₀-*t*BMA₅₀): ¹³C NMR (300 MHz, CDCl₃, δ , ppm): 176.34 (1C), 131.39 (4C), 124.32 (4C), 80.07 (1C), 46.47 (1C), 37.48 (2C), 29.33(7C), 25.66 (4C), 17.70 (1C). (Figure S10 in the supplementary information).

In a copolymer (MY₅₀- *t*-BMA₅₀) ¹H-NMR spectra, showed a narrow intense peak in δ =4.87 ppm is assigned to the protons of the of the vinyl group for myrcene and isopropylidene, and protons of methylene groups for myrcene and *t*-BMA monomer signaling at δ =2.04 ppm and δ =1.27 ppm, and follow it directly methyl groups for myrcene and *t*-BMA monomer at δ =1.96 ppm and δ =1.44-1.12 ppm (Figure S8 in the supporting information).

In the ¹³C NMR spectra for the copolymer (MY₅₀-*t*-BMA₅₀) spectrum shows the peak at δ = 176.34 ppm correspond to the group (O=C) for *t*-BMA monomer. The characteristic signal for olefinic carbon atom =C= (at atoms C₂ and C₈) appear at δ = 131.39 ppm for myrcene monomer, while the peak at δ = 124.39 ppm correspond to the vinyl carbon atom (at atoms C₃ and C₇). the signals for vinyl carbon atom C₃ and C₇ were recorded at δ = 124.32 ppm. The signature peak at δ = 80.07 ppm is attributed to the-OCH₂ group for *t*-BMA monomer, as for signal of quaternary carbon that belongs to moiety of *t*-BMA monomer was located at 46.47 ppm, and the rest of the signals for methylene carbon atom for myrcene and methylene carbon atom for *t*-BMA monomer were found at δ = 37.48-29.33 ppm. Student spectra were recorded from δ =25.66–17.70 ppm for methyl group (CH₃) carbon.

Conclusion

The copolymers (MY- THFMA), (MY- *iso*-BMA) and (MY- *t*-BMA) were successfully synthesized by emulsion polymerization, resulting product from the copolymerization reaction is a soft latex belonging to these copolymers, the apparent rate constant (K_{app}) was used to determine the conversion of monomers into copolymers by gravimetric method. It was found that the side chain methacrylate monomers influence to polymerization. The influence of temperature, time and solubility parameter was studied. Copolymers exhibited a T_g values in the range requested for an elastomeric (in rubbery state) were within (54–75) and suitable thermal stability with a decomposition temperature exceeding 400 °C, all the copolymers were fully characterized by FT-IR and NMR spectroscopy (¹H, ¹³C). In conclusion, our goal is replacement of fossil resources with bio-renewable monomers from terpenes.

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Supplementary information

The supplementary information is available any time after writing to us on the e-mail; esp.ali.sami@uoanbar.edu.iq

References

- Beher, A., Johnen, L. (2009). Myrcene as a Natural Base Chemical in Sustainable Chemistry: A Critical Review. *Chem. Sus. Chem.* 2(12), 1072-1095. <https://doi.org/10.1002/cssc.200900186>
- Coote, M.L., Davis, T.P., Willett, G.D. (1998). Effect of the Ester Side-Chain on the Propagation Kinetics of Alkyl Methacrylates an Entropic or Enthalpic Effect? *Macromolecules.* 31(4), 955-963. <https://doi.org/10.1021/ma9707291>
- Gandini A. (2008). Polymers from renewable resources: a challenge for the future of macromolecular materials, *Macromolecules*, 41(24), 9491-9504. <https://doi.org/10.1021/ma801735u>
- Grune, E., Bareuther, J., Blankenburg, J., Appold, M., Shaw, L., Müller, A.H.E., Floudas, G., Hutchings, L.R., Gallei, M., Frey, H. (2019). Towards bio-based tapered block copolymers: the behaviour of myrcene in the statistical anionic copolymerization, *Polym.Chem.*, 10(10), 1213-1220. <https://doi.org/10.1039/C8PY01711E>
- Holmberg, AL, Reno, KH, Wool, RP, Epps, III TH. (2014). Biobased building blocks for the rational design of renewable block polymers. *Soft Matter*, 10(38), 7405-7424. <https://doi.org/10.1039/C4SM01220H>
- Heuts, J.P., Forster, D.J., Davis, T.P. (1999). The effects of ester chain length and temperature on the catalytic chain transfer polymerization of methacrylates. *Macromolecules.* 32(12), 3907-3912. <https://doi.org/10.1021/ma9901341>
- Hulnik, M.I., Vasilenko, I.V., Radchenko, A.V., Peruch, F., Ganachaudc, F., Kostjuk, S.V. (2018). Aqueous cationic homo- and co-polymerizations of β -myrcene and styrene: a green route toward terpene-based rubbery polymers. *Polym. Chem.*, 9, 5690-5700. <https://doi.org/10.1039/C8PY01378K>
- Joseph, P. (2014). *Greene. Sustainable Plastics, Environmental Assessments of Biobased, Biodegradable, and Recycled Plastics*, by John Wiley & Sons, Inc.
- Krevelen, D.W.V., Nijenhuis, K.T. (2009). *Properties of polymers: Their correlation with chemical structure; Their numerical estimation and prediction from additive group contributions*, 4th ed.; Elsevier: Amsterdam, Ch. 7.
- Lei, W., Yang, X., Qiao, H., Shi, D., Wang, R., Zhang, L. (2018). Renewable resource-based elastomer nanocomposite derived from myrcene, ethanol, itaconic acid and nanosilica: Design, preparation and properties, *J. Eur. Polym.* 106, 1-8. <https://doi.org/10.1016/j.eurpolymj.2018.04.006>

- Marvel, S., Hwa, C.C.L. (1960). Polymyrcene. *J. Polym Sci. Part B.* 45(145), 1-10. <https://doi.org/10.1002/pol.1960.1204514503>
- Mojumdar, S.C., Prasad, R., Sun, L., Venart, J.E.S., Eichhorn, S.H., et al., (2009). An introduction to thermodynamic modeling, thermal analysis and calorimetry, *Res. J. Chem. Environ.* 13, 86-103.
- Noppalit, S., Simula, A., Ballard, N., Callies, X., Asua, J.M., Billon. L. (2019). Renewable Terpene Derivative as a Biosourced Elastomeric Building Block in the Design of Functional Acrylic Copolymers. *Biomacromolecules*, 20, 2241-2251. <https://doi.org/10.1021/acs.biomac.9b00185>
- Noppalit, S., Simula, A., Billon, L., Asua, J. (2020). On the nitroxide mediated polymerization of methacrylates derived from bio-sourced terpenes in miniemulsion, a step towards sustainable products, *Polym. Chem.* 11, 1151-1160. <https://doi.org/10.1039/C9PY01667H>
- Saleh, W.M., Ismail, A.S. (2020). Synthesis and Characterization of Sustainable Copolymers with Methacrylate Monomers based on B-Myrcene. *Solid State Technol.*, 63(2), 1380- 1400.
- Sarkar, P., Bhowmick, A.K. (2017). Terpene based sustainable methacrylate copolymer series by emulsion polymerization: Synthesis and structure-property relationship, *J. Polym. Sci., Part A: Polym. Chem.*, 55(16), 2639-2649. <https://doi.org/10.1002/pola.28661>
- Sahu, P., Sarkar, P., Bhowmick, A.K. (2018). Design of a Molecular Architecture via a Green Route for Improved Silica Reinforced Nanocomposite using Bio-resources. *ACS Sustainable Chem. Eng.*, 6(5), 6599-6611. <https://doi.org/10.1021/acssuschemeng.8b00383>
- Trumbo, D.L. (2018). Free radical copolymerization behavior of myrcene, *Polym. Bull.* 31(6); 1993: 629-636. *ACS Sustainable Chem. Eng.*, 6, 5, 6599-6611. <https://doi.org/10.1007/BF00300120>
- Wang, R., Ma, J., Zhou, X., Wang, Z., Kang, H., Zhang, L., Hua, K.C., Kulig, J. (2012). Design and preparation of a novel cross-linkable, high molecular weight and bio-based elastomer by emulsion polymerization, *J. Macromolecules.* 45(17), 6830- 6839. <https://doi.org/10.1021/ma301183k>
- Young, D.K., Leboeuf, J.E. (2000). Glass transition behavior in a peat humic acid and an aquatic fulvic acid. *Environ. Sci. Technol.* 34(21), 4549-455. <https://doi.org/10.1021/es000889j>