

Kinetics and Mechanism of Radical Copolymerization of Linalool with Methyl Methacrylate Initiated By AIBN

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ABSTRACT: Radical copolymerization methodology was explored by and making use of acyclic terpenoids namely linalool with methyl methacrylate (MMA) initiated by azobisisobutyronitrile (AIBN) in xylene at 80 ± 1 °C for 50 minutes under inert atmosphere of N_2 . The reaction results in alternating copolymer as evidenced from reactivity ratios. The system follows ideal kinetics. The overall activation energy is 65.0 kJ / mol. Alfrey Price, Q - e parameters for linalool have been evaluated as 5.08 and -2.27. The copolymer has been characterized by 1H -NMR, FTIR and DSC. The T_g of the copolymer is 70 °C.

Key words: Copolymerization, Linalool, Methyl methacrylate, Reactivity ratio.

Introduction

Polymers with unsaturated functional groups are applicable as reactive polymers which can be functionalized by polymer reactions. Polymerization of monomers with higher degrees of unsaturation is an attractive method to produce polymers bearing unsaturated moieties. These polymerizations, however, often include problems such as instability of monomers, and side reactions giving unregulated polymer structures. To construct well-defined polymers bearing unsaturated moieties, many efforts have been made in the polymerizations of dienes^{1,2} acetylenes³, cyclic olefins⁴, heterocumulenes⁵ and so on. In this aspects, we have developed the polymerization of monomers with high degree of unsaturation to give polymers containing unsaturated bonds.

A search of literature reveals that a voluminous literature is available on free radical copolymerization of vinyl monomers. Copolymerizations of acrylates, methacrylates, diacrylates and other vinyl monomers have been extensively studied⁶⁻⁸, but a very little attention has been devoted on polymerization of acyclic terpenoids⁹⁻¹². It is because acyclic terpenoids do not undergo homopolymerization due to steric hindrance^{13,14}, low stabilization energy between monomer and free radicals in transition state¹⁵, excessive chain transfer¹⁶, termination of cyclization as in case of 1,2 - disubstituted ethylenes¹⁷. The polymerization of few terpenoids like α / β - pinenes¹⁸⁻²¹, has attracted polymer chemists, since it yields optical active and functional copolymers. Therefore, the field of polymers of terpenoids is very challenging area of research with unlimited future prospects.

In the present article, acyclic monoterpenoid, namely linalool is copolymerized with methyl methacrylate using AIBN as radical initiator in xylene at 80 °C for 50 minutes and the kinetics, mechanism, the thermal properties have been evaluated.

Experimental

Materials

Reagent grade methyl methacrylate (MMA) (Merck Schuchardt) and solvents were purified by usual methods²²; stored over an anhydrous silica gel and distilled under vacuum before use. Azobisisobutyronitrile (M. P. = 104 °C) was recrystallized twice with methanol. Linalool²³ (B.P.=196 °C); $d_{150} = 0.8621$; specific rotation $[\alpha] = (-) 20.7^\circ$ was used after fractional distillation.

Polymerization Procedure

Polymerization of a solution containing requisite concentration of linalool with MMA in presence of AIBN was carried out in a dilatometric apparatus (capillary dia. = 2 mm; capillary length = 9.1 cm; lower bulb capacity = 2.5 ml). The copolymerization runs were performed for 50 min. at $80 \pm 1^\circ\text{C}$ under an inert atmosphere of N_2 . The copolymer, precipitated with acidified methanol, was dried to constant weight. It was refluxed with acetonitrile to remove poly(MMA) and then reprecipitated. The weight loss was negligible. Rate of polymerization (R_p) was calculated from the slope of linear portion of % conversion vs time plots.

Characterization

The copolymers were characterized by FTIR, $^1\text{H-NMR}$ and DSC.

$^1\text{H-NMR}$ spectra were recorded with Varian 100HA Joel LA 400 spectrometer using CDCl_3 as solvent and tetramethyl silane as internal reference.

The DSC runs were carried out using V4.013 Dupont 2100 analyzer, sample weight ~10 mg and heating rate 10 °C per minutes.

Results and Discussion

The kinetic studies have been studied by varying the concentrations of AIBN, monomer(s) and temperature. The effect of [AIBN] on rate of polymerization (R_p) is shown in Table 1. It is clear that the R_p increases with increasing concentration of AIBN as expected for free radical copolymerization. The order of reaction with respect to AIBN, calculated from the slope of the plot of $\log R_p$ vs $\log [AIBN]$, is 0.5 ± 0.03 .

TABLE 1

Effect of [AIBN] on the Rate of Copolymerization of Linalool and Methyl Methacrylate

[AIBN] x 10 ³ (mol/L)	% Conversion	R _p X10 ⁶ (mol/L/s)
1.3	6.7	4.6
2.6	10.7	4.0
4.0	15.6	3.3
5.2	16.3	3.0
6.5	19.2	2.7

[LIN] = 1.3 mol/l; [MMA] = 2.1 mol/l; Copolymerization time = 50 minutes;
Copolymerization temperature = 80 ± 1 °C.

The effect of [MMA] on the R_p has been studied by varying [MMA] from 1.5 mol / l to 3.1 mol / l where [LIN] and [AIBN] were kept constant (Tab. 2). A plot between $\log R_p$ and $\log [MMA]$ is linear, the slope of which gives relationship $R_p \propto [MMA]^{1.0 \pm 0.04}$.

TABLE2

Effect of [Comonomer(s)] on the Rate of Copolymerization using AIBN as an Initiator

[LIN] (Mol/L)	[MMA] (Mol/L)	Conversion (%)	Rp X 10 ⁶ (mol/L/s)
1.3	1.5	11.6	13.4
1.3	1.8	13.9	14.5
1.3	2.1	16.3	17.5
1.3	2.5	18.6	20.3
1.3	3.0	22.4	21.5
0.9	2.1	11.8	15.4
1.1	2.1	14.2	16.5
1.3	2.1	16.3	17.5
1.4	2.1	18.6	17.7
1.8	2.1	23.2	19.9

[AIBN] = 5.2×10^{-3} mol/l;

Copolymerization time = 50 minutes; Copolymerization temperature = 80 ± 1 °C.

The effect of [LIN] on Rp has been studied by varying [LIN] from 0.93 mol/l to 1.8 mol / l keeping [MMA] and [AIBN] constant (Table. 2). A plot between log Rp vs log [LIN] is linear , the order of reaction gives the relationship of unity .

$$R_p \propto [LIN]^{1.0 \pm 0.02}$$

The copolymerization runs were also carried out at 75 °C and 85 °C to evaluate the energy of activation. The Rp is direct function of temperatures and the apparent activation energy, determined from the slope of Arrhenius plot (Fig. 1), is 65.0 kJ/mol .

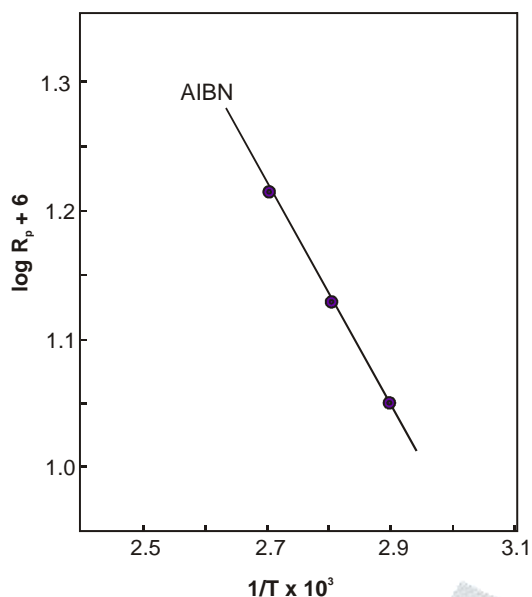


Fig. 1 Arrhenius plot of rate of copolymerization vs copolymerization temperature

[LIN] = 1.3 mol l⁻¹; [MMA] = 2.1 mol l⁻¹; [p- ABTAY] = 3.0 x 10⁻³mol l⁻¹;

Copolymerization time = 50 minutes.

Characterization of Copolymer(s)

¹H-Nuclear Magnetic Resonance Spectroscopy

The chemical shifts of protons, attached to elements other than carbon like -OH, -NH and -SH to a greater or lesser extent, is influenced by related phenomenon of intermolecular exchange and hydrogen bonding. Appearance of signals in the NMR spectra, due to -OH proton with species of smaller molecular weight, where intermolecular association is not hindered, generally, resonate in the region of $\delta = 3.0$ to 5.5 ppm (hydroxyl proton of CH₃OH appears at 3.3 δ whereas that of CH₃CH₂OH at 5.4 δ). However, with many large molecules, the hydroxyl proton often resonates near $\delta = 8.0$ ppm even at relatively high concentration. This is partially because of molar concentration and partially due to steric effect^{24,25}. Therefore, we have assigned the peak of -OH at 7.0 - 7.8 δ in the NMR spectra of linalool as well as in the copolymer of LIN-MMA.

The ¹H-NMR spectrum of copolymer shows peak at 7.0 - 7.8 δ of -OH group of linalool. The resonance signals at 3.6 δ were due to -OCH₃ protons of MMA, confirming the formation of poly(LIN-MMA) copolymer. The group peaks between 2.5 - 1.7 δ may originate from the back bone of -CH₂ and -CH protons.

Fourier Transform Infrared Spectroscopy

In the FTIR spectrum of copolymer, bands due to acrylate group of MMA is observed at 1735 cm^{-1} and band due to -OH group of linalool is observed at 3500 cm^{-1} . This confirms the incorporation of both the monomers in the copolymer.

Thermal Analysis

Differential Scanning Calorimetry

DSC scan of copolymer shows endothermic transition in the temperature range $70\text{ }^{\circ}\text{C}$. The endothermic transition in copolymers can be attributed to the copolymer formation for poly(MMA) and its copolymers^{26,27}.

The values of glass transition temperature (T_g), onset temperature (T_o) and peak temperature (T_p) of the copolymer are:

$$T_g = 70\text{ }^{\circ}\text{C}, \quad T_o = 175\text{ }^{\circ}\text{C}, \quad T_p = 181.39\text{ }^{\circ}\text{C}, \quad (T_p - T_o) = 5.79\text{ }^{\circ}\text{C}.$$

The onset temperature (T_o) be obtained at the intercept of the tangents to the base line at the lower temperature side of the endothermic peak. Peak temperature is the temperature at which the bulk of the copolymer has undergone dehydration reaction and the difference between the peak temperature and the onset temperature ($T_p - T_o$) is a measure of the overall rate of reaction. The smaller the difference, greater is the rate of reaction.

Copolymer Composition

$^1\text{H-NMR}$ analysis has been used to calculate the copolymer composition. The copolymer composition (Tab.3) was determined by the peak area at $7.0 - 7.8\ \delta$ due to -OH protons and at

TABLE 3
Composition of Copolymer

Molar ratio in monomer feed [MMA]/[LIN]	% Conversion	Molar ratio in copolymer composition [MMA]/[LIN]
1.62	16.80	1.03
1.90	11.13	1.04
1.50	13.30	1.02
2.30	16.50	1.07

3.6 δ due to $-\text{OCH}_3$. These were used to calculate the reactivity ratio value using Kelen-Tudos method²⁸, (Fig.2)

taking MMA (monomer 1) and linalool (monomer 2) as follows:

$$\eta = r_1\xi - r_2(1 - \xi)/\alpha$$

Where $\eta = G/(\alpha + H)$ and $\xi = H/(\alpha + H)$

The transformed variables G and H are given by -

$$G = \frac{[M_1]/[M_2][(d[M_1]/d[M_2]) - 1]}{d[M_1]/d[M_2]}$$

$$H = \frac{([M_1]/[M_2])^2}{d[M_1]/d[M_2]}$$

$$H = \frac{([M_1]/[M_2])^2}{d[M_1]/d[M_2]}$$

The parameter α is calculated by taking the square root of the product of the lowest and the highest values of H for the copolymerization series. The graphical evaluation for MMA/LIN yields values of $r_1 = 0.050$, $r_2 = 0.016$ (Tab. 4). These values are almost same per initiator set indicating that reactivity ratios are independent of nature of initiator. The product of r_1r_2 is nearly 0 which is the sign of nearly alternating copolymerization.

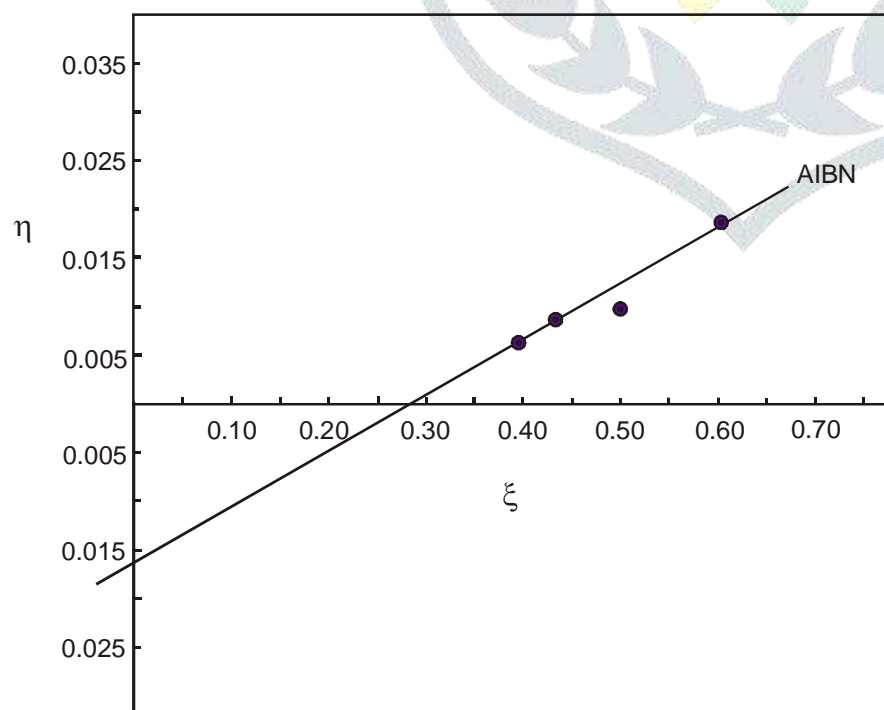


Fig 2. Kelen-Tudos plot of copolymer for determination of reactivity ratio.

TABLE 4
Reactivity Parameters using Kelen-Tudos Method

r^1	r^2	$r^1 r^2$	Q_2	e_2
0.050	0.016	0.0008	5.08	-2.27

According to the Alfery-Price Q-e scheme, the alternating tendency of the copolymer is given by a product of monomer reactivity ratios r_1 and r_2 with respect to monomers M_1 (MMA) and M_2 (LIN) in the four growing propagating reactions (PR) as:



$$r_1 = K_{11}/K_{12} \quad \text{and} \quad r_2 = K_{22}/K_{21}$$

By the values of r_1 and r_2 , it is clear that r_1 and r_2 are less than 1 i.e. the propagation reaction type 12 and 21 are preferred to type 11 and 22. The value of r_2 may be taken as zero, which shows that the probability of propagation reaction 22 is very less or somewhat impossible due to the fact that no homopolymerization of M_2 takes place and hence a chain ending with M_2^\bullet will add only a M_1 .

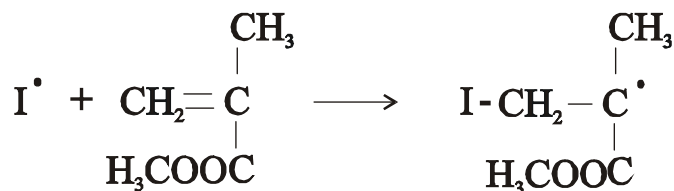
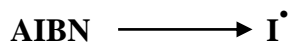
The e_2 and Q_2 values for linalool were calculated (Table 4), using $e_1 = 0.40$ and $Q_1 = 0.74$ for MMA, by following Alfrey - Price equation^{29,30} :

$$e_2 = e_1 \pm (-\ln r_1 r_2)^{0.5}$$

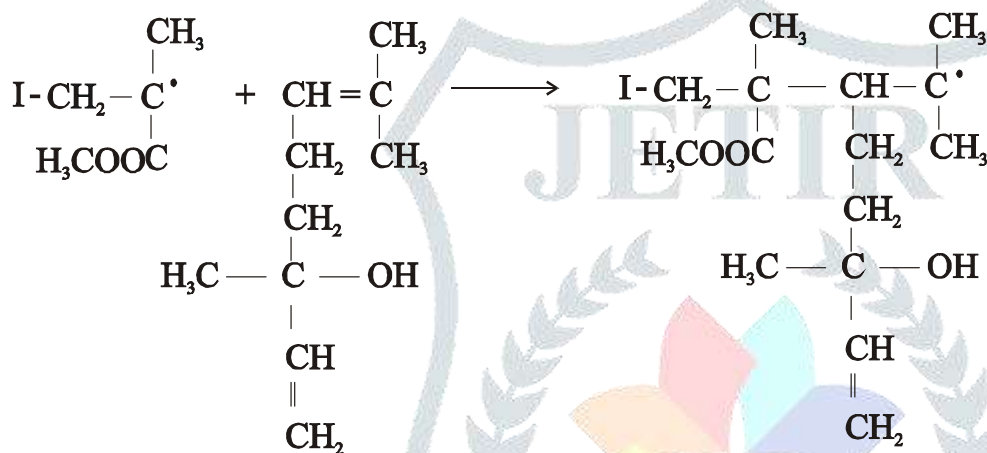
$$Q_2 = Q_1 / r_1 \exp[-e_1(e_1 - e_2)]$$

These equations express r_1 and r_2 in terms of constants Q and e , are assumed to be characteristic of each monomer. Q is related to the extent of resonance stabilization in the monomer i.e. its reactivity and e is related to the polarity of double bond. It has been found that strong alternating copolymers are formed when co monomers with widely differing polarities are reacted together. Thus an alternating copolymerization is suggested from high difference of e values of MMA and LIN.

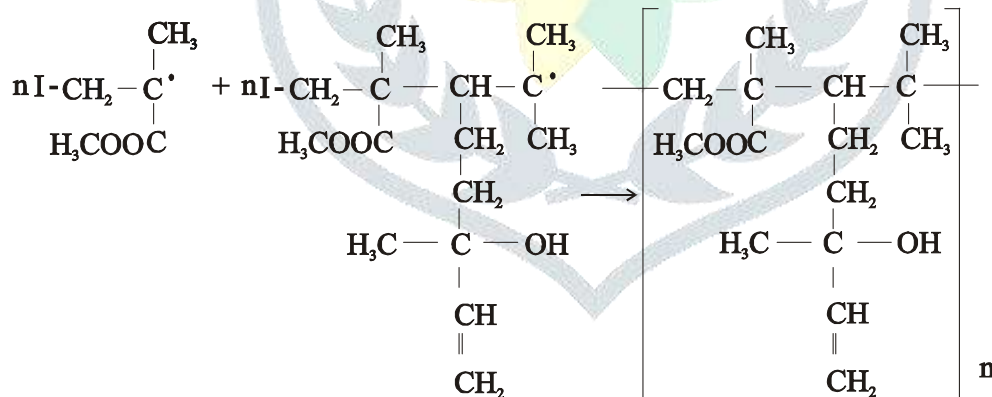
(i) Initiation



(ii) Propagation :



(ii) Termination :



Copolymer

Conclusion

Poly(LIN-alt-MMA) has been synthesized via free radical solution polymerization using AIBN as an initiator. The copolymer is stable thermally and has $T_g = 70^\circ\text{C}$. The system follows ideal kinetics and the energy of activation is evaluated as 65.0 kJ/mol .

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