

Measurement of Reactivity Ratios and Kinetics in Radical Copolymerization of Linalool with Methyl Methacrylate Initiated by Ylide

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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 p-acetyl benzylidene triphenyl arsonium ylide (p-ABTAY) in xylene at 80 ± 1 °C for 50 minutes under inert atmosphere of N₂. The reaction results in alternating copolymer as evidenced from reactivity ratios. The system follows ideal kinetics. The overall activation energy is 93.0 kJ/mol. Alfrey Price, Q - e parameters for linalool has been evaluated as 5.02 and -2.30. The copolymer has been characterized by ¹H-NMR, FTIR and TGA.

Keywords : Copolymerization, Linalool, Methyl methacrylate, Reactivity ratio.

I. INTRODUCTION

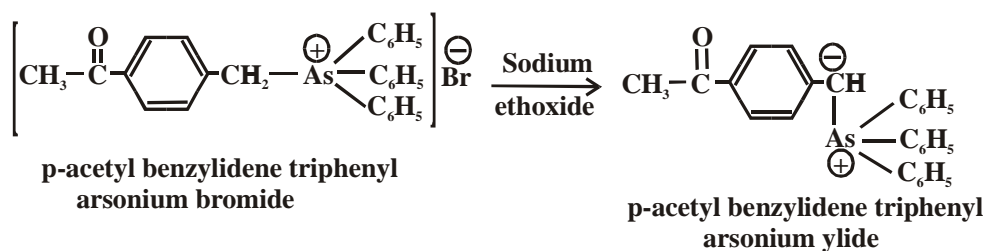
Polymers with unsaturated functional groups are applicable as reactive polymers which can be functionalized by polymer reactions. Polymerization of monomers with higher degrees of unsaturation is an attractive method to produce polymers bearing unsaturated moieties. These polymerizations, however, often 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, have 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.

Ylides can be viewed as species in which positively charged hetero atom is connected to a carbon atom possessing an unshared pair of electrons. The properties of ylides are very much dependent on the

2.0 gm of p-acetyl benzylidene triphenyl arsonium bromide in 100 ml of benzene was treated with sodium ethoxide in methanol, whereby a yellow suspension of ylide was obtained.



Characterization of ylide

Colour	-	Yellow - peach colour
Melting point	-	250 °C
Yield	-	20 %

Polymerization Procedure

Polymerization of a solution containing requisite concentration of linalool with MMA in presence of p-ABTAY 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±1°C under an inert atmosphere of N₂. 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 (Rp) was calculated from the slope of linear portion of % conversion vs time plots.

Characterization

The copolymers were characterized by FTIR, ¹H-NMR and TGA.

¹H-NMR spectra were recorded with Varian 100HA Joel LA 400 spectrometer using CDCl₃ as solvent and tetramethyl silane as internal reference.

The TGA runs were carried out using V5.1 Dupont 2100 analyzer, sample weight ~10 mg and heating rate 5 °C per minutes.

III. Results and Discussion

The kinetic studies have been studied by varying the concentrations of initiator (p-ABTAY), monomer(s) and temperature. The results have been illustrated in Tables 1 - 2 and Figure 1. The effect of [p-ABTAY] on rate of polymerization (Rp) is shown in Table 1. It is clear that the Rp increases with increasing concentration of p-ABTAY as expected for free radical copolymerization. The order of reaction with respect to initiator (p-ABTAY), calculated from the slope of the plot of log Rp vs log [p-ABTAY] (Fig. 1), is 0.5±0.03 .

TABLE 1

Effect of [p-ABTAY] on the Rate of Copolymerization of Linalool and MethylMethacrylate

[p-ABTAY] x 10 ³	% Conversion	Rp X10 ⁶
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(mol/L)		(mol/L/s)
1.52	06.2	4.5
2.20	08.7	3.6
3.00	10.9	2.5
3.80	13.4	2.1
4.50	16.0	1.9

[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 [p-ABTAY] was kept constant (Tab. 2). A plot between log R_p and log [MMA] is linear, the slope of which gives relationship $R_p \propto [MMA]^{1.0 \pm 0.04}$.

The effect of [LIN] on R_p has been studied by varying [LIN] from 0.93 mol/l to 1.8 mol / l keeping [MMA] and [p-ABTAY] constant (Table. 2). A plot between log R_p vs log [LIN] (Fig. 3) is linear, the order of reaction gives the relationship of unity.

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

TABLE 2

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

[LIN] (Mol/L)	[MMA] (Mol/L)	Conversion (%)	$R_p \times 10^6$ (mol/L/s)
1.3	1.5	08.4	11.7
1.3	1.8	09.2	12.8
1.3	2.1	10.9	14.4
1.3	2.5	12.3	15.8
1.3	3.0	16.5	18.1
0.9	2.1	07.2	12.8
1.1	2.1	09.3	13.8
1.3	2.1	10.9	14.4
1.4	2.1	12.6	14.7
1.8	2.1	15.2	16.5

[p-ABTAY] = 3.0 x 10⁻³ mol/l; Copolymerization time = 50 minutes; Copolymerization temperature = 80±1 °C.

The copolymerization runs were also carried out at 75 °C and 85 °C to evaluate the energy of activation. The R_p is direct function of temperatures and the apparent activation energy, determined from the slope of Arrhenius plot (Fig. 1), is 93.0 kJ / mol.

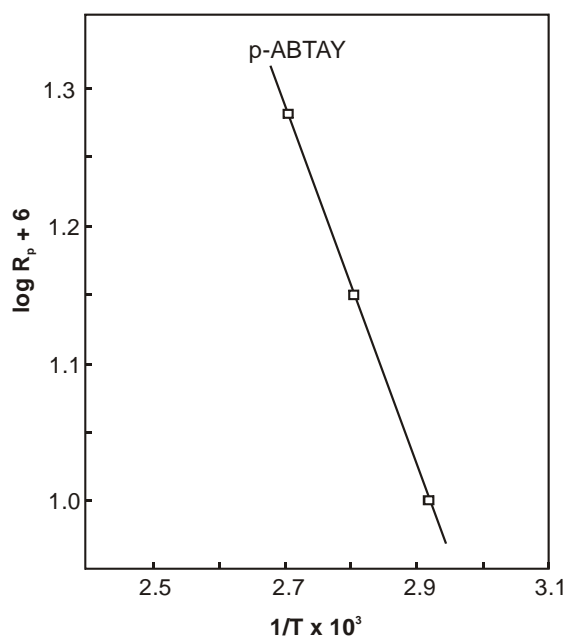


Fig 1. Arrhenius plot of rate of copolymerization vs copolymerization temperature
[LIN] = 1.3 mol l⁻¹; [MMA] = 2.1 mol l⁻¹; [p- ABTAY] = 3.0 x 10⁻³mol l⁻¹;
Copolymerization time = 50 minutes.

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^{27,28}. 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

Thermo Gravimetric Analysis

The TGA curve for copolymer using p-ABTAY as an initiator (Fig. 2) exhibits weight losses with temperature^{29,30}. The thermal behaviour data are as follows :-

(a) On set of major weight loss occurs between $300 - 400\text{ }^{\circ}\text{C}$; completion of weight loss $480\text{ }^{\circ}\text{C}$.

(b) The total weight loss in the range 40° to $400\text{ }^{\circ}\text{C}$.

(c) Weight losses at given stages of temperatures are as follows -

(i) $40 - 100\text{ }^{\circ}\text{C}$ = 1 %

(ii) $100 - 200\text{ }^{\circ}\text{C}$ = 8 %

(iii) $200 - 300\text{ }^{\circ}\text{C}$ = 26 %

(iv) $300 - 400\text{ }^{\circ}\text{C}$ = 45 %

(v) $400 - 480\text{ }^{\circ}\text{C}$ = 16 %

(d) Almost total volatilization of copolymer occurs at $389\text{ }^{\circ}\text{C}$.

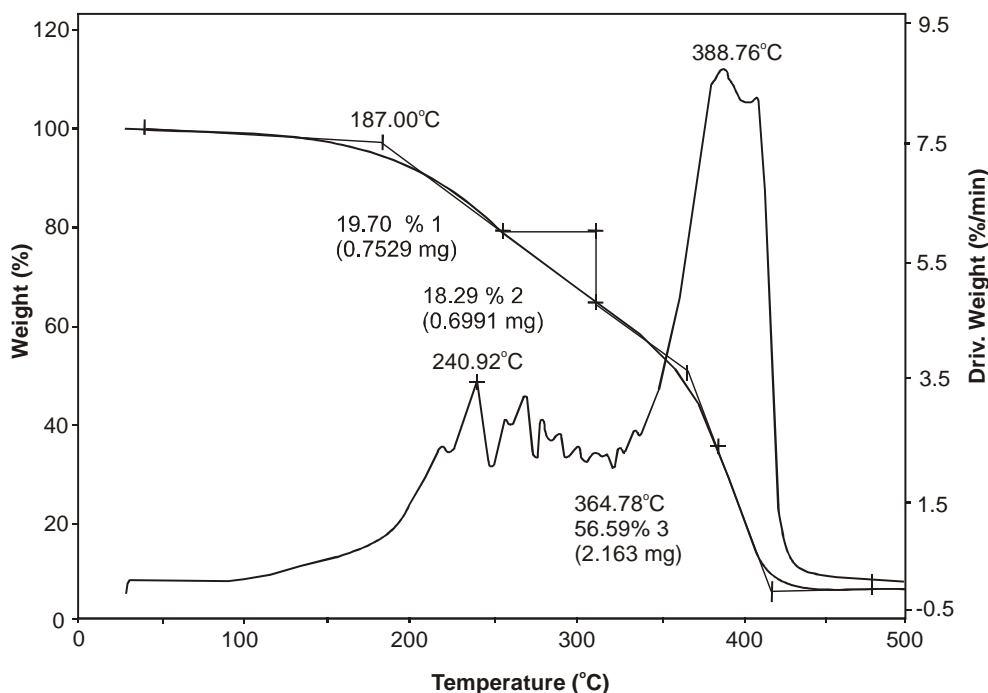


Fig 2. TGA curve of copolymer using p-ABTAY as an initiator.

Copolymer Composition

¹H-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 δ due to -OH protons and at 3.6 δ due to -OCH₃. These were used to calculate the reactivity ratio value using Kelen-Tudos method³¹ (Fig. 3), 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 -

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

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

TABLE 3. Composition of Copolymer

Molar ratio in monomer feed [MMA]/[LIN]	% Conversion	Molar ratio in copolymer composition [MMA]/[LIN]
1.62	14.50	1.03
1.90	14.40	1.04
1.50	13.60	1.09
2.30	12.20	1.06

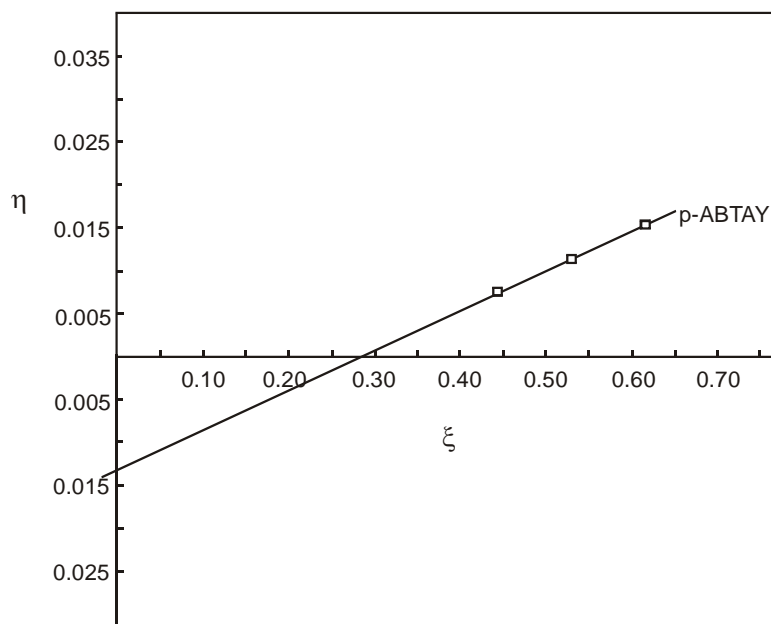


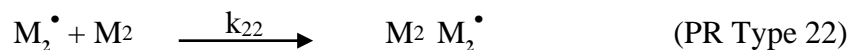
Fig 3. Kelen-Tudos plot of copolymer for determination of reactivity ratio.

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 $r_1 = 0.055$, $r_2 = 0.013$ (Tab. 4). These values are almost same per initiator set indicating that reactivity ratios are independent of nature of initiator. The product of $r_1 r_2$ is nearly 0 which is the sign of nearly alternating copolymerization.

TABLE 4
Reactivity Parameters using Kelen-Tudos Method

r_1	r_2	$r_1 r_2$	Q_2	e_2
0.055	0.013	0.0007	5.02	-2.30

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:



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

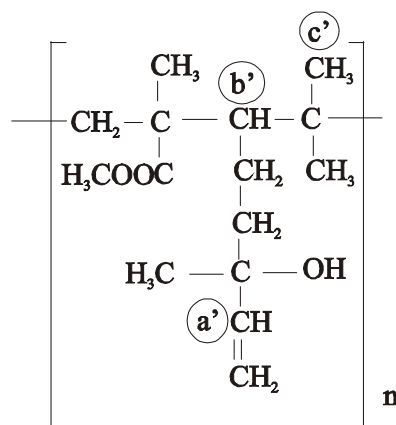
By the values of r_1 and r_2 , it is clear that r_1 and r_2 are less than 1 i.e. the propagation reaction type 12 and 21 are preferred to type 11 and 22. The value of r_2 may be taken as zero, which shows that the probability of propagation reaction 22 is very less or somewhat impossible due to the fact 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^{32,33} :

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

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

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



The participation of double bond in the copolymerization present between C-6 & C-7 is more likely because its homolysis form more stable tertiary free radical than the free radical formed by the homolysis of double bond present between C-1 & C-2.

The FTIR spectrum of linalool shows -

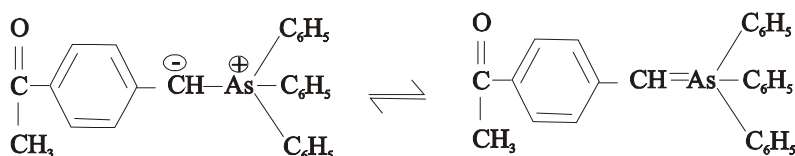
- $$\begin{array}{c} \text{CH}_3 \\ | \\ \text{CH}_3 - \text{C} = \text{CH} - \end{array}$$
- (A) Bands of $\text{CH}_3 - \text{C} = \text{CH} -$ group -
 = C - H stretching at 2971 cm^{-1}
 $>\text{C} = \text{C} - \text{H}$ stretching at 1668 cm^{-1}
 C - H bending at 835 cm^{-1}
- (B) Bands of $-\text{CH} = \text{CH}_2$ group -
 = C - C - H stretching at 3086 cm^{-1}
 $>\text{C} = \text{C}<$ stretching at 1643 cm^{-1}
 C - H bending at 996 cm^{-1}

The FTIR spectrum of copolymer also shows the bands of $-\text{CH} = \text{CH}_2$ group which confirms the no participation of this group in the copolymerization and confirms the formation of unsaturated copolymer.

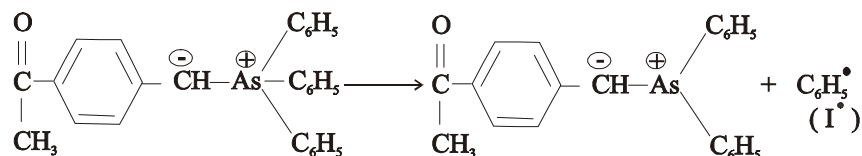
The proposed mechanism of copolymerization initiated by p-ABTAY is as follows-

(i) Initiation

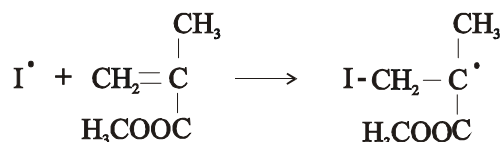
The p-ABTAY is considered to be resonance hybrid of the following two structures -



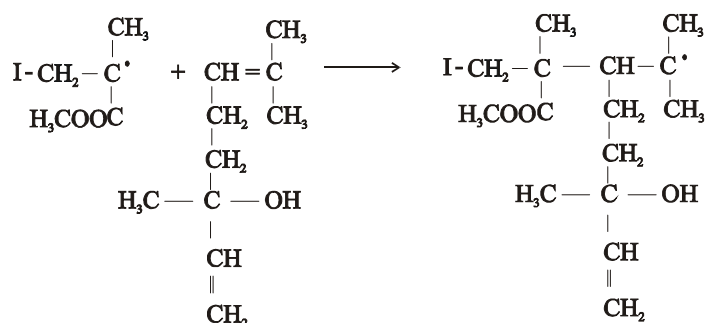
As reported in literature³⁴ p-ABTAY undergoes bond fission between the hetero atom and the phenyl group to produce phenyl radical which participates in the initiation of copolymerization as follows :



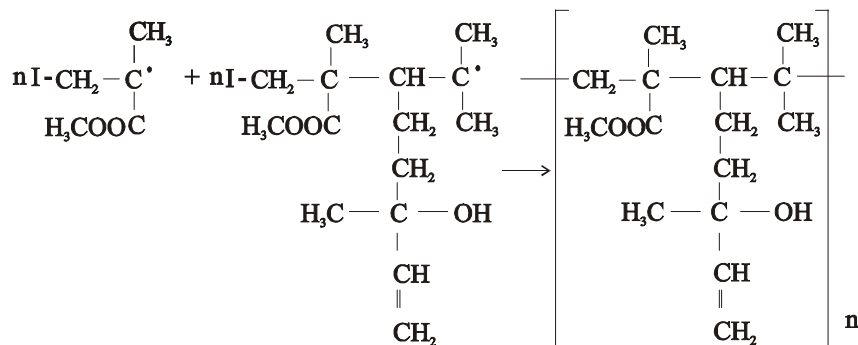
(i) **Initiation:**



(ii) **Propagation :**



(iii) **Termination :**



Conclusion

Poly(LIN-alt-MMA) has been synthesized via free radical solution polymerization using p-ABTAY as initiators. The system follows ideal kinetics and the energy of activation is evaluated as 93.0 kJ / mol .

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Cite this article as :

Akshay Kumar Shukla, Yousuf Akhtar Roomi, "Measurement of Reactivity Ratios and Kinetics in Radical Copolymerization of Linalool with Methyl Methacrylate Initiated by Ylide", *International Journal of Scientific Research in Science and Technology (IJSRST)*, Online ISSN : 2395-602X, Print ISSN : 2395-6011, Volume 7 Issue 3, pp. 492-503, May-June 2020.
Journal URL : <https://ijsrst.com/IJSRST2083217>