



## Benzoyl Peroxide-Initiated Free-Radical Copolymerization Of $\alpha$ -Terpineol With Vinyl Acetate

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**Abstract** – Today, the potential world-wide demand for designing polymers and developing polymerization processes that are safe, reduce pollution and provide efficiency in the use of materials and energy is quite significant. The synthesis of new monomers and polymers from plant based oils and their transformation into novel polymers has received much attention in recent years. Also, vinyl acetate [VA] is a commercially important monomer and has been frequently copolymerized with terpenes, the polymer that is formed is significant because it is likely biodegradable in nature. This article highlights the solution copolymerization of  $\alpha$ -terpineol and vinyl acetate [VA] in xylene at  $60 \pm 0.1$  °C for 90 minutes in presence of benzoyl peroxide [BPO] under inert atmosphere of nitrogen. The kinetic expression is,  $R_p \propto [I]^{0.5} [VA]^{1.0} [\alpha\text{-TER}]^{1.0}$ . The overall activation energy is calculated as 37KJ/mol. The copolymer(s) were characterized by NMR, FTIR and DSC. The formation of copolymer(s) is evidenced by FTIR and NMR spectrum as it shows bands at  $3400\text{cm}^{-1}$  due to hydroxy group of  $\alpha$ -terpineol and  $1750\text{cm}^{-1}$  due to acetoxy group of VA. and at 1.2-1.5 $\delta$  due to acetoxy group of VA. The value of reactivity ratios  $r_1 [VA] = 0.0246$  and  $r_2 [\alpha\text{-terpineol}] = 0.0082$  using Kelen-Tudos method are evaluated. The glass transition temperature ( $T_g$ ) from differential scanning calorimetry (DSC) is 50°C. The mechanism of copolymer has been elucidated. The copolymer(s) of VA and  $\alpha$ -terpineol are susceptible to further hydrolysis and oxidation.

**Index Terms** –  $\alpha$ -terpineol, vinyl acetate, copolymerization, kinetics, reactivity ratios.

### I. INTRODUCTION

Today, one of the important current incentives for the study of biodegradable polymers is their easier disposal. Moreover, biodegradable polymers are useful for applications such as sutures, surgical implants, controlled release formulations of drugs, agriculture chemicals and mulch. Poly (vinyl acetate) reportedly undergoes biodegradation<sup>1</sup> and its copolymers are also found susceptible to degradation<sup>2</sup>.

A search of literature reveals that vinyl acetate has been frequently copolymerized with many vinyl monomers such as MMA<sup>3</sup>, AN<sup>4</sup> are voluminous. However, it is almost devoid of reports regarding copolymers of VA with terpenoids although in recent years, the copolymerization of monocyclic monoterpenoids as functional comonomer has been achieved to yield new class of functional copolymers<sup>5</sup>.  $\alpha$ -terpineol, a typical monocyclic monoterpenoid, is the oxygenated derivative of terpene, having hydroxyl functional group as well as double bond. Therefore, this article highlights the synthesis and characterization of VA with  $\alpha$ -terpineol in xylene initiated by BPO at  $60 \pm 0.1$ °C for 90 min. Furthermore, this copolymer is significant because it is likely biodegradable in nature. Design of Bio-Based Block Copolymers via one-step Anionic Copolymerization was enabled by Temperature Variation<sup>6</sup>.

### II. EXPERIMENTAL

Reagent-grade VA (Merck Schuchardt) and solvents were purified with the usual method<sup>7</sup>, stored over anhydrous silica gel and dried under vacuum.  $\alpha$ -terpineol (Fluka: M=154.25g/mol, B.P.217°C and  $[\alpha]_D=1.4183$ ) was used after fractional distillation. BPO was recrystallized twice from methanol.

#### A. Copolymerization procedure:

The copolymerization in xylene as a solvent under inert atmosphere of nitrogen gas was carried out at  $60 \pm 0.1$ °C for 90 min with a dilatometric technique under oxygen free conditions. The polymer, isolated with acidified methanol and dried in vacuo, was refluxed with toluene for the removal of poly (vinyl acetate) when no detectable weight loss was observed. Finally, the copolymer was dried to a constant weight, and the conversion percentage was calculated from the slope of the graph between the conversion percentage and time(min).

The FTIR spectra were recorded on a Perkin-Elmer 599B spectra (with KBR pellets), and <sup>1</sup>H-NMR spectra were recorded with Varian 100HA spectrometers with CDCl<sub>3</sub> as a solvent and tetramethyl-silane as an internal reference, respectively. Differential scanning calorimetry (DSC) was

carried out on a Perkin-Elmer thermal analyzer at 10°C/min heating rate under a nitrogen blanket.

#### B. Result and Discussion:

The solution copolymerization of VA and  $\alpha$ -terpineol was carried out to a maximum conversion of 11.1% through the variation of the BPO,  $\alpha$ -terpineol and VA concentration. In all cases the polymerization runs were associated with short induction period of 2-4 min. The effect of monomer concentration on  $R_p$  is found to be direct function of monomers and the order of reaction, calculated from the slope of linear proportion of  $\log R_p$  Vs  $\log [M]$  is unity for both the monomer(s). The intrinsic viscosity of the copolymer(s) increases with an increase of comonomer concentration.

$R_p$  increases with increasing temperature. The overall energy of activation has been calculated to be 37KJ/mol from the slope of an Arrhenius plot of  $\log R_p$  Vs 1/Kelvin.

#### Characterization of the copolymer:

The FTIR spectra of the copolymer (Fig.1) shows bands at 3400  $\text{cm}^{-1}$  for alcoholic group of  $\alpha$ -terpineol, at 1750  $\text{cm}^{-1}$ .

$^1\text{H-NMR}$  spectra of the copolymer (Fig.2) shows that the peak due to acetoxy protons at  $\delta=1.2-1.5$  and the appearance of signal in NMR spectrum due to  $-\text{OH}$  protons with the species of small molecular weight, where intermolecular association is not hindered, generally appears in the region of 3.0-5.5  $\delta$ . However, with many large molecules, the  $-\text{OH}$  protons often appear near  $\delta=8$  even at high concentration partially due to steric effects. Therefore, the peaks of  $-\text{OH}$  group have been assigned in the range of 7.0-7.7  $\delta$  in the NMR spectrum of  $\alpha$ -terpineol as well as copolymer(s) of  $\alpha$ -terpineol and VA.

The DSC curve indicates that the glass transition temperature of the copolymer is 50°C. The glass-transition temperature of a copolymer of reaction between limonene and VA, determined by DSC was reported to be 32.4 °C<sup>9</sup>.

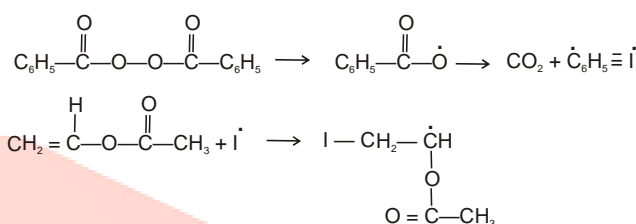
#### Copolymer composition and values of the reactivity-ratios:

The composition of copolymers have been evaluated from high resolution  $^1\text{H-NMR}$  spectra. The relative peak at  $\delta=1.2-1.5$  due to acetoxy protons of VA and at  $\delta=7.0-7.7$  due to hydroxyl protons of  $\alpha$ -terpineol have been used to calculate the copolymer compositions. The value of  $r_1(\text{VA})$  and  $r_2(\alpha\text{-terpineol})$  have been computed to be 0.0246 and 0.0082, respectively, by the use of Kelen-Tudos method<sup>7</sup> with the help of least square method.

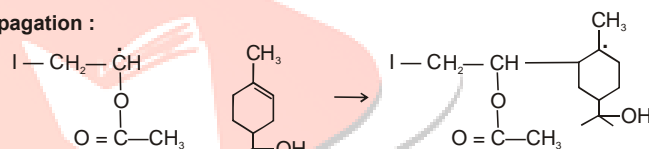
#### C. Mechanism:

It has been already reported the  $\text{C}=\text{C}$  is the active site in organic reactions of  $\alpha$ -terpineol<sup>10</sup>. On the basis of this evidence, it is concluded that,  $>\text{C}=\text{C}<$  is the active site for polymerization because of the presence of  $-\text{OH}$  group in NMR spectra and the copolymer does not decolorize bromine water. The proposed step of mechanism is shown as:

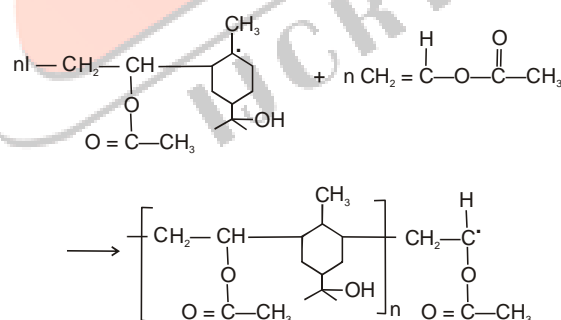
##### Initiation :



##### Propagation :



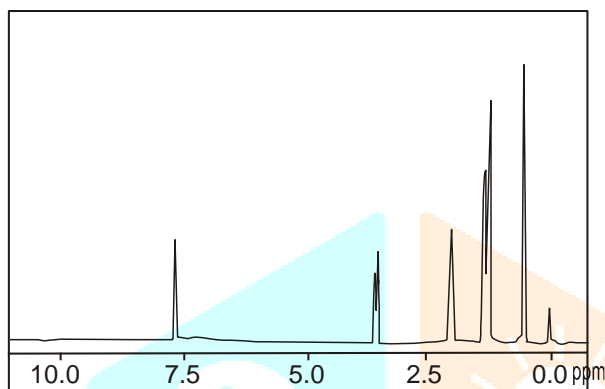
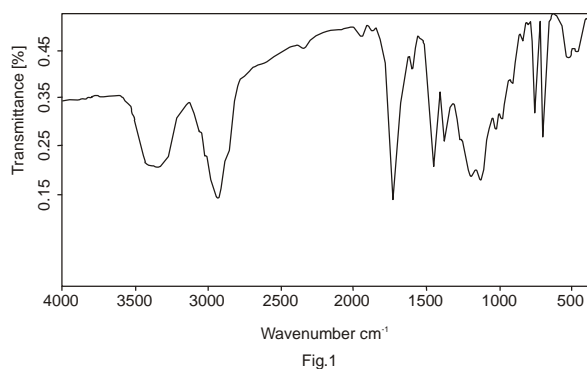
##### Termination :



### III. CONCLUSION

Poly ( $\alpha$ -terpineol-co-vinyl acetate) has been synthesized via free radical solution polymerization with BPO as an initiator. The synthesized polymer is functional and biodegradable in nature.

### Figures:



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