



RESEARCH ARTICLE

SYNTHESIS AND CHARACTERIZATION OF TERPOLYMER OF STYRENE, ACRYLONITRILE AND VINYL ACETATE INITIATED BY TRIPHENYLBISMUTHONIUM 1,2,3,4-TETRAPHENYLCYCLOPENTADIENYLIDE

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ABSTRACT

The radical terpolymerization, consisting of two electron donating monomers, viz. styrene and vinyl acetate, with one electron accepting monomer, viz. acrylonitrile, using triphenylbismuthonium 1,2,3,4-tetraphenylcyclopentadienylide as the radical initiator and dioxan as diluent at 70°C for 90 min., follows ideal kinetics, with an overall activation energy of 22 kJ/mol. The ¹H-NMR spectrum of the terpolymer showed the peaks at 7.15 to 7.28 δ because of phenyl group of styrene and at 2.06 δ because of acetoxy group of vinyl acetate. The bands at 2306 cm⁻¹, 3056 cm⁻¹, and 1676 cm⁻¹ in FTIR spectrum of terpolymer, evidence the presence of cyano, phenyl and acetoxy group, respectively. The terpolymer composition was estimated to calculate the values of reactivity ratios as r₁(AN)= 0.0066, and r₂(styrene + VA)= 0.0152 by the Kelen-Tüdös method.

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INTRODUCTION

Polymerization reactions, involving more than two monomers, have been under investigation since the systematic study of polymer science began in the 1930s. Terpolymerization has continued to evoke interest to both academic and industries like and provides a convenient method of synthesizing a new polymeric material with wide range of properties. Multicomponent polymerization, especially terpolymerization, allows the development of information on a certain class of monomer not otherwise available. A search of literature reveals that the terpolymerization of styrene-AN with some vinyl monomers like tri-n-butyltin-4-acryloyloxy benzoate-styrene-acrylonitrile¹, acrylonitrile-butadiene-styrene², styrene-methyl methacrylate-acrylonitrile³, acrylonitrile-styrene-acrylic acid⁴, styrene-acrylonitrile and 2, 4, 6-tribromophenyl acrylate⁵, styrene-acrylonitrile-vinyl pyrrolidone⁶, and terpolymerization of styrene-AN with some metal acrylates like styrene-AN-chromium acrylate⁷ and styrene-AN-copper acrylate⁸. Though much of the work has been done on the terpolymerization using AIBN/BPO as the radical initiators but very less work has been reported on the terpolymerization using ylide as the radical initiator.

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Ylides are 1, 2-dipolar compounds (>C—X, where, X = N, P, S, As, Sb, Bi, Se, Te) in which a carbanion is attached directly to a heteroatom bearing a positive charge. The properties of ylides are very much dependent on the identity of the heteroatoms⁹. The use of ylides containing N¹⁰, P^{11,12,13}, S¹⁴ and As¹⁵ as heteroatom in the domain of polymer science are sufficient and those containing Bi as heteroatom are rare, eg. the homopolymerization of methyl methacrylate¹⁶, styrene¹⁷ and methyl acrylate¹⁸. Also, copolymerization of vinyl pyrrolidone with methyl methacrylate¹⁹ and copolymerization of styrene with methyl methacrylate²⁰, methacrylic acid²¹ and acrylonitrile²². Therefore, this paper reports the terpolymerization of styrene, AN, VA using triphenylbismuthonium 1, 2, 3, 4-tetraphenylcyclopentadienylide as the radical initiator.

EXPERIMENTAL

Materials: Styrene, AN and VA (Merck-Schuchardt) were purified by treating it with 4% NaOH and distilled water^{23,24} followed by vacuum distillation before polymerization. Triphenylbismuthonium 1, 2, 3, 4-tetraphenyl cyclopentadienylide was synthesized by the method given by Lloyd²⁵

Polymerization procedure: The solution terpolymerization in dioxan was carried out with a dilatometric apparatus for 90 min. at $70 \pm 0.1^\circ\text{C}$ under an inert atmosphere of nitrogen. The terpolymer was precipitated with distilled water and dried to a constant weight, these were then refluxed with cyclohexane, dimethyl formamide (DMF) and benzene to remove the homopolymers and copolymers. The terpolymers were dissolved in dioxan and reprecipitated with distilled water and dried to a constant weight to calculate the percent conversion. The rate of polymerization (R_p) was calculated from the slope of linear plot of the percent conversion versus time plot.

The Fourier transform infrared (FTIR) and $^1\text{H-NMR}$ spectra were recorded with a Perkin–Elmer 599 B (with KBr pellets) spectrophotometer and a Varian 100 HA Jeol 400 LA spectrophotometer with CDCl_3 as the solvent and tetramethylsilane as an internal reference respectively. The monomer reactivity ratios were determined by using the Kelen-Tüdös method²⁶.

RESULTS AND DISCUSSION

The kinetics of terpolymerization was studied by varying [ylide] from $4.1 \times 10^{-6} \text{ mol l}^{-1}$ to 37.6 mol l^{-1} ; [AN] from 0.503 mol l^{-1} to 4.25 mol l^{-1} ; [Sty] from 0.576 mol l^{-1} to 2.306 mol l^{-1} and [VA] from 0.36 mol l^{-1} to 2.523 mol l^{-1} . The reaction proceeds with a short induction period of 2-5 min (Fig.1).

Effect of initiator concentration: The effect of [ylide] on the R_p was studied by varying the [ylide] from $4.1 \times 10^{-6} \text{ mol l}^{-1}$ to $37.6 \times 10^{-6} \text{ mol l}^{-1}$ keeping [AN], [Sty] and [VA] constant at 2.515 mol l^{-1} , 1.153 mol l^{-1} and 1.081 mol l^{-1} respectively. [Table-1] reveals the relationship between percent conversion and [ylide] for a fixed monomer concentration. The rate of polymerization [R_p] increases with increasing [ylide]. It is clear that the initiator exponent value, obtained from the linear graph of $\log R_p$ vs \log [ylide], is 0.5 (fig.2). The intrinsic viscosity of the terpolymer decreases with increasing [ylide].

Effect of monomer concentration: The effect of [monomer] on the rate of polymerization is summarized in [Table-2]. It reveals that the R_p is a direct function of [AN], [Sty] and [VA] and the exponent values, calculated from the slope of $\log R_p$ and \log [monomer], in all three cases is unity [fig.3-5]. The initiator and the monomer exponent values shows that the system follows ideal kinetics. The intrinsic viscosity (η) of the terpolymer increases with increasing [monomer].

Effect of temperature: Polymerization runs were also carried out at 60, 65, 75 and 80°C to evaluate the energy of activation because no polymerization occurred below 60°C . The R_p increases with increase in polymerization temperature. The overall activation energy, calculated from the linear Arrhenius plot of $\log R_p$ Vs $1/T$ is 22 kJ/mol (Fig.6).

CHARACTERIZATION OF THE TERPOLYMER

Fourier Transform Infrared Spectroscopy: The FTIR spectrum of terpolymer (Fig.7) shows the bands at 2306 cm^{-1} due to the cyanide group of acrylonitrile, at 3056 cm^{-1} due to C-H stretching of phenyl group of styrene and at 1676 cm^{-1} due to acetoxy group of vinyl acetate, indicating the

incorporation of all three monomers in the formation of terpolymer.

$^1\text{H-Nuclear Magnetic Resonance Spectroscopy}$: The $^1\text{H-NMR}$ spectrum of the terpolymer (fig.8) showed multiplets at 7.15 to 7.25 δ due to phenyl protons of styrene and the peak at 2.06 δ due to the acetoxy protons of VA.

$^{13}\text{C-Nuclear Magnetic Resonance Spectroscopy}$: The $^{13}\text{C-NMR}$ spectrum of the terpolymer (fig.9) showed peaks at 172 ppm due to the carbonyl carbon of VA, at 141 ppm due to the quaternary aromatic carbon resonance of the styrene residue and at 124 ppm due to the nitrile carbon (-CN) of AN.

REACTIVITY RATIOS: In order to calculate the reactivity ratios, the styrene and VA contents have been calculated from the peak area of phenyl protons and acetoxy proton respectively and acrylonitrile content from nitrogen percent by the elemental analysis. The composition is shown in Table-3. The slope of the plots of η versus ξ in the Kelen-Tüdös method (fig.10) gives the value of r_1 (AN) = 0.0066 and r_2 (styrene + VA) = 0.0152.

MECHANISM: It has been well reported in the literature¹⁴⁻¹⁶ that the ylide dissociates to form a phenyl radical which brings about the polymerization.

The mechanism is as follows:

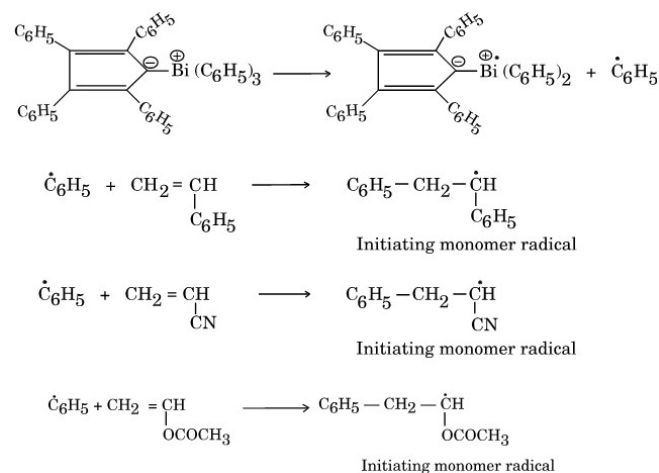


Table 1. Effect of ylide concentration on the rate of terpolymerization of AN, Sty and VA

| Sample | [ylide] x 10 ⁶ mol l ⁻¹ | Conversion % | R _p x 10 ⁶ mol l ⁻¹ s ⁻¹ | [η] dL/g |
|--------|--|-----------------|---|-------------|
| 1. | 4.1 | 7.6 | 6.33 | 0.080 |
| 2. | 12.5 | 8.2 | 7.91 | 0.070 |
| 3. | 20.9 | 8.9 | 8.7 | 0.056 |
| 4. | 29.3 | 10.0 | 10.29 | 0.040 |
| 5. | 37.6 | 12.4 | 12.66 | 0.024 |

Terpolymerization time = 90 min.
Terpolymerization temperature = $70 \pm 0.1^\circ\text{C}$
[AN]= 2.515 mol l^{-1}
[Sty]= 1.153 mol l^{-1}
[VA]= 1.081 mol l^{-1}

Table 2. Effect of termonomer (s) on R_p

| Sample | [AN] mol ⁻¹ | [Sty] mol ⁻¹ | [VA] mol ⁻¹ | Conversion % | $R_p \times 10^6$ mol ⁻¹ s ⁻¹ | $[\eta]$ dL/g |
|--------|---------------------------|----------------------------|---------------------------|-----------------|--|------------------|
| 6 | 0.503 | 1.153 | 1.081 | 6.0 | 4.014 | 0.026 |
| 7 | 1.509 | 1.153 | 1.081 | 8.6 | 6.612 | 0.042 |
| 3 | 2.515 | 1.153 | 1.081 | 8.9 | 8.708 | 0.056 |
| 8 | 3.522 | 1.153 | 1.081 | 11.6 | 12.47 | 0.058 |
| 9 | 4.528 | 1.153 | 1.081 | 13.0 | 18.048 | 0.074 |
| 10 | 2.515 | 0.576 | 1.081 | 7.0 | 6.118 | 0.048 |
| 3 | 2.515 | 1.153 | 1.081 | 8.9 | 8.705 | 0.056 |
| 11 | 2.515 | 1.730 | 1.081 | 10.0 | 11.53 | 0.066 |
| 12 | 2.515 | 2.307 | 1.081 | 12.1 | 15.74 | 0.082 |
| 13 | 2.515 | 1.153 | 0.360 | 7.9 | 5.907 | 0.046 |
| 3 | 2.515 | 1.153 | 1.081 | 8.9 | 8.708 | 0.056 |
| 14 | 2.515 | 1.53 | 1.802 | 10.6 | 11.85 | 0.062 |
| 15 | 2.515 | 1.153 | 2.523 | 12.5 | 16.50 | 0.078 |

Terpolymerization time = 90 min. Terpolymerization temperature = $70 \pm 0.1^\circ\text{C}$.
 $[\text{ylide}] = 20.9 \times 10^{-6} \text{ mol l}^{-1}$.

Table 3. Terpolymer composition

| Sample | Monomer feed | Polymer feed | Terpolymer composition (mole fraction) | | |
|--------|--------------------|------------------|---|------------------|------------------|
| | AN (F) (Sty+VA) | AN (f) Sty+VA | AN ^a | Sty ^b | VAc ^c |
| 3 | 1.25 | 1.058 | 0.51 | 0.148 | 0.33 |
| 7 | 0.675 | 1.012 | 0.505 | 0.127 | 0.372 |
| 8 | 1.576 | 1.064 | 0.511 | 0.25 | 0.238 |
| 10 | 1.517 | 1.024 | 0.502 | 0.261 | 0.235 |
| 11 | 0.894 | 1.079 | 0.515 | 0.31 | 0.170 |
| 13 | 1.662 | 1.032 | 0.507 | 0.139 | 0.352 |
| 14 | 0.351 | 1.022 | 0.501 | 0.107 | 0.391 |

^aCalculated from elemental analysis; ^bCalculated from NMR peak
^cCalculated from NMR peak.

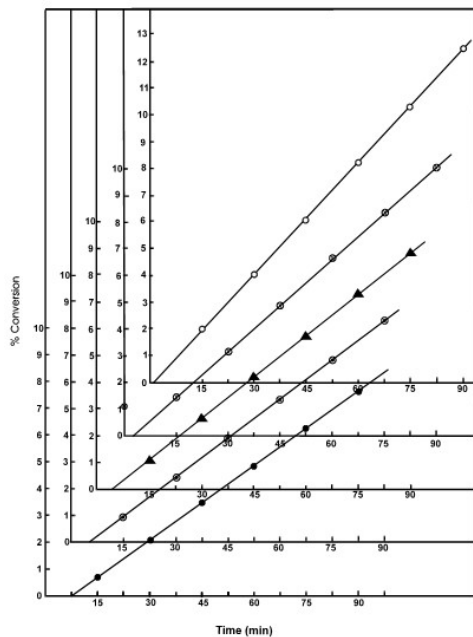


Fig.1 Relationship between percentage conversion and time(min). [AN] = 2.515 mol l^{-1} ; [Sty] = 1.153 mol l^{-1} ; [VA] = 1.081 mol l^{-1} ; [ylide] = $4.1 \times 10^{-6} \text{ mol l}^{-1}$; $=12.5 \times 10^{-6} \text{ mol l}^{-1}$; $=20.9 \times 10^{-6} \text{ mol l}^{-1}$; $=29.3 \times 10^{-6} \text{ mol l}^{-1}$; $=37.6 \times 10^{-6} \text{ mol l}^{-1}$; terpolymerization time = 90 min; terpolymerization temperature = $70 \pm 0.1^\circ\text{C}$.

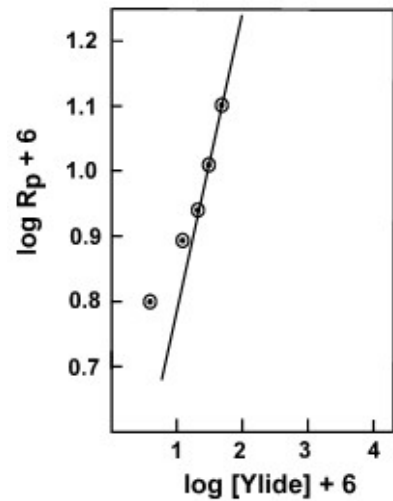


Fig.2 Relationship between the rate of terpolymerization and [ylide] [AN] = 2.515 mol l^{-1} ; [Sty] = 1.153 mol l^{-1} ; [VA] = 1.081 mol l^{-1} ; terpolymerization time = 90 min; terpolymerization temperature = $70 \pm 0.1^\circ\text{C}$.

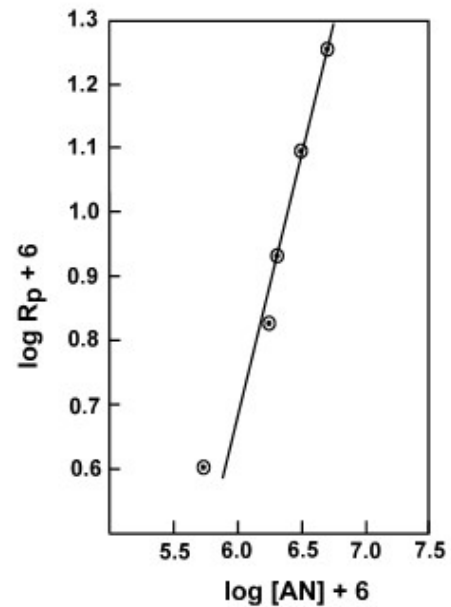


Fig.3 Relationship between the rate of terpolymerization and [AN]. [ylide] = $20.9 \times 10^{-6} \text{ mol l}^{-1}$; [Sty] = 1.153 mol l^{-1} ; [VA] = 1.081 mol l^{-1} ; terpolymerization time = 90 min; terpolymerization temperature = $70 \pm 0.1^\circ\text{C}$.

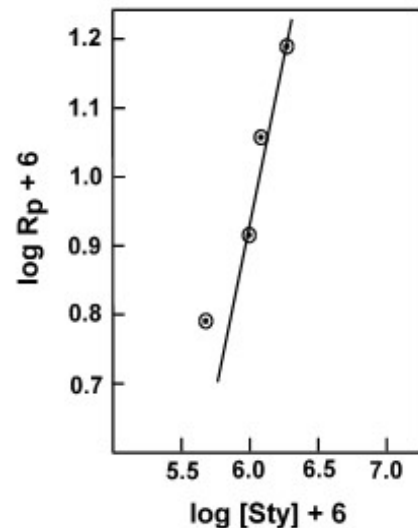


Fig.4 Relationship between the rate of terpolymerization and [Sty]. [ylide] = $20.9 \times 10^{-6} \text{ mol l}^{-1}$; [AN] = 2.515 mol l^{-1} ; [VA] = 1.081 mol l^{-1} ; terpolymerization time = 90 min; terpolymerization temperature = $70 \pm 0.1^\circ\text{C}$.

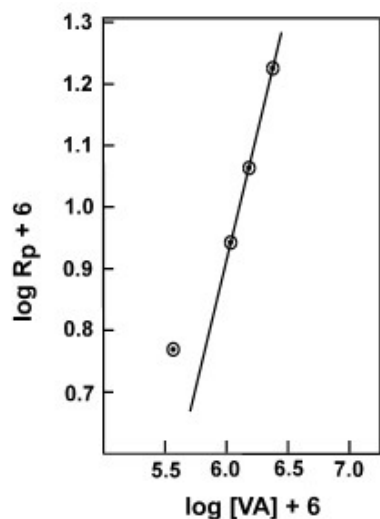


Fig.5 Relationship between the rate of terpolymerization and [VA]. $[y_{\text{lide}}] = 20.9 \times 10^{-6} \text{ mol l}^{-1}$; $[\text{AN}] = 2.515 \text{ mol l}^{-1}$; $[\text{Sty}] = 1.153 \text{ mol l}^{-1}$; terpolymerization time = 90 min; terpolymerization temperature = $70 \pm 0.1 \text{ }^\circ\text{C}$.

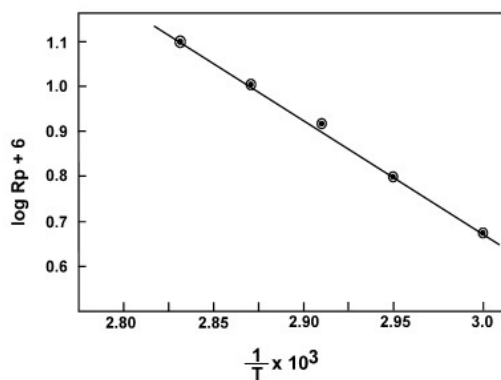


Fig.6 Arrhenius plot of the rate of terpolymerization and terpolymerization temperature. $[y_{\text{lide}}] = 20.9 \times 10^{-6} \text{ mol l}^{-1}$; $[\text{AN}] = 2.515 \text{ mol l}^{-1}$; $[\text{Sty}] = 1.153 \text{ mol l}^{-1}$; $[\text{VA}] = 1.081 \text{ mol l}^{-1}$; terpolymerization time = 90 min

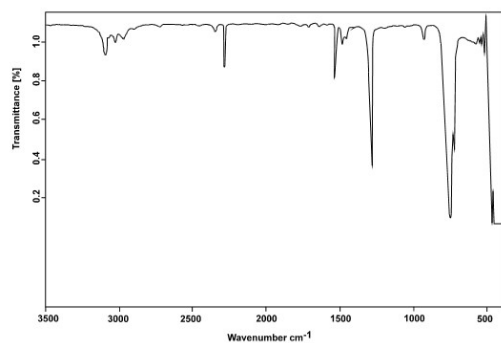


Fig.7 FTIR spectrum of terpolymer (samle-3)

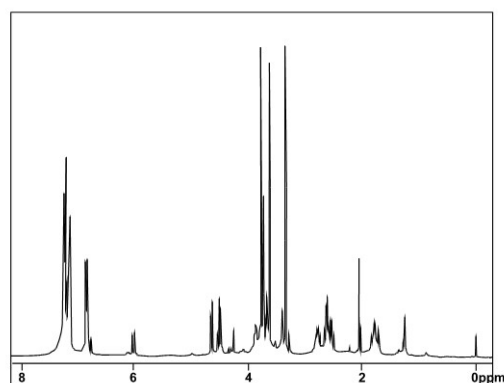


Fig.8 $^1\text{H-NMR}$ spectrum of terpolymer (sample-3).

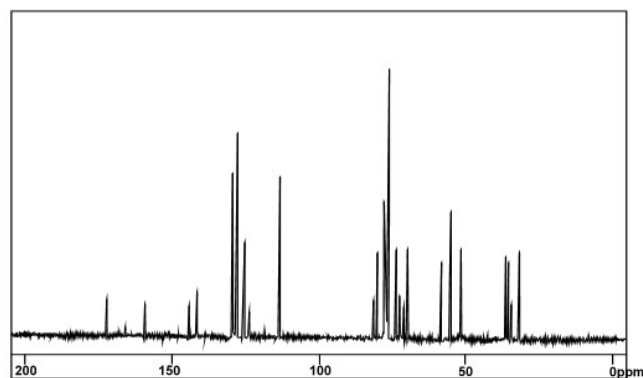


Fig.9 $^{13}\text{C-NMR}$ spectrum of the terpolymer (sample-3).

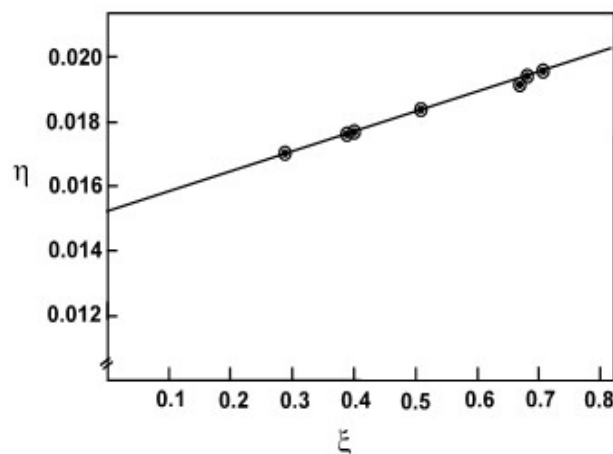


Fig.10 Kelen-Tüdös method for the determination of reactivity ratios

CONCLUSION

The terpolymerization of AN, styrene and VA initiated by triphenylbismuthonium 1, 2, 3, 4-tetraphenylcyclopentadienylide in dioxan, follows ideal kinetics.

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