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 terpolymerzation, consisting of two electron donating monomers, viz. styrene and vinyl acetate, with one electron accepting monomer, viz. acrylonitrile, using triphenylbismuthonium1,2,3,4-tetraphenylcyclopentadienylide as the radical initiator and dioxan as diluent at 70^0C for 90 min., follows ideal kinetics, with an overall activation energy of 22 kJ/mol. The ^{1}H-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 r_1 (AN)= 0.0066, and r_2(styrene + VA)= 0.0152 by the Kelen-Tüdos method.

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-acrylonitrile[1], acrylonitrile-butadiene-styrene[2], styrene-methyl methacrylate-acrylonitrile[3], acrylonitrile-styrene-acrylic acid[4], styrene-acrylonitrile and 2, 4, 6-tribromophenyl acrylate[5], styrene-acrylonitrile-vinyl pyrrolidone[6], and terpolymerization of styrene-AN with some metal acrylates like styrene-AN-chromium acrylate[7] and styrene-AN-copper acrylate[8]. 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.

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 heteroatoms[9]. The use of ylides containing N[10], P[11,12,13], S[14] and As[15] as heteroatom in the domain of polymer science are sufficient and those containing Bi as heteroatom are rare, eg. the homopolymerization of methyl methacrylate[16], styrene[17] and methyl acrylate[18]. Also, copolymerization of vinyl pyrrolidone with methyl methacrylate[19] and copolymerization of styrene with methyl methacrylate[20], methacrylic acid[21] and acrylonitrile[22].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 Lloyd [25]

Polymerization procedure: The solution terpolymerization in dioxan was carried out with a dilatometric apparatus for 90 min. at 70 ± 0.1^0C 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}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-Tüdos method[26].

RESULTS AND DISCUSSION

The kinetics of terpolymerization was studied by varying [ylide] from 4.1×10^{-6} moll^{-1} to 37.6 moll^{-1}; [AN] from 0.503 moll^{-1} to 4.25 moll^{-1}; [Sty] from 0.576 moll^{-1} to 2.306 moll^{-1} and [VA] from 0.36 moll^{-1} to 2.523 moll^{-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 4.1×10^{-6} moll^{-1} to 37.6×10^{-6} moll^{-1} keeping [AN], [Sty] and [VA] constant at 2.515 moll^{-1}, 1.153 moll^{-1} and 1.081 moll^{-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 termonomer 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 80^0C to evaluate the energy of activation because no polymerization occurred below 60^0C. 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}H-Nuclear Magnetic Resonance Spectroscopy: The ^{1}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}C-Nuclear Magnetic Resonance Spectroscopy: The ^{13}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-Tüdos 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 literature[14-16] that the ylide dissociates to form a phenyl radical which brings about the polymerization.

The mechanism is as follows:
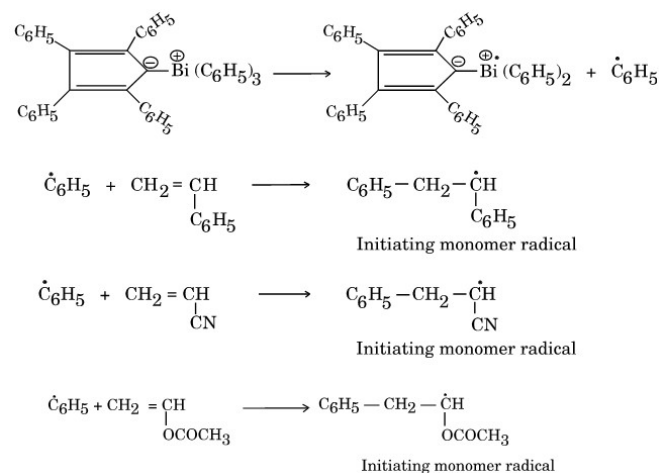
Table 1. Effect of ylide concentration on the rate of terpolymerization of AN, Sty and VA

Sample	[ylide] x 10^6 moll^{-1}	Conversion %	R_p x 10^6 moll^{-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 ± 0.1^0C
[AN]=2.515 moll^{-1}
[Sty]=1.153 moll^{-1}
[VA]=1.081 moll^{-1}

Table 2. Effect of termonomer (s) on R_p

Sample	[AN] moll^{-1}	[Sty] moll^{-1}	[VA] moll^{-1}	Conversion %	$R_p \times 10^6$ moll^{-1}s^{-1}	[η] 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 ± 0.1^{0}C. [ylide] = 20.9 x 10^{-6} moll^{-1}.

Table 3. Terpolymer composition

Sample	Monomer feed AN (F) (Sty+VA)	Polymer feed AN (f) Sty+VA	Terpolymer composition (mole fraction) AN[a]	Sty[b]	VA[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

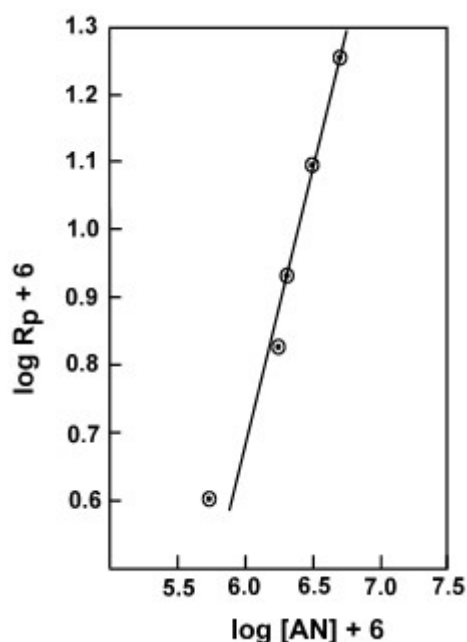[a]Calculated from elemental analysis; [b]Calculated from NMR peak
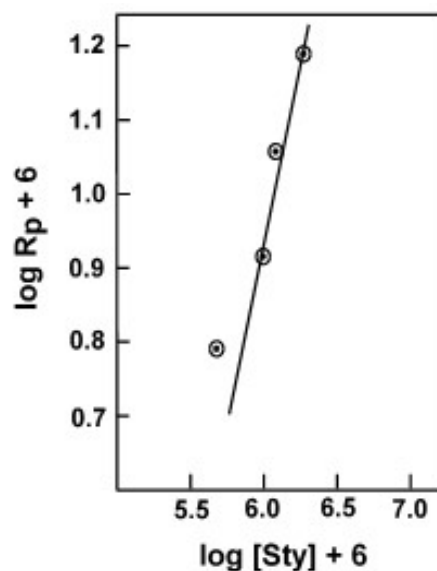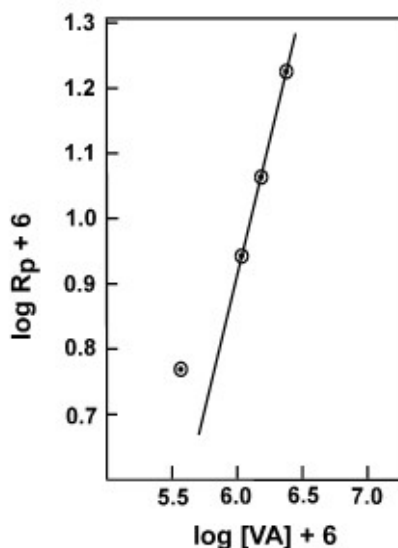[c]Calculated from NMR peak.
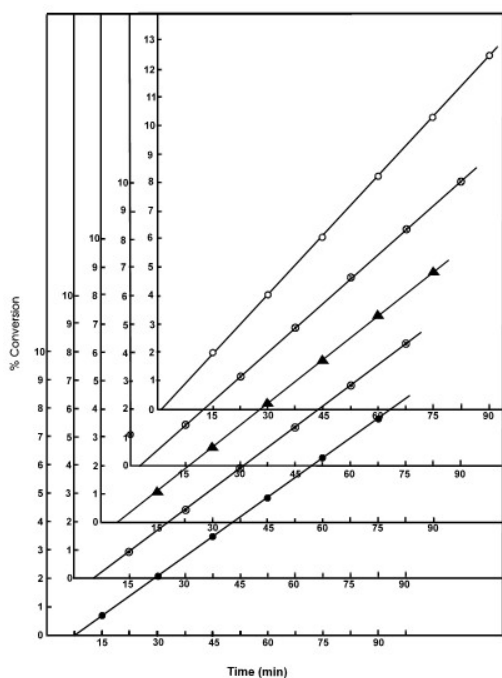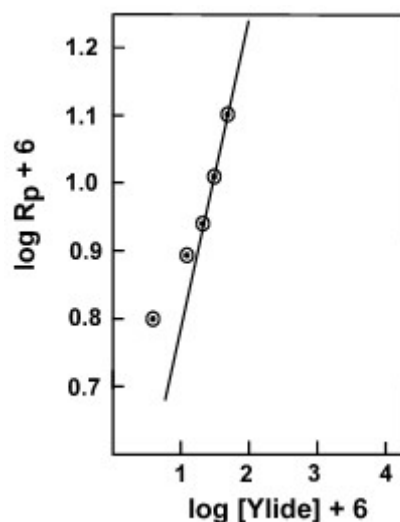
Figure 2.

Figure 3.

Figure 1.

Figure 4.

Figure 5.
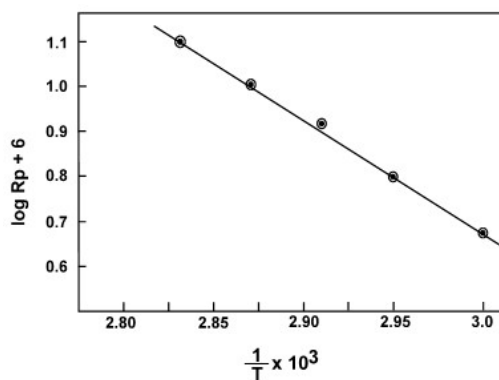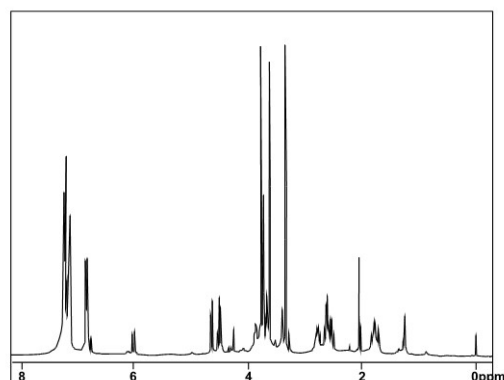

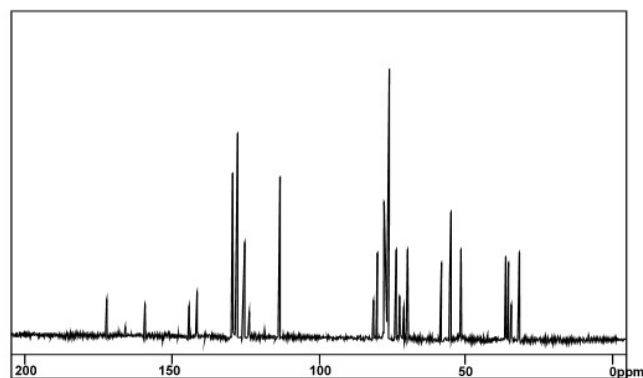**Figure 6.**
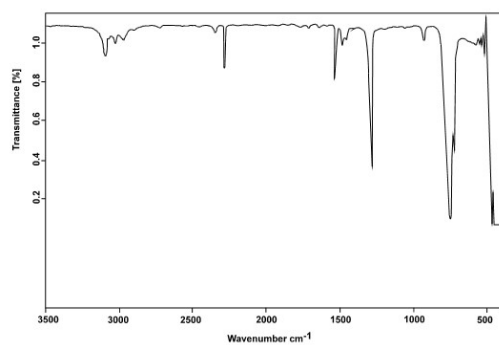
Figure 7.

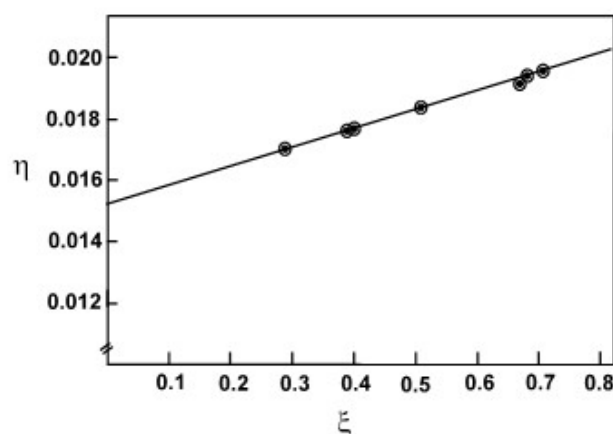**Figure 8.**

Figure 9.

Figure 10.

CONCLUSION

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

REFERENCES

1. Mahmoud A. A. F. Shabaan and M. M. Azab, Polym. Int., 28, 245 (1992).
2. Fahmy T and M. T. Ahmed, J. Polym. Mater., 20(4), 367 (2003).
3. Shukla P and A. K. Srivastava, Macrol. Reports, A (31), 315 (1994).
4. Brar A.S. and D. R. Pradhan, J. Polym. Mater., 20, 31 (2003).
5. Janovic Z. and K. Saric, J. Polym.Sci: Polym.Chem. Ed., 21, 2713 (1983).
6. Kumar P. D. Narain and A. K. Srivastava, Polym. Int., 337, 221 (1993).
7. Shukla P. and A. K. Srivastava, Polym. Int., 41, 407 (1996).
8. Shukla P. and A. K. Srivastava, Polymer, 35, 4665 (1996).
9. Freeman B. H. D. Lloyd and M. I. C. Singer, Tetrahedron, 28, 343 (1972).
10. Saini S. R. Vasistha, P. Shukla and A. K. Srivastava, Macromol., 22(3), 1025 (1989).
11. Vasistha R. and A. K. Srivastava, Polym. Engg. Sci., 31(8), 567 (1991).

12. Prajapati K. and A. Varshney, *J. Polym. Res.,* 13(2), 97 (2006).

13. Prajapati K. and A. Varshney, Polym-Plast Technol. 46, 629 (2007).

14. Bhatnagar U. and A. K. Srivastava, Polym. Int., 25, 13 (1991).

15. Daniel N. and A. K. Srivastava, Adv. Polym. Tech., 21(2), 108 (2002).

16. Bajpai R. and A. K. Srivastava, *Ind. J. Chem.* Tech., 8, 301 (2001).

17. Bajpai R. and A. K. Srivastava, *Ind. J. Chem.*, 40(A), 479 (2001).

18. Tripathi S. and A. K. Srivastava, *J. Polym. Sci. Part-A: Polym. Chem.,* 42, 2060 (2004).

19. Tripathi S. and A. K. Srivastava, Int. J. Current Res., 13(12), 20114 (2021).

20. Bajpai R. and A.K. Srivastava, J. Appl. Polym. Sci., 80, 2774 (2001).

21. Tripathi S. and A. K. Srivastava, *J. Appl. Polym. Sci.,* 98 (4), 1838 (2005).

22. Tripathi S. and A. K. Srivastava, *Polym. Plast. Technol. Engg.,* 46, 213 (2007).

23. Overburger C. G. and N. Yamamoto, J. Polym. Sci. Part - A: Polym.Chem., 3101 (1966).

24. Vogel A. E. A Text Book of Practical Organic Chemistry. Longman:: London, (1966).

25. Lloyd D. and C. Glidewell, Synthesis, 319 (1988).

26. Kelen T. and F. Tudos, J. Macromol. Sci. Chem. Edn., A (9),1 (1975).

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