

Diphenylselenonium 2,3,4,5-Tetraphenylcyclopentadienylide-Initiated Polymerization of Styrene and Acrylonitrile: Synthesis, Characterization, Reactivity Ratios, and Thermal Properties

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ABSTRACT: Solution copolymerization of styrene (Sty) and acrylonitrile (AN) was carried out in dioxane at $60 \pm 1^\circ\text{C}$ for 90 min using diphenylselenonium 2,3,4,5-tetraphenylcyclopentadienylide (selenonium ylide) as radical initiator. The kinetic expression is as follows: $R_p \sim [\text{Ylide}]^{0.5} [\text{Sty}]^{1.0} [\text{AN}]^{1.0}$. The overall activation energy is $28.72 \text{ kJ mol}^{-1}$. The composition of copolymer calculated from $^1\text{H-NMR}$ and elemental analysis was used to evaluate reactivity ratio as $r_1 (\text{Sty}) = 0.351$ and $r_2 (\text{AN}) = 0.0185$, using Kelen-Tudos method. It confirmed the alternating nature

of the copolymer. The copolymer was characterized using Fourier transform infrared (FTIR) spectroscopy, $^1\text{H-NMR}$, $^{13}\text{C-NMR}$, differential scanning calorimetry, and thermal gravimetric analysis. Electron spin resonance spectroscopy confirmed the presence of the phenyl radical responsible for initiation. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 121: 1052–1058, 2011

Key words: copolymerization; selenonium ylide; kinetics; mechanism

INTRODUCTION

Copolymerization is the most successful and powerful method for effecting systematic changes in polymer properties.¹ The incorporation of two different monomers having diverse physical and/or chemical properties in the same polymer molecule in varying proportions leads to the formation of new materials with great scientific and commercial importance.^{2,3} Copolymerization modulates both the intramolecular and intermolecular forces exercised between like and unlike polymer segments and consequently properties such as glass transition temperature, thermal stability, etc. may be varied within wide limits. The utility of the copolymerization is exemplified on the one hand by the fundamental investigations of structure–property relations^{4–9} and on the other hand by the wide range of commercial applications.^{10,11} The kinetics and elucidation of copolymer structure are the major concerns for the prediction of copolymer properties and the correlation between structure and properties. Among the various copoly-

merization reactions, radical copolymerization is the most important because it does not demand rigorous experimental conditions and can be applied to a large variety of monomers, leading to the formation of new materials.

Poly(styrene-*co*-acrylonitrile) (PSAN) is a widely used thermoplastic because of its excellent properties such as solvent resistance, thermal stability, transparency, and processability.¹² In addition to the application as a structural material, PSAN is often used as component in polymer blends with polyurethanes,¹³ polyamides,¹⁴ polyesters,¹⁵ poly(methacrylates),¹⁶ and polyolefin.¹⁷

The copolymerization of acrylonitrile (AN) with styrene (Sty) and different conjugate diene monomers by kinetic treatment has been a subject of interest for many authors.^{18–22} Thermooxidative degradation kinetics was also studied.²³ Srivastava et al.^{24,25} studied the copolymerization kinetics and mechanism of acrylates with Sty in the presence of Lewis acid complexes.

Ylides are dipolar compounds in which a carbanion is attached directly to a heteroatom carrying a high degree of positive charge. Ylides have applications in synthetic and theoretical chemistry.²⁶ They are important intermediate²⁷ in organic synthesis and also have some useful practical applications, e.g., as polymerization catalyst.²⁸ Ylides are very

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versatile in their behavior; they act as retarders,²⁹ initiators,³⁰ and degradative chain transfer agents³¹ in the polymerization of vinyl monomers. The application of ylides containing N,³² P,³³ Sb,³⁴ As,³⁵ Bi,³⁶ and S³⁷ in the domain of polymer science is a current topic of interest with a recent history of 25 years. However, a search of literature reveals that the selenium ylide has been successfully used as an initiator in the homopolymerization of MMA³⁸ in our laboratory only. The advantage of selenium ylide as initiator is that at a definite temperature and reaction period, higher yield of polymer can be obtained using its lower concentration (10^2 – 10^3 times less) in comparison with common radical initiators. Therefore, we have extended our studies to synthesize and characterize an alternating copolymer of Sty and AN in the presence of selenium ylide as a new radical initiator.

EXPERIMENTAL

Materials

Sty (Merck-Schuchardt) and AN (Ranbaxy) were purified by the standard methods.³⁹ Tetraphenylcyclopentadiene (Acros), *p*-toluenesulphonylhydrazide (Aldrich), diphenyl selenide (Lancaster), and solvents (Merck) were used as received. Selenium ylide was prepared by the method of Lloyd and Singer.⁴⁰

Copolymerization procedure

A solution containing Sty, AN, and ylide was injected in dilatometer and polymerization was carried out at $60 \pm 1^\circ\text{C}$ for 90 min under an inert atmosphere of nitrogen. The progress of the reaction was monitored as meniscus movement using cathetometer and the contraction was converted into % conversion. The copolymers were isolated with acidified methanol and dried to constant weight. Then, it was refluxed with cyclohexane and Dimethyl formamide (DMF) to remove polystyrene and polyacrylonitrile. The polymer was again dissolved in dioxane and reprecipitated with acidified methanol. Finally, the

TABLE I
Effect of Concentrations of Initiator on
the Rate of Polymerization

S. No.	[Ylide] $\times 10^6$ (mol L ⁻¹)	Percentage conversion	$R_p \times 10^6$ (mol L ⁻¹ s ⁻¹)	$[\bar{M}_v]$
1	12.61	4.40	25.06	114,000
2	25.21	6.10	35.30	64,268
3	50.40	8.70	50.70	58,479
4	75.63	10.40	60.13	37,025

[Sty] = 1.318 mol L⁻¹, [AN] = 1.388 mol L⁻¹, Time = 90 min, Temperature = $60 \pm 1^\circ\text{C}$.

TABLE II
Effect of Concentrations of Monomers on
the Rate of Polymerization

S. No.	[Sty] (mol L ⁻¹)	[AN] (mol L ⁻¹)	Percentage conversion	$R_p \times 10^6$ (mol L ⁻¹ s ⁻¹)
5	1.054	1.388	5.4	28.83
2	1.318	1.388	6.1	35.30
6	1.582	1.388	6.8	42.65
7	1.845	1.388	7.8	53.88
8	2.11	1.388	9.3	68.02
9	1.318	0.925	5.2	25.4
10	1.318	1.85	7.9	53.2
11	1.318	2.313	8.6	66.4
12	1.318	2.776	9.5	81.5

[Ylide] = 25.21×10^{-6} mol L⁻¹, Time = 90 min, Temperature = $60 \pm 1^\circ\text{C}$.

copolymer was dried to constant weight. The intrinsic viscosity $[\eta]$ of the copolymers, determined in tetrahydrofuran at 25°C using an ubbelohde viscometer. The viscosity average molecular weight $[\bar{M}_v]$ of the copolymers was determined by using Mark-Houwink equation.

Instrumental analysis

The copolymers were characterized by FTIR, NMR, differential scanning calorimetry (DSC), and thermal gravimetric analysis (TGA) analysis. FTIR spectra of the samples were recorded with Vertex 70 (Bruker) spectrophotometer using KBr pellets. ¹H-NMR and ¹³C-NMR spectra were recorded on an ECX 500 JEOL NMR spectrometer using CDCl₃ as solvent and TMS as an internal reference. DSC and TGA both were carried out on Universal V3.9A TA instrument at heating rate of $10^\circ\text{C}/\text{min}$ under nitrogenous atmosphere.

RESULTS AND DISCUSSION

The copolymerization of Sty with AN was studied by varying the concentration of Ylide, Sty, and AN. Temperature effect was also studied, keeping other parameters as constant. The rate of polymerization (R_p) was calculated from the graph of % conversion with time at different concentrations of initiator and monomers. The order of reaction was determined with the help of graph plotted between $\log R_p$ and \log of concentrations of initiator and monomers. The energy of activation was calculated from the plot of $\log R_p$ and temperature inverse. The polymerization conditions and results are summarized in Tables I–III and Figures 1–11.

Effect of initiator concentration

The effect of [Ylide] on the rate of polymerization was studied by varying its concentration from

TABLE III
Composition of Copolymer

S. No.	Molar ratio in monomer feed	Molar ratio in copolymer composition	Percentage conversion	copolymer composition	
				Molar fraction of Sty	Molar fraction of AN
2	0.95	1.032	6.1	0.508	0.492
6	1.14	1.051	6.8	0.513	0.487
7	1.33	1.103	7.8	0.525	0.475
9	1.43	1.133	5.2	0.531	0.469

12.61×10^{-6} to 75.63×10^{-6} mol L⁻¹ (Fig. 1) at the fixed concentration of Sty and AN (Table I). The percentage conversion as well as rate of polymerization increases with increase in concentration of initiator. The rate of polymerization is a direct function of [Ylide]. The initiator exponent value, calculated from the slope of log R_p vs. log [Ylide] is 0.5 (Fig. 2). The molecular weight of the copolymers decreases with the increase of ylide concentration.

Effect of monomer concentrations

The effect of monomer concentration on the rate of polymerization was studied by varying its concentration and keeping the initiator concentration constant at 25.21×10^{-6} mol L⁻¹ (Table II). The percentage conversion as well as rate of polymerization increases with increase in monomer(s) concentration.

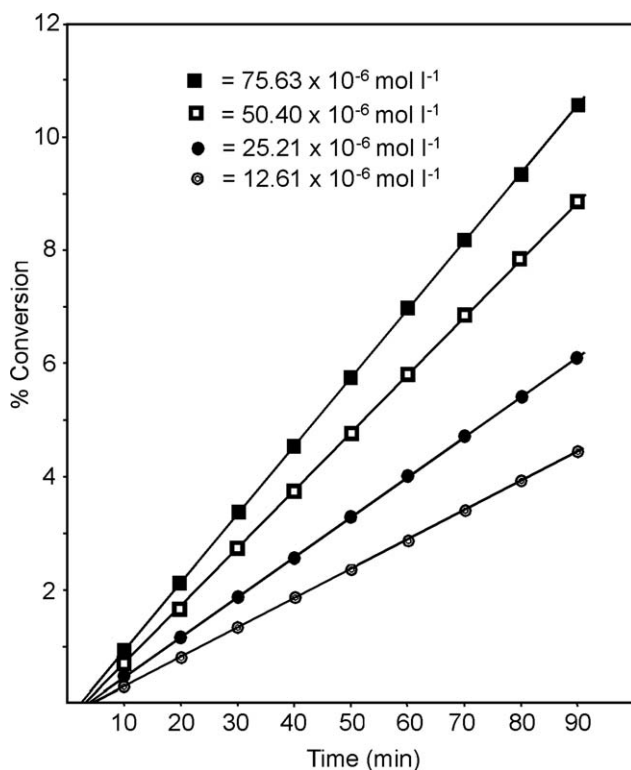


Figure 1 Percentage conversion vs. time plots of radical copolymerization of styrene and acrylonitrile using selenium ylide. [Sty] = 1.318 mol L⁻¹, [AN] = 1.388 mol L⁻¹, Time = 90 min, Temperature = 60 ± 1°C.

The monomer exponent value calculated from the slope of log R_p vs. log [M] in [Sty] is 1.0 and in [AN] is 1.0 (Figs. 3 and 4). The kinetic expression is:

$$R_p \sim [\text{Ylide}]^{0.5}[\text{Sty}]^{1.0}[\text{AN}]^{1.0}$$

Effect of temperature

The polymerization reactions were also carried out at different temperatures (60–90°C) for 90 min at fixed concentrations of [Sty] = 1.318 mol L⁻¹, [AN] = 1.388 mol L⁻¹, and [Ylide] = 25.21×10^{-6} mol L⁻¹. The rate of polymerization increases with increase in temperature. The overall activation energy calculated from a linear Arrhenius plot is 28.72 kJ mol⁻¹ (Fig. 5).

Characterization of copolymer

Spectral analysis

The FTIR spectrum of the formed copolymer (Fig. 6) exhibits characteristic absorption bands at 2238 cm⁻¹ and 3028 cm⁻¹ due to nitrile (—C≡N) group of AN and aromatic ring of phenyl group in Sty, respectively, indicating both the monomers are

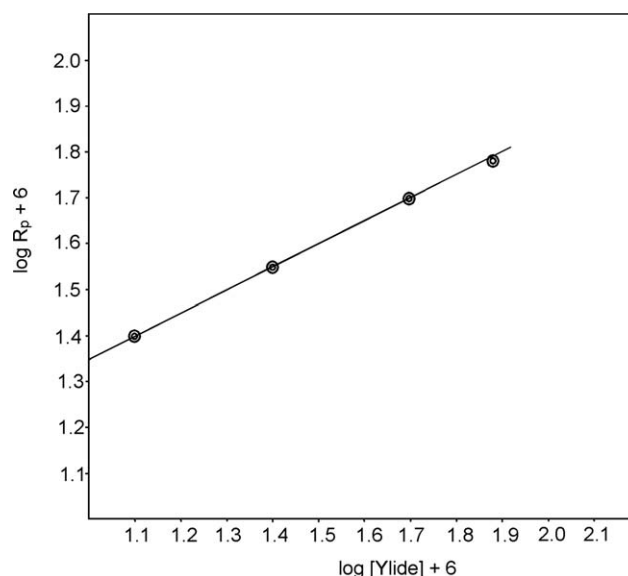


Figure 2 Plot of log R_p vs. log [Ylide]. [Sty] = 1.318 mol L⁻¹, [AN] = 1.388 mol L⁻¹, Time = 90 min, Temperature = 60 ± 1°C.

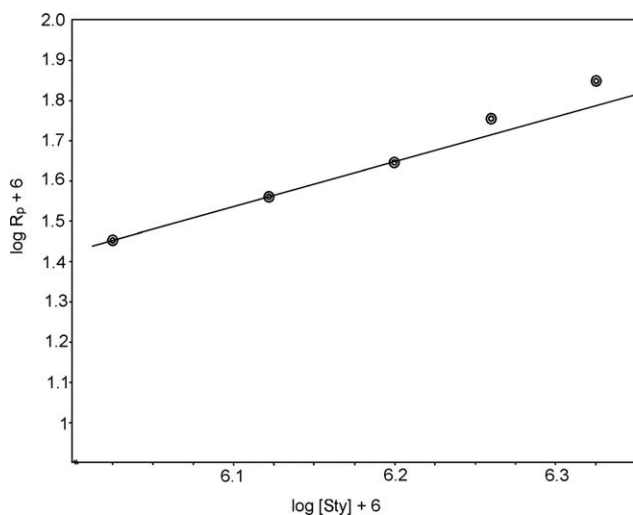


Figure 3 Plot of $\log R_p$ vs. $\log [\text{Sty}]$. $[\text{Ylide}] = 25.21 \times 10^{-6} \text{ mol L}^{-1}$, $[\text{AN}] = 1.388 \text{ mol L}^{-1}$, Time = 90 min, Temperature = $60 \pm 1^\circ\text{C}$.

incorporated in the synthesized copolymer. $^1\text{H-NMR}$ of the copolymer (Fig. 7) shows peaks at 1.2–2.2 ppm due to aliphatic methylene and methine protons and 6.9–8.28 ppm for aromatic protons of Sty, respectively. $^{13}\text{C-NMR}$ spectrum (Fig. 8) shows two distinct peaks at 142 ppm and 27–30 ppm due to aromatic phenyl group and methine group of Sty, respectively, and at 127 ppm due to nitrile ($-\text{C}\equiv\text{N}$) group of AN. The presence of nitrogen in the formed copolymer is confirmed by elemental analysis.

Thermal analysis

Differential scanning calorimetry. The glass transition temperature (T_g) is an important characteristic of a

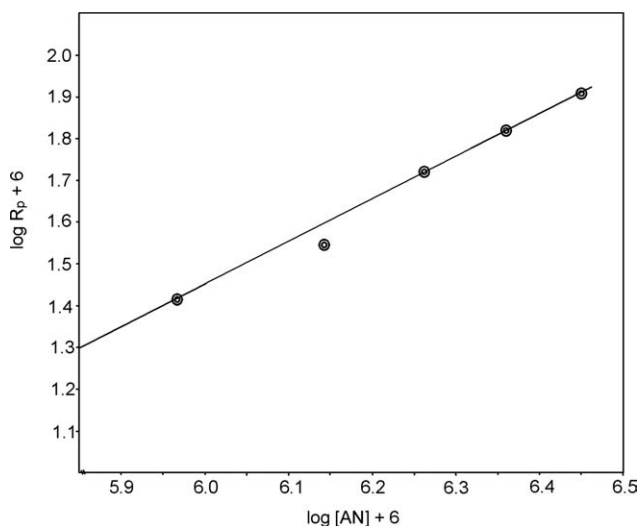


Figure 4 Plot of $\log R_p$ vs. $\log [\text{AN}]$. $[\text{Ylide}] = 25.21 \times 10^{-6} \text{ mol L}^{-1}$, $[\text{Sty}] = 1.318 \text{ mol L}^{-1}$, Time = 90 min, Temperature = $60 \pm 1^\circ\text{C}$.

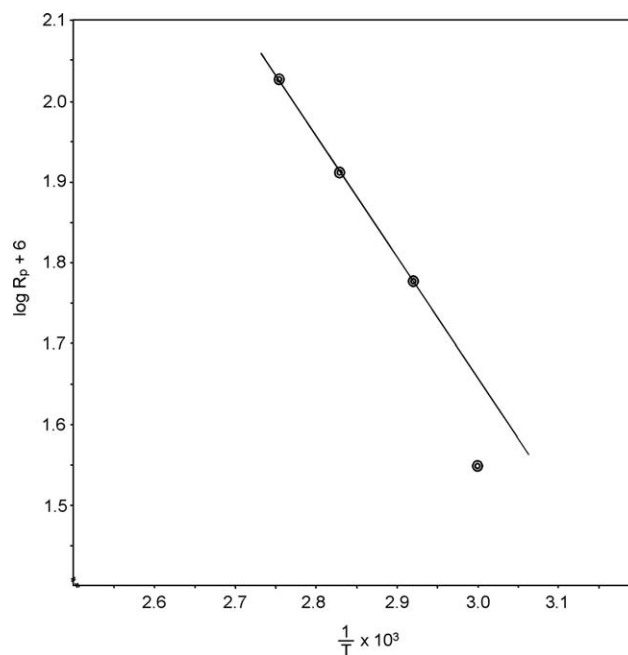


Figure 5 Plot of $\log R_p$ vs. $1/T$. $[\text{Ylide}] = 25.21 \times 10^{-6} \text{ mol L}^{-1}$, $[\text{Sty}] = 1.318 \text{ mol L}^{-1}$, $[\text{AN}] = 1.388 \text{ mol L}^{-1}$, Time = 90 min.

polymer for its applications. The T_g depends upon the copolymer composition and its correlation with the chain stiffness, tacticity,⁴¹ solvents used, and molecular weight.⁴² We observed the T_g of the copolymer as 117.25°C (Fig. 9). The T_g was calculated from the following copolymer equation:⁴³

$$100/T_g = (W_1/T_g) + (W_2/T_g)$$

T_g was also calculated by using simplest equation describing the effect of composition on T_g is the Gibbs-Di Marzio equation,⁴⁴ i.e.,

$$T_g = \phi_S T_{gS} + \phi_A T_{gA}$$

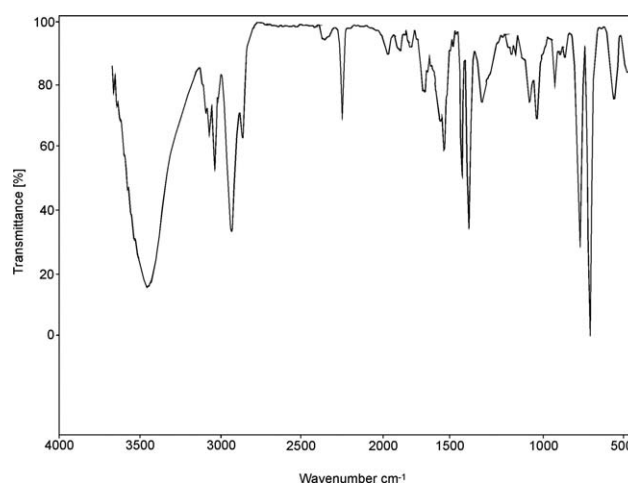


Figure 6 FTIR spectrum of copolymer.

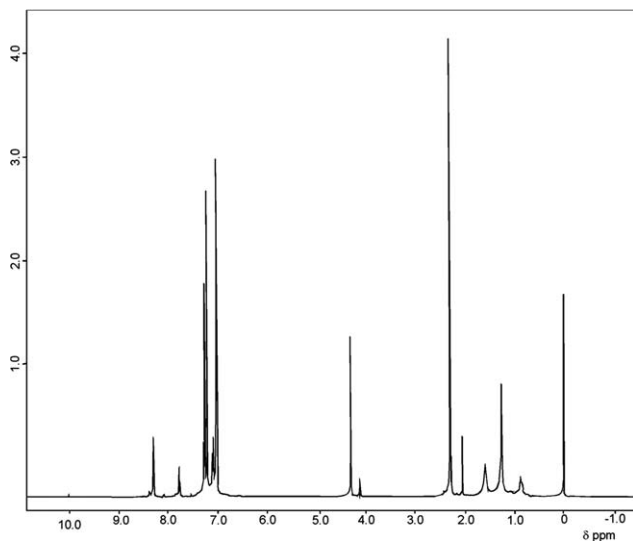


Figure 7 ^1H -NMR spectrum of copolymer.

where ϕ_S and ϕ_A are the molar fractions of Sty and AN monomers, respectively, in the copolymer and T_{gS} and T_{gA} are the glass transition temperature of the corresponding homopolymers, respectively.

The experimental value, i.e., 117.25°C , is in closer agreement with the values calculated by these equations, i.e., 108.68°C (calculated from copolymer equation) and 112.2°C (calculated from Gibbs-Di Marzio equation).

Thermal gravimetric analysis. TGA curve of the copolymer (Fig. 10) exhibits weight loss with the increase in temperature. The observed thermal behavior is as follows:

- Onset of major weight loss occurs at 350°C and completes at 460°C .
- Total weight loss in the temperature range of 300 – 500°C is 92.53%.

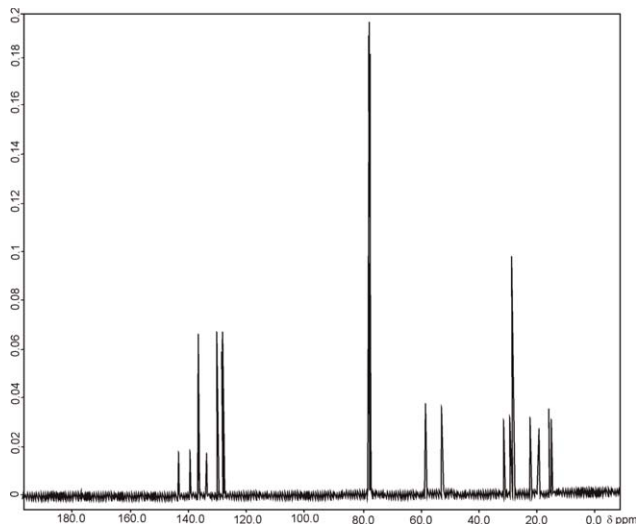


Figure 8 ^{13}C -NMR spectrum of copolymer.

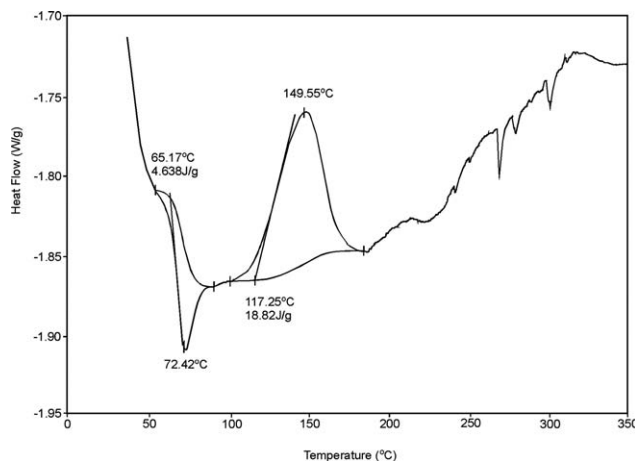


Figure 9 DSC curve of copolymer.

- Weight loss at different temperatures calculated by a plot of % weight and temperature is as follows:

- 50 – $100^\circ\text{C} = 0\%$
- 100 – $300^\circ\text{C} = 6.856\%$
- 300 – $500^\circ\text{C} = 92.53\%$

The weight loss of 6.856% up to 300°C , which is attributed to the loss of absorbed water. Above 300°C is the region of major weight loss and appears to be due to dehydration and to the extensive degradation of backbone chain.

For comparison, the thermograms of polystyrene, PAN, and poly[Sty-co-AN] were also studied (Fig. 10) It shows that copolymer is more stable than the homopolymers. The degradation of copolymer is controlled by its comonomer. The sequence of thermal stability is as follows:

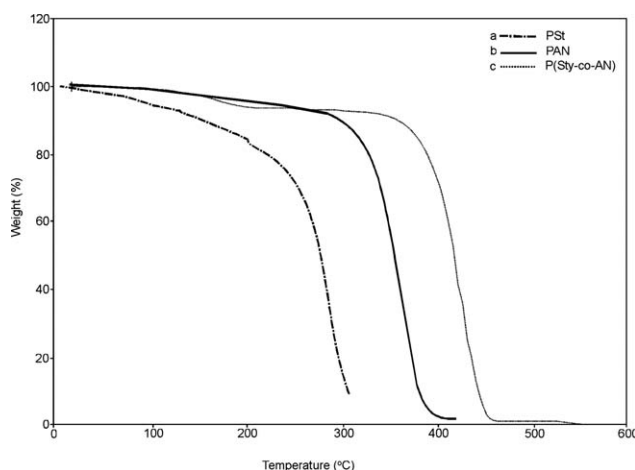


Figure 10 TGA curve of (a) polystyrene, (b) polyacrylonitrile, and (c) poly(Sty-co-AN).

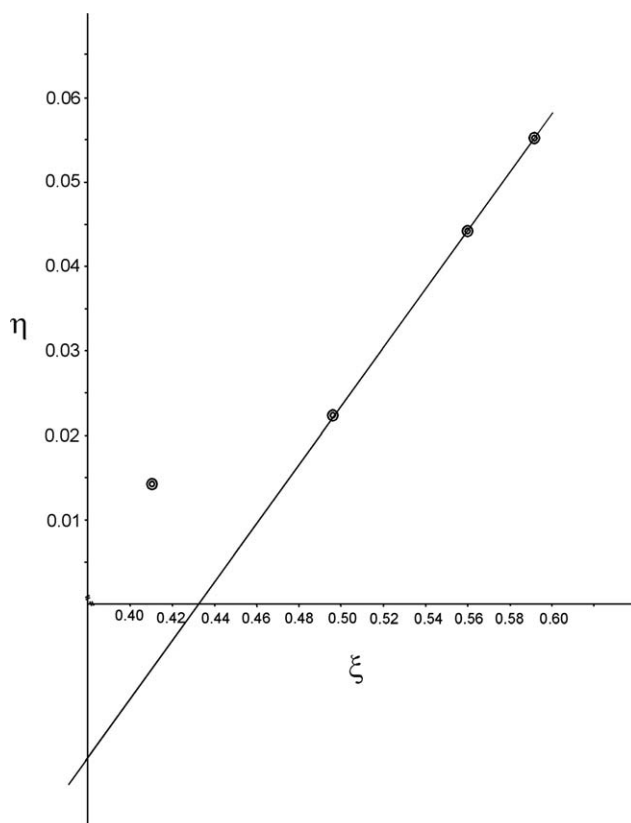


Figure 11 Kelen-Tüdös plot for the determination of reactivity ratios.

The advantage of the copolymer is that it is thermally more stable than the corresponding homopolymers of Sty and AN.

Copolymer composition and reactivity ratios

The composition of the copolymer was evaluated from high resolution $^1\text{H-NMR}$ and elemental analysis (Table III). The relative peak area at 6.9–8.28 ppm for phenyl protons of Sty and nitrogen percent of cyanide group of AN has been used to calculate the copolymer composition.

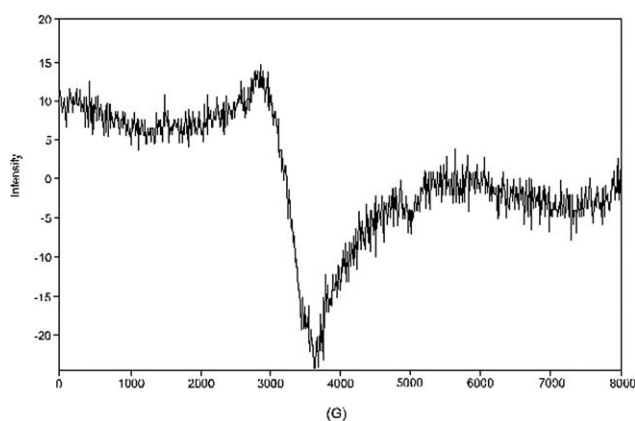


Figure 12 ESR spectrum of copolymer.

These values are used to calculate monomer reactivity ratios using Kelen-Tüdös⁴⁵ method. The values of r_1 and r_2 were calculated by the graph plotted between η and ξ (Fig. 11).

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

where,

$$\eta = G/(\alpha + H) \text{ and } \xi = H/(\alpha + H)$$

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

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

$$\alpha = (H_{\max} \times H_{\min})^{1/2}$$

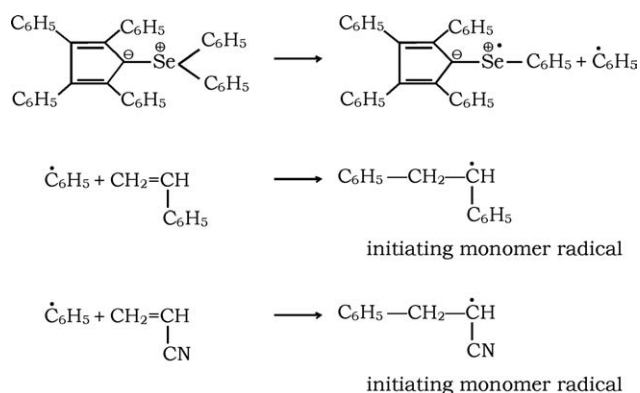
The parameter α is calculated by taking the square root of the product of the lowest and the highest values of H for copolymerization series. The slope of the plot of η vs. ξ gives the value of r_1 (Sty) = 0.351 and the intercept gives the value of r_2 (AN) = 0.0185. The product of r_1 and r_2 is nearly zero. This is an indication of an alternating copolymer taking AN as an electron acceptor and Sty as an electron donor monomers.

Mechanism of copolymerization

The free radical mode of polymerization is checked by the effect of hydroquinone which inhibits the polymerization reaction. The Electron spin resonance spectroscopy (ESR) spectrum (Fig. 12) further confirms that ylide dissociates to give phenyl free radical, which is responsible for the initiation of polymerization reaction. The value of gyromagnetic ratio (g) was calculated from the following relationship is 2.12.

$$g = \nu h / \beta H$$

where, H is the field set, ν is the modulation frequency, h is Planck's constant, and β the Bohr



Scheme 1 Mechanism of copolymerization.

magneton. The value of g matches well with that given for free radical polymerization. The absence of peak of selenium in the ^{77}Se NMR spectrum confirms that the synthesized copolymer does not contain selenium. The mechanism of copolymerization is given in Scheme 1.

CONCLUSIONS

Alternating poly[Sty-*co*-AN] has been synthesized via free radical polymerization using selenonium ylide as an initiator without using any lewis acid and the system follows ideal kinetics. To the best of our knowledge, this initiator is used first time for this system. The glass transition temperature of the copolymer is 117.25°C. The formed copolymer is significant because of more thermal stability than that of the corresponding homopolymers of Sty and AN. Selenium is not incorporated in the polymer matrix.

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