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RESEARCH ARTICLE

ALTERNATING COPOLYMERIZATION OF VINYL PYRROLIDONE WITH METHYL METHACRYLATE USING TRIPHENYLBISMUTHONIUM 1,2,3,4-TETRAPHENYLCYCLOPENTADIENYLIDE AS A RADICAL INITIATOR

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ABSTRACT

The radical copolymerization of methyl methacrylate with vinyl pyrrolidone in dioxan at $60 \pm 0.1^\circ\text{C}$ for 1 hr. in the presence of triphenylbismuthonium 1,2,3,4-tetraphenylcyclopentadienylide follows ideal kinetics and results in the formation of alternating copolymer. The activation energy is 51 kJ/mol. The FTIR spectrum of the copolymer(s) shows the bands at 1730 cm^{-1} and 1681 cm^{-1} for methoxy group and carbonyl group of methyl methacrylate and vinyl pyrrolidone, respectively. The $^1\text{H-NMR}$ spectra of the copolymers show peaks in the range 3.70-3.75 δ due to methoxy protons of methyl methacrylate. The values of reactivity ratios calculated by Kelen-Tüdös method are $r_1(\text{VP}) = 0.0035$ and $r_2(\text{MMA}) = 0.081$. The ESR spectrum shows that the ylide dissociates to form a phenyl radical, which brings about the polymerization. The glass transition temperature (T_g) of the copolymer determined by DSC, is 130°C .

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INTRODUCTION

In the past few years, the industrial uses of vinyl pyrrolidone (VP) based polymers have grown enormously. It has been copolymerized with a variety of comonomers in both solution and emulsion systems. The copolymers of VP have shown a number of properties which lend themselves to a variety of industrial applications of growing importance, i.e., those related to use as hair spray resins, tablet excipients and adhesives. VP has easily been copolymerized with variety of monomers such as vinyl-acetate¹, methyl methacrylate², N-hydroxy phthalimide (HPIE) and N-hydroxy succinimide (HSIE) esters of acrylic (AA), methacrylic (MAA) and crotonic (CA) acids³, 2-phenyl-1,1-dicyano-ethene⁴, styrene and butyl acrylate⁵ using AIBN^{3,4}/4,4-cyanopentanoic acid⁵ as the radical initiator. VP also copolymerized with methyl methacrylate using diphenyl- ditelluride as the radical initiator⁶ and by using titanium (III) – dimethylglyoxime [Ti(III)-DMG] as redox initiator⁷. However, there is a lack of literature on

Ylides are 1,2-dipolar compounds in which a carbanion is attached directly to a heteroatom bearing a positive charge ($\text{C}^- - \text{X}^+$), where, X = N, P; As, S, Sb, Bi, Se, Te). The properties of ylides are very much dependent on the identity of the heteroatoms⁸. The use of ylides containing N⁹, P^{10,11}, S¹², As¹³, Sb¹⁴ as heteroatom in the domain of polymer science are sufficient and those containing Bi, as heteroatom are rare e.g., the homopolymerization of methyl methacrylate¹⁵, styrene¹⁶, methyl acrylate¹⁷ and copolymerization of styrene with methyl methacrylate¹⁸, methacrylic acid¹⁹ and acrylonitrile²⁰. Therefore, this paper reports the copolymerization of VP with methyl methacrylate using triphenylbismuthonium 1,2,3,4-tetraphenylcyclopentadienylide, as the novel initiator.

EXPERIMENTAL

Materials: Methyl methacrylate (Merck-Schuchardt) was purified by treating it with NaOH and distilled water, followed by vacuum distillation before polymerization^{21,22}.

Vinyl pyrrolidone (Merck-Schuchardt) was used as such. Triphenylbismuthonium 1,2,3,4-tetraphenylcyclopentadienylide was synthesized by the method given by Lloyd²³.

Polymerization procedure: A dilatometric technique was used to follow the copolymerization runs under oxygen-free conditions. Copolymerization in dioxan was continued upto 1 hr to limit the conversion range between 5 to 16% at 60°C. The polymer, isolated in diethyl ether and dried under vacuum, was treated with benzene and methanol to remove PMMA and PVP respectively. Finally, the copolymer was dried to constant weight and percent conversion was calculated. The rate polymerization (R_p) was calculated from the slope of the graph between percent conversion and time. The intrinsic viscosity (η) of the copolymers, measured in dimethyl formamide (DMF) at 30°C using Ubbelohde Viscometer, was expressed in deciliter/gram. The FTIR spectrum was recorded with Perkin-Elmer 599B (with KBr pellets) spectrophotometer and ¹H-NMR and ¹³C-NMR spectra were recorded with a Varian 100 HA JEOL 400 LA spectrophotometer using CDCl₃ as a solvent and tetramethyl silane as an internal reference. Thermogravimetric analysis (TGA) was performed on a Stanton Redcroft instrument with a heating rate of 10°C/min in nitrogen. Differential scanning calorimetry (DSC) was carried out using DuPont V4.1C Model 2000 analyzer at a heating rate of 10°C/min, sample weight = 10 mg. The monomer reactivity ratios were determined by using the Kelen-Tüdös method²⁴.

RESULTS AND DISCUSSION

The kinetics of copolymerization was studied by varying [ylide] from $2 \times 10^{-6} \text{ mol l}^{-1}$ to $14.6 \times 10^{-1} \text{ mol l}^{-1}$, [MMA] from 0.313 mol l^{-1} to 2.82 mol l^{-1} and [VP] from 0.312 mol l^{-1} to 2.81 mol l^{-1} . The reaction proceeded with a short induction period of 1-3 min (Fig.1).

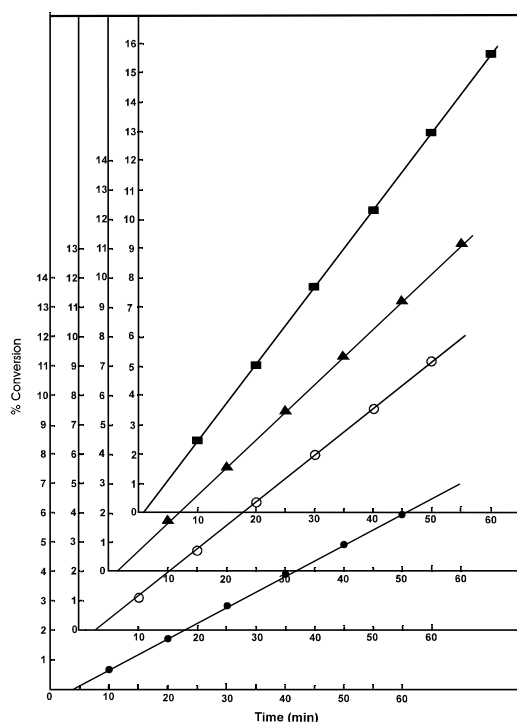


Fig.1 Relationship between percentage conversion Vs time (min); [VP] = 1.56 mol l^{-1} ; [MMA] = 1.56 mol l^{-1} ; [Ylide] ● = $2 \times 10^{-6} \text{ mol l}^{-1}$, ○ = $6.2 \times 10^{-6} \text{ mol l}^{-1}$, ▲ = $10.4 \times 10^{-6} \text{ mol l}^{-1}$; ■ = $14.6 \times 10^{-6} \text{ mol l}^{-1}$.

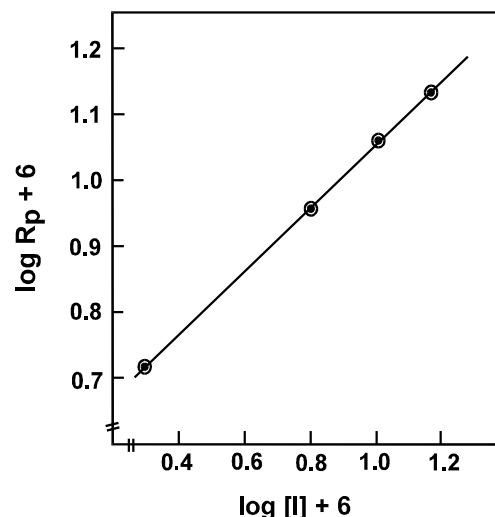


Fig.2 Relationship between the rate of copolymerization and [Ylide]. [VP] = 1.56 mol l^{-1} ; [MMA] = 1.56 mol l^{-1} ; polymerization time = 1hr. and copolymerization temperature = $60 \pm 0.1^\circ\text{C}$

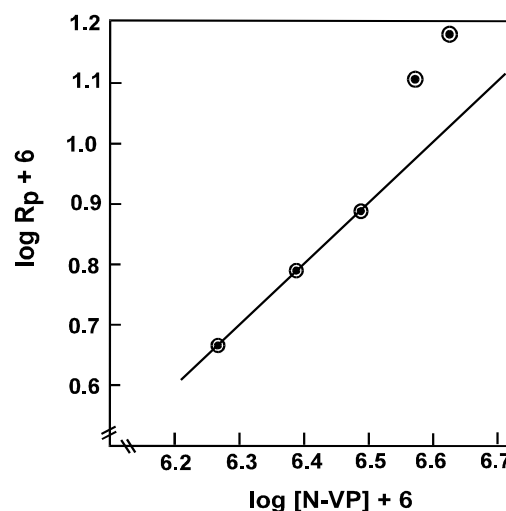


Fig. 3. Relationship between the rate of copolymerization and [VP] with constant [MMA] = 1.56 mol l^{-1} ; [Ylide] = $6.2 \times 10^{-6} \text{ mol l}^{-1}$; copolymerization time = 1hr. and copolymerization temperature = $60 \pm 0.1^\circ\text{C}$

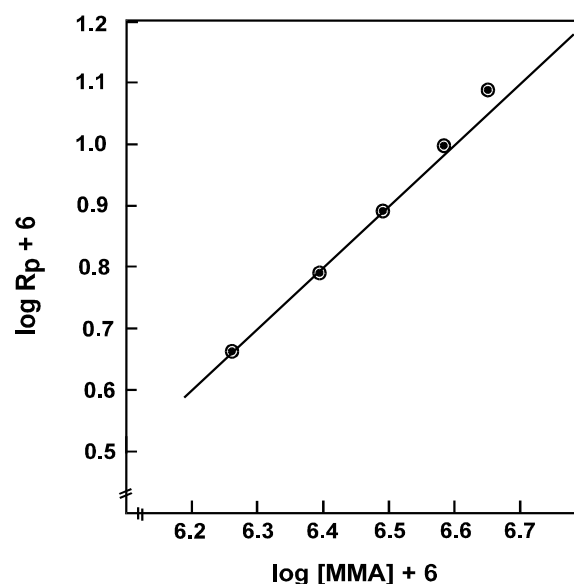


Fig.4. Relationship between the rate of copolymerization and [MMA] with constant [VP] = 1.56 mol l^{-1} ; [Ylide] = $6.2 \times 10^{-6} \text{ mol l}^{-1}$; copolymerization time = 1hr and copolymerization temperature = $60 \pm 0.1^\circ\text{C}$

Table 1. Effect of ylde concentration on the rate of copolymerization of vinyl pyrrolidone and methyl methacrylate

Sample	[Ylide] x 10 ⁶ mol l ⁻¹	Conversion %	R _p x 10 ⁶ mol l ⁻¹ s ⁻¹	[η] dL/g
1	2.00	5.90	5.20	0.027
2	6.20	9.20	9.20	0.020
3	10.40	11.20	11.59	0.014
4	14.60	15.70	13.50	0.007

Copolymerization time = 1 hr. Copolymerization temperature = 60 ± 0.1°C [VP] = 1.56 mol l⁻¹ [MMA] = 1.56 mol l⁻¹

Table 2. Effect of concentration of comonomer on the rate of copolymerization

Sample	[VP] mol l ⁻¹	[MMA] mol l ⁻¹	Conversion %	R _p x 10 ⁶ mol l ⁻¹ s ⁻¹	[η] dL/g
5	1.56	0.313	6.20	3.42	0.006
6	1.56	0.94	7.80	5.83	0.008
2	1.56	1.56	9.20	9.20	0.020
7	1.56	2.19	10.50	12.5	0.033
8	1.56	2.82	11.60	16.79	0.047
9	0.312	1.56	5.70	3.11	0.009
2	1.56	1.56	9.20	9.20	0.011
10	0.936	1.56	8.00	5.81	0.020
11	2.186	1.56	14.60	14.3	0.038
12	2.81	1.56	15.70	17.5	0.050

Copolymerization time = 1 hr. Copolymerization temperature = 60 ± 0.1°C [Ylide] = 6.2 x 10⁻⁶ mol l⁻¹

Table 3. Composition of copolymers

Sample	Molar ratio in monomer feed [VP/MMA] (F)	Conversion %	Mole fraction of [VP] in copolymer	Mole fraction of [MMA] in copolymer	Molar ratio in copolymer (f) [VP/MMA]
6	1.65	7.80	0.55	0.45	1.22
2	1.00	9.20	0.51	0.49	1.04
7	0.71	10.5	0.52	0.48	1.08
10	0.59	8.00	0.56	0.44	1.27
11	1.39	14.6	0.53	0.47	1.12

Effect of initiator concentration: The effect of [ylide] on the R_p was studied by varying the [ylide] from 2 x 10⁻⁶ to 14.6 x 10⁻⁶ mol l⁻¹, keeping [MMA] and [VP] constant at 1.56 mol l⁻¹ each. 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 (η) of the copolymers decreased with increasing [ylide].

Table 4. Reactivity ratios

r ₁	r ₂	r ₁ r ₂
0.0035	0.081	0.0002835

Effect of comonomer concentration: The effect of [VP] on the R_p was studied by varying [VP] from 0.312 to 2.820 mol l⁻¹, while MMA and [ylide] were kept constant at 1.56 mol l⁻¹ and 6.2 x 10⁻⁶ mol l⁻¹, respectively. It is noted that the R_p is a direct function of [VP].

A plot of log R_p Vs log [VP] is linear, given in on order with respect to VP as unity (Fig.3). The intrinsic viscosity of the copolymers increases with increasing [VP] (Table-2). The effect of [MMA] was studied by varying [MMA] from 0.313 to 2.82 mol l⁻¹ while [VP] and [ylide] were kept constant at 1.56 mol l⁻¹ and 6.2 x 10⁻⁶ mol l⁻¹, respectively. The R_p is a direct function of [MMA]. A plot of log R_p Vs log [MMA] is linear and the order of reaction with respect to MMA as unity (Fig.4). The intrinsic viscosity of the copolymer increases with increasing [MMA] (Table-2).

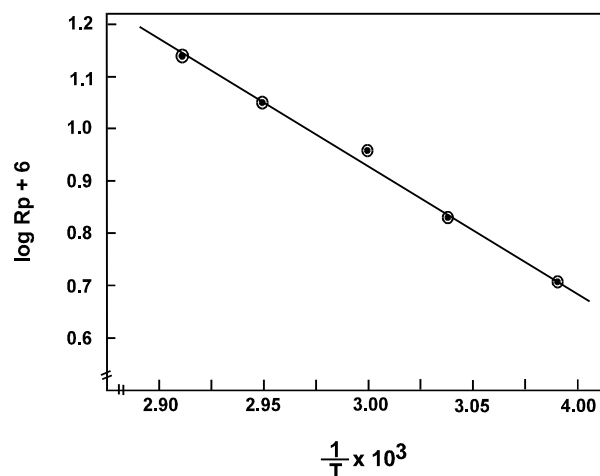


Fig. 5. Arrhenius plot of the rate of polymerization Vs polymerization temperature. [Ylide] = 6.2 x 10⁻⁶ mol l⁻¹; [VP] = 1.56 mol l⁻¹; copolymerization time = 1hr.

Effect of temperature: Polymerization runs were also carried out at 50, 55, 65 and 70°C to evaluate the energy of activation because no polymerization occurred below 50°C. The R_p is direct function of temperature and the apparent activation energy, determined from the slope of the Arrhenius plot of log R_p Vs 1/T, is 51 kJ/mol (Fig.5).

CHARACTERIZATION OF THE COPOLYMER

Fourier Transform Infrared Spectroscopy

The FTIR spectra of the copolymers (Fig.6) consists of following groups of bands:

- C-H stretching band at 2953 cm⁻¹
- OCH stretching band of MMA at 1730 cm⁻¹
- C=O stretching band of VP at 1681 cm⁻¹

- C–C H bending band of MMA at 1434 cm^{-1}
- C–O–C stretching band of MMA at 1265 cm^{-1}

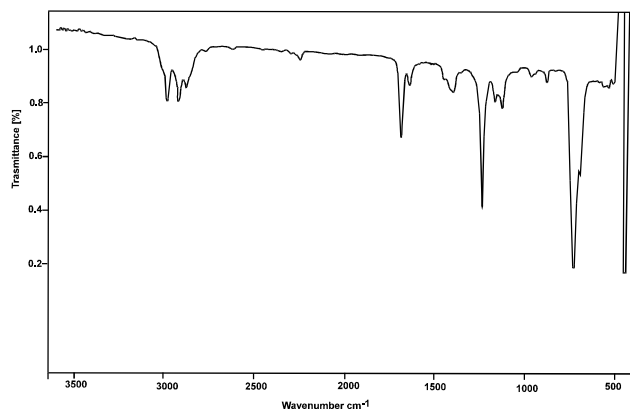


Fig.6 FTIR spectrum of the copolymer (sample 2).

^1H -Nuclear Magnetic Resonance Spectroscopy: The ^1H -NMR spectrum of the copolymer (Fig.7) shows peaks in the range 3.70 to 3.75 δ due to methoxy protons of methyl methacrylate.

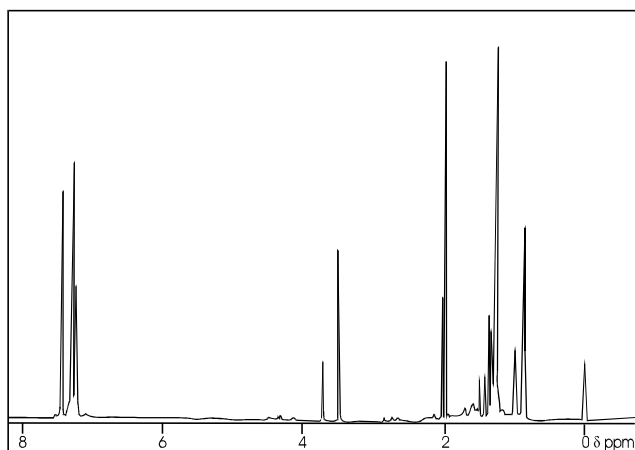
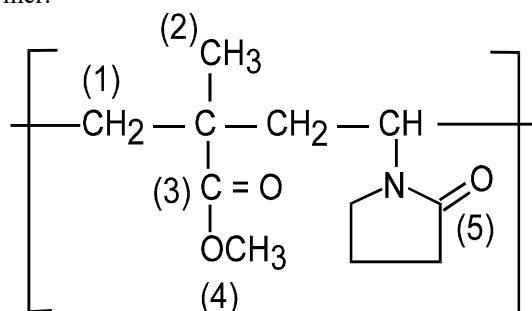


Fig.7 ^1H -NMR spectrum of the copolymer (sample 2).

^{13}C -Nuclear Magnetic Resonance Spectroscopy: The ^{13}C -NMR spectra of the copolymer (Fig.8) show signals at:

- ppm = 39.7 (C_1)
- ppm = 18.2 (C_2)
- ppm = 167 (C_3) (due to MMA)
- ppm = 67.5 (C_4)
- ppm = 200 (C_5) (due to VP)

Therefore, the following structure may be assigned to the copolymer.



Differential Scanning Calorimetry: The DSC curve (Fig.9) indicates the glass transition temperature (T_g) of the copolymer as 130°C .

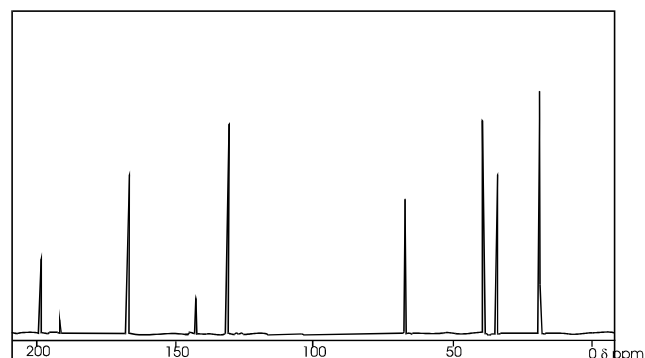


Fig.8 ^{13}C -NMR spectrum of the copolymer (sample 2).

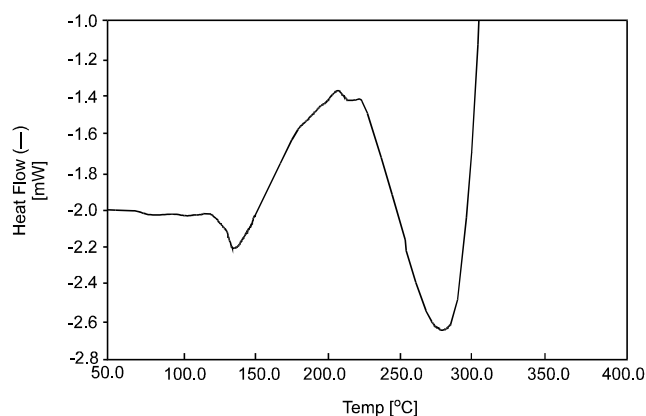


Fig.9 DSC curve of the copolymer (sample 2)

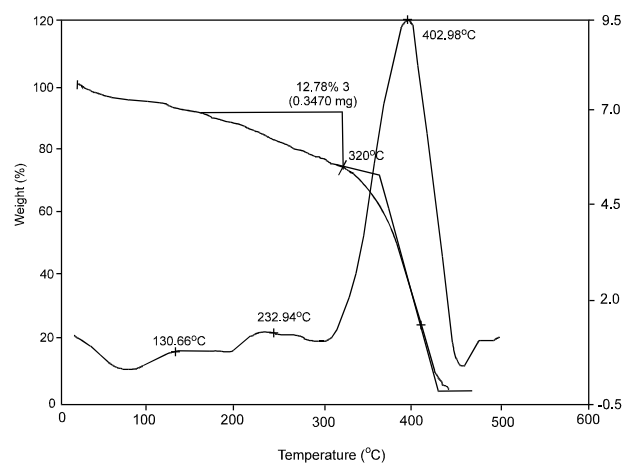


Fig.10 TGA curve of the copolymer (sample 2)

Thermogravimetric Analysis: The TGA curve for copolymer (Fig.10) exhibits weight loss with temperature. The thermal behaviour data are as follows:

- Onset of major weight loss at 320°C , Completion of major weight loss at 475°C .
- The total weight loss in the range $25\text{--}475^\circ\text{C} = 94\%$
- Almost total volatilization of copolymer occurred at 402.98°C .

COPOLYMER COMPOSITION AND VALUES OF REACTIVITY RATIOS: The composition of the copolymer (Table-3) was evaluated from the band depth of the carbonyl

group of vinyl pyrrolidone in the FTIR spectra and the peak area of methoxy protons in the $^1\text{H-NMR}$ spectra of methyl methacrylate. The values were used to calculate the monomer reactivity ratios using the Kelen-Tüdös method. The values of $r_1(\text{VP})$ and $r_2(\text{MMA})$ were calculated, using the least square method as 0.0035 and 0.081 respectively (Fig.11) (Table-4). The product $r_1r_2 = 0.0002835$ indicates that the copolymer is alternating in nature.

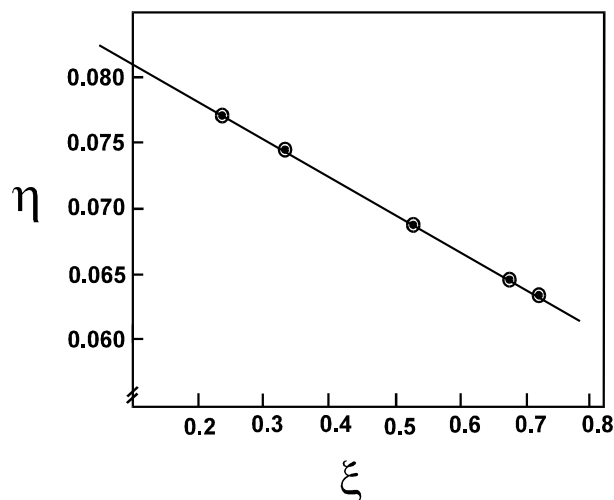


Fig.11. Kelen-Tüdös plot of VP and MMA for determination of reactivity ratio

MECHANISM: It has been reported in the literature¹⁵⁻²⁰ that the ylide dissociated to form a phenyl radical, which brings about polymerization. This has also been confirmed from the ESR spectrum²⁵ (Fig.12), which shows six hyperfine lines due to phenyl radical (the ESR spectrum was recorded on X-band EPR 109 E-line centaury series spectrometer at room temperature) and the value of hyperfine constant is 3.73 gauss.

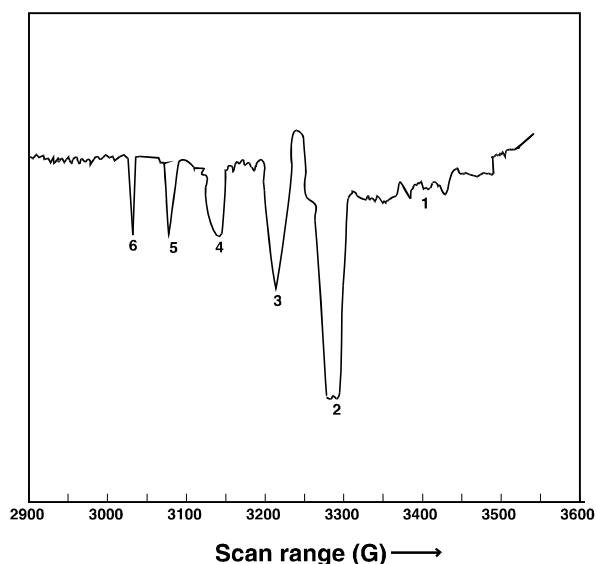
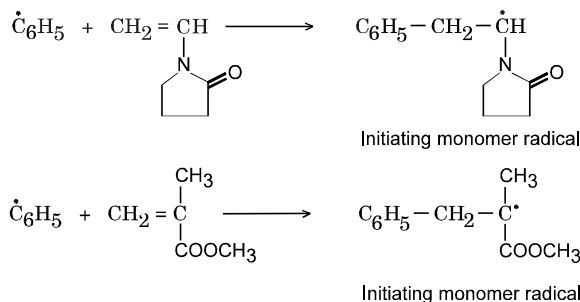
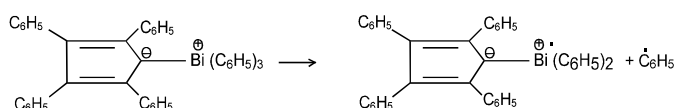


Fig.12. ESR spectrum of the copolymer

The mechanism is as follows:

Initiation



CONCLUSION

The copolymerization of vinyl pyrrolidone with methyl methacrylate, initiated by triphenylbismuthonium 1,2,3,4-tetraphenylcyclopentadienylide in dioxan, follows ideal kinetics & results in the formation of an alternating copolymer.

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