

Kinetics and Mechanism of the Radical Copolymerization of 4-Vinyl Pyridine with Methyl Acrylate Initiated by *p*-Acetylbenzylidene Triphenylarsonium Ylide

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ABSTRACT: The free-radical copolymerization of 4-vinyl pyridine (4-VP) with methyl acrylate (MA) initiated by *p*-acetylbenzylidene triphenylarsonium ylide at $60 \pm 0.1^\circ\text{C}$ with dioxane as an inert solvent yielded random copolymers. The kinetic equation was $R_p \propto [\text{Ylide}]^{0.83} [4\text{-VP}]^{0.33} [\text{MA}]^{0.40}$ (where R_p is the rate of polymerization); in other words, the system followed nonideal kinetics. The values of the energy of activation and k_p^2/k_t (where k_p is the rate constant of propagation and k_t is the rate constant of termination) were 23.21 kJ/mol and $1.212 \times 10^{-5} \text{ mol L}^{-1}$

s^{-1} , respectively. The reactivity ratios calculated with the Kelen–Tüdös method were 0.14 ± 0.0075 for 4-VP and 0.56 ± 0.0078 for MA. The copolymers were characterized with Fourier transform infrared, proton nuclear magnetic resonance, differential scanning calorimetry, and electron spin resonance methods. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 113: 3354–3359, 2009

Key words: copolymerization; differential scanning calorimetry (DSC); ESR/EPR; FT-IR; radical polymerization

INTRODUCTION

Copolymerization¹ is the most general and powerful method of making systematic changes in polymer properties, and it is widely used in the production of commercial polymers and in fundamental investigations of structure–property relationships. Within the past 2 decades, the area of polymer–ylide chemistry has become one of the most fruitful realms of polymer science. Ylides are 1,2-dipolar compounds in which a carbanion is attached directly to a heteroatom bearing a positive charge ($> \overset{\oplus}{\text{C}}-\overset{\ominus}{\text{X}}$, where X is N, P, As, S, Bi, Se, or Te). The properties of ylides are very dependent on the identity of the heteroatoms.² A literature survey has shown copolymerizations of methyl acrylate (MA) with styrene,³ 5-ethyl-2-vinyl pyridine,⁴ and acrylonitrile⁵ and copolymerizations of 4-vinyl pyridine (4-VP) with methyl methacrylate⁶ and styrene⁷ with imidazolium-*p*-chlorophenacylide,³ azobisisobutyronitrile,^{4,5} and β -picolinium-*p*-chlorophenacylide^{6,7} used as radical initiators.

There are several reports on the possible use of *p*-acetylbenzylidene triphenylarsonium ylide (*p*-ABTAY) as a radical initiator for the homopolymerization of MA,⁸ methyl methacrylate,⁹ and vinyl acetate¹⁰ and for the copolymerization of styrene with

citronellol,¹¹ styrene with vinyl acetate,¹² citronellol with methyl methacrylate,¹³ linalool with styrene,¹⁴ and so forth. However, research is still needed on the copolymerization of MA with 4-VP. Therefore, this system using *p*-ABTAY as a new radical initiator was studied, and this article highlights the kinetics and mechanism of the copolymerization of 4-VP and MA with dioxane as the solvent at 60°C for 90 min.

EXPERIMENTAL

4-VP (Aldrich, India) was distilled *in vacuo*, and MA (Merck, India) was purified by the method of Overberger and Yamamoto.¹⁵ The ylide (*p*-ABTAY) was prepared by the published method.¹⁶

Polymerization procedure

The copolymerization of 4-VP with MA was carried out in dioxane at $60 \pm 1^\circ\text{C}$ for 90 min with the dilatometric technique¹⁷ (capillary diameter = 2.0 mm and lower bulb capacity = 2.5 mL) under an inert atmosphere of nitrogen. The copolymer was precipitated in ethanol. The rate of polymerization (R_p) was calculated from the slopes of plots of the conversion percentage versus the time.

Measurements

The intrinsic viscosity [η (dL/g)] of the copolymers in dimethyl sulfoxide was measured at $30 \pm 0.2^\circ\text{C}$ with an Ubbelohde viscometer.

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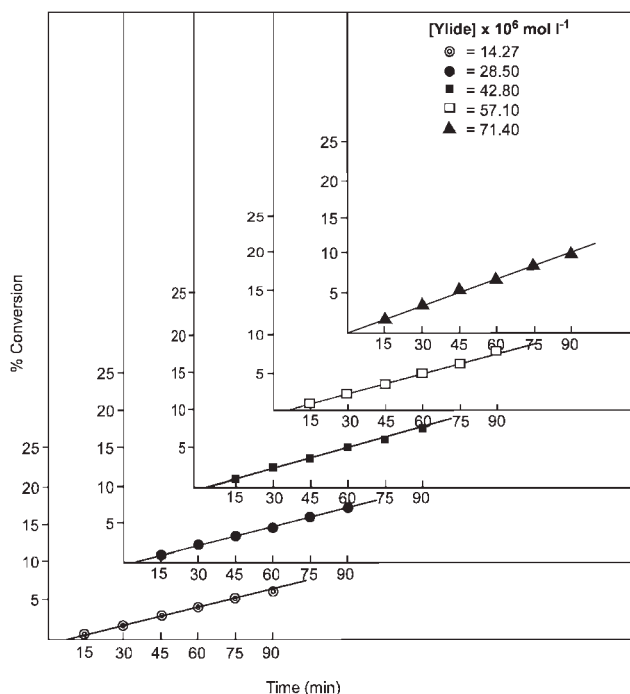


Figure 1 Conversion percentage versus the time for the copolymerization of 4-VP with MA as a function of the ylide concentration ([4-VP] = 1.159 mol/L; [MA] = 1.372 mol/L; copolymerization temperature = $60 \pm 0.1^\circ\text{C}$; copolymerization time = 90 min).

Characterization

The Fourier transform infrared (FTIR) and proton nuclear magnetic resonance ($^1\text{H-NMR}$) spectra were recorded with the help of a PerkinElmer (Waltham, MA) 599B spectrometer and a Varian 100 HA spectrometer, respectively, with CDCl_3 as the solvent and tetramethylsilane as the internal reference. The differential scanning calorimetry (DSC) runs were carried out with a VA.0B 2100 analyzer with a sample weight of 5.3 mg at a heating rate of $10^\circ\text{C}/\text{min}$. The electron spin resonance (ESR) spectrum was recorded on an X-band EPR-109 E-Line Century series spectrometer at room temperature. The reactivity ratios were determined with the help of the Kelen-Tüdös method.¹⁸

RESULTS AND DISCUSSION

The copolymerization runs were limited to 9.80% conversion by the variation of the monomer and ylide concentrations. The volume contraction data were converted into conversion percentages with the help of a master graph (Fig. 1). The system obeyed nonideal kinetics. The copolymerization runs were associated with a short induction period of about 2–10 min, and the results are presented in Tables I–IV and Figures 1–9.

Effect of the initiator concentration

The effect of the ylide concentration on R_p was studied by the variation of the ylide concentration from 14.270×10^{-6} to 82.800×10^{-6} mol/L, with the 4-VP and MA concentrations kept constant at 1.159 and 1.372 mol/L, respectively (Table I and Fig. 1). R_p increased as the ylide concentration increased. The results are presented in (Table I). The order of reaction, calculated from the slope of $\log R_p$ versus $\log [\text{Ylide}]$, was 0.83 ± 0.01 . It was more than the expected value (0.5) for ideal kinetics. η of the copolymers decreased with the initiator concentration increasing from 0.189 to 0.045 (Table I). The value of the rate constant ratio k_p^2/k_t (where k_p is the rate constant of propagation and k_t is the rate constant of termination), determined from the slope of a linear plot of $1/\eta$ versus $R_p/[\text{M}]^2$ (where [M] is the monomer concentration), was 1.212×10^{-5} mol $\text{L}^{-1} \text{s}^{-1}$.

Effect of the monomer concentration

The effect of the 4-VP concentration on R_p was studied by the variation of the 4-VP concentration from 0.580 to 2.898 mol/L while the MA and *p*-ABTAY concentrations were kept constant at 1.372 and 28.500×10^{-6} mol/L, respectively (Table II). R_p was a direct function of the 4-VP concentration. A plot of $\log R_p$ versus $\log [4\text{-VP}]$ was linear, yielding an order of reaction of 0.33 with respect to 4-VP. It was less than the expected value (1.0) for ideal kinetics.

TABLE I
Effect of the *p*-ABTAY Concentration on the Rate of Copolymerization of 4-VP with MA Initiated by *p*-ABTAY and the η Values of the Copolymer

Run	[<i>p</i> -ABTAY] $\times 10^6$ (mol/L)	Volume contraction (cm)	Conversion (%)	$R_p \times 10^6$ (mol $\text{L}^{-1} \text{s}^{-1}$)	η (dL/g)
1	14.27	2.55	6.12	20.21	0.189
2	28.50	2.82	6.78	21.49	0.150
3	42.80	3.00	7.20	24.60	0.105
4	57.10	3.10	7.45	29.20	0.090
5	71.40	3.54	8.50	36.20	0.065

[4-VP] = 1.159 mol/L; [MA] = 1.372 mol/L; copolymerization temperature = $60 \pm 0.1^\circ\text{C}$; copolymerization time = 90 min.

TABLE II
Effect of the 4-VP Concentration on the Rate of Copolymerization of 4-VP with MA Initiated by *p*-ABTAY and the η Values of the Copolymer

Run	[4-VP] (mol/L)	Volume contraction (cm)	Conversion (%)	$R_p \times 10^6$ (mol L ⁻¹ s ⁻¹)	η (dL/g)
6	0.580	2.37	5.69	23.23	0.020
7	1.159	2.82	6.78	24.70	0.030
8	1.739	2.92	7.01	27.13	0.045
9	2.319	3.18	7.65	30.59	0.085
10	2.898	3.33	8.01	36.27	0.135

[*p*-ABTAY] = 28.500 × 10⁻⁶ mol/L; [MA] = 1.372 mol/L; copolymerization temperature = 60 ± 0.1°C; copolymerization time = 90 min.

η (dL/g) of the copolymers increased with both monomer concentrations increasing (Tables II and III).

The effect of the MA concentration on R_p was studied by the variation of the MA concentration from 0.6861 to 3.400 mol/L while the 4-VP and ylide concentration were kept constant at 1.159 and 28.500 × 10⁻⁶ mol/L, respectively (Table III). R_p was a direct function of the MA concentration. A plot of log R_p versus log [MA] was linear, yielding an order of reaction of 0.40 with respect to MA. It was less than the expected value (1.0) for ideal kinetics.

The ideal kinetics¹⁹ are enormously simplified by certain assumptions. Chief among these are the following:

1. The velocity coefficients are independent of the radical size.
2. A stationary state is established for all radical intermediates.
3. The mean kinetic chain length is large.

The system obeys ideal kinetics²⁰ if the exponent values of the initiator and monomer concentrations are 0.5 and 1.0, respectively, so that $R_p/[I]^{0.5}[M]^{1.0}$ (where [M] is the monomer concentration and [I] is the initiator concentration) is a constant at a particular temperature for a particular monomer. Nonideality in vinyl polymerization is shown by exponent values of the initiator and monomer concentrations

other than 0.5 and 1.0. The nonideal case is particularly useful for analyzing the primary radical termination and degradative chain transfer.²⁰ It is also useful in kinetically treating chain-transfer processes. Therefore, the exponent values ([*p*-ABTAY] = 0.83, [4-VP] = 0.33, [MA] = 0.40) obtained in the copolymerization of 4-VP with MA showed that the system obeyed nonideal kinetics.

Effect of temperature

The activation energy was determined by the performance of the polymerization reactions at three more temperatures (50, 70, and 80°C) while the *p*-ABTAY, MA, and 4-VP concentrations were kept constant at 28.500 × 10⁻⁶, 1.372, and 1.159 mol/L, respectively. The overall activation energy, calculated with the help of an Arrhenius plot of log R_p versus 1/*T* (where *T* is the temperature), was 23.21 kJ/mol/L.

Spectral analysis

FTIR spectroscopy of the copolymer

The FTIR spectrum of (Fig. 2) of the copolymer (Table I, run 5) shows a band at 1736 cm⁻¹ due to an ester group of MA. A band at 1594 cm⁻¹ due to C=C stretching and a band at 1260 cm⁻¹ due to the C—N vibration of 4-VP are present.

TABLE III
Effect of the MA Concentration on the Rate of Copolymerization of 4-VP with MA Initiated by *p*-ABTAY and the η Values of the Copolymer

Run	[MA] (mol/L)	Volume contraction (cm)	Conversion (%)	$R_p \times 10^6$ (mol L ⁻¹ s ⁻¹)	η (dL/g)
11	0.6861	2.54	6.10	19.83	0.015
12	1.372	2.82	6.78	21.49	0.025
13	2.058	2.91	7.00	24.46	0.080
14	2.744	3.12	7.50	28.65	0.090
15	3.400	3.43	8.25	35.04	0.110

[*p*-ABTAY] = 28.500 × 10⁻⁶ mol/L; [4-VP] = 1.159 mol/L; copolymerization temperature = 60 ± 0.1°C; copolymerization time = 90 min.

TABLE IV
Composition of the Copolymer of 4-VP with MA

Run	Molar ratio in the monomer feed ([MA]/[4-VP])	Molar fraction of 4-VP in the copolymer	Molar fraction of MA in the copolymer
5	1.18	0.51	0.49
7	2.36	0.37	0.63
10	0.59	0.55	0.45
12	2.93	0.35	0.65

NMR spectroscopy of the copolymer

The $^1\text{H-NMR}$ spectra of the copolymers (Tables I–III, runs 5, 7, 10, and 12) are shown in Figures 3–6. The protons of 4-VP in the copolymer appear at δ values of 8.78–8.53, 7.37, 7.09, and 6.29 ppm, and the methoxy protons of MA appear at δ values of 3.59, 2.89–2.50, and 1.90 ppm.

DSC of the copolymer

The glass-transition temperature (T_g) value of the copolymer (Table I, run 5), determined by DSC, was 156.60°C (Fig. 8). According to the literature, the T_g value of poly(4-vinyl pyridine) is 142°C,²¹ and the T_g value of poly(methyl acrylate) is 10°C.²²

The composition of the copolymer (run 5) that had a T_g value of 156.6°C was as follows:

- p -ABTAY concentration: 71.400×10^{-6} mol/L.
- 4-VP concentration: 1.159 mol/L.
- MA concentration: 1.372 mol/L.
- Copolymerization temperature: $60 \pm 1^\circ\text{C}$.
- Copolymerization time: 90 min.

The aforementioned value of T_g is not the same because T_g changes with the tacticity,²³ molecular weight,²⁴ and polarity of the main chain.²⁵

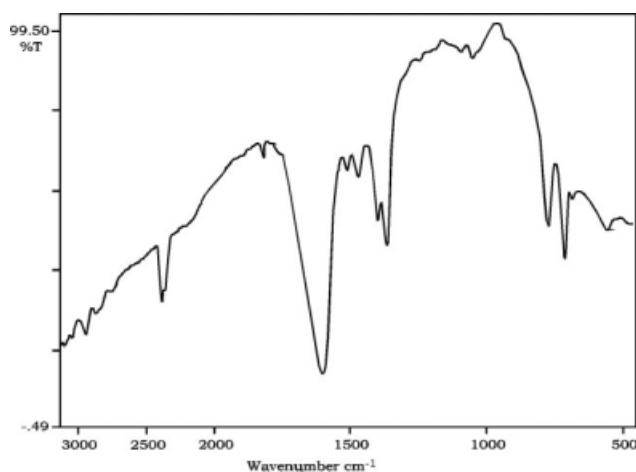


Figure 2 FTIR spectrum of the copolymer of 4-VP with MA (run 5).

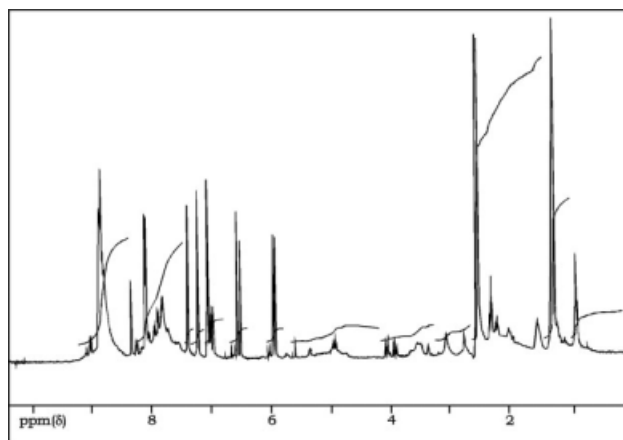


Figure 3 $^1\text{H-NMR}$ spectrum of the copolymer of 4-VP with MA (run 5).

Copolymer composition and values of the reactivity ratios

The composition of the copolymers (Table IV) was evaluated on the basis of high-resolution $^1\text{H-NMR}$ spectra. The peaks at 7.37 and 3.47 due to 4-VP and MA, respectively, were used to calculate the molar fractions of 4-VP and MA in the copolymer. The copolymer compositions were used to calculate the reactivity ratios by the Kelen–Tüdös method.¹⁸ The reactivity ratios were 0.14 ± 0.0075 for 4-VP and 0.56 ± 0.0078 for MA (Table IV and Fig. 7) in this system. The corresponding standard deviation and relative standard deviation (%) of the reactivity ratios of 4-VP and MA were calculated with error analysis.²⁶

The Kelen–Tüdös approach¹⁸ was used for the evaluation of the reactivity ratios (r_1 for 4-VP and r_2 for MA) as follows:

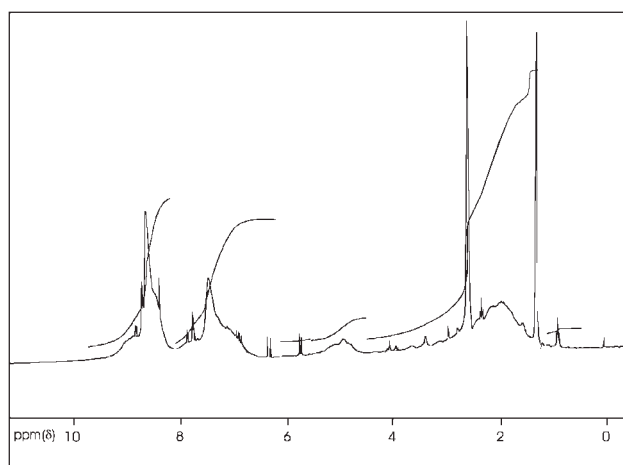


Figure 4 $^1\text{H-NMR}$ spectrum of the copolymer of 4-VP with MA (run 7).

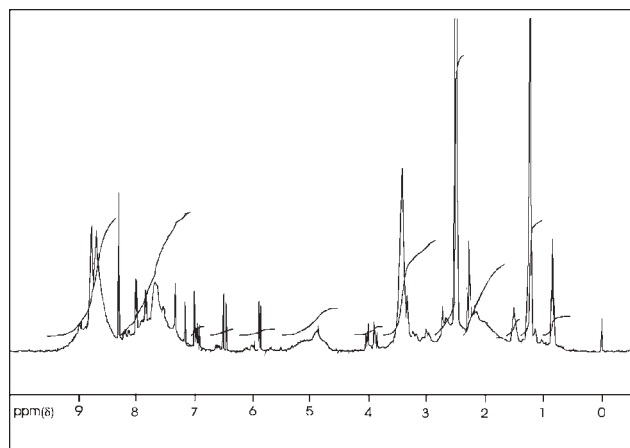


Figure 5 $^1\text{H-NMR}$ spectrum of the copolymer of 4-VP with MA (run 10).

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

where ξ is the ratio of H with $\alpha + H$, H is the relationship between F^2 and f , $\alpha + H$ is the sum of the ratio of F^2 with f , to square root of the product of lowest and highest value of H for copolymerization series

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

where G ($G + F/f(f - 1)$) is the relationship between mole ratio of monomer feed (F) and ration mole fraction (f) of first and second monomer. The transformed variables G and H are given by

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

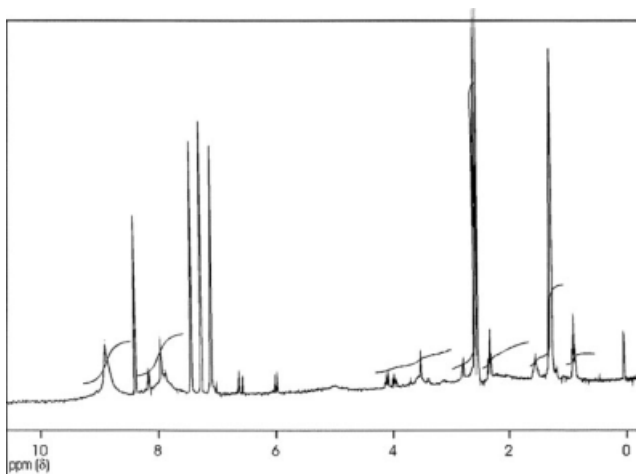


Figure 6 $^1\text{H-NMR}$ spectrum of the copolymer of 4-VP with MA (run 12).

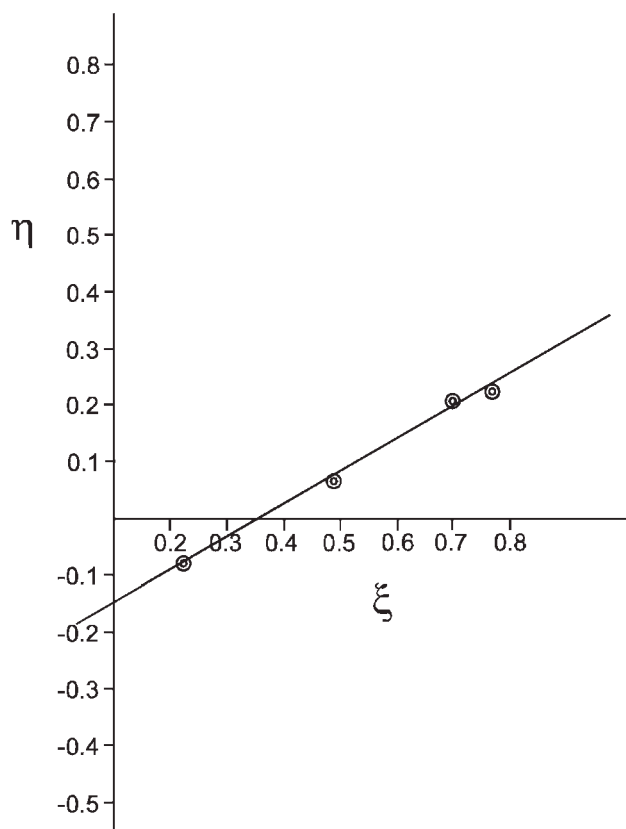


Figure 7 Kelen-Tüdös plot used for the determination of the reactivity ratios.

$$H = \frac{[M_1]/[M_2]}{d[M_1]/d[M_2]}$$

where $[M_1]$ is the concentration of the first monomer and $[M_2]$ is the concentration of the second monomer. The parameter α was calculated as the square root of the product of the lowest and highest values of H for the copolymerization series. A graphical evaluation of 4-VP and MA yielded reactivity ratios

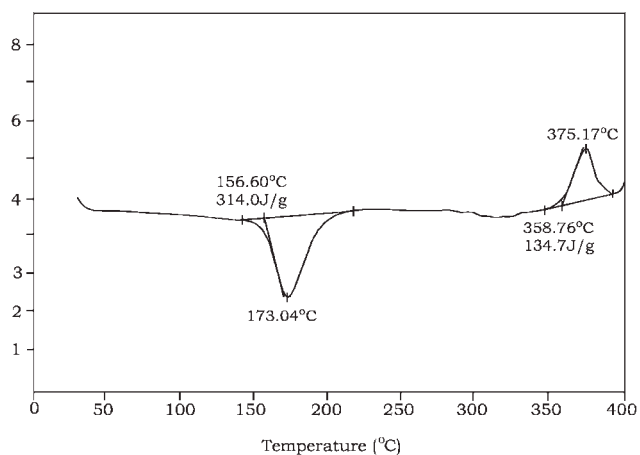


Figure 8 DSC curve for the copolymer of 4-VP with MA.

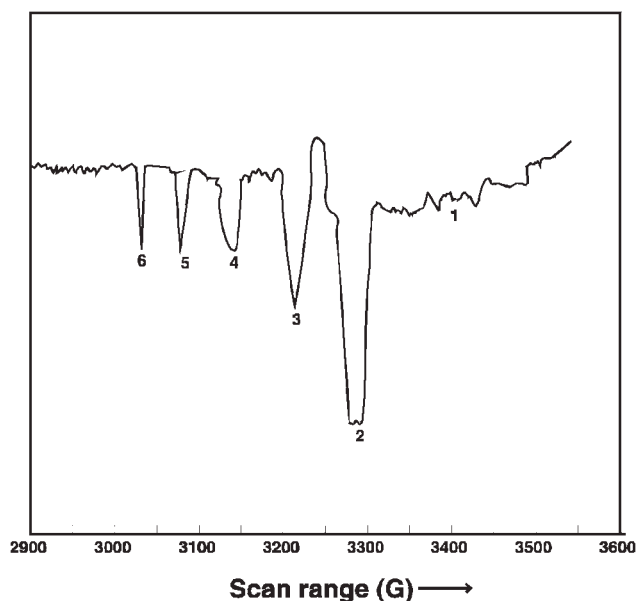


Figure 9 ESR spectrum for the copolymer of 4-VP with MA.

of 0.14 ± 0.0075 for 4-VP and 0.56 ± 0.0078 for MA (Fig. 7) for this random copolymer.

Mechanism

As reported in the literature,²⁷ the ylide dissociates to yield a phenyl free radical, which is responsible for the initiation of the polymerization reaction. The copolymerization was confirmed with the ESR spectrum²⁸ (Fig. 9, run 5), which showed six hyperfine lines due to phenyl radicals.

CONCLUSIONS

The copolymerization of 4-VP with MA, initiated by *p*-ABTAY in 1,4-dioxane, followed nonideal kinetics. The ESR spectrum, which showed six hyperfine lines, confirmed that the copolymer was random in nature. The T_g value and the conversion per-

centage of the copolymer were 156.6°C and 8.50, respectively.

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