in domains smaller than the wavelength of visible light.

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**Registry No.** (NB)(S) (graft copolymer), 108771-86-4; $WCl_6$, 13283-01-7; $SnMe_4$, 594-27-4; 1-octene, 111-66-0.

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# Ylide-Initiated Polymerization of 4-Vinylpyridine

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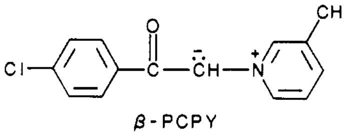
ABSTRACT: Ylide-initiated radical polymerization of 4-vinylpyridine using $CCl_4$ as diluent has been carried out at 60 °C. The system follows ideal kinetics at low [initiator]; however, it follows nonideal kinetics at high [initiator] which is attributed to active-center deactivation by chain transfer to solvent.

## Introduction

In recent years, there has occurred a wide spread upsurge of interest in the application of ylides in polymer chemistry. This activity has undoubtedly stimulated interest in the use of nitrogen ylides partially due to inherent difficulties in synthesis and characterization. A number of papers using ylide as an initiator/accelerator/retarder for the polymerization of methyl methacrylate,[1,2] methyl acrylate,[3] styrene[4], and vinyl acetate[5] have been published by us. Moreover, the effect of ylides on copolymerization systems has also been investigated from this laboratory.[6,7] In this continuation, we report in this paper the first example of a nitrogen ylide (β-picolinium *p*-chlorophenacylide) to be used as an initiator for the polymerization of 4-vinylpyridine (4-VP).



β-PCPY

## Experimental Section

Purified reagent grade 4-vinylpyridine (Fluka) and solvents were used. β-Picolinium *p*-chlorophenacylide (β-PCPY) was prepared by the method of Krohnke[8,9] and Lumb.[10]

The solution polymerizations of 4-VP using carbon tetrachloride as diluent were carried out in a borosilicate glass tube under nitrogen atmosphere. The polymer, precipitated with deionized water, was dried to a constant weight. The latter was used to calculate the conversion (%). Average rates of polymerization ($R_p$) for a series of initiator and monomer concentration are then calculated from the slope of linear conversion–time plot (Figure 1). All $R_p$'s were measured at low conversions (<10%).

The intrinsic viscosity [η] of the polymer(s), determined in ethanol at 25 °C by using an Ubbelohde viscometer, was used to calculate the average molecular weight ($\bar{M}_v$) with the help of following equation:[11]

$$[\eta] = 2.5 \times 10^{-4} M^{0.68}$$

## Results and Discussion

The results of the kinetic investigations of the solution polymerization of 4-VP initiated by β-PCPY at 60 °C for 120 min have been presented in Figures 1–5.

The dependence of $R_p$ of 4-VP in $CCl_4$ as a function of initiator concentration is investigated by varying [β-PCPY] from $2.04 \times 10^{-3}$ to $12.22 \times 10^{-3}$ mol $L^{-1}$ at constant [4-VP] (2.34 mol $L^{-1}$). The polymerizations were associated with short induction periods (<15 min), depending on [β-PCPY] (Figure 1). The $R_p$ gradually increases with increasing [β-PCPY] and the initiator exponent, calculated from the slope of the log $R_p$ versus log [β-PCPY], is 0.5 at low [initiator], i.e., upto $6.11 \times 10^{-3}$ mol $L^{-1}$, above which it is effectively 1.20 order (Figure 2), indicating that some additional termination occurs along with the usual bimolecular termination. The $\bar{M}_v$ decreases with increasing [β-PCPY] as expected for radical polymerization. A plot of $1/\bar{M}_v$ versus $R_p$ shows a straight line passing through origin

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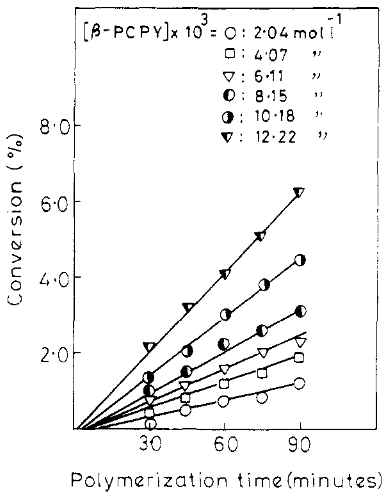

**Figure 1.** Time–conversion plot for the polymerization of 4-VP initiated by β-PCPY: [4-VP] = 2.34 mol $L^{-1}$; polymerization temperature = 60 °C; polymerization time = 90 min.

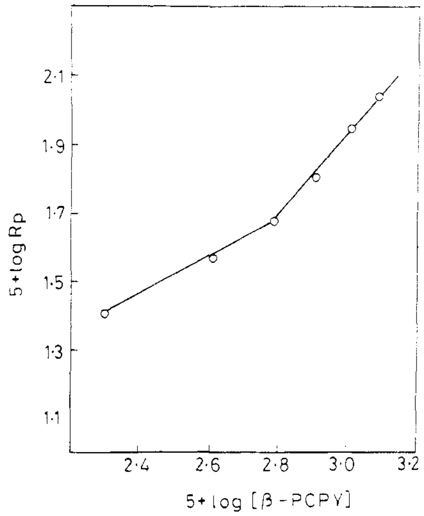

**Figure 2.** Plot between log $R_p$ and log [β-PCPY] for the polymerization of 4-VP initiated by β-PCPY: [4-VP] = 2.34 mol $L^{-1}$; *polymerization temperature = 60 °C; polymerization time* = 90 min.

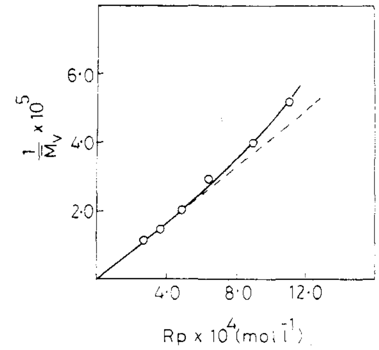

**Figure 3.** Plot between $1/\bar{M}_v$ and $R_p$ for the polymerization of 4-VP initiated by β-PCPY: [4-VP] = 2.34 mol $L^{-1}$; polymerization temperature = 60 °C; polymerization time = 90 min.

up to 6.11 × $10^{-3}$ mol $L^{-1}$, above which it becomes curved (Figure 3).

Since the curve in Figure 2 consists of two well-defined portions, we have studied the dependence of $R_p$ on [4-VP] at values of [β-PCPY] corresponding to these two regions. The system behaves ideally, i.e., first-order reaction, in both the regions (Figure 4).

The polymerizations were also carried out at 55 and 65 °C. The experimental data were used to calculate the energy of activation ($\Delta E$) with the help of an Arrhenius plot (Figure 5), and the value of $\Delta E$ is found as 58.0 kJ $mol^{-1}$.

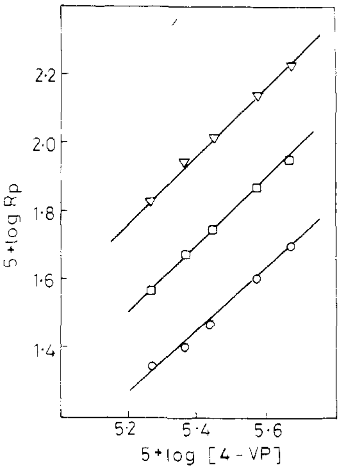

**Figure 4.** Plot between log $R_p$ and log [4-VP] for the polymerization of 4-VP initiated by β-PCPY: [β-PCPY] = (○) 2.04 × $10^{-3}$, (□) *6.11* × $10^{-3}$, (▽) *12.22* × $10^{-3}$ mol $L^{-1}$; *polymerization* temperature = 60 °C; polymerization time = 90 min.

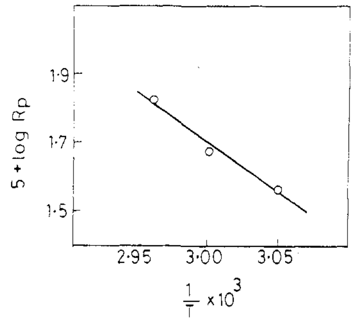

**Figure 5.** Arrhenius plot for the polymerization of 4-VP initiated by β-PCPY: [4-VP] = 2.34 mol $L^{-1}$; [β-PCPY] = 6.11 × $10^{-3}$ mol $L^{-1}$; polymerization time = 90 min.

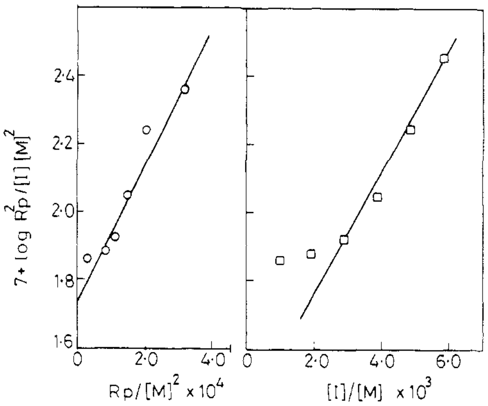

**Figure 6.** Plots of (○) log $R_p^2/[I][M]^2$ versus $R_p/[M]^2$ and (□) log $R_p^2/[I][M]$ versus [I]/[M] for the polymerization of 4-VP initiated by β-PCPY: [4-VP] = 2.34 mol $L^{-1}$, polymerization temperature = 60 °C; polymerization time = 90 min.

The rather high initiator exponent indicates some sort of nonideality such as (i) primary radical termination, (ii) degradative chain transfer to initiator, (iii) degradative additions, and (iv) chain transfer to solvent in the system.

To analyse primary radical termination, the following equation developed by Deb and Meyerhoff[12] is used:

$$\log \frac{R_p^2}{[I][M]^2} = \log \frac{2f_k k_d R_p^2}{k_t} - 0.8684 \frac{k_{prt}}{k_i k_p} \frac{R_p}{[M]^2}$$

Here I and M represents initiator and monomer respectively. The plot of the left-hand side of the above equation against $R_p/[M]^2$ (Figure 6) gave a positive slope, indicating the absence of a primary radical termination effect.

Deb[13] deduced a suitable expression which was further simplified by Ghosh and Mitra[14] to analyze the degradative chain transfer to initiator:

$$\ln \frac{R_p^{\,2}}{[I][M]^2} = \ln \frac{2f_k k_d k_p^{\,2}}{k_t} - \frac{k_p^{\,2}}{k_t}\,\frac{k_{rtI}}{k_{iI}k_p} C_I \frac{[I]}{[M]}$$

$$\log \frac{R_p^{\,2}}{[I][M]^2} = \log \frac{2f_k k_d k_p^{\,2}}{k_t} - 0.434 \frac{k_p^{\,2}}{k_t}\,\frac{k_{rtI}}{k_{iI}k_p} C_I \frac{[I]}{[M]}$$

Here $C_I$ is the initiator transfer constant. It is noticed that the experimental points fall on a straight line with a positive slope on the plot of left-hand side of above equation against [I]/[M] indicating the absence of degradative chain (initiator) transfer (Figure 6).

The system does not follow retardation at high [initiator]; hence the possibility of degradative addition is also ruled out.

Therefore the high initiator exponent at high [β-PCPY] is attributed to active-center deactivation by chain transfer to solvent ($CCl_4$) as confirmed by molecular weight data above $6.11 \times 10^{-3}$ mol $L^{-1}$ of [β-PCPY].

The mechanism[3] of dissociation of β-PCPY into radicals via triplet carbene formation has already been established. In conclusion, the experimental data on the polymerization of 4-VP in $CCl_4$ are all consistent with chain transfer to solvent.

**Acknowledgment.** We thank Prof. A. K. Vasishtha, Director, and Prof. R. S. Tewari, Head of the Chemistry Department, H.B.T.I., Kanpur, for providing necessary facilities. S.S. acknowledges financial support from the CSIR, New Delhi.

**Registry No.** β-PCPY, 92592-50-2; 4-VP, 100-43-6; 4-VP (homopolymer), 25232-41-1.

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# Thallium in the Synthesis of Phosphazene Derivatives: Donor-Substituted Polyphosphazenes

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ABSTRACT: Organothallium salts have been used to prepare a series of phenoxy-substituted cyclotriphosphazenes $[-N{=}P(OC_6H_4\text{-}4\text{-}R)_2-]_3$ and polyphosphazenes $[-N{=}P(OC_6H_4\text{-}4\text{-}R)_2-]_x$, with R = Et, ${}^tBu$, OMe, SMe, and $NMe_2$. Two new donor-substituted polyphosphazenes (R = SMe and R = $NMe_2$) undergo iodine doping, and the latter polymer is the most highly conducting polyphosphazene yet to be reported ($10^{-4}$ S/cm).

The high level of interest in polyphosphazene chemistry[1] may be attributed, mainly to two factors. First, a wide variety of different phosphazene macromolecules can be prepared by substitution reactions on the parent system, poly(dichlorophosphazene), $[NPCl_2]_x$, according to the Allock procedure[2-5] or by a condensation polymerization.[6] Second, the resultant polyphosphazene derivatives are generally tractable materials with excellent mechanical and chemical stability properties.[2-7]

The nature of the substituents which can be attached to the polyphosphazene backbone via direct substitution reactions is ultimately limited by the properties of the reactive intermediates which are required to effect the appropriate transformation. The largest class of polyphosphazenes is comprised of the aryloxy and alkoxy derivatives and some of these polymers are finding commerical application.[1-5,7] These compounds are usually prepared by the substitution reaction of the sodium salt of the appropriate aryloxide or alkoxide on polydichlorophosphazene.[2,4,5] The sodium salts are prepared as solutions or slurries in an ether solvent by a heterogeneous reaction of the alcohol or phenol with sodium metal or sodium hydride.

In the present work we report investigations into the utility of thallium alkoxides and aryloxides as reactive intermediates for the synthesis of substituted cyclo- and polyphosphazenes. The study is motivated by the work of Taylor, McKillop, and co-workers, who have pioneered the use of thallium in organic synthesis.[8] In particular, they showed that thallium(I) salts of phenols could be alkylated, acylated, aroylated, or tosylated under mild conditions in quantitative yield by treatment with the appropriate halide precursor. In addition the following was found:[9] "thallium(I) salts of phenols are readily prepared in quantitative yield by the addition of thallium(I) ethoxide to a solution of the phenol in a solvent such as benzene or ethanol. They are crystalline, sharp melting, stable solids which may be conveniently recrystallized from water or aqueous ethanol." On this basis we decided to test the thallium salts as nucleophiles for reaction with

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