

# BULK ANIONIC RADICAL POLYMERIZATION OF 4-VINYLCYCLOHEXENE-- 1 INITIATED BY p-NITRO BENZYL TRIPHENYL PHOSPHONIUM YLIDE

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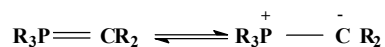
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## ABSTRACT

The present work details the bulk anionic radical polymerization of 4-vinyl cyclohexene-1 (VCH) initiated by p-nitrobenzyl triphenyl phosphonium ylide (p-NBTPY) at 5+0.1°C in ultra cryostat under nitrogen blanket for 144 hours. The  $R_p$  has been calculated from the slope of percent conversion vs. time plots. The various kinetic parameters have been evaluated and a suitable mechanism has been proposed.

## 1. INTRODUCTION

The interest in chemistry of phosphorus ylides is due to the great theoretical and practical importance of these reactive compounds in organic chemistry because these have been widely used in Wittig synthesis of olefins, synthesis of strained cycloalkanes, macrocyclic compounds, cyclic dienes and heavy metal complexes (Wittig, 1974; Becker, 1980; Bestmann, 1977; Schmidbauer, 1975; Boyd, 1971). Structurally phosphorus ylides are carbanion stabilized by the neighboring phosphonium group



The stability and reactivity of phosphorous ylide depends to a large extent on the substituents 'R' at the carbocationic centre. By varying these substituents, it is possible to obtain all possible types of C-substituted phosphorus ylides with exceptionally varied properties. However, the substituents R at the phosphonium centre also exert a significant influence on the properties of phosphorus ylides.

Although much information is available (Kondo, 1983; Daniel, 2002; Srivastava, 2004; Prajapati, 2006; Vasishtha, 1991) on radical as well

as ionic (both cationic and anionic) polymerization of different vinyl monomer such as styrene, methyl methacrylate, methyl acrylate, vinyl acetate, etc. yet it is difficult to search papers reporting polymerization of 4-vinyl cyclohexene-1.

## 2. EXPERIMENTAL PROCEDURE

VCH (Fluka) was used as such without further purification. p-NBTPY was prepared according to the method given in the literature (Mc Donald, 1959). The sample of VCH and p-NBTPY contained in a glass ampoule (6 ml) made of borosilicate glass was flushed with nitrogen for 3 minutes. The filled glass ampoule was then placed in a ultra cryostat at 5°C. The experiment was terminated after 144 hours. The polymerization tube was opened in a large amount of water to precipitate the polymer. The resulting polymer was dried in a vacuum oven.

## 3. RESULTS AND DISCUSSION

No polymer was obtained when VCH alone was put in ultra cryostat nor when VCH and p-NBTPY were kept at room temperature. Further investigations were carried out to study polymerization of this monomer using different initiator, such as AIBN, benzoyl peroxide and p-NBTPY in DMSO at different temperatures (30°C to 80°C), but in no case polymer was obtained.

Although by analogy to styrene the monomer was expected to undergo radical polymerization. However when p-NBTPY was added to the

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monomer (2.5 mole litre<sup>-1</sup>) and the content was kept at 5°C for 144 hours the polymer was obtained in low yield. The effect of further addition of monomer after certain interval of time effected the  $R_p$  and hydroquinone did not completely inhibit the polymerization reaction. These results prompted us to investigate kinetics and mechanism of bulk polymerization of VCH using p-NBTPY as anionic radical initiator. The results are mentioned in Table 1 and illustrated in fig.1.

### Effect of (p-NBTPY)

The polymerization runs were carried out by varying (p-NBTPY) from  $0.75 \times 10^{-3}$  to  $4.50 \times 10^{-3}$  mole litre<sup>-1</sup> as a result the  $R_p$  increased from  $5.8 \times 10^{-8}$  to  $12.4 \times 10^{-8}$  mole litre<sup>-1</sup> second<sup>-1</sup>. A study of Fig. 1 shows that practically the polymerization runs were associated with large induction period of about 1 to 15 hours. The order of reaction was determined by using least square method as 0.12, which excludes possibility of this ylide as radical initiator (Vasishtha, 1990). A study of Table 2 further shows that variation of intrinsic viscosity of polymer as a function of concentration of initiator does not have a regular trend and it varies from 0.12 to 0.08.

### Effect of temperature

Fig. 2 shows effect of temperature on polymerization of VCH. In contrast to radical polymerization the  $R_p$  decreases as polymerization increases (Vasishtha, 1990). The overall energy of activation has been calculated from Arrhenius plot (Fig. 2) as 2.5 kJ mole<sup>-1</sup> is quite low, but it matches well with those reported in literature (Vasishtha, 1997).

### Effect of hydroquinone

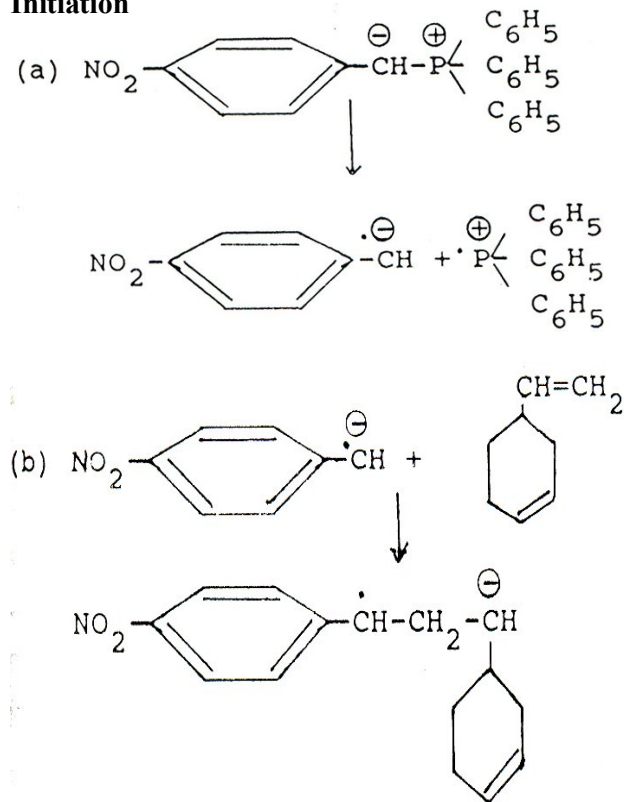
The effect of hydroquinone has been studied by varying its concentration from  $2.27 \times 10^{-3}$  to  $4.54 \times 10^{-3}$  mole litre<sup>-1</sup> at constant [p-NBTPY] ( $4.50 \times 10^{-3}$  mole litre<sup>-1</sup>). The  $R_p$  values were  $10.7 \times 10^{-8}$  and  $8.9 \times 10^{-8}$  mole litre<sup>-1</sup> second<sup>-1</sup>, respectively. Thus, hydroquinone could not act as a radical scavenger in this system which further excludes possibilities of radical polymerization.

### Mechanism

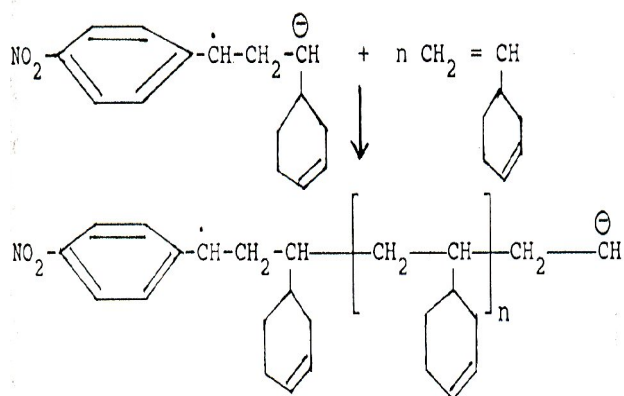
The initiator exponent value, occurrence of polymerization at low temperature, inverse effect of

polymerization temperature on rate of polymerization, low energy of activation, and variation of intrinsic viscosity of polymers as a function of concentration of ylide shows that the ylide acts as an anionic radical initiator and the following mechanism may be proposed for the present system.

#### Initiation



#### Propagation



#### (v) Conclusion:

It may, therefore, be concluded, that p-NBTPY acts as an anionic radical initiator for the polymerization of 4-vinyl cyclohexene-1.

Table-1 Effect of (p-NBTPY) on percent conversion, rate of polymerization and intrinsic viscosity for the polymerization\* of 4-vinyl cyclohexene-1.

Run. No.	(P-NBTPY) X103 mol. lit.-1	TIME (HOURS)						RPx108 mol. lit.-l sec.-1
		24	48	72	96	120	144	
		Percent conversion of VCH to polymer						
1.	0.75	0.05	0.15	0.25	0.39	0.52	0.65	5.80
2.	1.50	0.07	0.25	0.45	0.55	0.75	1.01	6.02
3.	2.25	0.20	0.51	0.75	0.85	1.11	1.32	7.20
4.	3.00	0.25	0.55	0.81	1.11	1.41	1.72	8.30
5.	3.75	0.32	0.67	1.01	1.42	1.74	2.05	11.60
6.	4.50	0.42	0.85	1.25	1.65	2.01	2.51	12.40

**\* Polymerisation conditions:**

VCH=2.50 moles, Temperature=  $5 \pm 0.1$  °C, Time=144 hours

Table -2 Effect of (p-NBTPY) on the intrinsic viscosity for the polymerisation\* of 4-vinyl cyclohexene-1.

Run. No.	(P-NBTPY) X103 mol. lit.-1	( $\eta$ )
1.	0.75	0.12
2.	1.50	0.11
3.	2.25	0.11
4.	3.00	0.10
5.	3.75	0.08
6.	4.50	0.08

**\* Polymerisation conditions:**

VCH=2.50 moles, Temperature=  $5 \pm 0.1$  °C, Time=144 hours

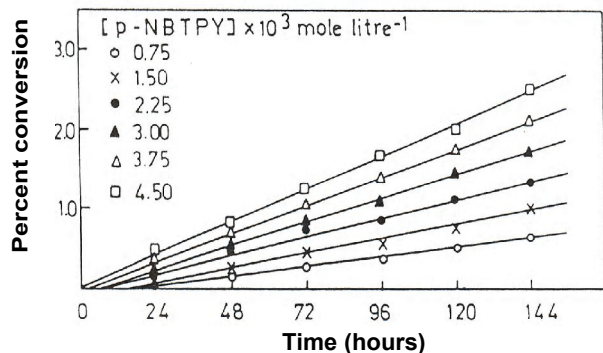


Fig.1. Percent conversion vs time plots, during the polymerisation of 4-vinyl cyclohexene-1 at 5°C, in presence of varying concentration of p-NBTPY, using 2.50 moles of [4-VCH].

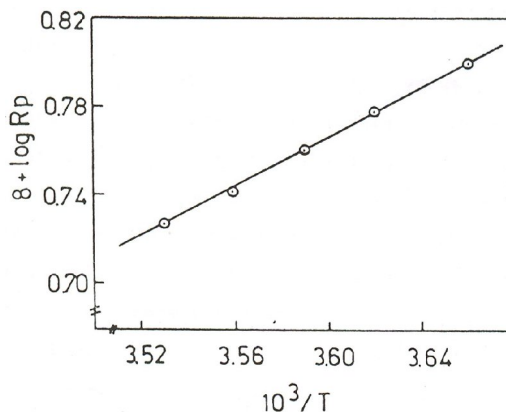


Fig. 2. Arrhenius plots, during the polymerization of 4-Vinyl cyclohexene-1, using 2.5 moles of (4-VCH) and  $0.75 \times 10^{-3}$  mole litre<sup>-1</sup> of (p-NBTPY)

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