

KINETICS AND MECHANISM OF HETERO-PHASE SOLUTION POLYMERIZATION OF *N*-VINYLCARBAZOLE ON VANADIUM PENTOXIDE CATALYST

by MRINAL M. MAITI*, N. D. GANGULY** and MUKUL BISWAS, *Department of Chemistry, Indian Institute of Technology, Kharagpur, West Bengal*

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N-Vinylcarbazole undergoes hetero-phase solution polymerization on vanadium pentoxide catalyst. Polymerization is cationic in nature, being inhibited by electron donors like alcohols and amines, and has a very low energy of activation, 1.77 k. cal. The reaction follows Hinshelwood-Langmuir mechanism with single-point adsorption of monomer molecule. Termination by solvent molecule is believed to be operative during polymerization. A generalised rate expression,

$$R_p = \frac{\alpha_1 [M]^2}{[M]^2 + \beta_1 [M] + \gamma}, \quad \bar{D}_p = \frac{[M]}{\alpha_2 [M] + \beta_2}$$

based on the steady-state concept of each individual reactive intermediate and taking into account all the possible termination steps, reproduces the rate-data satisfactorily. This polymerization activity of vanadium pentoxide establishes the presence of inherent active acid-sites on the surface of the catalyst.

INTRODUCTION

So far as the heterogeneous catalytic polymerization over solid surface is concerned, hardly any serious attempt has been made to study the kinetics of such reaction. A very limited information is available, excepting a few with Ziegler catalyst system (Solomon *et al.* 1961), on the elucidation of the mechanism of polymerization in relation to the physicochemical properties of the solid like the atomic or ionic arrangements, the surface and bulk acid-base characteristics, the electronic structure of individual ionic species in the solid, the nature and the extent of the induced or intrinsic semiconductivity exhibited by it and the nature of physico-chemical changes involved during the pretreatment of the same. In this respect, little is known about the so-called oxide catalysts like MoO₃, CrO₃, V₂O₅, CaO etc., although their activities have been critically studied and successfully utilised, even on the industrial level, in other types of reactions.

An understanding of the mechanism of the hetero-phase catalytic polymerization as well as the role of solid catalysts in relation to their physico-chemical properties can be achieved from the study of the polymerization characteristics

*To whom all correspondence should be addressed.

Present Address: Department of Chemistry, Indian Institute of Technology, Kharagpur-721302.

***Present Address:* Production Manager, Synthchem Ltd., 33A, Laxmibai Nagar Industrial Estate, Indore-452002.

of a vinylic monomer on a certain oxide catalyst. *N*-vinylcarbazole can be selected as the monomer due to its unique, yet controversial, polymerization characteristics (Biswas & Ghosal 1966; Ellinger 1964; Scott *et al.* 1963; 1964; and Heller *et al.* 1963). The choice of vanadium pentoxide as the catalyst has been guided largely by the dearth of information regarding the mechanism of hetero-catalytic polymerization particularly over metal oxides having inherent π -acidity and also by the fact that a more detailed and consistent information on the physico-chemical properties are available with this oxide. On the other hand, the general inferences, which can be drawn about its role in bringing about the polymerization of *N*-vinylcarbazole (NVC), may be extended to other types of reactions. In this communication is reported a kinetic study of the polymerization of *N*-vinylcarbazole catalysed by vanadium pentoxide and the general conclusions drawn therefrom have been discussed in the light of the theories of heterogeneous catalysis.

EXPERIMENTAL

Materials : Preparation of V_2O_5 catalyst (Bhattacharyya *et al.* 1967) and purification of NVC (Biswas *et al.* 1969) (gift from BASF, Germany) have been detailed elsewhere.

Benzene, toluene, and methanol (AnalaR, B. D. H.), acetic acid and formic acid (pro Analyti, E. M.), acetaldehyde, aniline and dimethylphthalate (Redeal de Haen), and ethanol were purified and dried prior to use following standard procedures (Vogel 1962).

Polymerization Procedure : Polymerizations were carried out in a ground-glass stoppered pyrex Erlenmeyer flask in which required amounts of catalyst, monomer and solvent were introduced under an atmosphere of oxygen-free nitrogen. The inside mass was kept well-stirred with the help of a magnetic stirrer. Desired temperature of reaction was maintained by immersing the flask in a constant temperature water-bath. Recovery and purification of the product polymer were made as per procedure detailed by Ellinger (1964).

The number average molecular weight of the resulting polymer, being very low, was determined by cryoscopic method, using benzene as solvent.

RESULT AND DISCUSSION

Preliminary Investigations : It was found that in solution, V_2O_5 catalysed NVC polymerization only to a low value of conversion and degree of polymerization. However, the reproducibility of the reaction was quite excellent. Also the contribution of thermal polymerization was insignificant, being only about 0.04 per cent of that of the catalyzed one. Thus no correction was introduced for thermal polymerization.

Diffusional resistance to polymerization was found to be negligible with catalyst particle-size ranging between $-150 + 240$ B. S. S. (0.1040 to 0.3430 mm.). Accordingly all the experiments were carried out using catalyst of particle-size $-200 + 240$ B. S. S.

Activation energy of polymerization was found to be 1.77 kcal/mole. This appreciably low value clearly points out the ionic nature of the propagating species. This fact was further corroborated by the observation that the rate and the degree of polymerization increased in a medium of higher dielectric constant.

The effect of several additives on the rate and degree of polymerization was studied to ascertain the nature of the ionic propagating species. The additives include water, ethanol, acetaldehyde, aniline, triethylamine, formic acid and acetic acid. Ethanol and acetaldehyde had a retarding effect on both the rate and the degree of polymerization. Aniline and triethylamine showed an acute inhibitory action. In fact, triethylamine in concentration as low as $10^{-4} M$, completely quenched the polymerization. Acetic acid and formic acid accelerated the rate of polymerization. Water showed no co-catalytic activity but retarded the rate of polymerization only after a concentration of $2 \times 10^{-2} M$. These facts clearly establish the cationic nature of the propagating species.

Effect of Monomer Concentration : Effect of monomer concentration on the rate and the degree of polymerization was studied at $35^{\circ}C$ in two solvents, benzene and toluene. Concentration was varied from 0.02072 to 0.24860 M . Fig. 1 (a) and (b) illustrate the variation of conversion to polymer as a function of time at different monomer concentrations in benzene and in toluene respectively. The corresponding variations of the average degree of polymerization (\bar{D}_p) have been represented in Fig. 2 (a) and (b). From Figs. 1 and 2 the initial rate of polymerization (R_p) and the instantaneous average degree of polymerization (\bar{D}_p) have been calculated graphically. The values are listed in Table I. It is evident from the data in Table I, that the rate is of the order of more than unity with respect to monomer at low values of monomer concentration, first order in the later stage and finally of zero order at still higher concentration of monomer.

TABLE I
Rate and degree of polymerization as functions of initial monomer concentration
(Temperature— $35^{\circ}C$)

Monomer concentration	Benzene Medium		Toluene Medium	
	$R_p \times 10^5$	\bar{D}_p	$R_p \times 10^5$	\bar{D}_p
0.02072	3.87	4.19	2.80	2.96
0.04144	10.86	5.70	9.16	5.57
0.06216	18.70	8.12	16.95	6.06
0.08288	25.40	9.83	23.77	9.12
0.1036	40.20	11.24	30.85	10.64
0.1244	42.21		36.00	
0.1451	44.13		38.98	
0.1658	51.39		41.40	
0.1866	54.52		42.60	
0.2073	71.78		45.95	
0.2280	61.77			
0.2488	65.85			

Analysis of Kinetic Data : These unique features of polymerization were critically examined in the light of different plausible mechanisms. After preliminary screening,

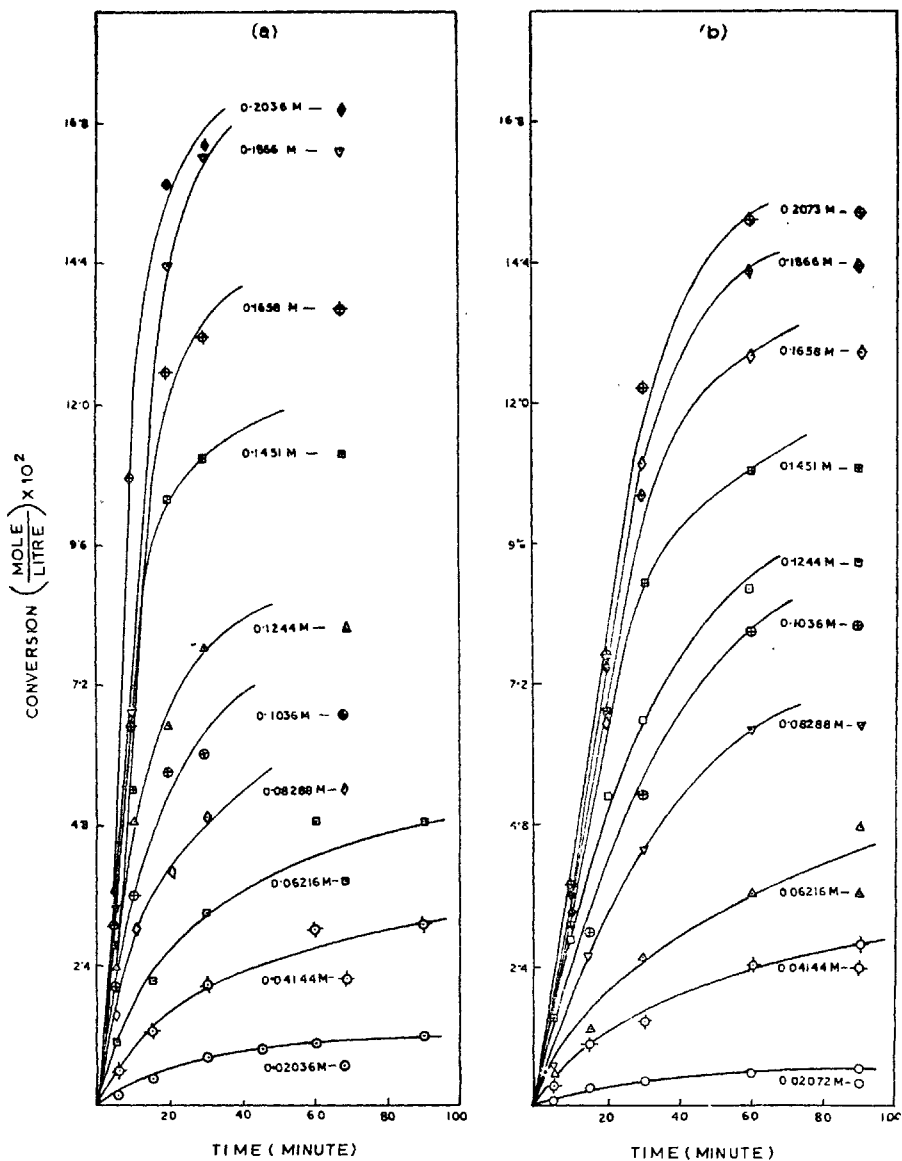


FIG. 1. Conversion to polymer as a function of time. Catalyst—12 g./l., temperature—35°C; (a) benzene medium, (b) toluene medium.

only two mechanisms were selected to verify their general validity in reproducing the rate data. These are (i) Rideal-Walker mechanism and (ii) Hinshelwood-Langmuir mechanism with single-point adsorption of monomer.

For Rideal-Walker mechanism, the rate expression is

$$R_p = k_p \frac{K_M [M]^2}{1 + K_S [S] + K_M [M]} \quad \text{or} \quad \frac{[M]^2}{R_p} = A + B[M]$$

where $A = (1 + K_S [S])/k_p K_M$ and $B = 1/k_p$; i.e., plot of $[M]^2/R_p$ against $[M]$ should produce a straight-line.

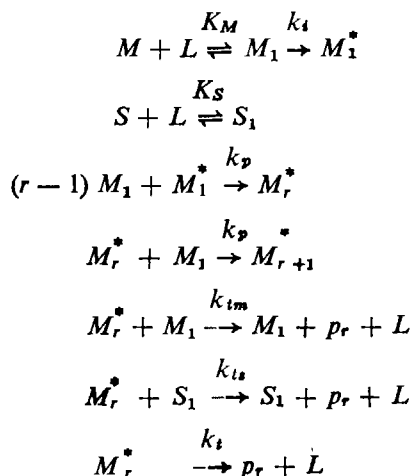
For Hinshelwood-Langmuir mechanism, the rate expression is

$$R_p = k_p \frac{K_M^2 [M]^2}{(1 + K_S [S] + K_M [M])^2} \text{ or } \frac{1}{R_p^{1/2}} = A^1 + B^1 \frac{1}{[M]}$$

where $A^1 = 1/k_p^{1/2}$ and $B^1 = (1 + K_S [S])/k_p^{1/2} \cdot K_M$ i.e., the plot of $1/R_p^{1/2}$ against $1/[M]$ should produce a straight-line. The validity of these two mechanisms is tested graphically in Figs 3 and 4. An excellent straight line relationship between $1/R_p^{1/2}$ and $1/[M]$ as is evident from Figs. 3 and 4, clearly points out the preference of the Hinshelwood-Langmuir mechanism over the Rideal-Walker mechanism in describing the course of the polymerization of NVC over V_2O_5 .

However, a point of difference should be noted between the rate data obtained in benzene and in toluene medium. While the data obtained in benzene are in excellent agreement with the simple Hinshelwood-Langmuir mechanism upto a monomer concentration of 0.25 *M*, deviation of the experimental rates from the theoretical ones is observed in toluene medium after a monomer concentration of 0.10 *M*. The discrepancy could be accounted for as being due to the role of adsorbed toluene molecule, which have the same dielectric constant but bigger size and higher donor property arising out of a hyperconjugative structure, in terminating the chain propagation and thereby decreasing the overall rate of polymerization.

A generalized rate expression, based on the Hinshelwood-Langmuir mechanism and taking into consideration all the steps involved during polymerization and their contributions in determining the ultimate concentration distribution of surface species at the steady state, as derived below, is expected to reproduce the rate data of polymerization in benzene and particularly in toluene. The course of polymerization may be represented as :



Proceeding in the same way as Clark and Bailey (1963) and assuming steady state condition of all the reactive intermediates during polymerization we have

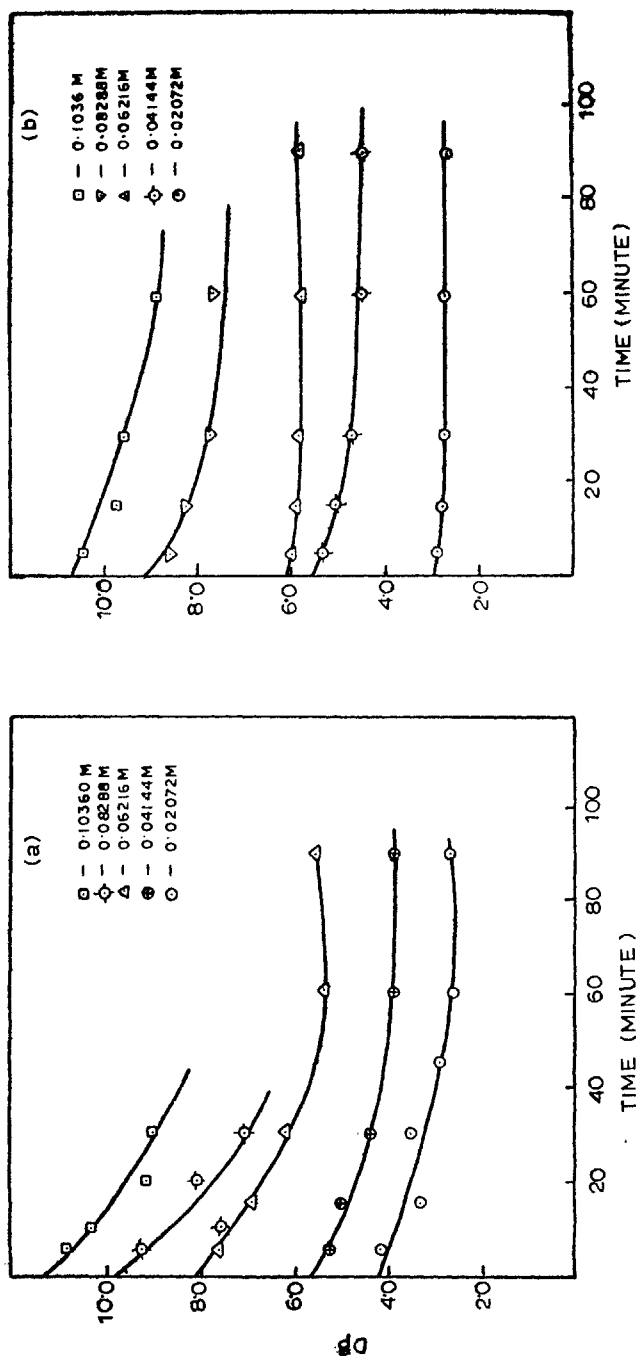


Fig. 2. Variation of \bar{D}_p with time. Catalyst—12 g./l., temperature—35°C; (a) benzene medium, (b) toluene medium.

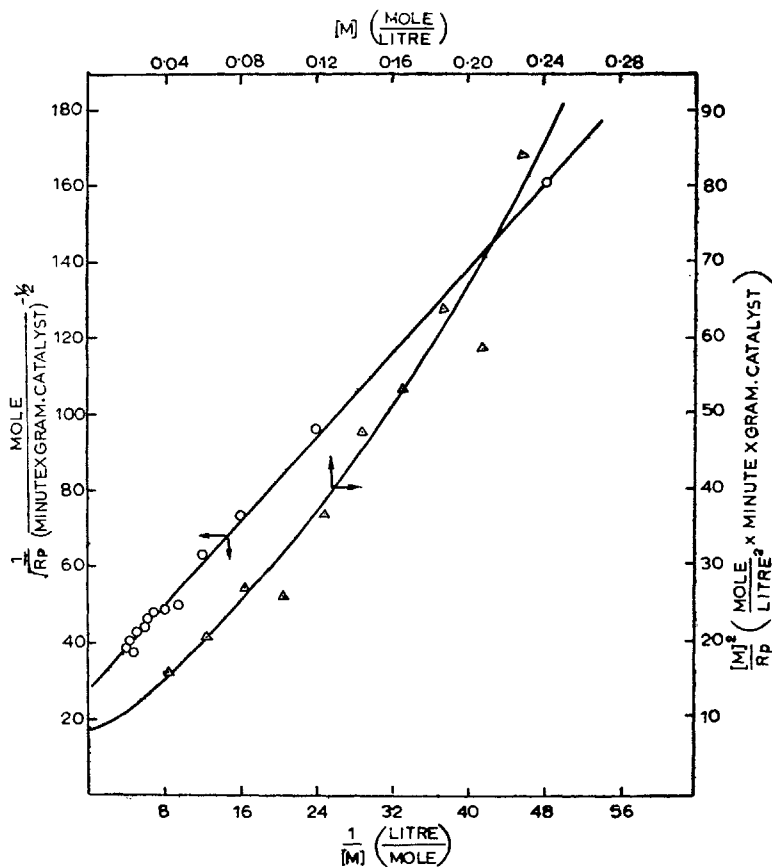


FIG. 3. Plot of $[M]^2/R_p$ vs. $[M]$ and 1 vs. $\sqrt{R_p} 1/[M]$. Temperature— 35°C , Medium—benzene.

$$[M^* T_R] = \frac{k_i [M_1]}{(k_p + k_{tm}) [M_1] + k_{ts} [S_1] + k_t} \quad \dots (1)$$

$$\text{and } \sum_{r=1} [M_r^*] = \frac{k_i [M_1]}{k_{tm} [M_1] + k_{ts} [S_1] + k_t} \quad \dots (2)$$

To evaluate $[M_1]$ and $[S_1]$ in terms of $[M]$, which is a known quantity, it is necessary to assume that the total concentration of propagating species $\sum_{r=1} [M_r^*]$ may be

neglected compared to $[M_1]$ and $[S_1]$. The assumption is justified since, in a sequence of steps going through active centres as intermediates, the concentrations of active intermediates are very small compared to those of the stable species and the steady state concentration of them could be maintained throughout the course of reaction.

$$\text{Therefore, } [M_1] = \frac{L_o \cdot K_M [M]}{1 + K_S [S] + K_M [M]} = \frac{L_o [M]}{R + [M]}$$

$$\text{and } [S_1] = \frac{L_o \cdot K_S [S]}{1 + K_S [S] + K_M [M]} = \frac{T}{R + [M]}$$

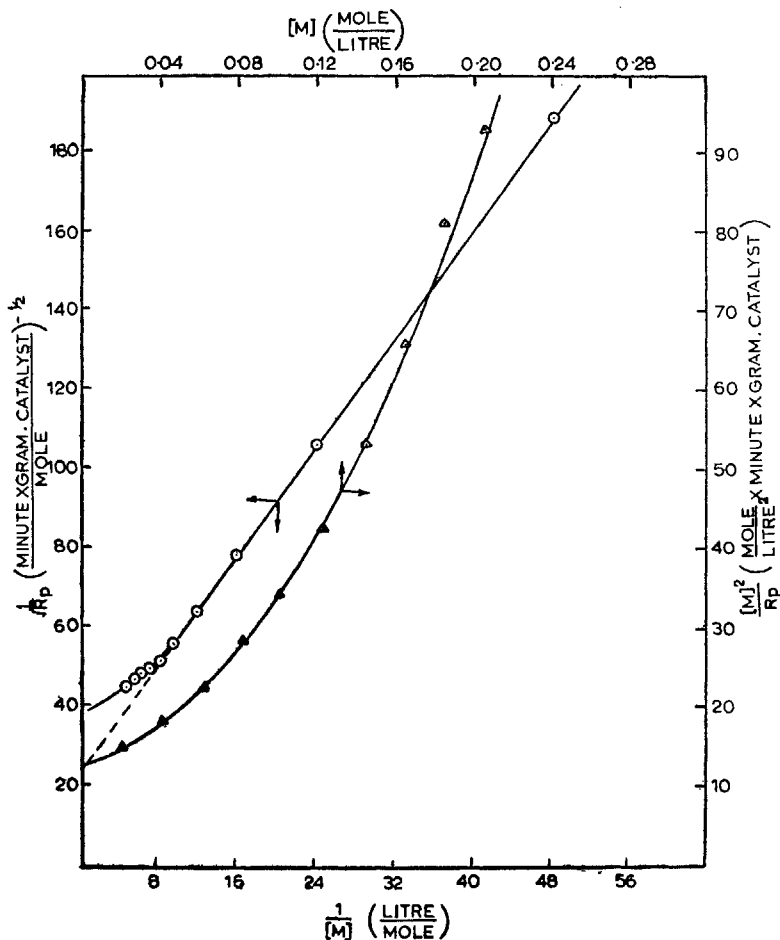


FIG. 4. Plot of $[M]^2/R_p$ vs. $[M]$ and $1/\sqrt{R_p}$ versus $1/[M]$. Temperature— 35°C , Medium—toluene.

where
$$R = \frac{1 + K_S [S]}{K_M} \quad \text{and} \quad T = \frac{L_0 \cdot K_S [S]}{K_M}$$

So
$$\sum_{r=1} [M_r^*] = \frac{k_1 \cdot K_M \cdot T \cdot [M]}{(k_{tm} \cdot K_M \cdot T + k_t \cdot K_S [S]) [M] + k_t \cdot K_S [S] + T \cdot k_{ts} \cdot K_S [S]}$$

$$= \frac{P [M]}{Q + [M]} \quad \dots (3)$$

and
$$R_p = \frac{k_p \cdot P \cdot L_0 \cdot [M]^2}{(R + [M]) (Q + [M])} = \frac{\alpha_1 [M]^2}{[M]^2 + \beta_1 [M] + \gamma} \quad \dots (4)$$

where
$$P = \frac{k_1 \cdot K_M \cdot T}{K_{tm} \cdot K_M \cdot T + k_t \cdot K_S [S]}$$

$$Q = \frac{k_t \cdot K_S \cdot R \cdot [S] + k_{ts} \cdot K_S \cdot T \cdot [S]}{k_{sm} \cdot K_M \cdot T + k_t \cdot K_S [S]}$$

$$\alpha_1 = k_p \cdot P \cdot L_0, \beta_1 = (R + Q) \text{ and } \gamma = RQ$$

$$\text{Also } R_T = R_i + R_{ts} + R_{tm}$$

$$= \frac{P[M] [(k_t + k_{tm}L_0) [M] + (Rk_t + Tk_{ts})]}{(R + [M]) (Q + [M])} \quad \dots (5)$$

$$\text{and } \bar{D}_p = \frac{R_p}{R_T} = \frac{k_p P L_0 [M]^2}{P [M] [(k_t + k_{tm}L_0) [M] + (Rk_t + Tk_{ts})]}$$

$$= \frac{[M]}{\alpha_2 [M] + \beta_2} \quad \dots (6)$$

$$\text{where } \alpha_2 = \frac{k_k + k_{tm}L_0}{k_p L_0} \text{ and } \beta_2 = \frac{Rk_t + T.k_{ts}}{k_p L_0}$$

The values of the constants involved in the expressions (4) and (6) have been calculated by Least Squares method and are tabulated in Table II. The experimental and calculated values of the rate and degree of polymerization have been compared in Table III. The agreement between the calculated and the experimental values is

TABLE II
Values of constants involved in the kinetic expressions (4) and (6)
(Temperature—35°C)

Constants	α_1	β_1	γ	α_2	β_2
Benzene Medium	1.322×10^{-3}	1.98×10^{-1}	9.9×10^{-3}	2.66×10^{-2}	6.182×10^{-3}
Toluene Medium	5.821×10^{-4}	2.45×10^{-2}	7.96×10^{-3}	3.24×10^{-2}	6.346×10^{-3}

TABLE III
Comparison of the theoretical and observed rate and degree of polymerization
(Temperature—35°C)

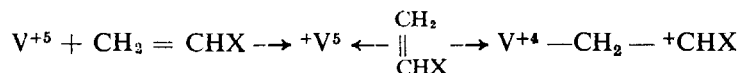
Monomer Concentration (Moles/Litre)	Benzene Medium				Toluene Medium			
	$R_p \times 10^5$		\bar{D}_p		$R_p \times 10^5$		\bar{D}_p	
	Observed	Calculated	Observed	Calculated	Observed	Calculated	Observed	Calculated
0.02072	3.87	3.92	4.19	3.08	2.80	2.80	2.96	2.95
0.04144	10.86	11.45	5.70	5.69	9.16	9.35	5.57	5.39
0.06216	18.70	19.64	8.12	7.93	16.95	16.85	6.06	7.44
0.08288	25.40	27.51	9.83	9.88	23.77	23.67	9.12	9.16
0.1036	40.20	34.74	11.24	11.59	30.85	29.44	10.64	10.66
0.1244	42.21	41.26			36.00	34.00		
0.1451	44.13	47.12			38.98	37.62		
0.1658	1.39	52.41			41.40	40.50		
0.1866	54.52	57.10			42.60	42.86		
0.2073	71.68	61.35			45.95	44.86		
0.2280	61.77	65.19						
0.2488	65.85	68.68						

quite satisfactory. This establishes the validity of the generalized Hinshelwood-Langmuir mechanism in explaining the course of polymerization.

CONCLUSION

Considering its activity in polymerizing NVC and the kinetics followed over its surface, several conclusions may be drawn about the surface property of V_2O_5 .

Polymerization on V_2O_5 is effected mainly by two properties. Firstly, the n -type conductivity of V_2O_5 , arising out of anion deficiency, favours a large cumulative adsorption of NVC to take place on the surface. This is necessarily a prelude to the formation of a propagating surface species. Adsorption occurs through partial charge-transfer from the vinylic double bond to the catalyst, which involves only one adsorption site. Secondly, the conversion of the adsorbed charge-transfer complex to an active propagating species is aided by the strong π -acidity of V^{+5} ion. Not all the surface vanadium ions have got the same acid strength. Only those having acid-strength much above the average, would accept electron pairs from the vinylic double bond and accommodate in the vacant d -orbitals, with the ultimate formation of NVC cations.



Propagation of this NVC cation may then proceed on the surface. The structural orientation of the substituents on the vinylic carbon atom is, however, solely dependent on the stereo-chemical environment of V^{+5} ion on the surface. Considering a highly distorted octahedral arrangement of oxide ions around vanadium ion and the presence of bulky carbazole group, it is quite unlikely that a high molecular weight and stereo-specific polymer will be obtained in this system. Low molecular weight poly-NVC and its very low degree of crystallinity, as observed in the present system of study, are in agreement with the above contentions.

Amines exhibit acute inhibitory effect on the polymerization through strong preferential adsorption on these active centres on V_2O_5 surface. The apparent increase in the rate of polymerization observed in the presence of carboxylic acids is caused by two simultaneous effects. Adsorption of acid produces surface carboxylate radical and hydroxyl group (Clark *et al.* 1964; Peri 1964), the latter furnishing proton for initiating polymerization. At the same time, the proton initiated polymerization of NVC in the homogeneous phase also takes place. The cumulative effect of these two phenomena is an ultimate increase in the rate of polymerization. Action of water on the polymerization is well understood in the light of the fact that its limited solubility in benzene or in toluene permits a very low degree of adsorption on V_2O_5 surface. Also, this extremely thin adsorption of water occurs only on the most active centres. As a result, a very shallow retarding influence is observed in the case of water. The surface proton which may originate as the ultimate species of water adsorption has much less activity and cannot augment the overall rate. On the other hand, an active participation of the adsorbed water molecule in the chain termination contributes considerably in lowering the rate of polymerization.

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NOMENCLATURE

- M = Monomer
 S = Solvent
 X = Carbazole group
 L = Adsorption site
 L_0 = Total concentration of adsorption sites
 M_1 = Unimolecularly adsorbed M
 S_1 = Unimolecularly adsorbed S
 M_r = Active propagating chain of length 'r'
 P_r = Polymer of chain length 'r'
 R_p = Rate of propagation
 Moles of monomer polymerized/litre
 Time of reaction in minute \times g. catalyst/litre
 Moles of monomer polymerized
 Minute \times g. catalyst
 D_p = Instantaneous average degree of polymerization at a certain initial monomer concentration.
 \bar{D}_p = Average degree of polymerization of the product after certain time of reaction.
 R_t = Rate of spontaneous termination
 R_{tm} = Rate of termination by monomer
 R_{ts} = Rate of termination by solvent
 R_T = Total rate of termination
 = $R_t + R_{tm} + R_{ts}$
 K_i = Adsorption equilibrium constant of the species 'i'
 k_i = Rate constant for initiation
 k_p = Rate constant for propagation
 k_t = Rate constant for spontaneous termination
 k_{ti} = Rate constant for termination by species 'i'.

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