

This article was downloaded by:

On: 24 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

Polymerization of N-Vinylcarbazole by SK-500 Molecular Sieve

Mukul Biswas^a; Narayan C. Maity^a

^a Department of Chemistry, Indian Institute of Technology, Kharagpur, Kharagpur, India

To cite this Article Biswas, Mukul and Maity, Narayan C.(1982) 'Polymerization of N-Vinylcarbazole by SK-500 Molecular Sieve', *Journal of Macromolecular Science, Part A*, 18: 3, 477 – 492

To link to this Article: DOI: 10.1080/00222338208056516

URL: <http://dx.doi.org/10.1080/00222338208056516>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Polymerization of N-Vinylcarbazole by SK-500 Molecular Sieve

MUKUL BISWAS and NARAYAN C. MAITY

Department of Chemistry
Indian Institute of Technology, Kharagpur
Kharagpur 721302, India

ABSTRACT

The polymerization of N-vinylcarbazole (NVC) by SK-500 molecular sieve obeys the relation, rate of polymerization (R_p) = $[NVC]^{1.0}$ (weight of SK-500) $^{0.70}$ at 30°C. Stirring increases the rate but the reaction order does not change. The highest catalytic activity, observed at 500°C precalcination temperature, does not correspond to the highest solid acidity of the sieve, realized at 200°C precalcination temperature. Pyridine and n-butylamine ($\approx 10^{-3}$ M) inhibit and hydrogen chloride ($\approx 10^{-3}$ M) and phosphoryl chloride ($\approx 10^{-4}$ M) cocatalyze the polymerization. Both R_p and the degree of polymerization (\bar{P}_n) increase up to a maximum at ~ 9 -10% uptake of water (g/g of dry zeolite) and thereafter fall. Alumina and silica increase R_p . \bar{P}_n decreases with an increasing alumina content and rises initially at low silica content, falling at a high concentration of the latter. Nitrobenzene retards the polymerization. \bar{P}_n is independent of $[NVC]$, percentage conversion, and weight of SK-500. It appears that the polymerization is initiated through Brönsted acid sites as well as through direct interaction of RE^{3+} centers with a vinyl double bond of the monomer by a conventional cationic mechanism.

INTRODUCTION

In earlier publications we have reviewed [1] the present status of vinyl polymerization by molecular sieves and reported [2] the polymerization behavior of isobutyl vinyl ether (IBVE) in the presence of Linde SK-500 (rare earth exchanged Y-type) molecular sieve and the effect of metal ion loading on the activity of 13X sieves [3]. In order to determine the monomer selectivity of SK-500 and endorse the cationic mechanism and other kinetic conclusions of the IBVE-SK-500 system, the work has now been extended to study the polymerization of N-vinylcarbazole (NVC) by SK-500. This paper discusses the salient kinetic and mechanistic aspects, and highlights certain unique features of the NVC-SK-500 polymerization system.

EXPERIMENTAL

Materials

NVC (BASF, West Germany) was recrystallized three times from hot n-hexane and dried in vacuo at 30°C for 2 d (mp 65.6°C). Solvents such as benzene and other chemicals used were all analytical grade materials. They were dried and fractionally distilled by recommended procedures. SK-500 molecular sieve (Union Carbide), supplied as a white, crystalline pellet containing no clay binder, was pulverized into powder (100 mesh). Directly before the experiment the catalyst was activated [4] at desired temperatures.

Polymerization

Polymerizations were conducted under nitrogen atmosphere with constant/intermittent stirring and followed gravimetrically. The general procedures followed for pretreatment of the reaction vessels, preparation of monomer solution in the dry glove-box, and charging of the reaction vessels with monomer solution in dry condition were essentially similar to those adopted earlier [2, 4-6]. Total volume of the reaction mixture was 25 mL unless stated otherwise.

Molecular weights were determined cryoscopically in benzene using a standard Beckman freezing point apparatus, with a thermometer precision of 0.001°C. In most determinations, concentration of the polymer solutions in benzene was kept below 5% to avoid nonideality complications, the depressions being in the 0.03 to 0.05°C range. Reproducibility from run to run was about 1%.

The solid surface acidity was measured by following the procedure of Johnson [2, 7].

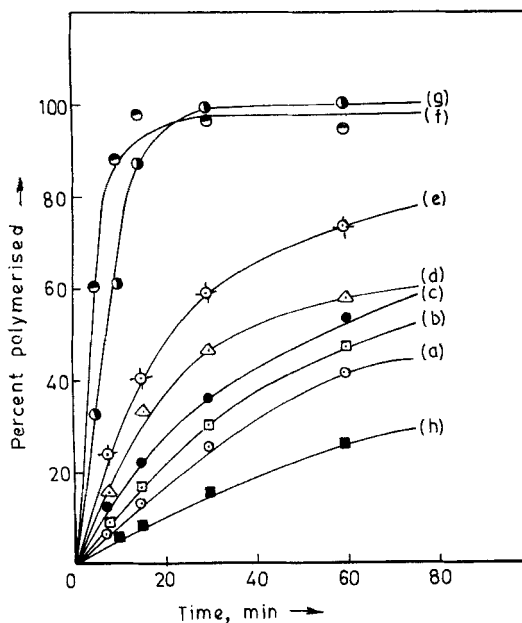


FIG. 1. Time-conversion curves for SK-500 catalyzed polymerization of N-vinylcarbazole in benzene at 30°C. $[NVC] = 0.1$ mol/L, weight of SK-500 = (a) 0.010 g, (b) 0.013 g, (c) 0.019 g, (d) 0.028 g, (e) 0.064 g, (f) 0.028 g in the presence of CO_2 , (g) 0.028 g with constant stirring, and (h) same as in (g) in the presence of n-butylamine.

RESULTS AND DISCUSSION

General Characteristics of the Polymerization

Figure 1 presents some characteristic time-conversion curves for a wide range of conditions. Carbon dioxide increases the rate to an appreciable extent, which can be ascribed to the formation of additional active centers responsible for the initiation reaction whereas n-butylamine acts as a retarder. Activation of the molecular sieve in the presence of carbon dioxide, sulfur dioxide, etc. has also been observed in other instances [8, 9]. The present results are consistent with these observations and particularly with the fact that the enhancement of catalytic activity is realized when carbon dioxide is added to the reaction mixture and not when the sieve is pretreated [9, 10] with carbon dioxide. The polymers obtained are white solids, soluble in most common solvents. The polymerizations are not accompanied by any typical color development, suggesting that the

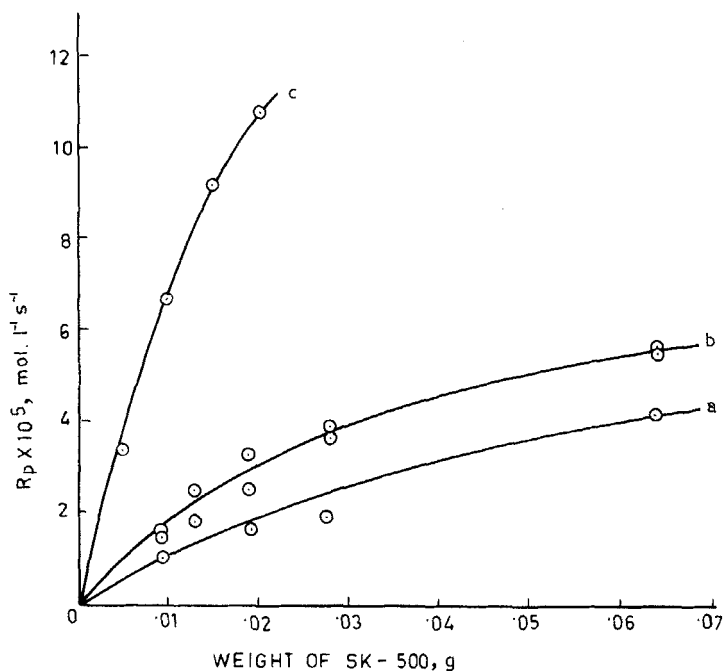


FIG. 2. Dependence of R_p on the weight of SK-500. $[NVC] =$ (a) 0.05 mol/L (intermittent stirring), (b) 0.10 mol/L (intermittent stirring), and (c) 0.05 mol/L (constant stirring). Solvent, benzene; temperature, 30°C.

charge transfer initiation [2, 11] through the interaction of NVC and rare earth centers is not important in the present polymerization. The IR spectrum of the polymer is identical to that of polyNVC obtained by aprotic acid initiation [7, 12].

Rate Dependence on the Weight of SK-500

Figure 2 shows the effect of the weight of SK-500 sieve on the rate, using the sieve precalcinated at 100°C for 2 h. From the results in Fig. 2a, b, and c it can be shown that

$$R_p \propto (\text{weight of SK-500})^{0.70}$$

for polymerizations performed with intermittent stirring and also with constant stirring. Significantly, stirring increases the overall

rates of polymerization but does not change the reaction order. Barson et al. [13] observed that the rate is proportional to the 2/3rd power of the weight of a 13X sieve for the polymerization of styrene in cyclohexane.

The fact that the rate is not directly proportional to the weight of the zeolite used indicates [13] that all the activated sites on the external surface of the sieve and on the internal pores are not equally involved in the polymerization. Presumably, in the present instance the external surface sites appear to participate in the reaction in preference to the internal pore sites. The liquid in contact with the molecular sieve contains a bulky molecule as NVC and this may discourage its diffusion to the interior pore sites, which is perhaps the reason why even with constant stirring the reaction order does not change. The less viscous the liquid, the more the chance of penetration. This should presumably explain the direct dependence of the rate on SK-500 for IBVE [2] polymerization.

Rate Dependence on Monomer Concentration

Figure 3 shows that the rate (intermittent stirring, Fig. 3a and b) increases in a first-order manner up to a certain [NVC] and falls thereafter. With constant stirring (Fig. 3c) these features are retained although the rates are higher. For the IBVE-SK-500 system, Biswas and Maity [2] reported a similar first-order dependence of the rate on [IBVE] but no such maximum.

The occurrence of the maximum in the rate vs [NVC] plot has been previously reported by Biswas et al. in NVC-aprotic acid [7, 12] and NVC-Grignard reagents [14, 15] polymerization systems, the rate being first order in NVC up to a certain threshold concentration. It is possible that at higher concentrations NVC, a tertiary amine, may act as a poison for the active sites on the catalyst surface. Significantly, \bar{P}_n is not affected. The possible implication of this feature is discussed later.

Effect of Preheating Temperature of SK-500

Figure 4 reveals the variation of R_p , \bar{P}_n , and solid acidity which represents the total acidity (Brönsted) of the solid catalyst phase with the preheating temperature of the SK-500 sieve. Initially, as the preheating temperature is increased, the rate also increases, a maximum value of R_p is realized at $\sim 500^\circ\text{C}$ and further preheating causes a fall in the rate. \bar{P}_n also shows an exactly parallel trend whereas solid acidity shows a maximum at 200°C only.

For the IBVE-SK-500 system [2] however, the rate exhibits a maximum at a preheating temperature of 200°C as against 500°C

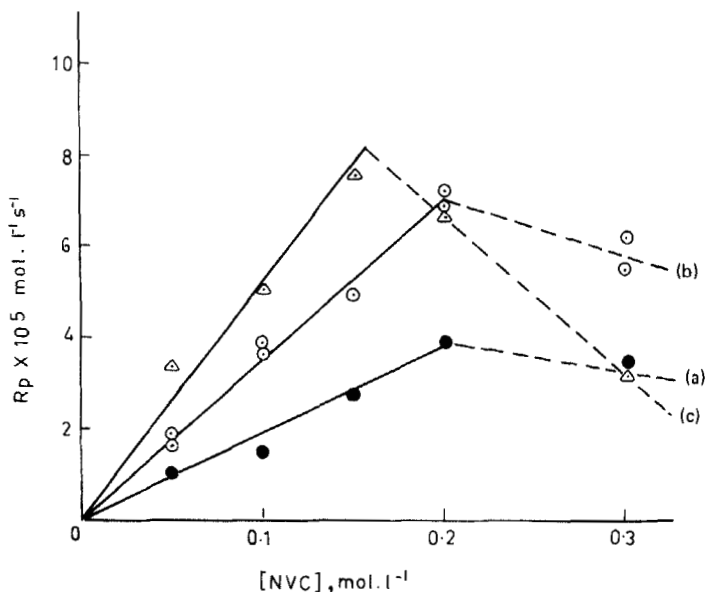
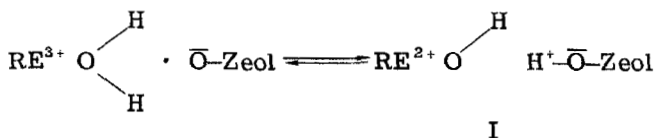


FIG. 3. Dependence of R_p on $[NVC]$. Weight of SK-500 = (a) 0.010 g (intermittent stirring), (b) 0.028 g (intermittent stirring), (c) 0.005 g (constant stirring). Solvent, benzene; temperature, 30°C.

observed in this instance. This difference in the behavior of the two monomers is quite significant and it possibly implies some difference in the nature of the initiating moieties in these two cases. The initiation in the IBVE-SK-500 system is believed to be due mainly to Brönsted acid sites formed by the reaction [16, 17]



which assumes its highest value at 200°C, the maximum point in the solid acidity vs preheating temperature curve [2]. In the present system the maximum occurs at 500°C and consequently it seems that Brönsted sites alone are not fully responsible for the initiation. Lewis acid initiation may also not be significant in the present system since the Lewis acid sites are believed to be formed at temperatures as high as 680°C and above [16, 17]. It appears that the rare earth

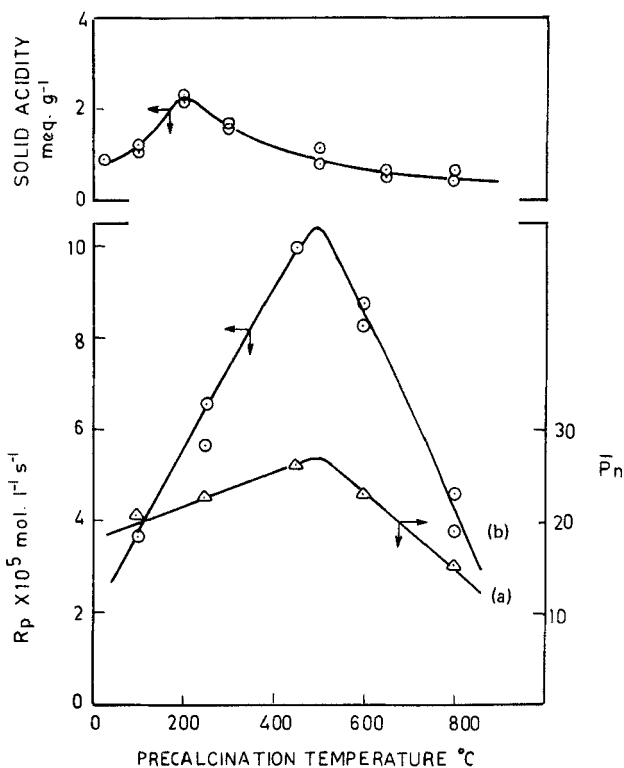


FIG. 4. Effect of preheating temperature on R_p , \bar{P}_n , and solid surface acidity of SK-500. $[NVC] = (a) \text{ and } (b) 0.1 \text{ mol/L}$; weight of SK-500 = (a) and (b) 0.028 g. Solvent, benzene; temperature, 30°C .

metal ion centers probably directly participate in the initiation of NVC polymerization by the SK-500 sieve, particularly at temperatures above 200°C . Further, the screening effect of water molecules [18] surrounding the RE^{3+} ions would be diminished as the precalcination temperature is increased in the range of 100 to 500°C . This also would tend to increase the rate. The situation becomes more complicated above $\sim 500^\circ\text{C}$ when the rate is controlled by desorption of water [18], Lewis acid site formation [16, 17], and a reversible redistribution of cations [19, 20] affecting the cation accessibility of the monomer in the sieve cage.

The increase in the value of \bar{P}_n up to 500°C may be attributed to continuous removal of residual surface [2, 24] or intracrystalline channel water from the sieve. As a consequence, the possibility of

transfer of the growing chains with water would be likely to decrease so that \bar{P}_n should increase. Beyond 500°C the fall in \bar{P}_n possibly results from the pronounced decrease in rate.

Effect of Additives

Basic Additives

Pyridine and n-butylamine totally inhibit the polymerization at 10^{-3} M and give a very low rate and \bar{P}_n at 10^{-4} M. These highly basic additives apparently destroy the growing carbonium ions and also at higher concentrations consume the Brönsted sites on the catalyst surface.

Brönsted and Aprotic Acids

Hydrogen chloride enhances the rate considerably and acts as a cocatalyst (Fig. 5). However, \bar{P}_n is rather slightly affected. Interestingly, phosphorus oxychloride, itself a fairly active initiator for polymerization of vinyl monomers [21, 22], also enhances the rate but decreases \bar{P}_n to a limiting value (Fig. 5). The trend in \bar{P}_n variation in either instance implies the predominance of transfer of growing chains with the acids or with the corresponding anions.

Water

Figure 6 represents the influence of zeolitic water on R_p and \bar{P}_n . Small amounts of water increase both the rate and \bar{P}_n to a maximum (around 9-10% uptake of water), but at still higher concentrations of water both these quantities fall. Addition of small amounts of water can enhance the Brönsted acidity. The initial catalytic effect of water declines above ~9% uptake of water. This behavior indicates that polymerization on the water-free catalyst occurs not only at the polymer-catalyst interface but also at sites within the crystals. As the amount of zeolitic water increases the intracrystalline channels become blocked [2, 23], and hence they become still less accessible to monomer so that the overall rate of polymerization decreases. Figure 6 also shows that at high water concentration polymerization tends to stop, which suggests that preferential adsorption of water may take place at surface sites, blocking access of monomer to the active centers on the surface. Consequently R_p will be seriously impaired. The fall in \bar{P}_n at high water content is conventionally explained in terms of termination as well as transfer of the growing chains by water [2].

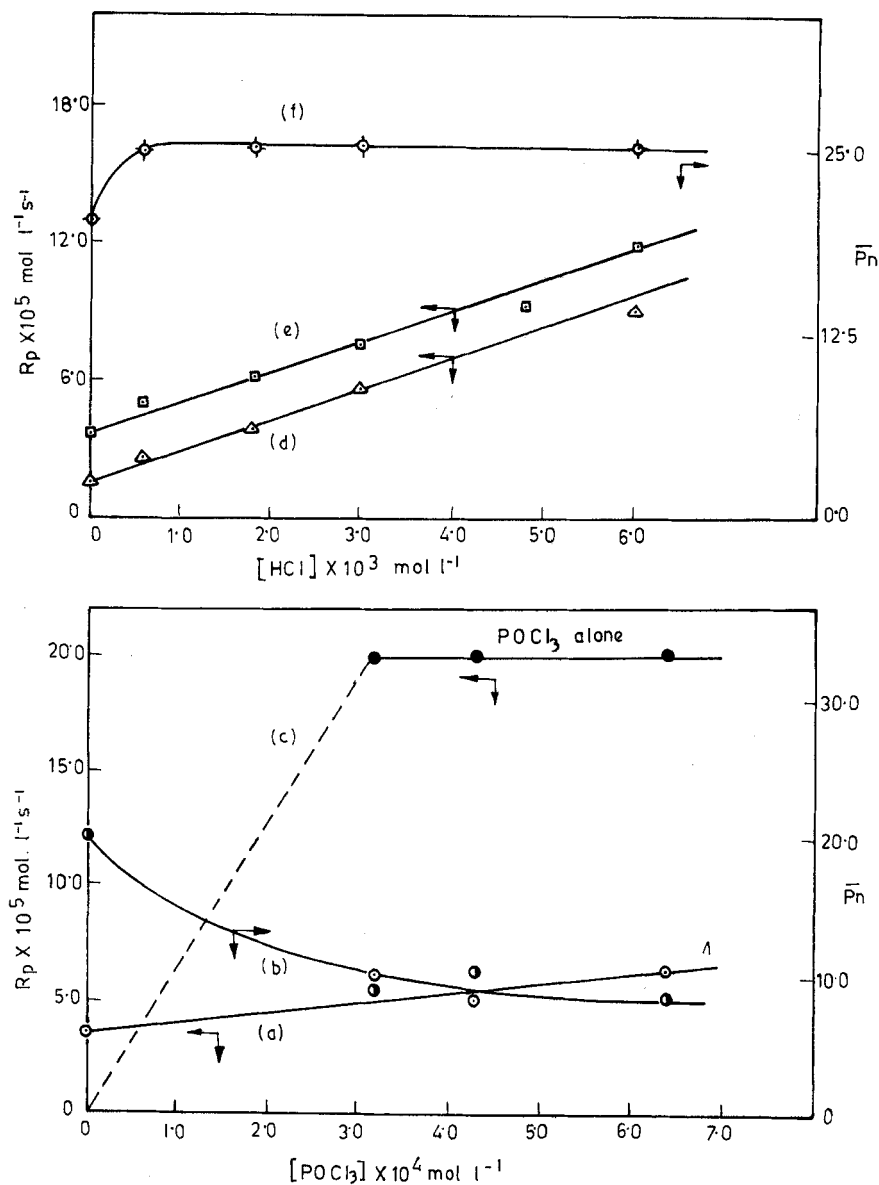


FIG. 5. Effect of hydrogen chloride and phosphorus oxychloride on R_p and P_n . [NVC] = (a), (b), (c), (d), (e), and (f) 0.1 mol/L; weight of SK-500 = (a), (b), (e), and (f) 0.028 g; (c) nil; (d) 0.010 g. Solvent, benzene; temperature, 30°C.

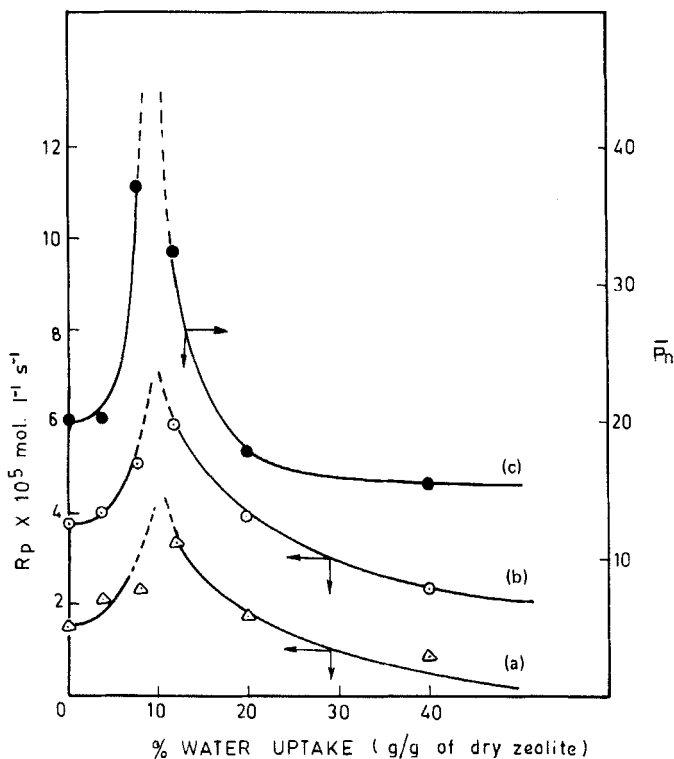


FIG. 6. Effect of sorbed water on R_p and \bar{P}_n . $[NVC] = (a), (b),$ and $(c) 0.1 \text{ mol/L}$; weight of SK-500 = $(a) 0.010 \text{ g}, (b) \text{ and } (c) 0.028 \text{ g}$. Solvent, benzene; temperature, 30°C .

Alumina and Silica

Table 1 summarizes the effect of alumina and silica on SK-500 catalyzed polymerization of NVC. The oxides increase the rate in the order silica > alumina. However, \bar{P}_n decreases consistently with increasing alumina content, and rises initially at low silica content, falling at high concentrations of the latter. The increase in rate in either instance is consistent with the usual action of these oxides as supporters. However, the trend in \bar{P}_n suggests the presence of transfer reaction in these systems involving the growing carbonium ion chains and exchangeable OH^- ions likely to be formed through adventitious hydrolysis of these oxides [24].

TABLE 1. Effect of Alumina and Silica on the SK-500 Catalyzed Polymerization of N-Vinylcarbazole^a

% Alumina ^b	% Silica ^b	$R_p \times 10^5$ (mol/L·s)	\bar{P}_n
-	-	3.70	20.30
5	-	5.00	9.10
15	-	5.00	8.03
50	-	5.00	6.90
-	2.50	5.00	35.80
-	5.00	6.60	32.50
-	15.00	6.10	14.80
-	50.00	6.60	9.00

^aWeight of SK-500 = 0.028 g and [NVC] = 0.1 mol/L in all runs. Solvent, benzene. Temperature, 30°C.

^bSilica and alumina were mixed mechanically with SK-500 activated at 100°C for 2 h and used in the polymerization.

Effect of Polymerization Solvent

The aprotic acid initiated cationic polymerizations of NVC are accelerated when the polymerization solvent is changed from benzene to nitrobenzene [7, 12]. Surprisingly, for the present system both R_p and \bar{P}_n fall sharply up to ~25% nitrobenzene concentration and thereafter remain virtually the same up to 100% nitrobenzene concentration (volume/volume) in a nitrobenzene-benzene solvent mixture (Fig. 7). The solvent dielectric constant progressively increases from benzene (100%) to nitrobenzene (100%).

The trend in the variation of rate and \bar{P}_n with increasing nitrobenzene in the solvent indicates that the initiation process must be seriously impaired. The solvent molecules are adsorbed, along with the monomer molecules, on the catalyst surface. Since nitrobenzene is an acceptor, a charge transfer interaction is likely to occur between NVC and the nitrobenzene, as actually reported by Okamura et al. [25]. However, in the absence of any radiation [25] the interaction will be too weak to initiate any polymerization but probably sufficient to decrease the π -electron density of the vinyl double bond. In consequence, the effective monomer concentration available for reacting with the Brønsted acid sites will be reduced, more so with increasing nitrobenzene in the medium, to a limiting value.

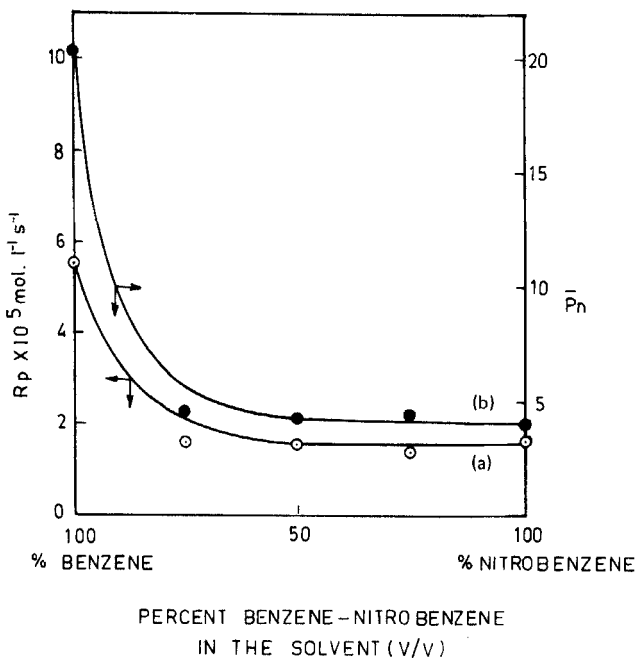


FIG. 7. Effect of nitrobenzene on R_p and \bar{P}_n . $[NVC] = (a), (b)$ 0.1 mol/L; weight of SK-500 = (a) and (b) 0.064 g. Temperature, 30°C .

Trend in \bar{P}_n

The variation of \bar{P}_n has been examined as a function of weight of SK-500, $[NVC]$ and increasing conversion (Fig. 8). \bar{P}_n at limiting conversion is found to be independent of all the three parameters. This feature is consistent with the behavior of this monomer during polymerizations by aprotic acids [7, 12] with the IBVE-SK-500 system [2]. \bar{P}_n is also independent of percent conversion or $[SK-500]$ but increases with $[IBVE]$, attaining a limiting value after a threshold monomer concentration. Since \bar{P}_n is independent of the percentage conversion, termination or transfer reactions are important [13, 25]. The independence of \bar{P}_n on $[SK-500]$ suggests that the catalyst does not participate in the chain-breaking mechanism [26]. Finally, the observation that \bar{P}_n does not depend on $[NVC]$ in the

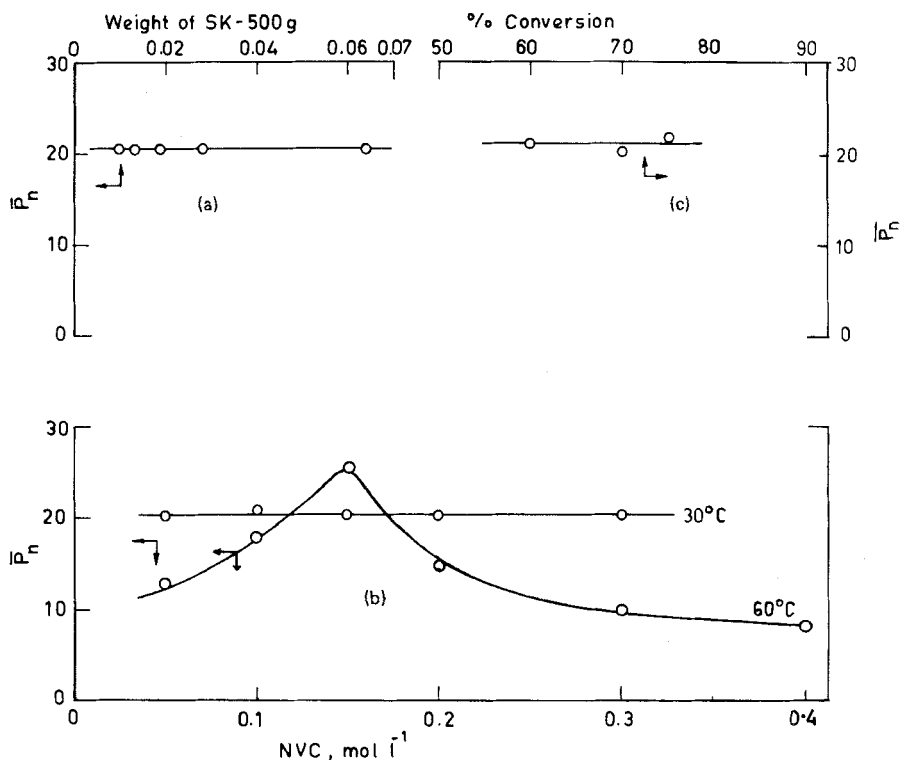


FIG. 8. Dependence of \bar{P}_n on $[NVC]$, the weight of SK-500 and increasing conversion. $[NVC] =$ (a) and (c) 0.1 mol/L; weight of SK-500 = (b) and (c) 0.028 g. Solvent, benzene; temperature, 30°C.

entire range up to 0.3 M (rate showing a maximum at ~ 0.2 M of NVC) implies that monomer transfer is important at low $[NVC]$ while termination [26] predominates at $[NVC]$ beyond ~ 0.2 M. At 60°C, \bar{P}_n tends to increase with NVC concentration (0.05–0.15 M) and ultimately falls to a limiting steady value (0.3–0.4 M NVC). The initial increase in \bar{P}_n may be due to an increase in R_p (both initiation and propagation) which is understood by the fact that R_p at 60°C is more than the rate at 30°C. Moreover, under these conditions the monomer transfer/termination is seemingly outweighed by spontaneous termination. Beyond 0.15 M NVC, chain breaking by monomer again becomes significant.

TABLE 2. Molecular Weight Distribution by GPC^a

Sample ^b	$D = \overline{M}_w / \overline{M}_n$
I	1.2
II	1.3
III	1.1

^aDetermined in Waters Associates Gel Permeation Chromatograph through the courtesy of C. A. Barson, Birmingham University, U.K. Solvent, THF. Calibration, polystyrene.

^bPolymerization recipe for I, II and III are, respectively: (I) [NVC] = 0.05 M, SK-500 = 0.064 g (precalcination temperature 100°C); (II) [NVC] = 0.09 M, SK-500 = 0.028 g (precalcination temperature 450°C); and (III) [NVC] = 0.15 M, SK-500 = 0.064 g (precalcination temperature 250°C).

Molecular Weight Dispersion

Table 2 suggests that the value of dispersion as obtained by GPC is less than 1.5 and within the limits of experimental accuracy, independent of the weight of zeolite, the concentration of NVC, and the precalcination temperature.

Regeneration of the Catalyst

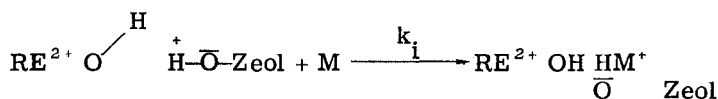
The relative loss in the catalytic activity of SK-500 following its use in a single polymerization has been determined to be about 40% at a precalcination temperature of 600°C. However, further studies are in progress in this direction.

Mechanism

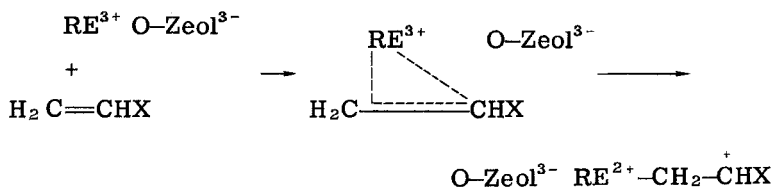
The cationic nature of the polymerization of NVC in the presence of SK-500 is well endorsed by the decelerating influence of basic additives, acceleratory effect of Brønsted and aprotic acids, and water.

Initiation

As discussed earlier, the precalcination temperature of the sieve appears to determine the nature of the initiating moiety. Accordingly, Brønsted acid initiation is supposed to occur predominantly on SK-500, precalcined up to ~ 200°C, as under



On the other hand, at precalcination temperatures of $\sim 200^\circ\text{C}$, initiation involving the adsorption of NVC on the active RE^{3+} centers becomes important and takes place through the interaction of π -electron clouds of vinyl double bond with RE^{3+} centers, a process similar to what occurs in 3d-metal oxide initiated polymerization of vinyl monomers studied by Biswas et al. [27-29]. Schematically,



where X = carbazole group.

Propagation

The polymer chains initiated at the zeolite surface would be held in contact with the surface by intermolecular interaction [12]. Consequently, propagation steps also occur on the zeolite surface.

Termination

\bar{P}_n trends indicate that termination by proton detachment is overweighed by monomer transfer or termination which is a very typical feature of NVC polymerization by aprotic and other systems [6, 11, 13, 14].

CONCLUSIONS

The polymerization of NVC by SK-500 molecular sieve proceeds by a conventional cationic mechanism. The unique features of the system include deceleration of the rate in nitrobenzene solvent and the influence of the precalcination temperature of the catalyst on the initiation mechanism.

ACKNOWLEDGMENTS

The authors thank the authorities of the Indian Institute of Technology, Kharagpur, for facilities and CSIR, India, for financial support in the form of a research scheme.

REFERENCES

- [1] M. Biswas and N. C. Maity, Adv. Polym. Sci., **31**, 47 (1979).
- [2] M. Biswas and N. C. Maity, J. Macromol. Sci.-Chem., **A15**(8), 1553 (1981).
- [3] M. Biswas and N. C. Maity, Polymer., **21**, 1344 (1980).
- [4] R. A. Rhein and J. S. Clarke, Ibid., **14**, 333 (1973).
- [5] M. Biswas and G. M. A. Kabir, Eur. Polym. J., **14**, 861 (1978).
- [6] M. Biswas and G. M. A. Kabir, J. Polym. Sci., Polym. Chem. Ed., **17**, 673 (1979).
- [7] M. Biswas and D. Chakravorty, Ibid., **11**, 7 (1973).
- [8] O. Johnson, J. Phys. Chem., **59**, 827 (1955).
- [9] C. Mirodatos, P. Pichat, and D. Barthomeuf, Ibid., **80**, 1335 (1976).
- [10] C. Mirodatos, A. Abau Kais, J. C. Vedrine, P. Pichat, and D. Barthomeuf, Ibid., **80**, 2366 (1976).
- [11] L. P. Ellinger, Advances in Macromolecular Chemistry, Academic, New York, 1968, p. 169.
- [12] M. Biswas and P. Kamannarayana, J. Polym. Sci., Polym. Chem. Ed., **14**, 2071 (1976).
- [13] C. A. Barson, J. R. Knight, and J. C. Robb, Br. Polym. J., **4**, 427 (1972).
- [14] M. Biswas and K. J. John, J. Polym. Sci., Polym. Chem. Ed., **16**, 3025 (1978).
- [15] M. Biswas and K. J. John, Ibid., **16**, 971 (1978).
- [16] H. W. Haynes, Jr., Catal. Rev.-Sci. Eng., **17**(2), 273 (1978).
- [17] J. W. Ward, J. Catal., **13**(3), 321 (1969).
- [18] H. W. Haynes, Jr., Personal Communication, 1979.
- [19] T. I. Barry and L. A. Lay, J. Phys. Chem. Solids, **27**, 1821 (1966).
- [20] Kh. M. Minachev, Kinet. Catal., **11**, 342, 412 (1970).
- [21] M. Biswas and P. K. Mishra, Polymer., **16**, 621 (1975).
- [22] M. Biswas and P. K. Mishra, J. Polym. Sci., Polym. Lett. Ed., **11**, 639 (1973).
- [23] R. M. Barrer and A. T. T. Oei, J. Catal., **30**, 460 (1973); **34**, 19 (1974).
- [24] C. J. Norton, Ind. Eng. Chem., Process Des. Dev., **3**, 230 (1964).
- [25] S. Tazuke, M. Asai, S. Ikeda, and S. Okamura, J. Polym. Sci., **B5**, 453 (1967).
- [26] J. Pac and P. H. Plesch, Polymer, **8**, 237 (1967).
- [27] M. Biswas, M. M. Maiti, and N. D. Ganguli, Makromol. Chem., **124**, 263 (1969).
- [28] M. Biswas and P. K. Mishra, Ibid., **163**, 37 (1973).
- [29] M. Biswas, G. M. A. Kabir, and S. S. Bhagawan, Ibid., **179**, 1209 (1978).

Accepted by editor August 10, 1981

Received for publication August 28, 1981