Polymerization of *N*-vinylcarbazole over cobalt (II) exchanged 13X molecular sieves

Mukul Biswas and Madhusudan Banerjee
Department of Chemistry, Indian Institute of Technology, Kharagpur 721 302, India

and Mrinal M. Maiti
Materials Science Centre, Indian Institute of Technology, Kharagpur 721 302, India
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Polymerization of *N*-vinylcarbazole over Co(II)-13X molecular sieves in toluene solution has been studied. The rate of polymerization has been observed to be second order both in monomer concentration and in the exchange level of Co(II), and linearly dependent on catalyst loading. An apparent activation energy of 8.71 kcal mol^{-1} (36.41 kJ mol^{-1}) has been found for the polymerization. The effect of different parameters on molecular weight has also been studied. The general kinetic features of the reaction are somewhat different from those reported for monomers like isobutyl vinyl ether, styrene etc. on simple and rare earth exchanged 13X molecular sieves.

(Keywords: Polymerization; *N*-vinylcarbazole; poly(*N*-vinylcarbazole); Co(II)-13X zeolite; activation energy)

INTRODUCTION

In an earlier publication the application of molecular sieves as polymerization catalysts was reviewed by Biswas and Maity[1] who in subsequent communications[2,3] reported some kinetic and mechanistic aspects of polymerization of *N*-vinylcarbazole (NVC) and isobutyl vinyl ether (IBVE) on an SK-500 rare earth exchanged molecular sieve. It was also reported that the rate of polymerization $(R_p) \propto [\mathrm{NVC}]^{1.0}$ [weight of SK-500]$^{0.70}$ in the NVC-SK-500 system and $R_p \propto [\mathrm{IBVE}]^{1.0}$ [weight of SK-500]$^{1.0}$ in the IBVE-SK-500 system. Barson *et al.*[4] observed that the rate is proportional to the 2/3rd power of the weight of 13X sieve in the polymerization of styrene in cyclohexane. It has also been observed[2,3] that the activity of SK-500, which is a rare earth exchanged 13X molecular sieve, is much superior to its sodium exchanged analogue which is virtually inactive. The activity of SK-500 is presumably due to the presence of rare earth cationic centres at +3 state. It would be interesting to investigate how the metal ions in +2 state alter the activity of 13X molecular sieves in the polymerization of NVC.

In this paper we highlight the activity and some kinetic features of Co(II) exchanged 13X molecular sieve in NVC polymerization which are quite different from those observed in the NVC-SK-500 polymerization system.

EXPERIMENTAL

Materials

NVC (BASF, West Germany) was recrystallized from methanol by the standard procedures[2,3]. Solvents such as toluene, methanol and other chemicals used were all analytical grade materials. They were dried and fractionally distilled by standard procedures. Linde 13X (Union Carbide, USA) supplied as a white powder containing no clay binder was activated at 500°C for 2 h prior to the experiments.

Preparation of Co(II) exchanged 13X zeolite

Metal exchange reactions were performed as per details provided in the bulletin from Union Carbide[5] and by Breck[6] using cobalt(II) chloride solution[7] (strength 0.2 M) at 35°C. The degree of ion exchange was determined by chemical analysis[8].

Polymerization

The polymerization technique was essentially the same as described in our earlier communications[2,3].

Viscosity measurements

The inherent viscosities of poly(*N*-vinylcarbazole) (PNVC) were determined with an Ubbelhode viscometer in toluene at 35° ±0.1°C in 0.5% solution.

RESULTS AND DISCUSSION

General features of polymerization

General features of polymerization are essentially the same as with copper(II) exchanged 13X-NVC system reported elsewhere[7]. However, certain differences are discernible in Co(II)-13X-NVC systems, which are discussed in appropriate places.

Dependence of rate on the extent of metal-ion exchange

Figure 1 represents the dependence of the initial rate of polymerization (averaged over initial 5 min of polymerization) of NVC on the extent of cobalt ion exchanged in 13X molecular sieve. The rate is close to second order with respect to the cobalt(II) content, the calculated slope in

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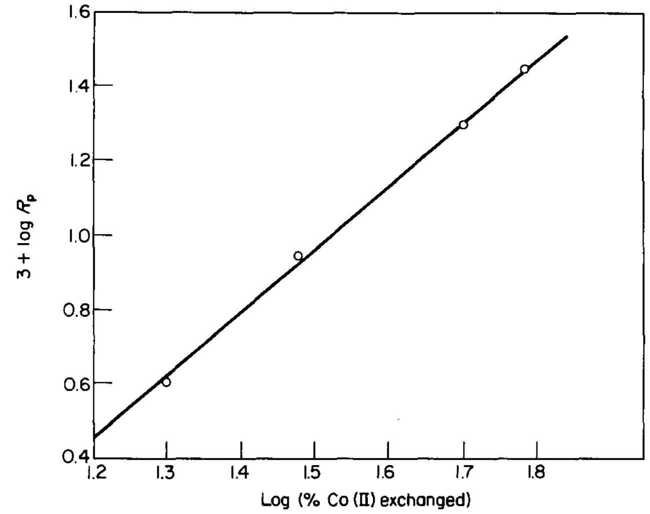

Figure 1 Dependence of log R_p on the logarithm of percentage of Co(II) in the 13X molecular sieve for the polymerization of NVC at 60°C: [NVC] = 0.15 mol l^{-1}; catalyst = 25 g l^{-1}

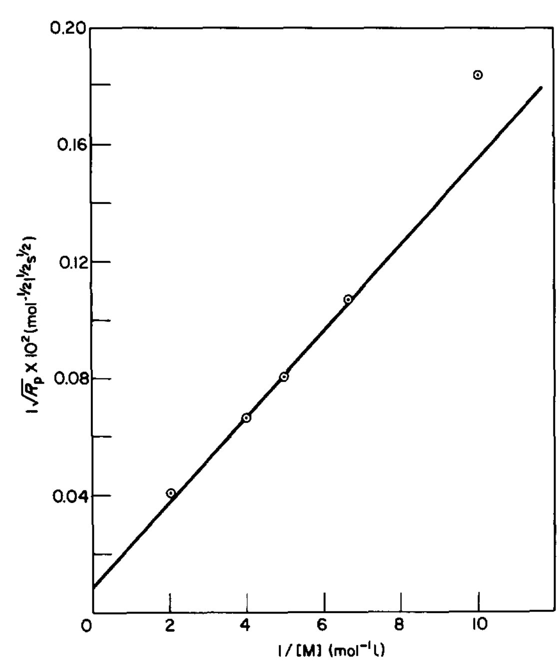

Figure 2 Plot of $1/\sqrt{R_p}$ against 1/[NVC]: catalyst = 25 g l^{-1}; percentage of Co(II) in the 13X = 30; temperature, 60°C

the plot of log R_p vs. log Co(II) exchange level being 1.82 ± 0.01. The increase in the rate of polymerization with increasing cobalt content of the molecular sieve is apparently understood on the basis of enhanced initiation and/or propagation processes which are aided by 3d-metal centres on the inner cage surface of the zeolite.

This feature of polymerization in the Co(II) system sharply contrasts with that observed in the Cu(II)-13X-NVC system[7] in which a rate maximum was observed at a certain percentage of Cu(II) in the 13X molecular sieve beyond which the rate started to decline.

Effect of monomer concentration

The effect of increasing the monomer concentration is illustrated in *Figure 2*. It has been observed that the rate increased with increase in monomer concentration; however, a tendency to level off was very apparent at higher concentrations of NVC (0.50 mol l^{-1}). The trend can be explained in terms of the concentration of adsorbed monomer onto the zeolite surface. In ideal cases, the concentration of adsorbed monomer is governed by the Langmuir adsorption isotherm, which predicts a saturation of the catalytic surface at higher concentration of the adsorbate.

Since the polymerization reaction in the present system takes place on the zeolite surface, the rate will be dependent on the surface concentration of the monomer and the propagative species, the latter originating initially from a single adsorbed monomeric species. Thus a second order dependence of the rate in the surface concentration is very likely to be obeyed. Application of the Hinshelwood–Langmuir mechanism in its simplest form would then lead to

$$R_p = k\theta^2$$

$$= k\frac{K^2[\mathrm{NVC}]^2}{(1 + K[\mathrm{NVC}])^2}$$

where k is the rate constant for propagation on the zeolite surface, θ the fractional coverage of the surface by monomer and active propagating chain and K is the adsorption equilibrium constant of NVC at a particular temperature. On linearization,

$$R_p^{-1/2} = (k.K)^{-1/2}[\mathrm{NVC}]^{-1} + k^{-1/2}$$

i.e. the plot $R_p^{-1/2}$ against $[\mathrm{NVC}]^{-1}$ should produce a straight line. This anticipated linear relation is clearly borne out in *Figure 2*.

The observed dependence of rate on monomer concentration is different from those reported for NVC or IBVE polymerizations on SK-500[2,3], and also of styrene on 13X molecular sieves[4]. In the cases of SK-500-NVC or SK-500-IBVE a first order dependence on the monomer has been reported; whereas in the 13X–styrene system an order of 1.6 has been observed. Also, in none of the above reported studies, which represent heterogeneous catalytic systems, due consideration has not been paid to adsorption of the monomer onto the zeolite surface.

Dependence of rate on the weight of molecular sieve

Figure 3 suggests that the rate of polymerization is proportional to the first power of the weight of the molecular sieve in the range studied. Interestingly, for SK-500 initiated polymerization of this monomer, a 2/3 order with the catalyst has been reported[2] as against the first order dependence[3] of IBVE polymerization with the same catalyst. A fractional order (2/3) with catalyst loading has also been reported by Barson *et al.*[4] in the 13X–styrene polymerization system. In contrast, we have observed in the present system an order of 1.10 ± 0.08 with catalyst loading.

The general kinetic features of catalysed polymerization on 13X molecular sieves, as reported in this study and in other published literature, suggest that the exchanged metal ion can significantly alter the polymerization mechanism on molecular sieve catalysts.

Effect of temperature

Figure 4 shows the Arrhenius plots for R_p. R_p increases steadily with increasing temperature over the range 40°–60°C. Apparent activation energy of 8.71 ± 0.01 kcal mol^{-1} (36.41 kJ mol^{-1}) and

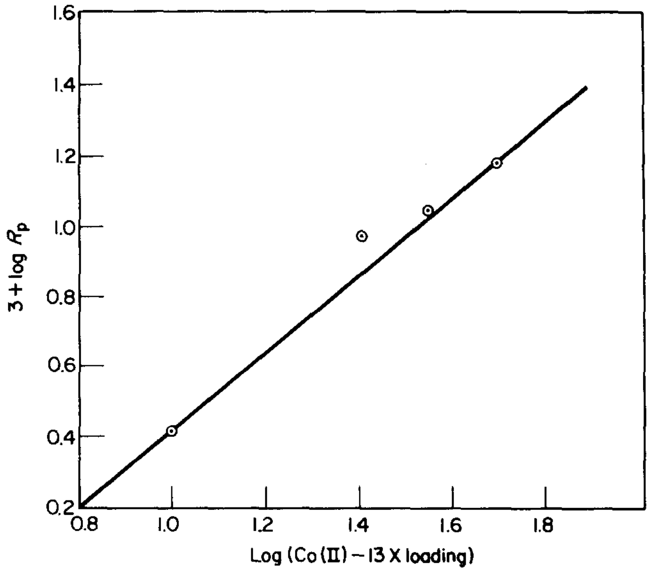

Figure 3 Variation of R_p as a function of the weight of Co(II)–13X molecular sieve catalysts at 60°C: [NVC] = 0.15 mol l^{-1}; percentage of Co(II) in the 13X = 30

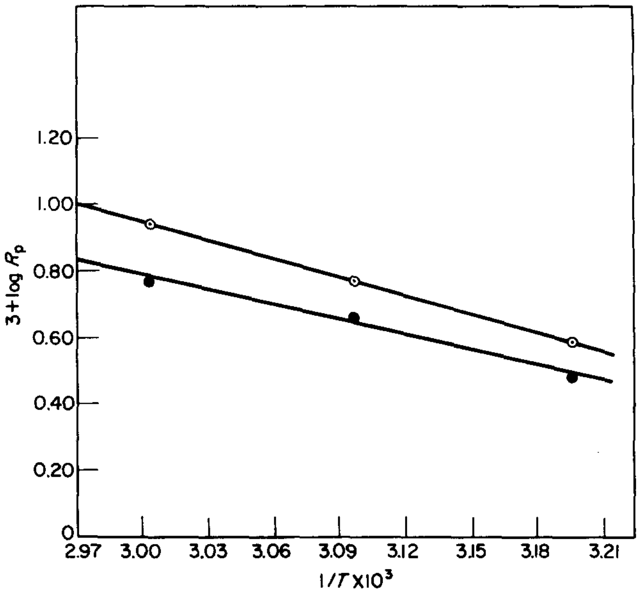

Figure 4 Arrhenius plot for polymerization of NVC on Co(II)–13X molecular sieve catalysts: [NVC] = 0.15 mol l^{-1}; percentage of Co(II) in the 13X = 30; amount of Co(II)-13X = 25 g l^{-1}; (○) at 5 min; (●) at 10 min

6.75 ± 0.02 kcal mol^{-1} (28.22 kJ mol^{-1}) have been calculated with the rates averaged over the initial 5 min and 10 min respectively. Lower activation energies observed with rates averaged over a 10 min period of the reaction compared with the rates over a 5 min period, is an indication that the contribution of less temperature-sensitive (lower activation energy) processes to the overall rate of polymerization gradually predominates as the concentration of the polymer increases with time. Considering a low molecular weight material, as in this system, the steric factors are perhaps operative which restrict longer chain growth in the zeolite cavity. On this premise, diffusion of the monomer into and/or escape of polymer from the zeolite pores are believed to be simultaneously operative during polymerization.

Dependence of rate on preheating temperature and adsorbed water of the catalyst

Figure 5 shows the effect of preheating temperature of the Co(II)–13X molecular sieves on the rate of polymerization. The rate gradually increases with increasing precalcination temperature and attains a maximum value at about 500°C. Further increase in the precalcination temperature resulted in the loss of activity of the zeolite. It has also been observed that the activity of the sieve is consistently depressed with the increase in the amount of externally added water to the zeolite.

These observed effects of water on the activity of zeolite suggest that water strongly adsorbs on the zeolite surface, thereby suppressing the available surface for the adsorption of the monomer. The maximum activity of the Co(II)–13X catalyst, observed around 500°C corresponds to a situation where the surface is virtually devoid of any adsorbed water. Fall in activity beyond 500°C is possibly due to the change in the structure of the zeolite itself under thermal influence[9].

It is also interesting to note that the colour of the Co(II)–13X zeolite which is pink under normal storage conditions, changes to blue after precalcination at 120°C, which is retained up to 500°C. Beyond 500°C, it gradually darkens and becomes completely black at 750°C. The pink colouration corresponds to hydrated Co(II) species, whereas the blue colour is due to free Co(II) ions. The black colouration is presumably due to the formation of cobalt oxide(s).

Trend in molecular weight of PNVC

The molecular weights of PNVC obtained with Co(II)–13X zeolite catalyst under various experimental conditions, are quite low, as evidenced by small inherent viscosity values. The following general observations, however, can be made about the dependence of the viscosity values on different experimental parameters (*Table 1*).

The inherent viscosity is higher when the percentage of Co(II) in the 13X sieve or the monomer concentration is

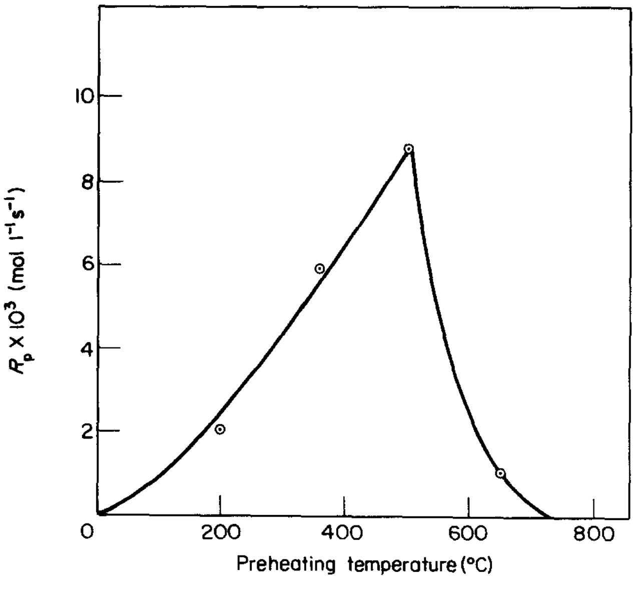

Figure 5 Effect of preheating temperature on R_p of polymerization of NVC at 60°C: [NVC] = 0.15 mol l^{-1}; percentage of Co(II) in the 13X = 30; catalyst = 25 g l^{-1}

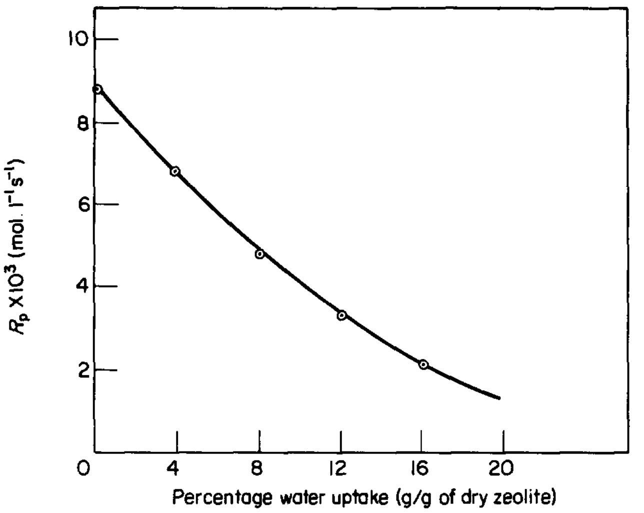

Figure 6 Effect of water content of the Co(II)–13X catalyst on R_p of the polymerization of NVC at 60°C: [NVC]=0.15 mol l^{-1}; catalyst=25 g l^{-1}; percentage of Co(II) in the 13X=30

increased. Increase in temperature resulted in a decrease in inherent viscosity. Increased catalyst loading, however, has no significant effect on the viscosity of PNVC.

All these trends are in general agreement with theoretically predicted kinetic features of addition polymerization.

MEK insolubility of PNVC

Tani[10] has reported that stereoregularity in an addition polymer can be indexed with the fraction of the polymer which is insoluble in methyl ethyl ketone (MEK). In fact, we have observed in the Co(II)–13X–NVC polymerization system that a certain fraction of PNVC is indeed insoluble in MEK. However, we have failed to record any significant differences either in the ^{1}H n.m.r. ($CDCl_3$, 90 Hz) spectra or in the X-ray diffractographs of the MEK soluble and insoluble fractions of PNVC. Also, no distinct correlation between the amount of MEK insoluble fractions and such reaction parameters as the exchange level of the Co(II) ion, monomer concentration, catalyst loading, reaction medium and the temperature of polymerization could be traced. The only recognizable difference has, however, been observed in the molecular weight; the MEK insoluble fractions always having higher molecular weight than those of the corresponding soluble fractions.

Although the occurrence of stereoregularity is not unequivocally established in the present system, some general comments can, however, be made. The cage environment of the sieves possibly provide some conformationally favoured adsorbed monomeric species which leads to some stereoregularity in the polymer formed.

Since the cage volume is very small, crowding of polymer chains may lead to local strains whereby both the molecular weight and the stereospecificity would suffer appreciably. These facts are reflected in lower molecular weight and formation of only a partially MEK-insoluble polymer.

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Table 1 Dependence of inherent viscosity of PNVC on different parameters

Percentage of cobalt	Monomer conc. (mol l^{-1})	Amount of catalyst^a (g l^{-1})	Reaction temperature (°C)	Inherent viscosity (dl/g)
20	0.15	25	60	0.100
30	0.15	25	60	0.130
50	0.15	25	60	0.156
60	0.15	25	60	0.171
30	0.10	25	60	0.113
30	0.20	25	60	0.147
30	0.25	25	60	0.167
30	0.50	25	60	0.207
30	0.15	10	60	0.131
30	0.15	35	60	0.130
30	0.15	25	50	0.137
30	0.15	25	40	0.143

^{a}Catalyst was preheated at 500° C/2 h before each experiment