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Polymerization of Isobutyl Vinyl Ether by SK-500 Molecular Sieve

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ABSTRACT

The polymerization of isobutyl vinyl ether (IBVE) by SK-500 is first order in monomer and directly proportional to the weight of the sieve. Catalytic activity and the solid surface acidity of SK-500 are maximum when the sieve is precalcined at 200°C for 2 h. Pyridine ($\approx 10^{-4}$ mol/L) inhibits and hydrogen chloride ($\approx 10^{-4}$ mol/L) cocatalyzes the polymerization. Both the rate and molecular weight increase to a maximum at ~7% uptake of water (g/g of dry sieve) and thereafter fall to a limiting value. Molecular weights increase as the monomer concentration increases up to ~1.0 mol/L and attain a limiting value. Molecular weights increase with precalcination temperature up to 500°C and decline thereafter. Rate increases steadily with temperature over the range 2-60°C while molecular weights increase only up to 30°C, above which a sharp fall is observed. The initiation of the polymerization appears to involve the Brönsted acid sites on the SK-500 molecular sieves through a proton transfer to the monomer molecule and follows a conventional cationic mechanism.

INTRODUCTION

A recent review by Biswas and Maity [1] revealed that there is, by now, considerable information on molecular sieve catalyzed

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polymerization and postpolymerization reactions. In this respect, the work of Barrer et al. [2, 3] on alkyl vinyl ether polymerization by H-mordenite and H-faujasite, by Barson et al. [4] on the polymerization of styrene by 13× molecular sieves, and a few other reports [5-7] have attempted a comprehensive characterization of the systems concerned. Nevertheless, these studies leave open some pertinent questions as to the molecular weight ranges of the polymers formed, the monomer selectivity of the prospective molecular sieve catalysts, and the sieve specificity of the vinyl monomers, which apparently warrant further studies. Accordingly, the kinetic, mechanistic, and some related aspects of the polymerization of some typical vinyl monomers by Linde SK-500 molecular sieve were studied. The latter is a rare earth exchange Y molecular sieve reported [8] to be a highly active catalyst for reactions occurring by an ionic mechanism. This paper describes the polymerization characteristics of IBVE by SK-500.

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EXPERIMENTAL

Materials

Isobuty vinyl ether (BASF, West Germany) was purified and distilled following standard procedures. Solvents, all analytical grade materials, were dried and fractionally distilled. SK-500 molecular sieves (Union Carbide) supplied as a white, crystalline pellet, containing no clay binder, were pulverized into powder (100 mesh). Prior to use, the catalysts were activated [8] at the desired temperatures.

Polymerization

Polymerizations were conducted in stoppered Pyrex reaction flasks (100 mL capacity) fitted with nitrogen inlet tubes under nitrogen atmosphere. The general procedures followed for pretreatment of the reaction vessels, preparation of monomer in the dry glove box, and charging of the reaction vessels with monomer solution in dry conditions were essentially similar as adopted earlier [9, 10]. The catalyst after appropriate activation was transferred to the monomer solution under nitrogen atmosphere. The progress of the polymerization was followed gravimetrically. Intrinsic viscosities ($[\eta]$) were determined in toluene.

Solid Surface Acidity

This was determined by following the procedure of Johnson [11].

The IR absorption characteristics of the polymer were measured on a Perkin-Elmer 237B Recording Spectrophotometer.

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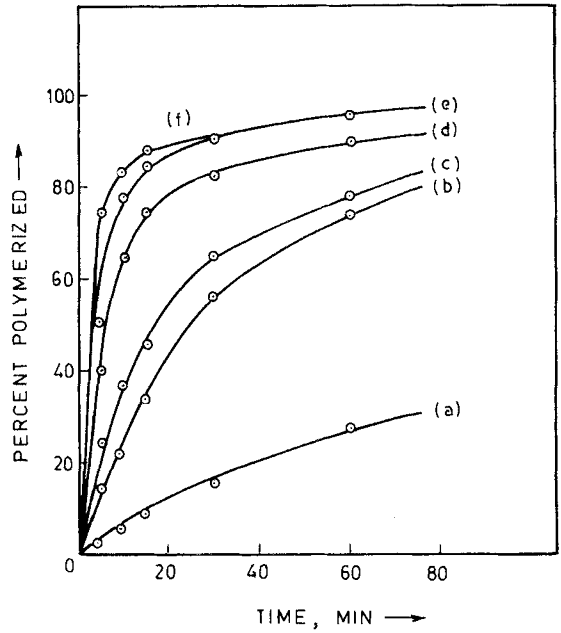

FIG. 1. The time-conversion curves for SK-500 catalyzed polymerization of IBVE in benzene at 30°C, using [IBVE] = 1.0 mol/L and weight of the sieve: (a) 0.02 g, (b) 0.10 g, (c) 0.15 g, (d) 0.25 g, (e) 0.30 g, and (f) same as (c) with stirring.

RESULTS AND DISCUSSION

General Characteristics of the Polymerization

A typical set of some characteristic time-conversion curves for a fixed IBVE concentration (1 mol/L) and different amounts of sieve is shown in Fig. 1. The curves are characterized by initial steady zones followed by leveling off from 40 min onward. At high concentrations of SK-500 and IBVE, the conversions tend to be complete (100%) in 1 h. These trends, though somewhat similar to observations of Barrer et al. [2, 3] for the IBVE-H-mordenite system, are conspicuously different from those reported for IBVE polymerization by aprotonic acids [9] where the polymerizations hardly reach completion. Figure 1 further reveals that the polymerization rate increases with stirring, implying diffusion is significant. The polymerization is exothermic, and the catalyst changes its color from white to light brown during polymerization. The polymers were obtained as a

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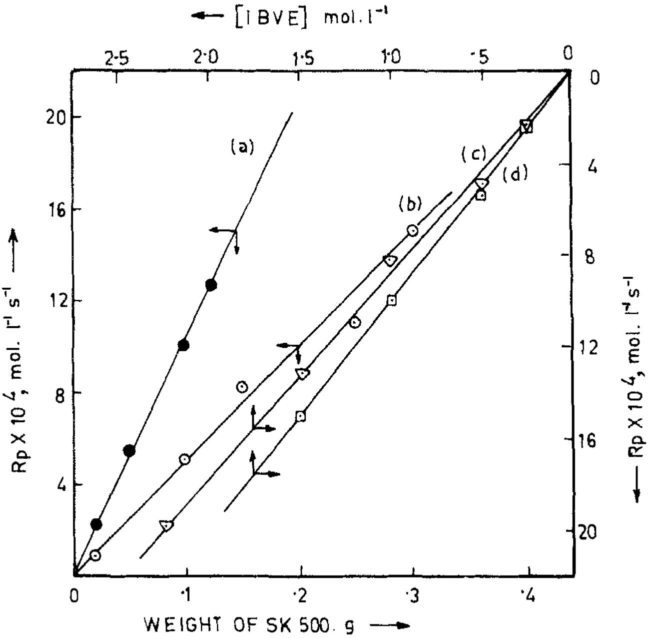

FIG. 2. Dependence of R_p on weight of the sieve and on [IBVE]: (a) [IBVE] = 1.0 mol/L (with stirring), (b) [IBVE] = 1.0 mol/L (no stirring), (c) [SK-500] = 0.15 g (no stirring), and (d) [SK-500] = 0.10 g (with stirring). Solvent, benzene; temperature, 30°C.

colorless sticky mass, soluble in all conventional solvents. The polymerizations were not accompanied by any color development, suggesting that charge transfer initiation [12, 13] through the interaction of IBVE and the rare earth centers is not important in the present polymerization. The IR spectra of the polymer are identical to those of polyIBVE obtained by aprotonic acid initiation.

Rate Dependence on the Weight of SK-500 and IBVE Concentration

Figure 2 shows the effect of variation of the weight of SK-500 and of IBVE concentration on the rate of polymerization (R_p). These results suggest that $R_p \propto$ (weight of SK-500)$^{1.0}$ [IBVE]$^{1.0}$, both when the system is stirred continuously during polymerization (Figs. 2a and 2d) and when there is no stirring (Figs. 2b and 2c). Barson et al. [4]

observed R_p to be proportional to $\sim\frac{2}{3}$ power of a 13× molecular sieve for the bulk polymerization of styrene. Regarding the monomer dependence of the rate, Barrer et al. [2, 3] reported a linear dependence of the rate coefficient on the pressure of IBVE. Barson et al. [4] found an order of 1.5 with respect to styrene for styrene-13×-cyclohexane polymerization system. Interestingly, the conventional cationic polymerization of IBVE by aprotonic acids [9] reveals an initial second-order dependence of the rate on IBVE concentration, followed by a fall, a trend which is conspicuously absent in the present system.

Effect of Preheating Temperature of SK-500 on Rate

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Figure 3 reveals the effect of preheating temperature of the molecular sieve on the rate of polymerization. It is evident that maximum rate is realized at 200°C. It is interesting to note that the solid-surface acidity [11] also exhibits an exactly parallel variation with the preheating temperature, the maximum acidity being realized at ~200°C. This behavior implies that at this temperature the concentration of the entities responsible for the polymerization attains a maximum value. The above observation is consistent with that of Hickson and Scicsery [14] who reported maximum catalytic activation of SK-500 molecular sieve at ~200°C for certain isomerization reactions, the catalyst activity being, however, associated with a weak dehydration process. The polymerization in the present instance appears to involve a cationic mechanism since it is retarded/inhibited in the presence of pyridine (Table 1). It is believed that Brönsted acid centers are responsible for the initiation. This is justified since pyridine is known [15-17] to react preferentially with the Brönsted acid sites on a molecular sieve surface and eliminates [17] the characteristic IR bands due to acidic OH groups. Moreover, for the rare earth Y zeolites, Ward [17] reported that Brönsted acidity may be significant up to a precalcination temperature of ~ 480°C, whereas above 700°C Lewis acidity may be important [17, 18]. On the basis of these observations it further appears that the contribution of Lewis acid centers to the initiation of the polymerization in the present system is unimportant.

Figure 3 also shows that the $[\eta]$ values increase up to a precalcination temperature of ~ 500°C and fall thereafter. This may be due to the continuous removal of residual surface or intracrystalline channel water from the sieve. The significance of intracrystalline water in such reactions has also been pointed out by Barrer [2, 3]. However, as a result of this process, transfer possibilities of growing chains with water would be reduced so that $[\eta]$ would increase. Beyond 500°C, the fall in $[\eta]$ possibly results from the pronounced decrease in the rate of propagation.

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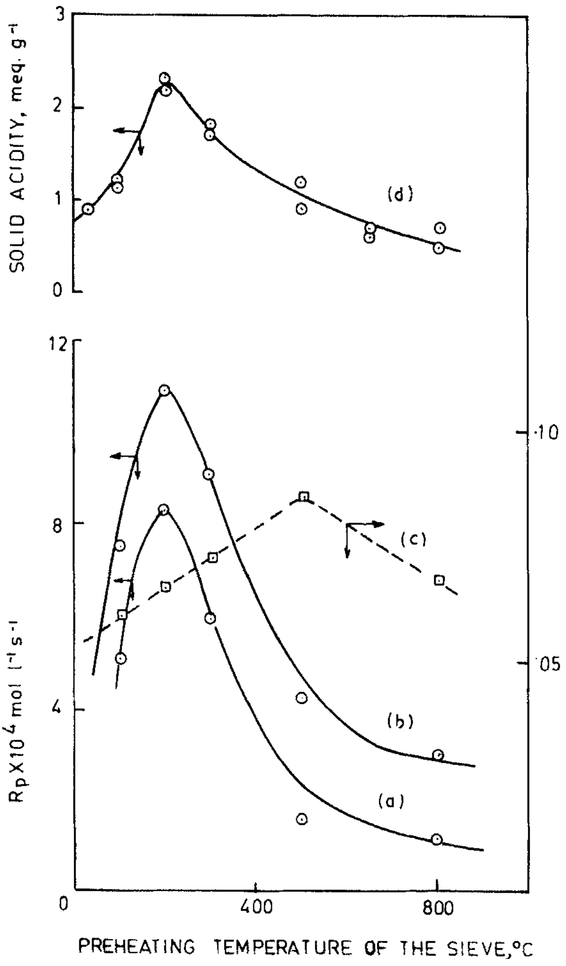

FIG. 3. The variation of R_p with the preheating temperature of the sieve, using (a) 0.15 g, (b) 0.25 g of sieve and [IBVE] = 1.0 mol/L in benzene at 30°C. The variation of (c) [η] using [IBVE] = 1.0 mol/L and a 0.15 g sieve, and (d) solid surface acidity with precalcination temperature of the sieve.

TABLE 1. Effect of Additives on the Polymerization[a] of IBVE by SK-500 Molecular Sieve

	Additives			
Weight[b] of SK-500 (g)	Name	Concentration $\times 10^4$ (mol/L)	$R_p \times 10^4$ (mol/L s)	$[\eta]$ (dL/g)
0.15	None	-	8.30	0.066
0.15	Pyridine	0.19	1.30	0.004
0.15	Pyridine	1.90	No polymerization	-
-	Hydrogen chloride	0.80	No polymerization	-
0.15	Hydrogen chloride	0.80	11.60	0.090
0.15	Hydrogen chloride	1.60	15.00	0.110
0.15	Hydrogen chloride	2.40	18.00	0.110
0.15	Hydrogen chloride	3.20	21.60	0.120

[a] [IBVE] = 1 mol/L. Temperature, 30°C. Solvent, benzene.
[b] The amount of catalyst added to the 25 mL of the reaction mixture.

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Effect of Additives

Pyridine and Hydrochloric Acid. To endorse the cationic nature of the polymerization, the effect of pyridine and hydrochloric acid was examined (Table 1). Pyridine, a typical inhibitor of cationic polymerization, totally inhibits the polymerization in the concentration range 10^{-4} mol/L. HCl ($\approx 10^{-4}$ mol/L) cocatalyzes the reaction. These observations clearly endorse the view that polymerization proceeds by a conventional cationic mechanism through initiation by Brönsted acid sites.

Water. Figure 4 shows the dependence of the polymerization rate and the intrinsic viscosity on the concentration of zeolitic water. Small amounts of water increase both the rate and the molecular weight to a maximum (near 7% uptake of water), but at still higher concentrations of water both these quantities fall. This trend in rate is reminiscent of the situation encountered by Barrer [2, 3] for the IBVE-H-mordenite system. However, he did not examine the molecular weight variation with added water. In small amounts, added water acts as a cocatalyst for the polymerization, but beyond an optimum

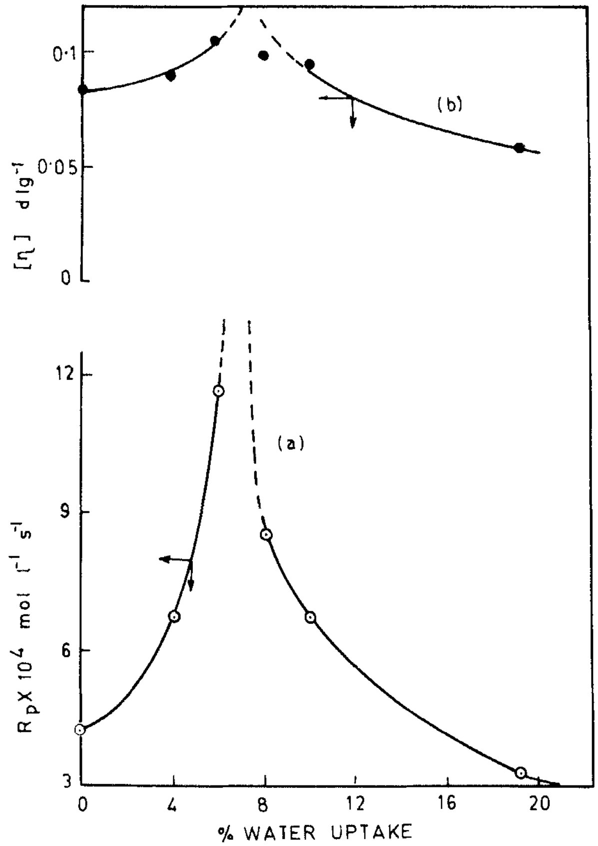

FIG. 4. The effect of sorbed water on (a) R_p and (b) $[\eta]$ using a 0.25 g sieve (precalcined at 500°C for 2 h) and [IBVE] = 1.0 mol/L in benzene at 30°C.

concentration, water retards the polymerization. This feature is atypical [19, 20] of the cocatalytic behavior of water. Figure 4 further reveals that at ~20% uptake of water the polymerization is practically inhibited totally. It is possible that under these conditions intracrystalline channels in the molecular sieve become blocked and there may also be preferential adsorption of water at surface sites. Consequently, propagation would be seriously impaired. The fall in $[\eta]$ at high water uptake limits is conventionally explained in terms of termination as well as transfer of growing chains by water [9, 19].

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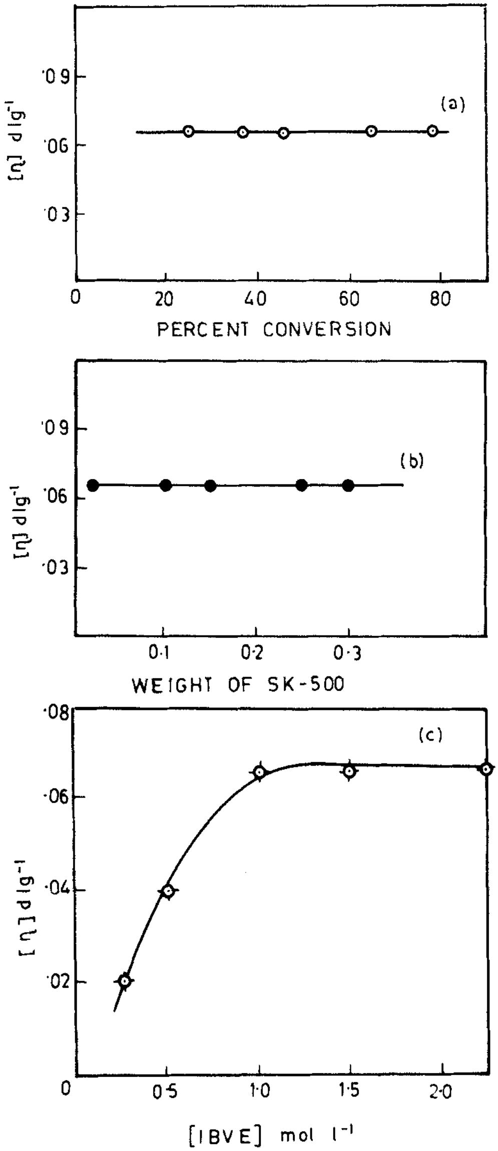

FIG. 5. The variation of [η] with (a) increasing conversion using 0.15 g of sieve and [IBVE] = 1.0 mol/L in benzene at 30°C, (b) weight of the sieve using [IBVE] = 1.0 mol/L, and (c) monomer concentration using 0.15 g sieve. [η] determined in toluene solution at 30°C.

Molecular Weight Trends

The variation of intrinsic viscosities ([η]) of the polymers has been examined as a function of (a) increasing conversion (b) the weight of SK-500 and (c) the concentration of IBVE.

Figure 5(a) reveals that [η] remains constant with conversion, suggesting that termination and or transfer reactions are operative [4, 19].

Figure 5(b) indicates that [η] is independent of the weight of SK-500, which confirms that the latter does not participate in chain-breaking reactions [9, 10, 21].

Figure 5(c) shows that with increase in IBVE concentration, [η] initially increases up to an IBVE concentration of 1.0 mol/L and thereafter tends to a limiting value. Such a trend was also reported by Biswas et al. [9, 10] for the alkyl vinyl ether-chromyl chloride system and also by Eley and Coombes [22] for the alkyl vinyl ether-$BF_3.Et_2O$ system. It appears that termination/transfer reactions involving monomer are important in the present system and, above ~1 mol/L, IBVE monomer transfer becomes predominant.

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Effect of Temperature

Figure 6 shows the Arrhenius plots for R_p and [η]. R_p increases steadily with temperature over the range 2-60°C (overall activation energy 24.15 kJ/mol) while the molecular weights increase up to ~30°C and fall sharply thereafter. Interestingly, for the IBVE-aprotonic acid system [9, 10] both the rate and the molecular weight reveal such maxima at ~47°C. However, as for the present system, the increase in rate and [η] is consistent with enhancement in initiation and propagation rates, while above the threshold temperature of ~30°C termination and transfer [9] become more significant, thereby decreasing the molecular weight.

Mechanism

The polymerization of IBVE in the presence of SK-500 is initiated through proton transfer from the Brönsted acid sites to the monomer. Several possibilities [23-25] have been suggested as to how Brönsted acid sites may be formed in rare earth zeolites. The polymer chains could be held in contact with the zeolite surface by intermolecular interaction [4]. Consequently, propagation would continue on the surface. Termination would involve proton detachment, forming an unsaturated chain end and reforming the zeolite site. A similar mechanism was used to explain the results of Benson and co-workers [26] who used an acid clay catalyst for the polymerization of styrene.

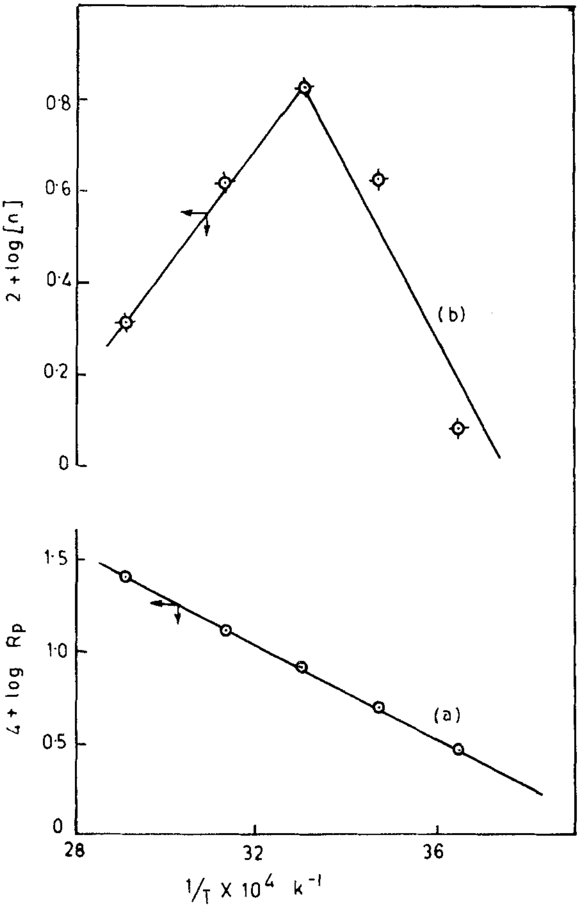

FIG. 6. Arrhenius plot for polymerization of IBVE by SK-500 molecular sieve, using 0.15 g of sieve and [IBVE] = 1.0 mol/L: (a) log R_p vs 1/T, and (b) log [η] vs 1/T.

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The following polymerization scheme is suggested for the system.

$$(\text{SK-500.H}_2\text{O}) \underset{k_2}{\overset{k_1}{\rightleftharpoons}} (\text{SK-500})\text{OH}^-\text{H}^+$$

Initiation:

$$(\text{SK-500})\text{OH}^-\text{H}^+ + \text{M} \xrightarrow{k_i} (\text{SK-500})\text{OH}^-\text{M}_1^+$$

Propagation:

$$(\text{SK-500})\text{OH}^-\text{M}_1^+ + \text{M} \xrightarrow{k_p} (\text{SK-500})\text{OH}^-\text{M}_2^+$$

$$\cdots$$

$$\cdots$$

$$(\text{SK-500})\text{OH}^-\text{M}_{n-1}^+ + \text{M} \xrightarrow{k_p} (\text{SK-500})\text{OH}^-\text{M}_n^+$$

Termination:

$$(\text{SK-500})\text{OH}^-\text{M}_n^+ \xrightarrow{k_t} \text{M}_n + (\text{SK-500.H}_2\text{O})$$

Transfer:

$$(\text{SK-500})\text{OH}^-\text{M}_n^+ + \text{M} \xrightarrow{k_{trM}} (\text{SK-500})\text{OH}^-\text{M}^+ + \text{M}_n$$

Monomer Specificity of SK-500

The polymerization initiating activity of rare earth exchanged Y sieves toward IBVE polymerization does not differ significantly from that of H-mordenite or H-faujasite. This may imply that polymerization through direct rare earth cation-monomer interaction due to stronger electrostatic field/potential surrounding the cations is not as important as the Brönsted acid initiation.

As to the monomer selectivity of SK-500, it has been found that N-vinylcarbazole and styrene, which are readily susceptible to cationic polymerization, polymerize in the order N-vinylcarbazole > IBVE > styrene under otherwise identical conditions. As in the case with H-mordenite or H-faujasite catalysts, the molecular weights in these systems are rather limited, the maximum degrees of polymerization of polystyrene and poly-N-vinylcarbazole being 27 and 37, respectively.

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