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Polymerization with Zeolite Catalysts

I. Polymerization of *n*-Butylvinylether by H-Mordenite

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n-Butylvinylether sorbed from the vapor phase onto hydrogen mordenite powder has been found to polymerize readily near room temperature. In a polymer sample from this reaction the polymer molecules were found to contain a number average of ten monomer units. The reaction over a considerable time interval followed the relations

$$Q_t = k\sqrt{t} + \gamma$$

$$k = (ap + b)F(H_2O)$$

where Q_t is the mass uptake (mainly as polymer) at pressure p in time t; k, γ, a and b are coefficients and $F(H_2O)$ is a function of the amount of water in the zeolite. The kinetics have been taken to indicate partial control by a diffusion process in which the monomer penetrates a growing layer of polymer formed around each catalyst particle. The monomer migrates to the catalyst–polymer interface and polymerizes at or near the interface. In small quantities water functioned as a cocatalyst, but around 5% weight uptake $F(H_2O)$ passed through a maximum. The rate of the reaction appeared to reach a maximum between 28 and 30°C. A carbonium ion mechanism of polymerization is proposed.

INTRODUCTION

Good adhesion between filler particles and polymer matrix is an important requirement in most composites. If polymerization of monomer can be effected in situ around the filler particles and if these particles, for example, molecular sieves, are suitably porous then polymer chains might grow into the crystals and improve adhesion. In situ polymerization might be effected by mixing an outgassed filler with monomer and adding an initiator; or one could try to use the filler as a polymerization catalyst (*1*). In the present work the second approach was investigated, using molecular sieve crystals as fillers and potential catalysts. In such crystals the type and location of cation, silicon-to-aluminium ratio and presence of proton donors may be important factors in catalysis (*2–4*).

Hydrogen mordenite was chosen as one possible catalyst. The crystal structure of mordenite is known (*5, 6*). Wide channels, which if devoid of metal ions have free dimensions of 6.7–7.0 Å, run parallel to the c axis. These free dimensions are found in hydrogen mordenite (*7*), although not in its Na, Ca, or Ba forms (*8–10*). The monomer investigated was *n*-butylvinylether which should be readily imbibed by hydrogen mordenite and have access to catalytic sites both at the surface and within the crystal.

EXPERIMENTAL

The reaction was followed gravimetrically with silica spring balances. A set of eight balances was constructed each with a separate manometer. Every balance and manometer was housed in a separate air thermostat in which the temperature variation of interest was within ±0.2°C. The zeolite samples, of about 0.1 g, were placed in small glass buckets suspended from the calibrated silica springs. The crystals were outgassed for 7 days at temperatures rising to 360°C, using removable tubular furnaces which fitted over the balance cases. The *n*-butylvinylether was freshly distilled before admission as vapor from a reservoir of its liquid through the vacuum line to the balance cases. The air thermostats were set at various appropriate temperatures and the reservoir containing the monomer was also thermostatted. This served to maintain a constant but adjustable vapor pressure of monomer in the balance cases.

Three sets of experiments were performed: (i) the air thermostats were set at 30°C and the vapor pressure of monomer in contact with the catalyst was systematically altered; (ii) the vapor pressure of monomer was held constant while the temperature of the catalyst was systematically changed between 22 and 50°C; and (iii) at constant temperature (30°C) and vapor pressure of monomer (1.26 cm Hg) the amount of water in the zeolite was altered in steps from zero upwards. The regulated amount of water was admitted to the zeolite at 30°C and the zeolite was then heated to ~135°C for 24 hr followed by slow cooling of the sample to 30°C. This treatment helped to distribute the intracrystalline water as uniformly as possible.

RESULTS

Hydrogen mordenite proved to be a good catalyst for the polymerization of *n*-butylvinylether. Figure 1 shows the fractional mass increase at time t, Q_t, as a function of $\sqrt{t}$. The temperature was 30°C and the constant pressures were changed

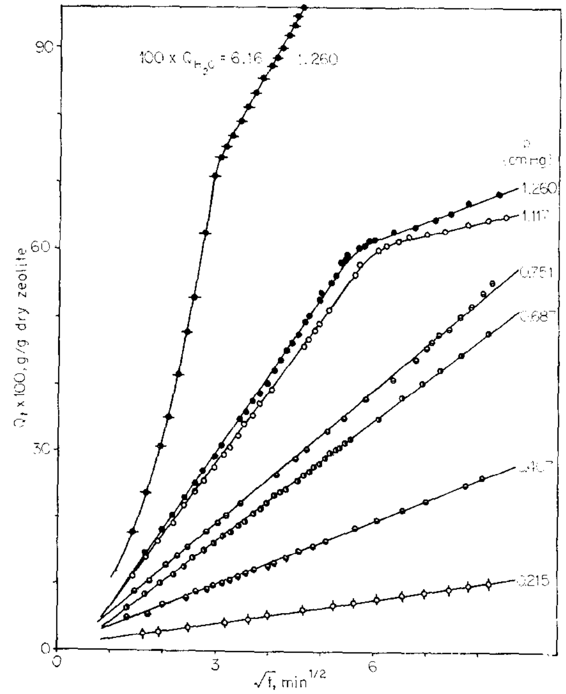


FIG. 1. The mass increase due to monomer uptake, Q_t vs $\sqrt{t}$, where t is the time in minutes. For comparison, the kinetic curve for a zeolite containing 6.16% water (w.r.t. mass of dry zeolite) is also shown. The reactions were carried out at 30°C at the several constant vapor pressures of monomer indicated at the top right of each curve.

systematically between 0.2 and 1.3 cm Hg. Over a considerable range in time t the measurements obeyed the relationship

$$Q_t = k\sqrt{t} + \gamma, \tag{1}$$

where k and γ are coefficients. The nonzero values of γ are due to the experimental difficulty of establishing instantly the constant pressure of monomer over the catalyst. After a certain period of time and for larger uptakes, the curves showed a break and a second line

$$Q_t = k_1\sqrt{t} + \gamma_1 \tag{2}$$

tended to be followed (lines for $p = 1.117$ and 1.260 cm Hg in Fig. 1).

As illustrated in Fig. 2, the coefficients k were very good linear functions of pressure

$$k = ap + b, \tag{3}$$

where a and b are coefficients. Where two straight lines were obtained in Fig. 1 [Eqs. (1) and (2)], k for that having the greater slope (Eq. 1) is plotted in Fig. 2.

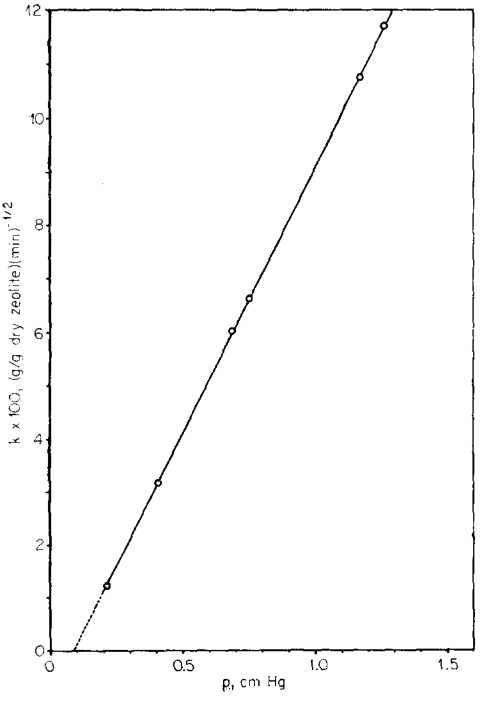


FIG. 2. The slopes of k of the curves in Fig. 1 vs monomer vapor pressure, p.

TABLE 1
EFFECT OF TEMPERATURE ON THE RATE CONSTANTS a

Set	t, °C	$k \times 100$[a]	p, cm Hg	$a \times 100$[b]
A1	25.0	12.72	1.430	9.6
A2	30.0	11.68	1.260	10.0
A3	38.5	11.63	1.450	8.6
A4	47.2	9.09	1.375	7.3
B1	22.9	7.47	1.273	6.6
B2	28.2	13.86	1.354	10.9
B3	39.4	10.93	1.354	8.8
B4	43.2	8.28	1.273	7.3

[a] The unit for k is (g/g dry zeolite) (min)$^{-1/2}$.

[b] a was calculated by taking $b = -0.9786 \times 10^{-2}$ (g/g dry zeolite)(min)$^{-1/2}$. Thus we have assumed b to be constant w.r.t. temperature. The unit for a is (g/g dry zeolite)(cm Hg)$^{-1}$(min)$^{-1/2}$.

The influence of temperature is shown in Tables 1 and 2. Columns 3 of each table record the values of k or k_1 and columns 4 give the corresponding pressures. Column 5 of Table 1 gives the constant a of Eq. (3), calculated assuming that b was temperature-invariant; the same column in Table 2 gives k_1/p. The constants a tend to show a maximum value in the range 28–30°C, while k_1/p goes through a minimum near 39°C.

The effects of sorbed water upon the kinetics are shown in the curve at the left of Fig. 1 and in Fig. 3. As the amount of zeolite water increases the kinetics change. The first straight line of Eq. (1) is replaced by a curve with an upward inflexion. The break after which the second straight line of Eq. (2) appears becomes less pronounced and at the highest water loading the plots of Q_t vs $\sqrt{t}$ are sigmoid. The initial rates of reaction were expressed as the mean

TABLE 2
EFFECT OF TEMPERATURE ON THE SLOPE OF THE SECOND LINE

Set	t, °C	$k_1 \times 100$[a]	p, cm Hg	$(k_1/p) \times 100$
A1	25.0	2.89	1.430	2.023
A2	30.0	2.29	1.260	1.818
A3	38.5	1.59	1.450	1.098
A4	47.2	2.02	1.375	1.474

[a] The unit for k_1 is (g/g dry zeolite)(min)$^{-1/2}$.

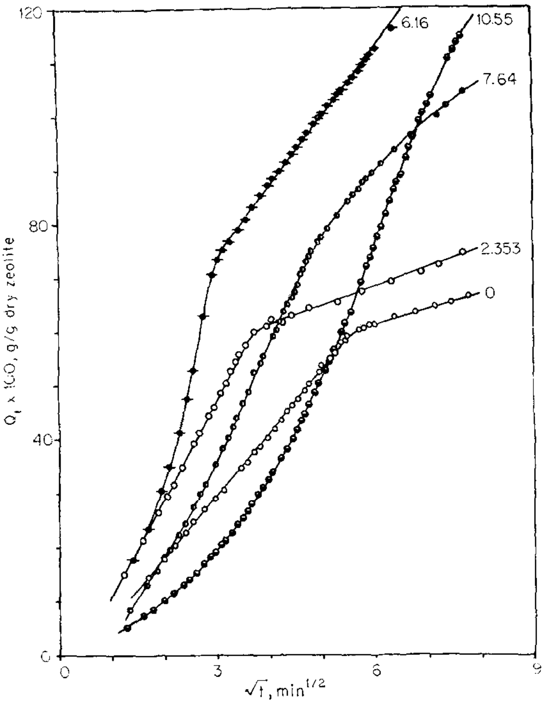


FIG. 3. Typical kinetic curves of Q_t vs $\sqrt{t}$ obtained with H-mordenite having different amounts of water. Temperature of reaction: 30°C. Monomer vapor pressure: 1.260 cm Hg. The figures at the top right hand side of the curves give the water contents of the zeolite [(g/g of dry zeolite) × 100].

slopes of the first parts of the curves of Fig. 3. In the case of the curve with 10.55 wt % of added water the mean slope was evaluated for the interval $1.2 < \sqrt{t} < 2.4$ min$^{1/2}$. The results are presented in Fig. 4, and indicate that a maximum value occurs around 4–6 wt % of zeolite water.

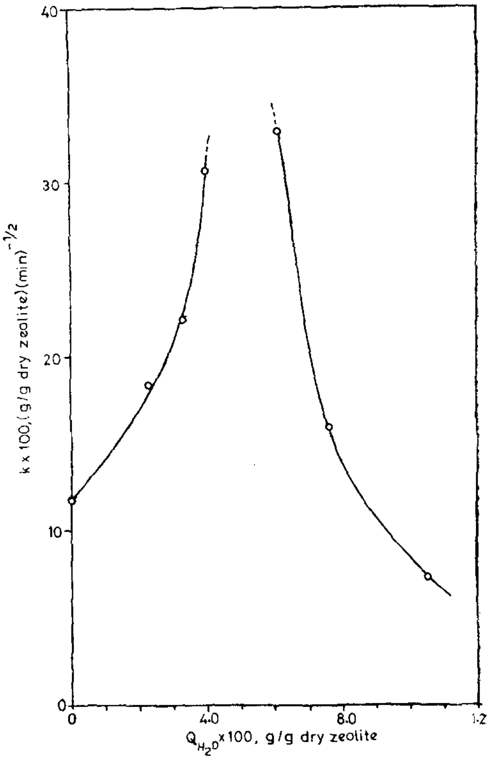


FIG. 4. The rate constant k as a function of the water content of the zeolite.

DISCUSSION

Interpretation of Polymerization Kinetics

The form of Eq. (1) suggests that the reaction is partially diffusion controlled. As soon as the first polymer forms, it coats the surface of each catalyst crystal with a film which increases in thickness as the reaction proceeds. The monomer reaches the catalytic centers on the surface of the zeolite (or within the zeolite) by dissolving in the polymer and diffusing through it to the catalyst. A one-dimensional analog of such a process is represented by tarnishing reactions at plane metal surfaces. Oxygen replaces the monomer and the coherent oxide film the polymer. With the boundary conditions for monomer

$$\left.\begin{array}{ll} C = C_0 \text{ at } x = 0 & \text{for all } t \\ C = 0 \text{ at } x = X(t) & \text{for } t > 0 \end{array}\right\}, \quad (4)$$

where $x = 0$ is the interface between the vapor and polymer and $x = X(t)$ is the interface between the polymer and zeolite crystals, one obtained for the one-dimensional diffusion and for the amount of polymer formed (*11*)

$$Q_t = AX(t) = 2A\alpha(Dt)^{1/2}, \quad (5)$$

where A is the area of the film and α is defined by

$$C_0 = \pi^{1/2}\alpha \exp \alpha^2 \operatorname{erf} \alpha. \quad (6)$$

C_0 in Eq. (6) is the concentration of the monomer at the outer surface of the film, expressed as mass of monomer per unit mass of polymer, and D is the constant diffusion coefficient of monomer in polymer.

In the polymerization reaction, the condition $C = 0$ at $x = X(t)$ may not be satisfied, since this condition implies that the polymerization at the interface is so much faster than the diffusional flow that the kinetics are totally controlled by the slow diffusion step. However, the cocatalysis by water, considered later, suggests an influence of the chemical rate process. Also D will not be constant but a function of monomer concentration in the polymer and diffusion is more nearly radial than linear. Nevertheless, Eqs. (5) and (6) provide a physical basis for linear plots of Q_t vs $\sqrt{t}$. They also show that α should be a function of C_0 and hence of pressure. For small values of α, $\exp \alpha^2 \operatorname{erf}\alpha \to 1$ and so α and C_0 are proportional. If, therefore, C_0 and p are also proportional, conditions for the linear dependence of k upon p (cf. Fig. 2) are approached. These criteria oversimplify since the plot of k vs p does not pass through the origin.

The breaks in the plots of Q_t vs t (Fig. 1) have their most probable explanation in a change in the physical configuration of the polymer film once the amount of the film has increased sufficiently. Instead of coating each catalyst particle separately the tacky films cohere under surface tension forces and reduce the area A through which monomer diffuses to the catalyst surfaces. It is of interest that the region of discontinuity corresponded approximately with the time at which the polymer films on the zeolite became clearly visible.

The Influence of Temperature

Temperature affects the rate of reaction in a rather complex way (Tables 1 and 2). In a diffusion-controlled mechanism, the temperature coefficients of D and α in Eq. (5) should determine the behavior. D increases with temperature but α, if proportional to C_0, will at constant pressure decrease because solution of monomer vapor in the polymer is exothermal. In view of the several approximations involved in applying Eq. (5) to the present systems, the exact net result of these opposing influences is not readily evaluated.

Cocatalysis by Zeolite Water

The acceleration of reaction rate by smaller amounts of sorbed water would not be expected if the reaction in absence of water was wholly controlled by diffusion of monomer through the polymer. This means that the boundary condition

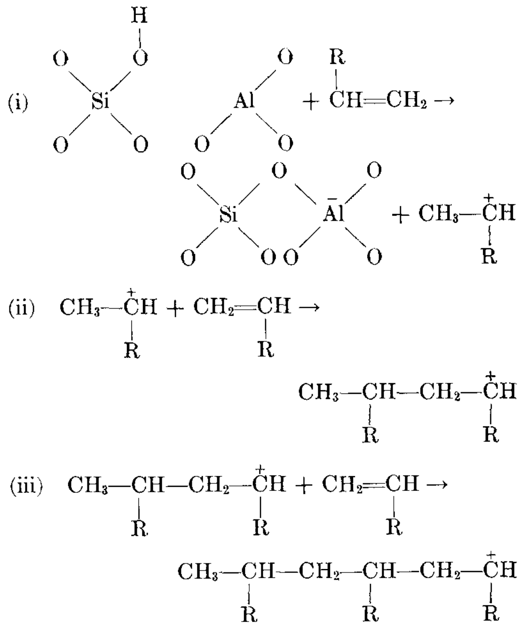
$$C = 0 \text{ at } x = X(t) \text{ for } t > 0$$

may, as already noted, be incorrect, and both diffusion and polymerization may occur at comparable rates. However, the faster the polymerization the more nearly will diffusion exert full control over the total observable rate and the more nearly will the above boundary condition be satisfied.

The initial catalytic effect of water as shown in Fig. 4 declines above about 5% by weight (g/g of dry zeolite). In part this behavior could indicate that polymerization on the water-free catalyst occurs not only at the polymer–catalyst interface but also at sites within the crystals. Intracrystalline sites are less accessible and therefore less effective than those at the surface. In particular, as the amount of zeolite water increases the intracrystalline channels become blocked and hence still less accessible, so that the overall rate of polymerization decreases. Also the water molecules, if present in excess, may by preferential adsorption at surface sites block access of monomer to the active centers on the surface.

Mechanism of Catalysis

Controversy still exists concerning the source of activity and the nature of active sites in zeolites. One view is that both Brønsted and Lewis acid sites are required, with optimum activity coinciding with equal numbers of each (*12, 13*). Hydrogen mordenite is rich in adjacent Lewis and Brønsted acid sites. A feasible reaction mechanism for the system involves proton transfer from the Brønsted acid sites to the monomer to give carbonium ions, followed by polymerization:

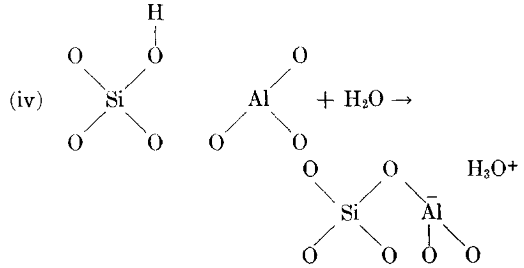


$$\text{(ii)}\quad CH_3\text{—}\underset{R}{\overset{+}{C}H} + CH_2{=}\underset{R}{CH} \rightarrow CH_3\text{—}\underset{R}{CH}\text{—}CH_2\text{—}\underset{R}{\overset{+}{C}H}$$

$$\text{(iii)}\quad CH_3\text{—}\underset{R}{CH}\text{—}CH_2\text{—}\underset{R}{\overset{+}{C}H} + CH_2{=}\underset{R}{CH} \rightarrow CH_3\text{—}\underset{R}{CH}\text{—}CH_2\text{—}\underset{R}{CH}\text{—}CH_2\text{—}\underset{R}{\overset{+}{C}H}$$

. . . etc.

In the above reactions R = n-butoxide. The zeolitic water in presence of the Brønsted sites may also yield some hydronium ions by proton transfer:



and the hydronium ions by proton transfer can yield carbonium ions of the kind seen in reaction (i), followed by reaction (ii), (iii), etc. The cocatalytic action of water can be understood if reaction (iv) followed by proton transfer from hydronium ion to the monomer occurs more readily than the direct transfer according to reaction (i).

In a sodium mordenite of unit cell composition (*5*, *6*) $Na_8\,[Al_8\,Si_{40}\,O_{96}]24H_2O$ the ideal outgassed hydrogen form should have 1.61×10^{21} Brønsted acid sites per gram of dry zeolite. The maximum reaction rate corresponds with $\sim 1.7 \times 10^{21}$ molecules of water added to the zeolite. This quantity of water is just sufficient to convert the hydrogen mordenite to hydronium mordenite. Such agreement could be fortuitous. Nevertheless, if this is the explanation of the cocatalysis by water it should have general validity. That is, maximum reaction rates should appear in other hydrogen zeolite catalysts when the water added is equal to the number of Brønsted acid sites. This property is being examined with the hydrogen form of zeolite *Y*.

Additional Observations

The polymerization continued indefinitely with slowing down over the later stages as the polymer accumulated in quantity. Some darkening of the catalyst was observed which was attributed to a side reaction involving carbon deposition. The polymer, even when outgassed to remove monomer, remained tacky and did not, for n-butylvinylether, harden on heating at about 100°C.

The tackiness of the polymer suggests a rather low molecular weight. A sample prepared at 30°C and 1.26 cm pressure of monomer vapor was extracted with chloroform and the latter as well as any monomer was removed by evacuation. The molecular weight of the polymer obtained was then determined by means of a Hewlett-Packard Vapor Pressure Osmometer (Type 300-B) using chloroform as solvent. A number average value of ~990 was obtained, indicating a mean value of ten monomer units per polymer molecule.

In order to find out how far the presence of polymer changes the uptake of zeolitic water, and hence whether the polymer exists in the intracrystalline channels, water sorption isotherms were measured at 30°C on the zeolite alone and on zeolite samples with 6.37 and 15.82 weight per cent of polymer, respectively. The uptakes of water in g/g of dry zeolite are shown in Fig. 5. At low water vapor pressures the water sorption is significantly reduced by the presence of polymer. Thus there is some evidence from the low-pressure section of the isotherm, where sorption will

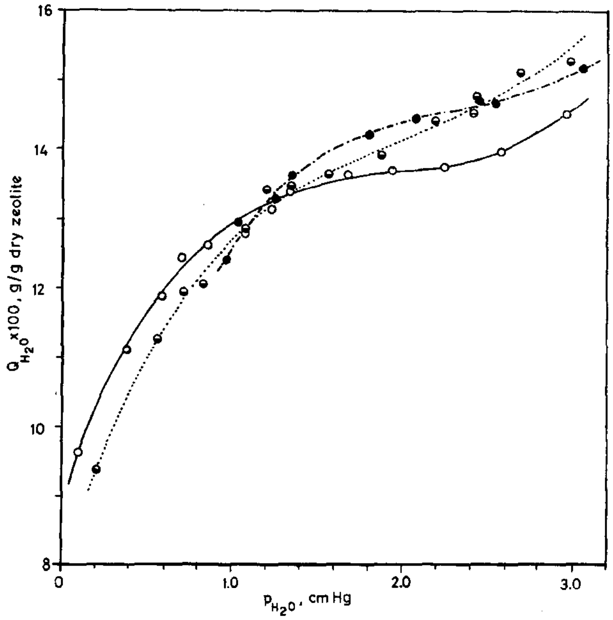


FIG. 5. The amount of water sorbed vs equilibrium water vapor pressure at 30.0°C for pure H-mordenite (○), and two composite samples with 6.37 (◒) and 15.82 (●) mass % polymer (w.r.t. mass dry zeolite).

be primarily intracrystalline, that a fraction of the channel space is not available to water in the polymer-bearing samples. However, the isotherms for pure hydrogen mordenite and for the mordenites with poly-(*n*-butylvinylether) cross at $p \sim 1.4$ cm Hg so that a second factor comes into play near and after the stage where available space in the intrazeolitic channels is expected to be filled. The sorption of water in the polymer-bearing mordenites includes any water sorbed by the polymer.

CONCLUSION

Near room temperature hydrogen mordenite is an interesting catalyst for polymerization of *n*-butylvinylether to polymers of rather low molecular weight. It seems likely that other vinylethers will also polymerize in the presence of hydrogen zeolites other than hydrogen mordenite. This aspect is at present being investigated.

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