

Cationic Polymers as Templates in Zeolite Crystallization

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Received August 18, 1977

Abstract: The ability of quaternary ammonium polymers to influence and to direct crystallization of zeolites is described for a series of 1,4-diazabicyclo[2.2.2]octane-based polyelectrolytes. Examples are shown in which polymers force crystallization of large-pore zeolites (mordenite) where small-pore species would otherwise have resulted (analcite). It is shown that polymeric cations can prevent stacking faults in a synthetic gmelinite, faults which have hitherto restricted access to the 12-ring channels of both natural and synthetic samples of this zeolite. It is proposed that these polyelectrolytes function as templates in the crystallization.

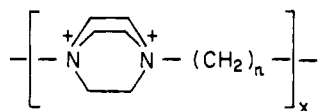
Introduction

In the synthesis of zeolites, cation distribution in the crystallization mixture strongly influences the product obtained. Flanigen recently reviewed the literature on template effects by cations in zeolite crystallization and identified a correlation between sodium, potassium, and possibly tetramethylammonium (TMA) cations and the structural building units of resultant aluminosilicate frameworks.¹ Except for TMA, however, the role of organic cations in directing crystallization is a topic open to debate. Numerous quaternary ammonium cations have been studied and a large number of new zeolites have been obtained, but in general there is little evidence in the literature that these organic cations (other than TMA) function as templates.

Quaternary ammonium polymers represent an unexplored, special class of organic cations in that a growing crystal must accommodate not just a single cation but a complete, linked chain of defined structure. It was with this thought in mind that a series of polymers was prepared and studied for effects in zeolite crystallization.

The synthesis of quaternary ammonium polymers dates back to the 1930s.^{2,3} Recently, a renewed interest in such polyelectrolytes has been reported and the generic term "ionene polymers" was applied to this class of materials.⁴ These ionene polymers, which have shown useful antimicrobial and antifungal properties, as well as clay (kaolin) flocculating abilities, have been reported to have molecular weights as high as 87 000.⁵ Most were synthesized by direct reaction of monomeric ditertiary amines with α,ω -dibromides, recognizing the low reactivity of dibromoethane and the tendency toward side reactions in short-interval or high charge density polymers.⁶

For the present example, polymers were synthesized by reaction of 1,4-diazabicyclo[2.2.2]octane (Dabco) with the compounds $\text{Br}(\text{CH}_2)_n\text{Br}$, where $n = 3, 4, 5, 6,$ and 10 .⁷ The products had a structure as shown, and were designated by the



bromide used. With 1,4-dibromobutane, for example, the polymer was designated "Dab-4Br".

Two zeolites will be central to the discussion, gmelinite and mordenite, both large-pore structures whose channels are defined by 12-membered rings ("12-rings") of SiO_4 and AlO_4 tetrahedra.¹¹ In their sorptive properties, however, both natural and synthetic gmelinites behave like small-pore zeolites, a behavior attributed to chabazite stacking faults. Chabazite fault planes, observable by x-ray diffraction, effectively block or restrict access to the large gmelinite channels.¹³ Reported

attempts to synthesize a pure (chabazite- or fault-free) gmelinite have failed,¹⁴ but it is recognized that substantial changes in sorptive properties should result if these fault planes could be eliminated.

Mordenite is a second 12-ring zeolite whose sorptive properties do not always correspond to expectations based on structure. Two synthetic types of mordenite have been reported by Sand, "large-port" and "small-port" mordenite.¹⁵ The former, synthesized from only a narrow range of reaction mixture compositions, exhibits the sorptive properties expected of a 12-ring channel (having a diameter of 7–8 Å). The latter, first synthesized and studied by Barrer,¹⁸ has an adsorption diameter of only about 4 Å. It is indistinguishable from large-port mordenite by x-ray diffraction and may coexist with dense structures such as analcite. Sorptive properties will thus be central in the characterization of the zeolites obtained and in an identification of the role played by the polyelectrolytes in the following experiments.


Experimental Section

Polymers were synthesized according to the procedures developed by Salamone and Snider.⁷ Monomer concentration was high and initial reaction temperature was low in order to maximize polymer chain length.⁸ For example, 92 g (0.82 mol) of Dabco was dissolved in 800 mL of dimethyl sulfoxide (Me_2SO) at 45 °C. To this stirred solution 177 g of 1,4-dibromobutane (0.82 mol) was added dropwise over a period of about 20 min. The temperature was controlled with cooling to below 70 °C. After 1 h the temperature was raised to 110 °C and maintained for 6 h. Stirring was stopped and the mixture was left to cool overnight.

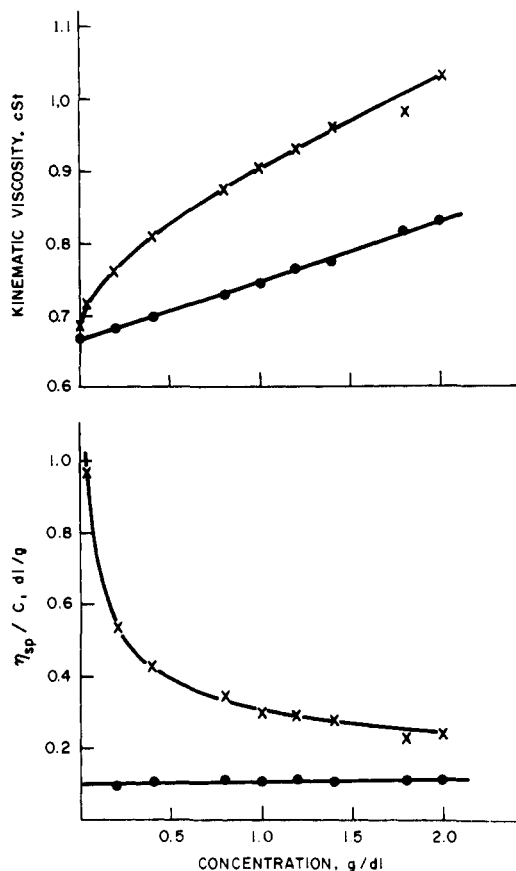
The resulting solid was filtered and was exhaustively extracted with ether (~10 L), then methanol, and again ether until the solid contained less than 0.2% sulfur. (The initial polymer occluded copious quantities of Me_2SO and was soluble in methanol, whereas the purified polymer was not.) After air drying the material was a fine white or faintly yellow, nontacky powder. The monomeric analogues, Dab-Pr₂ and Dab-Bu₂, were prepared by reaction of 1-iodopropane and 1-iodobutane, respectively, with Dabco in absolute ethanol.

When purified, both monomers and polymers contained bromide (or iodide) and nitrogen in the molar ratios of $\text{Br}(\text{I})/\text{N} = 0.95\text{--}1.06$, as compared with a theoretical value of 1.0. The C/N ratios, with calculated values in parentheses, follow: Dab-3Br, 4.68 (4.50); Dab-4Br, 5.07 (5.00); Dab-5Br, 5.56 (5.50); Dab-6Br, 5.85 (6.00); Dab-10Br, 8.17 (8.00); and Dab-Pr₂, 6.10 (6.00). As found by Salamone and Snider⁷ the polymers absorbed and retained about 10% water during purification. All polymers were highly soluble in water (some as much as 2 M) and, in keeping with their ionic nature, were readily precipitated by added bromide salts. Proton chemical

Table I. Chemical Shifts for Ionene Polymers 10% in D₂O, vs. DSS^c

Polymer		NCH ₂ CH ₂ CH ₂		
Dab-3	4.2	3.8	<i>a</i>	
Dab-4	4.1	3.8	2.0	
Dab-5	4.1	3.7	2.0	
Dab-6	4.1	3.7	1.9	
Dab-10	4.0	3.6	1.8	
Dab-Pr ₂ ^b	4.0	3.6	1.8	
Dab-Bu ₂ ^b	4.0	3.5	1.7	

^a Too broad and too weak for measurement. ^b Monomer, terminal methyl group. ^c 2,2-Dimethyl-2-silapentane-5-sulfonate, sodium salt.

**Figure 1.** Kinematic and reduced viscosities of Dab-6Br, 38 °C. Dots are in 0.4 M KBr; crosses in distilled water.

shifts were measured on a Varian T-60A NMR spectrometer. Kinematic viscosity was determined by ASTM procedure D-445 (38 °C).

Crystallization experiments were conducted at 85–90 and at 170–180 °C in polypropylene and in Teflon FEP bottles, respectively. Experiments at the higher temperature were conducted in an autoclave, several crystallizations being performed simultaneously to ensure uniform temperature for comparison.

Gels were prepared by mixing 30% silica sol with aqueous solutions of polymer and of NaOH and NaAlO₂. The polymer solution was combined with the silica sol prior to addition of the aluminate solution. The procedures for preparing the reaction mixtures are described by the following example: To 100 g of 30% silica sol (MCB or Du Pont Ludox, 0.50 mol of SiO₂) were added solutions of 23.2 g of Dab-4Br (0.14 equiv) in 67 mL of H₂O and of 21.5 g of NaOH (0.54 mol) and 4.5 g of

Table II. Viscosity Data and Molecular Weight Estimates of Dabco-Based Polyelectrolytes

Polymer	<i>M_v</i>	<i>M_w</i>
Dab-3Br	1400	2500
Dab-4Br	>6000	10 100
Dab-5Br	>6000	15 400
Dab-6Br	6100	9900
Dab-10Br	2100	5500

NaAlO₂ (0.05 mol of NaOH, 0.017 mol of Al₂O₃) in 50 mL of H₂O. After mixing, the gel was placed in a chest at 90 °C to crystallize.

Samples were taken periodically, filtered, washed, dried, and analyzed by x-ray diffraction. After 9 days the diffraction pattern showed no amorphous material and the intensity of the reflections had ceased to grow. The entire mixture was filtered, boiled in 100 mL of water, filtered, washed, and dried under a heat lamp to yield about 9 g of zeolite.

Zeolite products were characterized by elemental analysis and by x-ray powder patterns (Siemens diffractometer).¹¹ Their sorptive capacities and thermal properties were determined on a Du Pont Model 951 thermogravimetric analyzer. Reaction mixture compositions were defined by molar (or equivalent) ratios of the materials employed. The above example would be described by the ratios, SiO₂/Al₂O₃ = 30, H₂O/SiO₂ = 21, OH/SiO₂ = 1.2, Na/SiO₂ = 1.2, R/SiO₂ = 0.28, where R represents quaternary cation.

Results

Polymers. NMR spectra of the polymers clearly showed the changing structure of the materials, as listed in Table I. In addition to the ever-present Dabco protons at about 4.1 ppm, the protons on the α, β, and γ+ carbons linking these Dabco units were observed at 3.7, 1.9, and 1.5 ppm, respectively. The intensities of the 1.5-ppm absorption increased with increasing interval between nitrogen atoms (increasing number of protons three or more carbons removed from the Dabco moiety). The polymer spectra showed two noteworthy characteristics, a shift to higher field with increasing interval between charges (attributed to conformational effects within the polymer chain⁹) and a line broadening not found with monomers.

Viscosity behavior provides the most direct measure of the molecular weight of a polyelectrolyte, and kinematic viscosity data with and without added salt were obtained on all samples. Figure 1 shows these data for one example, the Dab-6Br, both as measured and when normalized for concentration [to yield reduced viscosities, η_{sp}/c , where $\eta_{sp} = (\eta - \eta_0)/\eta_0$].

In the absence of added salt, viscosity-average molecular weights, *M_v*, were calculated from the relationship⁵

$$M_v \approx (1.9 \times 10^3) \sqrt{A} \quad (1)$$

where *A* was obtained from the concentration dependence of the reduced viscosity (Fuoss' equation, ref 10).

When the charge on a polyelectrolyte was neutralized by addition of salt, weight-average molecular weights, *M_w*, were estimated from intrinsic viscosities [η] using the equation^{5,10}

$$[\eta] \approx 4 \times 10^{-4} M_w^{0.6} \quad (2)$$

As shown in Table II, molecular weights of the polymers studied were in the range 5000–15 000 (except for Dab-3Br).

It should be noted that the monomeric species, Dab-Pr₂ and Dab-Bu₂, showed a completely different behavior. Intrinsic viscosities were zero, and reduced viscosities were not concentration dependent. Such behavior is that expected for monomer salts.

Table III. Zeolite Crystallization Experiments with Polyelectrolytes: Silica Sol, 85–90 °C, SiO₂/Al₂O₃ = 30, H₂O/SiO₂ = 21, OH/SiO₂ = 1.2, Na/SiO₂ = 1.2, Unless Noted

Run	Reaction mixture			Product			Notes
	R	R/SiO ₂	Days	Zeolite	SiO ₂ /Al ₂ O ₃	R ₂ O/Al ₂ O ₃	
1		0	4	Y + P	3.91		
2		0	4	Y + P	3.61		Na/SiO ₂ = 1.4
3		0	11	Y + P	3.69		Na/SiO ₂ = 1.8
4		0	10	Y + P	4.41		Na/SiO ₂ = 1.4, H ₂ O/SiO ₂ = 44
5	Dab-4Br	0.01	9	Gmelinite + chabazite			
6	Dab-4Br	0.14	5	Gmelinite + chabazite	5.15	0.15	
7	Dab-4Br	0.23	9	Gmelinite only	7.05	0.43	
8	Dab-4Br	0.43	60	Amorphous			
9	Dab-4Br	0.24	7	Gmelinite only	5.52	0.44	H ₂ O/SiO ₂ = 44
10	Dab-4Br	0.11	3	Gmelinite only	5.78	0.33	SiO ₂ /Al ₂ O ₃ = 15
11	Dab-4Br	0.23	13	Gmelinite only	5.69	0.25	SiO ₂ /Al ₂ O ₃ = 15
12	Dab-4Br	0.11	13	Gmelinite + chabazite			SiO ₂ /Al ₂ O ₃ = 75
13	Dab-3Br	0.24	7	P	5.21	0.04	H ₂ O/SiO ₂ = 44
14	Dab-4Br	0.24	9	Gmelinite only	5.97	0.56	H ₂ O/SiO ₂ = 44
15	Dab-5Br	0.24	7	Gmelinite + chabazite	5.29	0.24	H ₂ O/SiO ₂ = 44
16	Dab-6Br	0.24	9	Gmelinite + chabazite	4.69	0.12	H ₂ O/SiO ₂ = 44
17	Dab-10Br	0.24	9	Y + P			H ₂ O/SiO ₂ = 44
18	Dab-Pr ₂	0.24	6	Y + P ^a	4.51	0.03	H ₂ O/SiO ₂ = 44
19	Dab-Bu ₂	0.24	6	Y + P ^a	5.24	0.01	H ₂ O/SiO ₂ = 44
20		0	7	Analcite			170–180 °C
21	Dab-4Br	0.11	7	Analcite	5.37	0.01	170–180 °C
22	Dab-4Br	0.23	7	Analcite + mordenite	8.46	0.16	170–180 °C
23	Dab-4Br	0.43	7	Mordenite only	20.8	0.40	170–180 °C
24		0	7	Analcite			170–180 °C, Na/SiO ₂ = 1.5

^a Trace chabazite.

Zeolites. Crystallization experiments are detailed in Table III. An initial survey of reaction mixture compositions was made at 85–90 °C to identify conditions for facile crystallization, using the synthesis of Y as a criterion.¹¹ As shown in runs 1–4, neither addition of salt (NaBr was used in amounts equivalent to the polyelectrolytes to be tested) nor dilution altered the zeolites obtained. That two zeolites, Y and P, were produced was expected since it is well known that both may form in the same overall composition field, their respective amounts depending on relative nucleation and growth rates.¹² The significant point is that *only* these two zeolites were observed in these polymer-free, low-temperature experiments.

The subsequent experiments in Table III show the effects of polyelectrolytes and can be summarized as follows:

(1) Even small amounts of polymer can produce a completely different product zeolite. Addition of Dab-4Br at R/SiO₂ = 0.01 yielded a mixture or an intergrowth of chabazite and gmelinite.

(2) The effectiveness of polymers in producing large-pore structures increases (up to some optimum) with increasing concentration. With Dab-4Br, pure gmelinite was obtained at R/SiO₂ = 0.23. (Figure 2 presents the x-ray pattern of pure gmelinite. The three most intense lines of chabazite, if it had been present, would have been at 9.4, 15.9, and 20.4° 2θ.)

(3) Effectiveness in the synthesis of a specific zeolite framework is dependent upon polymer structure. Dab-4, -5, and -6 produced gmelinite (in varying degrees of purity) while Dab-3 and -10 and the monomers had essentially no effect.

(4) These effects, to direct crystallization of large-pore structures, are not specific to a single phase such as gmelinite. At 170–180 °C, the product shifted from analcrite (small-pore) to mordenite (large-pore) on addition of increasing amounts of Dab-4Br.

Compositions of the gmelinite and mordenite samples prepared with Dab-4Br are listed in Table IV and confirm both

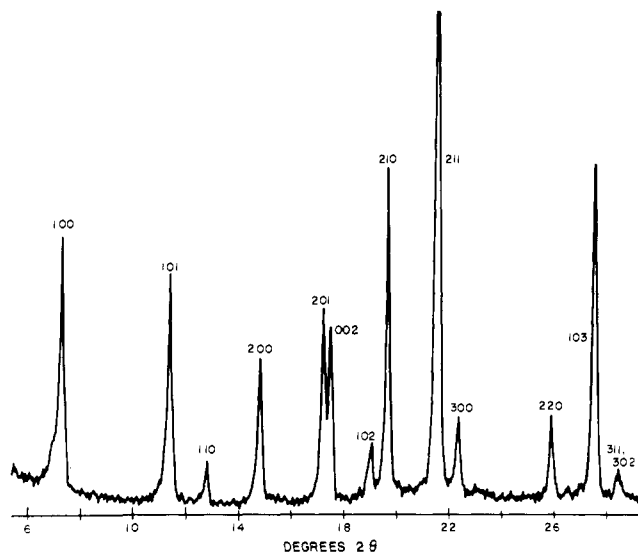


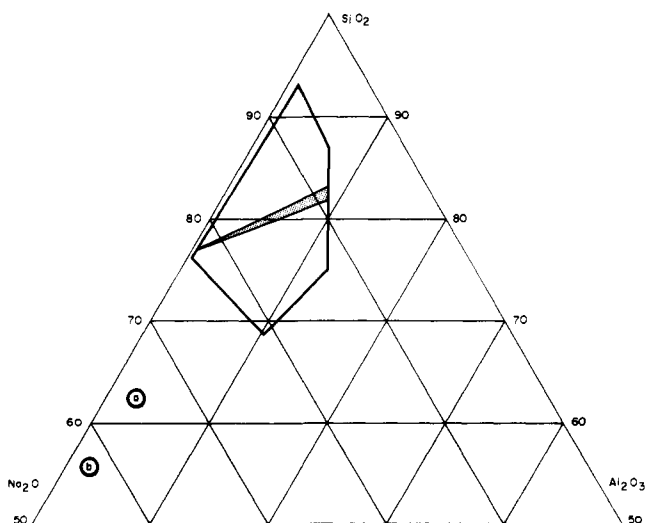
Figure 2. X-ray diffraction pattern of Dab-4 gmelinite. Lattice parameters are $a = 13.71$ and $c = 10.07 \pm 0.03$ Å.

the presence and the structure retention of the polymer. On the average, quaternary nitrogen accounted for 34% of the cations in the product zeolite. The carbon/nitrogen ratio of the gmelinite samples provided evidence for structure retention of the polymer during the crystallization process. This ratio averaged 5.4, as compared with an analytical value of 5.07 for the Dab-4Br used. A higher C/N ratio, indicating some polymer degradation, was observed and was expected in the 170–180 °C mordenite preparations.

Cyclohexane sorption completes the evidence for a fault-free gmelinite. The synthesized, calcined zeolite sorbed 7.3% cy-

Table IV. Composition of Zeolites Prepared with Dab-4Br

Zeolite	SiO ₂ /Al ₂ O ₃	Al/uc	Na/uc	N/uc	C/N
Gmelinite	7.05	5.3	3.5	2.3	5.0
	5.52	6.4	4.2	2.8	6.3
	5.78	6.2	6.2	2.0	5.2
	5.69	6.2	5.4	1.6	6.1
	5.97	6.0	4.1	3.3	4.5
	6.71	5.5	3.3	2.1	5.2
Mordenite	5.31	6.6	4.4	2.0	5.6
	20.8	4.2	3.3	1.7	6.8

**Figure 3.** Conditions for producing large-port mordenite—dark wedge.¹⁵ Molar composition of Dab-4 mordenite preparations (a); plotted as equivalents of quaternary + sodium (b).

clohexane (25 °C, $p/p_0 = 0.67$), exhibiting an initial rapid sorption of 3.7% and reaching the limiting capacity of 7.3% in about 1 h. Helium did not rapidly desorb hydrocarbon from the loaded zeolite. For comparison a natural gmelinite (Na, Ca form) sorbed only 1.0%.¹⁶

The mordenite prepared was of the large-port variety, although, as shown in Figure 3, the reaction mixture composition was clearly outside the range defined in the literature.¹⁵ It was stable to calcination (550 °C overnight), yielding a product which readily sorbed cyclohexane (6.3%, 25 °C, $p/p_0 = 0.67$). Sand reported a value of 7.8% (weight) for benzene on large-port mordenite, corresponding to about 6.9% for cyclohexane.

Discussion

That only a small number of polymers were effective in the synthesis of gmelinite suggests the possibility of templating. In support of this suggestion is the fact that the product zeolite contained polymer, a polymer which could not have exchanged into the zeolite after crystallization because all conventionally prepared gmelinites contain stacking faults.

Further evidence for templating comes from a consideration of the size of these polymers as that size compares with the dimensions of the zeolite pore systems. Both the gmelinite and

the mordenite structures contain one-dimensional, 12-ring channels having crystallographic free diameters of 7–8 Å.¹⁷ A unit cell in each is traversed by a single 12-ring channel in the c direction for a distance of 10.0 (gmelinite) and of 7.5 Å (mordenite).

The Dabco unit is cylindrical with a diameter of ~6.1 Å, a diameter which would fit comfortably within the 7–8 Å dimensions of the channels. In length the repeating units of Dab-3, -4, -5, -6, and -10 measure 7.5, 8.7, 9.9, 11.0, and 14.5 Å. In other words, all of the polymers which effected gmelinite (or gmelinite-chabazite) synthesis had repeating units of about 9–11 Å, as compared with 10.0 Å for the gmelinite unit cell. The corresponding dimension in mordenite is 7.5 Å, as compared with 8.7 for the effective Dab-4 polymer. Thus the spatial requirements of the polymer are in good agreement with the volume available within the gmelinite and the mordenite pore system.

The next question involves the quantity of polymer retained by the zeolites. A repeating unit of the Dab-4 polymer contains 2 equiv of cations and extends ~8.7 Å. The unit cell of gmelinite contains a single 12-ring channel 10 Å in length and could therefore contain little more than two quaternary cations. The data in Table IV show an average of 2.3 N/unit cell. The mordenite unit cell, on the other hand, extends only 7.5 Å along the 12-ring channel and could accommodate even less quaternary. Analysis of Dab-4 mordenite (Table IV) shows 1.7 N/unit cell, in excellent agreement.

One final note is appropriate. If, as suggested by the above analysis, an entrapped polymer is extended more or less linearly within a zeolite channel, one should compare polymer length with zeolite crystal size. The products of these crystallizations were 0.2–1 nm in diameter as judged by SEM photographs. A Dab-4 polymer of molecular weight 10 000 would have an extended length of only about 0.06 nm. It is therefore impossible that a single polymer strand could traverse an entire crystallite particle.

Acknowledgments. Particularly appreciated has been the advice of I. J. Heilweil and G. H. Kuehl. Thanks go to J. E. Fontinell and R. R. Jones for their assistance in these experiments and to D. H. Olson for the SEM photographs.

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