

Novel Polyvinyl Ether–HY Zeolite Hybrid Materials: General Features

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The application of a specific surface-mediated cationic polymerization technique under well-defined reaction conditions yields a series of polyvinyl ether (PVE)–HY–zeolite hybrid materials containing polyenylium sequences. The key to the success of this synthetic approach is the use of a Na/HY–zeolite with a controlled Na/H ratio and a vinyl ether component ($\text{CH}_2=\text{CHOR}$) with selected size of the substituent R (ethyl, isobutyl, and cyclohexyl) or 2,3-dihydrofuran. The novel PVE–HY–zeolite hybrid materials display outstanding optical properties. The length of the polyenylium sequences is correlated with the size of the substituent on the vinyl ether component. The properties of the solid samples and the mechanisms of the structure transformation of the PVE chain inside the zeolite supercage were investigated by means of $^{13}\text{C}\{^1\text{H}\}$ CP-MAS NMR, UV–vis, and DRIFT spectroscopy, GC, and DTG measurements.

Introduction

The chemistry of nanocomposites and hybrid materials has become of considerable interest during the past decade as evidenced by novel monographies,¹ review articles,^{2–4} and original contributions.^{5,6} One field of study is the development of novel nanocomposites from zeolites and synthetic polymers.^{3,7} The encapsulation of polymers into inorganic hosts offers the opportunity to study optical and electrical properties of individual chains.^{8–11}

The penetration of flexible polymer chains into porous inorganic materials with narrow pore size distribution, i.e., zeolites or mesoporous silicas, is not a trivial process.^{3,7}

There are in principle two different synthetic strategies to put a polymer chain as guest into an existing zeolite channel that serves as the host:

(1) The polymer is dissolved in a suitable solvent and then adsorbed to the inorganic material.^{3,7} This procedure is the simplest one. The problem is that it is difficult to distinguish between the chains being adsorbed at the outside of the zeolite crystal and those inside the supercage.

(2) The polymer chain is synthesized by a host–guest polymerization inside the zeolite channel.

There are in principle two types of selectivity to take into account to achieve a host–guest polymerization. If the monomer reactants are too large to diffuse through the catalyst pores, no polymer is produced inside the pore. Restricted transition selectivity occurs when the propagation reaction is prevented because the corresponding transition state requires more space than is available in the cavity or pore. In catalysis a third selectivity type is known: the product selectivity. This occurs when of the formed products are too bulky to diffuse out of the zeolite. The product selectivity principle is reversed to yield polymer–zeolite hybrid materials. In acid catalysis the products can be converted again to less bulky products or can deactivate the catalyst. This latter option is important to understand the effects resulting from interactions between the guest polymers and the acidic host zeolite surface.

Host–guest polymerizations were successfully developed for the electropolymerization of aniline and pyrrole derivatives and radically induced polymerization of styrene in the presence of zeolites.^{8–11} Ionic polymerization processes have still not been reported for host–guest polymerizations. The cationic polymerization technique seems suitable because the generation of carbocations on zeolite materials is a well-established process in catalysis.^{11–16} The application of cationic polymerizations to synthesize polymer silica hybrid

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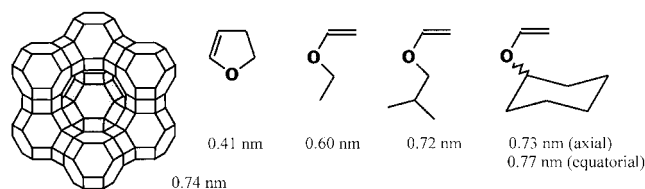
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Scheme 1. Dimension of the Gate of the HY Zeolite Host Compared to the Maximum Extension of the Vinyl Ether Components



particles has been reported for various cationically polymerizable monomers such as *p*-methoxystyrene,^{17,18} furfuryl alcohol,^{19–21} and cyclopentadiene.^{22,23} The use of photoinitiated cationic polymerization combined with sol–gel technique to produce novel organic–inorganic hybrid materials was reported by Crivello et al.^{24,25}

In this paper we will report on the cationic polymerizations of various substituted vinyl ethers at HY zeolites. The synthetic strategy was to use the zeolite supercage as both initiator and hybrid component. HY zeolites were selected because the penetration of the monomer into the gate of the zeolite was expected to be strongly controlled by the size of the monomer due to the similar size of the faujasite supercage. The size of the vinyl ether can be easily controlled by the substituents. The size of the gate of an HY zeolite is 7.4 nm (Scheme 1).

Enol ethers are electron-rich π -systems that are easily protonated by moderate solid acids.^{26,27}

Experimental Section

Materials. The NaY zeolite used was commercially available from Degussa AG (Frankfurt/Main). The exchange reaction of the NaY zeolite with protons was carried out using a 0.1 M ammonium nitrate solution. The HY zeolite was calcinated by heating at a rate of 1 K/min to 550 °C (kept for 5 h). HY-zeolite was dried carefully by heating to 400 °C for 24 h at a rate of 1 K/min. The sodium content of the calcinated HY zeolite was determined with the help of a HNO₃/HCl (1:1) treatment in a microwave oven. The specific surface of the HY zeolite was determined to 715 m² g⁻¹ by the BET method.

2,3-Dihydrofuran (DHF), isobutyl vinyl ether (IBVE), ethyl vinyl ether (EVE), and cyclohexyl vinyl ether (CHVE) (Aldrich, >99%) were dried over CaH₂, distilled, and stored under argon.

Dichloromethane was used as solvent for the synthetic procedure and for the UV–vis measurements. It was dried over CaH₂ and freshly distilled before use. The suspension of HY zeolite in this solvent is transparent, which allows UV–vis absorption spectra to be taken by means of an immersion cell with glass fiber optics under inert conditions.

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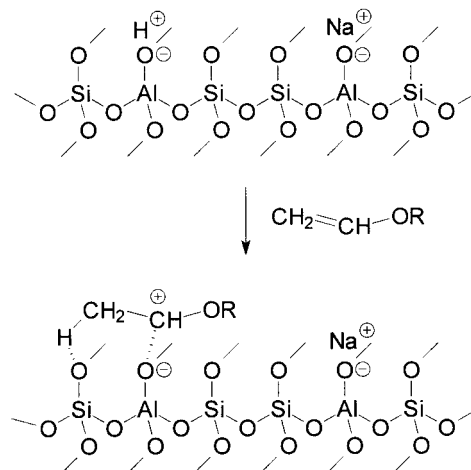
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Scheme 2. Part of the H/Na–Y Zeolite Framework^a



^a It is suggested that the VE is protonated and the resulting cation is stabilized by the framework.

Procedure. The dried HY zeolite (1.0 g) was poured into a flask under argon and immediately covered with 20 mL of dichloromethane. The resulting suspension was shaken for 5 min at room temperature, and the desired amount of monomer was added (0.1 to 3 mL). After continuous shaking for 24 h, the suspension was filtered and the filter residue was washed with 15 mL of dichloromethane three times. The colored polymer fraction could not be extracted from the HY zeolite. The organic fractions were combined and concentrated by rotary evaporation. The soluble polymers and the solid hybrid materials were dried in a vacuum.

Measurements. The equipment employed was an MCS 400 UV–vis spectrometer equipped with a TS 5A immersion cuvette (Zeiss).

The solution-state ¹³C NMR spectra (75 MHz) were recorded by use of a Varian 300 spectrometer. The chemical shifts were related to the solvent peaks used as internal standard (CDCl₃; $\delta = 77.0$ ppm). The solid state ¹³C{¹H}CP-MAS NMR spectra (75 MHz) of the solid hybrid materials were recorded by use of Bruker 300 equipment. We thank Dr. Komber, IPF Dresden, for his friendly cooperation.

Gel permeation chromatography measurements of the soluble polymer part were carried out at 25 °C under a pressure of 30 kPa using Knauer instrumentation with Ultrastaygel columns, THF as eluent, and polystyrene calibration.

The elemental analyses were carried out with a Vario EL from Elementaranalysen GmbH.

The IR measurements were carried out with a DRIFT unit for the FTS 165 spectrometer from Bio-Rad. The samples were measured as powders.

GC studies were carried out with a Shimadzu GC-14B and Class-VP 4.2. software. An HP-5 column was used to detect products derived from the polymerization of DHF, EVE, and IBVE. A DB–FFAP column from J&W Scientific was used to analyze the conversion products from CHVE.

SEM pictures were obtained by use of an SEM 515 from Philips with a voltage of 30 keV.

DSC was carried out by use of Perkin-Elmer equipment with a heating rate of 10 K/min from 30 to 150 °C.

The TGA 7 thermogravimetric analyzer used was from Perkin-Elmer. The heating rate was 10 K/min from 30 to 500 °C under helium.

Results and Discussion

Na/HY zeolite with a 70% (H) exchange ratio was used. The protonation reaction of the vinyl ether component by the Na/HY zeolite as discussed is shown in Scheme 2.

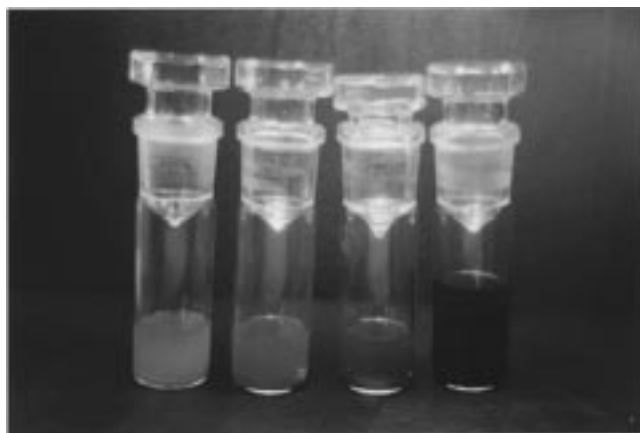


Figure 1. PVE-HY zeolite samples in dichloromethane after 24 h reaction time. From left to right: CHVE, DHF, IBVE, and EVE.

UV-Vis and GC Studies during Polymerization.

The zeolites become colored immediately after the monomers were added to the suspension of the carefully dried HY zeolite in dichloromethane. Completely colorless PVE is obtained in the solution phase. The structures of the soluble polymers were investigated by GPC as well as ^1H and ^{13}C NMR spectroscopy in each case. PVE structures without defects were confirmed in the soluble fractions in each case.²⁸ The M_n of the PDHF-soluble polymer fraction varied from 1000 to 20 000 g mol^{-1} depending on amounts of solid acid and monomers used. Typical results were as follows: for PCHVE, $M_n = 20\,000\text{--}40\,000\ \text{g mol}^{-1}$ with a broad distribution; for PIBVE, $M_n = 8000\text{--}10\,000\ \text{g mol}^{-1}$ with a broad distribution; and for PEVE, $M_n = 20\,000\text{--}100\,000\ \text{g mol}^{-1}$ with a distribution ratio (M_w/M_n) from 1.2 to 1.6.

The color formation takes place exclusively at the HY zeolite and depends on the size of the vinyl ether component (the larger the substituent the shorter the polyenylium sequence), the reaction time, and the reaction temperature. The colors range from blue through brown and orange-red to yellow, respectively, from EVE, DHF, IBVE, and CHVE (Figure 1).

Figure 2 shows a UV-vis spectral series monitored by means of an immersion cell placed directly in the suspension. The spectra were taken during the polymerization of DHF at the HY zeolite with respect to the reaction time (for details of the UV-vis technique, see ref 28 and Experimental Section).

It is important to note that the color formation also occurs in the presence of an excess of polyvinylpyridine base (PVP) ($M_w/M_n = 1.5$, $M_n = 176\,120\ \text{g mol}^{-1}$) in the surrounding solvent. PVP is strongly adsorbed to the HY zeolite and covers the acidic sites outside the nanopores due to its strong basicity. The gyration radius of PVP in the solution was approximately 7.3 nm. Therefore, we conclude that the large PVP coil cannot penetrate directly inside the nanopores of the HY zeolite, while the vinyl ether can do so.

An aluminosilicate with broad pore size distribution like siral 40 can also be used to initiate cationically vinyl ethers (VE). Siral 40 was chosen as reference solid acid catalyst because it bears the same acidic strength as

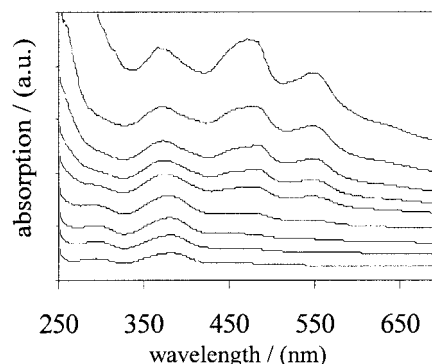
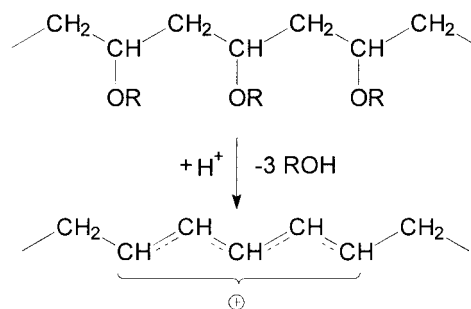


Figure 2. Time-dependent UV-vis spectroscopic study of the host-guest polymerization of DHF with HY zeolite at 20 °C (from bottom to top: 0.13, 0.50, 1.00, 3.00, 14.5, 33.0, 82.5, and 230.0 min and 24 h). The spectra were taken by means of an immersion cell placed in the suspension. The supernatant solution shows no absorption in the measured region.

Scheme 3. Acid-Induced Ether Transformation of a PVE Chain into a Polyenylium Structure



the HY zeolite used. A $\text{p}K_{\text{R}^+}$ range from -8.1 to -10.5 was estimated by Hammett indicators for both aluminosilicates. In the case of initiation of VE by siral 40, a soluble PVE fraction and a solid PVE-aluminosilicate hybrid were obtained. In contrast to the colored PVE-HY zeolite hybrid, the PVE-siral 40 hybrid materials are colorless white powders.

The UV-vis spectral series were recorded for different PVE-HY zeolite hybrids and were compared with similar spectral series from the literature.²⁹ It is proposed that polyenylium sequences are formed. In principle, polyenylium sequences can be obtained by acid-induced elimination of the corresponding alcohol R-OH from $(-\text{CH}_2-\text{CHOR}-)_n$ chains (Scheme 3).³⁰

GC studies of the reaction mixtures suggest that an acid-induced ether cleavage of the PVE chain takes place. Characteristic GC diagrams taken during the HY zeolite induced VE polymerization are shown in Figure 3 for three samples; EVE (A), IBVE (B), and DHF (C).

In the case of CHVE as monomer, the cleavage products cyclohexene and cyclohexanol were detected (not shown). Ethanol and diethyl ether or isobutene and isobutyl alcohol were detected during EVE and IBVE polymerization, respectively. Those are typically expected products of acid-induced ether cleavage and subsequent elimination reactions of VE chains. These products can diffuse out of the zeolite pores, but the PVE chains containing polyenyliums cannot do so and remain inside the pores. Acetaldehyde as product could not be

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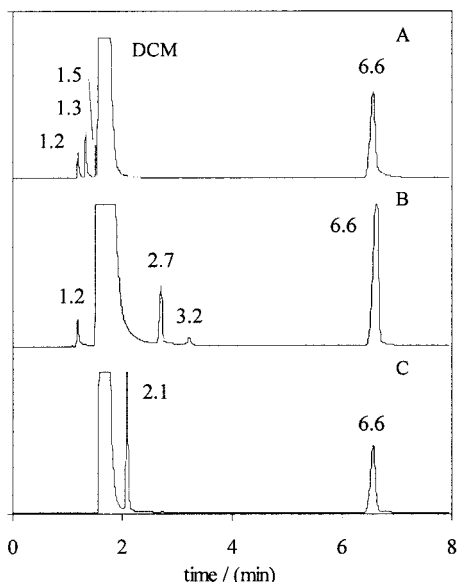


Figure 3. GC studies of the polymerization process of VE induced by the HY zeolite. The GC signals were interpreted by comparison to reference substances as follows: (A) 1.2 min EVE, 1.3 min ethanol, 1.5 min diethylether; (B) 1.2 min isobutene, 2.7 min isobutylalcohol, 3.2 min IBVE; (C) 2.1 min DHF. In each chromatogram, toluene (6.6 min) was used as a reference.

Table 1. UV–Vis Absorption Maxima of the Carbenium Ions Obtained after Polymerization (24 h) of Various VEs at HY Zeolites Compared to Polyenylium in Superacid Solution

carbenium ion	λ_{\max} (nm)				
	solution ²⁹	DHF	EVE	IBVE	CHVE
dienylium	397	385	377	379	383
trienylium	473	470	465	464	448
tetraenylium	550	550	554	550	
pentaenylium	675		619		

detected. This result showed that the conjugated sequences were derived from the generated polymer chain and did not result from acid-induced monomer decay. In the case of DHF polymerization, decay products could not be detected.

Similar polyenylium structures have been studied in superacid solution by Olah.²⁹ Stable polyacetyleniums were also observed by cationic polymerization of acetylene at H-ZSM-5 zeolite.³¹ A comparison of the measured UV–vis absorption maxima of the different PVE–HY zeolite hybrids with polyenylium compounds measured in superacids²⁹ is compiled in Table 1.

It was observed that the smaller the size of the substituent of the VE, the greater the extent of conjugated double bonds in the polymer chain. Polymerization of CHVE in the zeolite only yields short sequences of conjugated double bond due to the sterically hindered cyclohexyl substituent. In the case of DHF, longer conjugated sequences were expected. As seen from the GC in this case, diffusion of decay products from the pores during polymerization was not detected. It is possible that the side chains, which are formed after the ether cleavage, are strongly adsorbed to Lewis acid

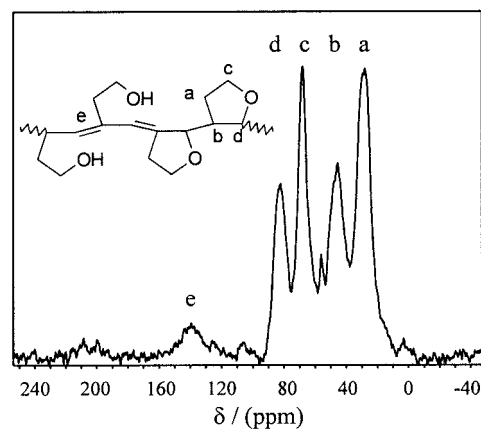


Figure 4. Representative solid-state $^{13}\text{C}\{^1\text{H}\}$ CP-MAS NMR spectrum of a PDHF–HY zeolite hybrid material.

sites in the zeolite. Thus the deeper penetration of the PDHF chain into the channel is prevented. In the case of EVE polymerization the ether cleavage products can easily diffuse out of the zeolite pores, and longer conjugated sequences are formed compared to the PDHF–HY zeolite hybrid material (Table 1). This is indicated by the bathochromic shift of the polyenylium absorption observed.

Solid Hybrid Materials. (A) $^{13}\text{C}\{^1\text{H}\}$ CP-MAS NMR Spectroscopy. Figure 4 shows a typical $^{13}\text{C}\{^1\text{H}\}$ CP-MAS NMR spectrum of a PDHF–HY zeolite hybrid sample. The four ^{13}C signals of the tetrahydrofuran rings in the vinyl ether chain are clearly detectable at 30, 45, 70, and 80 ppm.³³ These signals agree completely with those signals in the solution NMR spectrum of the extracted polymer fraction.

The formation of the π double bonds can be detected in the solid-state $^{13}\text{C}\{^1\text{H}\}$ CP-MAS NMR spectrum of the hybrid material by the ^{13}C signals at about 140 ppm (Figure 4). In the solution spectra the signals at 140 ppm are not observed. The solid-state $^{13}\text{C}\{^1\text{H}\}$ CP-MAS NMR spectrum of the PDHF–siral 40 hybrid bears the same signals as the solution spectra of PDHF. As expected, no signals appear that indicate double bonds in the $^{13}\text{C}\{^1\text{H}\}$ CP-MAS NMR spectrum of the white PVE–siral 40 hybrid materials.

(B) DRIFT Spectroscopy. The DRIFT spectra of the samples show the characteristic signals of PVE (wavenumbers: $(\text{C}-\text{H})_{\text{as}} = 2949 \text{ cm}^{-1}$; $(\text{D}-\text{H})_{\text{sy}} = 2871 \text{ cm}^{-1}$; $(\text{C}-\text{O}-\text{C})_{\text{as}} = 998 \text{ cm}^{-1}$) and of the double bonds ($(\text{C}=\text{C}) = 1644 \text{ cm}^{-1}$). The DRIFT spectra of the PVE–zeolite hybrid materials support the results from solid-state NMR spectroscopy.

(C) SEM Pictures. The neutralized dried PVE–HY zeolite hybrid materials are yellow and ochre powders. The shape of the crystals is not changed after the host–guest polymerization, as can be seen in the SEM pictures.

(D) DSC Measurements. For these measurements we selected the PDHF–HY zeolite hybrid because the glass transition temperature of PDHF can be used to determine the tacticity of the polymer.³² The glass transition temperature (T_g) of PDHF is evidently higher

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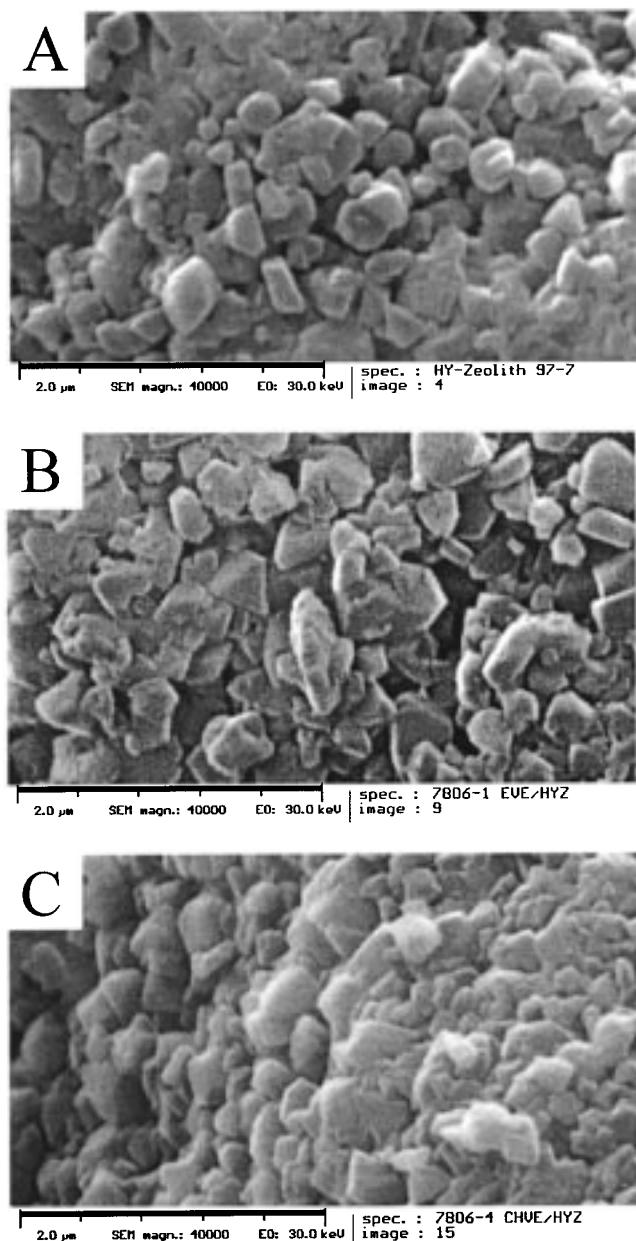
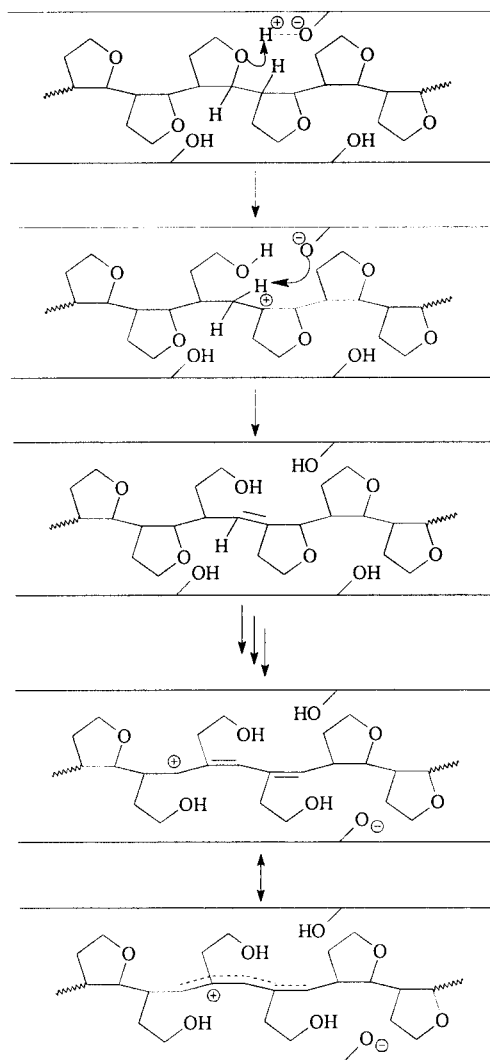


Figure 5. SEM pictures of PVE-HY zeolite hybrid crystals at 40000 \times magnification (A) HY zeolite before being treated with VE. (B) PEVE-HY zeolite (7.7% carbon). (C) PCHVE-HY zeolite (8.2% carbon).

than for other VEs and can be easily measured in the temperature range from 50 to 100 $^{\circ}\text{C}$. The T_g of the extracted polymer ($M_n = 6000 \text{ g mol}^{-1}$; broad distribution) was 85 $^{\circ}\text{C}$. However, the T_g characteristics of the PDHF-HY zeolite hybrid materials could not be detected. Three runs were carried out from 30 to 150 $^{\circ}\text{C}$. This result shows that the bulk properties of the PDHF are lost in the HY hybrid materials. Polystyrene chains in layered silicas similarly do not show a T_g characteristic of the bulk material.^{3,33} This result, interpreted in qualitative terms, indicates that the long-range motions of the polymer are restricted. Perhaps a similar effect is responsible for the PDHF-HY zeolite material; however, the consistency of our results together with those of other authors shows that the polymer is strongly restricted in its motion.³

(E) Thermogravimetric Studies. Because of the conjugated sequences, the thermal stability of the poly-

Scheme 4. Proposed Mechanism for the Transformation of PDHF into Polyenylium^a



^a The first step is the protonation of the oxygen followed by the ether cleavage, together with hydride rearrangement, and H^+ -elimination; further protonation takes place, and a second double bond is formed in the same steps.

mer component in the novel PVE-HY materials is lower than that of bulk PVE. The thermally induced decay of the PVE-HY zeolite occurs at 350–370 $^{\circ}\text{C}$. The thermal decomposition of the pure PVE (extracted fraction) occurs at 400–420 $^{\circ}\text{C}$. Due to the low activation barrier for thermal decomposition of the PVE component, the transformation of the PVE-HY zeolite hybrids to carbon-HY zeolite hybrids can be carried out by thermal treatment up to 500 $^{\circ}\text{C}$. The signals of the former $-\text{CH}_2-$ valency vibrations of the PVE chains disappeared in the DRIFT spectrum of the black material. The thermally induced transformation of the PVE-HY zeolite hybrids to novel carbon-zeolite hybrids is now being systemically studied.³⁴

Final Discussion

The results reported in this paper have shown that VEs can be cationically polymerized in pores of HY

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zeolites to produce novel hybrid materials. These materials are colored due to the presence of polyenylium sequences that are yielded during the host–guest polymerization process. The color of the materials is controlled by the size of the vinyl ether component. The observed effect is specific for cationic polymerization of VE induced by a Y zeolite with an Na/H exchange ratio of $70\% \pm 10\%$. It has been demonstrated by GC that the formation of the polyenylium sequences is attributed to acid-induced ether cleavage of the PVE chain in the zeolite pores. A mechanism is suggested in Scheme 4 that is in accordance with the results from UV–vis and solid-state NMR spectroscopy and GC studies.

Immediately after polymerization, the ether oxygen of a discrete PVE unit becomes protonated and oxygen carbon cleavage takes place. The carbenium intermediate is not stable, and proton transfer to the zeolite frame (negatively charged oxygen places) occurs rapidly. Of course, rapid hydride rearrangement shifts should also occur. As a consequence, a single double bond is formed at first. That structure becomes protonated again, and the same reaction cycle takes place. These reactions should only occur in the pore of the zeolite because two effects are required. First, the carbocation is stabilized by the controlled negative charge of the supercage, and second, disturbing reactions of the polyenylium to dormant PVE and vinyl ether monomers are prevented. In the case of CHVE due to the large rigid cyclohexyl substituents, the polymer chain cannot penetrate so deep into the pore. Therefore only a short part of the chain is transformed to polyenyliums. In contrast, PDHF is a compact monomer with restricted rotation of functional groups. It should diffuse more easily into the pore than expected for ethyl vinyl ether. Despite

this argument, EVE yielded larger conjugated sequences in the HY zeolite pores than DHF did. The explanation for this result is that the products derived from the acid-induced ether cleavage of PEVE can diffuse out of the pores, but the similar products from PDHF remain covalently linked to the polymer backbone. It is expected that the motion of the PDHF chain is already strongly restricted after the first ether cleavage step of PDHF.

Conclusions

The cationic polymerization of vinyl ethers in HY zeolites is a suitable approach to producing novel hybrid materials with combined properties. The synthetic strategy is based on two assumptions: controlled catalytic activity of the zeolite materials and required size of the cationically polymerizable monomer. It is expected that this concept can be applied to other vinyl monomers and zeolites.³⁴ The key to success will be to control gradually both the reactivity of the monomer (electron density of the carbon–carbon double bond) to the zeolite component (Brønsted versus Lewis acidity strength) and the monomer shape and size. The PVE–zeolite hybrid materials can be used as precursor materials to produce novel carbon–HY zeolite hybrids as well as for other applications.³⁴

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