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Acidolytic Ring Opening of Cyclic Siloxane and Acetal Monomers. Role of Hydrogen Bonding in Cationic Polymerization Initiated with Protonic Acids

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ABSTRACT: The kinetics of ring-opening reactions between trifluoroacetic acid and hexamethylcyclotrisiloxane (D$_3$), octamethylcyclotetrasiloxane (D$_4$), and dioxolane (DXL) was studied in the inert solvent methylene chloride and in some cases in *n*-heptane. The equilibrium constants of hydrogen-bond formation in the reaction system were determined by an independent method—infrared spectroscopy. Consideration of these constants in kinetic analysis proved to be necessary to obtain a consistent interpretation of the kinetic data. The competition between acid–acid interaction and acid–monomer interaction dominates the kinetic pattern and is suggested as a common phenomenon in cationic polymerization initiated with protonic acids. The role of H-bonded polymeric complexes in the process, including charge stabilization, multifunctional action, and cooperative hydrogen-bond migration, is discussed.

Introduction

The polymerization of a heterocyclic monomer initiated by a protonic acid usually starts with opening of the monomer ring, with the acid acting either as catalyst or simultaneously as both reagent and catalyst. One of the most common schemes of analogous reactions in polar amphiprotic solvents—which is also operative in the acid-catalyzed solvolytic opening of cyclosiloxanes[1,2]—involves the protonation of a heteroatom X followed by nucleophilic attack at the adjacent atom in the ring skeleton, resulting in ring opening, and finally a fast proton return (Scheme I). The solvent may function as the nucleophile and also as the base if HA is the solvent conjugate acid SH⁺.

Similar schemes are often applied to cationic polymerization. This may be, however, done only in a formal way. The polymerization usually takes place in a nonpolar aprotic medium, where association phenomena have a strong impact on the process,[3,4] making its kinetics far from being consistent with Scheme I. In particular, the role of acid H-bonding homocomplexation has often been observed in cationic polymerization systems.[5–8] However,

Scheme I
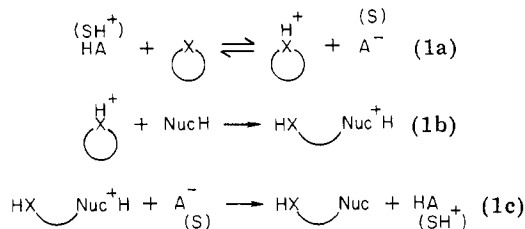
facts concerning the real mechanism are scarce. In order to progress further in understanding the cationic polymerization of heterocycles initiated with a Brønsted acid, kinetic studies of simple ring-opening reactions of heterocyclic monomer rings by acids in nonpolar aprotic and nonbasic solvents (inert solvents) are urgently needed. The reactions of monomers of weak nucleophilicity with an acid of medium strength were chosen here as models.

We have studied the kinetics of the acidolytic cleavage of hexamethylcyclotrisiloxane (D$_3$) and octamethylcyclotetrasiloxane (D$_4$) with trifluoroacetic acid in methylene chloride and in some cases in *n*-heptane. This reaction

Table I

Parameters of the Uninomial Approach Kinetics Equation (4) Involving Total Reagent Concentrations for the Acidolysis of Siloxane and Acetal Monomers with CF_3CO_2H in Methylene Chloride or Heptane at 35 °C

| monomer | $k_t{}^a$ | | m^b | | n^b | | $E_a{}^c$ |
	CH_2Cl_2	heptane	CH_2Cl_2	heptane	CH_2Cl_2	heptane	CH_2Cl_2
1,3-dioxolane	$(1.0-7.0) \times 10^{-7}$		0.7-3.8		-0.9 to -1.7		
D$_3$	1.7×10^{-3}	5.3×10^{-4}	3.5 ± 0.2	2.9 ± 0.3	-1.3 ± 0.2	-0.7 ± 0.2	56 ± 3
D$_4$	1.5×10^{-4}		3.3 ± 0.2		0 ± 0.1		46 ± 6
MM	5.8×10^{-3}	2.1×10^{-3}	3.1 ± 0.1	2.9 ± 0.3	0.2 ± 0.3	0.8 ± 0.2	

^{a} Unit, mol^{1-m-n} $dm^{3(m+n-1)}$ s^{-1}. ^{b} m and n are apparent orders in the catalyst and in the monomer, respectively. ^{c} E_a is the apparent energy of activation; unit, kJ mol^{-1}.

constitutes the initiation of cationic polymerization of these monomers.[9,10] Included also were studies of the cleavage of linear hexamethyldisiloxane (MM), as it was considered to be the simplest model reaction of acidolysis of the siloxane bond.

These studies were extended to a representative of acetal monomers, dioxolane (DXL), which is widely used as a model monomer in studies of cationic ring-opening polymerization. We hoped that this extension would make our results interesting in a more general sense.
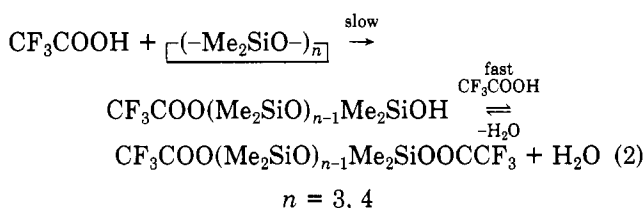
Hydrogen-bonded complexes formed in the reaction system were investigated separately and they were considered in the kinetic analysis as a relevant part of the mechanism of the ring-opening reactions studied.
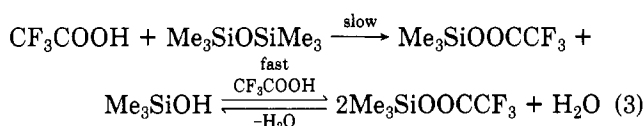
Results and Discussion

Kinetic Studies. The kinetics of the reaction of DXL, D$_3$, D$_4$, and MM with CF_3COOH in CH_2Cl_2 and in n-heptane was investigated with ^{19}F NMR spectroscopy. The decrease of the intensity of the signal of the acid and the increase of the intensity of the signal of the ester were followed.

Kinetic analysis is based only on the initial rates obtained by extrapolation to zero time of the reaction. In this way complications from consecutive and reverse processes affecting the reaction course are mostly avoided. In its initial stage the reaction is assumed to proceed according to eq 2 and 3.

Reaction of Cyclic Monomers

$$CF_3COOH + \boxed{\text{(–Me}_2\text{SiO–)}_n} \xrightarrow{\text{slow}}$$

$$CF_3COO(Me_2SiO)_{n-1}Me_2SiOH \underset{-H_2O}{\overset{\text{fast} \atop CF_3COOH}{\rightleftharpoons}}$$

$$CF_3COO(Me_2SiO)_{n-1}Me_2SiOOCCF_3 + H_2O \quad (2)$$

$$n = 3, 4$$

Reaction of Model Acyclic Disiloxane

$$CF_3COOH + Me_3SiOSiMe_3 \xrightarrow{\text{slow}} Me_3SiOOCCF_3 +$$

$$Me_3SiOH \underset{-H_2O}{\overset{\text{fast} \atop CF_3COOH}{\rightleftharpoons}} 2Me_3SiOOCCF_3 + H_2O \quad (3)$$

Our results, which will be reported separately,[11] proved that the esterification reaction is fast compared to acidolysis. Thus the initial rate of the acid consumption in the absence of water is equal to twice the initial rate of monomer acidolysis.

We found a close similarity of the kinetics in two reaction systems, one involving the cyclic monomers (eq 2), and the other involving the model acyclic compound (eq 3), which is unable to undergo polymerization. This observation indicates that the possible complications due to other processes[42] in the polymerization system do not cause uncertainties in the use of eq 2 in interpreting the kinetic
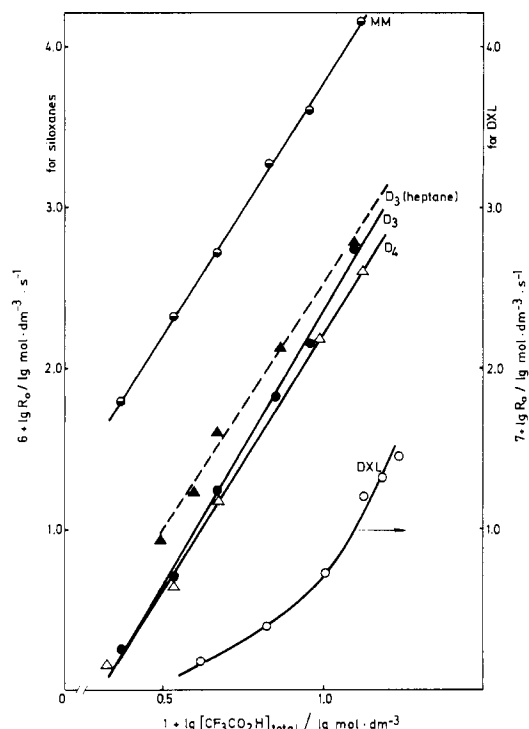

Figure 1. Dependence of the initial rate of acidolysis of siloxane and acetal monomers with trifluoroacetic acid in methylene chloride (continuous line) and in heptane (dashed line) at 35 °C on the total initial concentration of the acid. Initial concentration of the monomer is a constant 2.0 mol dm^{-3}. Experimental points: (O) DXL; (◉) MM; (△) D$_4$; (●) D$_3$ (all in CH_2Cl_2); (▲) D$_3$ (in heptane). The ordinate scale for DXL is marked at the right side.

data. In the first approach the kinetic law of the acidolysis was approximated by the uninomial equation (4), involving

$$R_0 = (-d[CF_3COOH]/dt)_{t=0} = (d[ester]/dt)_{t=0} =$$

$$k[CF_3COOH]^n{}_{0 \text{ total}}[monomer]^m{}_{0 \text{ total}} \quad (4)$$

total initial concentrations of the substrates. At first this approximation seems reasonable for siloxanes, as shown in Figures 1 and 2, where results of two series of experiments at constant acid concentration and at constant monomer concentration are compared. The values of exponents n and m are collected in Table I. The above approach is often applied to complex processes and values of exponents are interpreted in terms of molecularity. However, this interpretation is not straightforward here because of the following unusual features of the process studied:

(1) The apparent order in monomer (exponent m) is unexpectedly low. Particularly in the case of D$_3$ it acquires a negative value -1.4. Similarly a decrease of the reaction rate with increasing monomer concentration is observed for dioxolane.

(2) Reactions of all siloxanes show a high apparent order in acids. The exponent n is variable in the range 3.1–3.5.
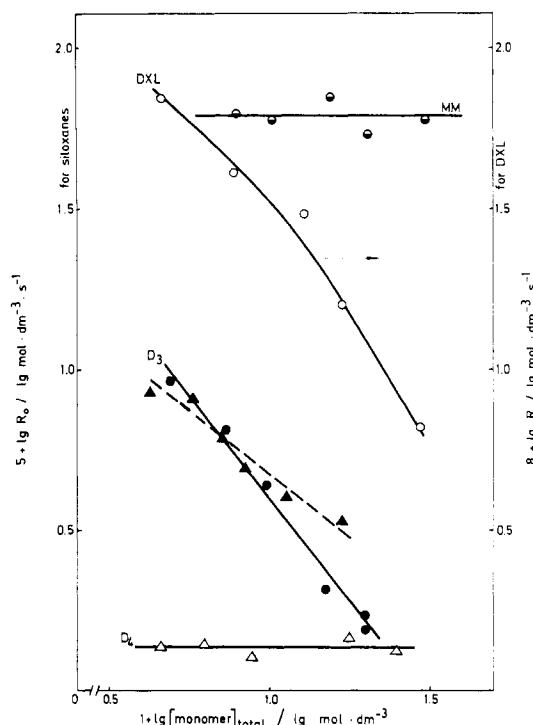
Figure 2. Dependence of the initial rate of acidolysis of siloxane and acetal monomers with trifluoroacetic acid in methylene chloride (continuous line) and in heptane (dashed line) at 35 °C on the total initial concentration of the monomer. Initial concentration of the acid is constant. $[CF_3COOH]_{0\ total} = 0.5$ mol dm^{-3}. (O) DXL; (⊖) MM; (△) D$_4$; (●) D$_3$ (all in CH$_2$Cl$_2$); (▲) D$_3$ (in heptane). The ordinate scale for DXL is marked at the right side.

It may seem strange that, on the average, a larger number of acid molecules is required to open the weaker siloxane bond in the strained ring of D$_3$ ($n = 3.5$) than in strainless D$_4$ ($n = 3.2$).

(3) The apparent value of the activation energy of the opening of an SiOSi bond is unexpectedly larger for strained D$_3$ (56 kJ mol^{-1}) than for unstrained D$_4$ (45 kJ mol^{-1}).

(4) Considerable deviations from linearity in the plots of Figures 1 and 2 for DXL are observed.

In addition the reaction shows other features reflecting the inadequacy of Scheme I.

(1) D$_3$ reacts at a comparable rate to D$_4$ (see Figure 1), though the acid-catalyzed solvolytic cleavage of D$_3$ in alcohol was found to proceed 10^3–10^4 times faster.[2] The kinetic experiment was also performed with a 1:1 (mol/mol) mixture of D$_3$ and D$_4$. The total consumption in initiation and in propagation of both D$_3$ and D$_4$ was followed by GLC. Although concentrations were chosen at which the rates in separate systems were the same, the reaction in the mixed system occurred almost exclusively with D$_3$ (see Figure 3).

(2) The addition of amphiprotic water strongly increases the rate of the conversion of the trifluoroacetic acid into the ester (Figure 4). In contrast, the addition of a species acting as a proton acceptor in hydrogen bonding and having no ability to yield a proton to another acceptor, like ethers, strongly decreases the reaction rate (Figure 4).

(3) The reaction in most of the concentration range used goes slightly faster in n-heptane (dielectric constant $\epsilon = 1.9$) than in more polar methylene chloride ($\epsilon = 9$). Siloxane monomers themselves have low values of dielectric constant about 2.4.

The main factor responsible for the complication of the kinetics is the hydrogen-bonding phenomenon. The reason
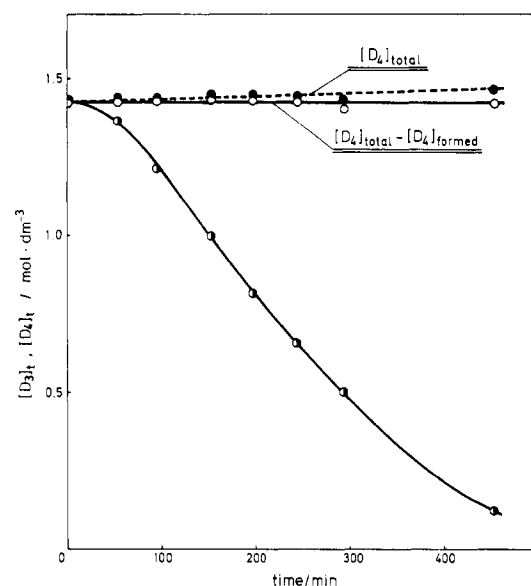

Figure 3. Conversion (due to initiation and propagation) of hexamethylcyclotrisiloxane (D$_3$) and octamethylcyclotetrasiloxane (D$_4$) in the system D$_3$–D$_4$–CF$_3$COOH in CH$_2$Cl$_2$ at 35 °C as measured by GLC. The dashed line corresponds to the amount of D$_4$ directly observed in the system. The continuous line corresponds to the amount of D$_4$ corrected for D$_4$ produced in the polymerization of D$_3$ as determined in a separate experiment.
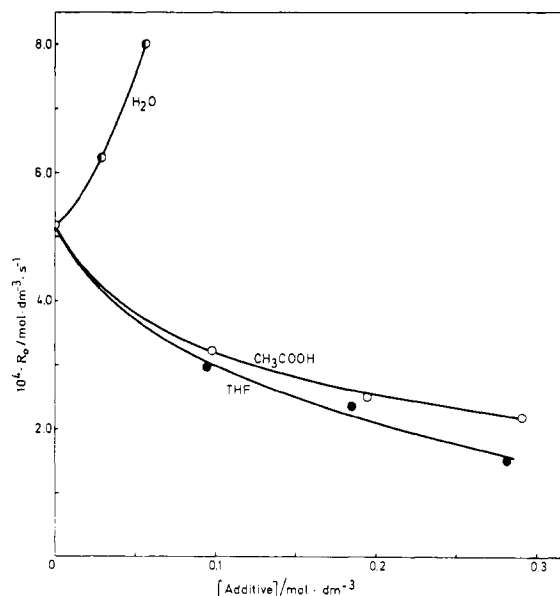

Figure 4. Effect of additives A on the initial rate of acidolysis of MM in methylene chloride at 35 °C. $[CF_3COOH]_{0\ total} = 0.474$ mol dm^{-3}, $[MM]_{0\ total} = 2.0$ mol dm^{-3}. (O) CH$_3$COOH; (●) THF; (◎) water.

for the inadequacy of eq 4 lies in the fact that the total concentrations which appear in this equation do not correspond to actual concentrations of uncomplexed species. Considering the equilibria of formation of H-bond complexes, it is thus necessary to obtain a more consistent interpretation of the kinetic results. This led us to study the hydrogen-bonding interaction in this system.

Hydrogen-Bonding Studies. Hydrogen-bonding complexation of trifluoroacetic acid with DXL, D$_3$, D$_4$, and MM in methylene chloride and self-association of the acid in this solvent were studied by IR spectroscopy. Studies of the complexation with water and tetrahydrofuran (THF) were also included. Water usually appears in the polymerization of oxygen heterocycles initiated with protonic
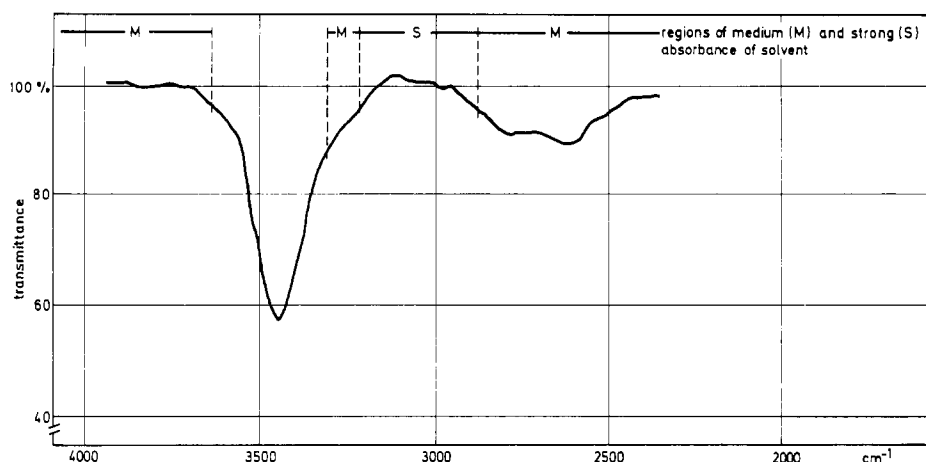
Figure 5. IR spectrum of the ternary system acid–base–solvent. $[CF_3COOH] = 0.02$ mol dm^{-3}, $[D_4] = 0.1$ mol dm^{-3}; in methylene chloride, at 35 °C; path length 0.2 cm.

acids,[9,11] while THF is one of the most frequently used monomers in studies of cationic polymerization.[3]

The formation constants of H-bonded complexes have been evaluated from the absorbance maximum of the band due to stretching vibrations of the uncomplexed O–H in the COOH group of the acid, which appears at 3500 cm^{-1}.[12,13] The absorbance can be measured with reasonably good precision, as the solvent absorbs only weakly at this wavelength. This contrasts with the case for complexed OH, where the main part of the band due to the complexed OH lies in the range of very strong CH_2Cl_2 absorption and elimination of the background absorbance cannot be done with sufficient precision. A typical spectrum of the acid–base solution in CH_2Cl_2 in the range of the O–H stretching vibration band is presented in Figure 5.

The molar absorption coefficient for the free OH group of the acid was determined by extrapolation to infinite dilution to account for self-association of the acid (Figure 6).

In the concentration range studied the system is dominated by two equilibria: (1) free acid HA ⇌ acid dimer $(HA)_2$ (eq 5) and (2) free acid + free base B ⇌ 1:1 acid–base complex (eq 6).

$$HA + HA \xrightarrow{K_1} (HA)_2 \qquad (5)$$

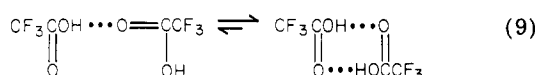$$HA + B \xrightarrow{K_2} (B \cdot HA) \qquad (6)$$
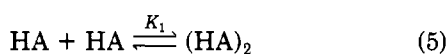
This is confirmed by the fact that the formation constants K_1 and K_2, calculated from eq 7 and 8 on the assumption that binary complexes are exclusively formed, tend to keep constant values with changing acid and H-acceptor concentration.

$$K_1 = ([HA]_{total} - [HA]_f)/2[HA]_f^2 \qquad (7)$$

$[HA]_f$ = concentration of uncomplexed acid

$$K_2 = \frac{[HA]_{total} - [HA]_f - 2K_1[HA]_f^2}{[HA]_f([B]_{total} - [HA]_{total} + [HA]_f + 2K_1[HA]_f^2)} \qquad (8)$$

There are two possible forms of acid dimer which are in equilibrium

$$CF_3\underset{\underset{O}{\|}}{C}OH \cdots O{=}\underset{\underset{OH}{|}}{C}CF_3 \rightleftharpoons CF_3\underset{\underset{O\cdots HOCCF_3}{\|}}{C}OH\cdots O \qquad (9)$$

The cyclic structure strongly predominates, as the experimental points can be fitted to the curve of absorbance change due to dilution only under the assumption that the
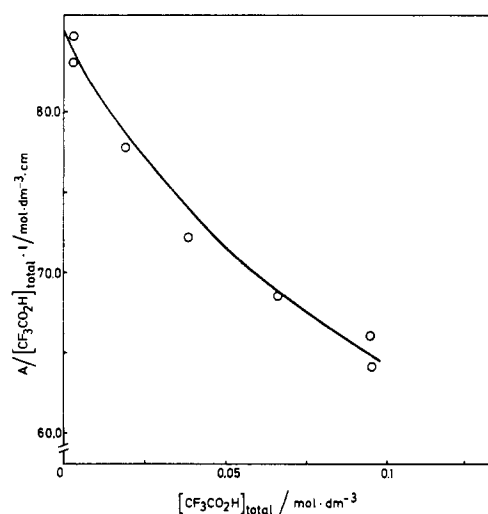

Figure 6. CF_3COOH homoassociation effect in methylene chloride on the apparent molar absorption coefficient at the maximum of the stretching vibration band of free OH of the acid. Marked are the experimental points and the theoretical curve calculated for $K_1 = 2.1$ mol^{-1} dm^{-3}, assuming a cyclic structure for the complex.

cyclic form appears exclusively (see Figure 6). This is also in agreement with the literature data.[14,15]

Instead, the complex of trifluoroacetic acid with water appears mainly in the open-chain form

$$\underset{H}{\overset{H}{>}}O \cdots HOCCF_3 \rightleftharpoons \underset{H}{\overset{H}{>}} \underset{O}{\overset{O\cdots HOCCF_3}{|}} \qquad (10)$$
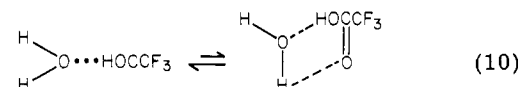
This was concluded from the observation that the intensity of the free-OH band of water at 3700 cm^{-1} increases proportionally to the amount of water introduced to the solution of trifluoroacetic acid in CH_2Cl_2. The open structure of the $CF_3COOH-H_2O$ complex was also postulated earlier.[16]

Values of formation constants of the complexes of trifluoroacetic acid with the oxygen bases studied are presented in Table II.

Inspection of the data leads to the conclusion that these siloxanes form much weaker complexes with the acid than the ether and the acetal, which is in agreement with earlier observations of IR band shifts due to complexation of alcohols with ethers and siloxanes.[17] This small basicity of siloxanes is explained by the electron back-donation from the oxygen free electron pair to the d orbital of silicon (p_π–d_π effect). D_3 forms stronger complexes with the acid

Table II
Equilibrium Constants K_2 (K_1) for H-Bond Binary
Complex Formation of CF_3COOH with Some Oxygen
Bases B in Methylene Chloride at 35 °C

B	$K_2{}^a$	$K_2{}'{}^{a,b}$	$[B]_{total}{}^c$
CF_3CO_2H	2.1 (K_a)	2.1	0.005–0.5
MM	1.4	1.4	0.02–4.5
D_4	2.1	0.5	0.10–3.1
D_3	5.0	1.7	0.07–0.6
H_2O	19	19	0.01–0.09
1,3-dioxolane	31	16	0.02–0.15
THF	220	220	0.01–0.10

^{a} Unit, dm^3 mol^{-1}. ^{b} K_2' is the equilibrium constant
taking into account the total number of basic centers in
the monomer. ^{c} Unit, mol dm^{-3}.

Table III
Parameters of the Kinetics Equation (12) (Obtained by
Three-Parameter Regression Analysis) Involving
Uncomplexed Species Concentrations for the Reaction of
Siloxane and Acetal Monomers with CF_3CO_2H in
Methylene Chloride at 35 °C

monomer	$k_f{}^a$	p^b	q^b
1,3-dioxolane	7.0×10^{-4}	1.7 ± 0.3	0.9 ± 0.3
D_3	7.1×10^{-2}	3.1 ± 0.2	1.0 ± 0.2
D_4	2.2×10^{-2}	3.5 ± 0.3	1.5 ± 0.2
MM	5.2×10^{-1}	3.5 ± 0.1	1.6 ± 0.1

^{a} Unit, mol^{1-p-q} $dm^{3(p+q-1)}$ s^{-1}. ^{b} p and q are orders in
the catalyst and in the monomer, respectively.

than MM and D_4, which is related to the strain in its
six-membered ring, making p_π–d_π conjugation less effective
than for strainless D_4 and MM. The absolute value of the
free energy of the acid–acid interaction is close to that for
the interaction of the acid with D_4 but is lower than that
for the interaction with D_3 and DXL.

It may be concluded from the literature data that H-
bonded complexes in methylene chloride are weaker than
the same complexes in heptane,[18,19] which is connected with
the competitive interaction of the former solvent with the
acid.

Interpretation of the Kinetic Results. Infrared data
point to a strong competition between acid homocom-
plexation and acid–monomer heterocomplexation in the
reaction systems studied. This competition must be also
responsible for the strange kinetics observed. A more
detailed kinetics analysis fully confirms this conclusion.

Equations 11a,b are derived from equilibria 5 and 6,

$$2K_1K_2[HA]_{0f}{}^3 + 2(K_1 + K_2)[HA]_{0f}{}^2 +$$
$$(K_2[M]_{0f} - K_2[HA]_{0\ total} + 1)[HA]_{0f} - [HA]_{0\ total} = 0$$
(11a)

$$[M]_{0f} = [M]_{0\ total} - [HA]_{0\ total} + 2K_1[HA]_{0f}{}^2 + [HA]_{0f}$$
(11b)

neglecting H-bond complexes other than binary ones. The
initial concentrations of free acid $[HA]_{0f}$ and free monomer
$[M]_{0f}$ were calculated from the above equations for all runs.
Correlation of rates with these concentrations, presented
in Figures 7 and 8, correspond well with the uninomial
kinetic equation (12). Values of k, p, and q were obtained

$$R_0 = k[CF_3COOH]_{0f}{}^p[M]_{0f}{}^q \qquad (12)$$

by rigorous regression analysis of the data in terms of the
three parameters in eq 12. They are presented in Table
III. The errors in p and q are given at a confidence level
of 0.9. The kinetic results can be understood when in-
terpreted in terms of eq 12. The complex including H-
bonded polymer of p molecules of acid being also H-
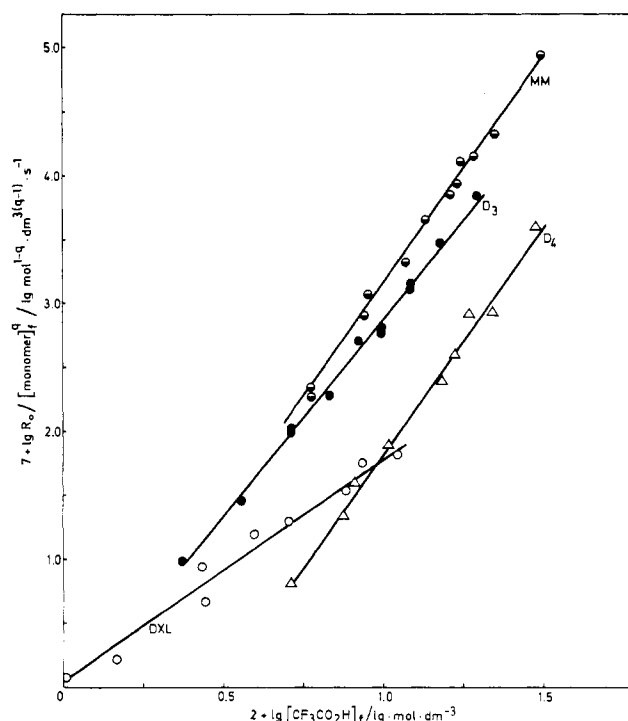bonded to one or eventually more monomer molecules is

Figure 7. Correlation of the initial rate of the siloxane and acetal
monomer acidolysis by CF_3COOH in CH_2Cl_2 at 35 °C with the
concentration of uncomplexed CF_3COOH. $[M]_{total} = 0.4$–3.0 mol
dm^{-3}, $[CF_3COOH]_{total} = 0.2$–1.3 mol dm^{-3}. (O) DXL; (◕) MM;
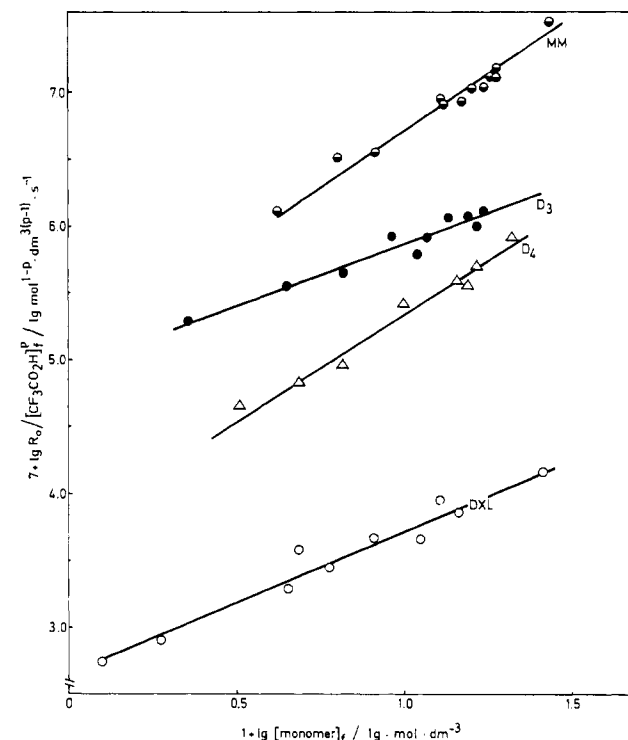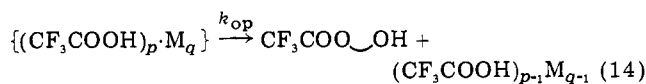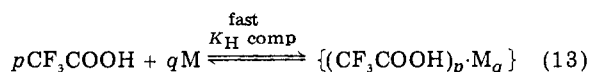(△) D_4; (●) D_3.

Figure 8. Correlation of the initial rate of the siloxane and acetal
monomer acidolysis by CF_3COOH in CH_2Cl_2 at 35 °C with the
concentration of uncomplexed monomer. $[M]_{total} = 0.4$–3.0 mol
dm^{-3}, $[CF_3COOH]_{total} = 0.2$–1.3 mol dm^{-3}. (O) DXL; (◕) MM;
(△) D_4; (●) D_3.

formed in fast reversible steps and is in equilibrium with
other H-bonded complexes as well as with the uncom-
plexed species. This complex is able to ring open (eq 13).

The reactions of D_3 and DXL both show first-order
kinetics with respect to the monomer ($q = 1$), which is

$$pCF_3COOH + qM \underset{K_{H \text{ comp}}}{\overset{\text{fast}}{\rightleftharpoons}} \{(CF_3COOH)_p \cdot M_q\} \quad (13)$$

$$\{(CF_3COOH)_p \cdot M_q\} \xrightarrow{k_{op}} CF_3COO\_OH + (CF_3COOH)_{p-1}M_{q-1} \quad (14)$$

$$k = k_{op}K_{H \text{ comp}}$$

consistent with a simple acidolysis involving only one monomer molecule. This permits rejection of the ester-forming mechanism via the tertiary oxonium ion, which is operative in the polymerization of THF.[13] The acidolysis of D_3 is third order in acid, while the reaction of DXL, within the limits of error, is second order in acid. Thus the acid trimer is the species which opens the six-membered siloxane ring of D_3 and the acid dimer the species which opens the dioxolane ring. Exponents $p = 3.5$, observed in the D_4 acidolysis, and $p = 3.6$, observed in MM acidolysis, may be interpreted as reflecting a crossover between the participation of the acid trimer and the acid tetramer in the range of the concentrations studied. In these cases the polynomial approach would be more consistent, as two parallel reactions of acidolysis occur, one involving acid trimer and the other involving the tetramer. It is reasonable that a more reactive larger H-bonded acid polymer, tetramer, participates in the cleavage of the SiOSi bond in strainless D_4. This tetramer is not important in the D_3 opening because its concentration must be smaller in this system. D_3 is a stronger base, and therefore acid homocomplexation cannot compete as effectively with acid–monomer heterocomplexation. The lower concentration of the H-bonded acid polymer species in the D_3 polymerization system is reflected in a relatively low reaction rate which is comparable to the rate of the D_4 cleavage, although under solvolytic conditions D_3 opening proceeds much faster. Also in the mixed D_3–D_4 system, where the availability of the acid pseudopolymer is the same for both monomers, D_3 is much more reactive.

The same argument can be used in comparing the reactions of DXL and D_3. Dioxolane interaction with the acid is so strong that a larger H-bonded polymer than dimer does not appear in kinetically significant concentration. Consequently, the reaction involves only the acid dimer of relatively low reactivity and this is one of the reasons that the acidolysis goes very slowly.

The order in monomer is sometimes higher than 1 (for D_4 and MM $q > 1$). Evidently the participation of another monomer molecule in the transition state is important in those cases.
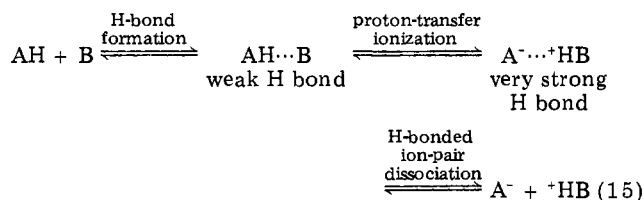
Now, the higher apparent energy of activation for D_3 acidolysis than for D_4 acidolysis can be understood better. Clearly, the ring-strain effect is more than compensated by the effect concerned with competition between homo- and heterointeractions. Lowering the temperature favors stronger D_3–HA interaction over a weaker interaction, leading to H-bonded acid polymer. Moreover, the participation of additional monomer species and the larger H-bonded acid aggregate contribute to the decrease of the energy barrier in the case of D_4 acidolysis.

Role of Hydrogen-Bonded Polymeric Complexes of Acid in the Acidolytic and Acid-Catalyzed Ring Opening in Inert Media

(1) Charge Stabilization. Effects of Additives Having Only Basic Centers. There are at least two reasons for which the mechanism of catalysis by acids in inert solvents (hydrocarbons, chlorinated hydrocarbons) differs from the mechanism depicted in Scheme I. First, there is strong intervention from an amphiprotic solvent

in the acid–base equilibria, forming solvent conjugate acid and base as well as solvent–solute H-bonded complexes. This permits treatment of the solute–solute interaction as a perturbation which may be allowed for by thermodynamic activity factors. No such intervention is possible in an inert solvent,[19] where the only acid–base interactions are those between solute molecules. Therefore, H-bond complexes should be treated as distinct chemical species in the kinetic analysis of these systems. Second, nonpolar solvents will favor a reaction route involving the least possible separation of charge. Thus preferred are mechanisms involving ion pairs. Also possible are synchronous mechanisms which do not require full ionization.

Inert solvents reveal a particularly important role of hydrogen bonding in acid-catalyzed reactions. The H bond can always be considered as a preliminary step in proton transfer between an acid and a base and the simplest model of the proton transfer can be expressed by eq 15.

$$AH + B \underset{\substack{\text{H-bond} \\ \text{formation}}}{\rightleftharpoons} \underset{\substack{\text{weak H bond}}}{AH\cdots B} \underset{\substack{\text{proton-transfer} \\ \text{ionization}}}{\rightleftharpoons} \underset{\substack{\text{very strong} \\ \text{H bond}}}{A^-\cdots{}^+HB}$$

$$\underset{\substack{\text{H-bonded} \\ \text{ion-pair} \\ \text{dissociation}}}{\rightleftharpoons} A^- + {}^+HB \quad (15)$$

There is much stronger H-bond interaction between charged species than between neutral ones. Therefore H bonding facilitates charge separation in the ionization step, leading to the formation of a stable ion pair which is very strongly H bonded.[19]

This H bonding renders the ion pair difficult to dissociate. Actually dissociation constants of acids even in aprotic solvents of relatively high dielectric constants are small.[20,21] Therefore, free ions are expected to be less important in the processes under consideration and, in consequence, the studies of the dissociation equilibria are not likely to give as much useful information as studies of the first two steps.

H-bond interaction between charged and neutral species is also strong and there are many observations of strong association of acids with their anions.[19,22-24]
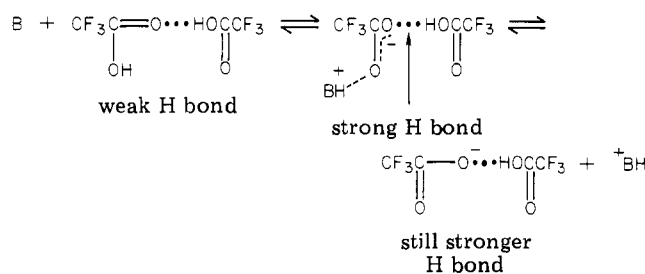
The above effect helps in both ionization and dissociation steps. Recent quantum mechanical calculations showed that the enthalpy of the H bond between a carboxylic acid and its anion exceeded by more than 100 kJ mol⁻¹ the enthalpy of the bond in the neutral dimer of the acid.[25] This excess energy is regained in the process of proton transfer from the dimer; thus it is only natural that an H-bonded polymeric complex more readily undergo proton-transfer ionization and H-bonded ion-pair dissociation than the monomeric form of the acid, which has been often reported.[5-7] The larger the H-bonded polymer, the better the stabilization of charge because of the cooperative effects of the remaining part of the complex.[26] Even in the case of partial charge separation in a synchronous process an H-bonded polymer can be very effective.

Addition to the reaction system of an agent which functions as a proton acceptor in H-bonding but is unable to act as a proton donor, like ether, results in the destruction of the acid H-bonded polymer by competitive association of the additive with the acid. This way ether addition impedes the reaction of CF_3COOH with siloxanes in CH_2Cl_2 (Figure 4). The same role is played by the monomer itself, which may lead to a negative apparent order in the monomer. This is the case for the reaction of CF_3COOH with DXL and D_3 in CH_2Cl_2.

We believe that this important role of the competition between the formation of the H-bond acid polymer and of the H-bond binary complex of acid with monomer is a rather common phenomenon in cationic polymerization with protonic acids. In general, weaker acids are more able to undergo homoassociation;[15] therefore, the stronger the acid and the more basic the monomer, the more effectively is the reaction involving the H-bonded acid polymer impeded by the acid–monomer interaction. Conversely, larger H-bonded acid aggregates are more likely to participate in the processes involving weaker acids and monomers of lower basicity. In fact, the idea of this competition is not a new one, as the formation of inactive catalyst–monomer complex in equilibrium with other active species has been postulated in the polymerization of styrene.[27,28] However, to our knowledge this complexation has not been studied in polymerization systems by independent methods and its nature has not been discussed.

(2) Cooperative Hydrogen-Bond Migration Mechanism. Effects of Additives of Amphiprotic Character. It should be pointed out that, apart from strongly acidic and electrophilic centers, the H-bonded acid polymer has weakly nucleophilic and basic centers, the strength of which may be strongly increased by putting a negative charge on them. It is known that charge displacement inside the H-bonded polymeric species is extremely fast due to cooperative hydrogen-bond migration.[29-31] Thus the negative charge formed as a result of the proton transfer to the monomer can be immediately shifted to the nucleophilic center which happens to be in contact with the electrophilic center of the reaction inside the ring (Scheme II). This charge migration may be induced by a weak interaction between these centers. This way the pseudopolymer can act as an effective multifunctional reagent. The H-bond migration step corresponds to the proton return step in Scheme I. H-bond migration may eventually occur synchronously with ring opening or with both ring opening and proton transfer via the transition state presented in 1. The addition of amphiprotic species
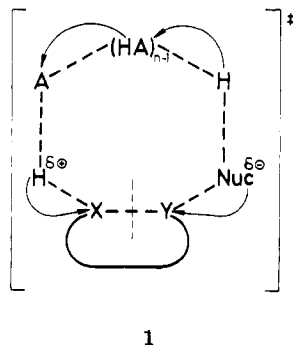

1

like water, which are able to function at the same time as proton donor and proton acceptor, may result in the formation of a more reactive H-bonded polymer, as the amphiprotic species built into the polymer may play some role in its cooperative or multifunctional action. For instance, addition of a weaker acid to the stronger one may enhance

Scheme II

$X = O$ $Y = C$ or Si $NucH = CF_3COOH$ (or H_2O)
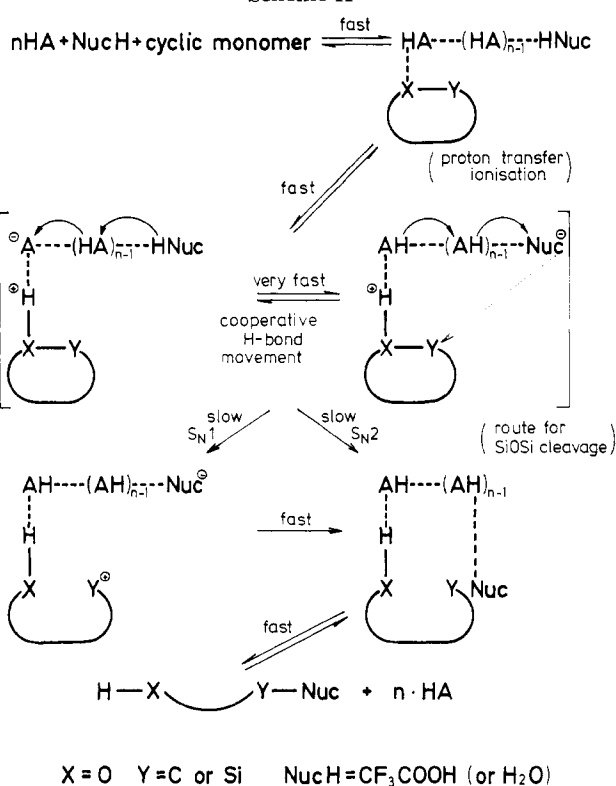
basic or nucleophilic properties of the polymer. Coactivation by weaker acid has been observed in cationic polymerization.[32] However, in the case under investigation the addition of acetic acid decreases the reaction rate.[43] This is presumably due to the formation of a strong and inactive 1:1 complex of acetic acid and trifluoroacetic acid (2),[33,34] which is connected with the decrease of the concentration of active polymeric form of CF_3COOH.
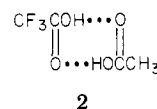
2

Water can play a particular role, as it can increase the acidity as well as the basicity and nucleophilicity of the H-bonded polymeric complex, which is shown in 3.
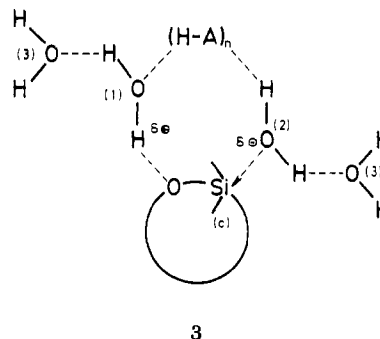
3

This may explain the very effective coactivation of the acid by water.[44] A consequence of the action of water as nucleophile would be hydrolytic opening of the ring. This reaction cannot be, however, distinguished from acidolytic opening because the product is controlled by a fast esterification–hydrolysis process (eq 3).

It should also be pointed out that H-bonded polymer forms a volume around the reaction center in which the local permittivity is higher. Thus a bulk dielectric constant
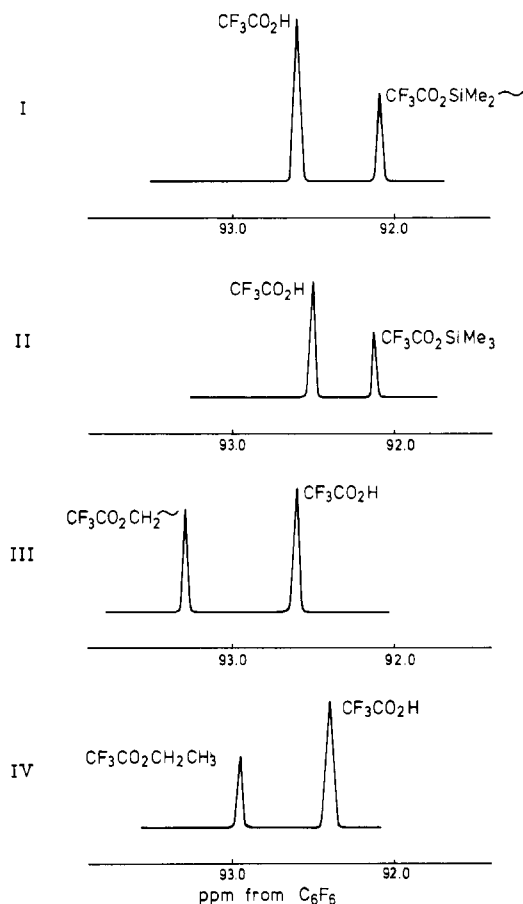
Figure 9. ^{19}F NMR 60-MHz spectra of the equilibrated system in CH_2Cl_2 (I, $[D_3]_{total}$ = 1.85 mol dm^{-3}, $[CF_3CO_2H]_{total}$ = 1.28 mol dm^{-3}; III, $[1,3\text{-DXL}]_{total}$ = 2.05 mol dm^{-3}, $[CF_3CO_2H]_{total}$ = 1.55 mol dm^{-3}) and of model systems in CH_2Cl_2 (II, 1:2 $CF_3CO_2SiMe_3$–CF_3CO_2H; IV, 1:2 CF_3CO_2Et–CF_3CO_2H).

of the medium is perhaps of minor importance in these ring-opening processes, so much that they presumably do not involve a full charge separation. This may partly explain the observation that ring opening in the system studied here occurs at a similar rate in methylene chloride and in n-heptane. However, it should be also taken into account that there exist better possibilities for the formation of H-bonded polymeric complexes in n-heptane than in methylene chloride, because the latter, being less inert, may somehow competitively interact with the acid.

Some Final Remarks. The main aim of this study is to draw attention to the diverse role of H-bonding-type association on kinetics and mechanisms of cationic polymerization with protonic acids. The acidolytic ring opening of siloxane and acetal monomers seems to be a good model for this purpose. However, we cannot consider this reaction as a general model of the initiation of ring-opening polymerization with protonic acids. Monomers used here, in particular, siloxanes, are weak nucleophiles and the acid is only of medium strength; therefore the acidolytic cleavage is favored. As the monomers become more nucleophilic and the acids become stronger, the reaction involving nucleophilic attack of another monomer molecule on the protonated monomer species, resulting in the formation of the onium ion active center,[1] becomes more important. This mechanism is accepted for polymerizations of THF[35] and dioxolane[36] in the presence of very strong acids, e.g., HClO$_4$ and CF$_3$SO$_3$H. Indeed, THF does not react in the system studied here even at very high CF$_3$COOH concentration.

In the case of a very strong acid and a more basic mo-

nomer like THF, the weak acid–acid interaction cannot compete with the strong acid–monomer interaction. Therefore the concentration of acid homocomplexes may be negligible. On the other hand, the acid–monomer interaction may be sufficiently strong to lead to proton transfer to the monomer without the assistance of acid-to-acid H bonding, and the secondary oxonium ion formed may be transformed to a tertiary ion by another monomer molecule without the active participation of a counterion. Some recent results of Pruckmayr's group[37,38] imply that this mechanism is operative in the polymerization of cyclic ethers.

Experimental Section

Materials. All reagents, catalysts, and solvents used were purified on a high-vacuum line. Siloxane monomers D$_3$, D$_4$, and MM were prepared in a way analogous to that described earlier.[39] DXL and THF were purified by standard high-vacuum methods.[40] They were stored over Na–K alloy in an ampule with a Teflon stopcock. CF$_3$COOH (Fluka) was purified by a method similar to that described in ref 41. The acid was separated from its anhydride by distillation under nitrogen on a highly efficient column. CF$_3$COOH was collected in the ampule with a Teflon stopcock, from which it was distilled on a vacuum line into the vessel in which the solution of the acid in CH$_2$Cl$_2$ or n-heptane was prepared. Acetic acid was purified in an analogous way. Methylene chloride and n-heptane were purified by methods described in ref 9.

Kinetic Investigations. Solutions of D$_3$, D$_4$, MM, DXL, and THF in CH$_2$Cl$_2$ or n-heptane as well as the solutions of CF$_3$COOH and CH$_3$COOH in these solvents were prepared by standard high-vacuum techniques, distilling proper amounts of components of each solution into ampules fitted with Teflon stopcocks. Both the monomer and the catalyst solutions were mixed together in proper proportion in an NMR tube in order to start the reaction. This procedure was performed under prepurified nitrogen, using hypodermic Hamilton syringes fitted with long needles. The tube was immediately placed in a thermostated ^{19}F probe of an R-12 Perkin-Elmer 60-MHz NMR spectrometer, and spectra were successively recorded and integrated. The assignment of acid and ester signals was done in separate experiments (Figure 9).

IR Studies of H Bonding. Solutions for IR studies were prepared in a way analogous to those for kinetic studies. Infrasil glass and NaCl cells of various path lengths, ranging 0.015–0.5 cm, with tight closures were used. They were thoroughly rinsed with dry CH$_2$Cl$_2$ and then with a stream of prepurified nitrogen. The cells were filled under prepurified nitrogen to prevent the absorption of moisture from the atmosphere. The spectra of the acid–base–solvent ternary system in the range 2300–3900 cm^{-1} were recorded with a Unicam SP 1200 double-beam spectrophotometer with compensation on the base solution. The scanning conditions chosen were those which gave good photometric precision and good resolution in the region of the free-acid band. The instrument recorded the spectra linearly with the transmittance scale, which was then converted to the absorbance scale. Temperature was kept constant within ±1 °C, as measured with a thermocouple occasionally installed inside the cell.

Gas–Liquid Chromatographic Studies. These were mostly performed in the way described in earlier papers from this laboratory.[10,39]

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(42) We are aware of two factors which can affect the initial rate of the acid consumption in the system involving the cyclic monomers. The initial product of the ring opening, which has $\equiv$SiOSi$\equiv$ groups, may undergo some fast fragmentations, allowing for the introduction of more acid. On the other hand, the propagation, which is fast in comparison with the initiation, is accompanied by end-to-end ring closure in which some of the acid is regenerated.[10,11] Similar complications may arise in DXL acidolysis; this process is being further studied at our Center.
(43) The ester of acetic acid is not formed in appreciable amount, as found by ^{1}H NMR.
(44) It is our feeling that the role of water as proton donor to the monomer is most important.

Rare Earth Metal Containing Polymers. 3. Characterization of Ion-Containing Polymer Structures Using Rare Earth Metal Fluorescence Probes[1a]

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ABSTRACT: Eu^{3+}, Tb^{3+}, and Co^{2+} salts of polymers containing carboxylic acid and sulfonic acid ligands were prepared and characterized. The polymers investigated were poly(acrylic acid) (PAA), copolymers of styrene–acrylic acid (PSAA), styrene–maleic acid (PSM), and methyl methacrylate–methacrylic acid (PMM/MA), and partially carboxylated and sulfonated polystyrenes (CPS and SPS). The lanthanide salts of these polymers showed characteristic lanthanide ion fluorescence in the solid state on excitation with UV light. The fluorescence excitation and emission spectra of these salts excepting carboxylated polystyrene showed characteristic spectra of the free ions, indicating that no energy is transferred from the polymer matrix to the ions. The carboxylated polystyrene–Eu^{3+} and –Tb^{3+} showed broad excitation spectra similar to the spectrum of the polymer and emission from the lanthanide ions, suggesting energy transfer from the polymer to the ion. The fluorescence intensities of the lanthanide salts of PAA, PSM, CPS, and SPS were found to increase linearly with the metal ion content. However, the salts of PSAA and PMM/MA displayed typical fluorescence concentration quenching behavior, reaching a maximum at 4–6 wt % of metal and decreasing with further increases in metal content. These results suggest that PSAA and PMM/MA contain ionic aggregates in which Eu and Tb ions are located close together. The energy transfer from Tb^{3+} to Co^{2+} and Eu^{3+} was evaluated from the Tb^{3+} fluorescence quenching. This was much more efficient in PSAA than in CPS and SPS systems. These results confirm that ion aggregates exist in PMM/MA and PSAA but not in the CPS and SPS systems at low metal concentration (<6 mol %). The probability $P_{D\rightarrow A}$ of dipole–dipole transfer between Tb^{3+} and Co^{2+} statistically distributed in a polymer matrix and the quenching characteristics were calculated by using Förster's equation. Experimental fluorescence quenching behaviors for PASS, CPS, and SPS are discussed as compared with the calculated quenching curve.

Introduction

The structures of synthetic polymers containing metal ions have been extensively investigated in recent years.[2,3] A host of techniques, including small-angle X-ray scattering, electron microscopy, and Raman spectroscopy, have been brought to bear on the elucidation of the structures of ion-containing polymers. It has been proposed that certain polymers contain submicroscopic aggregations of ionic groups.[3,4] Various structures of the ionic aggregates have been proposed and these depend on the composition of polymers, nature and concentration of metal ions, temperature, etc.

In the arsenal of spectroscopic techniques, fluorescence measurements offer particular advantages since they are sensitive and can be employed at relatively low concentrations of the luminescent species.[5] Thus, we have initiated a study of the structures of ion-containing polymers, using trivalent lanthanide ions as fluorescent probes.