quence of the (1,3) torsion angle pair cooperativity. Similar cooperative behavior was noticed in many other chains also.

It is possible to estimate a wave velocity of about 4700 m/s from the slope of the diagonals in Figure 2. We note that this is on the order of magnitude of the sound velocity through various crystalline media. Therefore, we believe that these motions may be related to the damped torsional oscillator (DTO) model, which has been used to explain acoustic relaxation data in alkane liquids.[8]

In conclusion, we believe that these findings from full Cartesian MD demonstrate the ab initio existence of torsion angle cooperativity. We expect that this cooperativity may be a very important factor in the structural phase transitions that take place in these materials.

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Study of the Initiation of Cationic Polymerization by Trimethylsilyl Esters

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Introduction

Protonic acids such as triflic acid are effective initiators in the cationic polymerization of vinyl[1] and oxacyclic[2] compounds. We speculated that contributing factors to the complex kinetics often observed were the complicated dissociation equilibria of the acid, hydrogen bonding, limited solubility, mixing controlled kinetics, etc. Since a trialkylsilyl group can be regarded as a bulky proton,[3] trialkylsilyl esters are expected to give clean reactions free of the complications caused by hydrogen bonding. Therefore, we recently introduced trialkylsilyl esters as a new class of initiators for cationic polymerization.[4] At the same time, another research group independently also proposed this class of compounds for the same purpose.[5]

Trimethylsilyl triflate was found to be a very active initiator for cationic polymerization but was too reactive and the polymerization could not be controlled.[4] One method of reducing the reactivity of an initiator involves the use of more nucleophilic counterions, which leads to a growing species with more covalent character, hopefully resulting in slower propagation and greater control of the molecular weight.

In this paper, we chose trimethylsilyl diphenylphosphate and trimethylsilyl methanesulfonate as the initiators to investigate the initiation of the cationic polymerization of styrene derivatives and cyclic acetals.

Results

Experimental Design. In view of the ready hydrolysis of silyl esters, particular attention was paid to possible initiation by traces of protic acids. A hindered base, 2,6-di-*tert*-butylpyridine or 2,6-di-*tert*-butyl-4-methylpyridine, was used as a probe. Introduced in the early 1980s,[6] and recently reviewed,[7] this base reacts with protic acids to form salts. The growing carbocationic chain end must not react directly with the base if its use is to be diagnostic of the initiating species. Whether it actually does or not depends on the nature of the carbocation. Bulky ones, from isobutylene or α-methylstyrene, or stabilized ones, such as trioxane, do not react. Styrene itself is more problematic, while *p*-methoxystyrene had not yet been studied.

In view of the above, to make sure the hindered base criterion was applicable, we synthesized 4-isopropenylanisole; this compound is the α-methyl-substituted analogue of *p*-methoxystyrene. Due to steric hindrance, the hindered base should not be able to abstract a proton from the derived carbocation. The reactivity of *trans*-anethole, a nonpolymerizable analogue of *p*-methoxystyrene, was also examined.

Reactions of Trimethylsilyl Diphenyl Phosphate with *p*-Methoxystyrene, Anethole, and 4-Isopropenylanisole. If ordinary polymerization conditions were used (septum-capped reaction tubes, syringes, and nitrogen atmosphere), trimethylsilyl diphenyl phosphate initiated the cationic polymerization of *p*-methoxystyrene in dichloromethane. The molecular weights of these polymers were high and the molecular weight distributions were broad. Terminal trimethylsilyl groups could not be

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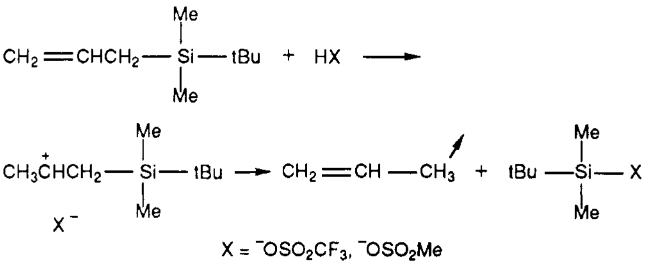
detected in the ^{1}H NMR spectrum of the polymers. We suspected that the real initiator in this system was diphenylphosphoric acid, which is formed from the reaction between a trace amount of water and trimethylsilyl diphenyl phosphate. Therefore, the reactions were carried out in the presence of a small amount of 2,6-di-*tert*-butylpyridine in sealed NMR tubes under vacuum. Under these conditions, no polymerization of *p*-methoxystyrene was observed after more than 4 days at low or ambient temperatures, strongly implicating the free acid.

The reactions of trimethylsilyl diphenyl phosphate with *trans*-anethole (nonpolymerizable) and 4-isopropenylanisole did not lead to any products either in vacuum and in the presence of hindered base.

Reactions of Trimethylsilyl Methanesulfonate with *p*-Methoxystyrene, Anethole, and 4-Isopropenylanisole. Because trimethylsilyl methanesulfonate is derived from a stronger acid than trimethylsilyl diphenyl phosphate, the former is expected to be a better initiator for polymerization of styrene derivatives. Therefore, the reactions of *p*-methoxystyrene, anethole, and 4-isopropenylanisole with trimethylsilyl methanesulfonate were studied. These reactions were carried out in sealed NMR tubes under vacuum. No polymerization was observed in the presence or absence of hindered base.

To clarify the reactivity of a carbocationic species β to a silicon, in the presence of a counterion, a model reaction was devised (see Discussion). The reaction of allyl-*tert*-butyldimethylsilane with triflic acid was very fast at 0 °C: no polymer was obtained, *tert*-butyldimethylsilyl triflate was obtained almost quantitatively. The reaction of allyl-*tert*-butyldimethylsilane with methanesulfonic acid was slow, at 26 °C, but after 24 h, more than 95% yield of (*tert*-butyldimethylsilyl) methanesulfonate was obtained.



Reactions of Trimethylsilyl Diphenyl Phosphate with 1,3-Dioxepane, 1,3-Dioxolane, and Trioxane. The reactions of cyclic acetals 1,3-dioxepane, 1,3-dioxolane, and trioxane with trimethylsilyl diphenyl phosphate were studied. When these reactions were carried out under normal polymerization conditions, high molecular weights and broad molecular weight distributions were obtained. When these reactions were carried out in the presence of hindered base, no polymer was obtained in any case.

Reactions of Trimethylsilyl Methanesulfonate with 1,3-Dioxepane, 1,3-Dioxolane, and Trioxane. The polymerization of 1,3-dioxepane with trimethylsilyl methanesulfonate was very slow in $CDCl_3$ at 0 °C (carried out in a sealed NMR tube), as shown in Table I. Even after 3 days, the conversion was only 35% and the initiation efficiency was less than 5%, as calculated from the NMR spectrum. The molecular weights were high and molecular weight distributions were broad. The presence of hindered base did not affect these results. The polymerization of 1,3-dioxolane and trioxane with trimethylsilyl methanesulfonate was not observed under the same conditions.

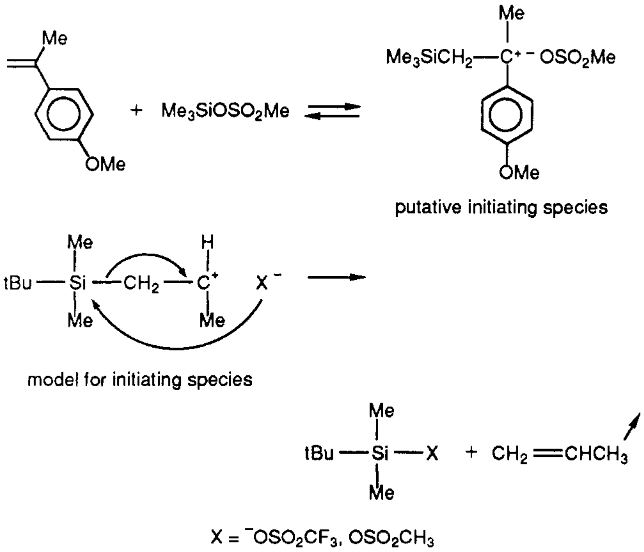
Table I
Reaction of 1,3-Dioxepane with Trimethylsilyl Methanesulfonate[a]

time, h	convrsn, %	$10^{-3}M_n$	$10^{-3}M_w$	MWD
6	0			
12	4			
24	9	3.20	1.03	3.2
36	17	19.11	5.46	3.5
48	21	20.92	6.75	3.1
60	29	43.47[b]	19.76[b]	2.2[b]
72	35	44.37[b]	21.13[b]	2.1[b]

[a] $[M_0] = 0.05$ M; $[I_0] = 0.05$ M; [2,6-di-*tert*-butylpyridine] = 0.01 M; solvent = $CDCl_3$; temperature = 0 °C. [b] Precipitated in methanol before analysis.

Discussion

Our results show that trimethylsilyl diphenyl phosphate and trimethylsilyl methanesulfonate are inefficient initiators for the polymerization of electron-rich styrene and oxacycle monomers. Only the more reactive trimethylsilyl methanesulfonate initiated the cationic polymerization of the very reactive 1,3-dioxepane in the presence of hindered base. The silyl initiators are much less effective than the corresponding protic acids. No ambiguity exists about the role of the hindered base. Bulky carbocationic propagating centers have been shown to be inert to hindered base and therefore 4-isopropenylanisole, a hindered equivalent for *p*-methoxystyrene, was also investigated. No addition of the silyl ester to the double bond was observed. *trans*-Anethole and 4-isopropenylanisole are electron-rich olefins and the question arises, why is there no reaction with the trimethylsilyl esters under investigation? In an attempt to answer this question, we generated an analogue of the putative initiating species from allyl-*tert*-butyldimethylsilane and triflic acid. Protonation of the allyl group leads to a cation β to a silicon; silicon is known to stabilize a β-cation. The rapid formation of *tert*-butyldimethylsilyl triflate shows that the oxygenated counterion clearly reacts at the silicon site and not at the carbocation, despite the steric hindrance at Si. The same reaction occurs between allyl-*tert*-butyldimethylsilane and methanesulfonic acid, albeit slower. This model reaction shows that the equilibrium of the proposed initiation step lies far to the left.



Thus, the initiating step never occurs in conditions where no methanesulfonic acid is formed by hydrolysis of the trimethylsilyl ester.

The fact that the oxacycle 1,3-dioxepane works better than the electron-rich styrenes might be traced to the greater affinity of Si toward O rather than toward C. Note that all the organic chemistry of trimethylsilyl triflate involves oxygen compounds, ketones and acetate, but not vinyls even if they are very electron rich.[8] So our polymer chemistry results are in accord with the known organic chemistry of these compounds. However, even in the successful case of 1,3-dioxepane with trimethylsilyl methanesulfonate, the initiation step is slow relative to propagation as shown by the long reaction times, high molecular weights, and broad molecular distributions.

Experimental Section

Methods. ^{1}H NMR spectra were recorded on a Brucker WM-250 spectrometer. Deuteriochloroform and dichlorodimethylsilane were used as the solvent and internal reference. Molecular weights of polymers were measured on a Shodex GPC A 804 column calibrated with polystyrene and THF standards, chloroform as eluent, and a Waters RI detector. Elemental analyses were performed by Desert Analytics, Tucson, AZ.

Monomers. *p*-Methoxystyrene, anethole, 1,3-dioxolane, and trioxane were purchased from Aldrich and purified by distillation over calcium hydride under reduced pressure. 1,3-Dioxepane was made from 1,4-butanediol and paraformaldehyde according to the method of Astle et al.[9] 4-Isopropenylanisole was made from 4-bromoanisole and acetone in the presence of magnesium.

Initiators. Trimethylsilyl diphenyl phosphate was made from the reaction of excess trimethylsilyl chloride with silver diphenylphosphate in acetonitrile in the dark at room temperature. After the silver chloride is filtered off, the solvent is evaporated and the viscous residue distilled (bp 119 °C (0.2 torr)). Yield 90%. Trimethylsilyl methanesulfonate was purchased from Aldrich.

Polymerization. A glass vessel with two arms containing small magnetic stirrers and an NMR tube were heated under 0.05 mmHg, until the magnets inside the stirrers could be seen (about 400 °C). The tube was then filled with argon and placed inside a glovebag. While argon was continuously purged into the tube, monomer, initiator, $CDCl_3$, and 2,6-di-*tert*-butyl-4-methylpyridine, which had been carefully purified, were put into the different arms: monomer, $CDCl_3$, and CaH_2 in one arm; *initiator, hindered base, and* $CDCl_3$ *in the other one. The tube* was closed and the contents stirred for about 20 h (argon was still continuously purged). The NMR tube was reheated to about 400 °C under 0.05 mmHg while the contents of the arms were cooled in liquid nitrogen. Under full vacuum (<0.05 mmHg) the NMR tube was cooled by liquid nitrogen and monomer, initiator, and $CDCl_3$ were distilled very carefully into the NMR tube, which was then sealed off.

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Registry No. Trimethylsilyl diphenylphospate, 25723-74-4; *p*-methoxystyrene, 637-69-4; anethole, 104-46-1; 4-isopropenylanisole, 1712-69-2; 2,6-di-*tert*-butylpyridine, 585-48-8; trimethylsilyl methanesulfonate, 10090-05-8; allyl-*tert*-butyldimethylsilane, 74472-22-3; triflic acid, 1493-13-6; *tert*-butyldimethylsilane, triflate, 69739-34-0; (*tert*-butyldimethylsilyl)methanesulfonate, 124156-70-3; 1,3-dioxepane, 505-65-7; 1,3-dioxepane (homopolymer), 25037-55-2; 1,3-dioxolane, 646-06-0; trioxane, 110-88-3; methanesulfonic acid, 75-75-2.

Modeling of the Epitaxial Crystallization of Poly(vinylidene fluoride): T_2, TGTG′, and T_3GT_3G' Chain Conformations on (111) CaF_2

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Introduction

In an earlier paper,[1] the epitaxial deposition of poly(vinylidene fluoride) (PVF_2) on a (111) CaF_2 substrate was modeled using molecular mechanics. A single PVF_2 chain segment consisting of 10 repeat units frozen into the all-trans (T_2) conformation was used to represent the polymer. It was found that the Coulombic contribution to the total polymer–substrate interaction energy was quite high (about 40%) as compared with other polymer epitaxial systems that have been modeled using this method. The orientation resulting in the lowest energy was one in which the plane of the planar zigzag backbone of the PVF_2 chain was parallel to the substrate and centered over a row of fluoride ions. The total interaction energy for this orientation was -55.4 kcal mol^{-1}/10 PVF_2 repeat units. The CF_2 dipoles in this orientation are parallel to the substrate. Another low-energy orientation ($E_{min} = -53.4$ kcal mol^{-1}/10 PVF_2 repeat units) was also found in which the CF_2 dipoles were normal to the substrate surface, with the polymer fluorine atoms next to the surface. Boltzmann statistics predicted that approximately 14% of the PVF_2 chain segments should deposit in the latter orientation. The other known chain conformations of PVF_2, TGTG′, and T_3GT_3G' were not considered. The purpose of this note is to summarize the results of these calculations for the last two chain conformations and to compare them with those of the T_2 conformation.

Theory and Methods

Details of the interaction energy calculations have been described in the earlier work and will only be summa-

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