

Reactions of Perfluorinated Compounds with Ethers: Evidence for Gas-Phase Cationic Polymerization

Jennifer S. Brodbelt,* Chien-Chung Liou, Simin Maleknia, Tzuhn-Yuan Lin, and Richard J. Lagow

Contribution from the Department of Chemistry and Biochemistry, University of Texas, Austin, Texas 78712-1167

Received December 21, 1992. Revised Manuscript Received April 13, 1993*

Abstract: Evidence for a novel type of gas-phase cationic polymerization process is described. Gas-phase ions consisting of a perfluorinated ion attached to an assembly of cyclic ether or thioether molecules, such as ethylene oxide, ethylene sulfide, and tetrahydrofuran, are formed in the chemical ionization source of a mass spectrometer. The ions contain up to five ether molecules depending on the size of the perfluorinated compound and the nature of the ether involved in the reaction. The highly strained ethylene oxide forms product ions containing the most ether molecules bound to a perfluorinated substrate, whereas the unstrained acyclic dimethyl ether results in product ions containing only a single ether molecule. The experimental results suggest that the cyclic ethers attach to a perfluorinated substrate ion and then undergo ring-opening gas-phase polymerization in the gas phase to form an extended polyether chain which is covalently bound to the perfluorinated substrate. Collisionally activated dissociation techniques were used to further characterize the structures of the ions.

Introduction

The variety of types of gas-phase clusters reported over the past decade has increased as new methods of forming and characterizing clusters have been developed.^{1–11} Although much attention has recently focused on the evaluation of carbon cluster chemistry,¹⁰ there also has been growing interest in the loosely-bound organic clusters typified by van der Waals and other molecular aggregates.^{1–19} Such clusters, bound by dispersive (induced dipole) and electrostatic interactions, represent an intriguing class of chemical species which may undergo internal reactions that can result in covalently bound ions.^{11–19} or may possess properties unlike those of the individual subunits. In this report, the formation and characterization of an unusual array of gas-phase ions consisting of perfluorinated ions bound to multiple ether molecules are described. The polymeric ions are generated through ion–molecule association and condensation reactions in the chemical ionization source of a triple-quadrupole

mass spectrometer. As shown herein, examination of the nature of the ethers that form product ions with the perfluorinated substrates supports the proposal that these ions are formed by a new gas-phase ring-opening cationic polymerization process. Cationic polymerization has been reported previously in the gas phase,^{11–19} especially for unsaturated molecular substrates such as acetylene, 1,1-difluoroethylene, propene, ethene, isoprene, and benzylacetate, and is a common mechanistic route in solution to produce polymers,^{20–27} especially of epoxides and other cyclic ethers. Gas-phase studies of cationic polymerization have provided new insight and a solvent-free perspective of the mechanisms and kinetics of ionic chain growth processes.^{11–19}

Perfluorocarbons afford an intriguing yet little studied class of compounds in gas-phase ion chemistry. The synthesis²⁸ and characterization of perfluorocarbons²⁹ have developed rapidly over the past two decades because of their unique properties as artificial blood substitutes.³⁰ Clearly perfluorinated compounds have very different reactive properties than their hydrocarbon counterparts because of the substitution of highly electronegative fluorine atoms for hydrogen atoms. The comparison of gas-phase reactions of perfluorocarbons to those of hydrocarbons provides an illustration of the types of distinctive association reactions that these two related classes of compounds undergo, and may provide insight into new ways to evaluate their novel binding

* Abstract published in *Advance ACS Abstracts*, November 1, 1993.

- (1) Castleman, A. W.; Keese, R. G. *Chem. Rev.* **1986**, *86*, 589.
- (2) Mark, T. D. *Int. J. Mass Spectrom. Ion Phys.* **1987**, *79*, 1.
- (3) Castleman, A. W.; Mark, T. D. In *Gaseous Ion Chemistry and Mass Spectroscopy*; Futrell, J. H., Ed.; Wiley: New York, 1986; p 259.
- (4) Schauer, M.; Berstein, E. R. *J. Chem. Phys.* **1985**, *82*, 726.
- (5) Schauer, M.; Law, K. S.; Berstein, E. R. *J. Chem. Phys.* **1985**, *82*, 736.
- (6) Kummel, A. C.; Haring, R. A.; Haring, A.; De Vries, A. E. *Int. J. Mass Spectrom. Ion Processes* **1984**, *61*, 736.
- (7) Hermann, V.; Kay, B. D.; Castleman, A. W. *Chem. Phys.* **1982**, *72*, 185.
- (8) Illies, A. J. *Org. Mass Spectrom.* **1989**, *24*, 186.
- (9) Iraqi, M.; Lifshitz, C. *Int. J. Mass Spectrom. Ion Processes* **1989**, *88*, 45.
- (10) O'Brien, S. C.; Heath, J. R.; Curl, R. F.; Smalley, R. E. *J. Chem. Phys.* **1988**, *88*, 220.
- (11) El-Shall, M. S.; Schriver, K. E. *J. Chem. Phys.* **1991**, *95*, 3001.
- (12) Meot-Ner, M.; Hunter, E. P.; Field, F. H. *J. Am. Chem. Soc.* **1977**, *99*, 5576.
- (13) Samy El-Shall, M.; Marks, C. *J. Phys. Chem.* **1991**, *95*, 4932.
- (14) Grossleil, J.; Herman, J. A. *Can. J. Chem.* **1971**, *49*, 363.
- (15) Kebarle, P.; Haynes, R. M. *J. Chem. Phys.* **1967**, *47*, 1676.
- (16) Coolbaugh, M. T.; Peifer, W. R.; Garvey, J. F. *Chem. Phys. Lett.* **1990**, *168*, 337.
- (17) Garvey, J. F.; Coolbaugh, M. T.; Whitney, S. G.; Peifer, W. R.; Vaidyanathan, G. *Physics and Chemistry of Finite Systems: From Clusters to Crystals*; 1992; Vol. II, p 1101.
- (18) Coolbaugh, M. T.; Whitney, S. G.; Vaidyanathan, G.; Garvey, J. F. *J. Phys. Chem.* **1992**, *96*, 9139.
- (19) Coolbaugh, M. T.; Vaidyanathan, G.; Peifer, W. R.; Garvey, J. R. *J. Phys. Chem.* **1991**, *95*, 8338.

- (20) Rajendran, A. G.; Timpe, H.-J. *J. Polym. Sci., Part A: Polym. Chem.* **1991**, *29*, 1491.
- (21) Becker, C.; Moussa, K. *J. Polym. Sci., Part A: Polym. Chem.* **1990**, *28*, 3429.
- (22) Crivello, J. V.; Fan, M. *J. Polym. Sci., Part A: Polym. Chem.* **1991**, *29*, 1853.
- (23) Kim, J. B.; Cho, I. *J. Polym. Sci., Part A: Polym. Chem.* **1989**, *27*, 3733.
- (24) *Carbocationic Polymerization*; Kennedy, J. P., Marechal, E., Eds.; John Wiley and Sons: New York, 1982.
- (25) *Principles of Polymerization*; Odian, G., Ed.; Wiley-Interscience: New York, 1970; Chapter 7.
- (26) *Developments in Polymerisation-1*; Haward, R. N., Ed.; Applied Science: London, 1979.
- (27) *Ring-Opening Polymerization*; Frisch, K. C., Reegen, S. L., Eds.; Marcel Dekker: New York, 1969.
- (28) Clark, W. D.; Lin, T. Y.; Maleknia, S. D.; Lagow, R. J. *J. Org. Chem.* **1990**, *55*, 5933.
- (29) Lagow, R. J.; Bierschenk, T. R.; Juhlke, T. J.; Kawa, H. In *Synthetic Fluorine Chemistry*; Olah, G. A., Chambers, R. D., Surya Prakash, G. K., Eds.; John Wiley and Sons: New York, 1992.
- (30) Reiss, J. G.; LeBlanc, M. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 621.

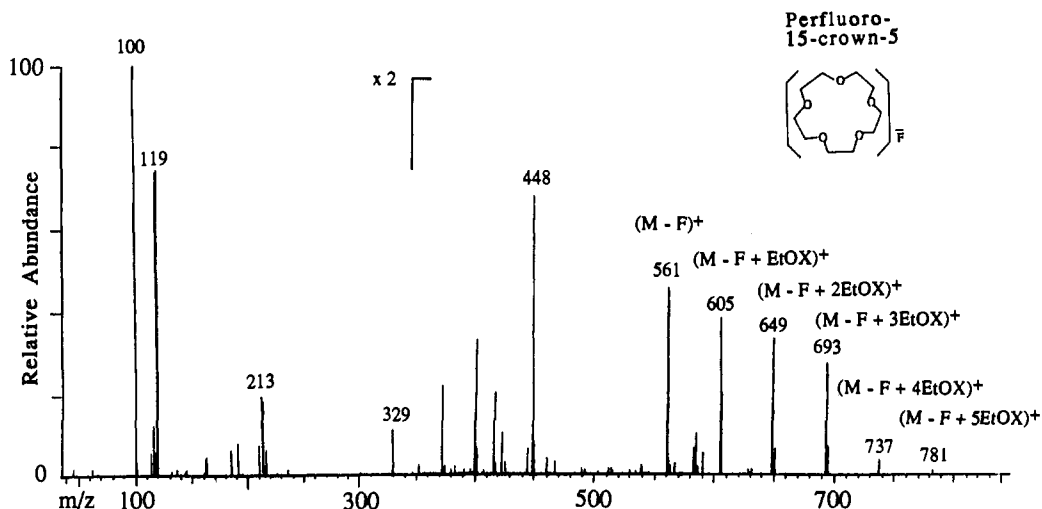


Figure 1. Positive ionization mass spectrum of a mixture of ethylene oxide and perfluoro-15-crown-5.

properties. In this study, collisionally activated dissociation³¹ (CAD) techniques are used to characterize the nature of the binding interactions of the ions, although the CAD spectra provide ambiguous information regarding the actual structures of the ions.

Experimental Section

Gas-phase product ions composed of perfluorinated ions condensed with various ether neutrals were formed via ion-molecule reactions in the chemical ionization source of a Finnigan TSQ-70 triple-quadrupole mass spectrometer. The ether neutrals were introduced into the source through a gas chromatographic inlet, and the pressure was varied from 2×10^{-6} to 1×10^{-5} Torr in the manifold, corresponding to 2–6 Torr in the chemical ionization ion volume, for optimal product formation. Perfluoro compounds were admitted via a variable leak valve to attain a manifold pressure of about 3×10^{-6} Torr. The source temperature was 50 °C. Higher source temperatures were avoided to prevent thermal decomposition of the perfluoro compounds. Under these conditions, the typical abundances of the product ions, $(M-F + n\text{Ether})^+$ relative to the $(M-F)^+$ ions were 5–40% or more depending on the number and type of ether reagent used.

The structures of the product ions were characterized by using low-energy collisionally activated dissociation techniques.³¹ A product ion was mass-selected with the first quadrupole, then accelerated into the second quadrupole, which was filled with an inert collision gas. The collision energy in the laboratory frame was 10 eV, and argon was used as the collision gas at 2 mTorr in the second quadrupole. The fragment ions resulting from the collisional activation process were mass-analyzed in the third quadrupole.

The perfluorinated ethers examined included perfluoro-12-crown-4, perfluoro-15-crown-5, perfluorotriethylene glycol monomethyl ether (perfluorotriglyme), and perfluoro-4,7,13,16,21,24-hexaoxa-1,10-diaza bicyclo[8.8.8]hexacosane (perfluorocryptand). These compounds were synthesized by the LaMar direct fluorination procedure.²⁸ Perfluorodecalin, 15-crown-5, and the ether reagents were obtained from Aldrich Chemical Co. (Milwaukee, WI) and used without further purification. Dimethyl ether was obtained from MG Industries. Ethylene oxide was obtained from Wilson Supplies.

Results and Discussion

Formation of Cluster Ions. In the positive ionization mode, perfluoro compounds by themselves typically form abundant $(M-F)^+$ ions and related fragment ions,³² but not molecular ions M^{++} . Upon addition of various ether neutrals to the ion source, product

Table I. Formation of Ethylene Oxide Product Ions^a

substrate	percent of product ion current: $(M-F + n\text{EtOx})^+$					
	$n = 0$	$n = 1$	$n = 2$	$n = 3$	$n = 4$	$n = 5$
perfluoro-12-C-4	50	25	10	10	5	0
perfluoro-15-C-5	30	25	20	20	<5	<2
perfluoro-18-C-6	35	20	25	10	5	5
perfluorotriglyme	65	20	10	<5	<2	<2
perfluorocryptand	40	15	10	25	5	5
perfluorodecalin	75	15	5	5	0	0

^a Values rounded to the nearest 5%.

ions identified as $(M-F + n\text{Ether})^+$ are formed. For each pair of perfluorinated compounds and ether reagents, the total relative contribution of these unusual product ions is 5–15% compared to the sum of the molecular-type ions and fragment ions of the perfluorinated substrate. A representative spectrum of the products formed from reactions of one perfluorinated compound, perfluoro-15-crown-5, and ethylene oxide (EtOx) is shown in Figure 1. A series of product ions assigned as $(M-F + n\text{EtOx})^+$ extends from $n = 0$ to $n = 5$ units. The ions at m/z 100, 119, 213, and 329 are common fragments of the perfluorinated ether $(M-F)^+$ molecular ion. The ions at m/z 329 and 213 are attributed to loss of one or two $\text{C}_2\text{F}_4\text{O}$ units, respectively, whereas the ions at m/z 100 and 119 likely involve loss of $\text{C}_2\text{O}_2\text{F}_3$ or $\text{C}_2\text{O}_2\text{F}_2$ in conjunction with $\text{C}_2\text{F}_4\text{O}$ units. The results obtained for the formation of ethylene oxide products with other perfluorinated substrates, including both perfluorinated cyclic and acyclic ethers and one perfluorinated alkane (decalin) are summarized in Table I. All of the perfluoro compounds form products with multiple units of ethylene oxide, and in each case, the products may be assigned as $(M-F + n\text{EtOx})^+$. One nonfluorinated substrate (hydro-15-crown-5) was also examined but formed no products with the ethers.

Reactions of the perfluoro compounds with a variety of other ether or thioether neutrals, such as ethylene sulfide, tetrahydrofuran, cyclohexene oxide, diethyl ether, dimethyl ether, and butadiene monoxide, were also evaluated to compare the product formation properties of these ethers. The results are summarized in Table II for reactions with perfluoro-15-crown-5. In each case, the pressure of the reactive ether was varied to promote optimal product formation in the ion source. Of all the ethers examined, the small cyclic ether ethylene oxide forms the most extensive array of products with the perfluorinated compounds, whereas its thioether analog, ethylene sulfide, demonstrates the second most abundant product formation. Reactions with ethylene sulfide result in addition of one, two, or three units, but not four or five units as observed for the ethylene oxide products. A larger cyclic ether, tetrahydrofuran (THF), shows a strong

(31) Busch, K. L.; Glush, G. L.; McLuckey, S. A. *Mass Spectrometry/Mass Spectrometry: Techniques and Applications of Tandem Mass Spectrometry*; VCH Publishers: New York, 1988.

(32) (a) Maleknia, S.; Liou, C.-C.; Brodbelt, J. *Org. Mass Spectrom.* 1991, 26, 997. (b) Bletsos, I. V.; Hercules, D. M.; Fowler, D.; vanLeyen, D.; Benninghoven, A. *Anal. Chem.* 1990, 62, 1275.

(33) *CRC Handbook of Chemistry and Physics*, 61st ed.; Weast, R. C., Astle, M. J., Eds.; CRC Press: Boca Raton, FL, 1980.

Table II. Extent of Cluster Formation with Perfluoro-15-crown-5

ether	number of ether molecules attached
ethylene oxide	$n = 1, 2, 3, 4, 5$
ethylene sulfide	$n = 1, 2, 3$
tetrahydrofuran	$n = 1, 2$
cyclohexene oxide	$n = 1, 2$
diethyl ether	$n = 1$
dimethyl ether	$n = 1$
butadiene monoxide	$n = 1, 2$
NH ₃	$n = 1$
2-methylaziridine	$n = 1$
CH ₄	$n = 0$
H ₂ O	$n = 1$

preference for attachment of two ether units to the perfluorinated compounds (*i.e.* typically the ratio $(M-F + 2THF)^+:(M-F + THF)^+$ is 20:1), but in fact does not promote formation of products containing more than two THF units. Butadiene monoxide shows limited product formation, such that the products containing one butadiene monoxide unit appear to be 5–20 times more abundant than those products containing two units, but products with three or more butadiene monoxide units are not observed. The acyclic ethers, diethyl ether (DEE) and dimethyl ether (DME), attach once to the perfluorinated ions, but larger products are not observed.

Further experiments indicated that products are only formed when the ether unit contains an electronegative sulfur or oxygen heteroatom because simple hydrocarbon molecules, such as methane, do not associate with the perfluorinated ions (see Table II). Additionally, certain amines are not effective in the ion-molecule association reactions with the perfluorinated ions. The perfluorinated substrates may attach a single unit of ammonia, forming $(M-F + NH_3)^+$, but further association is not observed. Likewise, reactions with the strained cyclic amine 2-methylaziridine, a nitrogen-containing analog to ethylene oxide, result in attachment of only one amine molecule, producing $(M-F + 2\text{-methylaziridine})^+$. The latter result suggests that these amines are in some way chemically nonreactive toward product formation.

Cyclohexene oxide is unusual in that it forms products with one or two cyclohexene oxide units in conjunction with losses of 26 amu (apparently loss of C₂H₂). The results for cyclohexene oxide formation are summarized in Table III.

In all cases, the reactions of the reactive ethers with nonfluorinated analogs to the perfluorocarbons, such as hydro-15-crown-5 and decalin, fail to produce product ions. This contrasting result highlights the importance of the highly electronegative nature of the perfluorinated substrates in selectively promoting the reactions.

With respect to the structures of the products, these initial results may be interpreted in two ways. First, each ether unit may be attached separately to the perfluoro substrate, such that there is a "cloud" of ether units surrounding each $(M-F)^+$ ion. This description is consistent with the model that the products consist of a loose electrostatically-bound van der Waals assembly of ether molecules around a central perfluorinated ion.

Alternatively, the spectra may suggest a growing polymer chain of ether units anchored to the perfluorinated substrate. A mechanism is shown in Scheme I which may conceptually represent the gas-phase cationic polymerization process. As shown, ethylene oxide attaches to the electropositive carbonium ion site of the perfluorinated substrate. This product ion presumably may rearrange to a more stable secondary carbonium ion or may continue to propagate via attack of a second ethylene oxide molecule via an S_N2-type reaction. Two conjectures regarding the limit of polymerization are offered. Eventually the cationic terminus may be stabilized by interaction with the electron-rich perfluorinated substrate, by a type of "self-solvation", resulting in termination of polymerization. Alternatively, the polymerization may terminate when the cationic tail becomes

too spatially distant from the activating fluorocarbon substrate. For this latter reason, the larger perfluorinated compounds would thus tend to promote a correspondingly longer polymerization sequence due to their greater electrostatic polarizability. Because the ether molecules by themselves do not undergo spontaneous ring opening and polymerization in the gas phase (as shown later experimentally), we speculate that interaction with an $(M-F)^+$ ion provides an *activating catalytic site* to initiate the polymerization process. The following sections explore in greater detail rationalizations for each of the two hypotheses.

Evidence for Gas-Phase Cationic Polymerization vs van der Waals Cluster Formation. The dipole moments of the various ethers were examined to correlate the electrostatic properties of the ethers with product formation (see Table IV). Presumably the ethers with the highest dipole moments may result in the most extensive van der Waals-type clusters due to their enhanced electrostatic interactions with the electropositive $(M-F)^+$ ions. This hypothesis appears to be a reasonable explanation for the great clustering abilities of ethylene oxide and ethylene sulfide, each of which have dipole moments larger than 1.8 D.¹⁸ However, it fails to explain the absence of products for H₂O (dipole moment 1.85 D) or NH₃ (dipole moment 1.47 D). This lack of correlation erodes support for the hypothesis that the products are van der Waals clusters.

From the preliminary results involving different ether units, the most highly strained cyclic ethers, such as ethylene oxide, result in the most extensive formation of products containing multiple ether units. Conversely, the acyclic ethers do not participate in these types of reactions. It is difficult to formulate a reason why this factor would affect the formation of van der Waals clusters, but an explanation related to polymerization processes is obvious. This effect may be related to the fact that the cyclic structures possess ring strain which specifically promotes ring-opening polymerization. This idea clearly explains the failure of NH₃ and H₂O, both of which have high dipole moments but lack sufficient covalent backbone structure, to react with the $(M-F)^+$ ions. None of the acyclic ethers would polymerize, and the larger cyclic ethers which are less strained would be correspondingly less reactive compared to ethylene oxide. Steric factors which would tend to inhibit polymerization are also suggested by the reduced cluster formation for the bulkier ethers, such as cyclohexene oxide and tetrahydrofuran.

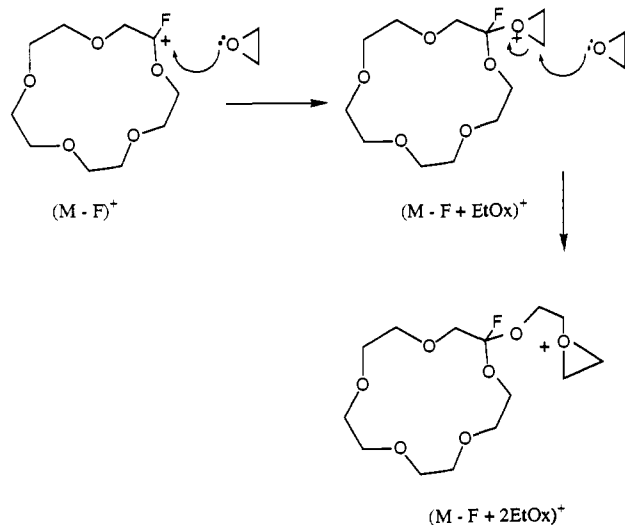
Some of the most convincing evidence in support of the cationic polymerization hypothesis is obtained from examination of the product spectra for the reactions of cyclohexene oxide (C₆O) with the perfluorinated substrate ions. These reactions result in formation of the unusual ions identified as $(M-F + C_6O - n26)^+$ products (Table III) where 26 Da must represent C₂H₂, suggesting that the association reactions are sufficiently exothermic to cause covalent bond rupture within the cyclohexene oxide units. This behavior is incompatible with that expected for formation of van der Waals clusters held by only weak electrostatic interactions, but is consistent for ions formed through a gas-phase eliminative polymerization process¹²⁻¹³ in which new covalent bonds are formed as the polymer chain is propagated.

The observations described above lend greater support to the proposal that the product ions are formed by gas-phase cationic polymerization rather than by van der Waals clustering. Several more experiments described in the following sections were done to further elucidate the nature of the reactions.

Pressure Dependence of Product Formation. The selectivity of product formation was evaluated by the examination of product distributions at variable ether reagent pressure. Shown in Table V are the product distributions for the ethylene oxide/perfluorotriethylene glycol dimethyl ether system at two different ethylene oxide pressures. The products containing more ethylene oxide units are favored at the higher ethylene oxide pressure, but even at the higher ethylene oxide pressure, addition of six or more

Table III. Formation of Cyclohexene Oxide (CxO) Product Ions

substrate	percent of product ion current: cluster formula					
	(M-F) ⁺	(M-F + CxO) ⁺	(M-F + CxO - 26) ⁺	(M-F + CxO - 26 - 26) ⁺	(M-F + 2CxO) ⁺	(M-F + 2CxO - 26) ⁺
perfluoro-15-C-5	50	10	5	30	5	0
perfluoro-18-C-6	55	5	10	30	0	0
perfluorotriglyme	65	10	5	15	0	5

Scheme I. Proposed Mechanism for Gas-Phase Polymerization of Perfluoro-15-crown-5^a

^a The multiple fluorine atoms attached to the polyether skeleton are omitted.

Table IV. Dipole Moments of Ethers^a

ether	dipole moment (D)
ethylene oxide	1.89
ethylene sulfide	1.85
tetrahydrofuran	1.63
diethyl ether	1.15
dimethyl ether	1.30
NH ₃	1.47
CH ₄	0
H ₂ O	1.85

^a From ref 33.

Table V. Cluster Formation of Perfluorotriglyme at Variable Ethylene Oxide Pressure

pressure of EtOx (Torr) ^a	percent of ion current of major ions formed: (M-F + nEtOx) ⁺					
	n = 0	n = 1	n = 2	n = 3	n = 4	n = 5
0.5	65	20	10	3	2	0
1.1	15	4	40	30	5	4

^a Nominal pressure measured in the ion source.

ethylene oxide units is not observed. This suggests that polymeric product formation is not merely a pressure-dependent function but also has a limit dependent on the size or geometry of the perfluoro substrate and/or the kinetics of competing chain termination reactions. For example, as shown in Table I, perfluoro-12-crown-4 can accommodate no more than four ethylene oxide molecules, and perfluorodecalin can accommodate only three ethylene oxide molecules. In fact, the perfluorinated ions may act as size-selective catalysts for cationic polymerization.

Intrinsic Clustering Capabilities of Ethers. The ion-molecule reactions of each ether alone were also examined to determine whether the ethers will polymerize spontaneously in the gas phase or whether they require an activating catalyst (such as a fluorocarbon) in order to polymerize. These results are summarized in Table VI. Most of the ethers form proton-bound dimers at 1 Torr in the chemical ionization source, but none show

Table VI. Mass Spectra of Ethers in a Chemical Ionization Source^a

ether	percent of ion current of major ions observed				
	M ⁺	(M + H) ⁺	(2M + H) ⁺	(3M + H) ⁺	related fragments
butadiene monoxide	0	50	0	0	50
ethylene sulfide	30	40	5	0	25
tetrahydrofuran	0	50	40	0	5
cyclohexene oxide	10	20	20	5	50
ethylene oxide	10	80	<5	0	5

^a At 1 torr of ether pressure; nominal pressure measured in the ion source.

the extensive association observed in the presence of the perfluoro ions. Proton-bound dimers are commonly observed at high pressures in an ion source; the unusual perfluoro/ether polymer-type ions described in this report, however, involve no proton interactions and thus are of a very different nature than any simple proton-bound adduct. These results suggest that the perfluoro substrates indeed *selectively* promote the polymerization process.

Collisionally Activated Dissociation of Polymeric Product Ions. Collisionally activated dissociation techniques were used to characterize the structures of the polymeric product ions. A representative CAD spectrum is illustrated in Figure 2, and Table VII summarizes the CAD spectra obtained for the (M-F)⁺ ion of perfluoro-15-crown-5 and its various ethylene oxide products (M-F + nEtOx)⁺. The bare (M-F)⁺ ion dissociates by loss of one or two C₂F₄O units (formation of 329⁺ and 213⁺, respectively) or by elimination of C₆O₂F₁₄, resulting in a dicarbonyl fluoroether fragment ion at *m/z* 191. In contrast, the (M-F + nEtOx)⁺ product ions predominantly fragment by loss of one of more ethylene oxide units, with low abundances of fragment ions analogous to dissociation of the bare (M-F)⁺ ion also observed. For each product ion, the loss of one ethylene oxide unit is favored over the loss of two or more units. Apparently fragmentation of the polymer chain is kinetically favored over the disruption of the macrocyclic structure. It is well-recognized that many types of polymer ions dissociate by elimination of a sequence of monomer units,³⁴ in many respects analogous to the series of ethylene oxide units observed in the CAD spectra shown herein. Thus, the CAD spectra are consistent with the behavior expected for dissociation of polymeric structures. However, electrostatically-bound cluster ions also tend to dissociate by elimination of a series of monomer units, so the CAD spectra are rather ambiguous in distinguishing the nature of the ion structures. CAD spectra could not be acquired for all of the product ions due to the relatively low abundance of some of the ions.

Cationic Polymerization in Solution. A comparison between cationic polymerization in solution and the present gas-phase results provides insight into their similarities and thus potentially gives many feasible explanations for some of the features observed in these gas-phase results. Ring-opening polymerization processes based on cationic mechanisms have been studied for years in solution²⁴⁻²⁷ and are routinely used in industrial processes. The generally accepted initiation and propagation steps for polymerization of epoxides, cyclic ethers, lactones, lactams, and other cyclic monomers containing heteroatoms involve S_N2 processes

(34) (a) Bletsos, I. V.; Hercules, D. M.; vanLeyen, D.; Benninghoven, A.; Karakatsanis, C. G.; Rieck, J. N. *Anal. Chem.* **1989**, *61*, 2142. (b) Lattimer, R. P.; Munster, H.; Budzikiewicz, H. *Int. J. Mass Spectrom. Ion Processes* **1989**, *90*, 119. (c) Schulten, H.-R.; Lattimer, R. P. *Mass Spectrom. Rev.* **1984**, *3*, 231.

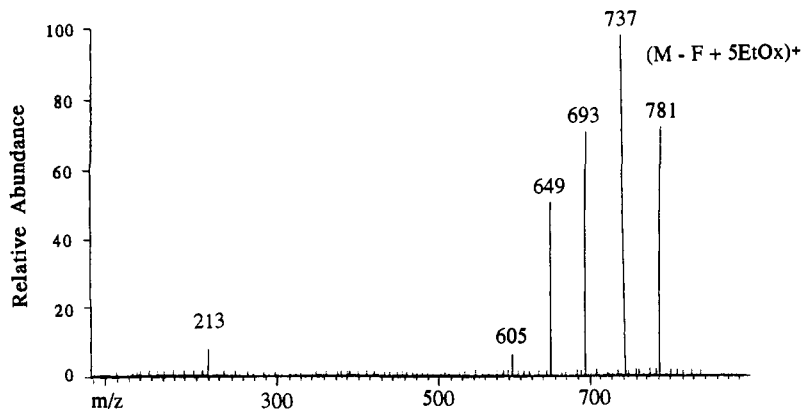


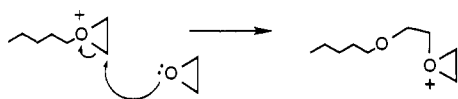
Figure 2. CAD spectrum of the (perfluoro-15-crown-5-F + 5EtOx)⁺ product, *m/z* 781.

Table VII. CAD Spectra of the Perfluoro-15-crown-5 Product Ions

precursor ion	percent of ion current of major fragment ions							
	191 ⁺	213 ⁺	329 ⁺	-C ₂ H ₄ O	-2C ₂ H ₄ O	-3C ₂ H ₄ O	-4C ₂ H ₄ O	others
(M-F) ⁺	20	45	15	na ^a	na	na	na	20
(M-F + 2C ₂ H ₄ O) ⁺	20	40	10	30	0	na	na	10
(M-F + 3C ₂ H ₄ O) ⁺	5	35	10	30	5	0	na	5
(M-F + 4C ₂ H ₄ O) ⁺	<2	5	<2	50	30	10	0	5
(M-F + 5C ₂ H ₄ O) ⁺	0	<2	0	45	30	20	5	<2

^a na: not applicable because a sufficient number of C₂H₄O units are not available in the ion to allow this loss.

in which a heteroatom of a monomer molecule promotes nucleophilic attack on an electron deficient α -methylene group of the polymeric ion,²⁶⁻²⁷ as illustrated here for an oxonium ion.



The addition causes ring opening and concomitant chain growth. Often cationic initiators, such as boron trifluoride, tin tetrachloride, or various other Lewis acids, are used.²⁶ Termination of the process is typically attributed to an intramolecular reaction, for example, forming a stable macrocyclic ion.²⁶⁻²⁷ The mechanism proposed in Scheme I seems feasible in light of the accepted mechanism in solution. Moreover, the same type of self-termination may be reasonable, although not provable, for the gas-phase reactions.

It is known that the ring strain of the monomer is the single most influential factor and thus the driving force for determining the extent of polymer chain growth in solution.²⁵⁻²⁷ For instance, tetrahydropyran does not polymerize, tetrahydrofuran shows limited polymerization, and ethylene oxide polymerizes extensively. This reactivity trend agrees with the gas-phase results described in Table III (*i.e.* compare ethylene oxide to tetrahydrofuran). Accurate quantitation of the trend is not possible due to the difficulty in monitoring the gas-phase concentrations of the extremely volatile ethers in the ionization source.

The presence of methyl or other alkyl groups on the cyclic monomers is also unfavorable for polymerization in solution because they restrict the rotation of the polymer and thus reduce its entropy.²⁶ Moreover, substitution of sulfur heteroatoms for oxygen heteroatoms in the monomer units reduces the strain energy of the ring system and thus decreases polymerizability.²⁶ Although nitrogen heterocycles have strain energies and thus polymerizabilities similar to their oxygenated counterparts,²⁶ methyl substitution at one of the ring carbon atoms greatly disrupts polymerization. Each of these factors observed in solution is

mimicked in the gas-phase results. Ethylene sulfide and 2-methylaziridine are less reactive than ethylene oxide, likely due to the sulfur heteroatom and methyl-substituent effects, respectively.

Temperature studies of polymerization have shown two predominant effects. As the temperature is raised, the rate of polymerization generally increases, but the degree of polymerization and overall conversion efficiency typically decrease due to the faster rates of competing termination reactions.²⁵ Temperature studies are not possible for the gas-phase experiments; however, the pressure study described in an earlier section tends to parallel the general effect seen in solution because the collision frequencies and therefore rates are greater at higher pressures in the gas phase. The contributions due to the competing polymerization and termination processes on the product distributions cannot be distinguished, yet this combined effect may explain the failure of the fluorocarbon ions to promote unlimited polymerization, even at higher pressures.

Conclusions. In summary, evidence suggests that a novel class of polymeric products consisting of a perfluorinated ion (M-F)⁺ and multiple ether molecules has been identified. The highly electronegative nature of the fully fluorinated substrate promotes the cationic polymerization process. A reasonable proposal for the mechanism of formation of the product ions is that they result from initial addition of a neutral ether unit to a (M-F)⁺ ion which has an activating electropositive carbonium ion site surrounded by many electronegative fluorine atoms. The subsequent mechanism of propagation of the larger ions represents a case of gas-phase ring-opening cationic polymerization, in which each ether unit is added to the growing polyether chain anchored to the perfluorinated substrate.

Acknowledgment. The support from the Welch Foundation (F-1155), the NIH (RO1 GM46723-01), the NSF (CHE-9122699), and an ACS-PRF grant (22270-G5) are acknowledged by J. Brodbelt. The support from the Air Force Office of Scientific Research (F49620-92-J-0L04) is acknowledged by R. Lagow. Discussions with John Isbell are acknowledged.