(9) Bokobza, L.; Monnerie, L. *Polymer* **1981**, *22*, 235.
(10) Wang, Y. C.; Morawetz, H. *Mackromol. Chem. Suppl.* **1975**, *1*, 283.
(11) Mark, J. E.; Ko, J. K. *J. Polym. Sci., Polym. Phys. Ed.* **1975**, *13*, 2221.
(12) Masegosa, R. M.; Hernández-Fuentes, I.; Horta, A.; Piérola, I. F. *Polymer*, in press.
(13) Rabek, J. K.; Sanetra, J.; Ranby, B. *Macromolecules* **1986**, *19*, 1674.
(14) Qian, R.; Cao, T. *Polym. Commun.* **1986**, *27*, 169.

Communications to the Editor

Radiation Degradation of Poly(1-butene sulfone). Mechanistic Data from Fourier-Transform Mass Spectrometry

Poly(olefin sulfone) polymers are important positive resists for microlithography, exhibiting unusually high sensitivity to electron beam irradiation.[1,2] Previously proposed mechanisms for their high-energy degradation involve an initial carbon–sulfur bond scission to produce cationic and radical chain ends followed by rapid depolymerization to volatile monomer species.[3-5] To study further this chemistry, we have employed mass spectrometry (MS), subjecting poly(1-butene sulfone) (PBS) to high-energy radiation under the high-vacuum ($<10^{-6}$ Torr) conditions of MS instruments. This should minimize secondary reactions, providing a direct analysis of the resulting fragment ions or initial neutral products ionized close to the site of formation. Utilizing similar MS conditions, a very recent study[6] of the thermal degradation of PBS postulated initial random cleavages at weak chain links,[7] followed by depolymerization to form monomers and the stable telomers $CH_2{=}CC_2H_5(SO_2C_4H_8)_nSO_2CH{=}CHC_2H_5$.

Our initial experiments carried out with a tandem double-focusing instrument[8] utilized a beam of neutralized 10-keV xenon ions from a fast atom bombardment (FAB) gun to irradiate the polymer. Surprisingly, the spectra of PBS gave no evidence for the monomers butene and SO_2; abundances at m/z 56 and 64 were $<10^{-4}$ of those of residual solvent peaks. However, scanning for higher mass products gave very poor sensitivity and reproducibility.

To reduce these problems, pulsed radiation with multichannel recording was employed, utilizing a Fourier-transform (FT) instrument[9-13] and two other forms of high-energy radiation, 11-keV cesium ion bombardment (secondary ion MS (SIMS))[12,14] and plasma desorption (PD) induced by the 100-MeV fission products of ^{252}Cf.[15-19] Laser desorption (LD)/FTMS[13] and Cs^+ bombardment/FTMS[12,14] have been successfully used to ionize polymers of lower molecular weight (up to 7000)[13] with varying degrees of accompanying degradation. Cs^+ bombardment and ^{252}Cf PD/FTMS of PBS again show no presence of any monomeric species (m/z 56 and 64 <0.1% of total ions), contrary to the prediction of a depropagation[1-5] mechanism. The peaks observed are consistent with oligomeric products, but not those expected from a weak-link mechanism.[6,7]

Experimental Section. The Nicolet FTMS-2000 with 3-T superconducting magnet used is described elsewhere.[14,19] For Cs^+ bombardment spectra[14] 20 μL of a 10 μg/mL solution (CH_2Cl_2) of PBS (Mead Technologies) is evaporated on a gold-coated tip for the sample inlet probe. A 120-μs pulse of 20-nA, 11-keV Cs^+ ions strikes the sample, producing positive secondary ions that are trapped with a +1.3-V potential. Before detection, most of the Cs^+ and Cs_2Cl^+ (m/z 301, 303) ions are ejected from the cell; Au_n^+ ions (n = 1, 3, 5, and 7) appear at m/z 197, 591, 985, and 1379.

Samples for ^{252}Cf PD spectra[19] are prepared by electrospraying 100 μL of a 0.5 mg/mL acetone solution with a 2-μm-thick aluminized mylar foil. The ions produced from a 50-μCi ^{252}Cf source are allowed to collect in the cell for 120 s with a –5-V trapping voltage followed by a 65-ms ion detection time for each of 460 co-added measurements.

Results and Discussion. The positive ion spectrum from Cs^+ bombardment of PBS (Figure 1) shows several ion series separated by 120 daltons, corresponding to C_4H_8 (56) + SO_2 (64). This is consistent with formation of the ionized products $CH_3CH{=}CHCH_2(SO_2C_4H_8)_nSO_2H$ (I), giving the molecular ion ($M^{+\bullet}$) series at m/z (120 + 120n); quite significant peaks are observed for n = 2–7. From their mass spectra,[20] these aliphatic sulfone ions should be expected to undergo cleavage of an S–C bond to give an alkyl ion $^+CH(C_2H_5)CH_2(SO_2C_4H_8)_mSO_2H$ (IIa) and a double hydrogen rearrangement producing $CH_3CH{=}CHCH_2(SO_2C_4H_8)_mS(OH)_2^+$ (IIb); by coincidence both are consistent with the ion series m/z (121 + 120m). Unimolecular loss of H_2O from either product ion produces the most abundant series (III) in Figure 1, m/z (103 + 120m), m = 0–10. Other lower mass peaks due to alkyl ($C_nH_{2n+1}^+$) ions are also present in the spectrum.

The dominant formation of these telomers, as well as the negligible formation of monomers, would appear to rule out the depropagation mechanism, which would predict low molecular weight products containing the original chain terminus from the azobis(isobutyronitrile) (AIBN) polymerization initiator. The dominant product of thermal degradation, also thought to involve depropagation,[6] is unimportant in Figure 1 as indicated by the absence of the m/z (175 + 120n)$^+$ series. Figure 1 also gives no evidence for substructures indicative of weak chain links[6,7] as sites of initial backbone rupture.

As a possible alternative mechanism consistent with these data, the RSO_2– radical or ionic reactive sites formed by the initial carbon–sulfur bond cleavage could react further by an *inter*molecular reaction, abstraction of a secondary hydrogen on an ethyl side chain. Hydrogen abstraction reactions in sulfone decompositions have been previously described in the literature.[21,22] The new radical site formed by this hydrogen abstraction is then stabilized by cleavage of the adjacent C–S bond to cleave a second polymer chain and form a terminal olefin, regenerating a new R′ SO_2–. Propagation of this *cross*-chain scission reaction then proceeds by further hydrogen abstraction, and so forth. It is even possible that the hydrogen transferred is already hydrogen-bonded in the original polymer to an oxygen on an adjacent polymer chain. Thus, radiation cleavage of a single C–S bond could cause a propagation reaction in two directions across polymer chains. A second C–S scission nearby on the chain from a second cross-chain reaction would then yield the product I.

0024-9297/87/2220-0698$01.50/0

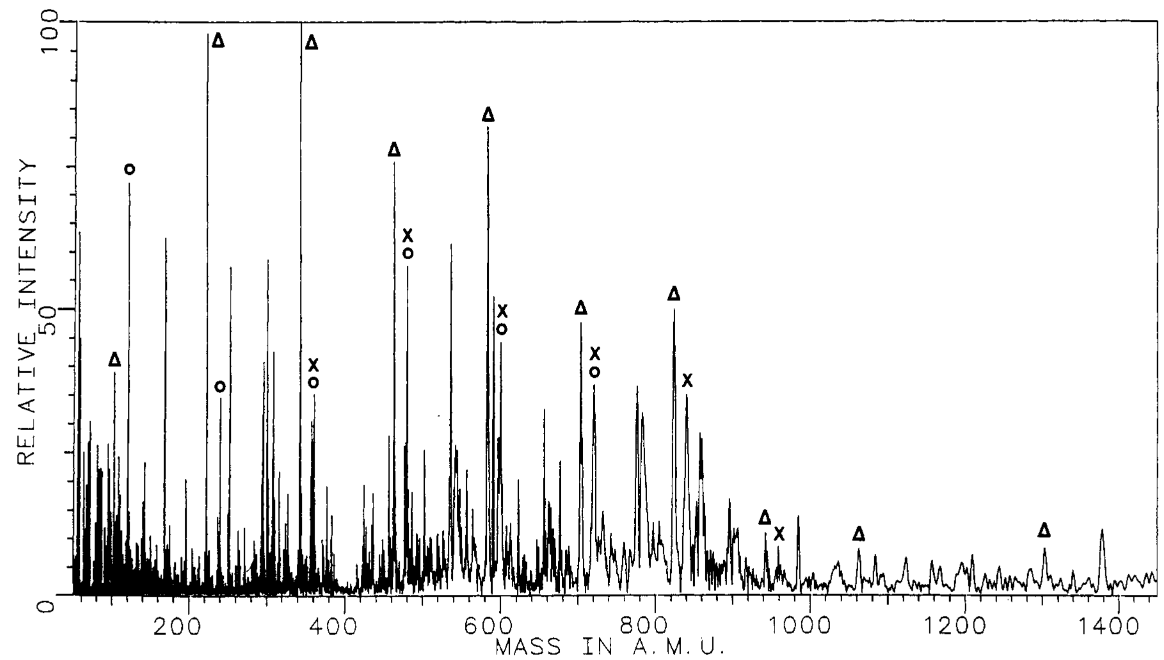

Figure 1. FTMS spectrum from bombardment of PBS with 11-keV cesium ions: (×) ion series I; (○) ion series II; (△) ion series III.

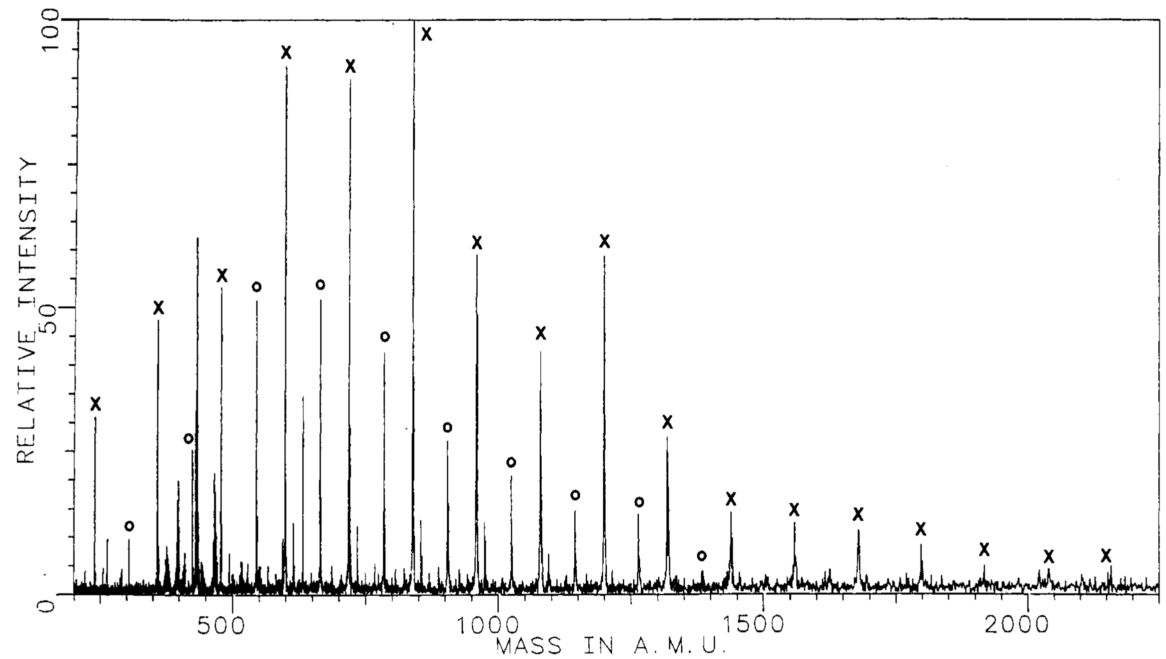

Figure 2. FTMS spectrum from bombardment of PBS with 100-MeV fission fragments from ^{252}Cf: (×) ion series IV; (○) ion series V.

Plasma desorption has affected ionization of even larger molecules than has SIMS; PD of trypsin, MW = 23 463, produces mainly molecular ion species.[23] In many cases the appearance of SIMS and PD spectra is similar.[16,19] With PBS, however, SIMS, but not PD, produces positive ions (for technical reasons we have not yet obtained the SIMS negative ion spectrum). The observation that 100-MeV fission fragments give only negative ions (Figure 2) suggests that positive ions are not formed in the initial ionization event. There is a negligible probability that a second fission fragment will ionize any desorbed neutral products; this is not true for the Cs$^+$ SIMS. However, in PD the "electron shower" thought to accompany passage of the fission fragment[15] could give negative ions through thermal electron capture by I. The fragmentation mechanism proposed above for degradation by Cs$^+$ bombardment can also explain the PD data. Again, no evidence for SO_2 or butene monomer formation was found. The most abundant ion series in Figure 2, extending beyond m/z 2000, is consistent with the loss of hydrogen from negative ions of I to give $CH_3CH{=}CHCH_2(SO_2C_4H_8)_nSO_2^-$ (IV) for m/z (119 + 120n), n = 1–17. The other relatively abundant series in the spectrum corresponding to m/z (185 + 120n) can be produced by RSO_2– abstraction of the tertiary, instead of the secondary, hydrogen from an adjacent chain, yielding $HO_2SCH(C_2H_5)CH_2(SO_2C_4H_8)_nSO_2H$ (V). Hydrogen loss from V produces the observed negative ion series. The formation of V requires the formation of a 1-olefin whereas the production of a 2-olefin accompanies product IV, consistent with the relative abundance of the two ion series.

Although the three types of high-energy bombardment used in this study gave no evidence for monomer formation, none of these types is identical with those that are reported to produce monomers.[3-5] If PBS is not unusually sensitive to the type of bombardment used, the latter monomer formation[3-5] could arise instead from secondary reactions of the initial products, reactions minimized under our conditions. Future experiments include collisionally activated dissociation[24] of the fragment ions to characterize them further, and testing the mechanism with poly(perdeuterio-1-butene sulfone) and other poly(olefin sulfones).

Acknowledgment. We are indebted to I. J. Amster, W. Moreau, T. N. Bowmer, J. M. J. Frechet, and C. G. Willson for helpful discussions, to IBM Corp. for generous financial support, and to the National Institutes of Health and the National Science Foundation for instrumentation.

References and Notes

(1) Brown, J. R.; O'Donnell, J. H. *Macromolecules* **1972**, *5*, 109–114.
(2) Bowden, M. J.; Thompson, L. F. *J. Appl. Polym. Sci.* **1973**, *17*, 3211–3221.
(3) Bowmer, T. N.; O'Donnell, J. H.; Wells, P. R. *Makromol. Chem., Rapid Commun.* **1980**, *1*, 1–6.
(4) Bowmer, T. N.; O'Donnell, J. H. *J. Polym. Sci., Polym. Chem. Ed.* **1981**, *19*, 45–50.
(5) Bowmer, T. N.; O'Donnell, J. H. *J. Macromol. Sci., Chem.* **1982**, *A17*, 243–263.
(6) Jardine, D. R.; Nekula, S.; Than-Trong, N.; Haddad, P. R.; Derrick, P. J.; Grespos, E.; O'Donnell, J. H. *Macromolecules* **1986**, *19*, 1770–1772.
(7) Bowden, M. J.; Thompson, L. F.; Robinson, W.; Biolsi, M. *Macromolecules* **1982**, *15*, 1417–1422.
(8) Amster, I. J.; Baldwin, M. A.; Cheng, M. T.; Proctor, C. J.; McLafferty, F. W. *J. Am. Chem. Soc.* **1983**, *105*, 1654–1655.
(9) Marshall, A. G. *Acc. Chem. Res.* **1985**, *18*, 316–322.
(10) Cody, R. B., Jr.; Kinsinger, J. A.; Ghaderi, S.; Amster, I. J.; McLafferty, F. W.; Brown, C. E. *Anal. Chim. Acta* **1985**, *178*, 43–66.
(11) Wilkins, C. L.; Weil, D. A.; Yang, C. L. C.; Ijames, C. F. *Anal. Chem.* **1985**, *57*, 520–524.
(12) Russell, D. H. *Mass Spectrom. Rev.* **1986**, *5*, 167–189.
(13) Brown, R. S.; Weil, D. A.; Wilkins, C. L. *Macromolecules* **1986**, *19*, 1255–1260.
(14) Amster, I. J.; Loo, J. A.; Furlong, J. J. P.; McLafferty, F. W. *Anal. Chem.* **1987**, *59*, 313–317.
(15) Macfarlane, R. D. *Acc. Chem. Res.* **1982**, *15*, 268–275.
(16) Ens, W.; Standing, K. G.; Chait, B. T.; Field, F. H. *Anal. Chem.* **1981**, *53*, 1241–1244.
(17) Tabet, J. C.; Rapin, J.; Poretti, M.; Gäumann, T. *Chimia* **1986**, *40*, 169–171.
(18) Viswanadham, S. K.; Hercules, D. M.; Weller, R. R.; Giam, C. S. *Biomed. Environ. Mass Spectrom.*, in press.
(19) Loo, J. A.; Williams, E. R.; Amster, I. J.; Furlong, J. J. P.; Wang, B. H.; McLafferty, F. W.; Chait, B. T.; Field, F. H. *Anal. Chem.*, submitted.
(20) Budzikiewicz, H.; Djerassi, C.; Williams, D. H. *Mass Spectrometry of Organic Compounds*; Holden-Day: San Francisco, 1967; p 556.
(21) Wellisch, E.; Gipstein, E.; Sweetin, O. J. *J. Appl. Polym. Sci.* **1964**, *8*, 1623–1631.
(22) Smakman, R.; deBoer, Th. J. *Org. Mass. Spectrom.* **1970**, *3*, 1561–1588.
(23) Jonsson, G. P.; Hedin, A. B.; Håkansson, P. L.; Sundqvist, B. U. R.; Säve, B. G. S.; Nielsen, P. F.; Roepstorff, P.; Johansson, K.-E.; Kamensky, I.; Lindberg, M. S. L. *Anal. Chem.* **1986**, *58*, 1084–1087.
(24) Cody, R. B., Jr.; Amster, I. J.; McLafferty, F. W. *Proc. Natl. Acad. Sci. U.S.A.* **1985**, *82*, 6367–6370.

Joseph A. Loo, Bing H. Wang, Frank C.-Y. Wang, and Fred W. McLafferty*

Department of Chemistry, Baker Laboratory
Cornell University
Ithaca, New York 14853-1301

Paul Klymko

IBM, East Fishkill
Hopewell Junction, New York 12433-0999

Received October 20, 1986

Light-Scattering Characterization of Poly(tetrafluoroethylene)

We have, for the first time, succeeded in determining the weight-average molecular weight M_w of a poly(tetrafluoroethylene) (PTFE) polymer, $-(CF_2CF_2)_x-$, commercially known as Teflon (a registered trademark of Du Pont), which was invented more than 40 years ago. Furthermore, we have succeeded in determining the z-average root-mean-square radius of gyration $\langle R_g \rangle$ and the second virial coefficient (A_2) for the PTFE polymer in a high-boiling-point solvent, made up mainly of poly(fluoroethylene/chloroethylene) oligomers, by means of light-scattering intensity measurements and in estimating the molecular weight distribution (MWD) by means of a time correlation function cumulants analysis. In this Communication, we briefly report our development of the light-scattering characterization of Teflon, leaving the details to a subsequent article that will be coauthored with W. Buck at Du Pont.

One of the ultimate challenges in determining the fundamental macromolecular parameters of polymers in solution is to be able to characterize Teflon, an important specialty polymer that has essentially defied an absolute determination of molecular weight over all these years. Radioactive tracers have been used to determine end groups and number-average molecular weights of several specially prepared PTFE polymers.[1] An obvious answer to this challenge is to find a solvent for Teflon, although it is not a trivial extension of any physical technique even if a solvent for Teflon does become available. In our search for a solvent for Teflon, we prefer to investigate the PTFE solution properties above the melting point of PTFE (~330 °C). Thus, we need a solvent that boils above 330 °C and high-temperature instrumentation.

From recent investigations on polymer probe dynamics[2] using a quaternary system consisting of a semidilute isorefractive polystyrene (PS) in a mixed solvent of α-chloronaphthalene and toluene with dilute poly(methylmethacrylate) (PMMA) as the optical probe, we found that we could characterize the PMMA polymer even in multicomponent solvents with complex structures.[2-4] Oligomers of PTFE could be a solvent for PTFE like alkanes could be solvents for polyethylene at high temperatures. Additional requirements for the PTFE solvent are that we need oligomers of sufficiently high molecular weight in order to achieve the high boiling point and with reasonable refractive index difference from the PTFE polymer in order to yield measurable scattered intensities for such a PTFE solution at dilute concentrations. The fractionally distilled solvents are oligomers of poly(chlorotrifluoroethylene) (to be denoted by MO as mixed oligomers and courtesy of W. Buck). The solvent has a boiling point of ~350 °C and a refractive index of ~1.32 at 340 °C and should suffice for the present demonstration. After completion of the present study, we note that the solvent quality could perhaps be improved by using oligomers of perfluoro polymers.

We have been able to overcome many of the difficulties encountered in the light-scattering characterization of specialty polymers[5-10] such as poly(1,4-phenyleneterephthalamide)[6-9] and an alternating copolymer of ethylene and tetrafluoroethylene (PETFE), commercially known as Kevlar (a trademark of Du Pont) and Tefzel (a trademark of Du Pont), respectively. In the light scattering characterization of Tefzel,[10,11] we constructed a dissolution/filtration apparatus capable of dissolving PETFE in diisobutyl adipate at 250 °C and subsequently filtering the PETFE solution in the same closed apparatus (under an