(22) D. Gaeckle, W. P. Kao, D. Patterson, and M. Rinfret, *J. Chem. Soc., Faraday Trans. 1*, **69**, 1849 (1973).
(23) D. E. G. Jones, I. A. Weeks, and G. C. Benson, *Can. J. Chem.*, **49**, 2481 (1971).
(24) P. de Saint-Romain, Ph.D. Thesis, McGill University, Montreal, 1977.
(25) M. Barbe, Ph.D. Thesis, McGill University, Montreal, 1978.
(26) H. Tra Van and D. Patterson, unpublished results.

ESCA and Mass Spectroscopic Studies of Degradations of Poly[bis(trifluoroethoxy)phosphazene]: Pyrolysis, Ultraviolet Light, and Electron Beam Induced Degradations

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ABSTRACT: Pyrolysis, UV light, and electron beam induced degradations of poly[bis(trifluoroethoxy)phosphazene] have been studied with ESCA and infrared and mass spectroscopic techniques together with gas chromatographic separation. The data obtained reveal the structural changes taking place in the polymer backbone due to the cross-linkage and the oxygen shift to the nitrogen upon the side group elimination. These studies support the mass spectroscopic data of the gaseous products formed in the side group removal.

Polyphosphazenes, polymers having repeating nitrogen–phosphor linkages as backbone chains, are recently gathering renewed interest because of their specific characteristics as processing materials.[1] Allcock and his co-workers reported UV light induced degradation of poly[bis(trifluoroethoxy)phosphazene] under vacuum, along with other polymeric and cyclic oligomer phosphazenes;[2] there they have found gaseous products such as trifluoromethane, 1,1,1-trifluoroethane, and carbon dioxide after a long irradiation at 254 nm. Although some molecular weight changes were observed after irradiation in air, there is no information available about the changes in the backbone. Mochel and Cheng reported a ^{13}C-NMR study of thermal rearrangement of poly[bis(methoxy)phosphazene] up to 150 °C, which involved migration of a methyl group from the methoxy position to the nitrogen.[3] No gaseous products were reported, but some cross-linking was inferred from increase of line widths.

We wish to report here our study of degradations of poly[bis(trifluoroethoxy)phosphazene] in pyrolysis, UV light, and electron beam exposures with ESCA, infrared, and mass spectroscopic techniques together with gas chromatographic product separation.

Our result on the gaseous products formed in the degradation agrees with the reported one.[2] We also observed significant oligomerizations of the high molecular weight polymer, particularly in pyrolysis. The most significant change is the one in the main chain, as revealed in ESCA data of the degradated polymer samples.

Experimental Section

Poly[bis(trifluoroethoxy)phosphazene]. The polymer was prepared from sodium trifluoroethoxide and poly(dichlorophosphazene) in tetrahydrofuran in the same way as reported by Allcock and his co-workers.[4] Its purification was carried out by several precipitations from acetone into water and finally a precipitation from acetone into benzene. The result of its elementary analyses is as follows[5] (the data in parentheses were calculated from the structure): C, 20.30 (19.6); H, 1.66 (1.6); N, 5.86 (5.7); P, 12.00 (12.6); Cl, 0. The fluorine and oxygen analyses were not carried out because of interference by the phosphorus present.[5]

A wide-band ESCA spectrum of the poly[bis(trifluoroethoxy)phosphazene] used in the study reveals the expected amounts of fluorine and oxygen in the sample, as shown in Figure 1. All major peaks of Figure 1 have been assigned to the elements present in the sample. No chlorine was detected at its binding energy of 200 eV even after the data accumulation of 120 time scans.

The purified white powder obtained was dissolved in methyl ethyl ketone, and the polymer films were spin-coated on either aluminum wafers for ESCA and mass spectroscopic studies under electron beams or on sodium chloride plates for infrared absorption studies in pyrolysis and UV light irradiations. The polymer films were then baked under vacuum at 80 °C for a few hours in order to remove any trace of the residual solvent.

Pyrolysis, UV Light, and Electron Beam Exposures. The pyrolysis was conducted under vacuum in a Pyrex glass tube with a break seal; after pyrolysis, the gaseous products were separated with a gas chromatograph with an 8-ft silica gel column at room temperature. Each peak was identified by its mass spectrum and retention time in the column in comparison with those of the authentic samples, trifluoromethane and 1,1,1-trifluoroethane (supplied by PCR Inc.).

The UV light exposures were carried out under vacuum with a Hanovia medium pressure mercury lamp with quartz windows. The gaseous products were analyzed in the same way as in the pyrolysis.

The electron beam exposures were conducted with a Varian scanning Auger gun at 3 KeV electron energy; the estimated dosage was 10^{-4} C/cm^2. The mass spectra of the gaseous products generated during the electron beam exposures were taken simultaneously with the exposures in a typical pressure range of 10^{-4} Pa; the equipment used was described previously.[6]

Analytical Instruments. ESCA measurements were carried out at room temperature under a vacuum better than 3×10^{-7} Pa with a Hewlett-Packard Model 5650B ESCA spectrometer, which had resolution better than 1 eV. The samples were flooded with thermal electrons during the data collections to neutralize the charge effect. The reported binding energies were referred to $Au_{4f7/2}$ transition at 83.9 eV.

[‡] Deceased in 1978.

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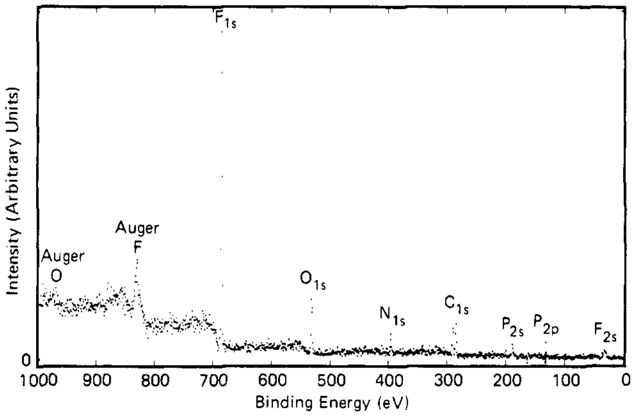
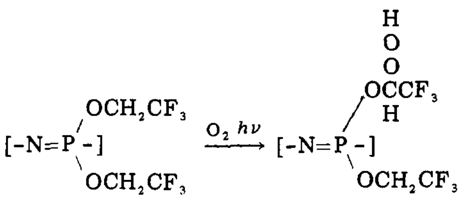


Figure 1. Broad-band ESCA spectrum of the poly[bis(trifluoroethoxy)phosphazene] used in the study.

An UTI quadrupole mass spectrometer was used for the measurements during the electron beam exposures, and a Hitachi Perkin-Elmer mass spectrometer was used for separated gaseous products.

Results and Discussion

1. UV Light Induced Degradation. The gaseous products formed under UV light irradiation were CF_3CH_3 and a trace of CF_3H with the main product CO_2 in agreement with the reported results.[2] A small reduction of the C–H absorption at 2975 cm^{-1} relative to the rest of the infrared absorption in 1450 to 600 cm^{-1} was observed after 30 h of UV light irradiation; this small change was caused by the removal of the side groups as CH_3CF_3. In order to explain the major photoproduction of CO_2, a direct oxygen addition, presumably in its singlet state, to the side groups of the polymer has been proposed as shown in the following:[2]



$$[\text{-N=P(OCH}_2\text{CF}_3)_2\text{-}] \xrightarrow{O_2\,h\nu} [\text{-N=P(OC(OOH)HCF}_3)(\text{OCH}_2\text{CF}_3)\text{-}] \qquad (1)$$

Traces of oxygen trapped in the polymer matrices are probably responsible for the above photooxidation. The infrared absorption study did not supply any supporting evidences for this proposed structural change. Our ESCA data, however, may support the above scheme of the direct oxygen attack to the polymer side group.

A 6 h UV light exposure under vacuum did not induce any significant changes in the binding energies of F_{1s}, N_{1s}, and P_{2p} of the polymer sample, although some broadenings and the intensity reduction for F_{1s} were observed relative to the unexposed, original polymer sample, as shown in Figures 2, 4, and 6.

In the O_{1s} signal of the photolyzed sample, a small but clearly discernible new signal appeared at a binding energy 0.6 eV lower than the original one at 534.7 eV. As shown in Figure 5, no such new separate signal appeared in the electron beam exposed sample nor in the pyrolyzed one. This new signal of O_{1s} may be derived from the oxygen of the peroxide group shown in reaction 1. The peroxide oxygen binding to the hydrogen may show a small shift to the lower binding energy due to a small minus charge on the oxygen generated by the charge transfer from the hydrogen; this notion of a local charge separation is well in accordance with the accepted bond theory,[7] and it is established that a charge accumulation shifts the binding energy to a lower value.[8] This assignment of the newly appearing signal of O_{1s} may substantiate the proposed direct attack of the oxygen to the polymer in the UV light induced photodegradation of poly[bis(trifluoroethoxy)phosphazene].

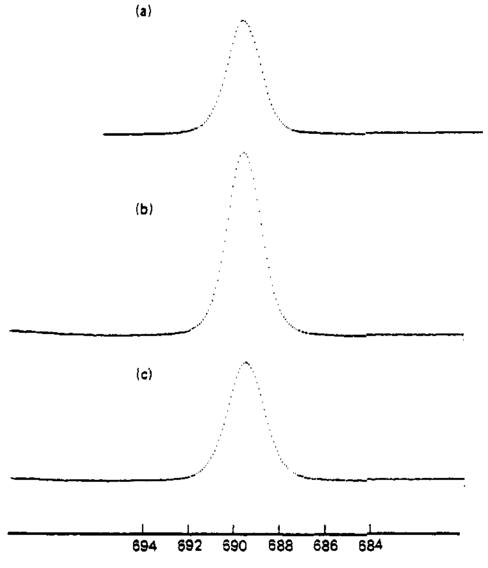


Figure 2. F_{1s} core level spectra of poly[bis(trifluoroethoxy)phosphazene]: (a) the original polymer film in half sensitivity relative to others; (b) the UV light exposed film; (c) the electron beam exposed film.

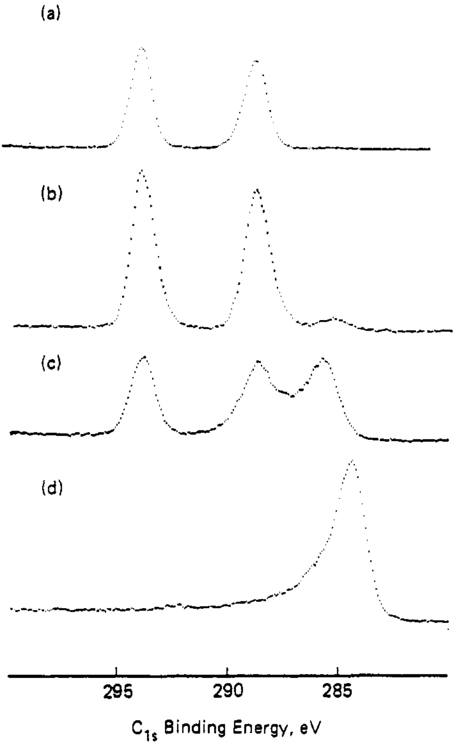


Figure 3. C_{1s} core level spectra of the polyphosphazene: (a) the original polymer in half sensitivity relative to all others; (b) the UV light exposed film; (c) the electron beam exposed film; (d) the pyrolyzed film at 500 °C for 1 h.

In the C_{1s} signals of the UV light exposed sample, not only were the intensity decreases of both C_{1s} signals for CF_3 at 293.7 eV and for CH_2 at 288.6 eV observed, but also a new olefinic C_{1s} signal at 285 eV appeared; this new C_{1s} signal may be derived from the cross-linking carbons formed by the elimination of CF_3H. The appearance of

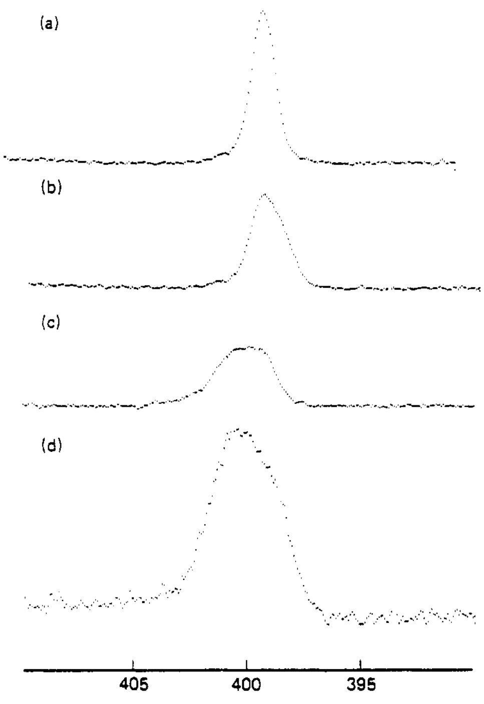


Figure 4. N_{1s} core level spectra of the polyphosphazene: (a) the original polymer film; (b) the UV light exposed film; (c) the electron beam exposed film; (d) the pyrolyzed film at 500 °C for 1 h in 2.5 × sensitivity relativity to (a), (b), and (c).

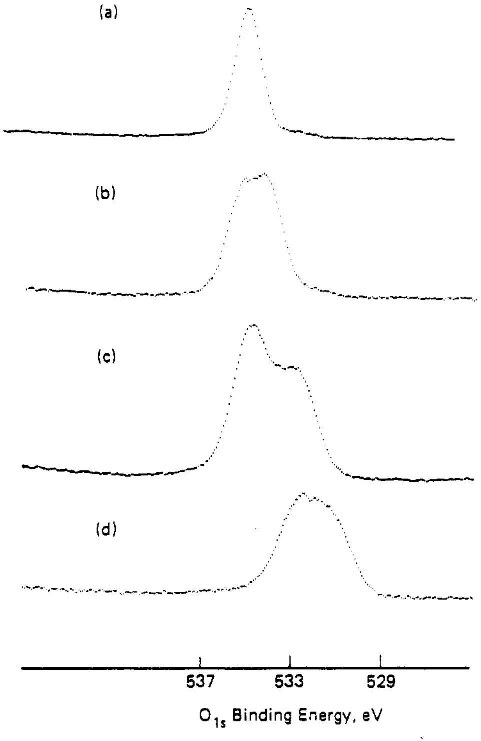


Figure 5. O_{1s} core level spectra of the polyphosphazene: (a) the original polymer film in half sensitivity relative to all others; (b) the UV light exposed film; (c) the electron beam exposed film; (d) the pyrolyzed film.

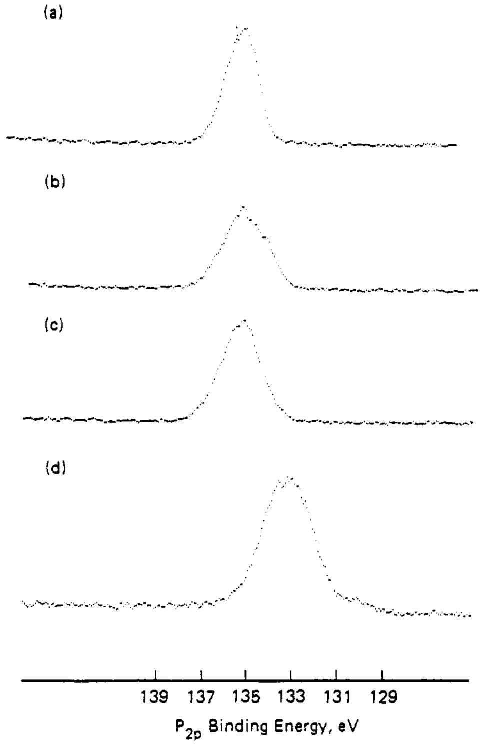


Figure 6. P_{2p} core level spectra of the polyphosphazene: (a) the original polymer film; (b) the UV light exposed film; (c) the electron beam exposed film; (d) the pyrolyzed film in 2× sensitivity relative to (a), (b), and (c).

the olefinic C_{1s} signal, shown in Figure 3, is more distinguished in the electron beam exposed polymer as well as in the thermally degraded samples. The formation of the olefinic cross-linkage is supported also by the infrared spectrum, as described in the pyrolysis section. The UV light or electron beam exposed parts of the polymer films became less soluble in methyl ethyl ketone, revealing cross-linkages in the exposed regions.

2. Electron Beam Induced Degradation. The mass spectra of the gaseous products formed during electron beam exposures showed a significant increase at m/e 69, which corresponded to CF_3, and the hydrogen peak. The fraction pattern of CF_3CH_3 with the parent peak at m/e 84 showed the major peak at m/e 69 together with a small peak at m/e 15 due to CH_3. If CF_3CH_2 were removed preferentially from the side groups, a corresponding increase at m/e 14 due to CH_2 would have been observed during the electron beam exposures. The mass spectra observed, however, did not show any significant increase at m/e 14, indicating that the CF_3 elimination was a dominant process in the electron beam induced reactions.

Corresponding to the CF_3 and CF_3CH_2 removals, the F_{1s} and C_{1s} signal intensities decreased under the electron beam exposures. Except for the intensity reduction, however, there is no significant shift in the binding energy of the F_{1s} transition; in addition, no change in the intensity and the position of the P_{2p} transition was observed, as shown in Figures 2 and 6. The importance of CF_3 and CF_3CH_2 eliminations from the side groups under electron beam exposures is revealed in the C_{1s} signals of the exposed sample. The olefinic linkages produced by the CF_3H elimination were more pronounced in the electron beam exposures than in the UV light irradiation as indicated by the newly formed C_{1s} signal at 285.5 eV. From the intensity decrease of the C_{1s} signals for CF_3 at 293.7 eV and for CH_2 at 288.6 eV, and the newly formed olefinic C_{1s} signal, the ratio of CF_3CH_2 to CF_3 elimination is estimated as follows: under the UV light irradiation $[CF_3CH_2]/[CF_3] = 5.5$, and under the electron beam exposures $[CF_3CH_2]/[CF_3] = 0.8$. The diminishing ratio with the increasing energy input is also observed in the pyrolysis.

Contrary to the C_{1s} signals, the intensity of the O_{1s} signals of the electron beam exposed samples did not decrease significantly. No appreciable change in the total signal intensities is observed for the O_{1s}, N_{1s}, and P_{2p}

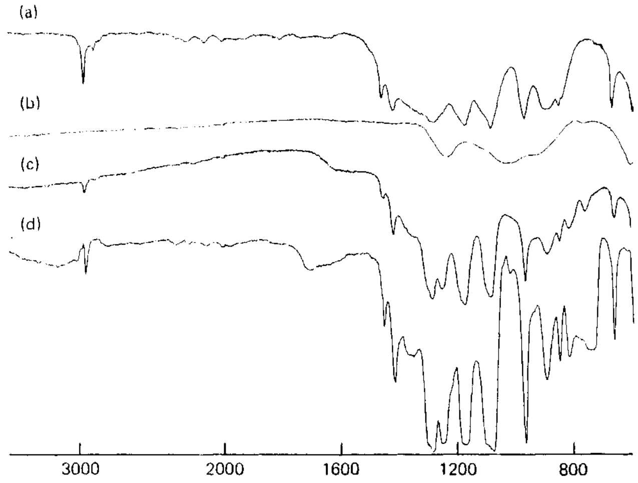


Figure 7. Infrared absorption spectra of poly[bis(trifluoroethoxy)phosphazene]: (a) the original polymer film on a sodium chloride plate; (b) the pyrolyzed film under vacuum at 500 °C for 1 h; (c) the pyrolyzed film under vacuum at 400 °C for 1 h; (d) a viscous liquid product dissolved in chloroform.

signals. A newly appearing O_{1s} signal, 2 eV lower than the original O_{1s} signal, under the electron beam exposures may belong to the oxygen next to the cross-linking olefinic bond generated by the CF_3H removal. The loss of the electron-withdrawing CF_3 group results in the increase in the charge population on the oxygen atom in the cross-linking bond, which in turn shifts the binding energy of the O_{1s} to a lower value. Hidden in the tailing of the above O_{1s} signal, another kind of oxygen atom, which is more apparent in the pyrolysis samples of the next section, appeared. This new kind of structural change is probably related to the change of the N_{1s} signal.

The N_{1s} signal of the electron beam exposed samples became not only broad but also its central position shifted to ≈400 eV, which was 0.9 eV higher than the original position. This N_{1s} shift is discussed in more detail in the discussion of the pyrolyzed samples.

3. Pyrolysis. The gaseous products formed in the pyrolyses were separated with a 2.4-m silica gel column, and each species was identified by comparing mass spectra and retention time with those of authentic samples. The identified products were CO_2, CF_3H, and CF_3CH_3. The pyrolysis was carried out for 5 h at 300 °C, for 1 h at 400 °C, and for 0.5 h at 500 °C. Their relative yields are the following: at 300 °C there was no evidence of CF_3H, $[CO_2]/[CF_3CH_3] = 22$; at 400 °C $[CF_3CH_3]/[CF_3H] = 4.0$, $[CO_2]/[CF_3H] = 7.6$; at 500 °C $[CF_3CH_3]/[CF_3H] = 1.6$, $[CO_2]/[CF_3H] = 0.3$. The pyrolysis results reveal an increasing tendency of the C–C bond breakage relative to the O–C bond scission with increasing temperature: C–C bond energy 347–356 J/mol and O–C bond energy 318–331 J/mol.[9] The larger energy input tends to break the stronger bonds more often than the lower energy input, as in the case for the UV light vs. the electron beam exposures in the previous sections. The CO_2 formation became less evident at higher temperatures, while in the photooxidation it was the major product, far more predominant over the CF_3CH_3 formation.

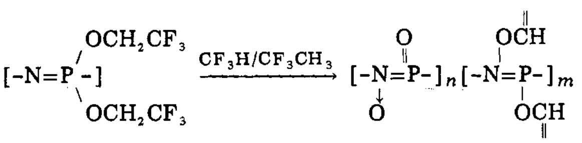
In the pyrolysis, the oligomerization took place. Viscous liquid deposited on a wall of Pyrex glass reactors. Figure 7d shows the infrared spectrum of the oligomeric viscous liquid dissolved in chloroform together with the spectra of the original polymer films of poly[bis(trifluoroethoxy)phosphazene] on a sodium chloride plate (Figure 7a), the spectra of the pyrolyzed films at 500 °C (Figure 7b), and the spectra at 400 °C (Figure 7c). The oligomeric liquid has a similar spectrum to that of the original polymer, except for the reduced intensity of CH absorption at 2960 cm^{-1}, a new absorption at 3020 cm^{-1} belonging to $-CH{=}CH-$, and new absorptions at 1300 and 1010 cm^{-1}. The new absorption at 1300 cm^{-1} is also observed in the pyrolyzed polymer films at 400 and 500 °C. The absorption at 1010 cm^{-1} appears as a broad band in the pyrolyzed films at 500 °C; because of the broadness this absorption may be hidden in the pyrolyzed films at 400 °C. A markedly reduced CH_2 absorption at 2970 cm^{-1} of the pyrolyzed films is the result of the elimination of the side groups. The new infrared absorptions at 1300 and 1010 cm^{-1} may be assigned to $P{=}O$ and $N{\to}O$ groups;[10] these structural changes in the backbone will be discussed with the ESCA data.

The CF_3 groups were completely eliminated from the side chains after a 500 °C pyrolysis, as substantiated by the disappearance of the F_{1s} signal and by the shift of the C_{1s} signals; only olefinic and amorphous carbon C_{1s} signal appeared with the maximum position at 284.3 eV, shown in Figure 3d. .

In addition to the O_{1s} signal of the cross-linking bond discussed in the previous section, another type of O_{1s} signal with a slightly lower binding energy, thereby belonging to the oxygen atom with a higher charge density, appeared at 531.8 eV, 1.0 eV lower than the cross-linking O_{1s} signal.

As shown in Figure 6, the P_{2p} signal shifted to a lower binding energy 133 eV from the original one at 135 eV. Contrary to the C_{1s}, O_{1s}, and P_{2p}, the maximum position of the N_{1s} signal shifted to a higher binding energy of 405 eV, 1.3 eV higher than the original one, with a small shoulder at the original position. A shift to a higher binding energy is caused by a loss of charge density on the nitrogen atom.[11]

The experimental data of these ESCA, infrared spectra, and gaseous product analyses suggest the following structural changes in the pyrolyzed films:



$$[-N{=}\overset{OCH_2CF_3}{\underset{OCH_2CF_3}{P}}-] \xrightarrow{CF_3H/CF_3CH_3} [-\underset{\overset{\downarrow}{O}}{N}{=}\overset{\overset{O}{\|}}{P}-]_n[-\overset{\overset{\|}{OCH}}{\overset{|}{N}}{=}\underset{\underset{\|}{OCH}}{\underset{|}{P}}-]_m \qquad (2)$$

The relative ratio of the above two structural units depends on the pyrolysis conditions.

The cross-linking reactions are also found in the UV light and electron beam exposed films. The reactions are initiated by the CF_3 removal, resulting in a reduced solubility in methyl ethyl ketone and formations of olefinic linkages. The exact mechanisms, however, are not clear.

The formation of the $N{\to}O$ bond increases the charge density on the oxygen atom, whereas it reduces the charge on the nitrogen, thus resulting in the higher binding energy of the N_{1s} signal, and in the lower binding energy of the O_{1s}; both shifts are observed in the ESCA data of the pyrolyzed films. The extended $P{=}O$ formation and cross-linking result in an increase of the charge density on the part of the phosphorus due to the loss of the electron withdrawing CF_3 groups, resulting in a shift to a lower binding energy of P_{2p}. These ESCA results, which are surface-limited data, agree well with the infrared spectra of the bulk samples.

The infrared absorption for $P{=}O$ is reported to be in a region of 1300 to 1250 cm^{-1}. The new absorption peak at 1300 cm^{-1} shown in Figure 7 agrees with this reported $P{=}O$ absorption. The $N{\to}O$ group is known to have the infrared absorption in a range of 1300 to 1200 cm^{-1} for aromatic compounds and in a range of 970 to 950 cm^{-1} for aliphatic compounds. The N→O group appearing in reaction 2 does not belong to any of these groups. However, part of the broad band observed at 1000 cm^{-1} may well be assigned to this group. Thus the ESCA data as well as the infrared spectra support the structural changes described in reaction 2. The P=O formation has also been reported in thermal rearrangement of poly[bis(methoxy)phosphazene].[3]

Conclusions

The ESCA data and the infrared spectra of poly[bis(trifluoroethoxy)phosphazene] exposed to pyrolysis, UV light, and electron beams reveal the structural changes taking place in the polymer backbone due to the cross-linkage and the oxygen shift to the nitrogen upon the side group elimination. These studies support the mass spectroscopic data of the gaseous products formed in the elimination of the side groups. The increasing energy input increases the relative yield of CF_3H to CF_3CH_3. The latter and CO_2 are the major products in low-temperature pyrolysis and UV light exposures. The ESCA data may support the photooxidation mechanism proposed.

References and Notes

(1) For a review, see H. R. Allcock, *Angew. Chem., Int. Ed. Engl.*, **16**, 147 (1977).

(2) J. P. O'Brien, W. T. Ferrar, and H. R. Allcock, *Macromolecules* **12**, 108 (1979); H.R. Allcock, J. P. O'Brien, W. Ferrar, and K. Kosydar, "Final Report to N.A.S.A. (Langley)", Grant NBG 1141, July 1977.

(3) V. D. Mochel and T. C. Cheng, *Macromolecules*, **11**, 176 (1978).

(4) H. R. Allcock and R. L. Kugel, *J. Am. Chem. Soc.*, **87**, 4216 (1965); H. R. Allcock, R. L. Kugel, and K. J. Valan, *Inorg. Chem.*, **5**, 1709 (1966); see also ref 2.

(5) The elementary analyses were carried out by Childers Microanalytical Laboratories, Milford, N.J. 08848.

(6) H. Hiraoka, *IBM J. Res. Dev.*, **21**, 121 (1977).

(7) L. Pauling, "The Nature of the Chemical Bond", 3rd ed., Cornell University Press, Ithaca, N.Y., 1960.

(8) K. Siegbahn, C. Nordling, G. Johansson, J. Hedman, R. F. Heden, U. Gelius, T. Bergmark, L. O. Werme, R. Manne, and Y. Baer, "ESCA Applied to Free Molecules", North-Holland Publishing Co., Amsterdam, 1969; see also D. T. Clark, *Adv. Polym. Sci.*, **23**, 125 (1977).

(9) B. Ranby and J. F. Rabek, "Photodegradation, Photo-Oxidation and Photo-Stabilization of Polymers", Wiley, New York, 1975, pp 45–48.

(10) K. Nakanishi, "Infrared Absorption Spectroscopy", Nankodo, Tokyo, 1960.

(11) H. Hiraoka and W. Lee, *Macromolecules*, **11**, 622 (1978).

High-Resolution Carbon-13 Nuclear Magnetic Resonance Studies of Polymers in the Solid State. Aromatic Polyesters

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ABSTRACT: High-resolution ^{13}C NMR spectra have been obtained for the insoluble, highly crystalline homopolymer of *p*-hydroxybenzoic acid, two methoxy derivatives of this polymer, and two copolymers with biphenylene terephthalate by use of proton dipolar decoupling, magic-angle spinning, and ^{13}C-{^{1}H} cross-polarization techniques. Resolution is sufficient that the majority of carbons in the homopolymer repeat units appear as individual resonance lines. The widths of resonance lines ($\leq$15 Hz) are 3–6 times more narrow than those obtained for glassy polymers—a result which is attributed to both the rigidity of these aromatic polyesters and the homogeneous local environment associated with crystal habit.

The design of polymers which possess a specific set of material properties requires understanding of structure–property relationships for macromolecules. Basic to the elucidation of these insights is the necessity of having characterization techniques which permit detailed analysis of polymer structure. In this regard, one of the more useful techniques in delineating the composition, conformation, and microstructure of chain molecules has been high-resolution NMR spectroscopy. The high resolving power of proton and carbon-13 NMR usually results in each of the nonequivalent proton or carbon nuclei of a repeat unit being individually identifiable in the respective spectrum, thereby providing either multiple sites for compositional analysis or specific main chain and side chain sites for assessment of the motional features of a polymer.

Unfortunately, in the past high-resolution NMR spectra have been obtainable only for polymer melts or polymers in solution. In the solid state, nonaveraged nuclear dipole–dipole interactions give rise to spectral broadening which results in only a single broad (tens of kilohertz) resonance line. This line width makes it impossible to utilize high-resolution NMR as a characterization technique for the many polymer systems which are essentially insoluble unless subjected to extensive degradation. However, in a recent set of papers, Schaefer et al.[1-3] have demonstrated that it is possible to obtain "high-resolution" carbon-13 NMR spectra for solid glassy polymers by combining line-narrowing techniques for solids (i.e., proton dipolar decoupling,[4] DD, to eliminate ^{13}C-^{1}H dipolar broadening and magic-angle spinning,[5] MAS, to eliminate chemical shift anisotropy broadening)[2] with a matched spin-lock cross-polarization (CP) experiment to enhance sensitivity.[4-6] For these experiments, the analytical sample consisted of compression-molded solid polymer plugs machined in the form of cylindrical rotors which were spun about an axle support by impingement of a driving gas (N_2) on the rotor. The approximate 100-Hz resolution achieved enabled many of the magnetically nonequivalent carbons both in the side and main chains of the polymer repeat units to be resolved as individual resonance lines. This degree of spectral resolution, of course, adds new potential for the use of ^{13}C NMR as a characterization technique for insoluble polymer systems.

In the work reported here, we have explored, in a preliminary manner, the use of ^{13}C NMR to characterize the highly insoluble polyesters based on *p*-hydrobenzoic

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