THE DIRECT FLUORINATION OF HYDROCARBON POLYMERS

A. J. OTSUKA and R. J. LAGOW

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Mass. 02139 (U.S.A.)

(Received September 5, 1973)

Summary

A new technique for direct fluorination has been used to prepare several new fluorocarbon polymers. The direct fluorination of poly-*p*-xylylene, poly-isobutylene, Novolac and a highly crosslinked phenolic resin has produced fluorocarbon polymers which bear a strong structural resemblance to their hydrocarbon polymer precursors, though some crosslinking may occur. The thermal properties of these polymers have been investigated by DSC and TGA techniques.

Introduction

In general, it has been found that substitution of fluorine for hydrogen or other functional groups improves thermal stability. Many methods of fluorination are now in use [1], however most are unfortunately unsuited to the fluorination of high polymers. Although it has been reported by Rudge [2] and others [3] that polyethylene surfaces may be fluorinated with a mixture of nitrogen and fluorine, the recent development of a direct fluorination technique by Lagow and Margrave [4] has facilitated the fluorination of many classes of compounds without extensive carbon-bond rupture or decomposition. Direct fluorination by this method yields complete addition of fluorine to double bonds and replacement of all hydrogen by fluorine in the polymers. Several polymers have been perfluorinated by this process to obtain new fluorocarbon polymers which exhibit improved thermal properties and resistance to oxidation [5].

While the general procedures for direct fluorination have been described previously [4], one of its principal features with respect to the fluorination of polymers is the initial infinite dilution of fluorine followed by gradient changes of fluorine concentration as the reaction moves towards completion. Most previous studies of direct fluorination reactions have used simple mixtures of fluorine with an inert gas. Polymer surfaces, and polyethylene surfaces in particular, require less careful control to prevent extensive fragmentation or combustion than powdered polymers and more complex polymeric

structures. However, when the direct fluorination of delicate organic or inorganic compounds or gaseous and liquid starting materials is investigated, many more factors are apparently important if success is to be achieved. In the case of polymers, it is very important to have an oxygen- and water-free reaction environment to prevent oxygen crosslinking or the fluorocarbon materials will be less stable thermally and less inert chemically. It is also necessary to start with hydrocarbon powders of less than 100 mesh size if complete conversion to fluorocarbons is to be obtained since the diffusion of fluorine is a limiting factor. Other aspects of the technique are discussed in the experimental section.

Poly-*p*-xylylene, polyisobutylene, Novolac (a low molecular weight phenolic) and a highly cross-linked phenolic resin were selected as starting materials in an attempt to gain further understanding of this technique. A study by Learmonth and Marriot [6] has shown some improvement in the thermal properties of phenolics when methylene bridges are replaced with $C(CF_3)_2$ linkages in these materials. It is their hypothesis that the electron-withdrawing effect of the trifluoromethyl groups reduces the electron density in the bridging bonds, thus shortening the bonds and reducing bond rupture. It was also proposed that the steric effect of the trifluoromethyl groups would reduce oxidative attack. Since the methylene bridge is subject to oxidation, protection or elimination of this bridge was found to improve thermal stability. In another study by Cotter *et al.* [7], several perfluoropolyphenylenes were synthesized. Even though these compounds have no methylene bridges or aromatic hydrogen, resistance to thermal degradation in oxygen was not dramatically superior to the polymer in the previous study. Wall and Fearn [8] of the National Bureau of Standards have prepared the non-aromatic poly-4-chloroperfluorohepta-1,6-diene by cobalt irradiation of the monomer. The carbon skeleton of the polymer is thought to be similar to the proposed structure of fluorine-saturated Novolac, except that a chlorine atom has been substituted at the 4 position. It was anticipated that the properties of a fluorinated Novolac would be similar to those of the poly-4-chloroperfluorohepta-1,6-diene.

The structures of the polymers chosen for fluorination are shown in Figure 1. Poly-*p*-xylylene and polyisobutylene are commerically available starting materials. Poly-*p*-xylylene is used for film and coating applications and polyisobutylene is primarily used as a self-sticking adhesive. Highly crosslinked phenolic resins are usually produced by acid- or base-catalyzed condensation of phenol and formaldehyde. By varying the reactor conditions, it is possible to obtain various degrees of polymerization, ranging from a "Resole" (mol.wt. 300 - 700) to a "Novolac" (mol.wt. 1200 - 1500) and finally a fully-cured crosslinked resin. The Novolac structure is, in general, bridged from the 2 and 6 positions, although 2,4 linkages may be found.

The highly crosslinked phenolic was a particularly interesting material because it has a structure with many advantages for thermal stability, including adequate space for conformational changes, an infinite highly crosslinked network structure and protection of the carbon skeleton by fluorine atoms.
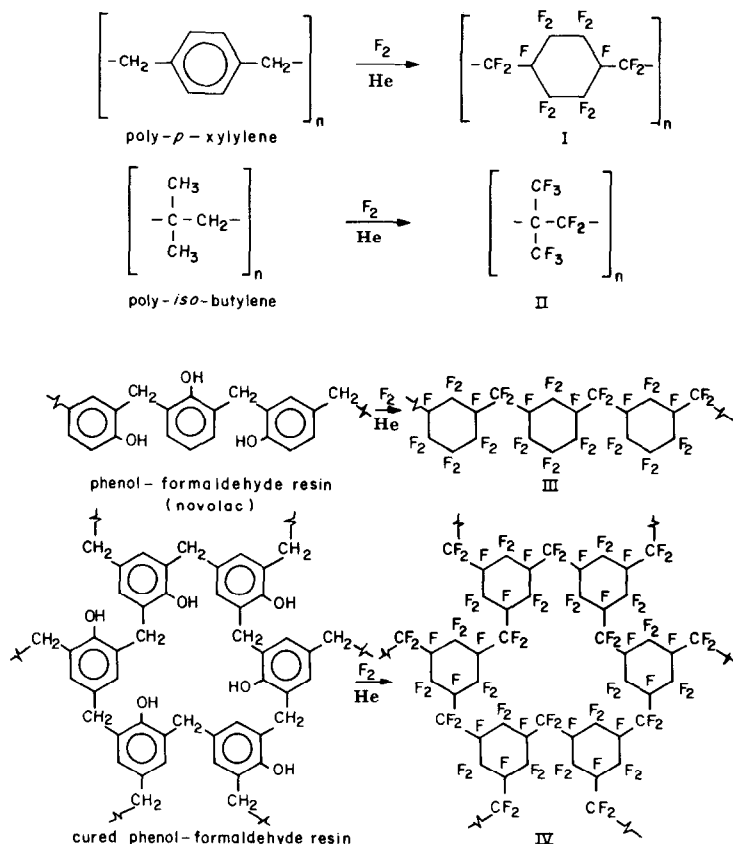
Fig. 1. Structures of polymers chosen for fluorination.

Experimental

Materials

Except for the cured phenolic resin, the polymeric starting materials were high-purity commercial chemicals. The poly-*p*-xylylene was obtained from Polysciences, Inc., Warrington, Pa. and both the Novolac and the poly-isobutylene were obtained from Monomer–Polymer Laboratories, Philadelphia, Pa. The fluorine used was supplied by Allied Chemical (99%) and contained 1.0% max. oxygen. To avoid additional contamination by oxygen or water, the flow system was leak-tested under high vacuum prior to use and exiting gases were driven with a nitrogen flow through a bubbler to ensure that no back-diffusion occurred to the reactor.

The preparation of phenolformaldehyde resin

The synthesis of the phenolic resin is that given by Sorensen and Campbell [9]. After curing for 9 days at 80 °C, a hard, insoluble, infusible

resin was obtained. The infrared spectrum of a cast film showed a strong 1,2,4,6-substitution peak at 850 cm^{-1} and a weaker 1,2,6-substitution peak at 740 cm^{-1} in agreement with the spectra reported by Hummel for a highly crosslinked polymer [10].

Apparatus

The fluorination apparatus has been described previously [4]. A nickel tube reactor (45 cm × 2.5 cm i.d.) containing a nickel boat filled with the starting material was used.

Analytical

Elemental analyses were made by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y. The infrared spectra were run as KBr disks on a Beckman IR20A spectrophotometer.

Thermal analysis

DSC and TGA thermograms were recorded with a Dupont 990 Thermal Analyzer fitted with appropriate attachments. Differential scanning calorimetry was undertaken on 10 - 20 mg samples using crimped pans in air and using pans with perforated caps in argon. The samples were heated at a rate of 5 °C min^{-1} over the temperature range 30 - 460 °C. Specific heat calculations were made by the method described by Jenkins and Slade [11]. Thermogravimetric analyses were made in a nitrogen atmosphere and in air with a heating rate of 20 °C min^{-1} over the temperature range 25 - 700 °C.

The fluorination of poly-p-xylylene

Powdered (120 mesh size max.) poly-*p*-xylylene was spread to a depth of about 3 mm in a nickel boat, dried at 100 °C for 4 h in vacuum and then dried in a reactor fitted with a resistance heater under helium flow for 8 h at 110 °C. After cooling the reactor to room temperature, a helium/fluorine mixture was passed over the sample. The sample was fluorinated for 63.7 h under a flow of 0.5 cm^3 min^{-1} of fluorine and 27 cm^3 min^{-1} of helium. The fluorine flow was then increased to 1.5 cm^3 min^{-1} and fluorination continued for 14.7 h. The fluorine flow was increased to 20.0 cm^3 min^{-1} and the helium flow decreased to 1.0 cm^3 min^{-1} for 56.6 h. The reaction was terminated and the reactor flushed with helium.

The infrared spectra of the product showed strong C—F stretching at 1210 cm^{-1}, and weak features at 950 cm^{-1} and 730 cm^{-1}. Analysis: Found: C,26.19; F,73.14%. Calculated for structure (I): C,26.54; F, 73.46%. Yield based on structure (I) = 99%.

The fluorination of polyisobutylene

Approximately 5 g of polyisobutylene was dissolved in 200 cm^3 of hexane and coated on aluminum foil. The solvent was evaporated, the sample placed in the reactor and the system flushed with helium for 30 min.

The sample was fluorinated for 24 h under a flow of 0.5 cm^3 min^{-1} of fluorine and 27 cm^3 min^{-1} of helium. The sample was further fluorinated at a flow rate of 1.0 cm^3 min^{-1} of fluorine and 11 cm^3 min^{-1} of helium for 48 h before the reaction was terminated. The unreacted portion was then dissolved with hexane and filtered. The insoluble portion was washed with hexane, passed through a 120 mesh size screen and fluorination continued at a flow rate of 0.5 cm^3 min^{-1} of fluorine and 11 cm^3 min^{-1} of helium for 27 h. The fluorine flow was then increased to 2.0 cm^3 min^{-1} and the helium flow decreased to 7 cm^3 min^{-1} for 44 h. The reaction was terminated as before.

The infrared spectra displayed strong C—F stretching from 1100 to 1400 cm^{-1} with a maximum at 1240 cm^{-1}, sharp medium C—C stretching at 980 cm^{-1} and a peak at 725 cm^{-1} due to the trifluoromethyl species. Very weak peaks at 510 and 2340 cm^{-1} were also present. Analysis: Found: C,27.35; F,71.51%. Calculated for structure (II): C,24.02; F,75.98%. Yield based on structure (II) = 95%.

The fluorination of Novolac

Powdered Novolac (120 mesh size max.) was dried for 24 h at room temperature under vacuum. A nickel boat filled to a depth of 2 mm was placed in the reactor, and after flushing the system for 30 min with helium, the fluorine flow was set at 1.0 cm^3 min^{-1} and the helium flow at 27 cm^3 min^{-1}. After 23.5 h, the fluorine flow was increased to 2.0 cm^3 min^{-1} and the helium flow reduced to 4 cm^3 min^{-1} for 25.8 h. Finally, the fluorine flow was increased to 4.0 cm^3 min^{-1} and the helium flow terminated. After 25.2 h the reaction was terminated.

The infrared spectra of the reaction product showed C—F stretching from 1050 to 1400 cm^{-1} with a maximum at 1240 cm^{-1} and a shoulder at 1300 cm^{-1}. A weak carbonyl peak could be seen at 1790 cm^{-1} and C—C stretching at 100 cm^{-1}. Analysis: Found: C, 29.77; F, 69.93%. Calculated for structure (III), *i.e.* C$_7$F$_{12}$: C, 26.94; F, 73.06%. Yield based on structure (III) = 98%.

Fluorination of phenolformaldehyde resin

The phenolic resin (120 mesh size max.) was dried for 4 h at 100 °C under vacuum. A nickel boat containing a 3 mm-deep layer of the resin was placed in a reactor, and after flushing for 30 min with helium, the fluorine flow was set at 1.00 cm^3 min^{-1} and the helium flow set at 27 cm^3 min^{-1}. After 19.5 h, the fluorine flow was increased to 2.0 cm^3 min^{-1} and the helium flow reduced to 4 cm^3 min^{-1}. After 18.6 h, the fluorine flow was increased to 4.0 cm^3 min^{-1} and the helium flow terminated. The reaction was terminated after 74.8 h. The infrared spectrum was identical to that of the fluorinated Novolac. Analysis: Found: C, 29.96; F, 69.92%. Calculated for structure (IV), *i.e.* C$_{7.5}$F$_{12}$: C, 28.32; F, 71.68%. Yield based on structure (IV) = 98%.

Results and discussion

Direct fluorination of the four starting materials resulted in the preparation of the new fluorocarbon polymers. The structures postulated for products (I) and (IV) are in agreement with the elemental analyses. The carbon analyses of the perfluorinated polyisobutylene material and the perfluorinated Novolac are 3% too high and the fluorine analyses are low. This discrepancy is due in part to crosslinking during fluorination. The polyisobutylene starting material has a rather strained structure and since the dimensions of the trifluoromethyl group which is produced upon fluorination is larger than that of the methyl, an even more highly strained structure may result. This, of course, increases the chances of degradation or crosslinking upon fluorination. The infrared spectra all exhibit a strong carbon–fluorine stretch, and features characteristic of carbon hydrogen and double-bonded species are absent from the spectra. The trifluoromethyl feature expected in the perfluorinated polyisobutylene is readily apparent at 730 cm^{-1}.

All the reaction products are white solid powders, and with the exception of (II) are all insoluble in common organic solvents or hexafluorobenzene. Product (II) is soluble in hexafluorobenzene and may be precipitated with water. It also softens to the point of flowing in acetone. Product (I) is relatively inert and resists attack by boiling aqueous 3 mol l^{-1} sodium hydroxide solution. Products (III) and (IV) are attacked by hot concentrated alkali solution. A powder of (II) may be melted and cooled to form a brittle translucent plastic.
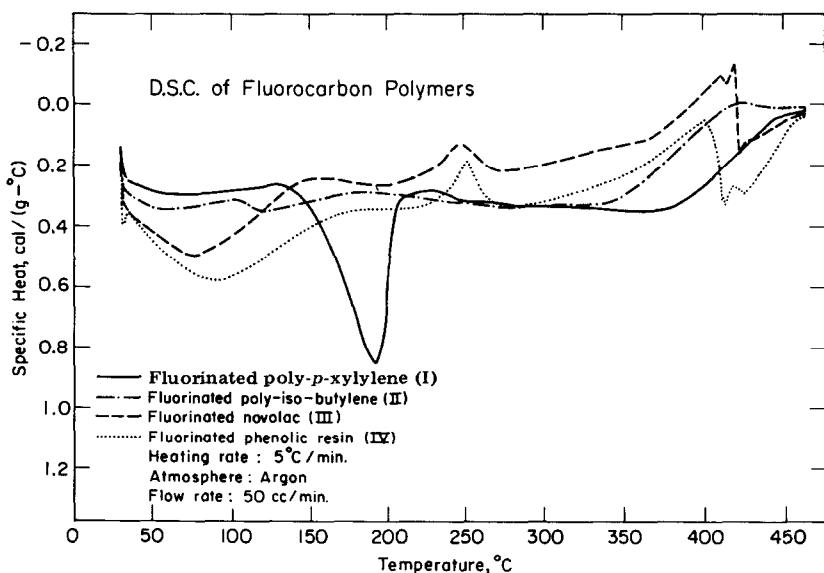

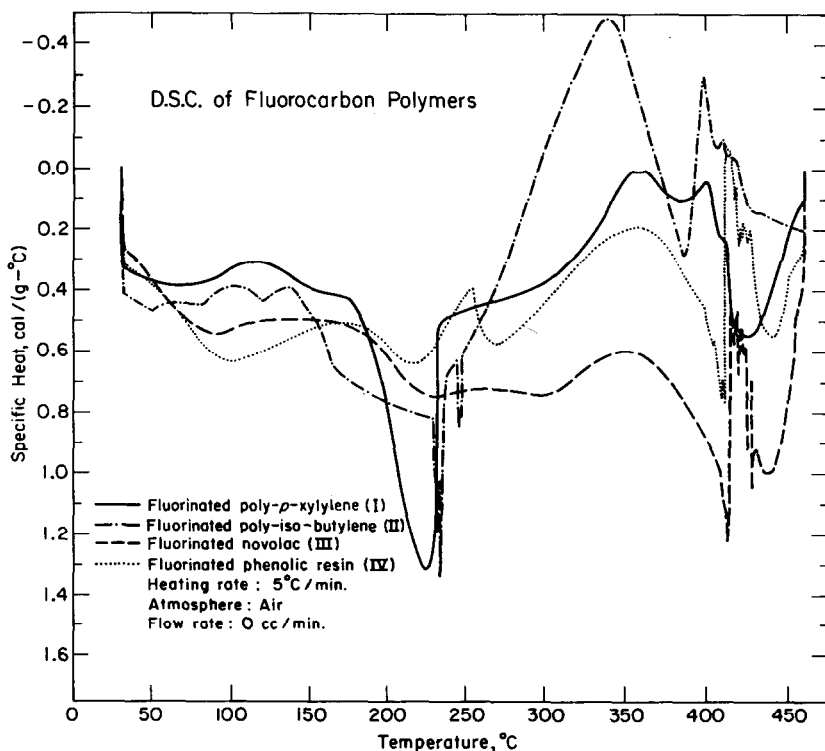Fig. 2. The DSC of fluorocarbon polymers in argon.

Fig. 3. The DSC of fluorocarbon polymers in air.

The thermal properties of the four poly.ners were studied by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) and found to vary widely. This data presented in Figures 2 - 5 gives primarily an indication of the thermal stability of the new materials. Product (II) begins to melt at approximately 77 °C, while product (I) does not melt at all but decomposes gradually above 205 °C in air. Of the four materials, products (III) and (IV) have the most similar properties.

Product (I) remains unchanged to *ca.* 200 °C at which temperature it begins to soften. The DSC scan shows a large peak at 195 °C in argon and at 230 °C in air (Figs. 2 and 3). Decomposition of (I) begins at 205 - 210 °C in air, as observed visually, with gradual darkening until 390 °C where rapid decomposition occurs. Finally, shrinkage and charring occur at *ca.* 420 °C. The DSC in air shows gradual decomposition to *ca.* 300 °C where an increased rate of decomposition occurs. In argon, the increased decomposition rate is delayed to *ca.* 375 °C. Because hermetically sealed cells were not used, the specific heats obtained after decomposition to gaseous products had occurred are not reliable. Product (I) does not melt but decomposes to volatile products and 12% carbon char as demonstrated by the results in Figure 4. Decomposition of poly-*p*-xylylene as the starting material begins at *ca.* 210 °C with gradual darkening to 286 °C where it begins to bubble. At *ca.* 370 °C, the starting material turned black and had
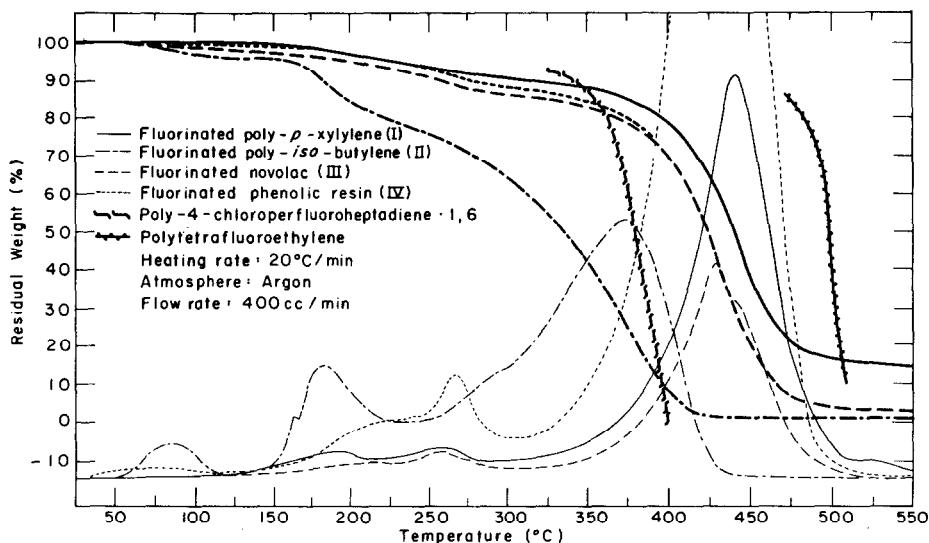
Fig. 4. The TGA of fluorocarbon polymers in argon.

lost considerable weight by volatilization. The TGA thermograms of (I) show three weight-loss regions. The first two at 10 °C and 225 °C are also present in the thermograms of (III) and (IV) and are presumed to be low molecular weight fragments. Major weight loss occurs above 400 °C with the maximum rate of weight loss in argon being at 440 °C. Oxidation in air occurs at a greater initial rate, leading to a maximum at 400 °C and then decreasing with gradual formation of char.

Product (II) softens at 77 °C with the release of volatile impurities at 110 °C. At *ca.* 135 °C, the material is a slightly viscous clear liquid. This is a marked improvement over the starting material which melts at 44 °C [12]. Product (II) has a wide liquid range, boiling at 225 °C, All these effects are observable in the DSC thermograms of the sample. Hence the peak at 120 °C represents the release of volatile materials, boiling begins at 230 °C with a gradual decrease in the specific heat as the sample is boiled away and finally discoloring and rapid decomposition occur at *ca.* 390 °C. The TGA thermograms of (II) show three major weight-loss regions. The first volatilization occurs over the temperature range 90 – 110 °C, the second at 185 °C corresponds to the volatilization of low molecular weight fragments in the melt while the third may be attributed to the gradual boiling of the liquid polymer About 1% char remains at 600 °C.

Products (III) and (IV) have very similar thermal properties. This is probably due to crosslinking of Novolac during the fluorination process. Very little decomposition of either (III) or (IV) occurs below 335 °C at which temperature they both yellow slightly. Gradual darkening occurs to *ca.* 390 °C where decomposition becomes rapid. Product (III) forms bubbles at *ca.* 410 °C and product (IV) forms bubbles at *ca.* 410 °C. Product (IV)
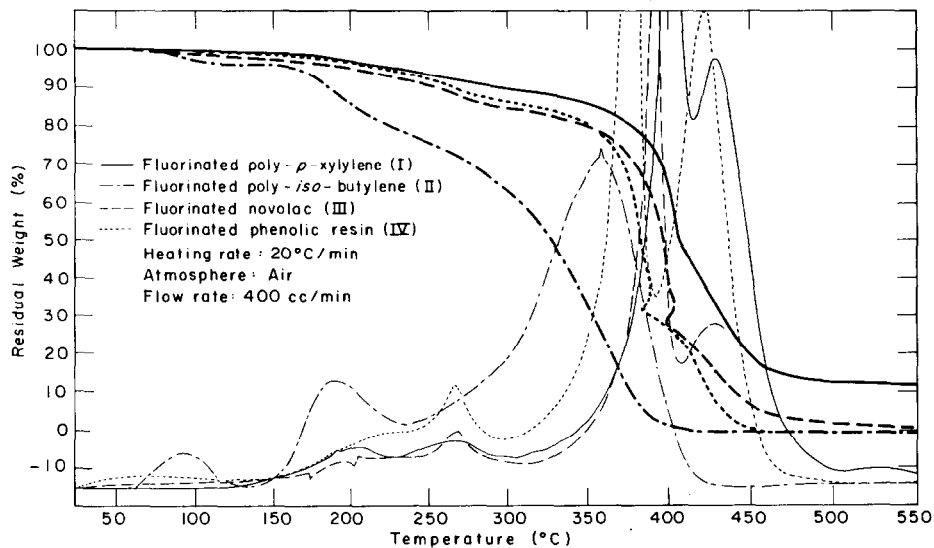
Fig. 5. The TGA of fluorocarbon polymers in air.

shows considerable thermal improvement when compared to the original Novolac which melted at 80 °C. The DSC curves for both samples are similar. The two peaks at 220 °C and 270 °C correspond to weight losses and are presumed to be due to the volatilization of low molecular weight impurities. Both fluorinated polymers soften in this region. As expected, the curves in air drop off at lower temperatures than those in argon. Boiling peaks are observed for both samples. Both (III) and (IV) display three weight-loss steps. As mentioned above, the first two correspond to low molecular weight fractions. The final rate attains a maximum value at *ca.* 43 °C. In air, an exothermic reaction was observed as the sample temperature rose above the cell temperature and then dropped back again. The sample of (IV) left no residue, while that of (III) left 1% char at 700 °C.

The structure of the phenolic starting materials usually contains many ether linkages and other imperfections. However, as can be seen from Figure 4, the thermal stability of (IV) is not as high as that of polytetrafluoroethylene which has been studied under vacuum [13]. The stability of (III) and (IV) is superior to that of poly-4-chloroperfluorohepta-1,6-diene which was tested under the same vacuum conditions as polytetrafluoroethylene.

A weak carbonyl peak at 1790 cm^{-1} is observed in the products of both the Novolac and crosslinked phenolic fluorinations. All the phenolic starting materials contained oxygen in hydroxyl and other groups. During fluorination, oxygen radicals are formed from these groups and because the oxygen is constrained by the polymer network, the formation of oxygen-containing groups such as carbonyl is likely on nearby sites. Although the percentage of these oxygen-containing groups is small, they provide the limiting factor in the thermal stability of the perfluorocarbon polymers produced. The decreased

activation energy for decomposition is, of course, a direct consequence of the decreased carbon–oxygen bond strength in comparison to the stronger carbon–fluorine bonds throughout the structure. Efforts are now in progress to obtain a starting phenolic containing no oxygen so that the potential high thermal stability of perfluorinated phenolics may be realized to a greater extent.

Acknowledgments

References

1 R. E. Banks, Fluorocarbons and Their Derivatives, MacDonald Technical and Scientific, London, 2nd ed., 1970.
2 A. J. Rudge, Brit. Pat., 710,523 (1954).
3 S. P. Joffre, U.S. Pat., 2,811,468 (1957); W. R. Siegart, W. D. Blackley, H. Chaftez and M. A. Mahow, U.S. Pat., 3,480,667 (1969).
4 R. J. Lagow and J. L. Margrave, Proc. Nat. Acad. Sci. USA, 67 (1970) 4, 8A; R. J. Lagow and J. L. Margrave, unpublished results; N. J. Maraschin and R. J. Lagow, J. Amer. Chem. Soc., 94 (1972) 8601; N. J. Maraschin and R. J. Lagow, Inorg. Chem., 12 (1973) 1459.
5 R. J. Lagow and J. L. Margrave, Polym. Lett., in the press.
6 G. S. Learmonth and A. G. Marriot, Eur. Polymer J., 5 (1969) 441.
7 J. L. Cotter, G. J. Knight, J. M. Lancaster and W. W. Wright, J. Appl. Polymer Sci., 12 (1968) 2481.
8 J. E. Fearn and L. A. Wall, Soc. Plastics Eng. J., July (1963) 231.
9 W. R. Sorenson and T. W. Campbell, Preparative Methods of Polymer Chemistry, Interscience, New York, 2nd ed., 1968, p. 456.
10 D. O. Hummel, Infrared Spectra of Polymers, Interscience, New York, 1966, p. 59.
11 P. E. Slade, Jr. and L. T. Jenkins, Techniques and Methods of Polymer Evaluation, Vol. 2, Marcel Dekker, New York, 1970, p. 1.
12 J. Brandrup and E. H. Immergut, Polymer Handbook, Interscience, New York, 1966, p. 3.
13 S. L. Madorsky, Thermal Degradation of Organic Polymers, Interscience, New York, 1964, p. 159.