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Direct Fluorination of Polymers

RICHARD J. LAGOW and HAN-CHAO WEI

14.1. INTRODUCTION

The direct fluorination of inorganic,[1,2] organometallic,[3–5] and organic compounds,[6–8] employing the LaMar[9,10] and Exfluor–Lagow[11] methods, has impacted the synthesis of fluorinated compounds over the past 25 years. Among the most important applications of direct fluorination are the synthesis of fluoropolymers from hydrocarbon polymers and the conversion of the surface of the hydrocarbon polymers to fluoropolymer surfaces.[12,13] The direct fluorination process is an excellent approach to the synthesis of fluoropolymers.

Idealized structures and reaction schemes for these fluorination studies of hydrocarbon polymers are shown in Figure 14.1 and other structures have been discussed in the literature.[10] The new fluoropolymers differ from the idealized structures primarily because, in such high-molecular-weight species, carbon–carbon cross-linking occurs to a significant extent during fluorination. This cross-linking may be controlled, but in general the fluoropolymer is of higher molecular weight than the hydrocarbon precursor. Polymer chain fission can be almost entirely eliminated under the proper conditions. Most of these fluoropolymers are white solids with high thermal stability. The elemental analyses indicate complete conversion to fluoropolymers and correspond closely to the idealized compositions. The infrared spectral analyses and other spectroscopic evidence are consistent with perfluorocarbon materials. A number of very interesting X-ray photoelectron spectroscopy studies by D. T. Clark et al.[14,15] have confirmed that hydrocarbon polymers are converted to fluoropolymers by direct fluorination with very few or no structural rearrangements. These studies, in addition to further

RICHARD J. LAGOW and HAN-CHAO WEI · Department of Chemistry and Biochemistry, University of Texas at Austin, Austin, Texas 78712–1167
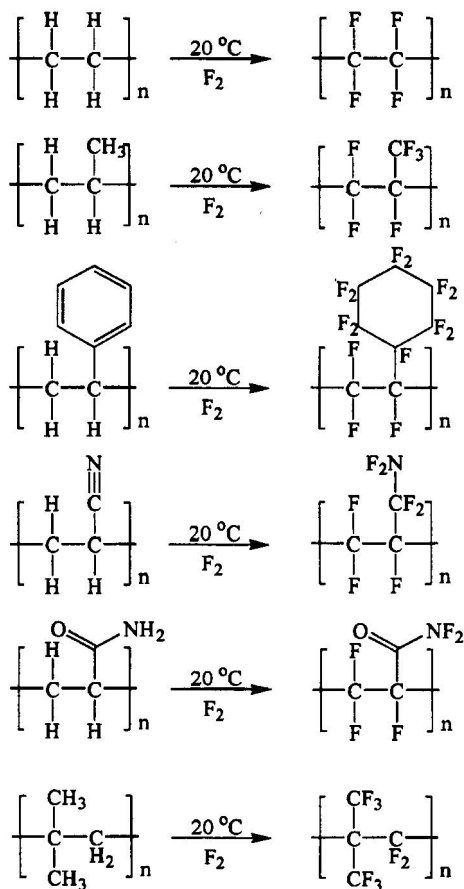
Figure 14.1. Direction fluonnation of polymers.

elucidating the structure of the fluoropolymers, provide information on subtle surface effects and comment on the rate and depth of the fluorination.

The primary advantage of direct fluorination for synthesizing fluoropolymers is that many monomers are difficult to polymerize because of the steric repulsion of fluorine, which leads to relatively low-molecular-weight species; also, it is difficult or impossible to synthesize many of the corresponding monomers.

If solid polymer objects are fluorinated or polymer particles much larger than 100 mesh are used, only surface conversion to fluoropolymer results. Penetration of fluorine and conversion of the hydrocarbon to fluoropolymers to depths of at least 0.1 mm is a result routinely obtained and this assures nearly complete conversion of finely powdered polymers. These fluorocarbon coatings appear to

have a number of potentially useful applications ranging from increasing the thermal stability of the polymer surfaces and increasing their resistance to solvents and corrosive chemicals, to improving their friction and wear properties. It is also possible to fluorinate polymers and polymer surfaces partially to produce a number of unusual surface effects.

We are going to discuss the syntheses of fluoropolymers, poly(carbon monofluoride), perfluoropolyethers, perfluorinated nitrogen-containing ladder polymers, and surface fluorination of polymers by direct fluorination.

14.2. POLY(CARBON MONOFLUORIDE)

Poly(carbon monofluoride), $(CF_x)_n$ (Figure 14.2) has been known since 1934 when Ruff and co-workers[16] prepared a gray compound of composition $CF_{0.92}$. In 1947 W. and G. Rodorff[17,18] reported a series of compositions of $CF_{0.68}$ to $CF_{0.99}$, varying in color from black in the case of $CF_{0.68}$ through gray to white in the case of $CF_{0.99}$.

Poly(carbon monofluoride) is a white compound, often reported to be explosive and unstable but found in our research results to be stable in air at temperatures up to at least 600°C. In fact, poly(carbon monofluoride) is the most thermally stable fluoropolymer known. It decomposes upon heating at 800°C or under a high vacuum at 580°C to form a series of polyolefinic fluorocarbons.[19] The compounds with compositions in the range of $CF_{0.68}$ to $CF_{0.8}$ are nearly black. The $CF_{0.8}$ to $CF_{0.95}$ compounds become gray and the $CF_{0.95}$ to $CF_{1.12}$
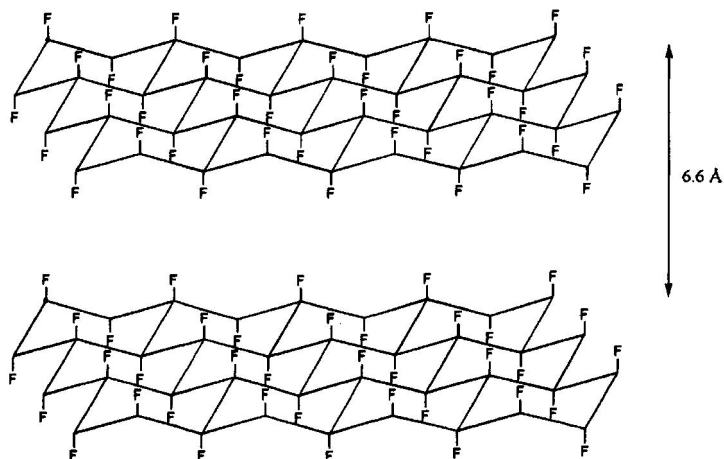

Figure 14.2. Structure of poly(carbon monofluoride),

develop into a snow-white solid. In earlier syntheses[16–18] poly(carbon mono-fluoride) was prepared by passing fluorine over graphite at 450-600°C for several hours. In some cases hydrogen fluoride is used as a catalyst, With these methods, a gray material of stoichiometry $CF_{0.68}$ to $CF_{0.8}$ is normally obtained.

Careful control of the reaction temperature at higher temperatures (627° ± 3°C) was necessary to reproducibly obtain a completely fluorinated pure white material. A snow-white material was obtained by direct fluorination of graphite at this temperature. Elemental analysis showed the calculated empirical formula to be $CF^{1.12\pm0.03}$.[20]

To produce $(CF_x)_n$ of the highest fluorine content, it was necessary to maintain a temperature of 627° ± 3°C. This 6°C range was very critical, which was not recognized in earlier work and consequently the process for reproduction of $(CF_x)_n$ gained a reputation for being irreproducible. $(CF_x)_n$ is formed from about 540 to 630°C at atmospheric fluorine pressure. It has been found that at higher pressures the critical temperature decreases.[21] At 540°C the empirical formula is $CF_{0.68}$ and the product is black. If the furnace has a hot zone within this 6°C range smaller than the length of the nickel boat, only the center region of the boat produces white $(CF_x)_n$ and on either side the color ranges from gray to bladck. At temperatures over 630°C, the compound is unstable in fluorine and burns to produce CF_4 and black soot. $(CF_x)_{1.1}$ is therefore a solid subfluoride of carbon that should be considered metastable with respect to CF_4. These observations of reaction variations with temperature can be explained by consequent changes in fluorine atom concentrations and subsequent kinetics.

Studies at the Lewis Research Center of the National Aeronautic and Space Administration[22] and at the Frankford Arsenal of the U.S. Army[23] have shown that poly(carbon monofluoride) is a superior solid lubricant under heavy loads, in high temperatures, in oxidizing atmospheres, and under other extreme conditions. Researchers at the U.S. Army Electronics Command at Fort Monmouth, N.J.[24,25] and industrial scientists in Japan have recently demonstrated a high potential for the use of poly(carbon monofluoride) as a cathode material in high-energy batteries.

14.3. PEFLUOROPOLYETHERS

Perhoropolyethers are the most extraordinary and exciting high-performance lubricants known today and represent perhaps the most important discovery in lubrication in the last 20 years.[26–30] For example, perfluoropolyether greases formulated from perfluoropolyether oils are used as the lubricants of choice for almost all civilian and military space activities (these greases often have fillers of either finely powdered Teflon or molybdenum disulfide) for lubricating bearings and other moving parts in satellites. The satellite grease applications are

very important because the satellites must often operate for 10 years in both high-temperatures and in unusually cold environments, and failure makes for severe losses. These lubricants are also used on the space shuttle and will soon find their way into use as jet engine lubricants in aircraft.

Perfluoropolyethers have extraordinary properties and the materials are stable in some cases to 430°C, i.e., stable at a temperature 60°C higher than poly(tetra-fluoroethylene), thus giving very high thermal performance, because carbon–oxygen bonds are thermochemically stronger than carbon–carbon bonds. In addition, the fluoropolymer backbones are protected by a sheath of fluorine and the cloud of projecting nonbonding electrons associated with protruding fluorine atoms covering the chains provide lubrication properties.

On the other hand, perfluoropolyethers are the most extraordinary low-temperature lubricants known because at very low temperatures the carbon–oxygen–carbon ether linkage acts as hinge for storing vibrational energy. At even lower temperatures, often less than — 100ºC, these materials still have free rotation around the ether linkages giving a lower operating temperature.

Perfluoropolyethers emerged on the market in the early 1970s. The first perfluoropolyether was the homopolymer of hexafluoropropylene oxide produced by DuPont, which has the structure $[—CF_2CF(CF_3)O—]_n$ and this new lubricant material was called Krytox.[31,32] Krytox was and is used in most of the vacuum pumps and diffusion oil pumps for the microelectronics industry because it does not produce any hydrocarbon or fluorocarbon vapor contamination. It also has important applications in the lubrication of computer tapes and in other data processing as well as military and space applications.

The second material to come onto the market was the Montecatini Edison fluoropolymer called Fomblin Z[33,34] with the structure $(—CF_2O—)_m$ $(—CF_2CF_2O—)_n$. This fluoropolymer has better low-temperature properties than Krytox, but is more expensive. Fomblin Z is made by photo-chemical polymerization of a mixture of oxygen and tetrafluoroethylene to prepare the random copolymer. The methylene oxide unit $(—CF_2O—)$ imparts even more extraordinary low-temperature properties than those derived from vibration and free rotation of other perfluoroether linkages.

The third material, Demnum,[35] was only introduced in 1984 with the structure of $(—CF_2CF_2CF_2O—)_n$ and no new materials had been commercia-lized since. It was clear that the full potential of this new area had not yet been fulfilled.

Work from our research group at the University of Texas on the synthesis of perfluoroethers and perfluoropolyethers by direct fluorination is revolutionizing and, in fact, has revolutionized this field. Our laboratory has been responsible for putting at least 30 new perfluoropolyethers into the literature and in some cases they are now on the commercial chemical market. Exfluor Research Corporation prepared several hundred new perfluoropolyethers expanding upon the work from
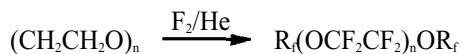
$$(CH_2CH_2O)_n \xrightarrow{\text{F}_2/\text{He}} R_f(OCF_2CF_2)_nOR_f$$

Figure 14.3. Direct fluorination of poly(ethylene oxide).

our laboratory. This represents great flexibility in the direct fluorination technique and substantially lower costs as well.

The Lagow group first entered the perfluoropolyethers field in 1977, by reacting fluorine with inexpensive hydrocarbon polyethers to prepare perfluoropolyethers. In the simplest case (Figure 14.3) poly(ethylene oxide) is converted to perfluoroethylene oxide polymer, a simple reaction chemistry that we first reported in the literature.[27] As will be seen later, this direct fluorination technology as well as many new patents from Exfluor Research Corporation have been non-exclusively licensed to the 3M Corporation by the Lagow research group.[36–39]

New perfluoropolyethers were important because the only differences in the physical properties among different Krytox and Fomblin Z materials were produced by varying the degree of polymerization. Direct fluorination technology offers great flexibility in controlling molecular weights as well as in providing as new structures.

Subsequently, we were able to make perfluorinated analogues of Krytox from the hydrocarbon poly(propylene oxide)[40] (Figure 14.4). In 1985, we published three interesting perfluoropolyethers. First we copolymerized hexafluoroacetone with ethylene oxide, propylene oxide, and trimethylene oxide. Subsequent fluorination yielded the new perfluoropolyethers (Figure 14.5).

We discovered another synthetic technique that involves the conversion by direct fluorination of hydrocarbon polyesters to perfluoropolyesters followed by treatment with sulfur tetrafluoride to produce new perfluoropolyethers.[42] The first paper in this area of reasearch reported that conversion of poly(2,2-dimethyl-1,3-propylene succinate) and poly(1,4-butylene adipate) by using the direct fluorination to produce novel branched and linear perfluoropolyethers, respectively. The structures are shown in Figure 14.6. The second paper concerns the application of the direct fluorination technology base directed toward oligomers, diacids, diesters, and surfactants.[43]

Two of the fluid structures are very interesting. The first structure is a strictly alternating copolymer of ethylene oxide and methylene oxide,
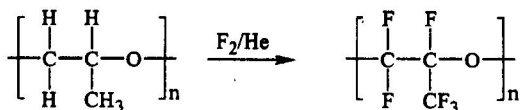

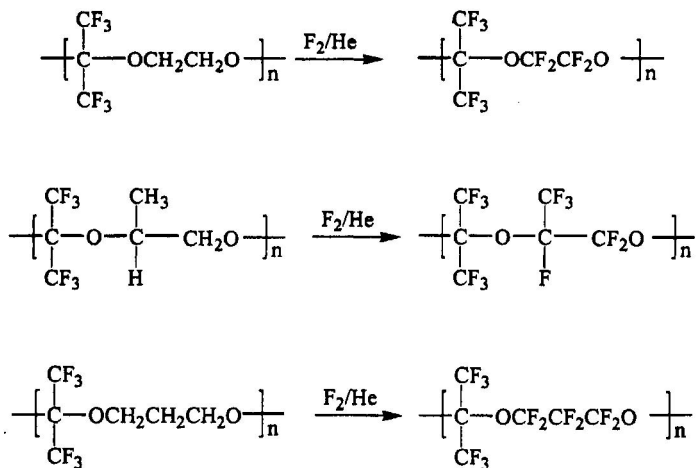**Figure 14.4.** Direct fluorination of poly(propylene oxide).

Figure 14.5. Direct fluorination of polyethers (copolymerization of hexafluoroacetone with ethylene oxide, propylene, and trimethylene oxide).
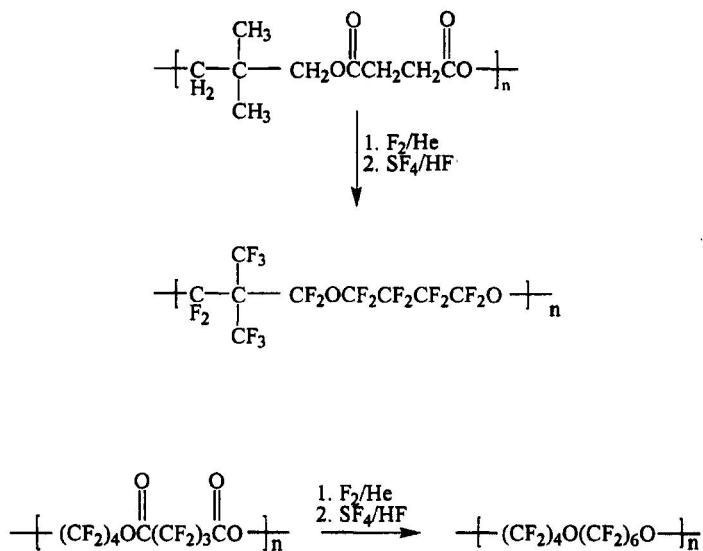

Figure 14.6. Syntheses of perfluoropolyethers from perfluoropolyesters.

($-CF_2O-CF_2CF_2O-)_n$, which currently is the longest liquid range of any carbon-containing molecule.[44] While it is a liquid down to as low as $-100°C$, its decomposition temperature is about 350°C. The second structure, ($-CF_2O-)_n$, was long sought by a number of laboratories. Other groups had attempted to polymerize carbonyl fluoride to synthesize material and had used a number of other approaches as well. We succeeded in capping this structure with a perfluoro-ethyl group to provide stability.[45] This is one of the lowest-temperature high-molecular-weight liquids known. It remains a liquid lubricant down to $-112°C$ but unfortunately when it is in contact with metals or in acidic or basic environments it is only stable to about 250°C. Our new perfluoropolyether lubricants where the subject of a paper published jointly with Bill Jones of the Tribology Branch at NASA's Lewis Research Center.[46]

The fluorination of chlorine-containing polyethers has given rise to a new class of materials that exhibit outstanding properties. For example, telomers of epichlorohydrin can be fluorinated to give perfluoropolyepichlorohydrin, ($-CF_2C(F)(CF_2Cl)O-)_n$.[47]

Functional perfluoropolyethers[11] (Figure 14.7) can also be prepared by direct fluorination in high yields. Difunctional perfluoropolyethers based on fluorinated poly(ethylene glycol) are of particular interest as possible precursors for elasto-mers, which should have outstanding high-temperature and low-temperature properties.

A breakthrough in our laboratory has involved the synthesis of perfluorinated crown ethers and cryptands.[48–51] Several manuscripts in collaboration with J. S. Brodbelt[52-55] describe syntheses in which both perfluoro crown ethers and perfluoro cryptands tenaciously encapsulate O^{2-} and F^-. It will be extremely interesting to make pertluoro crown ether polymers and investigate their binding abilities toward oxygen and other molecules. Recently, we have used the direct fluorination technique to make the first perfluorinated crown ether polymer (Figure 14.8).[56] The hydrocarbon polymer, poly[(dibenzo-18-crown-6)-coformaldehyde] (l), was reacted with fluorine in carbon tetrachloride with excess sodium fluoride to make the perfluoro crown ether polymer **(2).** The excess sodium fluoride was removed by washing the fluorinated product with excess water. The yield of perfluoro crown either polymer is 94%. The results of elemental analysis of the fluoropolymer $(C_{21}F_{36}O_6)_n$ is consistent with the proposed structure (Calcd: C,

$$CH_3CO(CH_2CH_2O)_nCCH_3 \xrightarrow{F_2} CF_3CO(CF_2CF_2O)_nCCF_3$$
$$n=1\sim50$$
$$\xrightarrow{H_2O} HOOCCF_2O(CF_2CF_2O)_{n-2}CF_2COOH + 2CF_3COOH + 2HF$$
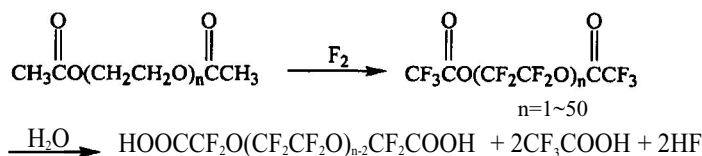
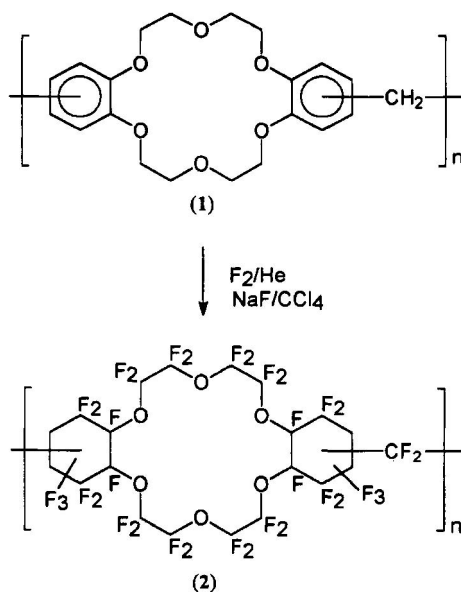**Figure 14.7.** Synthesis of functional perfluoropolyethers.

Figure 14.8. Synthesis of perfluoro crown ether polymer.

24.42; F, 66.28; H, 0. Found: C, 24.20; F, 66.44; H, 0.25). Trace hydrogen was found because of contributions from carboxylic acid end groups or hidden unfluorinated hydrogen. The results of thermal gravimetric anlaysis (TGA) showed that approximately 50% of perfluoro crown ether polymer's original weight is lost by 390°C and only 10% of fluoropolymer's original weight is lost at 261°C. XPS spectroscopy showed carbon, fluorine, and oxygen peaks at 289, 695, and 540 eV, respectively. No sodium peak was found. Solid state ^{19}F-NMR (external CFC13) δ –40.51, –57.47, –62.26, –74.81, –82.03, –88.84, –123.71, –165.35, and –207.00 ppm.

The new perfluoro crown ether polymer is currently under investigation in regard to its binding abilities of several gas molecules.

14.4. PERFLUORINATED NITROGEN-CONTAINING LADDER POLYMERS

Two nitrogen-containing polymeric materials with extended aromatic ladder structures have been chosen for direct fluorination studies (Figure 14.9).[57] Pyrolyzed polyacrylonitrile **(3)** and paracyanogen **(4)** [poly(pyrazinopryazine)] have been subjected to direct fluorination to produce perfluorinated analogues.
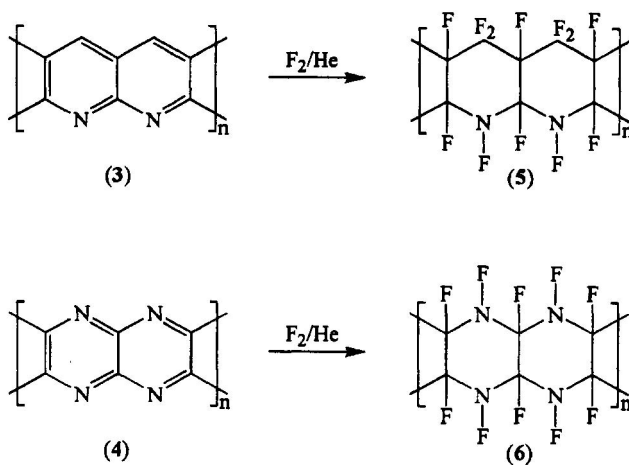
Figure 14.9. Synthesis of perfluoro nitrogen-containing ladder polymers.

Fluorination of **3** and **4** appears to have produced the saturated analogues **5** and **6**, respectively. Characterization of the perfluorinated products provides evidence that the fused polycyclic structures were retained.

The products of perfluorination are both white, very different from the original black hydrocarbon polymers. Both materials are moisture-sensitive powders and slowly degraded by atmospheric moisture, **6** more quickly than **5**. The materials oxidize iodide ion to iodine owing to the presence of the N—F moiety. A series of iodometric titrations showed that **6** required twice the number of equivalents of titrant as did **5**. This result supports the proposed structures **6** having twice as many N—F moieties as **5**.

Both IR spectra are dominated by the strong, broad absorbance between 1100 and 1300 cm^{-1} that is due to C—F stretching. A less prominent absorbance observed just below 1000 cm^{-1} is assigned to N—F stretching. The absence of absorbance in the 1500–2000 cm^{-1} region confirms that no unsaturation, either C═C or C≡N, remains in the final perfluorinated products. The results of mass spectral analysis of **5** showed m/z (formula), 69(CF_3), 81(C_2F_3), 95(C_2NF_3), 100(C_2F_4), 114(C_2NF_4), 119(C_2F_5), 131(C_3F_5), 152(C_2NF_6), and **6** showed m/z (formula), 69(CF_3), 76(C_2NF_2), 83(CNF_3), 95(C_2NF_3), 114(C_2NF_4), 121($C_3N_2F_3$), 135($C_3N_3F_3$), 159($C_3N_2F_5$), The absence of the characteristic C_nF_{2n+1} fragments of a perfluorinated straight-chain compound precludes the fused ring structure of products. The results of the elemental analysis of **5** (Calcd: C, 24.83. N, 9.65. F, 65.52; Found: C, 24.87. N. 9.34. F, 65.33) are in excellent agreement with the calculated values, those for **6** (Calcd: C, 18.75. N, 21.87. F, 59.37; Found: C, 22.02. N, 20.30, F, 53.66) show some deviation. This may reflect

the increased difficulty in maintaining the difunctional structure during fluorination or may simply be a result of greater sensitivity of **6** to decomposition after fluorination.

The thermal stability of these new materials was of special interest in regard to their possible use as high-performance lubricants. Material **5** melted sharply at 3 10°C producing a liquid that began to yellow at 340°C. Material **6** proved to be less thermally robust than **5,** exhibiting a melting point of 175°C with the liquid yellowing above 200°C. TGA confirmed that both these materials exhibit inferior thermal properties to poly(carbon monofluoride). Approximately 50% of the original weight of **6** is lost by 250°C compared to **5** having lost only 20% at that temperture. Material **5** has a region of maximum weight loss in the range 275–350ºC, while **6** shows an area of comparable degradation at 160–300°C.

These two new materials may find use as more reactive forms of solid graphitic fluoride compounds for fluorine-containing cathodes in high-energy lithium batteries. New synthetic methods to prepare higher-molecular-weight paracyanogen and pyrolyzed poly(acrylonitrile) may be a route to increase the thermal stability of the subsequent perfluorinated polymers. However, it can be expected that these fluoropolymers will always be less stable than graphite fluoride, $(CF_{1,12})_n$, which does not contain a carbon–nitrogen bond. Another possible application for these new fluoropolymers is as a solid source of fluorine. Making use of the reactive fluorine bound to nitrogen, these fluoropolymers act as mild fluorinating agents. Recent work has shown molecular N—F compounds to be useful selective fluorinating agents.[58–61]

14.5. SURFACE FLUORINATION OF POLYMERS

The best known aspect, and the first one to find commercialization in the direct fluorination area, was the fluorination of polymer surfaces. This Lagow–Margrave invention, trademarked "Fluorokote," involved many types of polymeric materials in various forms: e.g., polyethylene bottles, polypropylene objects, and rubber gloves. Polyethylene bottles are easily given fluorocarbon surfaces (> 0.1 mm), and this has been commercialized. Air Products has at least 20 licenses for what is known as their "Aeropak" process and Union Carbide has a "Linde Fluorination" process as well. Applications in chemical, pharmaceutical, and cosmetic storage are widespread.

Direct fluorination of polymer or polymer membrane surfaces creates a thin layer of partially fluorinated material on the polymer surface. This procedure dramatically changes the permeation rate of gas molecules through polymers. Several publications in collaboration with Professor D. R. Paul[62–66] have investigated the gas permeabilities of surface fluorination of low-density polyethylene, polysulfone, poly(4-methyl-1-pentene), and poly(phenylene oxide) membranes.

14.6. CONCLUSION

It is clear that many new fluoropolymers can be synthesized by direct fluorination technology that cannot be obtained through other routes. The information in this chapter should serve as a strong indication that perhaps the best and ultimate synthetic method for fluoropolymers on both laboratory and manufacturing scales in the future will be direct fluorination reactions.

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