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In celebration of the 60^{th} birthday of Dr. Andrew K. Galwey

FLUORINATION RATES OF POLYOLEFINS AS A FUNCTION OF STRUCTURE AND GAS ATMOSPHERE

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Abstract

Polyolefins and fluoropolymers were reacted with elemental fluorine under carefully controlled conditions in a thermobalance adapted to be compatible with fluorine gas. The fluorination reactions were monitored by measuring the mass increase as a result of hydrogen substitution by fluorine. The mass increase was directly proportional to the square root of the fluorination time, which indicates that fluorine gas diffusion to the unreacted surface is the rate determining step. The fluorination rate was increased by increasing the fluorine concentration and the fluorination temperature. The fluorination rate is higher when nitrogen rather than helium is used as diluting gas. The fluorination rate for the reaction in which CO_2 is used as diluting gas is the same as during fluorination with nitrogen as diluting gas, while the presence of oxygen dramatically decreased the fluorination rate. Oxygen is incorporated during fluorination with oxygen as diluting gas, while no functionalization was observed when CO_2 was employed as diluting gas. The effect of polymer structure on fluorination was studied. Poly(vinylfluoride) gained mass during fluorination, while no reaction was observed for poly(vinylidenefluoride). The reaction rate for polypropylene was higher than that of polyethylene.

Keywords: fluorination, kinetics, polymers, polyolefins

Introduction

Investigations into the fluorination of hydrocarbon polymers were originally undertaken with the intention of modifying the properties of the inexpensive and readily fabricated hydrocarbon polymers to resemble those of polytetra-

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fluoroethylene. Since a patent was issued to Rudge [1] in 1954 on the fluorination of polyethylene, elemental fluorination has become a successful alternative route to synthesize fluorinated polymers. Some research groups, like the group of Margrave and Lagow, directed their research to the synthesis of fluoropolymers by completely fluorinating very fine hydrocarbon polymer powders [2]. Other groups, like Air Products, focused on the surface fluorination of polymers to improve their barrier properties and adhesion [3, 4].

Fluorine is one of the most reactive elements and reacts in a highly exothermic reaction with hydrocarbons by a free-radical chain reaction mechanism [5]. Since Rudge fluorinated polyethylene, almost all the well known polymers have been reacted with fluorine gas. Surprisingly, little has been reported on the mechanism and kinetics of fluorination and the effect of polymer structure on fluorination. However, it is believed that fluorination results in the formation of a partially fluorinated surface layer and further reaction is controlled by the diffusion of the fluorine gas through this layer [6, 7, 8]. Although Lagow suggested that polyethylene is uniquely easy to fluorinate in comparison with other polymers [5], Shimada was the first to publish different fluorination rates for different polymers by measuring mass increases and fluorination depths [7]. Notwithstanding the reactivity of fluorine gas and the low activation energy for the initial abstraction of a hydrogen atom, it seems that elemental fluorination is selective with respect to primary, secondary and tertiary hydrogen atoms. Teddar found that the fluorination reaction of hydrocarbons is a function of fluorine substitution, because of the deactivation effect of substituted fluorine [9]. Lagow attributed the reduction in reaction rate to possible steric hindrance [5]. Wolf and Mallon observed cleavage of carbon-carbon bonds as well as crosslinking by recombination of macroradicals during fluorination [10].

Lagow and Margrave reported the importance of diluting the fluorine gas with an oxygen-free inert gas to prevent fragmentation of carbon-carbon bonds [5]. The use of various diluting gases, for example nitrogen, helium and argon, has been reported in the literature. Shimada studied the effect of the diluting gas on fluorination and observed an increase in reaction rate if helium is used instead of nitrogen [7]. Examination of the literature shows inconsistencies in proposed reaction mechanisms and properties of the fluorinated surfaces. Schonhorn and Hansen [11] described a fluorinated surface with a reduced surface tension, and similar results were claimed in a patent issued to Cohen in 1985, in which surface fluorination was assisted by ultraviolet radiation [12]. On the other hand, several studies revealed an increase in surface tension and wettability upon fluorination. Hayes studied the surface energy of fluorinated surfaces and found that fluorination is accompanied by oxidation, even in an atmosphere substantially free of oxygen [13]. It was then realised the desired properties could also be obtained by simultaneous fluorination and functionalization of the surfaces. Fluorination reactions are described in which fluorine was used in combination with various reactive gases such as CO_2, O_2, CO and SO_2 [3, 14, 15]. Infrared studies revealed the existence of acid fluoride groups on fluorinated surfaces [16], but there is uncertainty about the mechanism by which oxygen is introduced into these surfaces. Dixon observed that the rate of fluorination is dramatically affected by the presence of oxygen [17]. Lagow only observed functionalization in polymers which contained pendant methyl or other alkyl groups, while linear polymers such as high density polyethylene, failed to produce significant functionalization [18]. Uhse speculated that fragmentation of the carbon chains in the presence of oxygen could also lead to the formation of acid fluoride groups and consequently may cause functionalization in linear polymers [19].

Fluorine is an expensive reagent and, in commercial applications, it is of great importance to optimise the reactions with respect to economics and improved properties. It is reported that increases in reaction temperature and fluorine concentration accelerate fluorination reactions [8]. However, detrimental side-effects, such as serious degradation, were reported under such conditions [20].

A thermobalance, modified to be compatible with corrosive gases, was used for monitoring the fluorination reaction rates. This technique has the advantage of in-situ monitoring of kinetic processes. In this study, thermal analysis was used to study the effect of reaction conditions, gas mixtures and polymer structure on the fluorination rates of hydrocarbon polymers.

Experimental

Materials

Polypropylene, polyethylene, and a copolymer of ethylene and propylene were exposed to fluorine gas under various reaction conditions. High-density polyethylene was obtained from Plastomark and low-density polyethylene from AECI. Polypropylene and the copolymer were obtained from SASOL Polymers. The densities and the melt flow index values of the various polymers are given in Table 1. The polymers were hot pressed into sheets of thickness 0.3 cm. Sample discs with a diameter of 0.9 cm were punched from these sheets.

Thermogravimetry

The progress of the fluorination reactions was monitored with a thermobalance by measuring the mass increase as a result of hydrogen substitution by fluorine. Thermal analysis is usually conducted in an inert atmosphere and the protection of the microbalance is the biggest problem when it is done in reactive atmospheres. The design of the instrument that was used in this study is based on the principles described by Gimzewski [21]. The electronic weighing mechanism is protected by a stream of inert gas which flows through the balance chamber, while the reactive gas enters at a separate inlet and flows through the furnace. The disadvantage of the system of Gimzewski is that both gases leave the system through the same outlet, which could lead to dilution of the reactive gas by the inert gas. This possibility was eliminated by modifying the instrument according to Birks and Tattam by which the inert gas and reactive gas leave the system through separate outlets [22]. The resolution of the balance was 1 μg.

Table 1 Properties of the polymers exposed to fluorine gas

Polymer	Melt flow index / g/ 10 min	Density / $g \cdot cm^{-3}$
HDPE	1.5	0.950
LDPE	1.0	0.921
PP	1.8	0.907
PE–CO–PP	1.8	0.900

Surface roughness

Surface profiles and surface roughness parameters were measured on a Perthen surface roughness tester. In this method a stylus which generates electronic signals is pulled across the surface of a specimen. A surface profile is obtained from which surface roughness parameters can be determined.

Attenuated total reflectance infrared spectroscopy

Infrared spectra were recorded on a FTIR spectrophotometer equipped with an ATR attachment. A ZnSe crystal was used as the reflecting element and the angle of incidence of the infrared beam was 45°.

Neutron activation analysis

The results obtained from thermogravimetry were correlated with results obtained by neutron activation analysis. Neutron activation is based on the measurements of gamma rays emitted by radionuclides which are formed by the irradiation of stable nuclides with neutrons. In this study, gamma rays were detected with a Ge(Li) detector.

Results and discussion

Surface roughness

The kinetics of surface reactions are complicated by, inter alia, the large effects of surface topography. This is especially true when the reaction rates of different materials are compared. Obtaining surface profiles is therefore essential for normalization purposes when reaction rates of different specimens are compared.

The roughness factors of the polymer surfaces are given in Table 2. Polypropylene, high density polyethylene and the copolymer had uniformly rough surfaces, while low density polyethylene had a smooth surface. The true surface area for each polymer was calculated by the following expression:

$$A = fA_0$$

where A is the true surface area, A_0 is the apparent surface area and f the roughness factor. Corrections were made in the determination of the reaction rates for the various polymers.

Table 2 Relative surface roughness of the polymers exposed to fluorine gas

Polymer	Roughness factor
LDPE	1.06
HDPE	1.14
PP	1.13
PE–CO–PP	1.10

Kinetics of fluorination

Low density polyethylene film, 40 μm thick, was exposed to a gas mixture composed of 10% fluorine in nitrogen (% in *v/v*) at 50°C in the thermobalance. The increase in mass of the film during fluorination is shown in Fig. 1. Initially, the mass increases rapidly with time, but it becomes much slower as the reaction proceeds.

The fluorination of hydrocarbon polymers has been reported to proceed under the control of fluorine diffusion through the sample [6–8] and the results obtained in this study were therefore correlated with a diffusion-controlled model. Levenspiel describes rate equations for an unreacted core model in which the reaction occurs first at the outer skin of the particle and the zone of the reaction then moves into the solid [23].

$$\text{A(fluid)} + \text{bB (solid)} \rightarrow \text{fluid and solid products}$$

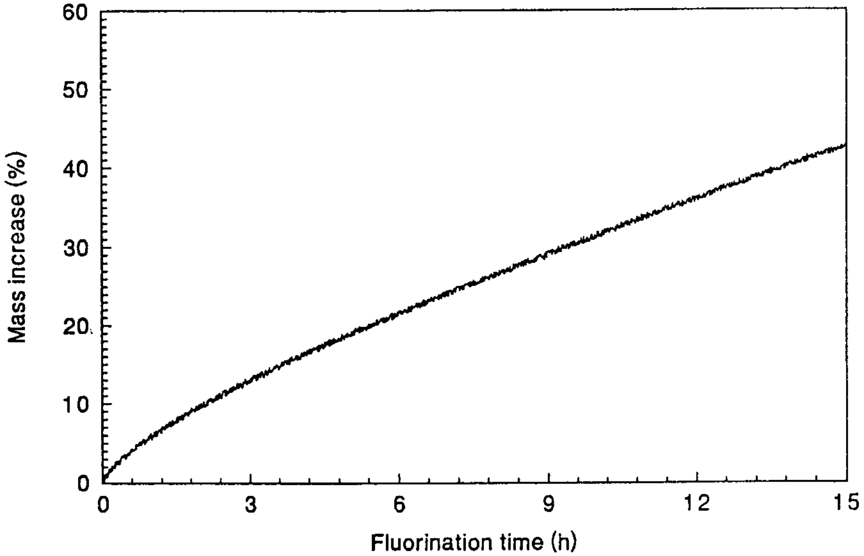

Fig. 1 Mass increase of low-density polyethylene as a function of fluorination time

In the case of a flat plate, the rate equations are

$$X_B^2 = \frac{t}{T} \tag{1}$$

and

$$X_B = \frac{t}{T} \tag{2}$$

in which X_B is the fractional conversion, t is the reaction time and T is the time for complete conversion. Equations (1) and (2), respectively, are applicable to diffusion control through the product layer and chemical reaction control.

The times for complete conversion for diffusion control and chemical reaction control, can be calculated from the expressions

$$T = \frac{\rho_B L^2}{2bD_e C_{ag}} \tag{3}$$

and

$$T=\frac{\rho_B L}{b k_s C_{ag}} \tag{4}$$

in which ρ_B is the density of the solid, D_e is the diffusion coefficient of the gaseous reactant in the converted layer, L is the sample thickness, C_{ag} is the concentration of the reactant gas and k_s the rate constant for the surface reaction.

In this model, Levenspiel [23] describes five possible rate-determining steps:

1. Diffusion of gaseous reactant through a surrounding gas film to the surface of the solid.
2. Diffusion of the reactant through the converted layer.
3. Reaction of the reactant at the reaction surface.
4. Diffusion of the gaseous products through the converted layer to the exterior surface of the solid.
5. Diffusion of the gaseous products to the main body of the fluid

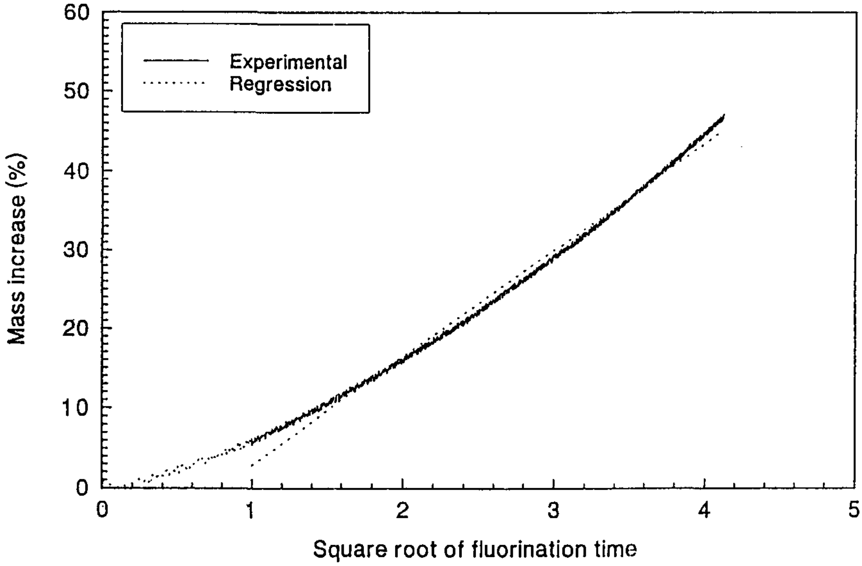

Fig. 2 Mass increase of low-density polyethylene as a function of the square-root of the fluorination time

The increase in mass of the low density polyethylene film *vs.* the square root of the fluorination time is shown in Fig. 2. The mass increase is directly proportional to the square root of the fluorination time, with the exception of the first part of the reaction. Fluorination reactions were carried out under dynamic flow conditions, which resulted in a forced convection mode of mass transfer from the gas bulk to the surface. Volkmann and Widdecke found that, under similar conditions, the reaction rate is independent of gas flow rate [8], which excludes the possibility that gas bulk diffusion could be rate determining. It seems therefore that the fluorination of polyethylene occurs in two stages. The initial stage is chemical reaction controlled. The progress ofthe reaction is unaffected by the presence of any reacted layer and is proportional to the available surface of the unreacted material. In the second stage the reaction zone moves into the solid, leaving behind completely converted material through which the fluorine must diffuse in order to reach the inner unreacted core. This is of course the idealized case. It is believed that fluorination results in the formation of only a partially fluorinated surface layer, and the boundary of the unreacted core is therefore not as sharply defined as in the model. Kinetic limitations, such as steric hindrance and deactivation effects of fluorine, polymer crystallinity and impurities in the reaction system, may complicate kinetic studies and cause a proposed model to differ from reality. It is clear from the rate equation that the reaction can be influenced by several factors and in this study, these and other factors and their effects on fluorination were studied.

The effect of fluorination temperature

The temperature dependence of the rate of fluorination of high density polyethylene is shown in Fig. 3. As can be seen in the figure and Table 3, an increase in temperature increases the rate of the fluorination reaction. Since it is stated in the literature that a minimum fluorine content is necessary before barrier properties towards organic liquids are obtained [24], it is possible to reach that value much sooner if the reaction temperature is increased. This is a possible advantage in the Airopak process of Air Products in which fluorine is reacted with high density polyethylene at an elevated temperature during the blow moulding process [3]. However, Eschwey *et al.* observed thermal degradation of the fluorinated surfaces at such high temperatures [20].

Table 3 Neutron activation results of fluorinated high density polyethylene as a function of fluorination temperature

Temperature / °C	Fluorine content / $\mu g \cdot cm^{-2}$
28	73.40
50	120.117
70	233.561

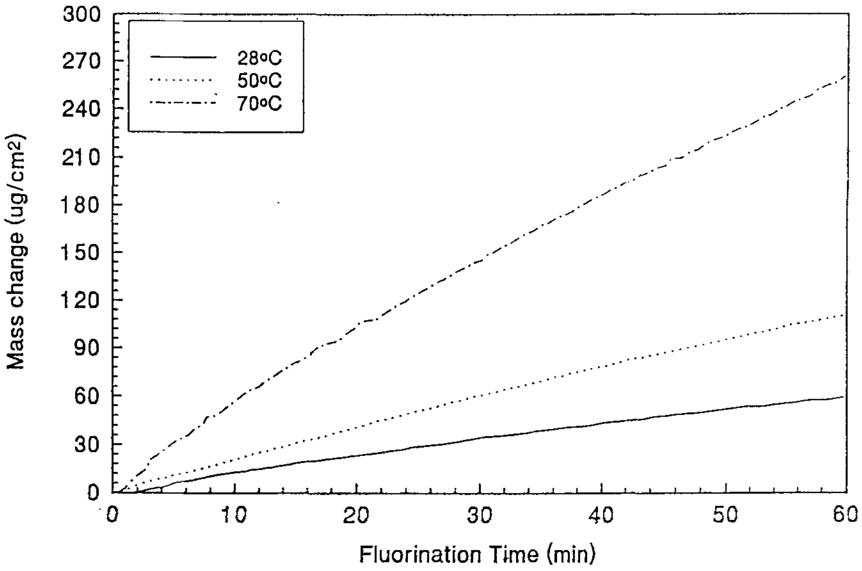

Fig. 3 Effect of the fluorination temperature on the fluorination rate of high-density polyethylene

The effect of fluorine concentration

Lagow and Margrave suggested that the probability of a polymer chain surviving a fluorine reaction on adjacent carbon atoms at approximately the same time is very low [5]. They placed emphasis on the importance of using low fluorine concentrations in the initial stages of the reactions to decrease the probability of fluorine collisions at adjacent reaction sites. The effect of fluorine concentration is shown in Fig. 4. The fluorination rate is increased considerably when the fluorine concentration is doubled. The difference in reaction rates for the two fluorine concentrations is even more evident at increased temperatures.

The effect of an inert diluting gas

High density polyethylene was fluorinated in the thermobalance at 28°, 50° and 70°C with various binary gas mixtures containing 10% fluorine. The effect of helium and nitrogen as inert diluting gases is demonstrated in Fig. 5. The rate of fluorination of high density polyethylene is higher when nitrogen, rather than helium, is employed as diluting gas. This is an agreement with results obtained by Shimada [7]. Gas bulk diffusion and laminate sublayer diffusion cannot provide a possible explanation for the difference in the reaction rates because, as was mentioned before, these effects do not occur under dynamic reaction conditions. However, the thermal conductivities of helium and nitrogen are 1.56 and 0.27 mW·cm^{-1}·K^{-1}, respectively [25]. The heat generated at the reaction centre of the highly exothermic reaction between polyethylene and fluorine will be removed more effectively by helium than by nitrogen. This might explain the slower reaction rate for helium as the diluting gas compared to nitrogen.

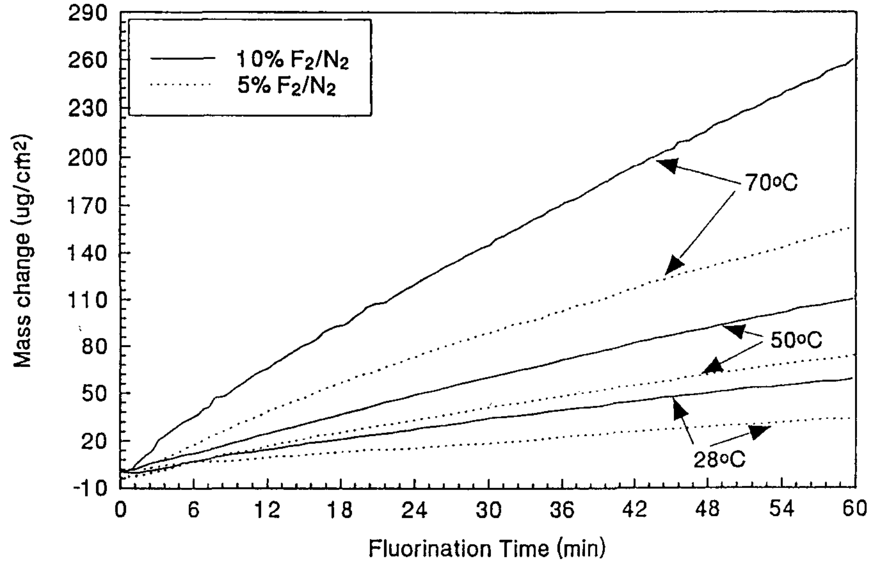

Fig. 4 Effect of fluorine concentration on the fluorination rate of high-density polyethylene

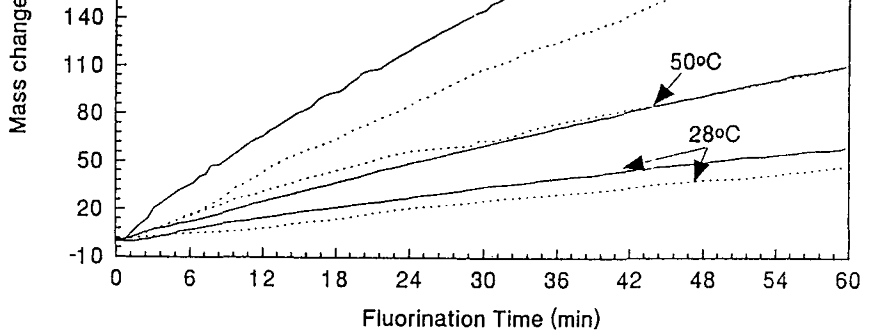

Fig. 5 Effect of an inert diluting gas on the fluorination rate of high-density polyethylene

The effect of a reactive diluting gas

The reaction rate of high density polyethylene, fluorinated with 10% fluorine in a nitrogen atmosphere, was compared with the reaction rate of an identical sample in an oxygen atmosphere (Fig. 6). The presence of oxygen dramatically decreases the reaction rate. Neutron activation analysis (shown in Table 4) also indicates a large decrease in fluorine substitution when oxygen was used as the diluting gas. ATR-infrared spectra of fluorination with different diluting gases are shown in Fig. 7. Oxygen is incorporated in the surface during oxyfluorination and was observed as hydrolysed –COF groups at 1727 cm^{-1}. This is in disagreement with results obtained by Lagow and Margrave who did not observe functionalization in high density polyethylene [18].

Table 4 Neutron activation results of fluorinated high density polyethylene as a function of the diluting gas

Temperature / °C	Fluorine content / $\mu g \cdot cm^{-2}$ F_2/N_2	Fluorine content / $\mu g \cdot cm^{-2}$ F_2/O_2	Fluorine content / $\mu g \cdot cm^{-2}$ F_2/CO_2
28	73.40	24.69	64.06
50	120.12	22.68	113.44
70	233.56	42.7	193.52

The following reaction scheme between a hydrocarbon and fluorine gas can be proposed

$$RH + F_2 \rightarrow R\cdot + HF + F\cdot$$

If no other reactive species are present, chain propagation occurs in which each reaction site consumes a reactive particle but again generates another radical.

$$R\cdot + F_2 \rightarrow RF + F\cdot$$

Oxygen (which is in the triplet ground state) is very reactive towards radicals and reacts quickly with a radical to form a new radical.

$$R\cdot + O_2 \rightarrow ROO\cdot$$

Florin observed peroxides with ESR spectroscopy during oxyfluorination [26]. The peroxy radical is much less reactive than the R· radical and can do little to continue the chain reaction. Subsequent reaction of the peroxide radical can lead to chain scission (and –COF formation), crosslinking (ROOR), and to the formation of various oxygen-containing species. Thus oxygen inhibits the reaction by reacting with the radicals that are formed during fluorination.

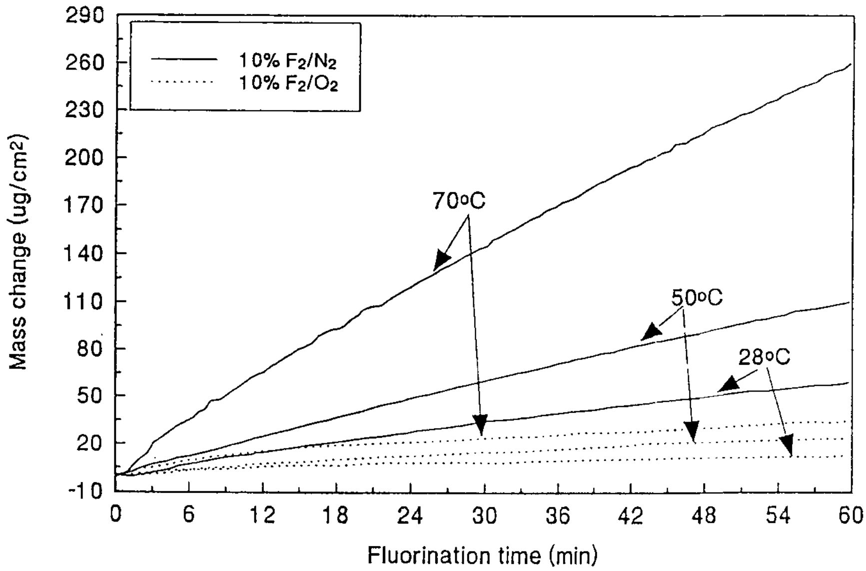

Fig. 6 Effect of oxygen as diluting gas on the fluorination rate of high-density polyethylene

Another possibility is that the polymer surface catalyses the reaction between fluorine and oxygen through the formation of fluorine radicals. This can also contribute to a decrease in radical concentration. It is further known that many polymers with good barrier properties towards gases contain oxygen in their repeat units (e.g. Surlyn) and the surface layer that is created during oxyfluorination may therefore passivate the material from fluorination by suppressing diffusion of the fluorine gas.

The effect of carbon dioxide as diluting gas on the fluorination of high density polyethylene is shown in Fig. 8. The fluorination rate for the reaction in which carbon dioxide is used as diluting gas is the same as during fluorination with nitrogen as diluting gas. Neutron activation results in Table 4 confirm these results. The degree of fluorination in carbon dioxide and nitrogen atmospheres is approximately the same. A small absorption band is visible at 1735 cm^{-1} in the infrared spectrum (Fig. 7), but it is not as prominent as during oxyfluorination.

The presence of oxygen during fluorination thus has an inhibiting effect on the fluorination rate, while the presence of carbon dioxide has little influence

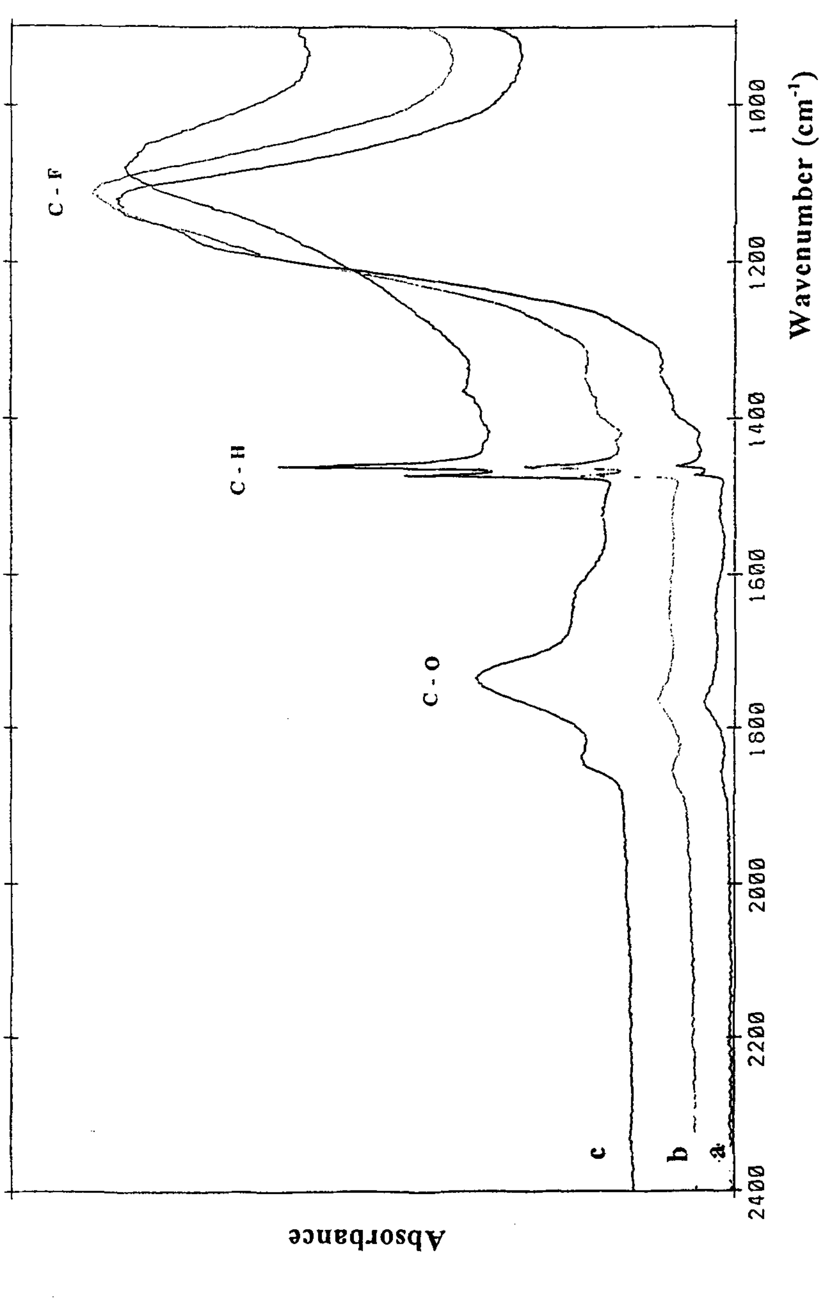

Fig. 7 ATR – infrared spectra of fluorinated high-density polyethylene. a) nitrogen as diluting gas; b) carbon dioxide as diluting gas; c) oxygen as diluting gas

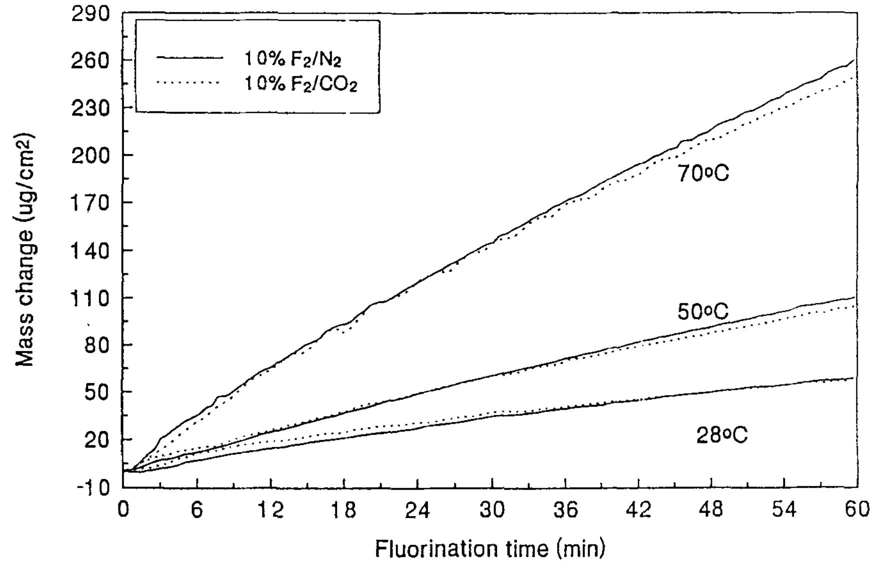

Fig. 8 Effect of carbon dioxide as diluting gas on the fluorination rate of high-density polyethylene

on the reaction rate (compared with nitrogen). However, if functionalization is required, oxygen is a much better candidate as diluting gas than carbon dioxide. The role of oxygen is important, because it is almost impossible to eliminate all the oxygen from the fluorine system since commercial fluorine contains oxygen as an impurity.

Effect of surface composition

It would be impossible to observe constant values of D_e, the diffusion coefficient, if the fluorinated layer depends on chemical and structural factors. Attempts have been made to determine the effect of substituted fluorine atoms on the fluorination of hydrocarbon polymers by reacting fluoropolymers and polyethylene with elemental fluorine. Corbin *et al.* studied surface fluorination of poly(vinylidene fluoride), poly(vinyl fluoride) and polyethylene and reported that, in none of the experiments, was the F/C ratio of the reaction product higher than 1 [27]. This was attributed to the deactivation effect of substituted fluorine. However, Scherer suggested that kinetic limitations do not exist and that PVDF could be fluorinated under 'normal conditions' [28].

Fluorination of PVF and PVDF at 50°C in the thermobalance with 10% fluorine in nitrogen is shown in Fig. 9. Poly(vinyl fluoride) gained mass during fluorination, although the rate was slow, but under the above reaction conditions, no fluorination was observed for poly(vinylidene fluoride).

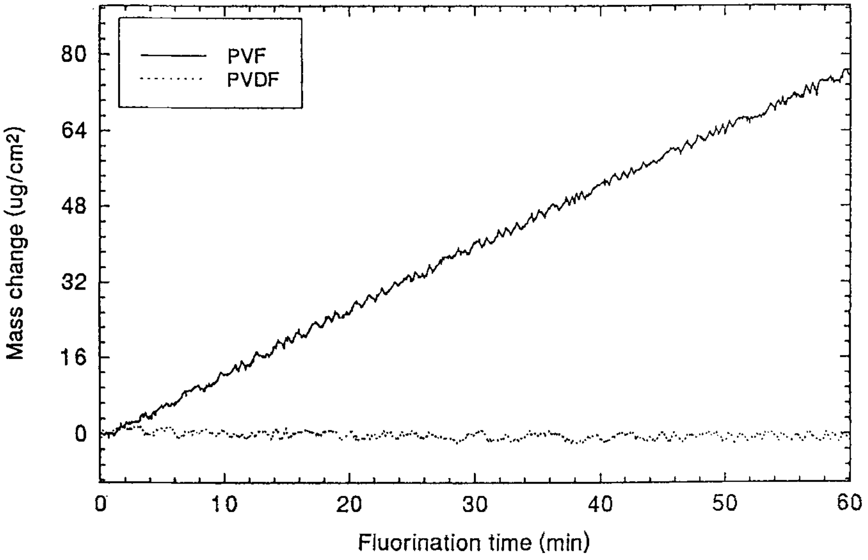

Fig. 9 Effect of fluorine gas on fluoropolymers

The effect of polymer structure

High density polyethylene is by far the most important candidate for fluorination from a commercial point of view and therefore most of the work reported in the literature has been done on this polymer. Little has been reported on the structure of other polymers, such as fluorinated polypropylene. In spite of the reactivity of fluorine gas, a perfluorinated layer is not achieved during surface fluorination and the reaction does not proceed uniformly through the surface layers. It is reported that the CH_2–CH_2 units of polyethylene are replaced by a complex structure during fluorination. ESCA studies reveal the presence of CH_2–CHF, CHF–CH_2, CF_2–CF_2, CH_2–CH_2 and CHF–CHF units in the surface of fluorinated polyethylene [6, 29]. One can therefore expect the fluorinated layer not to be independent of polymer structure and morphology.

It is known that certain additives have a detrimental effect on the barrier properties of fluorinated polyolefin containers. The relative mass increases of low density polyethylene containing no additives and low density polyethylene containing various antiblocking agents, slip agents and antioxidants are compared in Table 5. It is clear that the presence of additives at the surface of low density polyethylene does not affect its reactivity towards fluorine.

Table 5 The influence of additives on the fluorination rate of low density polyethylene

Fluorination time / min	Mass increase / μg·cm^{-2} LDPE: additives	Mass increase / μg·cm^{-2} LDPE: no additives
20	19.25	17.57
40	32.35	30.8
60	43.05	41.87

High and low density polyethylene, polypropylene and a block copolymer of ethylene and propylene were fluorinated at 28°C with 10% fluorine in nitrogen in the thermobalance. Although the highly reactive fluorine molecule is much less selective than the other halogens, branch points present the most likely points of attack by fluorine. ^{13}C NMR was used to determine the type and the frequency of branches in high and low density polyethylene. No branching was observed in high density polyethylene, but 5 ethyl branches and 17 longer branches per 1000 carbon atoms were observed in low density polyethylene. The relative reaction rates of the unpigmented polymers are compared in Fig. 10. Polymers containing propylene in the structural unit have a higher fluorination rate than polyethylene. In spite of the higher degree of crystallinity and the absence of tertiary carbon atoms in high density polyethylene, the reaction rate of high density polyethylene is higher than that of low density polyethylene. This confirms results obtained by Volkmann and Widdecke [8].

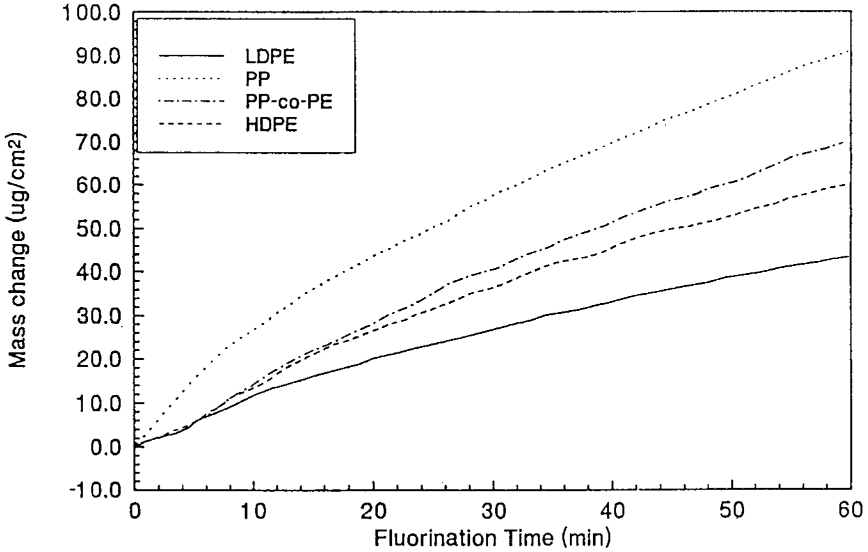

Fig. 10 Relative fluorination rates of polyolefins

The higher degree of fluorination of high density polyethylene compared to low density polyethylene is surprising, since one would expect the crystalline areas in high density polyethylene to suppress fluorine diffusion through the sample. Although Schonhorn observed no evidence of morphological rearrangement in the fluorination of monolayer single crystals of polyethylene [30], the effect of the larger fluorine atoms on crystallinity is not clear. Studies of the crystallinity at the surface of a polymer before and after fluorination may provide answers to this and other unaccountable results, such as the fact that fluorination of polypropylene fails to produce the same striking barrier properties towards organic liquids as fluorinated polyethylene.

The role of hydrogen fluoride in fluorination

Hydrogen fluoride is formed as a byproduct during fluorination. Questions arise as to what influence this product has on the fluorinated product and whether it is removed from the polymer matrix and surface during fluorination. Eschwey claims that a hydrogen fluoride film forms at the polymer surface during fluorination and inhibits the reaction [31].

High density polyethylene bottles (100 ml) were filled with water immediately after fluorination (60 μg/cm^2). The quantity of fluoride leaching from the bottles was determined over a period of 6 weeks with ion chromatography. As can be seen in Fig. 11, the quantity of F^1 leaching from the bottles increases

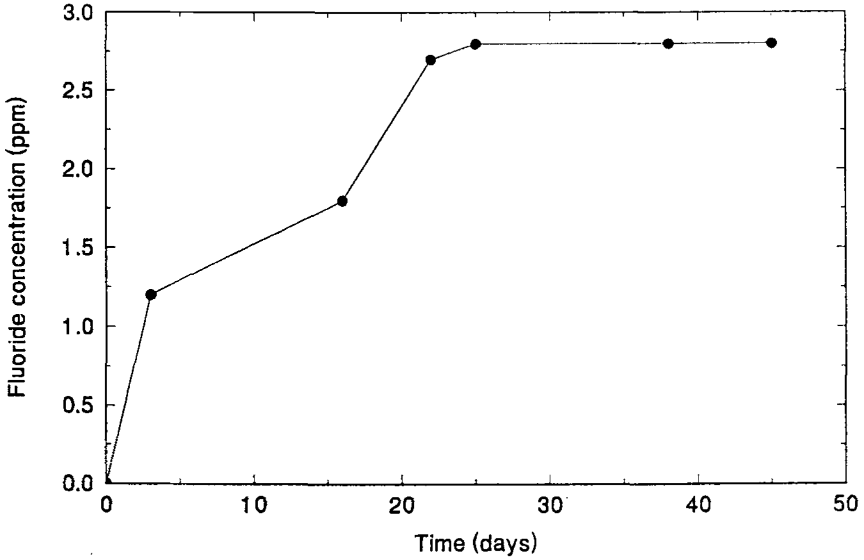

Fig. 11 Fluoride leaching from 100 ml fluorinated high-density polyethylene containers

with time, but levels off at 2.8 ppm. However, 2.8 ppm corresponds to only 3.38% of the total amount of fluorine in the fluorinated bottles. Desorption of small amounts of HF or hydrolysis reactions at the fluorinated surfaces may account for the loss of fluorine from the fluorinated products.

High density polyethylene was fluorinated with a 10% F_2/N_2 gas mixture in the thermobalance. The fluorinated samples were subjected to neutron activation analysis after 14 days. The mass increase that was measured in the thermobalance is correlated with neutron activation results in Table 6. There is a reasonable agreement between results observed in the thermobalance during fluorination and neutron activation results after fluorination. A standard deviation is reported from neutron activation analysis which may influence these results. These values are calculated from counting statistics during gamma ray detection and is higher for samples in which the fluorine concentration is low. The correlation in the results implies that the mass increase measured with the thermobalance results from fluorine incorporation in the sample and not from adsorbed hydrogen fluoride. The reaction temperature (28°C) in the experiments is well above the boiling point of HF (19.5°C at 101.3 kPa) and therefore, HF would be released from the polymer surface if no adsorption occurs.

Table 6 Correlation between mass increase in the thermobalance and neutron activation

Temperature / °C	Fluorine content NAA / $\mu g \cdot cm^{-2}$	Fluorine content thermobalance / $\mu g \cdot cm^{-2}$	Standard deviation NAA / %	Difference / %
28	69.53	61.28	9.1	11.86
50	113.77	113.38	5.6	0.34
70	221.15	260.12	5.7	-17.62

In addition, polyethylene and fluorinated polyethylene were exposed to HF gas in the thermobalance. No increase in mass was observed. This implies that HF does not adsorb on the polymer surface. One can therefore conclude that hydrogen fluoride desorbs from the polymer sample as it is formed.

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References

1 A. J. Rudge, British Patent, 710,523 (1954).
2 R. J. Lagow and J. L. Margrave, Polymer Lett. Ed., 12 (1974) 177.
3 Dixon *et al.*, United States Patent 3862, 284 (1975).

4 Bauman *et al.*, United States Patent, 4764, 405 (1988).
5 R. J. Lagow and J. L. Margrave, Progress in Inorganic Chemistry, 26 (1979) 161.
6 D. T. Clark, W. J. Feast, W. .K. R. Musgrave and I. Ritchie, Polym. Sci. Technol., 5A (1974) 373.
7 J. Shimada and M. Hoshino, J. Appl. Polym. Sci., 19 (1975) 1439.
8 T. Volkmann and H. Widdecke, Macromol. Chem. Macromol. Symp., 25 (1989) 243.
9 J. M. Tedder, Advances in Fluorine Chemistry, 2 (1961) 104.
10 F. Wolf and H. J. Mallon, Plaste Kautsch, 24 (1977) 617.
11 H. Schonhorn and R. H. Hansen, J. Appl. Polym. Sci., 12 (1968) 1231.
12 R. E. Cohen *et al.*, European Patent, 132, 407 (1985).
13 L. J. Hayes, J. Fluorine Chem., 8 (1976) 69.
14 Dixon *et al.*, United States Patent, 3940, 520 (1976).
15 Bauman *et al.*, United States Patent, 4771, 110 (1988).
16 H. S. Shinohara, M. Iwasaki and S. Tsujimura, J. Appl. Polym. Sci., Part A-1, 10 (1972) 2129.
17 Dixon *et al.*, United States Patent, 4020, 223 (1977).
18 J. L. Adcock, R. J. Lagow and S. Inoue, J. Amer. Chem. Soc., 100 (1978) 1948.
19 E. Uhse, A. Zimmerling, D. Hass and M. Schonherr, Z. Chem., 29 (1989) 313.
20 M. Eschwey *et al.*, United States Patent, 4869, 859 (1989).
21 E. Gimzewski, Thermochim. Acta, 84 (1985) 7.
22 N. Birks and N. Tattam, J. Sci. Instrum., 2 (1969) 628.
23 O. Levenspiel, Chemical Reaction Engineering, John Wiley and Sons, New York 1962,p. 357.
24 H. Sorek, J. Radioanal. Nucl. Chem. Lett., 93 (1985) 97.
25 R. C. Weast (Ed.), Handbook of Chemistry and Physics (57 ed.), CRC Press, Cleveland 1977, E-3.
26 R. E. Florin J. Fluorine, Chem., 14 (1979) 253.
27 G. A. Corbin, R. E. Cohen and R. F. Baddour, Polymer, 23 (1982) 1546.
28 G. G. Scherer and P. Pfluger, Makromol. Chem. Rapid Commun., 5 (1984) 611.
29 C. Bliefert, Metalloberflache, 41 (1987) 371.
30 H. Schonhorn, P. K. Gallagher, J. P. Luongo and F. J. Padden, Macromolecules, 3 (1970) 800.
31 M. Eschwey and H. Jastrow, Gas Aktuell, 32 (1986) 17.

Zusammenfassung — Unter sorgfältig überwachten Bedingungen ließ man in einer für Fluorgas geeigneten Thermowaage Polyolefine und Fluoropolymere mit elementarem Fluor reagieren. Die Fluorierungsreaktionen wurden über die als Ergebnis der Substitution von Wasserstoff gegen Fluor eintretende Massenzunahme verfolgt. Die Massenzunahme war der Quadratwurzel der Fluorierungszeit direkt proportional, was zeigt, daß die Diffusion des Fluorgases zur noch nicht reagierten Oberfläche der geschwindigkeitsbestimmende Schritt ist. Die Fluorierungsgeschwindigkeit wurde durch steigende Fluorkonzentration und Fluorierungstemperatur erhöht. Die Fluorierungsgeschwindigkeit ist größer, als Stickstoff anstelle von Helium als Gas zur Verdünnung angewendet wurde. Die Fluorierungsgeschwindigkeit bleibt gleich, wenn man als Verdünnungsgas anstelle von Stickstoff CO_2 verwendet, während die Gegenwart von Sauerstoff die Fluorierungsgeschwindigkeit drastisch verringert. Bei der Fluorierung mit Sauerstoff als Verdünnungsgas wird Sauerstoff eingebaut, während bei CO_2 als Verdünnungsgas keinerlei Funktionalisierung beobachtet werden konnte. Weiterhin wurde der Effekt der Polymerenstruktur auf die Fluorierung untersucht. Polyvinylfluorid wies bei der Fluorierung einen Massenzuwachs auf, während für Polyvinilydenfluorid keine Reaktion beobachtet werden konnte. Die Reaktionsgeschwindigkeit für Polypropylen war höher als die für Polyethylen.