Difluorocarbene Modification of Polymer and Fiber Surfaces

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Synopsis

Difluorocarbene (difluoromethylene, $:CF_2$) generated by the pyrolysis of sodium chlorodifluoroacetate has been shown to irreversibly modify the surfaces of polymers and fibers.   The critical surface tension values of several polymers are shown to decrease with increasing exposure to difluorocarbene vapors and ultimately approach the critical surface tension values of partially fluorinated polyethylenes.   The rate-controlling step appears to be the diffusion of difluorocarbene from the precursor to the polymer substrate.   The nature of the interaction between difluorocarbene and the polymer surface is unknown; however, the absence of infrared bands due to C—F bonds in attenuated total reflection measurements tends to establish the mono-molecular-like character of the modified surface.

INTRODUCTION

Carbenes have become well known compounds in recent yers.   They may be defined as divalent carbon intermediates in which the carbene carbon is linked to two adjacent groups by covalent bonds and possesses two un-bonded electrons.   One of the more common reactions of the parent carbene (methylene) is its insertion into a single bond,[1,2] viz.

$$:CH_2 + A—B \rightarrow A—CX_2—B$$
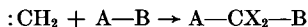
The "carbene" form of nomenclature while not conforming to the established rules of the International Union of Pure and Applied Chemistry has been nevertheless widely accepted because of its clarity and consistency. Additional arguments for its acceptance have been given by Kirmse.[2]   Accordingly we have used carbene nomenclature in the work reported here.

Insertion of a carbene into C—H and C—C bonds occurs readily while addition can occur at C=C bonds.   For insertion reactions the C—H bond is generally the more reactive.   Insertion of carbene (methylene) into C—H bonds has been found to occur by two different mechanisms that often operate concurrently.[1]   In one mechanism, the insertion occurs through a transition state.

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$$RC—H + :CH_2 \rightarrow RC\underset{\underset{\displaystyle \dot{C}\dot{H}_2}{}}{\diagdown\diagup}H \rightarrow RC—CH_2—H$$
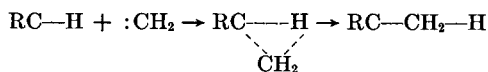
In the other mechanism, two intermediate radicals are formed and then combine.

$$RH + :CH_2 \rightarrow R\cdot + CH_3\cdot \rightarrow RCH_3$$
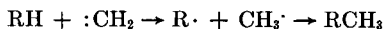
The reactivity of carbenes is also affected by substituent groups. Although the electronic effects of substituent goups on the insertion reactions are not fully known, it appears that carbenes substituted with electrophilic groups have longer half lives[2] with lessened reactivity.[3] The latter observation was made chiefly from the reactions involving the generation of dihalocarbenes in solution where little additional energy was put into the system. For $:CX_2$ generation by pyrolysis where the carbene receives additional energy the C—H insertion reaction should be more favorable. This has indeed been shown to be true.[4]

In view of the foregoing the initial carbene selected for the modification of surfaces was difluorocarbene $(:CF_2)$ since this carbene could be readily generated by pyrolysis and, more importantly, its reaction with a surface could be detected by determining the ciritical surface tension,[5] γ_c, of that surface. Insertion of $:CF_2$ into the surface of a hydrocarbon polymer should produce a surface group, as follows,

$$\text{▧}—H + :CF_2 \rightarrow \text{▧}—CF_2H$$
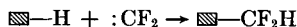
with a γ_c value approaching either that of polytetrafluoroethylene[5,6] or of other fluorinated polyethylenes.[7]

Experimental Procedure

Generation of difluorocarbene was first attempted by thermal decomposition of sym-difluorotetrachloroacetone[8] or chlorodifluoroacetic acid[9] in a nonreactive solvent such as CCl_4. The solvents roughened the polymer surfaces; therefore, the contact angle measurements necessary to determine critical surface tension values could not be made.

Pyrolysis of sodium chlorodifluoroacetate as a $:CF_2$ precursor was tried next with good results. The sodium salt was prepared by adding sodium bicarbonate to the free acid (General Chemical Div., Allied Chemical Corp.), until CO_2 evolution stopped. The $ClF_2CCOONa$ could then be used immediately or dried for storage.

The polymer sheets used in this study were of commercially available grades (Cadillac Plastics and Chemical Co.). Wettability measurements on cleaned samples of the polymers gave the critical surface tension values given in Table I for zero time. These values are in generally good agreement with those given in the literature[10] and thus establish that the polymer surfaces were free from contamination or surface oxidation. The polymer sheets were prepared for exposure to difluorocarbene as follows: the sheets were first washed in detergent followed by copious rinsing in tap water followed by a distilled water rinse;[6] glossy surfaces were then pre-

pared by pressing the cleaned polymer under moderate heat and pressure against glass similarly cleaned;[5] after peeling the polymer from the glass surface it was given a final rinse in distilled water.

In a typical batch preparation of a modified polymer surface about 10 g of $ClF_2CCOONa$ was placed in an open top pyrolysis chamber consisting in the most simplified form of a Petri dish on a hot plate. Other pyrolysis chambers of basically the same design and of both stainless steel and glass construction were used with no detectable difference in the pyrolysis. The usual pyrolysis temperature was 385°C. At this temperature the evolution of $:CF_2$ commenced within two minutes; however, pyrolysis also proceeds at lower temperatures. For surface modification the polymer sheet was placed over the pyrolysis chamber with ceramic insulation separating the sheet from the hot sides of the chamber. Samples were exposed to $:CF_2$ vapors for varying periods of time at a diffusion distance of 4 cm. (i.e., the distance from the precursor bed to the polymer surface). The surface temperature of the polymer during reaction with $:CF_2$ could not be determined since thermocouple leads mounted on the surface adsorbed radiant heat at rates differing from that of the polymer surface. The results given below for the continuous treatment of polyethylene suggest that the polymer surface must be softened before reaction with $:CF_2$ occurs.

For the continuous treatment of polyethylene surfaces with $:CF_2$ a strip of low density polyethylene ($5/8$ in. wide, 6 mils thick) was passed through a Pyrex glass tube (65 cm $\times$ 4.6 cm) inserted in a Lindberg Tube Furnace No. 241, equipped wtih an Automatic Furnace Control). Ten grams of $ClF_2CCOONa$ was spread out on a metal insert in the center 20 cm portion

TABLE I
Critical Surface Tensions of Difluorocarbene Modified Polymer Surfaces

Polymer	Time of exposure min	γ_c (dynes/cm)
Polyethylene	0	31.0
	3	27.0
	8	23.5
	14	21.0
Polypropylene	0	32.0
	3	30.0
	8	27.0
Polymethylmethacrylate	0	39.0
	3	35.0
	8	31.0
Nylon	0	41.0
	8	34.5
	14	24.5
Polystyrene	0	30.5
	8	24.0
Cellulose acetate	0	39.0
	3	26.0
	8	20.0

of the tube where isothermal conditions were approximated. During pyrolysis the polyethylene strip was passed through the tube and over the bed of the carbene precursor; the diffusion distance between the precursor bed and strip was 0.5 cm. As shown by the results given below the polyethylene surface must be softened before reaction with :CF_2 will occur.

Advancing contact angles were measured directly using an Eberbach telescopic cathetometer equipped with a circular protractor. The procedure was essentially that described by Schonhorn and Ryan.[11] The wetting liquids were reagent grade ethylene glycol and glycerol, and distilled water. The handbook values for the surface tensions of these liquids were verified by capillary rise measurements. Ethylene glycol and glycerol are known to be hygroscopic however there was no observed effect due to the hygroscopicity since drops of these liquids showed no variation in contact angle upon prolonged exposure to air.

For each drop of wetting liquid, three more more contact angle measurements were made on each side of the drop. The values thus obtained were averaged with the most extreme values being given as the error.

Commercial cloth samples were also exposed to :CF_2 vapors. The procedure was the same as above. For the fabrics, meaningful contact angles and, hence, γ_c values could not be obtained. Instead, the time of penetration of uniform water droplets was used as the criterion of :CF_2 reaction. The water penetration test (or water drop test) consists of placing a measured drop of water on the fiber and noting the time for complete absorption.[12,13]

Results

The effect of progressive modification of the various polymer surfaces with :CF_2 is given by the wettabilities shown in Figures 1 through 6 and summarized in Table I. If insertion does occur a —CF_2H surface group is expected which should have a γ_c value similar to that of a fluorinated poly-

TABLE II
Time of Penetration of Uniform Water Droplets on
Difluorocarbene Modified Fiber Surfaces

Fabric	Time for complete penetration	
	Unexposed samples	Exposed for 5 min
65% Dacron polyester/ 35% Cotton	53 sec	3 min 54 sec
100% Arnel triacetate	18 sec	1 min 24 sec
50% Arnel triacetate/ 50% Avron rayon	49 sec	4 min 35 sec
100% Rayon	15 sec	11 min 34 sec
100% Acetate-chromspun	12 sec	1 min 46 sec
100% Nylon	84 min	>120 min[a]

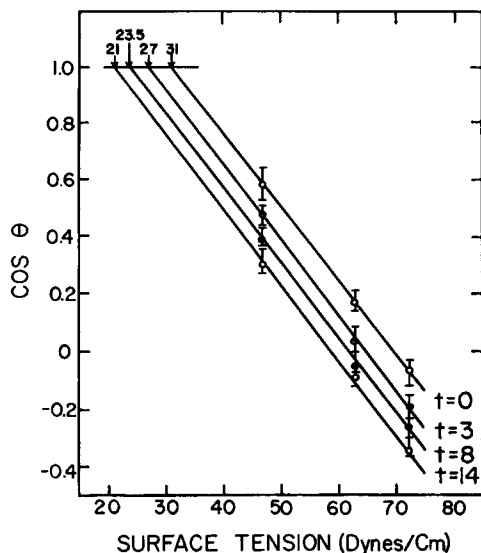[a] Complete evaporation would precede penetration.

Fig. 1. Wettabilities at 20°C of polyethylene exposed to :CF$_2$ for varying periods of time (minutes).
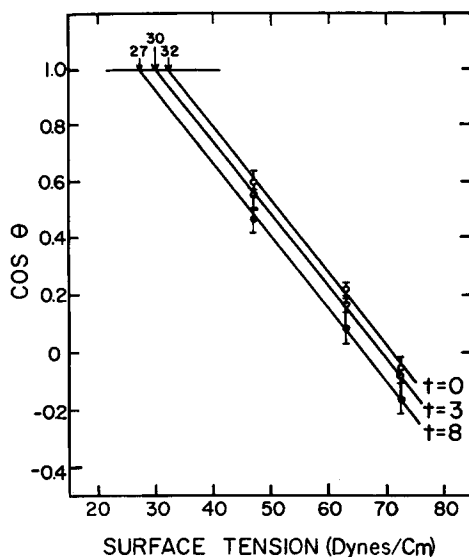

Fig. 2. Wettabilities at 20°C of polypropylene exposed to :CF$_2$ for varying periods of time (minutes).

ethylene. Since the γ_c values for the various :CF$_2$ modified surfaces are in the same range as for polytetrafluoroethylene[5]—18 dynes/cm, or for partially fluorinated polyethylenes[7]; viz., polyvinylfluoride—28 dynes/cm, polyvinylidene fluoride—25 dynes/cm, polytrifluoroethylene—22 dynes/cm, insertion may have taken place. It should also be noted that a γ_c value
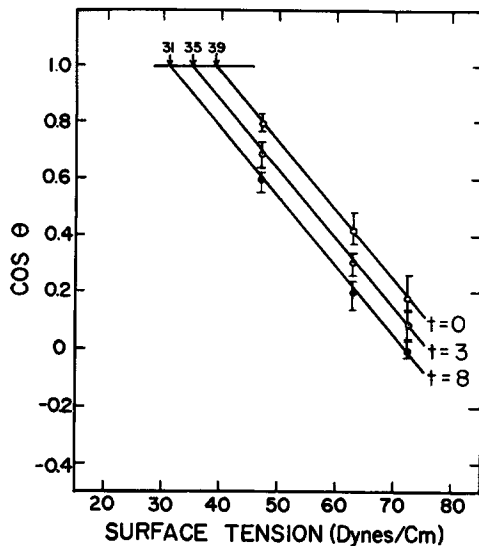
Fig. 3. Wettabilities at 20°C of polymethylmethacrylate exposed to: CF_2 for varying periods of time (minutes).
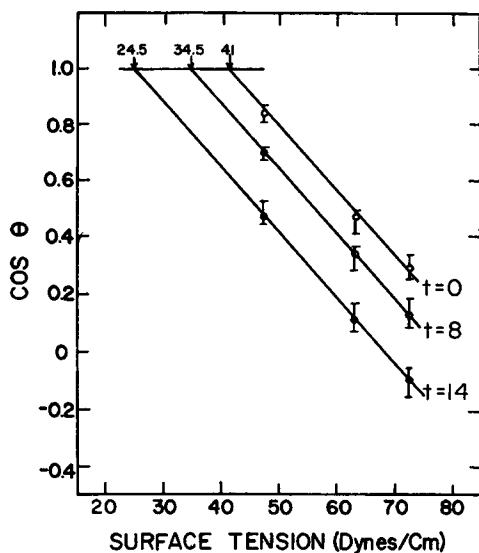

Fig. 4. Wettabilities at 20°C of nylon exposed to: CF_2 for varying periods of time (minutes).

is available for —CF_2H surfaces[14]; however, this value of 15 dynes/cm is for a terminal group of a close packed monolayer. Such surfaces generally have lower γ_c values than surfaces of polymers.[10]

The reacted : CF_2 layer on a polymer surface is stable in that no change in observed water contact angles was detected at any time during a two-week
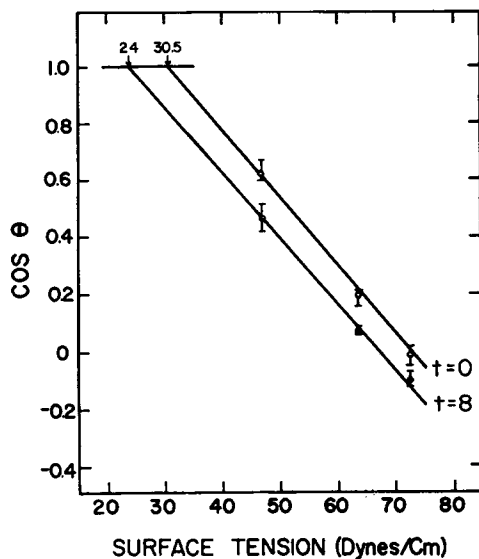
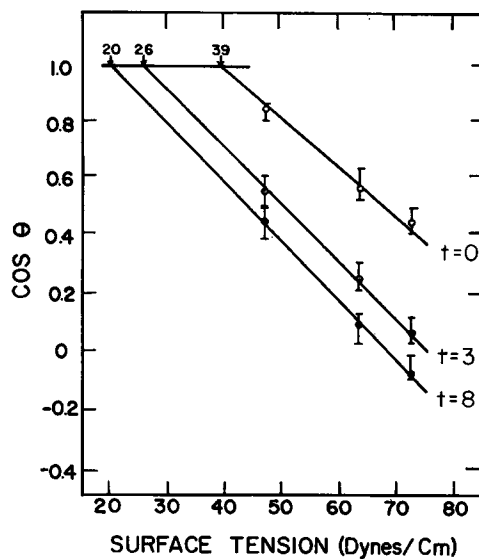Fig. 5. Wettabilities at 20°C of polystyrene exposed to: CF_2 for varying periods of time (minutes).

Fig. 6. Wettabilities at 20°C of cellulose acetate exposed to : CF_2 for varying periods of time (minutes).

soaking of : CF_2 modified polyethylene surfaces in 3M HNO_3 and 3M NaOH solutions.

Several fabrics were also exposed to : CF_2 in the same manner as the polymer surfaces. The results in terms of the time of penetration of uniform water droplets are shown in Table II. It should be noted that the

fiber spacing was different for each type of fabric; thus comparisons between fabric types are not valid. However, comparisons between treated and untreated samples of the some fabric are meaningful. From the data of Table II it is obvious that a considerable effect has taken place. While not given here, similar results were also observed for paper surfaces.

During the continuous runs it became apparent that successful modification of a polyethylene surface occurred at a residence time (i.e., time of pass through the furnace) just sufficient to allow the film to become elastic.
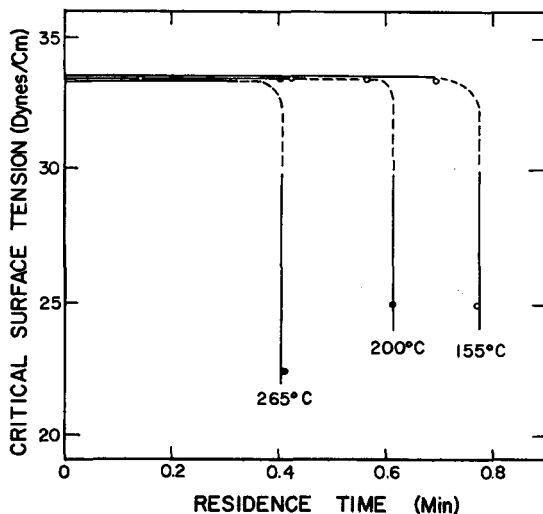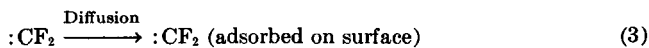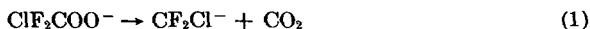

Fig. 7. Effect of furnace temperature on residence time for continuous: CF₂ modification of polyethylene strip. Successful surface modification occurs only upon softening of the polymer.

When the strip became elastic an immediate reaction took place as evidenced by the decrease in critical surface tension. These results are shown in Figure 7 for several furnace temperatures. As noted previously, the actual temperature within the polyethylene strip necessary for $:CF_2$ treatment is not known but it probably corresponds to the softening temperature between the rubbery state and the viscous melt.

Discussion

In view of the foregoing results the overall surface modification reaction probably involves at least the following equations:

$$ClF_2COO^- \rightarrow CF_2Cl^- + CO_2 \tag{1}$$

$$CF_2Cl^- \rightarrow :CF_2 + Cl^- \tag{2}$$

$$:CF_2 \xrightarrow{\text{Diffusion}} :CF_2 \text{ (adsorbed on surface)} \tag{3}$$

$$\boxed{\text{≋}}—H + :CF_2 \text{ (adsorbed)} \rightarrow \boxed{\text{≋}}—CF_2H \tag{4}$$

where eqs. (1) and (2) are inferred from the decarboxylation of trichloro-acetic acid in aprotic solvents.[15]   Simple diffusion is described by[16]

$$\overline{\Delta X^2} = 2Dt$$

where $\overline{\Delta X}$ is the diffusion distance, D is the diffusion constant and t is time. A corollary of eq. (5) is that the number of $:CF_2$ biradicals diffusing a constant distance increases linearly with the square root of time.   Thus the degree of surface modification as determined by γ_c values should be at least approximately proportional to root time.   The resulting linear relation between γ_c and root time values of Figure 8 (excepting nylon) thus shows that diffusion is indeed involved and that the slow step in the over-all surface modification reaction is most likely diffusion of $:CF_2$ to the polymer surface [eq. (3)].   (The nonlinear results for nylon are attributed to its relatively high softening point which, are shown above for polyethylene, must be exceeded in at least the surface layers before modification occurs.)
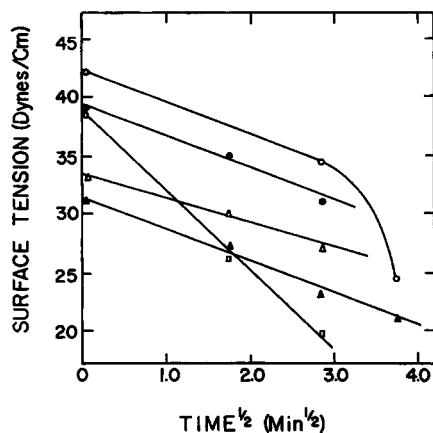

Fig. 8. Linear relation between critical surface tension values and the square root of time demonstrating diffusional control of the overall surface modification reactions.

Equation (4) is difficult to verify experimentally.   There is ample wettability data given above; however, critical surface tension values substantiate only qualitatively that surface modification has occurred.

Infrared attenuated total reflection (ATR) was also used to try to determine the structure of $:CF_2$ modified polyethylene surfaces.   The results are shown in Table III.   Difluorocarbene modified polyethylene surfaces showed no C-F bands using infrared attenuated total reflection.   In this technique the incident light penetrates the sample to about one wavelength before being reflected.   Since no C-F bands were found, the amount of reacted $:CF_2$ must be small and is probably concentrated only at the polymer surface.   Thus it is possible that the surface reaction involves only the outermost bonds in the polymer surface and may be no thicker than a reacted monomolecular layer or, at most, a few molecular layers.[17]

Infrared transmission spectra of eight to ten thicknesses of polyethylene film also failed to show any weak bands which might be attributed to insertion of $:CF_2$ into a C—H bond.   The critical surface tension values of these samples had decreased from 33 dynes/cm to about 25 dynes/cm, thus indicating that surface modification had indeed taken place.   These results reinforce the view that the surface reaction involves only a very few molecular layers.

Identical water vapor permeabilities for both unmodified and $:CF_2$ modified polyethylene also tends to confirm that modification is confined only to the surface layers.

TABLE III
Infrared Attenuated Total Reflectance Spectra

Polyethylene	CF$_2$ Modified polyethylene	Polytetrafluoroethylene
3530 cm^{-1}	3530 cm^{-1}	3520 cm^{-1}
2922 (s)	2922 (s)	—
2855 (s)	2855 (s)	—
1465	1465	—
—	—	1202 (s)
—	—	1149 (s)
716 (w)	716 (w)	—
	(s) strong band	
	(w) weak band	

Thus, the exact nature of a polymer surface reacted with a substituted carbene is not fully understood.   However, as shown from the wettability measurements above a definite and predictable change in the critical surface tension is observed.   For difluorocarbene modification of polyethylene surfaces (γ_c = 31–33 dynes/cm) a critical surface tension approaching that of a fluorinated polyethylene (γ_c = 18–25 dynes/cm) is predicted and is observed.   For carbethoxycarbene modification of a polyethylene surface[18] a critical surface tension approaching that of polymethylmethacrylate (γ_c = 40 dynes/cm) is predicted and is observed.   The question still remains whether the carbene reacts with the polymer surface by insertion or whether the carbene first dimerizes to a substituted ethylene which then polymerizes on the polymer surface.   The lack of infrared bands from total attenuated reflection measurements shows that the reacted layer on the polymer surface is thin.   A thin layer of surface polymerized substituted ethylene would probably not adhere well and should be easily removed by chemical means.   The inability to destroy a difluorocarbene modified polyethylene surface by alkaline hydrolysis (as verified by constant water contact angles) and the ability to run a sequence of classical reactions with rather drastic reaction conditions on a carbethoxycarbene modified polyethylene surface[18] shows that the modified layer is quite permanent. These results, then, support the conclusion that a separate layer due to the surface polymerization of substituted ethylene does not form.

It may also be doubtful whether any polymerization product of difluoro-carbene is formed other than its dimer, tetrafluoroethylene, since Lenzi and Mele[19] have shown that $:CF_2$ radicals show a low reactivity with tetra-fluoroethylene molecules.   Dalby[20] has shown that the major product from the photolysis of perfluoropropylene is tetrafluoroethylene while Cohen and Heicklen[21] have shown that photolysis of tetrafluoroethylene results in some cycloperfluoropropylene being formed.   Thus, in general, only dimers or trimers of difluorocarbene seem to be formed and further polymerization in the absence of a catalyst appears doubtful.

While dimerization of $:CF_2$ does occur, the foregoing discussions argue against further polymerization of the tetrafluoroethylene thus formed. This, then, would seem to preclude tetrafluoroethylene from participating in surface modification of polymers.

Insertion reactions involving difluorocarbene must be considered as the remaining possibility.   The immediate problem here is that carbenes are transitory intermediates with short half lives.   The half lives of difluoro-carbene are usually quoted as being 0.5 msec and 20 msec in solution and in the gas phase repsectively.[2]   These are extremely short half lives and would seemingly preclude the diffusion step shown above to occur in the surface modification of polymers.   Other authors, however, have estimated that the half life of difluorocarbene to be on the order of one second.[22]   The disparity in observed half lives is reasonable since it is most probable that difluorocarbene forms tetrafluoroethylene through a bimolecular process[20,21] and thus the observed half life should be strongly dependent upon concen-tration.[23]   It should also be noted that various authors[19,24,25,26] have ob-served no reaction, other than third body collisions, between CF_2 in the gas phase and O_2, N_2, H_2, CO, C_2H_4, and C_3H_8.

In the present work difluorocarbene is generated quite slowly from the precursor, thus the concentration in the pyrolysis chamber should be low and the half life relatively long.   Assuming for the moment that a half life of one second is attainable and that the diffusion constant for difluoro-carbene in air is $0.1 \ cm^2/sec$ (i.e., that of molecules of similar molecular weight[27]) the following shows that surface modification with difluoro-carbene is possible.   As a general rule a reactive species is active through at least six half lives, i.e., for $:CF_2$ six seconds.   Thus, from eq. (5) it can be calculated that active $:CF_2$ diffuses about 1.1 cm within six seconds.   This is ample time to reach a polymer surface at a diffusion distance of 0.5 cm.   It also explains why such fairly long exposure times as 8 to 14 min were neces-sary to obtain the critical surface tensions of Table I, viz. only the most energetic radicals had half lives long enough to diffuse 4 cm.

Thus, when the $:CF_2$ arrives at the polymer surface it is presumed to react with any unsaturation present and, more importantly, to undergo in-sertion reactions.   The literature shows that the relative rates of attack by $:CF_2$ on primary, secondary, and tertiary C—H bonds are in the ratio of $1:2:7$.[28]   For polyethylene which consists mostly of secondary C—H bonds the insertion reactions should proceed quite randomly on the surface.   This

would be true to a lesser extent for polypropylene and polystyrene. For nylon, polymethylmethacrylate, and cellulose acetate it is likely that selectivity is shown in the order in which the surface reactions occur. The final surface formed, however, should be independent of the relative rates.

Conclusions

Difluorocarbene has been shown to irreversibly modify the surfaces of polymers as determined by wettability measurements. The exact nature of the interaction between the carbene and the surface is not known; however, contrary to oxidative treatments which tend to penetrate and degrade the polymer, the modification is evidently limited to the surface. Contrary to a graft modification of the surface, no build-up of material occurs on the surface. The absence of infrared ATR results also tends to establish the monomolecular-like character of the modified surface.

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