

## Modification of Polyethylene Surfaces with Carboxy Substituted Carbenes and Nitrenes

A. JEAN OSTERAAS,\* and DOUGLAS A. OLSEN,† *Research Center, Ashland Chemical Co., Minneapolis, Minnesota 55420*

### Synopsis

Carboxycarbene, carboxynitrene, and nitrene generated respectively by the pyrolysis of ethyl diazoacetate, ethyl azidoformate, chloramine and sodium hydroxyl amine-*o*-sulfonate are shown to irreversibly modify the surface of polyethylene as shown by wettability measurements. The nature of the modification is not fully understood; however, insertion of the carbene or nitrene into a carbon-hydrogen bond appears likely. The modified surfaces thus formed are shown to undergo several classical organic reactions as again determined by wettability measurements.

### INTRODUCTION

Electron deficient moieties such as carbenes are well known for their ability to insert into C-H bonds of simple compounds.<sup>1</sup> Nitrenes have also been shown to react in a similar manner.<sup>2</sup> It has also been reported that carbenes and nitrenes react with polymer surfaces.<sup>3</sup> In this latter study Osteraas and Olsen suggested, as a result of comparing critical surface tension ( $\gamma_c$ ) values for polymer surfaces exposed to a variety of substituted electron deficient moieties with known polymer prototypes, that pendent groups apparently are incorporated onto a polymer surface. Difluorocarbene generated by the pyrolysis of sodium monochlorodifluoroacetate has also been shown to irreversibly modify the surfaces of polymers and fibers.<sup>4</sup> By increasing the exposure time of several polymer types to difluorocarbene vapors, the critical surface tension values progressively decreased and ultimately approached the critical surface tension values of partially fluorinated polyethylenes, i.e., 18-25 dynes/cm. The monomolecular-like character of the difluorocarbene modified surface was suggested by the absence of infrared bands due to C-F bonds in attenuated total reflection measurements.

In the present study surface modification by three other electron deficient moieties is reported. These are carboxycarbene (:CHCOOEt), nitrene (:NH) and carboxynitrene (:NCOOEt). The nature of the interaction

\* Present address: Research Division, Gould-National Batteries, Inc., Minneapolis, Minn. 55414.

† Present address: Applied Science Division, Litton Systems, Inc., Minneapolis, Minn. 55427.

between the electron deficient moiety and the polymer surface is unknown; however, the data suggests that electron deficient moieties are inserted at the polymer surface, thereby modifying the surface by incorporating new pendent groups. It should also be noted that we have used the carbene (and nitrene) system of nomenclature here because of its general acceptance in the chemical literature.

### Experimental Procedure

**Preparation of Precursors.** Ethyl diazoacetate was prepared according to the method of Womack and Nelson.<sup>5</sup> Monochloramine was prepared according to the method of Coleman and Johnson.<sup>6</sup> Hydroxylamine-*o*-sulfonic acid was obtained commercially (Eastman). Since the commercial product assayed 99.1%, it was used without further purification. Sodium hydroxylamine-*o*-sulfonate was prepared by neutralizing  $\text{NH}_2\text{OSO}_3\text{H}$  with an aqueous solution of  $\text{NaHCO}_3$  to pH 7 and then was air dried. Ethylazidoformate was prepared according to the method of Lwowski and Mattingly.<sup>7</sup>

**Substrate.** The polyethylene sheets used in this study were of a commercially available grade (Cadillac Plastic and Chemical Co.). Wettability measurements on cleaned samples of the polyethylene gave the expected value of 31 dynes/cm,<sup>8</sup> thus establishing that the polyethylene surface was free from contamination or surface oxidation. The polyethylene sheets were cleaned by washing in a detergent (Concentrate RBS-25, R. Borghgraef, Brussels, Belgium) followed by copious rinsing first in tap water and then in distilled water. After drying the samples were immediately exposed to pyrolysis vapors.

**Pyrolysis Equipment.** In its most simplified form, the pyrolysis chamber consisted of a Petri dish on a hot plate. Other chambers of basically the same design and of both stainless steel and glass construction were used with no detectable difference in the pyrolysis. In the following type A refers to a pyrolysis chamber 9 cm in diameter and of glass construction; type B refers to a stainless steel chamber 2.5 cm in diameter. A ceramic insulation separated the polymer from the hot sides of a type A pyrolysis chamber, whereas the polymer was placed directly over a type B pyrolysis chamber.

**Generation of Electron Deficient Moieties.** Carbethoxycarbene was generated by heating 0.5 ml ethyl diazoacetate in a type B pyrolysis chamber at various temperatures with the following results: detonation occurred at 400°C and over; pyrolysis or visible decomposition occurred between 240 and 350°C; evaporation occurred at temperatures below 225°C. Samples of clean low density polyethylene were exposed to the pyrolysis vapors of ethyl diazoacetate at 340 and 214°C. The exposure time of substrate to pyrolysis vapors was one to two minutes.

Nitrene was generated by heating 0.5 ml monochloramine in a pyrolysis chamber type B at 385°C. Exposure time of substrate to pyrolysis vapors was approximately one minute. Nitrene was also generated during pyroly-

sis of 1 gm of hydroxylamine-*o*-sulfonic acid or 1 gm of its sodium salt in a pyrolysis chamber type A at 250° to 350°C. Exposure time of substrate to pyrolysis vapors was approximately one minute.

Carbathoxynitrene was generated by heating 0.5 ml ethylazidoformate in a pyrolysis chamber type B at 325°C. Exposure time of substrate to pyrolysis vapors was approximately one to two minutes.

**Surface Reactions.** Samples of polyethylene exposed to carbethoxycarbene generated during the pyrolysis of ethyl diazoacetate at 425°C for one minute were subjected to several classical organic reactions and the resulting critical surface tension value ( $\gamma_c$ ) measured. Since the surface was immobile, the reaction conditions were more stringent than the classical analogs. The following reaction conditions were used: for neutralization reactions, 0.5 *N* KOH at 100°C for eight hours; for chlorination, thionyl chloride (SOCl<sub>2</sub>) at 20°C for ten minutes; for fluorination, 2,2,2-trifluoroethanol at 20°C for 30 min.

Attempts were made to quaternize samples of polyethylene exposed to nitrene by reacting the polymer surface with methylene iodide in a slurry of ethanol and CaCO<sub>3</sub> at 20°C for 67 hr.

**Wettability Measurements.** 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.<sup>9</sup> The wetting liquids were reagent grade *o*-xylene, benzaldehyde, ethylene glycol, formamide, and glycerol; freshly distilled aniline; and distilled water. The handbook values for the surface tension of these liquids were verified by capillary rise measurements.

For each drop of wetting liquid, three or 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.

## Results and Discussion

After exposure to carbethoxycarbene, the critical surface tension values ( $\gamma_c$ ) of polyethylene increased from 31 dynes/cm to about 40 dynes/cm. If carbethoxycarbene was inserted into the C-H bond at the surface of polyethylene then the new surface with a pendant ester group should be similar to the surface of polymethylmethacrylate which also has a pendant ester group. Critical surface tension values suggest this to be the case since the  $\gamma_c$  of polyethylene exposed to carbethoxycarbene was 40 dynes/cm while the value observed for polymethylmethacrylate is 41 dynes/cm.<sup>8</sup>

Another view of the foregoing is that the carbethoxycarbene may have dimerized to a maleic or fumaric acid which then further polymerized on the polyethylene surface.

To further elucidate the nature of the carbethoxycarbene-polyethylene surface samples of polyethylene exposed to carbethoxycarbene were subjected to a reaction scheme of classical organic reactions. Upon completion of each reaction in the reaction scheme,  $\gamma_c$  values were determined. The

reactions, products and  $\gamma_c$  values are as follows (with the reaction conditions given above):

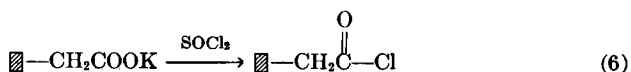
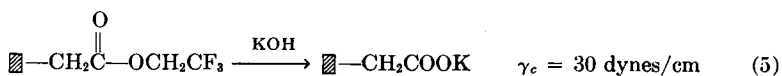
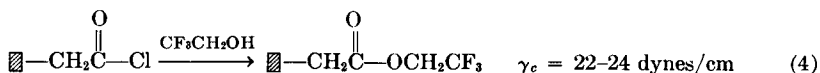
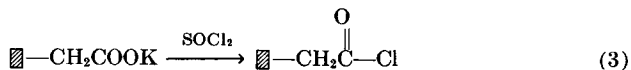
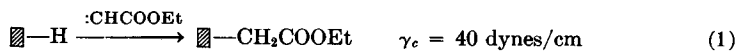


Figure 1 shows wettability measurements for eq. (1), (2), and (4). Each of these equations produces a surface with a lower critical surface tension value than the preceding equation. Considering the polar nature of the carboxylic acid surface of eq. (2) the  $\gamma_c$  value of 30 dynes/cm seems rather low. Repeated measurements, however, gave the same  $\gamma_c$  value. Because of the reactive nature of the acid chloride surface of eq. (3) no  $\gamma_c$  value was obtained. In eq. (4) 2,2,2-trifluoroethanol produces a fluorinated surface

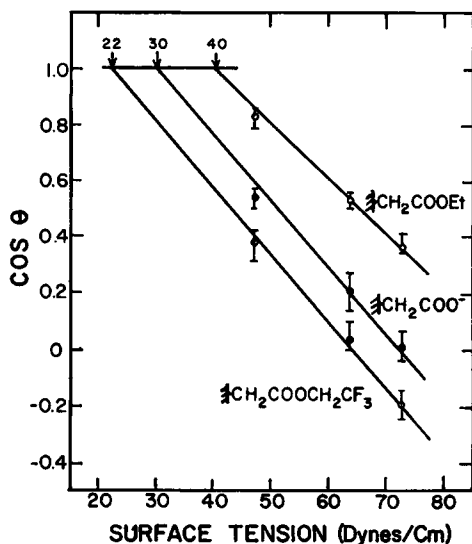
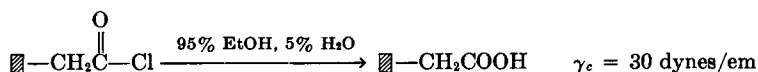


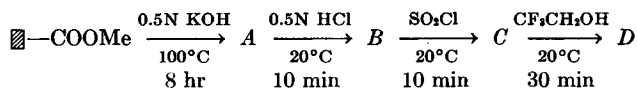
Fig. 1. Wettabilities at 20°C of polyethylene exposed first to carbethoxycarbene followed by other surface reactions.

which, as expected, has a very low  $\gamma_c$  value that approaches that of polytetrafluoroethylene, i.e., 22–24 dynes/cm compared to 18 dynes/cm for polytetrafluoroethylene. Eq. (5) through (7) regenerate the original carbethoxy surface and also produce higher  $\gamma_c$  values for each equation. The  $\gamma_c$  value for the regenerated carbethoxy surface [eq. (7)] is 37 dynes/cm rather than the expected 40 dynes/cm of eq. (1). The probable reason for this is that eq. (7) was found to be very sensitive to water and thus some carboxylic acid surface was also present, thereby giving a low  $\gamma_c$  value. When small amounts of water were known to be present, the  $\gamma_c$  value of the reacted surface was consistently 30 dynes/cm, thus suggesting that a carboxylic acid surface was indeed being formed, viz.



Untreated polyethylene subjected to reactions (2) through (7) showed no change in  $\gamma_c$ .

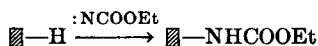
Since polymethylmethacrylate has a similar surface structure to that of polyethylene exposed to carbethoxycarbene, the following reaction scheme was attempted:



The values of the  $\gamma_c$ 's of products *A* and *B* were 39 dynes/cm as was the initial value of the polymethylmethacrylate ( $\gamma_c = 41$  dynes/cm is expected only for smooth surfaces). These data plus the large amount of stringy fiber generated on the polymer surface at *D* indicate that hydrolysis of the surface resulted in a layer by layer removal of polymethylmethacrylate molecules rather than a surface reaction of the type observed above for the carbethoxycarbene modified polyethylene surface.

Thus if only surface polymerization of the carbethoxycarbene had taken place on the polyethylene substrate, results similar to those for polymethylmethacrylate should have been observed. Instead the ability of the carbethoxycarbene treated substrate to withstand the strenuous conditions of the reaction cycle constitutes good evidence that carbethoxycarbene does insert into the C-H bonds of the polyethylene surface or, at least, reacts with unsaturation in the polymer surface.

Proceeding next to the treatment of polyethylene surfaces with carbethoxynitrene it was expected that results similar to above would be obtained. This was indeed the case since upon exposure to the pyrolysis vapors of ethylazidoformate, the  $\gamma_c$  value of polyethylene increased to 39 dynes/cm (Fig. 2) which is the same value as found for carbethoxycarbene treated polyethylene. Thus



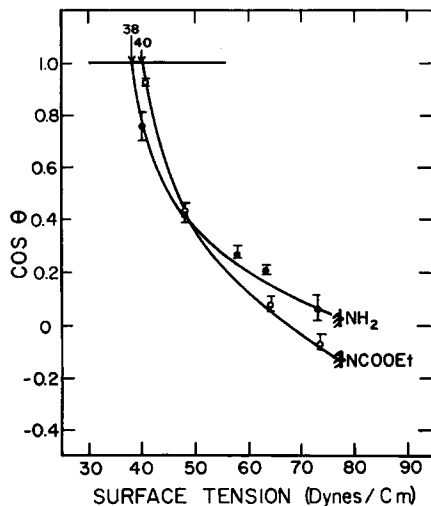


Fig. 2. Wettabilities at 20°C of polyethylene exposed first to carbethoxynitrene followed by hydrolysis.

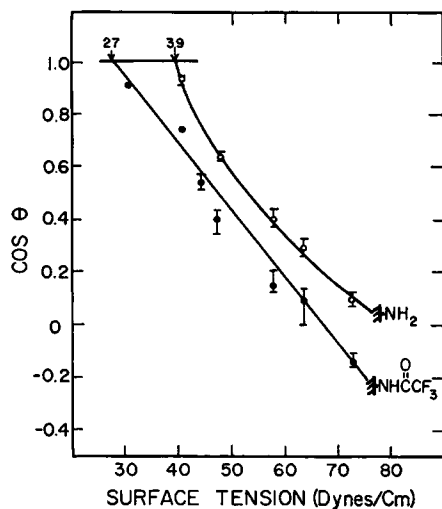
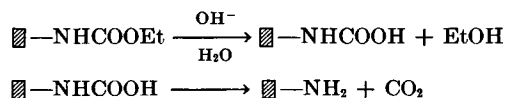


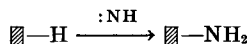
Fig. 3. Wettabilities at 20°C of polyethylene exposed first to nitrene followed by reaction with trifluoroacetic anhydride.

Hydrolysis causes little change in the  $\gamma_c$  value, 38 dynes/cm as shown in Figure 2; however, this is reasonable since upon hydrolysis an unstable carbamic acid is formed which gives an amine surface, viz.

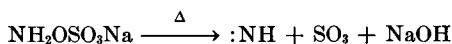


As will be shown below amine surfaces have a  $\gamma_c$  value of 39 dynes/cm.

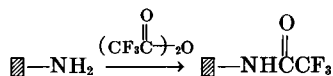
The  $\gamma_c$  value of polyethylene treated by the pyrolysis vapors of chloramine increased from 31 dynes/cm, the  $\gamma_c$  of untreated polyethylene, to 39 dynes/cm (Fig. 3). This value is also in agreement with that of the previous section. Thus:



Attempts to quaternize the surface were not successful. However, possible undesirable side reactions could occur during the pyrolysis of  $\text{NH}_2\text{Cl}$  including the formation of  $\text{NCl}_3$ ,  $\text{NHCl}_2$  and  $\text{Cl}^+$ . Since  $\text{NCl}_3$  and  $\text{Cl}^+$  are powerful oxidizing agents, the resulting change in  $\gamma_c$  could be the result of oxidation instead of nitrene insertion. Nitrene formation also occurs upon pyrolysis of hydroxyl amine-*o*-sulfonic acid or its sodium salt. Presumably, the following reaction for the salt takes place upon pyrolysis:



While  $\text{SO}_3$  is an oxidizing agent its formation should be somewhat inhibited, especially in the case of the salt. As with chloramine, quaternization was not possible. However, the nitrene treated surface did react with trifluoroacetic anhydride, giving a low  $\gamma_c$  value (27 dynes/cm) shown in Figure 3, in a manner similar to the carbethoxycarbene study. Thus:



The fact that this reaction proceeds and quaternization does not suggests that the nitrene inserts in a fairly close packed manner on the polyethylene surface so that steric effects prevent quaternization but do not inhibit reaction with trifluoroacetic anhydride.

### Conclusions

Carbethoxycarbene, carbethoxynitrene, and nitrene have been shown to irreversibly modify the surface of polyethylene. The ability of the modified surfaces to undergo organic reactions with rather strenuous conditions indicates that bonding between the carbene (or nitrene) and the polyethylene surface has indeed taken place.

This paper is based on work conducted at the Research Center, Ashland Chemical Co., Minneapolis, Minnesota. This paper is published with the approval of Ashland Chemical Co. Notice is hereby given that portions of this paper are covered by U. S. patents and patent applications of Ashland Chemical Co.

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Received December 11, 1968