

Gas Transport in Partially Fluorinated Low-Density Polyethylene

C. L. KIPLINGER, D. F. PERSICO, R. J. LAGOW, and D. R. PAUL,
*Departments of Chemistry and Chemical Engineering, and Center for
Polymer Research, University of Texas, Austin, Texas 78712*

Synopsis

Low-density polyethylene film was subjected to direct fluorination on one surface by exposure to a dilute fluorine gas stream for various periods of time. Various analyses indicate partial fluorination of a thin surface layer. The permeability coefficients for He, CO₂, and CH₄ were measured at 35°C. The permeability of He was not changed by fluorination; whereas, values for CO₂ and CH₄ were decreased by as much as two orders of magnitude. The selectivity of transport for gas pairs of different molecular size was greatly improved, suggesting applications of this technique for membrane separation processes.

INTRODUCTION

The control of permeation rates of small molecules through polymers has been of interest for some time because of the need for better barrier materials in packaging applications. *In situ* fluorination processes for polymers such as polyethylene¹⁻⁴ have been found to be effective for reducing the permeation of volatile liquids from fabricated articles such as bottles; although little attention seems to have been paid to the effect of such reactive treatments on gas permeation rates. With the advent of commercially viable membrane processes for gas separations, there is additional incentive to examine approaches, like fluorination, which may advantageously affect the *relative* rates at which one gas species permeates a polymer relative to another gas species.⁵ Important separations include the gas pairs CO₂/CH₄ and He/CH₄.⁶ Membrane materials should exhibit a high selectivity of permeation for obtaining purity while retaining high permeation rates for productivity. Usually there is a tradeoff in selectivity versus productivity when selecting membrane materials.

This paper reports on an exploratory effort to learn whether *in situ* fluorination of a polymer film might offer a useful approach to the control of gas permeation rates with particular reference to membrane separation applications. A simple polymer, low-density polyethylene, was selected for this study. Table I lists some literature data for the permeability of the gases He, CO₂, and CH₄ in low-density polyethylene and polymers which have been formed from ethylenic monomers with systematic replacement of hydrogen by fluorine atoms. Based on these limited data, it is clear that complete substitution with fluorine [i.e., poly(tetrafluoroethylene)] does not decrease the rate of gas permeation relative to polyethylene nor dramatically increase selectivity as seen by the ratios of permeabilities computed from these data and listed in Table II. However, partial fluorine substitution

TABLE I
Literature Values of Gas Permeabilities at 35°C

Polymer	Gas	$P \times 10^{10}$
		$\text{cm}^3 \text{ (STP) cm/cm}^2 \text{ s cm Hg}$
Low-density polyethylene ^a (den. = 0.914 g/cm ³)	He	7.7
	CO ₂	21.0
	CH ₄	5.3
Poly(vinyl fluoride) ^b	He	1.3
	CO ₂	0.12
	CH ₄	0.010
Poly(vinylidene fluoride) ^c	He	1.6
	CO ₂	0.63
	CH ₄	0.020
Poly(tetrafluoroethylene) ^b	He	32.5
	CO ₂	14.0
	CH ₄	not available

^a From Ref. 13.

^b From Ref. 14.

^c From Ref. 15.

does both. The data in these tables are useful for comparison with the results reported here.

EXPERIMENTAL

The polyethylene used in these experiments was commercially obtained in the form of film approximately 1.2 mil thick and had a density of 0.92 g/cm³.

Fluorination by plasma techniques have been described in the literature,⁴ but direct fluorination of the polymer using elemental fluorine has certain advantages of simplicity and of scale-up, and therefore, was the approach used here. However, the extremely rapid rate of fluorine reaction with hydrocarbon polymers and the very exothermic nature of the reaction dictate that steps be taken to dissipate or moderate the energy release to avoid structural degradation of the polymer. Lagow and Margrave^{4,8} and Persico et al.⁹ have developed a technique for accomplishing this, and the current work utilized a reactor and reaction protocol like those described previously.

The early stages of direct fluorination are the most critical, and the initial fluorine concentration in the gas phase must be kept low. Molecular processes such as rotational or vibrational relaxations need time to distribute the reaction energy throughout the system, and it is necessary to minimize the probability of simultaneous reaction of adjacent sites to avoid energy

TABLE II
Separation Factors Estimated from Data in Table I

Polymer	$P_{\text{He}}/P_{\text{CH}_4}$	$P_{\text{CO}_2}/P_{\text{CH}_4}$
Low-density polyethylene	1.45	3.96
Poly(vinyl fluoride)	130.0	12.0
Poly(vinylidene fluoride)	2.5	31.5
Poly(tetrafluoroethylene)	2.3	—

localization that would break chain bonds. In the present work, samples of polyethylene measuring approximately 15×15 cm were sealed to aluminum foil around the edges so that only the top surface would be exposed to fluorine when placed in the reaction chamber. After installation in the reactor, the chamber was purged by helium flow for one to two hours to remove oxygen, water, and other impurities. Next, a highly diluted flow of fluorine (2% in helium) was initiated and maintained at a total flow rate of $51 \text{ cm}^3/\text{min}$. Such high dilutions and flow rates are necessary to avoid perfluorination of the surface of the film. The reaction was carried out for various periods of time at 25 to 30°C .

Gas permeability coefficients of the resulting film were measured at 35°C using techniques described previously.¹⁰

FILM CHARACTERIZATION

As a rough indication of the changes occurring during the fluorination process, the change in mass of the film during this treatment was monitored with the results shown in Figure 1. The samples gained mass as would be expected for a simple replacement of hydrogen by fluorine with the amount of change leveling off after about 12 hours of fluorination under these reaction conditions. However, such a simple interpretation of these results is not fully consistent with other characterization information described later.

Transmission infrared (IR) spectroscopy of the treated films revealed small changes in the spectra relative to the untreated film in the $8\text{--}11 \mu\text{m}$ region. Comparison to published spectra for the fluorinated polymers listed in Table I¹¹ suggests relatively small total amounts of fluorine were incorporated into the film after 24 hours of treatment.¹²

Thermal properties of untreated and treated film were compared using differential scanning calorimetry (DSC). The melting point and heat of fusion of the untreated film were found to be 113°C and 28 cal/g , respectively. These values were unchanged within the limits of detection after the maximum fluorination time used (*viz.*, 24 hours). Similarly, the glass

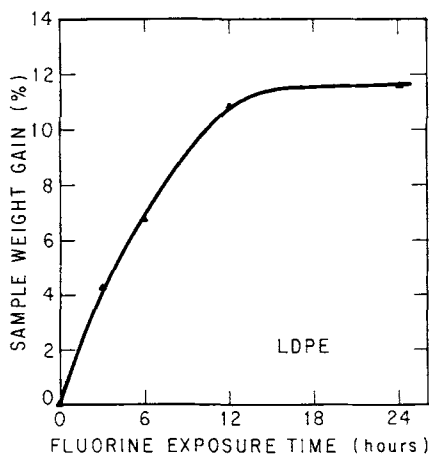


Fig. 1. Weight gain by low-density polyethylene during fluorination process.

transition region of the polyethylene thermogram did not show any discernible changes after fluorination.

Stress-strain diagrams were generated on a table model Instron at 0.5 in./min for samples measuring 3.0 in. long by 0.81 in. wide. The results are shown in Figure 2. The fluorination treatment apparently causes a slight alteration in the region of the yield point and progressively decreases the elongation at break. Physically, there was little difference in appearance and feel following fluorination, and Figure 2 confirms surprisingly little alteration in overall mechanical behavior.

Samples of film treated for 24 hours were submitted to two separate laboratories for bulk elemental analysis of carbon, hydrogen, and fluorine with the results shown in Table III. The two analyses agree reasonably well and indicate relatively little fluorine incorporation into the sample consistent with the IR, DSC, and mechanical property data but at some variance with the mass change results shown in Figure 1. These analyses indicate that carbon, hydrogen, and fluorine account for nearly all of the mass of these bulk samples.

Electron spectroscopy for chemical analysis (ESCA), was employed for more extensive chemical characterization. This technique provides an analysis of the sample surface with penetration of perhaps no more than 5 nm. The spectrum for untreated low-density polyethylene is shown in Figure 3. The principal feature is the carbon peak at 289 eV; however, an oxygen peak appears at 540 eV and it is estimated that there are about 12 oxygen atoms per 100 carbon atoms on the surface of this film. Evidently this oxygen stems from surface oxidation of the polyethylene since the high vacuum in the ESCA chamber would have removed any dissolved oxygen. The carbon peak is shown in more detail in Figure 4. The spectrum of a low-density polyethylene surface exposed to fluorine is shown in Figure 5 with the carbon peak shown in more detail in Figure 6. The carbon peak is shifted and broadened relative to that of the untreated sample shown in Figure 4. Fluorine peaks are observed around 695 eV. Peak analysis indicates 70

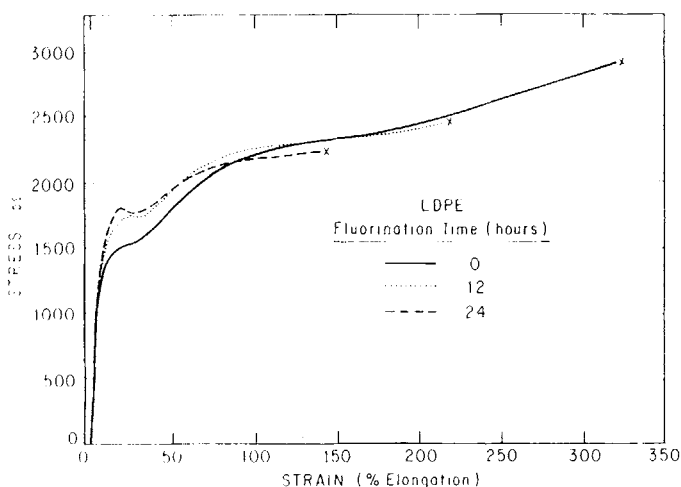


Fig. 2. Stress-strain diagram for fluorinated low-density polyethylene film.

TABLE III
Bulk Elemental Analysis of Low-Density Polyethylene Film Fluorinated for 24 Hours

	Laboratory A	Laboratory B
% Carbon	84.98%	84.64%
% Hydrogen	14.35	13.80
% Fluorine	0.66	1.39
Total	99.99	99.83

fluorine atoms per 100 carbon atoms on this surface. The bottom surface (not exposed to fluorine) was analyzed and showed no evidence of fluorine. Figure 7 summarizes the amount of fluorine found on the top surface as a function of exposure time. Table IV gives the fluorine and oxygen levels found on both the top and bottom surfaces. As indicated, no fluorine was detected on the bottom surface except in the case of the 24-hour sample which showed essentially the same level as the top surface. Evidence indicated that this occurred because of failure of the seal around the edge of the film permitting fluorine gas to contact this surface directly. Subsequent testing confirmed this conclusion.¹² The observed oxygen level tended to increase with treatment time which may reflect some unknown source of oxygen contamination in the fluorination process or a susceptibility of treated samples to react with atmospheric oxygen after removal from the reactor.

The evidence given here leads to the conclusion that incorporation of fluorine into the polyethylene structure is limited primarily to the outermost layer directly exposed to fluorine with little fluorination of the bulk of the material (i.e., there is a steep fluorination gradient restricted to the surface region of the film with the interior of the film unaffected as indicated

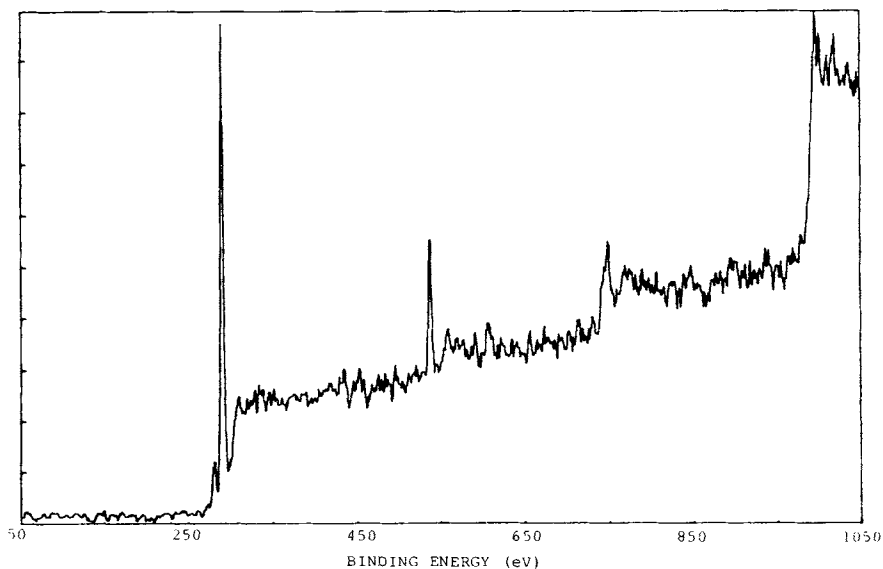


Fig. 3. ESCA spectrum for untreated low-density polyethylene.

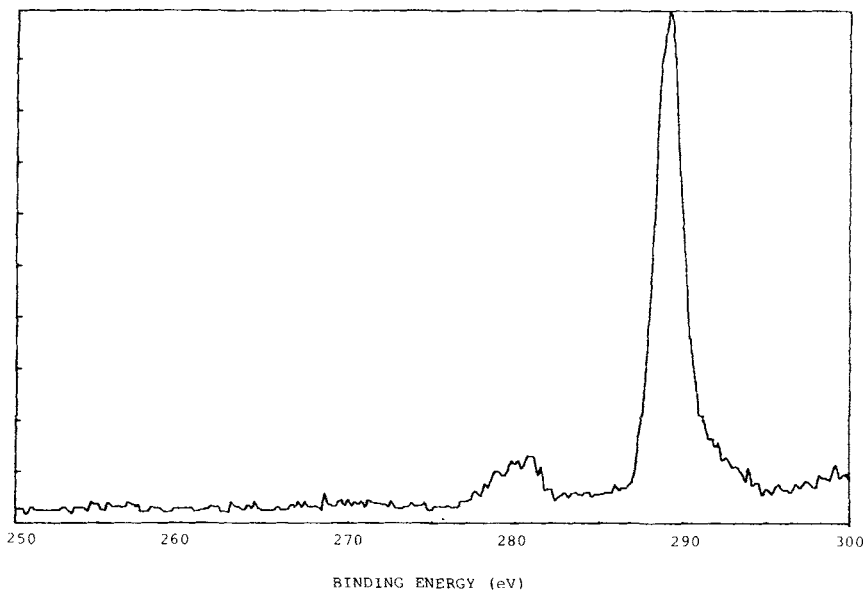


Fig. 4. Carbon spectrum of Fig. 3.

by bulk elemental analysis, IR, and DSC). The surface reaction could easily account for the change in mechanical properties shown in Figure 2. The origin of the oxygen observed by ESCA is unclear, but based on the evidence shown it too is primarily limited to the film surface. The majority of the fluorination obtained is accomplished within the first few hours with exposure longer than 12 hours producing little further effect. In this regard, there is general qualitative similarity between the results in Figures 1 and 7.

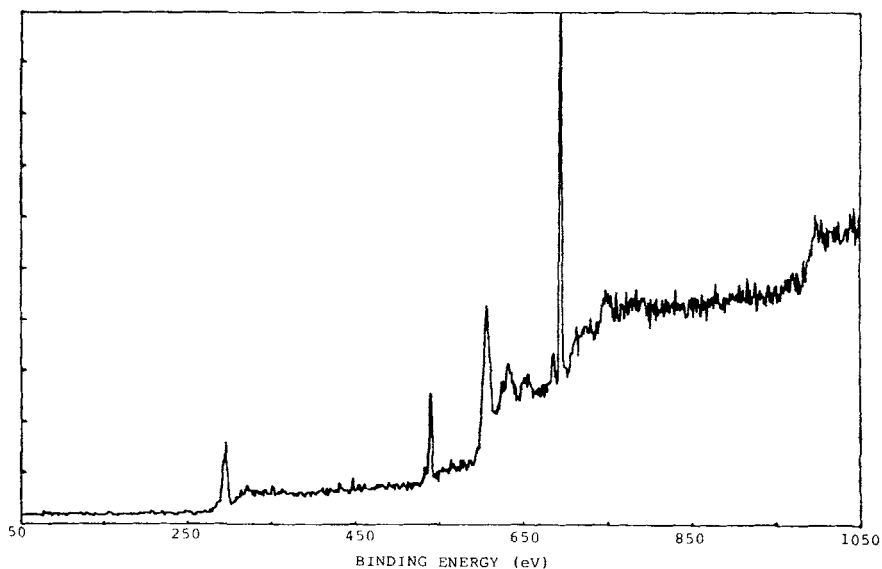


Fig. 5. ESCA spectrum of low-density polyethylene after 12 hours of fluorination (top surface).

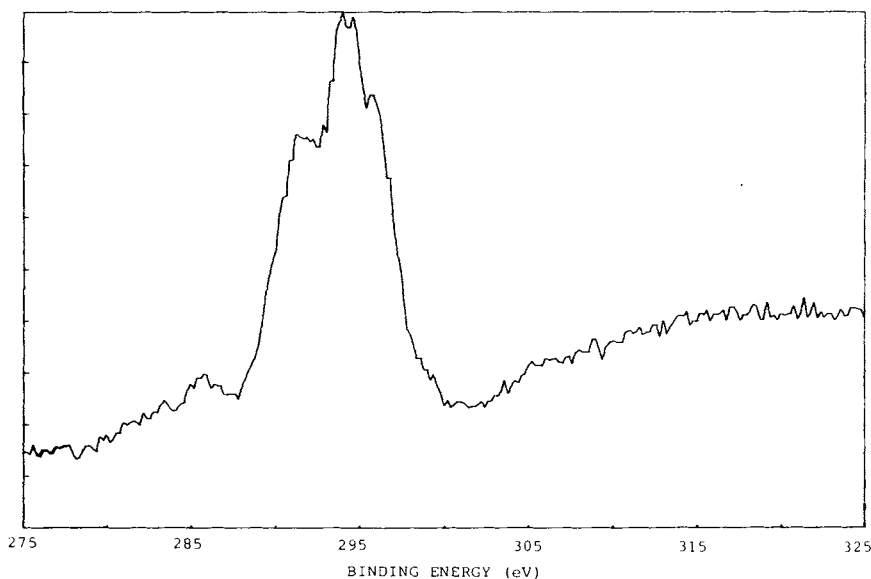


Fig. 6. Carbon spectrum of Fig. 5.

GAS PERMEATION RESULTS

Helium, CO_2 and CH_4 permeabilities of these films were measured at 35°C , using an upstream driving pressure of approximately one atmosphere. The results are shown in Figure 8 as a function of fluorine treatment time. Permeabilities of the untreated film agree well with those for low-density polyethylene from the literature (see Table I). The helium permeability is essentially unchanged by fluorination; whereas, the permeabilities to CO_2 and CH_4 drop very dramatically and level off after about 12 hours of treatment more or less in parallel with the fluorine levels noted on the surface

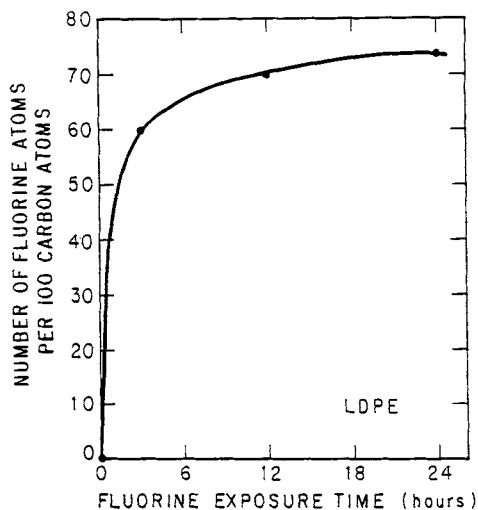


Fig. 7. Surface concentration of fluorine as a function of exposure time as computed from ESCA data.

TABLE IV
Surface Analysis for Fluorine and Oxygen Expressed as Number of Atoms per 100 Carbon Atoms Obtained by ESCA

Exposure time	Top		Bottom	
	F	O	F	O
0	0	12	0	12
3	60	30	0	6
12	70	29	0	12
24	77	20	77	18

(see Fig. 7). The drop in CH_4 permeability is roughly two orders of magnitude.

These dramatic changes in permeation characteristics caused by fluorination have an equally remarkable effect on the selectivity characteristics as may be estimated by ratios of the various pure gas permeability coefficients. The latter approximate the separation factors of interest in membrane applications. The corresponding separation factors for the gas pairs He/CH_4 , CO_2/CH_4 , and He/CO_2 computed from the data in Figure 8 are plotted versus fluorine treatment time in Figure 9. The separation factor for He relative to CH_4 is slightly less than 2 for low-density polyethylene and rises to about 150 after fluorination of 12 or more hours. The separation factor for CO_2 relative to CH_4 increases from less than 4 to about 10. Interestingly, CO_2 permeates low-density polyethylene more rapidly than does He; however, upon sufficient fluorination this situation is dramatically reversed.

While not tested, one might expect hydrogen to behave similarly to He since these molecules generally have about the same permeability coefficients for most polymers.⁵

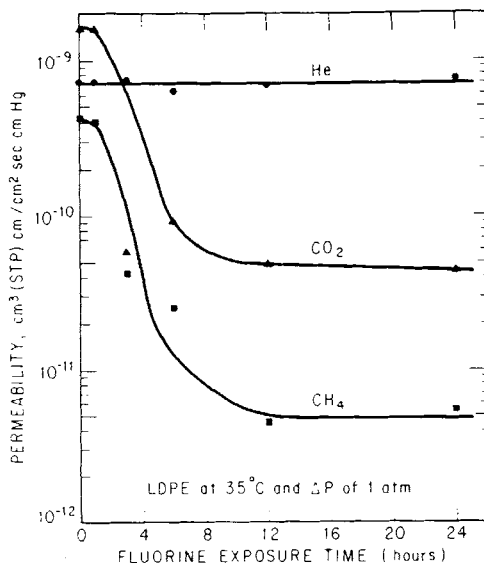


Fig. 8. Permeability of He, CO_2 , and CH_4 through low-density polyethylene after various times of fluorine treatment.

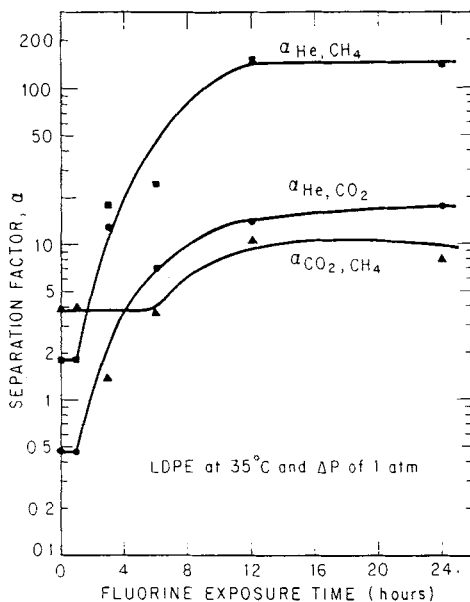


Fig. 9. Separation factors estimated from permeability data in Fig. 8.

As mentioned earlier, we believe this process fluorinates only the very outer surface of the polyethylene film based on surface versus bulk analyses. Therefore, the treated film might be viewed as a laminate³ of which the principal part is unaffected low-density polyethylene. The reacted surface layer may be composed of carbon atoms with the structures CH_2 , CHF , CF_2 or crosslinks. Adjacent carbon atoms may have different structures. An assembly of CH_2 units is nonpolar just as a complete assembly of CF_2 units, and as seen in Table I both result in rather high permeability coefficients for all gases (crystallinity is a physical factor which ought to be considered) with relatively poor selectivity of transport. On the other hand, repetition of $-\text{CH}_2\text{CHF}-$ and $-\text{CH}_2\text{CF}_2-$ units as in the case of poly(vinyl fluoride) and poly(vinylidene fluoride), respectively, are polar structures which result in lower permeabilities to all gases and better selectivity of transport as seen in Tables I and II. Based on this, we must conclude that the fluorination process used here does not produce a surface layer like poly(tetrafluoroethylene) but must result in a polar, partially substituted structure. The separation factors for He/CH_4 and CO_2/CH_4 of the fluorinated samples described here are rather similar to those of poly(vinyl fluoride), see Table II, but the overall permeability to He, CO_2 , and CH_4 is about five times larger than that of poly(vinyl fluoride). Since the fluorinated surface layer is thought to be quite thin and the relatively thick underlayer of polyethylene contributes to the permeation behavior,³ we conclude that the fluorinated layer must have remarkable permeation characteristics, such as very high selectivity, which apparently result from chemical structures that cannot be duplicated by polymers made from fluorinated monomers and are, therefore, not available for comparison. An example of such a structure would be a $-\text{CHFCHF}-$ unit. Cross-linked units may also be a factor.

SUMMARY

These preliminary experiments reveal that the current fluorination process creates a thin layer of partially fluorinated material on the surface of low-density polyethylene film. This dramatically reduces the overall permeability to CO₂ and CH₄ while not affecting the permeation rate of He. Thus, this treatment should be of value for improving the size selectivity of gas-separation membranes.

Clearly, further work is indicated especially with other polymers more appropriate than polyethylene for membrane applications. The process needs to be optimized and defined. Results not reported here¹² indicate that some important process parameters were not fully controlled, since apparently identical conditions sometimes led to different results. The data given here were obtained for samples made during one series of experiments where little change in the process occurred. Further characterization of the fluorinated product would be most helpful.

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