

Studies of Polymer Electrets. I. Factors Governing the Stabilities of Homoelectrets Obtained from Poly(1-olefin)s

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Synopsis

Various poly(1-olefin)s have been studied as homoelectrets and their stabilities under different environmental conditions have been determined. It has been found that the stabilities of the homoelectrets, prepared from these polymers, depend on their volume resistivities, degrees of crystallinity, and the temperatures at which the crystalline domains of these polymers undergo transitional motions. Excellent stabilities have been exhibited by the homoelectrets prepared from poly(3-methyl-1-butene), poly(4-methyl-1-pentene) and other similar isotactic poly(1-olefin)s with pendant branched side chains. It is postulated that the charged particles are trapped at the crystalline/amorphous interfaces in these polymers and the bulky alkyl substituents stabilize the charged particles by raising the transition temperatures of these polymers as well as by providing some additional chemical interaction sites.

INTRODUCTION

The first organic electret was prepared from carnauba wax, a mixture of long-chain fatty esters,¹ by the application of an intense electric field while the material was heated and successively cooled to room temperature. Very soon, it was found² that whether hetero- or homocharged electrets are formed depends on the nature of the net charge carried by an electret surface in relation to that of the forming electrode. It was also noted that heterocharging was the result of internal dipole orientation and migration of free charges inside the material, while homocharging was caused by charge injection from the ionized air space between the electrode and the electret surface.³

Although dipole orientation by strong electric fields can be very important for the pyro- and piezoelectric effects observed in organic dielectrics,⁴ it has not been found significant for those applications where stable external electric fields are needed.⁵ For these kinds of applications, homoelectrets are preferred because of the advantages that they offer, especially, their stabilities under humid atmospheric conditions.⁶

Among organic dielectric materials, only nonpolar polymers with certain structural features have been found to be the best materials for stable homoelectrets.⁷ The effect of humidity on polar polymer electrets is quite deleterious, thus rendering them useless for practical applications.

Polar polymers absorb much larger amounts of water than nonpolar polymers due to the presence of dipolar groups. Interactions between water, polymer molecules, and charged particles easily cause charge neutralization and transport in polar polymer homoelectrets. These interactions might arise for the following reasons:

- (a) Polar polymers such as polyesters, polycarbonates, polyamides, polyure-

thanes, etc., are invariably contaminated with the starting monomers or intermediate products that contain carboxylic acid, alcohol, amino, and other functional groups as well as the catalysts employed during condensation polymerization. These can increase electrical conductivity by "ionic transport" through absorbed water that generally increases the dielectric constant of the medium.⁸

(b) Water itself can dissociate into H^+ (or H_3O^+ , etc.) and OH^- ions and, thereby, provide as an important source of charge carriers, particularly at low concentration of moisture. For example, resistivity of pure *n*-hexane has been found to decrease to 10^{14} from 10^{19} ohm-cm in presence of 18 ppm of water by weight.⁹

(c) An increase in dielectric constant due to water absorption can affect the creation of various charge carriers including mobile electrons. The following equation is obeyed in some polar polymers, regardless of the nature of the carriers^{10,11}

$$\log \sigma = Cm + D, \quad \text{where } \sigma = \text{electrical conductivity}$$

m = amount of moisture absorbed by the polymer, C and D constants (1)

(d) Beside increasing electrical conductivity, developing interfacial polarizations and generating mobile charge carriers, water has been found to have plasticizing effects on certain polar polymers, thus decreasing the transition temperatures of these polymers.^{12,13}

At the present moment, the best material for the preparation of homoelectrets is DuPont's Teflon—FEP, a nonpolar polymer, containing fluorocarbon structure. Polyolefin materials are structurally analogous to the fluorocarbon polymers, except that the polyolefins contain carbon-hydrogen rather than carbon-fluorine units. The polyolefins therefore appear to be a useful class of material for a careful and systematic study to find out what determines charge stability in their homoelectrets.

EXPERIMENTAL

Materials

The commercial polyolefins studied are listed in Table I.

TABLE I
Commercial Polymers Used

Polymer	Source	Trade name	Density/other feature
Polyethylene	Johnston Plastics, Toronto	—	0.960, extruded film
Polyethylene	Celanese Company, U.S.A.	Fortiflex A-60	0.960
Polyethylene	Celanese Company, U.S.A.	Fortiflex B-50	0.950
Polyethylene	Celanese Company, U.S.A.	Fortiflex B-45	0.945
Polypropylene	Hercules Inc., U.S.A.	Profax	Isotactic polymer
Poly(1-butene)	Witco Chem. Corp., U.S.A.	Polybutylene BP131	Isotactic polymer
Poly(4-methyl- 1-pentene)	Imperial Chemical Industries (England) + Mitsui Petrochemicals (Japan)	TPX	Isotactic polymer

Other polymers used in this work were poly(1-hexadecene), poly(3-methyl-1-butene), poly(4-methyl-1-pentene) and poly(3-cyclohexyl-1-propene). They were prepared in the laboratory in the following manner.

In a 500-mL three-necked round bottom flask fitted with a nitrogen inlet, reflux condenser, and a Teflon-coated magnetic stirring bar was placed purified petroleum ether (35 mL) of boiling point 80–120°C. To this was added a solution of diethylaluminum chloride (5 mL) in petroleum ether (80 mL) and a suspension of α -TiCl₃ [Grade AA, 5 mL, prepared by suspending 10 g α -TiCl₃ in 100 mL petroleum ether]. After the mixture had been stirred at room temperature for 15 min, the resultant catalyst was ready for use.

The required 1-olefin monomer (20 mL) was added to the above catalyst suspension and polymerization was allowed to proceed for about 18–24 h with continuous stirring in an atmosphere of dry nitrogen. After this, the reaction mixture was treated with a solution of 2,4-pentanedione (50 mL) in reagent grade isopropanol (100 mL). The resulting mixture was then heated at 80°C for 2 h and filtered. The solid polymer obtained was once more treated with 2,4-pentanedione, isopropanol mixture at 80°C and filtered again. It was thoroughly washed with dry petroleum ether and dried in a vacuum oven at 60°C for 12 h.

The poly(1-olefin)s were studied as film electrets of thickness ranging from 10 to 20 mils. They were either commercially extruded materials or were processed in the laboratory by compression molding at appropriate temperatures and pressures.

Preparation and Evaluation of the Electrets

The polymer films were cut in 5.5 cm × 5.5 cm sizes and slid into appropriate sized photographic slide-holder frames. The mounted films were charged by the glass insert method¹⁴ as follows:

The polymer sample was placed over a 5-mm-thick soda glass plate, resting on a grounded metal electrode. It was covered with another 5-mm-thick soda glass plate, having a coating of evaporated aluminum film on its top side. This upper electrode was connected to the negative terminal of a high voltage dc power supply. All the films studied were charged at a potential of 30 kV for 1 min.

The films thus charged were wrapped with an aluminum foil for 5–10 min to eliminate excess and spurious charges. The electrets thus obtained were studied by following their apparent surface charge density as measured by a chopper electrode.¹⁵

The apparent surface charge density σ is given by $\sigma = KE_0V/d$, where K = dielectric constant of the electret material, E_0 = permittivity of free space (8.854×10^{-14} faraday/cm), V = externally applied voltage for null deflection in the ac circuit, and d = thickness of the film (cm). A replicate of five samples was used to calculate the average value of the voltage, V , of the electret.

The charge decay of the electrets was followed by subjecting them to different environmental conditions. Since σ is proportional to V when a particular electret sample (K , E_0 , d constant) is studied, σ_t/σ_0 is proportional to V_t/V_0 at time t . Therefore, for decay studies, the external negative voltage V_t of the electrets were followed with respect to time. The negative side was preferred since we used the negative electrode for breakdown purposes while the positive electrode was

grounded. It was found that during charge decay, the positive side behaved almost the same as the negative side.

Thermally stimulated discharge (TSD) current spectra were obtained by following standard techniques.³ The ^{60}Co source at the University of Guelph was utilized for γ -ray irradiation of polyethylene films.

RESULTS AND DISCUSSION

According to Van Turnhout,⁵ homocharging at room temperature leads to less stable electrets. This was concluded from his studies of thermally stimulated discharge (TSD) spectra of various electrets. Preparation of electrets at higher temperatures leads to more stable electrets. However, for our study, we preferred a room-temperature charging method because this would help us to eliminate effects due to orientation of intrinsic charge carriers inside the polymers as well as thermooxidation and other thermal effects that could affect compositions of a polymer at higher temperatures due to prolonged application of high voltages.

We employed the technique, discovered by Sessler and West,¹⁴ of applying breakdown voltage through dielectric inserts to form electrets. In order to have uniform conditions, we employed polymer films of thickness varying from 10 to 20 mils, a charging voltage of 30 kV and charging time of 1 min. We also eliminated excess and spurious charges on the surface of the polymer electrets by wrapping them with aluminum foils. Once stable initial charges were obtained, we followed the decay of these charges by measuring the surface voltage with respect to time.

We also considered that the decay of polymer electret charges should be studied under controlled conditions because external ion sources sometimes compensate the electret charges.¹⁶ For this reason, the electrets were put inside closed glass containers where they were subjected to different controlled environmental conditions. We studied them at room temperatures under dry conditions as well as at 98% and 100% relative humidity. For practical applications at room temperature, charge stabilities of these electrets may not have to be tested at temperatures much higher than 50–60°C. Therefore, the maximum test temperature we used fell in that range. Here again, the effect of humidity was also examined.

We know from studies done by others⁷ that DuPont's Teflon-FEP is the best electret material known to date. Therefore, we tested FEP electrets prepared by the glass insert method to determine whether stable electrets could be prepared. The results in Table II show that, indeed, stable electrets can be prepared by the application of this dielectric insert method. Therefore, we followed this technique to study the effects of variables on the charge stabilities of our polyolefin electrets.

We followed charge decay with respect to time at room temperature and 50°C, rather than employing thermally stimulated techniques. Although extrapolation to room temperatures on the basis of the Arrhenius equation is possible and an educated guess can be made about lifetime and other characteristics, most TSD studies are carried out under dry atmospheric conditions. Therefore, usually, the very significant effect of humidity is not studied in detail. From all indications, it seems that the real test of stability of an electret is under humid conditions.

TABLE II
Charge Decay Characteristics of Teflon—FEP (Type A) Electrets

Time (days)	Room temperature/100% relative humidity		50°C/100% relative humidity	
	Voltage (V)	V/V ₀	Voltage (V)	V/V ₀
0	1630	1.00	1550	1.00
1	1600	0.98	1530	0.99
15	1500	0.92	1470	0.95
29	1400	0.86	1420	0.92
43	1450	0.89	1430	0.92
111	1350	0.83	1430	0.92
174	1400	0.86	1390	0.90
230	1350	0.83	1350	0.87

Preliminary evaluation of stabilities of polyethylene electrets was made on those prepared from 15-mils-thick extruded high-density polyethylene samples. Table III lists the results.

This shows that polyethylene electrets are reasonably stable at room temperature even at high humidity.

The above electrets were prepared from materials obtained from commercial sources without much cleaning or purification of the surfaces. Therefore, it was decided to see whether there is any effect if the surfaces are cleaned with solvents, prior to electret formation. Table IV indicates the stabilities of polyethylene electrets at room temperature and 98% relative humidity. The solvents used for cleaning were ethanol and acetone. The polymer films were dipped in the solvents for 15 min, followed by removal of the solvents at 40°C/17 h in a vacuum oven. The blank samples were treated in the same manner except that they were not washed with a solvent.

It is clear from Table IV that surface cleaning does not add to electret stability. This indicates that it is the bulk property of the polymers that determines the electret behavior.

It is known that the effect of high energy radiation such as γ -radiation can affect polymer properties by altering chemical structures. High-density polyethylene is a semicrystalline polymer in which the crystals are usually in a folded chain configuration.¹⁷ Oxidation with strong oxidizing agents and high energy

TABLE III
Charge Decay Characteristics of High Density Polyethylene Electrets

Time (days)	Room temperature/dry		Room temperature/98% relative humidity	
	Voltage (V)	V/V ₀	Voltage (V)	V/V ₀
0	1200	1.00	1300	1.00
5	1170	0.98	1280	0.98
26	1170	0.98	1210	0.93
69	1180	0.98	1150	0.89
89	1150	0.96	1150	0.89
119	1150	0.96	1150	0.89
150	1140	0.95	1070	0.82
230	1130	0.94	975	0.75

TABLE IV
 Charge Decay Characteristics of Polyethylene Electrets: Effect of Solvent Cleaning of the Surface. Environment: 98% Relative Humidity, Room Temperature

Time (Days)	Solvent	Voltage (V)	V/V ₀	Solvent	Voltage (V)	V/V ₀	Solvent	Voltage (V)	V/V ₀
0	none	1200	1.00	ethanol	1520	1.00	acetone	1100	1.00
12	none	1080	0.90	ethanol	1450	0.95	acetone	970	0.86
42	none	1050	0.88	ethanol	1370	0.90	acetone	900	0.82
62	none	960	0.80	ethanol	1300	0.86	acetone	890	0.81
91	none	940	0.78	ethanol	1240	0.82	acetone	900	0.82
170	none	840	0.70	ethanol	1100	0.72	acetone	800	0.73

TABLE V
 Charge Decay Characteristics at Room Temperature of Electrets Prepared from Polyethylene
 Irradiated in Air with ^{60}Co γ -Rays (0.45 Mrad/h)

	Time (days)	Dry		98% relative humidity	
		Voltage (V)	V/V ₀	Voltage (V)	V/V ₀
Irradiated 7 h	0	1530	1.00	1230	1.00
	4	1400	0.92	1100	0.89
	7	1300	0.85	1010	0.82
	40	1030	0.67	600	0.49
	70	810	0.53	440	0.36
	110	710	0.46	360	0.29
	150	670	0.44	300	0.24
Irradiated 24 h	0	1320	1.00	1130	1.00
	4	1170	0.89	940	0.83
	7	1080	0.82	850	0.75
	40	670	0.51	480	0.42
	70	490	0.37	330	0.29
	110	390	0.30	270	0.24
	150	350	0.27	210	0.19
Irradiated 48 h	0	1140	1.00	1100	1.00
	4	980	0.86	790	0.72
	7	880	0.77	740	0.67
	40	410	0.36	300	0.27
	70	260	0.23	170	0.15
	110	160	0.14	110	0.10
	150	130	0.11	100	0.09

radiation in presence of air can attack the exposed folds very rapidly.¹⁸ Therefore, we became interested to determine how the electret behavior of polyethylene is affected by irradiation with γ -radiation in presence of air prior to electret formation. Table V summarizes the results.

The data from Tables III and V are represented in Figure 1. It shows that prior treatment of polyethylene with γ -radiation has drastic effects on the stabilities of polyethylene electrets. Apparently, alterations of bulk properties such as electrical conductivity, crystal characteristics, or oxidation of chemical groups have occurred.

It is quite obvious that the electret stabilities of a material will be affected adversely by increasing electrical conductivity of the medium. After all, the electret state is possible because of highly insulating characteristics of a dielectric. Therefore, our next enquiry was to find out whether the degree of crystallinity in these semicrystalline polymers has any bearing on electret behavior. For this study, we selected two groups of polyolefins. It is known that the density of polyethylene polymers roughly parallels the crystalline content. Therefore, first we determined the stabilities of electrets derived from polyethylenes of varying densities. The second group of polymers studied was poly(4-methyl-1-pentene) and poly(3-cyclohexyl-1-propene). Poly(4-methyl-1-pentene) is known to possess good semicrystalline structure,¹⁹ whereas poly(3-cyclohexyl-1-propene) is generally amorphous.²⁰ A comparison between their structures as given below

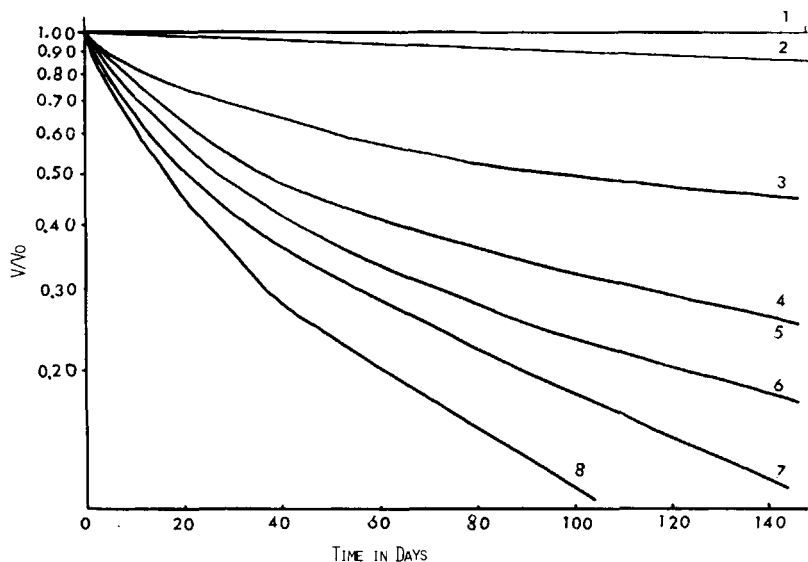
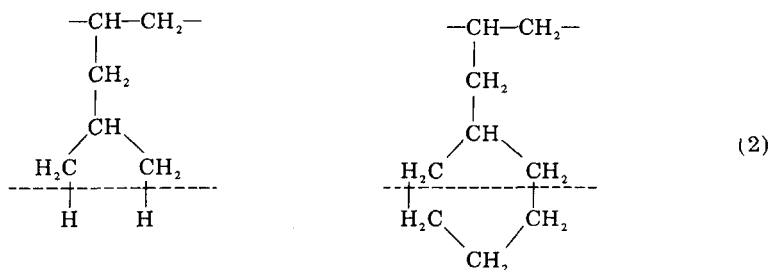


Fig. 1. Charge decay of polyethylene electrets at room temperature. (1) Extruded polyethylene: dry chamber; (2) extruded polyethylene: 98% relative humidity; (3) polyethylene irradiated with γ -rays: 7 h: dry chamber; (4) polyethylene irradiated with γ -rays: 7 h: 98% relative humidity; (5) polyethylene irradiated with γ -rays: 24 h: dry chamber; (6) polyethylene irradiated with γ -rays: 24 h: 98% relative humidity; (7) polyethylene irradiated with γ -rays: 48 h: dry chamber; (8) polyethylene irradiated with γ -rays: 48 h: 98% relative humidity.

shows their similarities:



Poly(4-methyl-1-pentene)
(semicrystalline)

Poly(3-cyclohexyl-1-propene)
(amorphous)

Therefore, any difference in their electret behaviors should be dependent on their abilities to develop appropriate crystalline structures.

Table VI summarizes the stabilities of various polyethylene electrets and Table VII indicates those of poly(4-methyl-1-pentene) and poly(3-cyclohexyl-1-propene).

It is obvious, then, that two important factors governing the charge stabilities of the polyolefin electrets are high volume resistivity and development of crystalline structure inside the polymers. Among organic dielectrics, polymers are better electret substrates than even high melting, crystalline materials of high volume resistivity but of low molecular weight.³ This implies that the long chains, characteristic of polymer structures are also important. Study of ther-

TABLE VI
Charge Decay of Electrets Prepared from Different Grades of Polyethylene [Fortiflex].
Environment: 100% Relative Humidity

	Time (days)	Room temp		50°C	
		Voltage (V)	V/V ₀	Voltage (V)	V/V ₀
Polyethylene, density 0.960	0	1500	1.00	2000	1.00
	1	1500	1.00	1200	0.60
	4	1440	0.96	1050	0.52
	44	1100	0.73	1000	0.50
	75	1000	0.67	700	0.35
	110	900	0.60	500	0.25
Polyethylene, density 0.950	0	1600	1.00	1300	1.00
	1	1570	0.98	300	0.23
	4	1510	0.94	100	0.08
	44	1270	0.79	—	—
	75	1150	0.72	—	—
	110	10.60	0.66	—	—
Polyethylene, density 0.945	0	1600	1.00	1500	1.00
	1	1250	0.78	150	0.10
	4	1040	0.65	60	0.04
	44	690	0.48	—	—
	75	650	0.41	—	—
	110	400	0.25	—	—

mally stimulated discharge of polymer electrets has shown that, at different transition temperatures of the polymers, discharge of electric charges occurs very rapidly.³ Thus, it is possible that the molecular chains and groups are sites where the charged particles are trapped and the onset of thermally activated motions in them would tend to dislodge them. In order to study this effect, we have determined the electret stabilities of polyolefins with pendant normal side chains, such as polypropylene, poly(1-butene), and poly(1-hexadecene). All these polymers were highly isotactic materials with high values of volume resistivity. Table VIII summarizes the results.

From Tables III and VIII, it appears that high density polyethylene and isotactic polypropylene produce fairly stable electrets at room temperature even under humid conditions, but polyolefins having long normal side chains such as poly(1-butene) and poly(1-hexadecene) are poor electret materials at room

TABLE VII
Charge Decay of Electrets Prepared from Poly(4-methyl-1-Pentene) ($T_g = 40^\circ\text{C}$) and Poly(3-cyclohexyl-1-Propene) ($T_g = 65^\circ\text{C}$). Environment: $50^\circ\text{C}/100\%$ relative humidity

Time (days)	Poly(4-methyl-1-pentene)		Poly(3-cyclohexyl-1-propene)	
	Voltage (V)	V/V ₀	Voltage (V)	V/V ₀
0	1600	1.00	1400	1.00
1	1500	0.94	370	0.26
4	1480	0.93	270	0.19
8	1400	0.88	210	0.15
20	1340	0.84	—	—
30	1280	0.80	—	—
40	1230	0.77	—	—

TABLE VIII
Charge Decay Characteristics of Various Isotactic Polyolefin Electrets. Environment: Room temperature, 100% relative humidity

Time (days)	Isotactic Polypropylene		Isotactic poly(1-butene)		Isotactic poly(1-hexadecene)	
	Voltage (V)	V/V ₀	Voltage (V)	V/V ₀	Voltage (V)	V/V ₀
0	1600	1.00	1800	1.00	700	1.00
1	1600	1.00	435	0.24	250	0.36
7	1550	0.97	260	0.14	250	0.36
15	—	—	200	0.11	130	0.19
21	—	—	160	0.09	80	0.11
28	1500	0.94	150	0.08	60	0.09

temperature. The effect of transition temperature is clearly important here because all these polymers possess high values of volume resistivity and isotactic semicrystalline structures. Obviously, the glass transition temperature (T_g) is not important because T_g of all these polymers are near or below 0°C. Therefore, the only important transition temperature that is affecting the stabilities of these polymer electrets is the one involved in the motion of the crystal domains in these polymers, the so-called T_α , found in the study of dynamic mechanical and dielectric loss properties of these polymers. T_α for these polymers are the following: Polyethylene, 40–60°C, polypropylene, 50–90°C, poly(1-butene) 0–20°C and poly(1-hexadecene), –60––10°C.²¹ The room temperature stabilities of the electrets prepared from these polymers correlate quite well with the T_α temperatures. The correlation also holds well when the electret stabilities of polyethylene and polypropylene are compared at 50°C (Table IX).

If the above arguments are valid, one can increase the stabilities of the polyolefin electrets by simply increasing the T_α temperature of the substrate. It is known that the presence of branched side chains in the polyolefins raises T_g and T_α temperatures.²⁰ Commercially, poly(4-methyl-1-pentene) is available as TPX, a product formerly from ICI, England and now from Mitsui Petrochemicals, Japan. Table X lists the charge decay characteristics of TPX electrets under different environments.

Table X indicates that TPX indeed gives rise to stable electrets. The stabilities of TPX electrets are quite comparable to those of Teflon—FEP electrets (Table I). At this stage, we thought that it would be interesting to compare the

TABLE IX
Charge Decay Characteristics of Polyethylene and Polypropylene Electrets at 50°C, 100% Relative Humidity

Time (days)	Polyethylene (high density)		Polypropylene (isotactic)	
	Voltage (V)	V/V ₀	Voltage (V)	V/V ₀
0	1300	1.00	1400	1.00
1	1200	0.92	1380	0.99
4	1050	0.81	1340	0.96
29	880	0.68	1230	0.88
75	700	0.54	740	0.53
110	500	0.28	660	0.47

TABLE X
Charge Decay Characteristics of TPX [Poly(4-methyl-1-Pentene)] Electrets

Time (days)	Room temp., 98% relative humidity		50°C, dry		50°C, 100% relative humidity	
	Voltage (V)	V/V ₀	Voltage (V)	V/V ₀	Voltage (V)	V/V ₀
0	1340	1.00	1590	1.00	1390	1.00
1	1340	1.00	1510	0.95	1450	1.04
15	1230	0.92	1530	0.96	1380	0.99
29	1090	0.81	1540	0.97	1320	0.95
57	1000	0.75	1540	0.97	1250	0.90
111	980	0.73	1520	0.96	1170	0.84
204	980	0.73	1520	0.96	1020	0.73
265	950	0.71	1490	0.94	1060	0.76
310	990	0.74	1480	0.93	940	0.68

TSD spectra of TPX and FEP electrets. It is shown in Figure 2. The high temperature peaks in both cases occur at about 175°C. Figure 3 shows the TSD spectrum of TPX electret after it was exposed to 100% relative humidity at 50°C for 50 days. The high-temperature peak remained the same, whereas the natures of low-temperature peaks had changed.

Therefore, it appears that the polyolefins and the poly(fluoroolefin)s have the

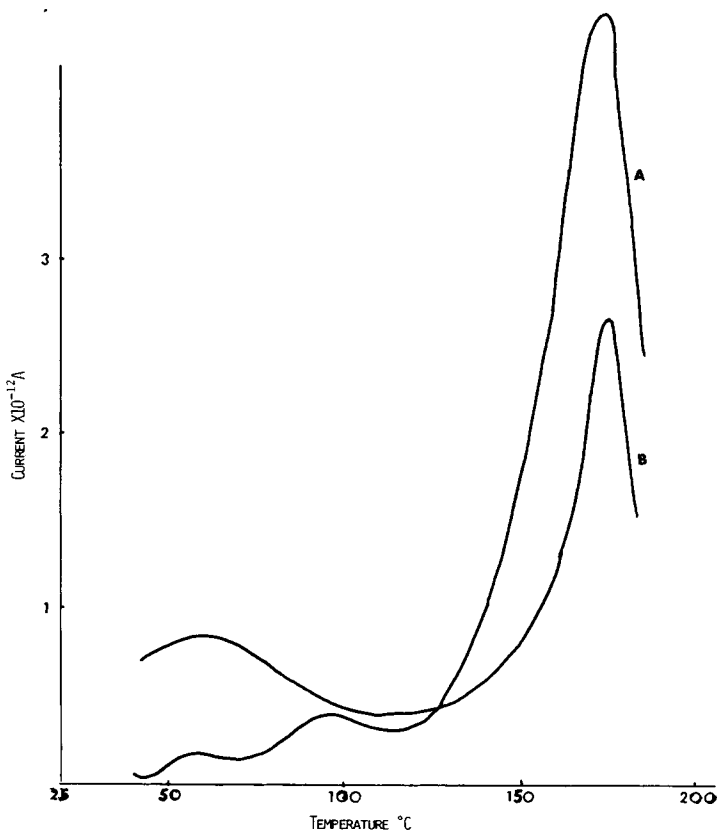


Fig. 2. TSD currents from Teflon FEP and TPX 20 mils thick. Electrets: heating rate, 2.2°C/min. (A) Teflon—FEP; (B) TPX.

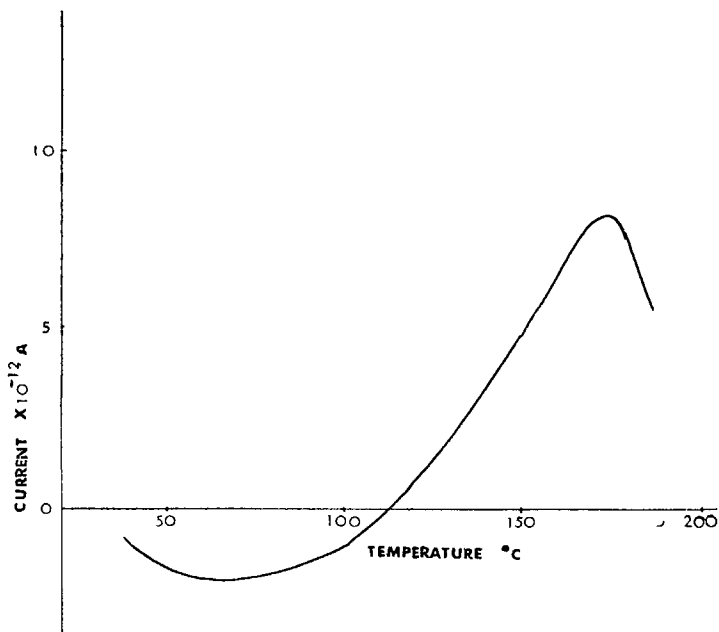


Fig. 3. Effect of 50 days' exposure at 50°C and 100% relative humidity on the TSD currents from TPX electrets. Heating rate: 2.2°C/min.

same general basis for electret formation and stability. The fact that electrets prepared from poly(fluoroolefin)s have in general much better stabilities than those prepared from similar polyolefins indicates that the fluorine atoms also stabilize electret charges.

The stability of an electret should depend on the interaction between the traps and the charge species involved. Unfortunately, we have not been able to determine the exact nature of the charged species involved in the electrets we have studied. It seems that only one investigation²² has attempted seriously to tackle this problem. According to this work, charged species derived from chemicals in the atmosphere are involved. However, most polymers would tend to react at room temperature with these reactive species such as O_2^- , NO_2^+ , etc., giving rise to chemical derivatives and most probably releasing electrons and holes in the process. The parallel behaviors exhibited by the electrets of a particular polymer prepared by different methods such as electron bombardment, corona discharge, dielectric breakdown, etc., implies that perhaps electrons and holes are the ultimate charged species that are trapped. There is a possibility, however, that polymers with stable chemical entities, such as fluorinated materials, may be able to stabilize the reactive species without undergoing chemical transformations. At lower temperature, also, these reactive species may remain intact in different polymer substrates.

If most homoelectrets do (a) involve trapping of electrons and holes through charge exchange via reactive chemical species obtained from the atmosphere or (b) trap these charged chemicals directly, the energetics and, thus, the stabilities of the electrets produced would then depend on the nature of the atmosphere present during electret formation. Unfortunately, we have not investigated this aspect at all, but, to avoid complications, all our electrets were prepared

under a standard atmospheric condition, especially at a constant relative humidity of 20–30%.

Not all fluoroolefin polymers are good electret substrates. Thus, although poly(tetrafluoroethylene), poly(tetrafluoroethylene-co-hexafluoropropylene), poly(chlorotrifluoroethylene) are excellent electret materials³, poly(vinylidene fluoride) is not.²³ The T_α temperature of this polymer is 50–80°C and, thus, similar to polypropylene.²⁴ Also, this polymer is basically polar because two fluorine atoms are on the same carbon atom (CF₂) alternating with a CH₂ group: [—CH₂—CF₂—].

Therefore, a balance of various factors governs the electret stabilities. From our study, the following factors are found to be important in governing the stabilities of polyolefin electrets: (a) a high value of volume resistivity, (b) a high degree of crystallinity, (c) a high value of the T_α temperatures, and (d) trapping of appropriate charged particles as well as the presence of suitable chemical groups acting as trapsites.

The combined effects of crystallinity and T_α temperatures indicate that the crystalline domains are involved in the trapping processes. There are two possibilities here. The charged species might be trapped either inside the crystalline phase or at the crystalline/amorphous interface.

We consider that the charged particles are trapped at the crystalline/amorphous interface. This is shown quite clearly by our study of γ -ray-irradiated polyethylene. The crystalline chain folds in polyethylene are susceptible to oxidation^{18a,18b,18c} and these regions are, therefore, affected by γ -rays much more easily than the inside of the crystal domains.^{18d,18e} That the γ -rays are affecting the crystalline segment of the polyethylene structure was also demonstrated by studying the loss peak at 30–70°C (T_α) in its dynamic mechanical spectrum. With increasing doses of irradiation with γ -rays, this peak was progressively reduced in intensity.

According to Keller^{18c}, 0.9 of all vinyl end groups in polyethylene lie in the surface layer of the chain folds. Thus, this might indicate that the vinyl end groups are the active trapsites for the charged particles. The same idea has been put forth by other workers.²⁵ It appears that the vinyl groups play an important part. We think, however, that stabilization of a charged species by interaction with only one vinyl group would not be too significant. Therefore, we propose that the chain folds provide appropriate geometrical arrangements for a number of vinyl groups as well as suitable alkyl groups, so that delocalization of π and

TABLE XI
Charge Decay Characteristics of Poly(3-methyl-1-Butene) Electrets Environment: 60°C, 100% Relative Humidity

Time (days)	Voltage (V)	V/V ₀
0	1200	1.00
1	1200	1.00
7	1100	0.92
15	1080	0.909
22	1020	0.85
43	930	0.78
70	800	0.67
90	800	0.67

σ orbitals can occur within a cagelike structure. In fluoropolymers, the "n" orbitals of the fluorine atoms will also take part. It is this cage structure where the charged particles are stabilized as well as shielded from deleterious materials such as moisture and low-molecular-weight solvents and impurities.

It is, of course, known that charged ions can be complexed by organic chelating agents.²⁶ Discoveries of crown ethers, cryptides, and other similar cagelike organic structures have shown that ionic species can be trapped inside and held strongly by secondary forces so that the caged ion is effectively separated from its counter ions.²⁷ In these instances, generally metal ions are complexed by organic groups through their anion, π -electrons or nonbonded "n" electrons. We believe that the charged species are similarly stabilized in polyolefin electrets, assisted by highly insulating properties of the polymer medium itself.

Finally, in order to verify that other polyolefins similar to TPX would follow the same stability pattern, we have prepared and studied the electrets of poly(3-methyl-1-butene). Table XI summarizes the results.

Table XI indicates that fairly stable electrets can also be prepared from poly(3-methyl-1-butene), thus providing support for our hypothesis.

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