

Polymethylene and the structure of polyethylene: Study of short-chain branching, its nature and effects

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Abstract

Model compounds in the form of polymethylenes, linear and branched, have been prepared and used to develop methods of measuring the numbers and lengths of branches in polymethylene. The polymethylenes used for calibration work contain deuterated butyl branches; the numbers of branches present in the polymers have been established by two independent methods: direct assay for deuterium and mass spectrometric analysis of the irradiation products. Using this series a new infrared technique has been calibrated absolutely to measure total number of methyl group and also butyl branches specifically. The infrared technique is a compensation method, using solid specimens in a double-beam spectrometer, in which the compensating material (linear polymethylene) is devoid of the structural features, namely branches, to be measured. Using the same technique and reference samples of ethyl-branched polymers (Hydropol), a method of estimating ethyl branch concentration has been developed. A study of the gaseous products of irradiation of the butyl-branched polymethylenes, using mass spectrometric analysis, has shown the extent to which this technique might provide a quantitative means of identifying and estimating branches in such polymers; it has also greatly strengthened the evidence of earlier workers that low density polymethylenes contain primarily ethyl and butyl branches. The same conclusion, in more quantitative terms, is drawn from an infrared study of various polymethylene-specimens: practically all the branches observed can be accounted for as ethyls and butyls present in the ratio of approximately 2:1. Some high density polyethylenes contain a few branches, which appear to be ethyl groups. The effects of the numbers and lengths of branches on degree of crystallinity, crystalline melting point, density, rate of oxidation,

and dynamic mechanical properties are illustrated and discussed. The status of theories concerning the mechanism of formation of short side chains in polymethylene is considered.

Keywords: Polyethylene, x-ray, temperature, charge, electret.

Introduction

There is enough literature available, giving the dependence of nature of the charge and general properties of electrets, on the electric field used in electret preparation (1,2,3,4). Good quality electrets were obtained when the specimen was subjected to high voltage in the molten state (5). It (6) have observed that the polarizing temperature affects the magnitude of hetero-charge. Tiku in his investigations observed a decrease in the electrocution when the field was maintained for a longer time after solidification of if switched off before complete solidification of wax. Cooling period of the dielectric under electric stress is also an important factor influencing the electret behavior (8,9). According to Wiseman and Feaster, all solid dielectric are capable of acquiring surface charge and volume polarization, provided they are subjected to proper conditions; hence all solid insulators can exhibit electret effect. The effect of thickness of the specimen also plays an important role in determining the general behavior of the electrets, such as nature of charge, period of charge reversal, and other properties of the electrets .

In general there are two ways of getting charged samples, firstly the charge acquired by friction, and secondly as exhibited by electrets. But there is marked difference in these charge acquiring processes. The charge acquired by friction is purely a surface charge effect while the charge acquired upon breaking the bond between metal and insulator is a volume charge distribution. In the case of electrets a volume charge distribution is obtained. An electret is a dielectric which can maintain a permanent electric to an electric stress at high and even at room temperature. In practice, hetero-charge appears first and in due course of time changes into homo-charge, which lasts for a longer time.

To establish the correlation between the observed surface charge of the electret and their various properties a number of workers have measured the surface charge. The maximum value of the surface charge observed by Shepperd and Stranathan 10 e.s.u./cm^2 , while Theissen and others have observed a value of 8 e.s.u./cm^2 , And Gemant found 4.6 e.s.u./cm^2 only . In plastic electrets Wieder and Kaufmann have reported surface charge densities as 16.5 e.s.u./cm^2 , whereas in ceramic materials value of $3 - 6 \text{ e.s.u./cm}^2$, or even more

have been reported . It has been found that Barium-titanate yields electrets having the maximum charge, which is retained for a longer period. Gemant and others have measured the field at various distances above the electret surface and have discovered that the values of the field decreases exponentially with distance. Surface charge of electrets were measured at various pressures in the and to 10 to 228 *cmHg* pressure, it was found that the density of charge is proportional to the pressure(14). At 150 *cm Hg* pressure, the density of charge attains nearly a constants value of about 15 e.s.u/cm^2 , It is therefore presumed that at such high pressure the polarizing field is not sufficient to produce an electrocution, which can give surface potential equal to the breakdown strength of air at that pressure.

Frei and Groetzinger have found that in the re-melting process of the electrets a discharge current appeared which was of the order of 10^{-8} amp/cm^2 , but no current was observed when the complete molten state was attained. Paraffin wax which is a non-polar substance, shows a discharge current that remains the same whether the substance is polarized in the solid of molten state. The discharge current has been observed even at temperature below the melting point.

Electret properties of the high polymers have been studied by very few worker; their surface charge measurements under different physical conditions were also done. It has been reported that there is a charge transfer from metal to the surface of high polymers, when the contact between the two is broken. The charge thus attained by the high polymer does not respond to any surface treatment. X-ray work made in the previous chapters of this thesis clearly show that there is some mechanism taking place which gives rise to enhancement in the orientation in the 110 and 200 diffraction rings, at $110^{\circ}C$. Hence the purpose of the studies in this chapter is to examine the properties of the electrified sample of Polyethylene and especially to know whether there is any correlation between the surface charge developed and the orientation obtained at $110^{\circ}C$.

Description of the apparatus

(i) Electret holder:-

The electret holder used for electret preparation was the same as that described in Chapter III, and shown in fig 3.1

(ii) D.C. high voltage Source:-

The required number of 90 volts Eveready Minimax dry batteries were connected in series. The positive potential was applied to the upper electrode, and the negative to the lower electrode. Every time the voltage was tested by KV meter.

Hetero-charge was observed on anode side of the Polyethylene electrets which were prepared at 110⁰C and 10kv/cm field, using Tin and Aluminum electrodes, whereas on the cathode side homo-charge was found. But in the case of Lead electrode, only homo-charge was observed on both the side. Appearance of homo-charge suggests that the charges due to internal polarization are being over-compensated by the charges arising from external polarization.

The polarizing current for different electrodes observed during the cooling process in electret formation for different temperature has been given. It clearly shows that among the three different metal electrodes used (Aluminum, Tin, and Lead) Aluminum is the best electrode showing more current than any other electrode. Tin comes next to Aluminum and Lead comes to last. The X-ray studies of electrets prepared with different metal electrodes given in chapter IV also suggest that the choice of the metal electrodes regarding orientation is in the same order as above. Hence it is evident that electrode material plays a very important role in polarization of dielectric and in determining the orientation of molecules in the electrets. From the above studies it can also be stressed that the orientation of molecules in the dielectric will increase with the polarizing current.

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