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Dielectric Behaviour of a γ-Irradiated Polycarbonate

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SUMMARY

Dielectric measurements on a γ-irradiated polycarbonate in a dose range 0-20 Mrad and at test frequencies of 10^3 and 10^4 Hz have been carried out. The glass transition temperature shows a maximum at 3.5 Mrad and then decreases at larger doses. This result is in line with other experiments (intrinsic viscosity, dynamic-mechanical measurements, etc) already reported: the Tg values are however larger in the present results. This is probably due to the plasticizing action of the absorbed moisture present in the previous tests. A Tg vs $\frac{1}{[\eta]^2}$ plot ($\frac{1}{[\eta]^2}$ is proportional to $\frac{1}{M_\eta}$) allows to find the value of the glass transition point at an infinite molecular weight and the dependency of Tg on molecular weight.

INTRODUCTION

The exposure of polymers to γ-radiation produces a large number of physical and chemical modifications. In particular either crosslinking or chain scission occurs, depending on the nature of the polymer and on the conditions of irradiation, i.e. temperature, moisture, dose rate, etc.

In a previous work (ACIERNO et al. 1979) the effect of γ-radiation on a commercial polycarbonate (Lexan) has been considered. Some unusual results with respect to other polymers have been obtained: namely the polycarbonate has shown crosslinking, with an increase in molecular weight when small doses were used and degradation when exposed to larger doses. As expected, however, a small sensitivity to the radiation has been evidenced, similarly to other aromatic polymers.

In this work preliminary data are reported, concerning the dielectric behaviour of irradiated polycarbonate. The present results qualitatively confirm the previous ones. Some differences, especially with

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regard to the quantitative determination of the glass transition temperature, are quite evident. A possible explanation, which deserves however further support, is advanced in terms of the absence of moisture in the samples of the present work.

EXPERIMENTAL

The material used was a bisphenol A polycarbonate (4-4' dioxydiphenyl - 2-2-propane carbonate) Lexan, manufactured by General Electric and supplied in the form of a sheet 0.9 mm thick. Samples, about 8 cm in diameter, cut out of the sheet were irradiated at room temperature (T ≃ 25°C) and in air at about 60%R.U. by the IGS-3, a panoramic 3000 Curie of ^{60} Co irradiator. Irradiations, in the range up to 20 Mrad, were performed always at a rate of about 0.8 Mrad/h. The disuniformity ratio of about 1.05 was accepted. Before the experiments the samples were held for at least seven days in a vacuum desiccator over silica gel to remove the moisture. The tests were also performed in presence of silica gel and under a moisture-free nitrogen flow.

An a.c. General Radio capacitance bridge and a three electrodes cell Balsbaugh LD-3 were the main parts of the experimental apparatus. The cell was taken in an environmental chamber, which was always heated at a rate of about 1.5 °C/min. The temperature was varied in the range 20-200°C at both the investigated frequencies (10^3 and 10^4 Hz).

RESULTS AND DISCUSSION

The dielectric constant and the dissipation factor for some of the irradiated materials and, for sake of comparison, for the not-irradiated polycarbonate are reported in FIG. 1 as a function of the temperature, at the 10^3 Hz frequency. The dielectric constant seems to be only slightly influenced by the γ-irradiation and in fact all the curves reported in FIG. 1 have the same shape and mostly do not differ in value. However the sample irradiated at 3.5 Mrad has a dielectric constant smaller than the one irradiated at 20 Mrad. As for the control material the values of the dielectric constant obtained in the present work, although similar to those reported for the same material elsewhere (HARPER, HANDBOOK OF PLASTICS AND ELASTOMERS, MC GRAW HILL, NEW YORK, 1975), are slightly smaller, possibly because the tests have been carried out on dry samples and under moisture free conditions.

More evident differences can be seen in the dissipation factor results and particularly in the temperature at which the maximum occurs. The highest temperature value is obtained for the samples irradiated at

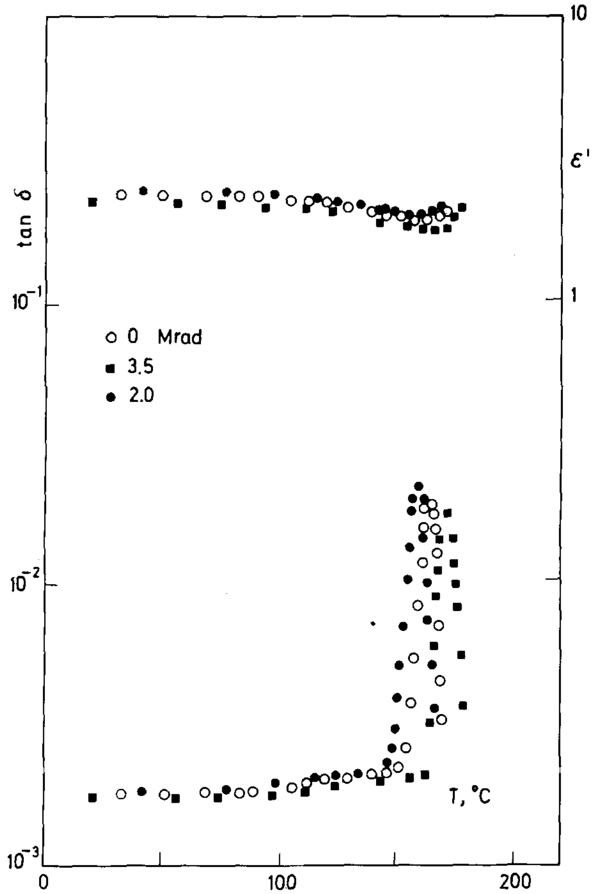

FIG. 1 Dielectric constant and dissipation factor as a function of temperature.

3.5 Mrad while at doses larger than 6 Mrad the temperature of the damping peak becomes even smaller than that of the control sample. Such a behaviour can be attributed to a crosslinking action of the γ-radiation at low doses and to a degradation occuring at larger doses. The slight decrease of the height of the maximum for the samples irradiated at 3.5 Mrad and the increase for other irradiated samples are in line with the above explanation.

More quantitative informations can be taken from the ε'' results, especially as far as the glass transition temperature is concerned, which is generally considered given by the temperature at which the maximum in ε'' occurs. Tg values are reported in TABLE 1 as a function of both irradiation dose and test frequency.

It is worth noticing that such Tg values are remarkably larger than those obtained by means of dynamic-mechanical measurements (ACIERNO et al. 1979): this is true also taking into account the different test frequency. The differences with the irradiation are also more significant in the present results. Both effects are probably due to the plasticizing action of the moisture which largely depress the transition temperature and makes less evident the effect of the change in molecular weight following the irradiation.

The Tg data (at 10^3 Hz) are reported in FIG.2 vs $\frac{1}{[\eta]^2}$. $[\eta]$ is intrinsic viscosity as measured in chloroform at 20°C (ACIERNO et al. 1979). Following previous works (DE CHIRICO 1960) $[\eta]$ for this system is proportional to the square root of viscosity average molecular weight and therefore $\frac{1}{[\eta]^2}$ is representative of the inverse of molecular weight. On the other side Tg is depending on number average molecular weight (FOX and FLORY 1950) through the relation

$$Tg = Tg^{\infty} - \frac{k}{Mn} \qquad (1)$$

Considering for the same polymer $M\eta$ proportional to Mn suggested the above plot, and in fact a straight line well interpolated the experimental data. This allowed to find the value of Tg^{∞} , i.e. the glass transition at an infinite molecular weight, and the dependency of Tg on molecular weight. In particular Tg^{∞} resulted 202°C and the proportionality factor k' in the expression

$$Tg = Tg^{\infty} - \frac{k'}{[\eta]^2} \qquad (1')$$

resulted 1.45×10^{-2} in $(g/ml)^2$ °C.

TABLE 1

Dose (Mrad)	$f=10^3$Hz	$f=10^4$Hz
0	Tg=166°C	Tg=174°C
2	169	178
3.5	172	180
6	167	174
10	164	173
20	160	169

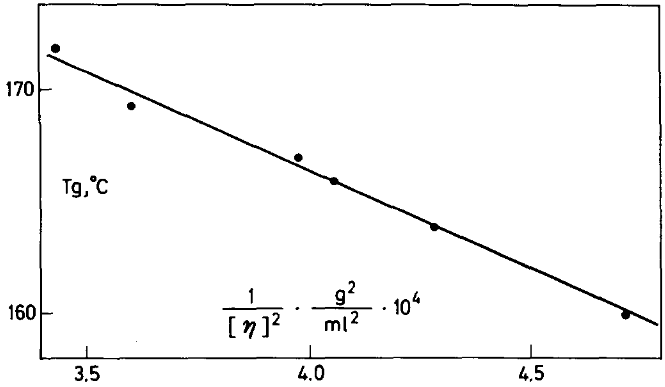

FIG. 2 The dependency of Tg on molecular weight as seen through the intrinsic viscosity.

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