*Eur. Polym. J.* Vol. 20, No. 11, pp. 1057–1059, 1984
Printed in Great Britain. All rights reserved

0014-3057/84 \$3.00 + 0.00

# DIELECTRIC PROPERTIES OF POLYESTER RESINS—1

F. LEGROS*†, A. FOURRIER-LAMER*, D. LE PENT† and A. GOURDENNE†
*Université Pierre et Marie Curie, Laboratoire de Dispositifs Infrarouge (ERA CNRS 365), tour 12, 2ème étage, 4 place Jussieu, 75230 Paris, Cedex 05 and †Ecole Nationale Supérieure de Chimie, Laboratoire de Physico-Chimie des Hauts Polymères, 118, rte de Narbonne, 31077 Toulouse, Cedex, France

(*Received* 29 *March* 1984)

**Abstract**—The dielectric properties of unsaturated polyester resins mixed with styrene have been investigated in the microwave 1–12 GHz range. The frequency dependence of the permittivity ($\varepsilon_r'$ and $\varepsilon_r''$) is typical of an orientational polarization relaxation process. A Davidson–Cole like model fits the experimental results reasonably well. A hypothesis on the molecular process is discussed, correlating the influence of temperature and sample composition.

## INTRODUCTION

Microwave heating of polyester resins mixed with styrene leads to copolymerization; experimental proof at the 2.45 GHz frequency has been recently given [1, 2]. The appearance of heat, when a non-conductive material is subject to an electromagnetic radiation, is generally conceived as caused by the dielectric losses. Our purpose has been to discover whether the loss factor is sufficiently high, in the vicinity of 2.45 GHz, to explain the possibility of an easy copolymerization process. Little is known about the dielectric properties of polyester/styrene in the microwave range. Measurements at 92 GHz [3] have led to high values of the loss factor, indicative of a strong polarization of the polymer.

In order to elucidate the frequency dependence of polarization, we have performed dielectric measurements in the gigahertz range on various low molecular weight samples, using a broadband system (HP Network Analyzer).

## SYNTHESIS

Polyester resins have been synthesized by thermal polycondensation of phthalic and/or maleic anhydrides with propylene or ethylene glycol. In any case, maleic residues are isomerized into fumaric in order to make radical copolymerization with styrene possible. In two samples ($R_1$ and $R_4$) propylene oxide has been used (Table 1).

The polyester chains are mixed with styrene (30% weight concentration). The chains are short, corresponding to very low molecular weight.

Table 1. Chemical composition of the initial unsaturated polyester resins

| Sample code | GP | PO | PA | MA (moles) | GE | $I_A$ | MW |
|---|---|---|---|---|---|---|---|
| $R_1$ | | 1.16 | 0.64 | 0.76 | 0.10 | | |
| $R_2$ | 1 | | | 1.00 | | 41 | 1300 |
| $R_3$ | 1 | | 0.50 | 0.50 | | 38 | 1400 |
| $R_4$ | | 1 | 0.66 | 0.33 | | 35 | 1400 |
| $R_6$ | 1.09 | | 0.37 | 0.63 | | | |

GP = glycol propylene; PO = propylene oxide; PA = phthalic anhydride; MA = maleic anhydride; GE = glycol ethylene; $I_A$ = acidity index; MW = molecular weight.

## EXPERIMENTAL

The determination of the permittivity is based upon reflexion coefficient measurements, provided by a non-automatic HP 8746 B Network Analyzer. A 50 Ω coaxial line is connected with the analyzer, the propagating mode being the TEM. The polyester/styrene mixtures, which are in a viscous liquid form, have been studied in a coaxial short circuit terminated cell.

The modulus and the phase of the reflexion coefficient are related to the real and imaginary parts of the permittivity by a system of two non-linear equations which may be numerically solved [4]. The measurements have been made in the 1–12 GHz frequency range. The real part of the permittivity of styrene has been found consistent with published values [5, 6]: $\varepsilon_r' = 2.40$ with a probable uncertainty of $= \pm 3\%$ and maximal uncertainty of $\pm 10\%$.

Statistical analysis of the data and comparison with values obtained by the resonant cavity perturbation technique (in the X band range) led to a probable uncertainty of $\pm 9\%$ and maximal uncertainty of $\pm 20\%$ on the imaginary part of the permittivity $\varepsilon_r''$. These large values are fundamentally caused by the manual operating procedure, which does not include automatic vectorial corrections.

The influence of temperature has been studied between 292 and 338 K. The cell was surrounded by a Joule effect heated ceramic. The temperature was measured by a Pt resistance thermometer, with an absolute error of $\pm 0.25$ K.

## RESULTS AND DISCUSSION

Initiating of grafting by microwave heating cannot be considered because of low values of electrical power (a few milliwatts); this is confirmed by the fact that all dielectric measurements are reproducible after recovering the initial experimental conditions, i.e. no chemical grafting occurs under this microwave analysis.

As examples of the dielectric measurements, dispersion and absorption of $R_1$ are shown in Fig. 1a and 1b. The experimental results may be fitted, within the uncertainty domain, by the Davidson–Cole like model

$$\varepsilon_r = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{(1 + j\omega\tau)^\beta}$$

as is shown by the Argand representation (Fig. 2).

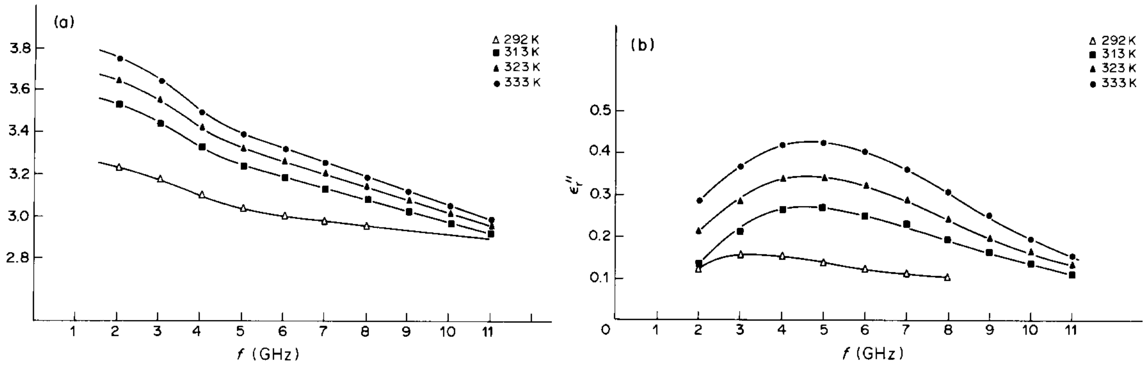


Fig. 1. Dielectric dispersion (Fig. 1a) and absorption (Fig. 1b).

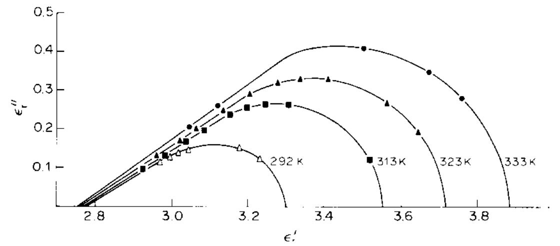


Fig. 2. Argand diagram.

Calculation of the Davidson–Cole parameter [7] leads to $\beta = 0.36$: this value is independent of temperature.

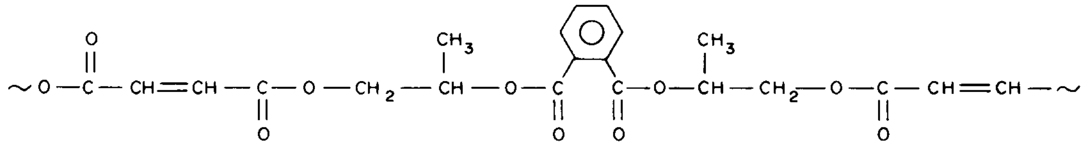
The absorption maximum shifts slowly towards higher frequencies as the temperature rises. The relaxation frequency is 3.5 GHz at 292 K and 5 GHz at 338 K. Intermediate values are consistent with an Arrhenius equation

$$f_r = f_0 \exp\left(\frac{W}{k_B T}\right)$$

(Fig. 3), where the activation energy $W$ is 7.1 kJ/mol. This value is compatible with Van der Waals bonding which induces aggregations of the chains mainly responsible for the thermoreversible viscosity of the medium.

The real and imaginary parts of the permittivity ($\varepsilon_r'$ and $\varepsilon_r''$) exhibit linear evolution over the studied temperature range (Fig. 4); the slope decreases as the frequency increases (Table 2). The dielectric responses of all the samples are qualitatively very similar. The large uncertainty inherent in the measurement technique [8] makes precise comparison difficult but the most important and less ambiguous feature is that the highest absorption values are observed in $R_2$ and the lowest in $R_4$ as shown in Fig. 5.

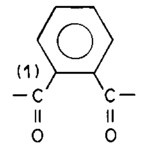
The chemical structure of the polyester chain may be represented thus:



The C=O units are known to be dipolar. The electric moment has been measured on carbon monoxide in the gaseous state [6] and is 0.112 D. They are involved as side chain groups coming from maleic and phthalic anhydrides.

From a mechanical point of view, the chain may be considered as a sequence of flexible segments connected by units having rigidity caused by double bonds. *A priori*, two elementary movements are possible. The C=O units may turn around the axis of the chain. The mass of these entities being small, easy displacement is expected.

Phthalic anhydride gives rise to the segment



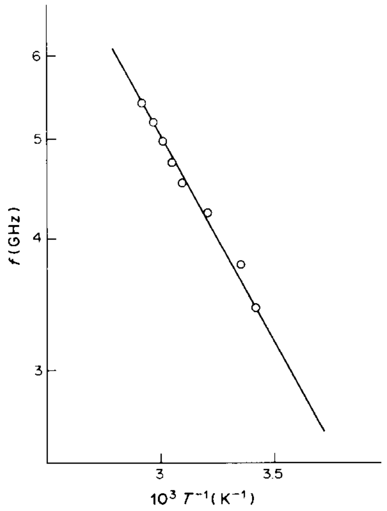


Fig. 3. Temperature dependence of the relaxation frequency of $R_1$.

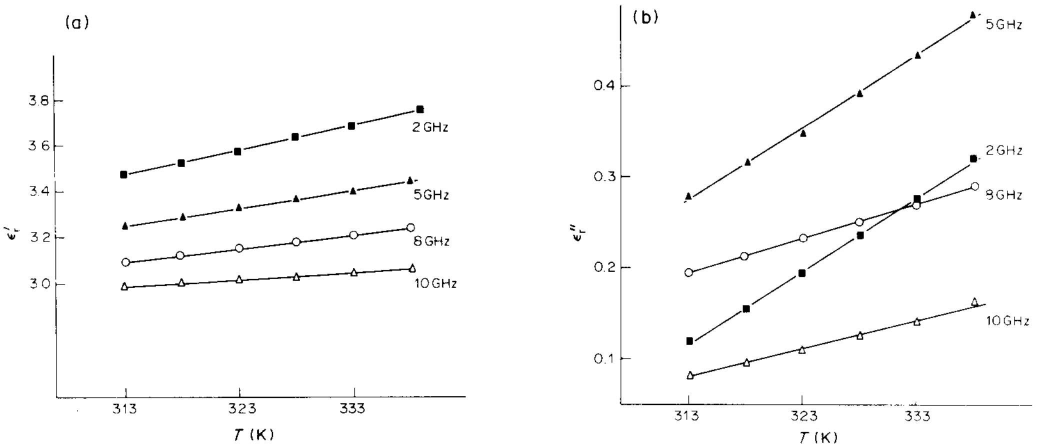


Fig. 4. Temperature dependence of the dielectric permitivity of $R_1$. $\varepsilon_r'$ (Fig. 4a), $\varepsilon_r''$ (Fig. 4b).

Table 2. Slope of dielectric permittivity vs temperature

| $f$(GHz) | $\frac{\partial\varepsilon_r'}{\partial T}10^3$ | $\frac{\partial\varepsilon_r''}{\partial T}10^3$ |
|---|---|---|
| 2 | 10.3 | 8.12 |
| 5 | 8.0 | 7.80 |
| 8 | 6.0 | 3.84 |
| 10 | 3.2 | 3.36 |

The possible rotation around the axis (1) involves the phenyl group so that, in comparison to the first case, it involves a heavy group. This displacement is probably hindered by interaction with the phenyl group of styrene, which superposes.

More complex movements than these two elementary processes may arise because of the flexibility of segments within the chain. Brownian motions are indeed responsible for strong deviation from linearity of the chains. So it is difficult to propose simple "crankshaft" motion as would be possible in solid polymeric materials.

The flexibility of the chain may introduce interaction between dipolar species. As Work *et al.* [9] recently reported, the Davidson–Cole parameter is a measure of intrachain interaction: $\beta$ has been found to be smaller than unity and indicates interactions within the chains.

The striking point is that, even in the absence of phthalic anhydride, relaxation processes occur. Comparison of the resins $R_2$ and $R_4$ indicates that the absorption grows as maleic concentration increases. This correlation gives logical support to the hypothesis by which C=O units coming from maleic anhydride play a fundamental role in the observed relaxation process.

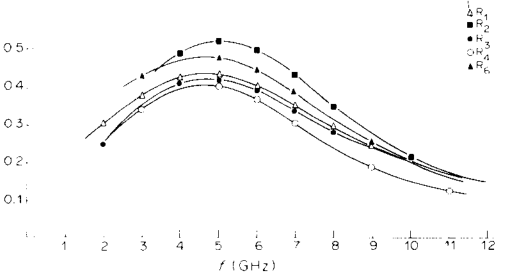


Fig. 5. Absorption at 333 K in the polyester/styrene samples.

Finally, we stress the following important point: contrary to the Debye [10] or Fröhlich [11] models which predict

$$\left(\frac{\partial\varepsilon_s}{\partial T}\right)_{p,v} = -\frac{1}{T}(\varepsilon_s - \varepsilon_\infty)$$

the experimental data lead to a positive slope

$$\left(\frac{\delta\varepsilon_s}{\delta T}\right)_{p,v} > 0$$

Accordingly to Daniel [12] this increase corresponds to a case where most of the free energy $F = U - TS$ of the field is stored in an energy content $U$ rather than in a $TS$ term where $S$ represents entropy.

## REFERENCES

1. S. Aussudre, A. H. Maassarani, L. Thourel and A. Gourdenne, *9th International Congress on Electroheat*, Section 4, Comm. III, A3. Cannes (1980).
2. A. Gourdenne, A. H. Maassarani, P. Monchaux, S. Aussudre and L. Thourel, *Polym. Prep.* **20,** 471 (1979).
3. P. Borderie, B. Chan Son Lint, A. Claverie and A. Gourdenne, *VIe Colloque Optique Hertzienne et Diélectrique*, Section III, p. 215. Toulouse (1981).
4. F. Legros, Thèse de Docteur-Ingénieur, Toulouse (1984).
5. A. von Hippel, *Les Diélectriques et Leurs Applications*. Dunod, Paris (1961).
6. *Handbook of Physics and Chemistry*, 53rd edn. CRC Press, West Palm Beach, FL (1972–1973).
7. A. K. Jonscher, *Physics of Thin Films*, Vol. 2, p. 205. Academic Press, New York (1980).
8. L. P. Ligthart, *IEEE, Trans. Microwave Theor. Tech.* **31,** 3 (1983).
9. M. Yoshihara and R. N. Work, *J. chem. Phys.* **72,** 5909 (1980).
10. P. Debye, *Polar Molecules*. Dover, New York (1945).
11. H. Fröhlich, *Theory of Dielectrics*. Clarendon Press, Oxford (1945).
12. V. V. Daniel, *Dielectric Relaxation*. Academic Press, London (1967).