reference materials to that of a polystyrene sample[8,9] of broad molecular weight distribution ($\bar{M}_w/\bar{M}_n = 3.4$) made available by this Laboratory as a means of calibration in g.p.c. In order to do so, account must be taken of dispersion, which is important for samples with $\bar{M}_w/\bar{M}_n < 2$, but can be neglected for the polystyrene reference material.

Some estimate of dispersion is possible from chromatograms of samples of narrow molecular weight distribution ($\bar{M}_w/\bar{M}_n \leqslant 1.1$). Smith's[10] 'molecular weight correction factors' were calculated from chromatograms of some commercial polystyrene reference materials (Pressure Chemical Company) of that sort, and lay between 1.06 and 1.09 for the elution volume range of the PVC samples. Since the difference is within the error of that determination, dispersion was taken to be symmetrical and invariant with elution volume. There is evidence[11] that dispersion is independent of polymer type under a given set of experimental conditions, and the result was assumed to hold for PVC.

For each of the PVC samples a linear calibration consistent with the classical number-and weight-average molecular weights was found by Frank's[7] method; $(\bar{M}_w)_{\mathrm{g.p.c.}}$ was used for the three samples without measured weight-average molecular weights. The effect of symmetrical dispersion is to rotate such a calibration about the peak molecular weight, M_0, so that the molecular weight identified in that way in invariant with dispersion. The M_0 values found are given in *Table 1*; the values for the NPL samples are within 10% of $(\bar{M}_n\,\bar{M}_w)^{1/2}$, so that by Berger and Schulz's criterion[12] the molecular weight distribution of those samples are close to log-normal. The same result was found[13] for a series of polypropylene reference materials produced in the same way. The peak molecular weights found in that way for the PVC samples were found to be directly proportional to the M_0 values found from the chromatograms and the polystyrene calibration established with the broad reference material; regression analysis gave a straight line through the origin with no residual exceeding 3% and no systematic deviation with molecular weight and sample source. The calibrations for polystyrene and PVC were therefore parallel, as is consistent with ample evidence[14,15] that tetrahydrofuran is a good solvent for both polymers. In that case the unperturbed dimensions can serve[16] as universal calibration parameters, and the slope of the relation described is given by the ratio of the root mean square end-to-end distances, $(\langle r_0^2\rangle/M)^{1/2}$, of the two polymers. With an averaged value[16] of that parameter for polystyrene (67 nm) under these conditions, the observed slope gives 84 nm for PVC. The agreement with a value (79 nm) determined[17] viscometrically is good, considering the approximations in both treatments.

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Changes in electric conductivity during the process of methyl methacrylate polymerization

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INTRODUCTION

As soon as the process of polymerization starts in the monomer, various quantities become functions of time i.e. the mass of the molecule, the number of free radicals, and the concentration of free admixture ions. This leads to variations in the macroscopic properties of the material undergoing polymerization[1–3].

In this paper, results are reported on changes in the electrical conductivity of methyl methacrylate (MMA) during the polymerization process at constant temperature and constant illumination. Moreover, the feasibility of inducing an electret effect when polymerizing MMA in static electric field is considered.

EXPERIMENTAL

MMA polymerization was initiated in chemically pure MMA using benzoyl peroxide. A special liquid condenser, filled with MMA, was placed in a thermostat at constant temperature. On partial polymerization of the material, a d.c. electric field was applied to the condenser and the current was measured over 10 days (*Figure 1*, switch K in position 1). Next, the field was removed, the system was short circuited, and the thermally stimulated discharge (*TSD*) current was measured when heating the sample at a constant rate.

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* Polish Pat. Application P-190261 (8 June 1976)

RESULTS

The current density (j) as a function of the time (t) of polymerization at constant temperature (~300K) in a constant d.c. electric field (10 kV/cm) is shown in *Figure 2*, where $\ln j$ is found to depend linearly on t:

$$j = j_0 \exp(-\beta t) \qquad (1)$$

j_0 and β being constants, to be determined from the slope of $\ln j = f(t)$. During the time interval of 0 to 2 days, $j_0 = 1.13 \times 10^{-5}$ A/cm^2, $\beta = 7.7 \times 10^{-6}$ sec^{-1}, whereas at the further stage of polymerization they take the values 2.13×10^{-6} A/cm^2 and 1.8×10^{-5} sec^{-1}, respectively. The electric conductivity varies in the course of 10 days from 7.6×10^{-10} to 2×10^{-13} cm^{-1} cm^{-1} i.e. by about 4 orders of magnitude.

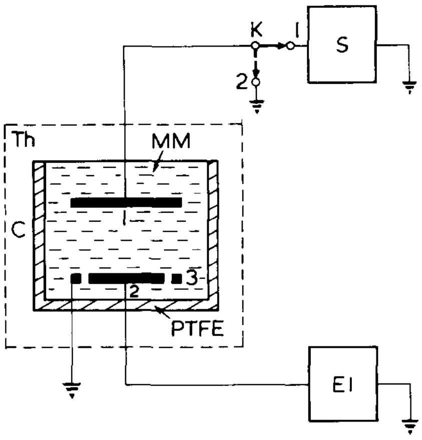

Figure 1 Block diagram of circuit for the measurement of current during the polymerization process of methyl methacrylate (switch K in position 1) and of *TSD* current (switch K in position 2): Th, thermostat; C, liquid condenser, made of PTFE, with nickel electrodes[1–3]; S, type ZWN-1A high voltage supply, made by BUTJ (Poland). El, type 219A electrometer, made by UNITRA (Poland)

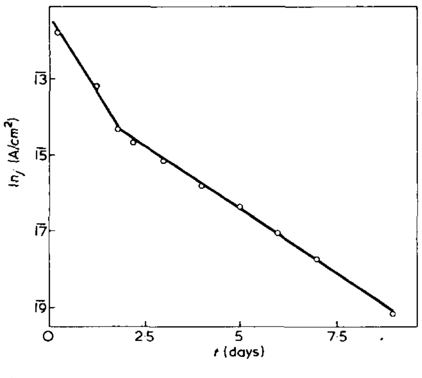

Figure 2 Logarithm of current density ($\ln j$) as a function of the polymerization time (t) of MMA

On removing the field, the sample was short circuited and the *TSD* current (j_d) was measured when heating the sample at a constant rate of $\lambda = 1$ degree/min. The current j_d is shown vs. the temperature T (upper axis of abscissae) and vs. the heating time t (lower axis of abscissae) in *Figure 3*. The *TSD* current varies from 4×10^{-11} A/cm^2 at 300K to a maximal value of 5.8×10^{-9} A/cm^2 at $T_m \approx 443$K. With regard to the scale applied, *Figure 3* does not show initial behaviour of the *TSD* current. From 300 to 400K, this current varies but insignificantly with increasing temperature.

Figure 4 shows $\ln j_d$ as a function of $1/T$ for the ascending portions of the *TSD* curve of *Figure 3*. We have here a straight line, pointing to an activational nature of the depolarization process. The activation energy of the process derived from the slope of $\ln j_d = f(1/T)$ amounts to $U = 1.9$ eV.

The amount of charge set free during depolarization can be evaluated by graphical integration of the $j_d(t)$ curve of *Figure 3*. Within the depolarization time interval from 115 to 145 min the integral yields $\sigma = 4.5 \times 10^{-6}$ C/cm^2.

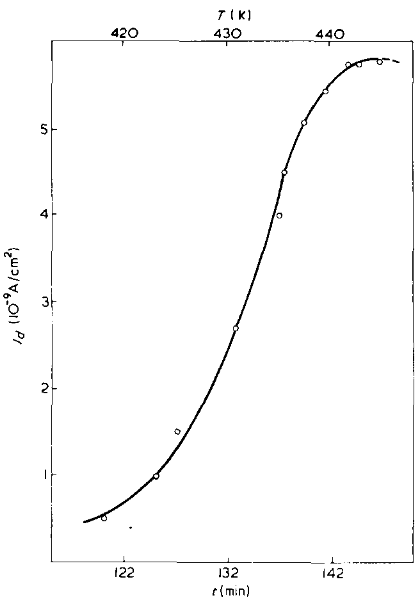

Figure 3 *TSD* current density (j_d) as a function of the temperature (T) and heating time (t) of the MMA sample

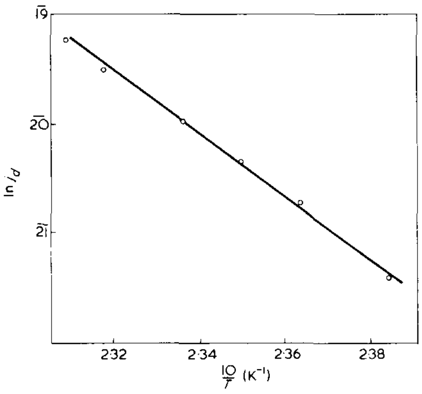

Figure 4 Logarithm of the *TSD* current density (j_d) as a function of the temperature (T), for the ascending portion of the $j_d(T)$ curve of *Figure 3*

DISCUSSION

In the opinion of many authors[4,5], the electric conductivity of polymers is probably due to some amounts of ionized impurities[4] and, maybe, to the presence of ions arising by thermal dissociation and background radiation[5].

The change in conductivity in the process of MMA polymerization is surely due to the decrease in concentration and mobility of the carriers. In the process of vitrification of the material, the polymerization rate decreases, as is apparent from the change in slope of the $\ln j = f(t)$ curve (*Figure 2*). These results are in qualitative agreement with those of Warfield and Petree[4] obtained in their study of isothermal polymerization of diallyl phthalate with 1.96% benzoyl peroxide.

The depolarization thermogram of *Figure 3* suggests the possibility of achieving a state of permanent polarization when polymerizing the material in a static electric field at room temperature. The effect observed resembles that reported by numerous authors[6–8] when studying samples polarized in a static electric field upwards of the glass transition temperature. Presumably, the nature of the mechanism underlying this effect is similar in both cases.

The linear $\ln j_d$ vs. $1/T$ dependence (*Figure 4*) points to the possibility of describing the changes in polarization at constant temperature in terms of a single relaxation time τ. Having recourse to the data for $U = 1.9$ eV $T_m = 443$K and $\lambda = 1$ degree/min, and using Arrhenius's formula, we obtain at $T = 300$K:

$$\tau = \tau_0 \exp\frac{u}{kT}$$

$$= \frac{kT_m^2}{\lambda u \exp(u/kT_m)} \exp\left(\frac{u}{kT}\right)$$

$$= \approx 10^{13} \text{ sec}$$

It is worth noting that, under our experimental conditions, no bubbles were formed in the samples. Therefore, the results were reproducible.

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Synthesis of poly {2,2 bis[4(*p*-aminophenoxy)phenyl] propane–terephthalic acid}

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INTRODUCTION

One of the greatest limitations of present commercial polymers is their inability to operate at elevated temperatures, due to their relatively low melting points. In recent years, therefore, intensive research programmes aimed at synthesising new thermally stable polymers have been initiated and many new organic polymers have been reported[1–7]. This report describes the synthesis of a new thermally stable aromatic polyamide containing phenylene oxide groups in the main chain. Several aromatic rings are present in the repeating unit, all of which are *para-para* linked. This is desirable, because, only then would the new polyamide be highly symmetric and hence thermally more stable than a non-symmetric structure[8–10]. Low temperature interfacial polycondensation technique was adopted in preference to high temperature melt condensation method because of its well-known advantages[11].

2,2-Bis[4(*p*-nitrophenoxy)phenyl] propane (II) containing the phenylene oxide linkage was first prepared from Bisphenol-A (I) and *p*-bromonitrobenzene. It was then reduced to the diamine (III) which was polycondensed with terephthaloyl chloride to form the polymer, poly {2,2-bis[4(*p*-aminophenoxy)phenyl] propane–terephthalic acid} (IV). As the complimentary compounds reacting are bifunctional, a condensation polymer (IV) is obtained. The reactions can be represented as follows by equation (1).

EXPERIMENTAL AND RESULTS

Dry sodium methoxide powder was allowed to react with Bisphenol-A in benzene medium and nitrogen atmosphere for 1 h. The methanol formed and benzene were distilled off and the pure dry sodium salt so obtained was then reacted with *p*-bromonitrobenzene in pyridine medium and nitrogen atmosphere. After about 9 h, the products obtained were extracted with ether, washed with alkali, and fractionated using column chromotography. The first fraction suspected to be the dinitro compound (II), on concentration gave yellow crystals. It was contaminated with *p*-bromonitrobenzene and this was removed using sublimation technique. The dinitro compound so obtained had a melting point of 117°–118°C. The analytical data, i.r. and n.m.r. spectra confirmed the structure (II). The i.r. spectra of the dinitro compound (II) showed peaks at 1018 and 1255 cm^{-1} corresponding to ether –C–O stretching frequency, in addition to all other expected group frequencies. The n.m.r. spectra of II showed a singlet at 1.75δ corresponding to 6 aliphatic protons, a quartet at $6.9–7.5\delta$ corresponding to 12 aromatic protons and a doublet at $8.1–8.45\delta$ showing that the 4-aromatic protons, *ortho* to the two nitro groups, are shifted to a lower field. The dinitro compound (II) was then reduced to give the diamine (III) with hydrogen in presence of Raney Nickel in tetrahydrofuran medium. The pale yellow crystals obtained had a melting point of 121°–122°C The i.r. spectra of the diamine (III) showed the important