Self-temperature-control heaters by graphite–poly(ethylene glycol) mixed systems: mechanism of electrical conduction

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We have found that graphite–poly(ethylene glycol) mixed systems constitute self-temperature-control heaters and that the self-controlled constant temperatures depend on the molecular weight of the poly(ethylene glycol). The mechanism of self-temperature-control for these systems cannot be explained in terms of volume expansion of the total system, which has hitherto been suggested for the self-temperature-control mechanism for systems such as carbon–rubber mixtures. It is found that the temperature dependence of the electrical resistance in a graphite–poly(ethylene glycol) system corresponds well to that of the dielectric constant in the corresponding pure poly(ethylene glycol) system. This leads to a model by which the mechanism of electrical conduction and self-temperature-control can be explained. The voltage dependence of the electric currents in graphite–poly(ethylene glycol) systems supports this model.

(Keywords: self-temperature-control; electrical resistance; dielectric constant; poly(ethylene glycol); graphite; plane heater)

INTRODUCTION

Many investigations concerning carbon-particle-loaded polymer resistors have been reported[1,2]. The resistances of these carbon-loaded polymer systems are reported to be moderately temperature-dependent[3]. However, some carbon-loaded polymer systems show switching characteristics: namely, the resistances of these systems show abrupt increases at certain temperatures[4-6]. The mechanism of electrical conduction in carbon-loaded polymer systems has been reported[1,7]. The switching characteristic, an anomalous increase in resistance, is explained in terms of volume expansion of the polymer matrix[4,5]. We have recently reported[8] that graphite carbon–poly(ethylene glycol) (GC–PG) mixed systems constitute self-temperature-control planar heaters, the operation of which depends on sharp increases in their resistances at certain temperatures. We have also reported that their self-controlled steady-state temperatures depend on the molecular weights of the constituent PGs. As is described later, the mechanism of self-temperature-control in GC–PG systems cannot be explained in terms of the volume expansion described above. In addition, GC–PG systems have unique characteristics. One of these is the sharp temperature response of the resistance: resistances vary by two orders of magnitude with a change of temperature of 1°C. Variations of the resistance, $\Delta R/R$, over the temperature range studied are 10^4–10^5. However, the mechanism of electrical conduction in GC–PG systems is not known. In this paper we will report the relation between the resistance of GC–PG systems and the dielectric constant in the corresponding pure PG systems. We will also report the effect of applied electric fields on electrical conduction in GC–PG systems. From these results the mechanism of electrical conduction in GC–PG systems will be tentatively presented.

EXPERIMENTAL

Several types of poly(ethylene glycol) (Dai-ichi Kohgyo Seiyaku) were used. These were nos. 600, 1000, 1540, 2000, 4000, 6000, 10000 and 20000, the number-average molecular weights of which were 600, 1000, 1450, 2000, 3050, 8200, 10900 and 21500, respectively. Graphite (Nishimura Kokuen) was 90–300M and the average particle size was 45 μm. PGs are crystalline polymers; it is easy to make spherulites of PGs. The particles of GC used are black scales, which consist of layers of planar crystals. Wako Pure Chemical n-hexatriacontane was used as received.

GC (28 wt%) was mixed with molten PG by a mechanical stirrer. Samples of GC–PG systems for resistance and current measurements were discs (2 mm diameter, 2 mm thickness) made by filling a through-hole in a Teflon plate with a GC–PG mixture in its molten state and sandwiching the plate with two Teflon plates. The top and bottom circular surfaces were painted with a silver paint in order to make them electrodes. Samples of rectangular shape (20 × 20 × 2 and 10 × 10 × 1 mm) were made by a similar procedure as described above. Plane heaters were made by sandwiching a GC–PG mixture in the molten state and copper-foil electrodes between two poly(ethylene terephthalate) films. The size of the plane heaters was 300 mm in length, 80 mm in width and

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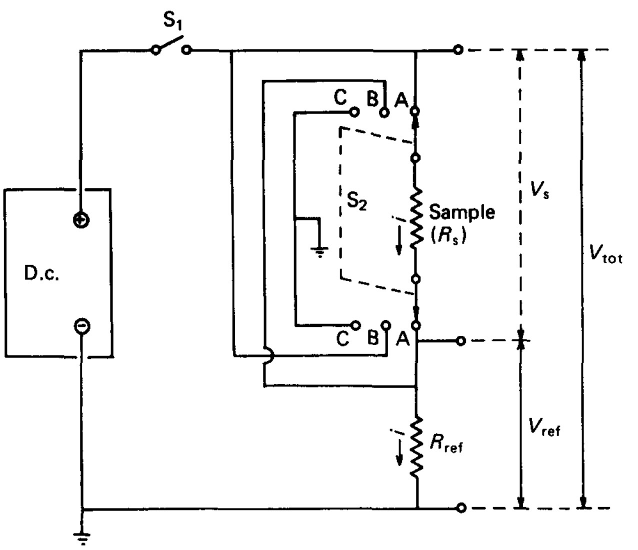

Figure 1 Electrical circuit for the measurements of resistances (R) and currents (i) in the sample

0.35 mm in thickness. The separation of the electrodes was 72 mm. In some cases, the resistances of the GC–PG samples were measured with a digital multimeter (Takeda TR 6841). In other cases, the resistances (or conductances) were obtained from the current (i) and the voltage applied to the sample (V_s). This was done with a series circuit, as shown in *Figure 1*, where R_{ref} is a reference resistor of metallic oxide (known value), V_{ref} and V_s are the voltages applied across the GC–PG sample and R_{ref}, respectively, and V_{tot} is the voltage applied to the circuit ($V_{tot} = V_s + V_{ref}$). D.c. power was supplied by a d.c. generator (A&D AD-8681) when the voltage was low and by a combination of 9 V dry cells when the voltage was high. The current (i) in GC–PG samples and the resistances of those samples (R_s) were obtained by measuring V_{ref} and V_{tot} as:

$$i = V_{ref}/R_{ref}$$

and

$$R_s = R_{ref}(V_{tot} - V_{ref})/V_{ref}$$

respectively. A digital oscilloscope (Nicolet 2090-204) was used for the measurement of V_{tot} and V_{ref}. The switch S_1 was kept on only during a one-shot pulse (about 0.3 s) for each measurement in order to avoid any increase in the temperature of the sample. The polarity of the sample was reversed by changing the position of the switch S_2 from A to B, and it was confirmed that the values of i and R_s were the same for both polarities. Samples were short-circuited in position C of S_2 when measurements were not performed.

The dielectric constants of pure PG systems were measured with an impedance meter (Mita Musen D-51S) using a hand-made cell. The cell consists of stainless-steel electrodes with a guard electrode (effective area $51 \times 51\,\mathrm{mm}^2$) and a silicone spacer (1 mm thick). Frequencies of 120 Hz and 1 kHz were used for the measurements. Since the results showed the same tendency for both frequencies, only the results for 120 Hz are given in this work.

GC–PG samples and pure PG samples were set in a temperature-controlled air bath (Komatsu-Yamato Coolnics CTR-520) during the electrical measurements. Samples were kept at the same temperature for at least 30 min in order to reach a steady-state temperature throughout the sample. Temperatures were measured by a chromel/alumel thermocouple and a digital multimeter (Takeda TR-6841).

RESULTS

Characteristic steady-state temperatures of plane heaters composed of GC–PG systems

When power (100 V a.c.) was supplied to a plane heater of GC–PG with a covering of polystyrene foam, the temperature on a surface of the heater increased gradually at first and then reached a plateau, at the latest within 10 min. Once the temperature reached the plateau, the temperature was maintained constant without any temperature-control device. The steady-state temperatures for those heaters of 27 wt% GC–PG systems are shown in *Table 1*. It is clearly seen in *Table 1* that the steady-state temperatures of the heaters depend on the molecular weights of their constituent PGs. As described below, the steady-state temperatures of GC–PG plane heaters result from abrupt increases in their electrical resistance at certain temperatures. These surface temperatures could be slightly lower than those inside.

Temperature dependence of the resistance of GC–PG systems and the dielectric constant in pure PG systems

Resistances for 28 wt% GC–PG systems were measured at various temperatures using a measuring voltage of 1 V. The results are shown in *Figures 2–6* as full circles for GC–PG nos. 20 000, 10 000, 6000, 4000 and 1540, respectively. In each system, the resistance increased gradually with increasing temperature over the lower-temperature region, then showed an abrupt increase (some of them of five orders of magnitude) at each characteristic temperature and finally decreased abruptly after passing through the maximum. Peak temperatures, at which resistances show maxima, are 65.2, 64.0, 62.8, 57.0 and 46.8°C for GC–PG nos. 20 000, 10 000, 6000, 4000 and 1540, respectively.

The dielectric constants (ε_r) of pure PG systems were obtained by measuring the capacitance of the cell filled with PG and that of the empty cell. Dielectric constants at various temperatures are shown together with resistances in *Figures 2–6* as open circles for pure PG systems nos. 20 000, 10 000, 6000, 4000 and 1540, respectively. The temperature dependence of the dielectric constant of pure PG systems is similar to that of the resistance in GC–PG systems: namely, the dielectric constant changes gradually over the lower-temperature region, increases

Table 1 Steady-state temperatures of plane heaters composed of 27 wt% GC–PG systems

PG	Number-average molecular weight	Steady-state temperature (°C)
no. 20 000	21 500	60.0
no. 10 000	10 900	58.0
no. 6 000	8 200	56.0
no. 4 000	3 050	51.9
no. 2 000	2 000	47.1
no. 1 540	1 450	40.0
no. 1 000	1 000	33.0

abruptly at each characteristic temperature, suddenly decreases after passing through the maximum and seems nearly constant in the higher-temperature region.

It should be noted from *Figures 2–6* that curves of the logarithm of resistances in GC–PG systems correspond

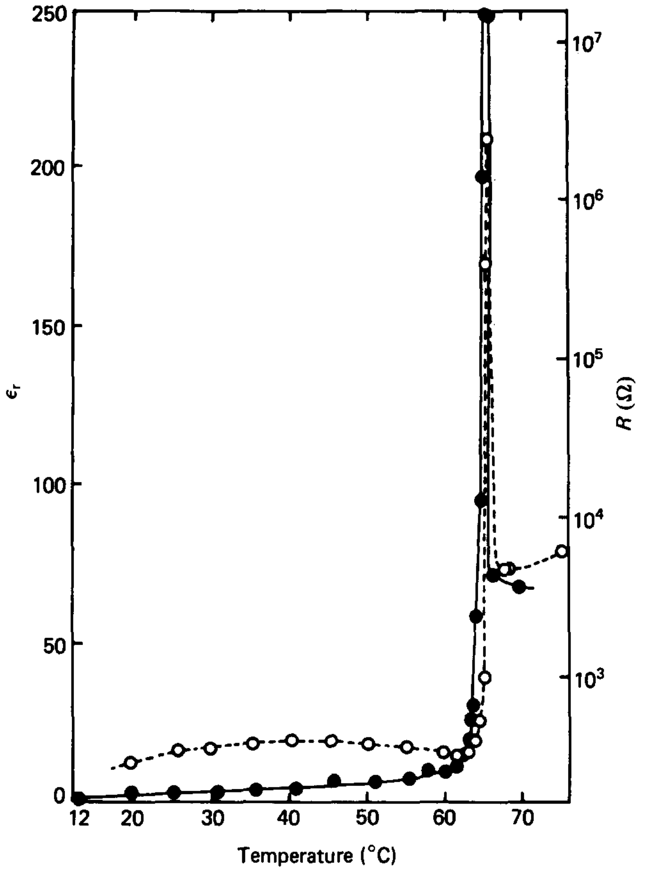

Figure 2 Resistance in 28 wt% GC–PG 20000 system (●) and dielectric constant in pure PG 20000 system (○) vs. temperature

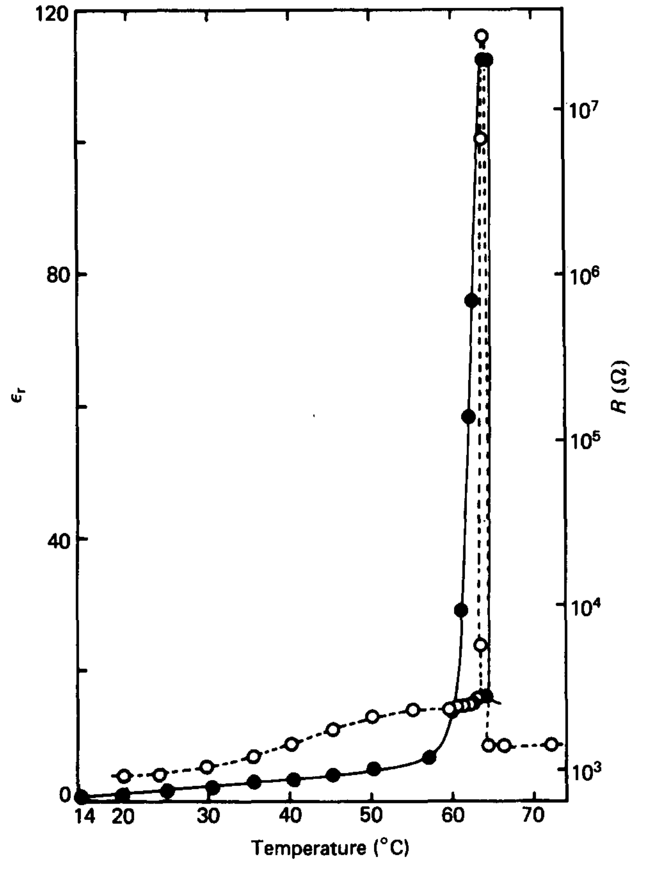

Figure 3 Resistance in 28 wt% GC–PG 10000 system (●) and dielectric constant in pure PG 10000 system (○) vs. temperature

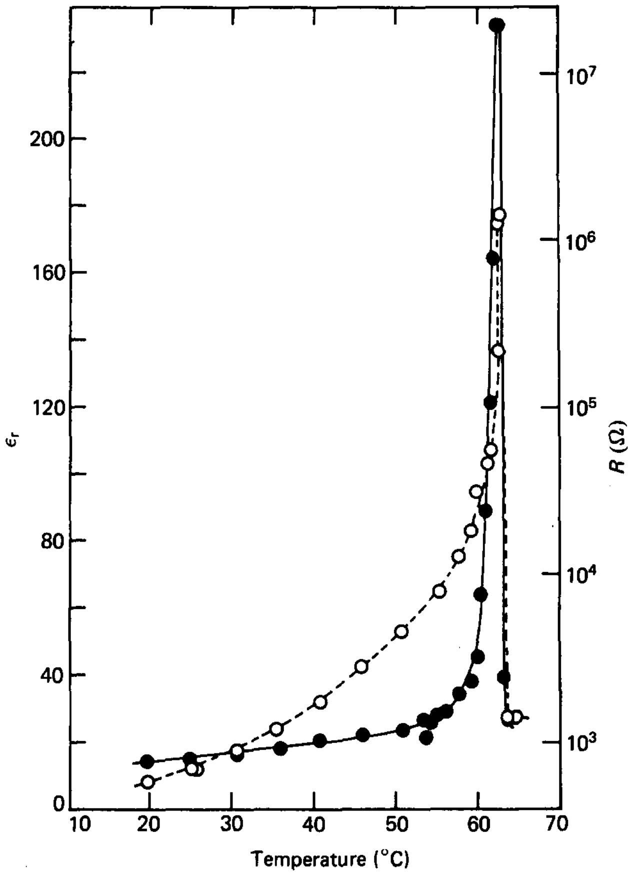

Figure 4 Resistance in 28 wt% GC–PG 6000 system (●) and dielectric constant in pure PG 6000 system (○) vs. temperature

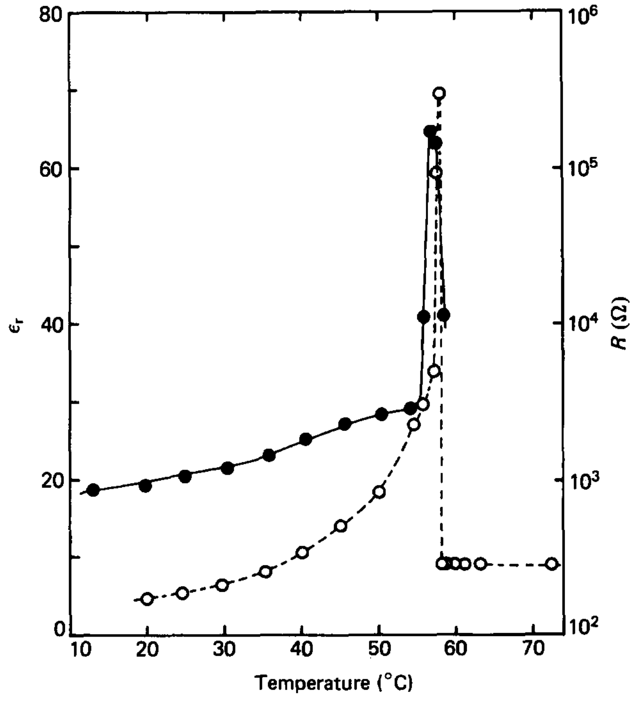

Figure 5 Resistance in 28 wt% GC–PG 4000 system (●) and dielectric constant in pure PG 4000 system (○) vs. temperature

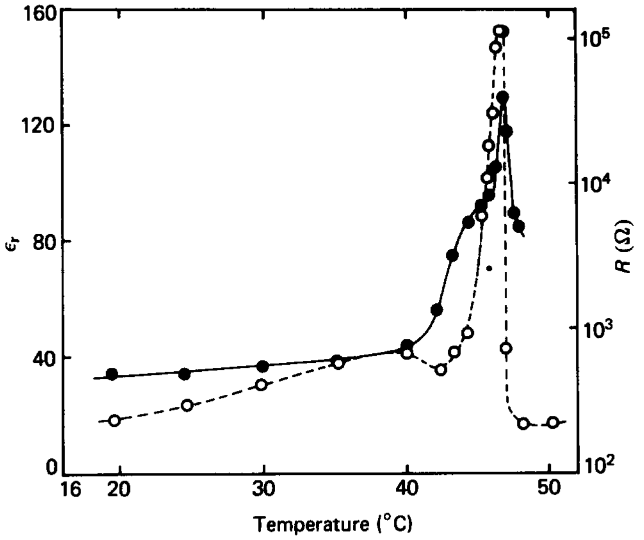

Figure 6 Resistance in 28 wt % GC–PG 1540 system (●) and dielectric constant in pure PG 1540 system (○) vs. temperature

well to those of dielectric constants in the corresponding pure PG systems; peaks of resistances in GC–PG systems overlap those of dielectric constants in the corresponding pure PG systems.

Agreement between the temperature dependences of the dielectric constant and the resistance is known for doped barium titanate ceramics[9,10]. In this sense the present GC–PG systems are similar to barium titanate ceramics. However, the characteristic of GC–PG systems differs from that of barium titanate ceramics in that the anomalous changes in the dielectric constant and resistivity in GC–PG systems appear over very narrow ranges around transition temperatures, whereas the changes in the dielectric constant and resistivity appear over a fairly wide temperature range in barium titanate ceramics.

The size of GC–PG samples for the measurement of resistance and current was much smaller than that of pure PG samples for the measurement of dielectric constant. Therefore, the heat capacity was different in those two systems. This might lead to small differences in peak temperatures of the resistance in GC–PG systems and of the dielectric constant in pure PG systems. The measurements were also carried out for GC–PG systems and for pure PG systems, where PGs were nos. 600, 1000 and 2000. These results were abbreviated because they showed similar tendencies.

Electric-field dependence of resistances

Resistances in the 28 wt % GC–PG 6000 system were obtained under various applied electric fields by the procedure described before. Resistances at various temperatures are plotted as a function of applied field in *Figure 7*. It is shown in *Figure 7* that resistances at all temperatures studied are constant at lower fields ($<10\,\mathrm{V\,cm^{-1}}$) and decrease with increasing applied field in the higher-field region. It is also shown that the decrease at higher field is greater at higher temperatures than at lower temperatures. These results are also similar to those for barium titanate ceramics[9].

Concerning the sample size, we have made thin samples (2 mm) in order to obtain high fields. However, since a large current is not desirable because of Joule heating, the cross section was also made small ($3.14\,\mathrm{mm^2}$). This results in a big difference in sample size between GC–PG systems and pure PG systems, as described already.

Field dependence of currents

Currents (i) in the 28 wt % GC–PG 6000 system at various temperatures are plotted as a function of applied field (E) in *Figure 8*. Experimental values of the log(i)–log(E) plot fit straight lines with slopes of 1 over the lower-field region, as shown in *Figure 8*. Thus, the samples are ohmic at all temperatures studied when the applied field is less than $10\,\mathrm{V\,cm^{-1}}$. The experimental points at higher fields deviate upwards from straight lines with slopes of 1.

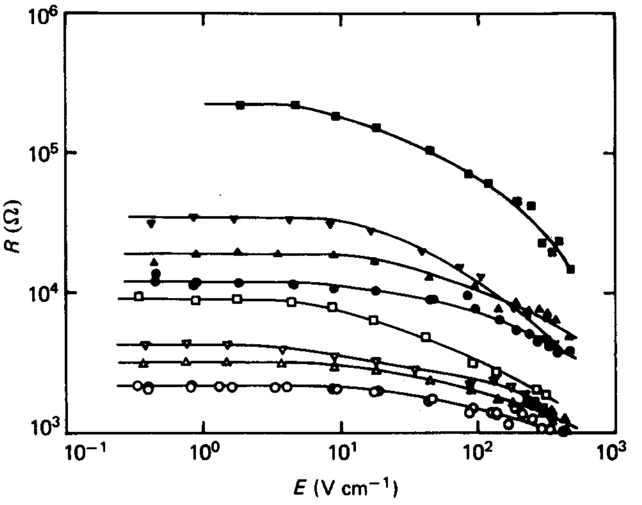

Figure 7 Resistances (R) in 28 wt % GC–PG 6000 system vs. electric field strength (E) at 19.8 (○), 40.5 (△), 50.1 (▽), 54.9 (□), 57.0 (●), 58.8 (▲), 60.1 (▼) and 60.9°C (■)

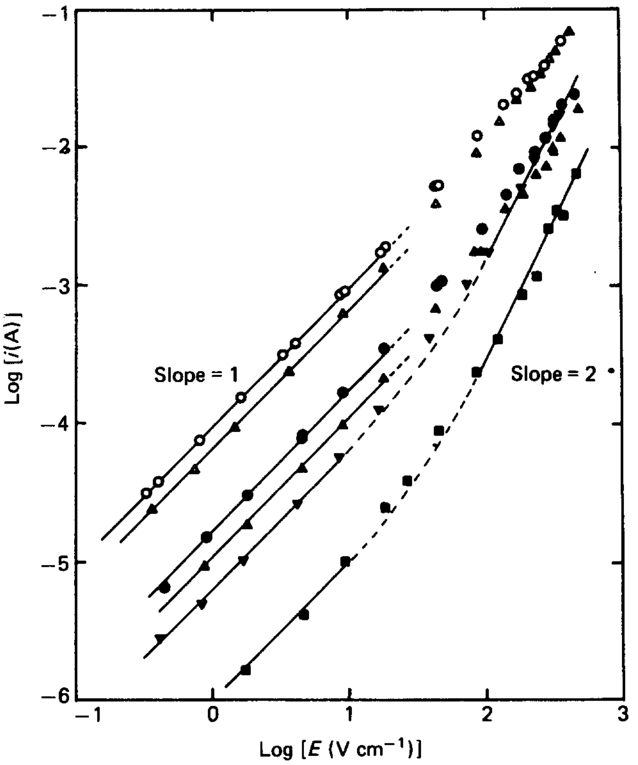

Figure 8 Logarithm of current (i) vs. logarithm of electric field strength (E) in 28 wt % GC–PG 6000 system at 19.8 (○), 40.5 (△), 57.0 (●), 58.8 (▲), 60.1 (▼) and 60.9°C (■)

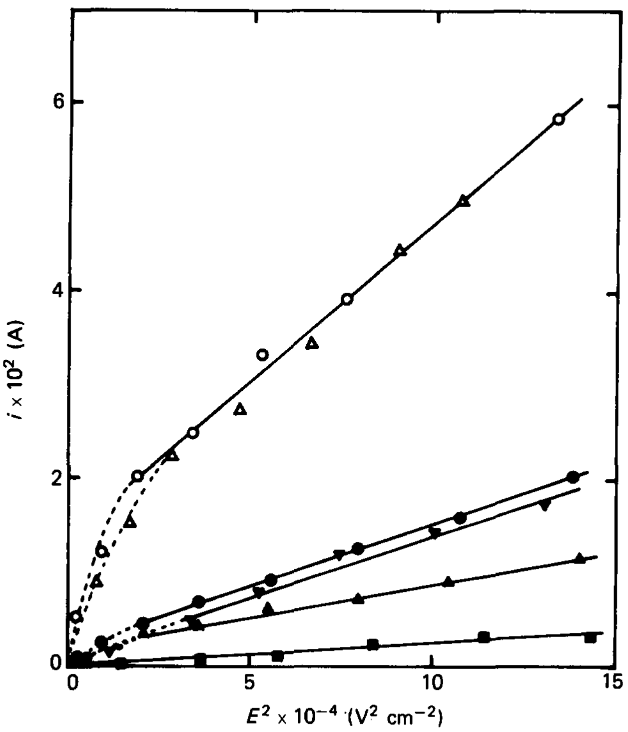

Figure 9 Current (i) vs. square of field strength (E^2) in 28 wt % GC–PG 6000 system at 19.8 (○), 40.5 (△), 57.0 (●), 58.8 (▲), 60.1 (▼) and 60.9°C (■)

It should be noted that the experimental points for GC–PG systems at higher temperatures fit a straight line with a slope of 2 when the electric field is higher, as shown in *Figure 8*.

DISCUSSION

Electrical conduction

In the first step, it is necessary to decide whether the electrical conduction in GC–PG systems is electronic or ionic. For GC–PG systems we have compared the resistances at 25°C with those at temperatures higher than the melting temperatures of constituent pure PGs. These higher temperatures were higher by 2–3°C than the melting points of the corresponding pure PGs. The samples for this purpose were made by putting a small amount of GC–PG mixture (28 wt % GC) into a glass test tube and also putting in copper plates with wires as electrodes. The results showed that for each GC–PG system the resistance at a temperature higher than the melting point of the constituent PG was higher by a factor of about 10 than that at 25°C. This means that resistances in liquids were higher than those in solids. Mobilities of ions are expected to be higher in liquids than in solids. The above results thus seems to indicate that electrical conduction in GC–PG systems is not ionic. However, we have to consider the possibility of charge accumulation as reported by Reboul[11]. If charges move faster to a contact region near an electrode than they are neutralized by giving up their carried charge to the electrode, then charge accumulates near one electrode. This causes a decrease in electric current and an increase in apparent resistance. Therefore, mobilities of ions cannot be directly related to total resistance if a space-charge layer exists near an electrode. We have applied a low voltage (1 V) to the sample described above at 25°C for 3 h and measured the current. In this case care was taken not to increase the temperature of the sample. The currents in GC–PG systems at 25°C were constant within experimental error for 3 h. The currents were also measured at temperatures higher than the melting point for 10 min. It was found that the currents were also constant for 10 min and that a change of polarity did not cause any change of the currents. The above two facts indicate that an ionic space-charge layer near an electrode does not exist in the GC–PG systems studied. Taking into consideration the above facts, i.e. (1) resistances are higher in liquids than in solids and (2) an ionic space-charge layer near an electrode does not exist, only electronic conduction is considered here.

Field dependence of currents

A change in slope from 1 to 2 for log(i)–log(E) curves, which is seen in *Figure 8* at higher temperatures, is reported by Reboul for carbon black–poly(ethylene chloride) and carbon black–rubber systems[2]. Although Reboul's result concerning the change in slope from 1 to 2 was obtained at 23°C, we did not find a change in slope of that size in our samples at 19.8 and 40.5°C within the range of fields studied. At first it seems that the currents at higher fields do not depend on the square of the field in the GC–PG 6000 system at lower temperatures. However, we found that this is not true, as is shown below. We have plotted i vs. E^2 in *Figure 9*. It is clear from *Figure 9* that i depends on E^2 at each temperature studied when E^2 is higher than 3×10^4 V^2 cm^{-2}, which corresponds to $E = 170$ V cm^{-1}. Therefore the i vs. E^2 plot in *Figure 9* clearly shows the E^2 dependence of i at higher fields, which is hard to see from *Figure 8* for GC–PG 6000 systems at 19.8 and 40.5°C. The deviation of plots from straight lines in *Figure 9* at lower fields is due to ohmic behaviour.

The results from *Figures 8* and *9* indicate that currents can be expressed as a linear combination of two terms, one including E and the other E^2, such as:

$$i = aE + bE^2 \qquad (1)$$

where a and b are coefficients. The requirement for a and b is that the first term of (1) must be dominant when E is low and the second term must be dominant when E is high. On the other hand, the following relation holds between i and E:

$$i = El\sigma \qquad (2)$$

where l is the distance between the electrodes and σ is the conductance (1/Ω) of the sample. In order for (1) to be compatible with (2), σ must be of the form:

$$\sigma = c + dE \qquad (3)$$

where c and d are coefficients.

In order to see whether (3) holds for the present systems, the values of σ are calculated for the GC–PG 6000 system and plotted as a function of E as shown in *Figure 10*. Since the values of σ at 19.8 and 40.5°C scatter at higher fields, these plots are shown at fields lower than 200 V cm^{-1}. This could be due to undesirable Joule heating because the resistances are lower at 19.8 and 40.5°C. The width of the one-shot pulse for measuring the resistances should have been shortened. Nevertheless, it is

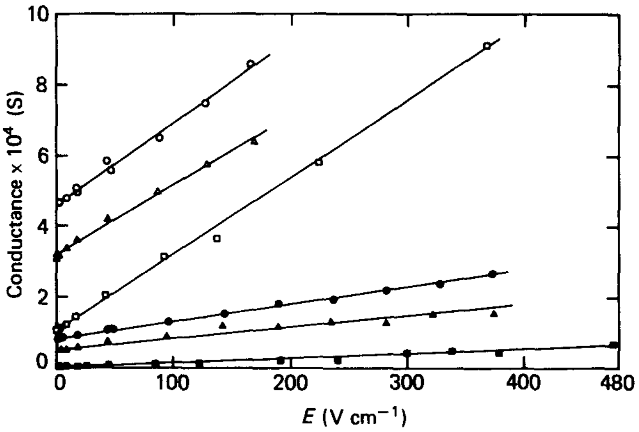

Figure 10 Conductance vs. electric field strength in 28 wt% GC–PG 6000 system at 19.8 (○), 40.5 (△), 54.9 (□), 57.0 (●), 58.8 (▲) and 60.9°C (■)

seen from *Figure 10* that relations such as (3) hold between σ and E for the GC–PG systems at each temperature studied.

We found in our experiments that the conductances of GC–PG systems can be expressed by a relation such as (3), as described already. This leads to a relation between i and E such as (1). As long as the requirement for the coefficients a and b is satisfied, the E and E^2 dependence of i, which is seen in *Figures 8* and *9*, can be explained.

Mechanism of self-temperature-control

The function of self-temperature-control in GC–PG heaters arises from an abrupt increase in resistance at each characteristic temperature. Let us imagine that electrical power is supplied to a GC–PG heater. If it overheats, resistance increases, the power dissipated (under a constant-voltage condition) drops precipitously and the sample cools. If it overcools, resistance decreases and the power dissipated increases, and so on. This is the common behaviour for the self-temperature-control heaters known at present. Hitherto, this behaviour has been explained in terms of volume expansion of the total system[4,5]. However, the mechanism of volume expansion is not applicable in our GC–PG systems, as described below.

We have compared the temperature dependence of resistance in 28 wt% GC–PG systems with that of resistance in 28 wt% graphite carbon–n-hexatriacontane (GC–HTC) systems. The sizes of the samples were 20 x 20 mm^2 in area and 2.5 mm in electrode distance for GC–PG systems and 10 x 10 mm^2 in area and 1 mm in electrode distance for GC–HTC systems. The results are shown in *Figure 11*. Resistance in the GC–PG system shows a much sharper increase than that in the GC–HTC system. Let us designate the temperature at which the resistance shows the maximum as $T_{R\max}$. It should be noted that resistance in the GC–PG system decreases abruptly after passing through the maximum whereas resistance in the GC–HTC system does not change too much in the corresponding temperature region. If the sharp increase in resistance results from volume expansion of the total system, then the resistance should not change too much at temperatures higher than $T_{R\max}$. Once distances between conducting particles increase by volume expansion, the resistance of the system should not decrease too much and should depend mainly on that of the polymer matrix. In the case of the GC–HTC system the abrupt increase of the resistance can certainly be explained in terms of volume expansion. On the other hand, the abrupt decrease in the resistance in the GC–PG system after passing through $T_{R\max}$ cannot be explained in terms of volume expansion, unless pure PG becomes conductive to such an extent that the decrease in the resistance by four orders of magnitude is explicable. Resistivity and density of pure PG 6000 are shown as a function of temperature in *Figure 12*. As is seen from *Figure 12*, the decrease in the resistivity of PG is only

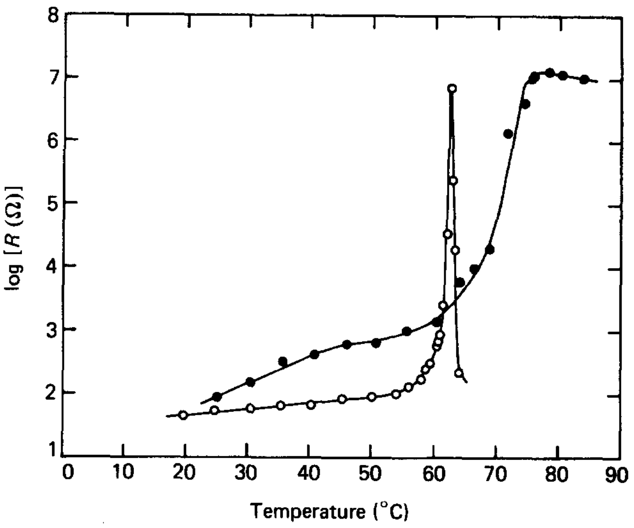

Figure 11 Log(R) vs. temperature in 28 wt% GC–PG 6000 system (○) and in 28 wt% GC–HTC (●)

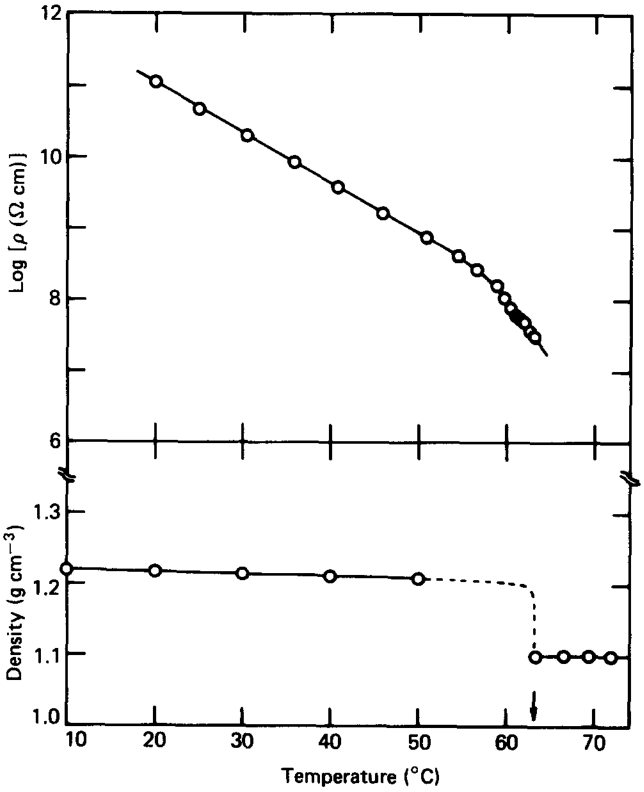

Figure 12 Resistivity and density of pure PG 6000 vs. temperature. Densities of solid PG were measured with a pycnometer and n-hexane as a solvent; those of liquid PG were done with a volumetric flask

small in the temperature region where the abrupt decrease in the resistance in the GC–PG system after passing through $T_{R\max}$ appears (*Figure 11*). Therefore the mechanism of volume expansion cannot give any reasonable explanation for the decrease in the resistance of GC–PG systems at temperatures higher than $T_{R\max}$.

On the other hand, it is necessary to consider the possibility that the abrupt increase in the resistance of GC–PG systems at temperatures lower than $T_{R\max}$ is due to volume expansion. When the volume of the total system expands, direct contacts between conducting particles cease and become gaps, and narrow gaps tend to be wider as a result of volume expansion. The electrical conduction in carbon-loaded polymer systems is composed of ohmic conduction by direct contacts of carbon particles and tunnelling conduction through narrow gaps between carbon particles[7]. As a result of volume expansion, ohmic conduction turns out to be minor and so tunnelling conduction is major. The relation between the electric current and the applied field at a temperature near $T_{R\max}$ is expected to be of the Fowler–Nordheim type. Therefore the electric current of these carbon-loaded systems at a temperature near $T_{R\max}$ is expected to show a strong field dependence when the field is high. This has been easily confirmed as follows. We took the data from Beuche's work[6] and replotted the logarithm of electric current (i) vs. the logarithm of electric field (E) in a carbon–(styrene–butadiene rubber)–wax system at 85°C and found that i is proportional to $E^{5.7}$ at electric fields around $40\,\mathrm{V\,cm^{-1}}$. We have also measured the relation between $\log(i)$ and $\log(E)$ in GC–HTC at 75°C, and a similar result ($i \propto E^{5.6}$, $E \approx 50\,\mathrm{V\,cm^{-1}}$) was obtained[12]. The GC used for GC–HTC systems was the same as for the present GC–PG systems. These two facts indicate that the abrupt increases in the resistance of these systems can be explained by volume expansion. However, in the case of GC–PG systems i depends only on E^2 at much higher fields at a temperature close to $T_{R\max}$. If the abrupt increase in the resistance in GC–PG systems is due to volume expansion, i should depend on E to a much higher power, as is the case for GC–HTC or carbon–(styrene–butadiene rubber)–wax systems.

The arrow in *Figure 12* indicates the temperature where the d.s.c. peak appears. The temperature where the resistance in a GC–PG system shows the maximum is slightly lower than the melting temperature of the constituent PG. In the case of the 28 wt% GC–PG system, the peak temperature at which the resistance shows the maximum is 62.8°C, whereas the d.s.c. peak of pure PG 6000 is 63.2°C.

In order to explain electrical conduction and the mechanism of self-temperature control in GC–PG systems, a new model is required. However the relation between conductance and electric field, such as (3), and the similarity between the temperature dependence of resistance and that of dielectric constant must be taken into account in this model.

We have assumed the following model in order to explain the field dependence of conductances for GC–PG systems such as (3). The total electrical resistance in a GC–PG system is the sum of the bulk resistance between the grains. The summation must be done through the total volume of the sample. At the present stage we do not intend to obtain a theoretical value of the sample resistance but we will try to give some theoretical explanation for the dependence of the conductivity on the applied electric field and temperature. Therefore, the summation is put aside. Since it is obvious that the resistances of boundary junctions are higher than those of bulk grains, we only consider the boundary junction between two GC grains in order to analyse the electrical conduction in GC–PG systems. We consider electronic conduction between two GC grains separated by a thin PG layer. Since GC grains are easily dispersed in PG matrices[8], GC grains could easily contact with each other through thin PG layers. It may happen that GC grains contact directly with each other without a PG layer between. We do not think such direct contact plays an important role in the present case. This will be discussed later. We assume electrons reside in the PG layers; in other words, PG acts in a sense as an electron acceptor. We consider unit area and take a one-dimensional model here. Let the number of filled acceptors per unit volume be n. The potential is given from Poisson's equation as:

$$\frac{\partial^2 \varphi_0}{\partial x^2} = -\frac{n(-e)}{\varepsilon_r} \tag{4}$$

which gives

$$\varphi_0 = \frac{nex^2}{2\varepsilon_r} \tag{5}$$

where x is the gap distance between two grains where electrons reside. Applied fields give an additional potential xE, so that the total potential φ is given as:

$$\varphi = \frac{nex^2}{2\varepsilon_r} + xE \tag{6}$$

Therefore the potential that an electron feels in the PG layer (ϕ) is given by:

$$\phi = \varphi(-e) = -\frac{ne^2x^2}{2\varepsilon_r} - exE \tag{7}$$

Then the conductivity through the PG layer can be expressed as:

$$\begin{aligned}\sigma &= \sigma_0 \exp(-\phi/kT)\\ &= \sigma_0 \exp\left(\frac{ne^2x^2}{2\varepsilon_r kT} + \frac{exE}{kT}\right)\\ &= \sigma_0 \exp\left(\frac{ne^2x^2}{2\varepsilon_r kT}\right)\exp\left(\frac{exE}{kT}\right)\end{aligned} \tag{8}$$

where k is Boltzmann's constant and T is the absolute temperature. Under the condition that $exE \ll kT$, (8) can be rewritten as:

$$\sigma = \sigma_0 \exp\left(\frac{ne^2x^2}{2\varepsilon_r kT}\right)\left(1 + \frac{exE}{kT}\right) \tag{9}$$

This is the same type of equation as (3). As already described, conductivity given by (9) under the condition $exE \ll kT$ results in a field–current characteristic such that i depends on E when E is low but on E^2 when E is high.

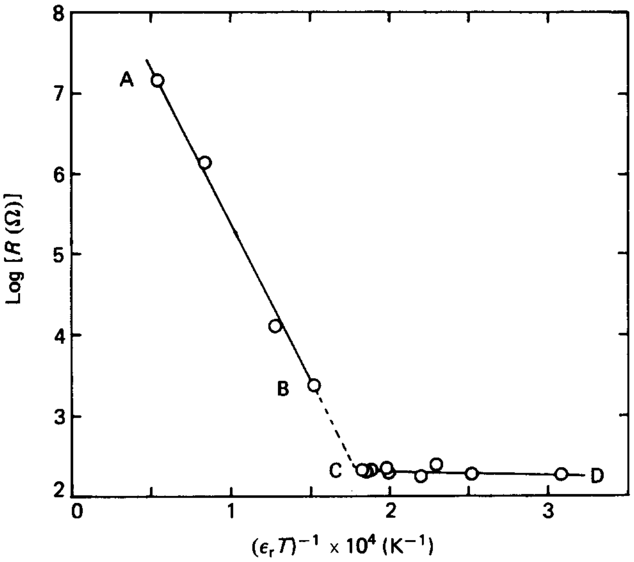

Figure 13 Log(R) vs. $(\varepsilon_r T)^{-1}$ in 28 wt% GC–PG 20 000 system

The values of field strengths in *Figure 10* are average ones throughout the sample. However, the field strength in (9) should be the one between two GC grains. At present it is not easy to obtain the field strength in a grain gap.

Unfortunately no evidence is available at present for PG as an electron acceptor. Electrons may be accepted in a PG layer by occupying an impurity level or by being trapped. Dodlet *et al.* have reported that electron mobilities in liquid ethers are approximately only twice those of anions at low temperatures and they explained this in terms of ion-like diffusion or phonon-assisted hopping between nearest-neighbour sites[13]. One of the present authors found that photoconductivity and optical photoabsorption spectra of trapped electrons in γ-irradiated PG (nos. 1000, 2000 and 20 000) at 77 K are similar to those in γ-irradiated alcohol glasses but not an ether glass such as 2-methyltetrahydrofuran (MTHF); the absorption maximum of trapped electrons in PG (nos. 1000 and 2000) is 700 nm whereas that in MTHF is 1200 nm and that in 2-propanol is 644 nm (ref. 14). These facts indicate that the electrons in PGs interact more strongly with matrices than do those in ethers. Therefore, electrons might reside in the PG layer between two GC grains. Further investigations are necessary on this point.

Using the model described above, we have expressed conductances as a function of dielectric constant (ε_r) and absolute temperature (T) by equation (8). From this it is possible to see whether the relation between dielectric constant in a PG system and resistance in a GC–PG system is like those shown in *Figures 2–6* and also whether resistance increases abruptly as shown in *Figures 2–6*. Resistivities of GC–PG systems are given from (8) as:

$$\rho = 1/\sigma = \rho' \exp\left(-\frac{ne^2x^2}{2\varepsilon_r kT} - \frac{exE}{kT} \right) \qquad (10)$$

Values of resistivities are generally obtained at lower fields where currents are ohmic so that the second term in the exponential in (10) can be neglected:

$$\rho = \rho' \exp\left(-\frac{ne^2x^2}{2\varepsilon_r kT} \right) \qquad (11)$$

In (11), x could be temperature-dependent because of the thermal expansion of PG and n is definitely a function of temperature (Fermi–Dirac distribution function which is included in (7)). Among the terms in the exponential, ε_r seems to show the biggest change in a very narrow temperature range. This is the range where the abrupt change in resistance is observed. So, this is the temperature region in which we are interested. From (11), it is clear that the resistivity in a GC–PG system increases or decreases with increasing or decreasing dielectric constant of PG, respectively. This agrees at least qualitatively with the results in *Figures 2–6*. If we can neglect the temperature dependence of n and x over the temperature range studied, then plots of log(R) vs. $(\varepsilon_r T)^{-1}$ should be linear.

Values of log(R) in the GC–PG 20 000 system are plotted as a function of $(\varepsilon_r T)^{-1}$ in *Figure 13*, where the values of R and ε_r are obtained from *Figure 2* at each specified temperature. The experimental curve in *Figure 13*, which is drawn to fit the points, consists of two parts, AB and CD, as shown in *Figure 13*. In region AB, the points fit the straight line AB, where R values vary by four orders of magnitude. Therefore it can be concluded that log(R) is proportional to $(\varepsilon_r T)^{-1}$ in region AB, which is expected according to (11). The variation of temperature in region AB is very small, namely 1.8°C. Thus, it can be expected that the temperature dependence of x and n is negligibly small in this temperature region of 1.8°C, which, according to (11), leads to the result that log(R) is proportional to $(\varepsilon_r T)^{-1}$.

It is difficult to discern whether the curve in region CD should be a straight line or not, because the variation in this region is small compared with the scatter in the experimental points. Since the variation of temperature in region CD is wide, n and x seem to be temperature-dependent. Then, values of n and x are no longer constant in region CD. This could be the reason for the change of curve from AB to CD. Further investigations are necessary on this point.

Direct contact of GC grains contributes to electrical conduction through the system. However, this does not contribute to the self-temperature-control except for the case of volume expansion. As described already, the mechanism of self-temperature-control in GC–PG systems cannot be explained in terms of volume expansion of the total system. Therefore we can say that direct contact of GC grains does not play an important role for the self-temperature-control process.

As described already, the present model explains satisfactorily the voltage dependence of conductivity (*Figure 10* and equation (9)), the agreement of temperature dependence of resistance in GC–PG systems with that of dielectric constant in constituent pure PG systems (*Figures 2–6*), and the relation between log(R) and $(\varepsilon_r T)^{-1}$. This model is similar to that for barium titanate ceramics[10]. However, this type of model has not been used for the explanation of electrical conduction nor of self-temperature-control in carbon-loaded plastic systems. Further investigations are necessary for n, x and their temperature dependence. Studies are now proceeding.

Anomalous peak of dielectric constant in poly(ethylene glycol)

The temperature dependence of the dielectric constant of a polymer is generally such that the dielectric constant decreases only bit by bit with increasing temperature but decreases remarkably at the melting point. Therefore PGs are extraordinarily different from other polymers.

In order to investigate the reason for the anomalous peaks of dielectric constant in PGs, we have performed experiments with the following two points in mind: (i) effect of electrodes and (ii) effect of impurity ion concentration. Three types of electrodes were used: stainless steel, silver paint and vapour-deposited aluminium. The cell with the stainless-steel electrodes was that used for the measurements shown in *Figures 2–6*. Casting samples of pure PGs were used and silver painted or vacuum-deposited with aluminium. Although the sizes of the samples were different for these three, the results were the same for the three types of electrodes: in each case anomalous peaks were obtained whose heights were about the same.

Impurity ions in PGs are Na^+ and K^+ and the concentration of these was about 300 ppm. We have used PG (CP-5000) as a sample of low ion concentration. The concentration of Na^+ and K^+ and the number-average molecular weight were 3 ppm and about 5000, respectively. We have measured the dielectric constant of PG (CP-5000) using the cell with stainless-steel electrodes and found an anomalous peak similar to those of other PGs. Therefore we can say that the reason for the anomalous peaks in PGs is not due to ions or electrodes.

Before we proceed with the discussion, we would like to remark on some points that we have noticed during our experiment. One is that the appearance of anomalous peaks is reversible: peaks are observed when the temperature is increased and peaks are also observed when the temperature is decreased from a temperature sufficiently above the peak temperature. The appearance of the peak when the temperature is decreased is affected by the rate of temperature decrease. The other remark is as follows. If we set the sample at the peak temperature and maintain the temperature constant, the dielectric constant shows a maximum. If we keep the temperature still the same after we get the maximum dielectric constant and wait for several hours, then the dielectric constant decreases very slowly. Taking the above two remarks into account, it seems that the appearance of the anomalous peak is a non-equilibrium phenomenon related to the phase transition between crystalline and molten states.

As described already, the existence of alcohol-type trapped electrons in γ-irradiated PG at 77 K indicates that there are microscopic portions that are as polar as alcohols. These polar portions probably result from ether (–O–) bonds orienting into favourable directions. In connection with this we think the anomalous peak of dielectric constant in a PG system is due to dipoles of –O– bonds oriented so that the summation of the vectors of all the dipoles has a component in one direction. Takahashi *et al.* reported studies of the crystal structure of PG and showed a (7/2) helix with symmetry isomorphous to the point group D_7, where (7/2) helix means that seven monomeric units turn twice per fibre period[15]. They later found[16] the (7/2) helix to be distorted from that whose symmetry is isomorphous to the point group D_7. According to their model, –O– bonds are oriented inside of the helix and O atoms look close to each other when the fibre is viewed cross-sectionally.

It is necessary to consider the phase transition of PGs from the crystalline to the molten state. It can be expected that the helices of PG fibres will be loosened when the phase is changed from crystalline to the molten state. According to the structure model of PG crystals described above, there is a possibility that the summation of vectors of all –O– dipoles has a component in one direction when the helices are loosened. Conversely the same situation could occur when disordered fibres of PG in the molten state turn to helices in the crystalline state. This explains well the appearance of the anomalous peaks of dielectric constant of PGs when the phase transition occurs. Unfortunately we do not have direct evidence for this at present. Further investigations are also necessary.

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