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An investigation into the low-frequency dielectric response of polyethylene glycols

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The dielectric response of a series of polyethylene glycols (PEGs) in the molecular weight range 3400–20 000 has been studied using low-frequency dielectric spectroscopy. In the molten state, a Maxwell–Wagner response was seen, indicating a conducting bulk in series with a barrier layer of high capacitance. The high-frequency conductance was shown to be activated, with a higher activation energy being seen for PEG 3400 than for the other three molecular weight samples, all of which possessed similar values. On solidification, the samples showed spectra which corresponded to a high-frequency response of comparatively small magnitude with a larger response being observed as the frequency was lowered. The low-frequency conductance decreased with chain length, although no other relationship was found between the components of the dielectric response and the molecular weight.

1. Introduction

Polyethylene glycols (PEGs) are water-soluble synthetic polymers which have the general formula $H(-OCH_2CH_2-)_nOH$. These materials have a wide range of applications, including use as pharmaceutical excipients, food additives and plasticizers [1]. It is important to develop methods of characterizing these materials in order both to control the quality of a particular batch and to understand the macroscopic properties of these systems. In the present study, the use of low-frequency dielectric spectroscopy in such an investigation will be described. While dielectric analysis is an established method of polymer characterization [2], comparatively little data are available regarding the low-frequency response (i.e. less than 100 Hz) of polymeric materials. This is largely because the low-frequency response was formerly considered to be an artefact of electrode polarization. However, there is a growing body of evidence [3, 4] that dielectric behaviour at very low frequencies may be characteristic of the material under study. Furthermore, it is often possible to ascribe the low-frequency response to specific regions within the sample, thus considerably extending the use of dielectric spectroscopy as an analytical tool.

2. Theory of dielectric analysis

The presence of charge separation within a molecule leads to the generation of a dipole moment. The charges giving rise to the moment may be present within the molecule irrespective of external factors, in which case the dipole is defined as being permanent, or alternatively may be induced by the presence of an electric field. In both cases the charges will tend to respond to the field in such a way as to reduce the free energy of the system to a minimum. It is the study of the nature and extent of this response that forms the basis of dielectric spectroscopy.

The dielectric behaviour may be measured by enclosing the sample between two parallel plate electrodes of area, A, and separation distance, d. The application of an electric field will cause the establishment of induced charges and the reorientation of dipoles, both of which will lead to a polarization, P, defined as the dipole moment per unit volume of sample. The overall charge on the plates, Q, is related to the applied voltage, V, i.e.

$$\mathrm{d}Q = C\mathrm{d}V \quad (1)$$

where C is the capacitance.

The response of the material may also be expressed as the relative permittivity, (ε_r), given by

$$\varepsilon_r = \frac{C}{C_o} \quad (2)$$

where C and C_o are the measured capacitance values in the presence and absence of the sample, respectively. The permittivity can be related to the polarization by

$$P = \varepsilon_o\varepsilon_r E \quad (3)$$

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where E is the field strength and ε_o is the permittivity of free space ($8.85 \times 10^{-12}\,\mathrm{Fm}^{-1}$). The relative permittivity can also be expressed in terms of the sum of individual susceptibility components, ie. $\varepsilon_r = \Sigma_\chi$.

The principal mechanisms of polarization can be summarized as follows.

(a) Orientational polarization; this involves the physical realignment of permanent or induced dipoles in the direction of the applied field. For a set of non-interacting dipoles, the total energy of the system, W is given by

$$W = kT - \mu E \cos\varphi \tag{4}$$

where μ is the dipole moment, kT is the thermal energy and φ the angle of the dipole relative to the field direction. Therefore, the energy of the system is at a minimum at any temperature when φ approaches zero.

(b) Molecular polarization; by this mechanism a dipole is induced either by distortion of the atomic electron cloud with respect to the nucleus or, in the case of ionic solids, by distortion of the charge lattice. Some degree of molecular polarization is invariably present when a sample is subject to an electric field.

(c) Charge carries polarization; in freely conducting materials such as metals, semiconductors at high temperatures or aqueous electrolyte solutions, a net flow of electrons or charged ions may be established between the electrodes, leading to direct current conduction. In insulating or purely semiconducting materials, charge may be transferred between localized sites by similar carriers or by charged molecular moieties. The energetics of this "charge hopping" mechanism bear a resemblance to both reorientational and d.c. conductivity processes, as the carrier behaves as both a relaxing dipole and as a moving charge particle [5].

On the application of an oscillating field to a dielectric material, the dipolar response becomes frequency dependent as the different polarization mechanisms exhibit varying degree of inertia with respect to the field. As molecular polarization is effectively instantaneous, this response follows the field irrespective of frequency when a low-frequency field is applied (10^4–10^{-2} Hz in the present study). Other polarization mechanisms, being non-instantaneous, lead to a phase lag between the field and the response, hence the degree to which these mechanisms apply vary with frequency. It is, therefore, often possible to distinguish between different polarization processes by monitoring the response over a range of frequencies.

The relationship between the polarization at time, t, and the susceptibility at a frequency, ω, is given by the one-sided Fourier transform

$$\chi(\omega) = \frac{\mathrm{d}}{\mathrm{d}E}\int_0^\infty \frac{\mathrm{d}P(t)}{\mathrm{d}t}\exp(i\omega t)\mathrm{d}t \tag{5}$$

For a single dominant process, the susceptibility can now be written in terms of the real and imaginary components

$$\chi(\omega) = \chi'(\omega) - i\chi''(\omega) \tag{6}$$

where $\chi'(\omega)$ is the real (storage) component, $\chi''(\omega)$ is the imaginary (loss) component at any given frequency and i is the square root of -1. The two components are related to the measured capacitance, C, and the dielectric loss G/ω, where G is the a.c. conductance of the system, via

$$\begin{aligned} C(\omega) &= \varepsilon_o \frac{A}{d}[\chi'(\omega) + \varepsilon(\infty)] \\ &= \frac{\varepsilon_o \varepsilon'_r A}{d} \end{aligned} \tag{7}$$

where $C(\omega)$ refers to the real part of the complex capacitance, $\varepsilon(\infty)$ is the permittivity at infinite frequency, A is the area of the electrodes and d is the inter- electrode distance (assuming an homogeneous sample). The dielectric loss is given by

$$\begin{aligned} \frac{G(\omega)}{\omega} &= \frac{\varepsilon_o A}{d}\chi''(\omega) \\ &= \varepsilon_o \varepsilon''_r \frac{A}{d} \end{aligned} \tag{8}$$

The qualitative significance of the complex permittivity may be seen by considering the applied voltage, V, and polarization current, I, which is the current generated by any movement of charges within the sample under an alternating field. For an ideal system whereby the energy dissipation (relaxation) is instantaneous, the two wave forms will be 90° out of phase and no energy loss occurs.

In practice, however, the physical inertia of the charge system effectively delays the polarization current, leading to an in-phase component between V and I. This component corresponds to a conductance process, resulting in energy loss via Joule heating. This process is therefore quantified by analysis of the conductance, G, of the system. It must be stressed, however, that the conductance represents a finite movement of charge between specific sites and does not involve a direct current. If a d.c. conductance is present, this will be seen in addition to the a.c. process described above.

3. Dielectric analysis of polymers

The dielectric behaviour of polymeric substances has been extensively reviewed [2, 6] and only a brief summary will be given here. Polymers are almost exclusively classified as insulators, with little direct current conductivity being in evidence. However, their dielectric properties are of interest for three reasons. Firstly, the absence of any sizeable d.c. conductivity renders the observation of a.c. relaxation processes, such as reorientation or charge hopping, comparatively simple, thus polymers are good model substances for examining dielectric behaviour in general. Secondly, the dielectric properties of polymers are of importance when choosing or designing insulators for cables and other applications. Thirdly, as we shall show, the dielectric response may give an indication as to the structure and behaviour of a particular sample, thus the technique may be used as an analytical tool in its own right.

Dielectric properties may be investigated by measuring the response over a range of temperatures at a single frequency. Any observed relaxations may then be defined according to the temperature at which the loss peaks occur. However, as several phenomena may occur at the same temperature depending on the frequencv of measurement, the processes may also be defined according to the frequency at which they occur at a constant temperature.

In the present study, the low-frequency response of a range of different molecular weight PEG samples will be investigated in both the molten and solid states. This has been performed in order to investigate the use of low-frequency dielectric spectroscopy as a means of characterizing these materials and also to examine the mechanisms associated with the dielectric response of polyethylene glycols over this frequency range.

4. Materials and methods

Polyethylene glycols (PEGs) 3400, 6000 (CSD, UK), 10 000 and 20 000 (BDH, UK) were ground in an end-runner mill and the < 250 μm fraction used. The materials were characterized by gel permeation chromatography, the measured number-average molecular weights and polydispersity values being reported elsewhere [7]. The dielectric responses of the PEGs were measured over the temperature range 273–373 K using a low-frequency dielectric spectrometer (Dielectric Instrumentation Ltd, UK). A voltage of 1 V r.m.s. was applied to the sample and subsequently analysed to allow calculation of the capacitance, C, and loss, G/ω. All reported data represent the average of at least three measurements taken by the instrument.

Measurements were performed using glass cells, prepared by depositing aluminium electrodes on to two glass slides using a vacuum evaporator (Edwards Ltd, UK). The size and shape of the electrodes were controlled by placing the slides in a template before coating. A U-shaped hole was cut out of a third slide. The three components were glued together in a staggered arrangement such that the opening was placed between the circular portion of the two electrodes, leaving sufficient aluminium exposed at either end to allow attachment of copper wires using Electrodag paint (Acheson Colloids Ltd, UK). Soda glass slides were used in all cases (76 mm × 22 mm, thickness 1.25 mm, electrode area 0.72 cm^2). The cell was mounted in a copper block and placed in a cryostat. A platinum thermocouple was placed in the copper block and the temperature measured and controlled (273–373 ± 0.5 K) by feedback to the heating coil via a Eurotherm temperature controller (Eurotherm Ltd, UK). The chamber was evacuated using a rotary pump to 10^{-1} torr (1 torr = 133.322 Pa) in order to improve temperature stability. For measurements below 313 K, cardice and acetone were used together as a coolant.

PEGs were added by heating the cells to a temperature just above the melting point of the sample, whereupon the powdered material was introduced into the aperture between the electrodes. The polymer component of the sample subsequently melted, allowing the material to flow into the inter-electrode gap. Preliminary studies indicated good reproducibility between samples prepared in this manner. The filled cell was left to solidify under ambient conditions before heating to the required temperature. In all cases, the samples were first heated to 373 K and then cooled sequentially to each of the desired temperatures. Solid state studies were conducted immediately after the molten studies, thus enabling the same sample to be used for each set of experiments. The cooling rate was approximately 20 °C h^{-1} for the molten studies and 10 °C h^{-1} for the solid studies.

5. Results and discussion

5.1. The molten response

Studies were carried out over the temperature range 333–373 K. For any particular molecular weight the spectra of log capacitance or loss against log frequency showed similar shapes at each temperature, but different displacements with respect to the axes. It was possible to superimpose the spectra, thus producing a master response curve, as shown for PEG 3400 in Fig. 1. The datum points in the diagram indicate the shift in a particular spectrum required to superimpose the curves on the response at 373 K. This normalization process is an established technique [8] and is useful for assessing the temperature dependence of the individual relaxation processes.

The results for PEG 3400 shown in Fig. 1 resemble the Maxwell–Wagner response for heterogeneous systems [4], which was developed to interpret the frequency-dependent behaviour of disperse systems and, in the simplest case, suggests a barrier capacitance, C_s, in series with a bulk resistance, $R_b(=1/G_b)$, thus giving a response with a relaxation time of R_bC_s. While this may be applicable to some electrode/electrolyte solution combinations, most systems show more complex responses. These may often be described by a series connected pair of parallel RC circuits where $C_s \gg C_b$ and the conductance $G_b \gg G_s$.

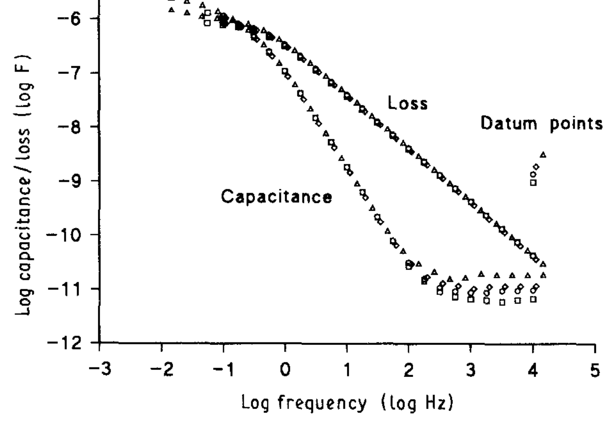

Figure 1 Dielectric response of molten PEG 3400 normalized to 373 K. (□) 373 K, (○) 363 K, (◇) 353 K, (△) 333 K.

The model describes a barrier layer with a high capacitance in parallel with a small conductance (seen at low frequencies) in series with the bulk sample, this having a small capacitance in parallel with a high conductance (seen at high frequencies). A typical response is illustrated in Fig. 2.

If one applies this model to the molten PEG 3400 system, the thickness of the two layers can be estimated using Equation 7. Examination of Fig. 1 shows the two corresponding capacitances to be approximately 10^{-11} and 10^{-6}F. The permittivity at 10^4 Hz for the sample at 373 K may be estimated from the capacitance and cell dimensions as being approximately 13. Assuming that this value applies to both the bulk and barrier layers, then using the above capacitance values to estimate the thickness of the surface and barrier layers yields values of approximately 1 mm and 10 nm, respectively. Such results imply that one RC circuit corresponds to the bulk response and the other to a much thinner layer, probably located at the electrodes. Surface barrier layers have been previously reported [4, 9] and may arise due to the adsorption of one or more layers of PEG molecules on to the aluminium electrodes. Chatham [9] has suggested that the adsorption process may occur via the unshared electron pair on the ether oxygen contributing to the electron pool of the metal surface. It should be noted that the presence of a thin barrier layer renders the calculation of permittivity values difficult, as it is necessary to know the exact thickness of the layer before ε may be derived accurately.

The response shown in Fig. 1 is described by the parameters given in Table I. These include the high- and low-frequency capacitances measured at 10^4 and 10^{-1} Hz in order to represent the response of the bulk and barrier layers, respectively. The logarithmic slopes of the loss and capacitance curves are close to the theoretical values of -1 and -2 required by the Maxwell–Wagner theory. Fig. 1 indicates that the normalized response does not superimpose over the whole frequency range, the high-frequency capacitance showing a different temperature dependence to the dispersive barrier/bulk mechanism. It can be seen from Table I that the high-frequency capacitance decreases disproportionately at 333 K, which is within the melting range of PEG 3400 (328–333 K). There may, therefore, be some crystallization at this temperature. Consequently, the system will become less mobile and the bulk permittivity will decrease, leading to the observed decrease in high-frequency capacitance.

The results for PEG 6000, 10 000 and 20 000 are given in Table II, with the characteristic parameters at 373 K being taken as representative. The shape of the curves obtained were similar to that shown in Fig. 1 for PEG 3400, hence it is assumed that the nature of the relaxation processes are also similar. The high-frequency conductance was found to be activated with the activation energies given in Table III. The values are somewhat lower than that of 0.62 eV previously reported for PEG 35 000 [10], although this may be due to differences in the PEG molecular weight. The high-frequency conductivity values were similar for PEGs 3400, 6000 and 20 000, although a lower value was found for PEG 10 000. The high-frequency capacitance slope was found to be greater

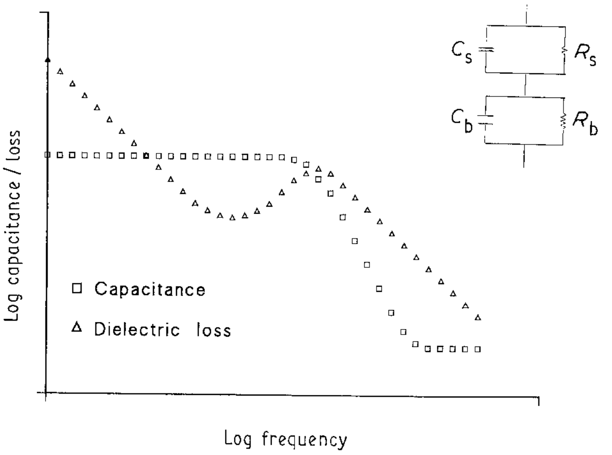

Figure 2 Maxwell–Wagner response corresponding to biphasic systems. C_s and C_b represent the barrier (surface) and bulk capacitances; R_s and R_b represent the barrier (surface) and bulk resistances.

TABLE I Characteristic values associated with the dielectric response of molten PEG 3400

Temperature	C(pF) at 10^4 Hz	C(μF) at − 1 log Hz	Conductivity (10^{-6} Mho) at 10^4 Hz	Slope G/ω 10^2–10^4 Hz	Slope C $10^{1/2}$–$10^{3/2}$ Hz
373	6.875	1.027	2.806	− 0.979	− 1.942
363	6.457	0.7463	1.776	− 0.993	− 1.948
353	6.191	0.5357	1.202	− 0.995	− 1.956
333	3.088	0.3088	0.5996	− 0.993	− 1.974

TABLE II Characteristic values associated with the dielectric response of molten PEGs at 373 K

Molecular weight	C(pF) at 10^4 Hz	C(μF) at 10^{-1} Hz	Conductvity (10^{-6} Mho) at 10^4 Hz	Slope G/ω 10^2–10^4 Hz	Slope C $10^{3/2}$–$10^{1/2}$ Hz
6000	8.135	0.7190	1.361	− 0.995	− 1.826
10 000	6.050	0.1535	0.3871	− 0.971	− 1.366
20 000	8.448	0.8837	1.423	− 0.998	− 1.769

for PEG 10 000, possibly indicating a different arrangement of PEG molecules at the electrode interface for this molecular weight sample, giving a dispersive nature to C_s [4].

The mechanism of the relaxation process may be assessed by considering the conductance values shown in Table I and Fig. 1. Conductivity values of this magnitude are unusual in saturated polymers [10] and are more likely to be due to localized charge migration than to reflect reorientation of the polymer chains alone. The exact nature of the charge itself is unclear, although trace impurities or absorbed water may act as carriers [11]. However, Binks and Sharples [10] indicated that the high conductance found for PEG 35 000 is an intrinsic property of the material. They proposed a model involving conduction via hydrogen ion generation and suggested that the process may be catalysed by trace amounts of carbonyl groups arising from oxidation of the sample. It is also noted that the capacitance (and hence permittivity) values are also high for a polymeric material and may further reflect the presence of impurities within the sample.

5.2. The solid response

Interpretation of the solid response of dielectric has been the subject of some debate. The ideal Debye model [12] is largely inapplicable to condensed materials as the underlying theory was designed for non-interacting systems. Jonscher [13] and Hill and Jonscher [8] have suggested a many-bodied model which allows interpretation of the solid response of a wide range of materials. It is this interpretation that will be assumed for subsequent discussions.

In the case of PEGs of this molecular weight range, the interpretation is complicated by the fact that these systems form lamellae which, in turn, are arranged to form spherulites [14]. The transition from the liquid to the solid state may therefore introduce a number of additional relaxing subsystems. The increase in viscosity and the establishment of long-range order within the system will considerably decrease the flexibility of the polymer chains, while the presence of spherulites and related structures in conjunction with amorphous material may cause the sample to act as a two-phase system, possibly resulting in interfacial phenomena at the crystallite surfaces.

The response of the solid may, therefore, differ from that of the melt in terms of both the energetics of similar relaxation mehanisms and the introduction of additional processes associated with the solidification of the sample. The assignment of the relaxation mechanisms according to their temperature dependence at a fixed frequency is not considered appropriate in the present case as the processes are not seen as discreet peaks when examined in the frequency domain. Moreover, the temperature range studied does not cover the glass transition temperature, as estimates of this value lie between 273 and 253 K [1], depending on molecular weight and crystallinity. The responses reported in the present study are therefore unlikely to be associated with glass transition phenomena.

The response for solid PEG 3400 is given in Fig. 3, normalized to 313 K, and the characteristic parameters of the responses of all four PEGs are given in Table IV. The spectra shown in Fig. 3 consist of two components, seen at high and low frequencies, with a crossover point between the capacitance and loss at approximately 10 Hz. The loss slope changes from − 0.535 to − 0.900 above and below the crossover point, with the capacitance increasing as the frequency is lowered. The low-frequency loss may reflect the onset of d.c. conductivity, which would be characterized by a constant capacitance and a slope of − 1. Alternatively, the slope may be a consequence of

TABLE III Parameters associated with the Arrhenius relationship between inverse temperature and log conductance at 10^4 Hz for molten polyethylene glycols

PEG molecular weight	Activation energy (eV)	Correlation coefficient
3400	0.405	0.9952
6000	0.249	0.9913
10000	0.253	0.9990
20000	0.235	0.9997

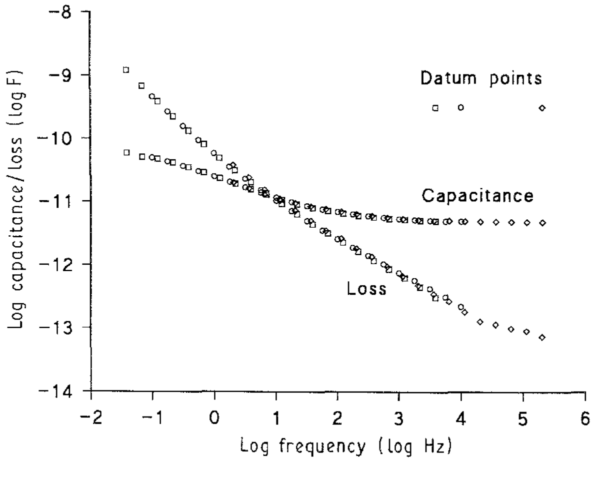

Figure 3 Dielectric response of solid PEG 3400 normalized to 313 K. (□) 323 K, (○) 313 K, (◇) 293 K.

TABLE IV Characteristic parameters associated with the dielectric response of solid PEGS

Molecular weight	C(pF) at 10^4 Hz	Conductance (10^{-9} Mho) at 10^4 Hz	Conductance (10^{-9} Mho) at 10^{-1} Hz	Capacitance (nF) at 10^{-1} Hz
3400	4.924	13.84	0.2911	0.05002
6000	6.233	21.68	0.1925	0.1339
10000	5.167	8.817	0.08831	0.05887
20000	5.525	7.557	0.07913	0.08547

strong low-frequency dispersion, as described by Dissado and Hill [15], which relates to charge hopping over relatively large distances. The two may be distinguished by examining the behaviour at low frequencies, as spectra showing low-frequency dispersion are characterized by an increase in capacitance as the frequency is lowered. There is therefore no evidence for the occurrence of such a process over the frequency range used in the present study.

Examination of Table IV indicates that the only clear relationship between the molecular weight of the samples and the response lies in the low-frequency conductance, whereby a decrease is seen with increasing chain length. This decrease can be ascribed to several factors. The increase in molecular weight tends to result in an increase in lamellar thickness, depending on the degree of chain folding [14]. Furthermore, the relative proportion of hydroxyl end groups decreases with molecular weight. Decossas *et al.* [16] have suggested that hydroxyl end groups in the amorphous fraction may contribute to the response, while Chatham [9] has suggested that the low-frequency response of PEG 4000 may be associated with the hydroxyl end groups which are rejected from the crystalline lamellae.

6. Conclusion

The study has suggested that the low-frequency dielectric response of molten PEGs comprises a conduction process in series with a barrier layer of PEG molecules adsorbed on to the electrodes. The conduction process was shown to be activated, while the high-frequency capacitance showed a marked decrease at lower temperatures, possibly due to crystallite formation within the sample.

On solidifying the PEGs, the shape of the spectra altered substantially. It is suggested that the solid response comprises two bulk processes; a high-frequency response of small magnitude and a lower frequency response which is considered to correspond to a d.c. conductivity process. This lower frequency response showed dependence on molecular weight, with a decrease in conductivity being observed with increasing chain length.

Overall, the study has demonstrated that low-frequency dielectric spectroscopy may be used to characterize PEGs in both the molten and solid states. Furthermore, it is suggested that the data obtained may be ascribed to various dielectric processes within the sample. While the nature of these processes is not yet fully understood, use of the low-frequency technique introduces the possibility not only of gaining a better understanding of the dielectric behaviour of the samples but also of providing characteristic parameters which may be compared to those of samples prepared under different conditions. As a result of such investigations, it should be possible to clarify the relationship between the dieletric response and the physical or chemical structure of the sample. Once this has been achieved, the application of the low-frequency technique to the study of polymeric systems would be extended considerably.

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