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Dielectric properties of poly(3-hydroxybutyrate) gels in dimethylformamide

F. Bordi
Dipartimento di Medicina Interna, Sezione di Fisica Medica, Università di Roma 'Tor Vergata', 00173 Roma, Italy

and C. Cametti*
Dipartimento di Fisica, Università di Roma 'La Sapienza', 00185 Roma, Italy

and A. Cesàro
Dipartimento di Biochimica, Biofisica e Chimica delle Macromolecole, Università di Trieste, 34127 Trieste, Italy

and G. Paradossi
Dipartimento di Scienze e Tecnologie Chimiche, Università di Roma 'Tor Vergata', 00133 Roma, Italy
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The thermal and dielectric properties of poly(3-hydroxybutyrate) in dimethylformamide at a concentration of $10\,\mathrm{g\,l^{-1}}$ have been investigated. This system shows a gel–sol transition as the temperature is raised from 25 to 90°C. Two endothermic peaks are revealed by differential scanning calorimetry at 70 and at 85°C respectively, which pair with two discontinuities in the electrical conductivity and in the permittivity when the sample undergoes annealing. A description of the observed process in terms of melting of microcrystalline domains is presented. Copyright © 1996 Elsevier Science Ltd.

(Keywords: poly(3-hydroxybutyrate); gels; dielectric behaviour)

INTRODUCTION

In recent years, the synergies of methodologies from different areas, such as from biotechnology and polymer science, have promoted a new boost in the research of new polymeric materials derived from genetically controlled microorganisms[1]. For example, it is now possible to obtain several biotechnological copolymers with regular composition and sequence of repeating units. Among these biopolymers, copolyesters of hydroxybutyrate and other similar alkanoates have led to systematic investigations of a large range of physical properties[2–6]. The naturally occurring poly(hydroxybutyrate) (PHB) still has a relevant role owing to its balance of production costs and physico-chemical properties. This polymer, known to microbiologists since the early 1950s, is industrially synthesized by fermentation of *Alcaligenes autrophus* under appropriately controlled conditions, and its copolymer with hydroxyvalerate is also obtained in good yield.

While the high crystallinity has been recognized for the homopolymer in its purified form[7] and it has been possible to deduce the molecular features from powder diffraction studies of the crystalline form[8], the experimental data on the PHB in the native granules have unambiguously proved a high mobility of the polymeric chains[9]. This amorphous state of 'living' PHB granules does not yet have a satisfactory explanation, but a kinetic hypothesis[10] and a plastifier effect[11] are proposed.

Given both the practical and scientific interest, the thermal behaviour of amorphous and crystalline morphologies of PHB under different conditions (e.g. quenched and spherulitic habits in blends with diluents) has been studied to a great extent[3–6,12]. The structural changes and the evaluation of the polymer–solvent interactions, induced in these mixed systems by temperature, have attracted interest in the attempt to understand the physical properties of these polymers, either in the solution state or in the gel state. In addition, owing to the biocompatibility and to biodegradability of PHB, possible applications of nano-crystalline matrices imbibed with a proper solvent may result in the field of biomedical and drug release technologies as well as in the alternative wet-spinning processing for packaging.

In this paper, a study of the audio to microwave dielectric properties of PHB in *N,N*-dimethylformamide (DMF) solution is presented. The formation of the gel phase and the occurrence of a thermal transition of PHB

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* To whom correspondence should be addressed

in dilute DMF solution have been recently shown by a number of optical techniques and by differential scanning calorimetry (d.s.c.)[13]. These studies attributed the endothermic peaks observed in the range 70–80°C to the fusion of small-size crystallites. In this solvent the polymer forms a gel consisting, at temperatures up to about 70°C, of a large ordered entanglement, due to three-dimensional networks of partially crystalline chains connected through amorphous chains, which may strongly interact with the solvent. At higher temperatures, these ordered crystalline domains undergo a melting process, eventually resulting in a sol state.

The aim of the present investigation is to characterize the gel phase and its phase transition by means of different experimental techniques in order to gain information on the structural changes occurring in the state at low polymer concentration. Dielectric measurements have been undertaken to determine whether or not the changes in the thermodynamic properties of the polymeric gel as a function of the temperature (as those shown by d.s.c.) result in a change of the electrical polarization, depending on the amount of the solvent involved in the melting of the polymer aggregates.

For this purpose, dielectric measurements have been extended over a wide frequency range, from 1 kHz to 1 GHz, and in the same temperature interval scanned in d.s.c. experiments. This approach aims at the distinct observations of the effect of the sol–gel transition on both the polymeric chain entanglements, at lower frequencies, and on the solvent, at higher frequencies.

Since PHB has a large total dipole moment along its axis due to the presence of a carbonyl group in each repeating unit, in analogy to poly(α-amino acid)s, dielectric polarization measurements should provide information on the chain arrangement, stabilized by attractive interaction between segments of chains involved in the build up of the entanglements in the gelling conditions adopted in this study. Moreover, dielectric measurements have been carried out at a fixed temperature as a function of time during the evolution of the overall system structure, in order to gain information of the gelation kinetics.

EXPERIMENTAL

Materials

The homopolymer PHB used in this study was obtained from the former Biopolymer Division of ICI (UK) with the trade name Biopol G08. The values of the molecular weight, M_w, and of the polydispersity ratio, M_w/M_n, of the sample investigated were 5×10^5 and 4.1, respectively. DMF was an RPE grade product from Carlo Erba (Italy) and it was used without further purification.

Gel samples were prepared by dispersing the polymer at a concentration of $10\,g\,l^{-1}$ in DMF at room temperature and gradually raising the temperature up to 110°C, under stirring. The clear PHB solution, slowly cooled at room temperature, yielded a firm opalescent gel. The gel was then transferred into the measurement cells of the microcalorimeter (or of the dielectric apparatus). The samples were equilibrated for at least two days at room temperature before the dielectric measurements were carried out. Gel formed directly in the conductivity cell showed the same dielectric features as the gel formed in the test tube and then transferred into the measuring cell.

Microcalorimetric measurements

A high-sensitivity micro-d.s.c. (Setaram) microcalorimeter was used. The two cells were filled with the sample and with the reference solvent, particular care being taken in reaching the proper weight balance of the two cells. In each measurement a cyclic heating and cooling programme was fixed with at least four heating scans in order to check for the reversibility.

The output signal of the microcalorimeter was connected to an IBM-PC through an interface Burr–Brown A/D, obtaining a parallel acquisition of the digital data and of the analogic data on the chart recorder[14]. The capability of the digital acquisition interface and real time software, coupled with the architecture of the IBM microprocessor, made it possible to select a frequency of up to 1000 data points s^{-1} with a real time control of the amplification up to 100 times. The software for data acquisition collects all data points in a single file of sequential data, normalized and formatted in such a way that the file can then be transferred to a larger computer for analysis. This solution was preferred in order to dedicate the acquisition function with higher controlling speed and to develop more sophisticated software for the data elaboration. Typically, a whole curve was scanned at $0.2\,K\,min^{-1}$ with a frequency of 1 or 10 Hz giving either 300 or 3000 data points per degree, with a total of 21 000 or 210 000 points for the interval from 25 to 95°C. Each of these segments was then subjected to a statistical and graphic analysis with commercial software.

Dielectric measurements

Complex dielectric measurements were carried out by means of two impedance analysers, Hewlett-Packard Models 4292A and 4191A in the frequency ranges 1 kHz–10 MHz and 1 MHz–1 GHz, respectively, and at different temperatures within the interval from 20 to 90°C. The input impedance (magnitude $|Z|$ and phase angle ϕ) was converted in the permittivity ϵ' and electrical conductivity σ of the sample by means of an appropriate equivalent circuit based on a parallel RC network. The cell constants, i.e. the capacitance of the cell, the stray capacitance and the inductance, were determined by calibration with standard liquids of known conductivity, following the procedure suggested by Bottomley[15] and Athey *et al.*[16]

Owing to the extremely wide frequency range investigated, two different dielectric cells were used. The first one consisting of fixed distance parallel plane electrodes at lower frequencies and the second one consisting of a short section of a coaxial cable fitted by means of a precision APC7-connector directly to the input of the meter, for the higher frequency range.

RESULTS AND DISCUSSION

Differential scanning microcalorimetry

The occurrence of a phase transition of PHB in DMF has already been reported elsewhere[13]. The existence of a large endothermic peak at around 70°C was attributed to a melting process. However, other findings have shown that samples with different thermal history or

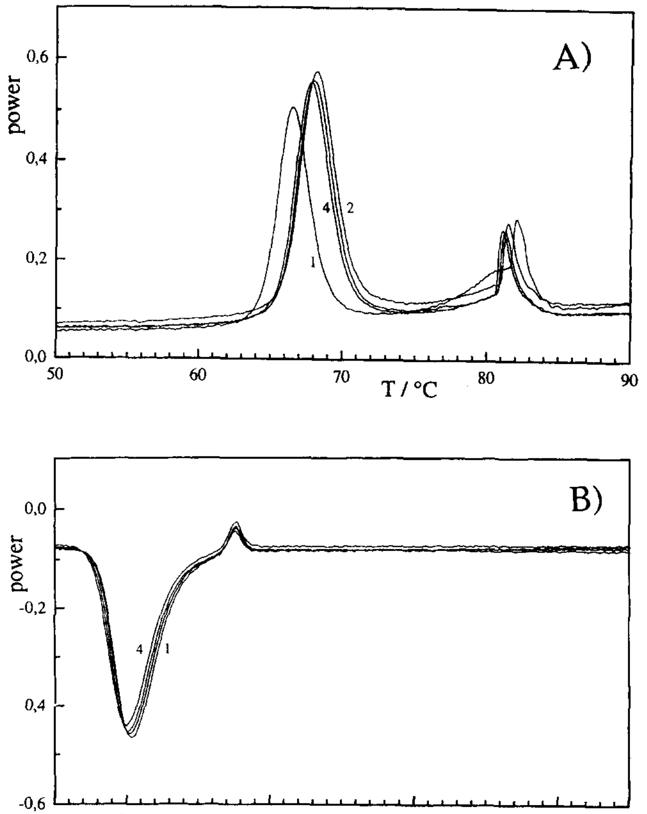

Figure 1 Thermograms recorded under repeated cycles of heating (A) and cooling (B) of the 10 mg ml^{-1} PHB–DMF system at a scan rate of 30 K h^{-1}. The thermograms clearly show that only the first 'heating run' (marked as 1) of the gel formed as described in the text discloses some slight difference from the other runs (marked as 2, 3 and 4)

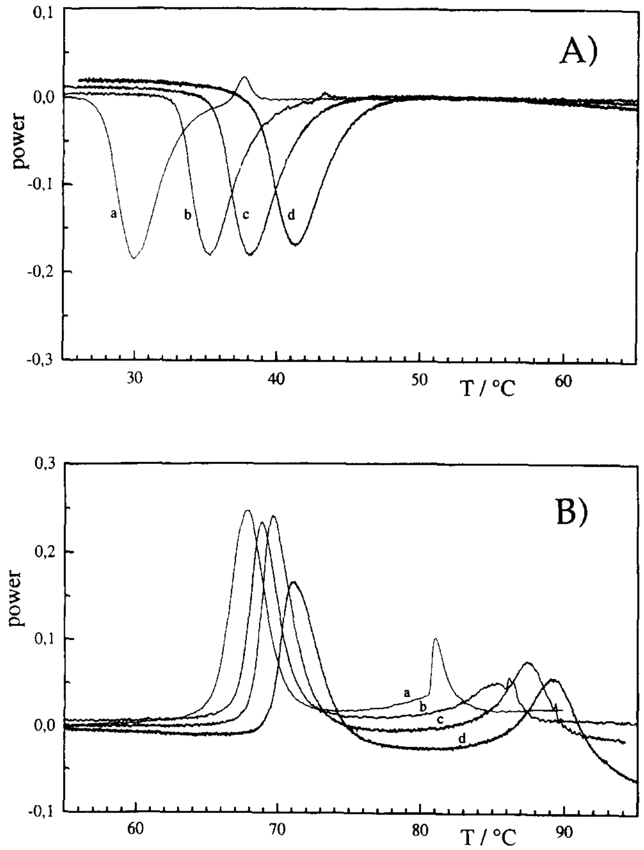

Figure 2 Dependence of the gel setting and melting temperatures on the scan rate. Cooling thermograms (A) and following heating thermograms (B) at scan rates 30 (curve a), 15 (curve b), 6 (curve c) and 3 (curve d) K h^{-1}. Note that the heating thermograms have been recorded with a heating rate equal to that used for cooling

concentration showed two endothermic peaks of different size, but with the total heat constant; in addition, several scanning cycles were shown to be reproducible, provided that a new gel phase was formed under reproducible cooling conditions after the thermal history of the solution was cancelled. Therefore, a full characterization of the gel–sol transition energetics and kinetics was carried out. Some of the original thermograms recorded under repeated cycles of heating and cooling the 10 mg ml^{-1} PHB–DMF system are reported in *Figure 1*. The 'first recorded' heating thermogram always discloses some slight difference from the other runs; this has been ascribed to the settlement of the gel in the calorimetric cell.

A cursory inspection of experiments carried out with different scanning rates (cooling and subsequent heating) provides the following observations. The temperature of gel formation on cooling is (obviously) a function of the scan rate, with the lower temperature at a higher scan rate. Within the explored interval, the instrument response has no effect on the recorded curve. The temperature range for the gel formation spans over 30–45°C for scan rate changing from 30 K h^{-1} down to 1 K h^{-1}. This dynamic cooling behaviour is commonly analysed by means of several semi-empirical theories as that proposed by Ozawa[17]. These theories predict an exponential dependence of the rate of transformation through an activation energy of the process. More interesting is the heating behaviour of gel formed at different cooling rates. In fact, the thermograms (either recorded with a constant heating rate or with a heating rate equal to that used for cooling) present a continuous change in the intensity and in the position of the two endothermic peaks, characteristic of the 'fusion-like' process of the gel phase. Most of the collected heating thermograms show two peaks, the area of the first peak approximately two-thirds of the total area. Only gels formed by very slow cooling or obtained at a temperature of 60°C show one peak only at higher temperature, which still depends on the crystallization conditions. *Figure 2* shows some thermograms obtained with different sets of cooling and heating scan rates.

This behaviour implies a difference in the morphology of the crystalline material involved. In our case, given the small size of the crystallites and the high crystalline content in the PHB gel, the bimodal fusion seems rather to be due to 'fringed micelles' interspersed in the 'lamella-like' crystallites.

As a final remark, the heat associated with the disruption of the gel (about 115 J g^{-1} for 10 mg ml^{-1}) has to be compared with the value of 146 J g^{-1} suggested for the heat of fusion of 100% crystalline PHB with $T_m = 186$°C[13]. Therefore, the value of the heat of transition suggests an estimation of the crystallinity of up to 80% in the gel phase. All these data confirm that a gel made of PHB at a concentration of 10 mg ml^{-1} forms a large amount of crystalline domains. The fact that an additional endothermic peak appears at higher temperatures suggests a diffuse non-homogeneity of density for the crystalline clusters dispersed in the system. The

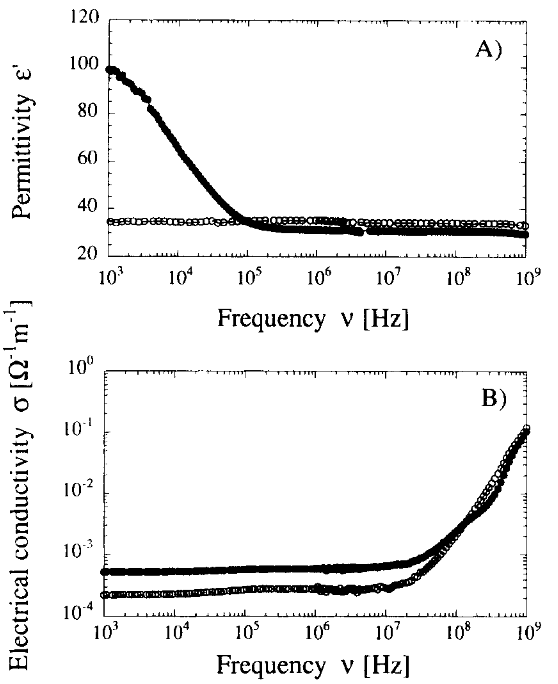

Figure 3 (A) The dielectric permittivity ϵ' of PHB in DMF gel at a concentration of $10\,\mathrm{mg\,ml^{-1}}$ in the whole frequency range investigated, from 1 kHz to 1 GHz, at a temperature of 25°C. The permittivity of the pure solvent (empty symbols) is also shown for comparison. (B) The electrical conductivity σ of PHB in DMF gel at a concentration of $10\,\mathrm{mg\,ml^{-1}}$ as a function of frequency, at a temperature of 25°C. The conductivity of pure solvent (empty symbols) is also shown for comparison

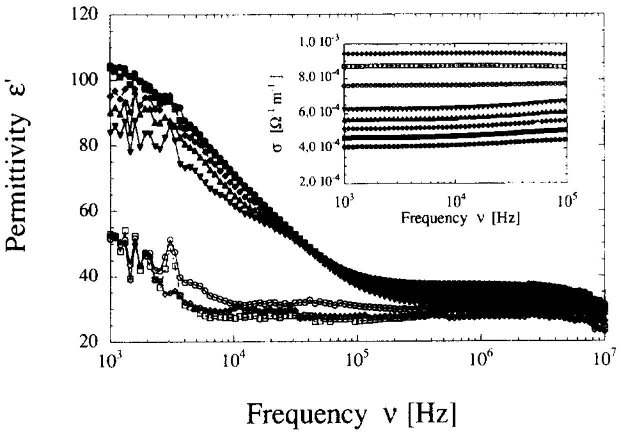

Figure 4 The permittivity ϵ' of PHB in DMF (polymer concentration: $10\,\mathrm{mg\,ml^{-1}}$) as a function of frequency, in the low-frequency region of the dielectric spectrum. The temperature has been varied from 20°C (●) to 90°C (◇) in steps of 10°C. The inset shows the low-frequency electrical conductivity as a function of frequency at the above quoted temperatures between 20 and 90°C. The full lines serve to guide the eye only

distribution of these crystalline clusters and of the 'interconnecting' amorphous fractions in the gel cannot be clarified solely by calorimetric data.

The dielectric spectrum

A typical dielectric spectrum of PHB in DMF at a concentration of $10\,\mathrm{mg\,ml^{-1}}$ and at a temperature of 25°C covering the whole frequency range investigated, from 1 kHz to 1 GHz, is shown in *Figure 3a*, compared to that corresponding to the pure solvent. *Figure 3b* shows the electrical conductivity of the PHB solution in the frequency range 1 kHz–1 GHz, at the same temperature.

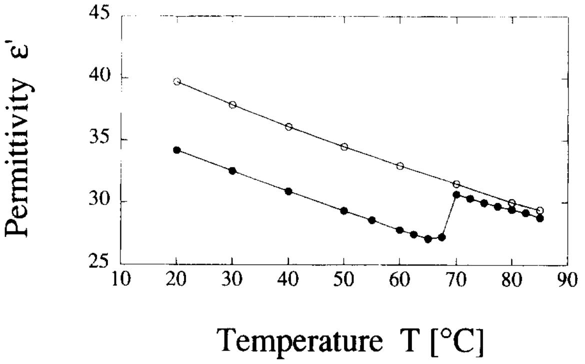

Figure 5 The permittivity ϵ' of PHB in DMF at a concentration of $10\,\mathrm{mg\,ml^{-1}}$ as a function of temperature. The permittivity of pure solvent (empty symbols) is also shown for comparison

As far as the permittivity ϵ' is concerned, the main feature emerging from the dielectric behaviour consists of a marked dispersion localized between 1 and 100 kHz followed by a further dispersion at frequencies higher than 5 GHz, the beginning of which is suggested by the small decrease in ϵ' at the high-frequency end of the spectrum. This low-frequency dispersion may be attributed to the presence of large polymer domains caused by ordered helical segments entangling on themselves, giving rise to heterogeneous regions in the polymer–solvent system. The presence of relatively rigid rod-like aggregates was suggested more than two decades ago by Cornibert *et al.*[18] on the basis of light scattering measurements.

It is worth noting that the magnitude of the low-frequency dispersion depends on the temperature, and the dielectric increment tends to become negligible as the temperature is increased towards that of the gel–sol transition. *Figure 4* shows the dielectric behaviour of PHB gel in the frequency range 1 kHz–10 MHz, at some selected temperatures below and above the transition temperature (about 70 °C). As can be seen, the large dispersion occurring at temperatures as high as 60°C disappears at 70°C, in correspondence with the endothermic peak shown by d.s.c. measurements and attributed to the melting of supramolecular domains of the gel state.

Dependence of the permittivity on temperature

After the initial decrease due to the presence of the low-frequency dispersion, the permittivity of the polymer gel remains nearly constant, up to approximately 100–500 MHz, indicating that the dielectric dispersion due to the polymer network does not contribute further to the observed dispersion. This means that, from an electrical point of view, a steady state condition is reached and any change in the value of the permittivity in this frequency range must be attributed to a modification of the solvent ordering in the neighbouring polymer. *Figure 5* shows the permittivity of the polymer solution averaged by the measured values in the frequency range 10–100 MHz, as a function of temperature. As can be seen, a marked increase in ϵ' occurs at a temperature around 70°C, where a phase transition takes place, the partial melting of the polymer network begins and the whole system evolves towards a sol state.

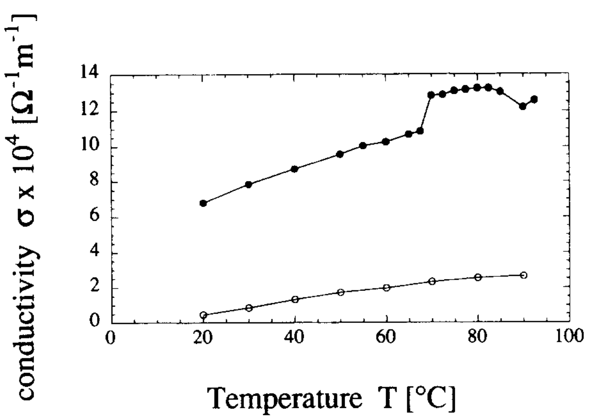

Figure 6 The electrical conductivity σ of PHB in DMF at a concentration of 10 mg ml^{-1} as a function of temperature. The conductivity of pure solution (empty symbols) is also shown for comparison

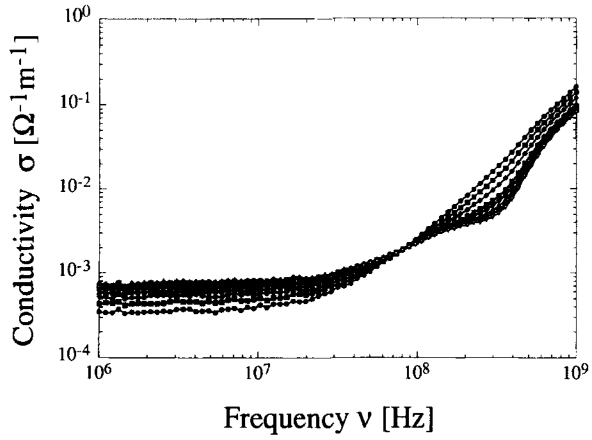

Figure 7 The electrical conductivity of PHB in DMF at a concentration of 10 mg ml^{-1} as a function of frequency from 1 MHz to 1 GHz at different temperatures, below and above the phase transition temperature, from 20°C (∇) to 85°C (●) in steps of 5°C. The curves evidence the presence of two different relaxation regions with relaxation frequencies of about 0.1–0.2 and 1 GHz, respectively. The full lines serve to guide the eye only

The increase in the permittivity towards the value of the pure solvent suggests that, in these conditions, the contribution due to the presence of large polymeric entanglements in the polymer–solvent system is gradually reduced and, to a first approximation, the solvent contribution to the permittivity remains the only relevant one. The apparent amount of the solvent involved in the microcrystalline structure can be evaluated using methods analogous to those used in the investigation of the dielectric properties of heterogeneous systems. The most widely used expression for heterogeneous mixtures that relates the complex dielectric constant of the bulk materials to that of the solution is given by the Maxwell–Fricke equation[19]:

$$\frac{\sigma^*}{\sigma_m^*} = \frac{f\sigma_m^* + \sigma_p^* - \Phi f(\sigma_m^* - \sigma_p^*)}{f\sigma_m^* + \sigma_p^* + \Phi(\sigma_m^* - \sigma_p^*)} \tag{1}$$

where σ_m^*, σ_p^* and σ^* are the complex conductivities of the solvent, the polymer and the solution, respectively, Φ is the volume fraction of the dry polymer and f is a shape factor whose value depends on the geometry of the solute molecule ($1.5 < f < 2.5$). Assuming thin aggregates of rod-like polymer chains with random orientation ($f = 1.5$) and for the permittivity of the polymer molecules a value of 3.5 with a density of 0.812 g cm^{-3}, it is possible to evaluate the fractional volume of the system 'immobilized' in the gel structure. For temperatures below that of the sol–gel transition, an amount of about 7% w/w (approximately constant) of solvent is strongly immobilized and does not contribute to the permittivity of the system. This value falls to about zero at temperatures higher than 70°C.

In correspondence to the peak of the permittivity at the transition temperature, a similar behaviour occurs in the electrical conductivity, as shown in *Figure 6*, when the conductivity rapidly increases at around 70°C.

The conductivity dispersion

Figure 7 shows the conductivity behaviour of PHB solutions as a function of the frequency at different temperatures between 20 and 95°C. As can be seen, each curve displays the typical conductivity dispersion of a heterogeneous system composed of regions with different conductivities. The main feature that emerges from the observed behaviour of the conductivity as a function of frequency is the appearance of two separate conductivity dispersions whose relaxation times heavily depend on the temperature.

Low-frequency dielectric relaxation of annealed sample

Finally, it must be noted that the gel time is probably a function of the temperature, since lower temperatures result in a shorter time of gelation, as suggested by similar results obtained by measurements of turbidity at controlled temperatures[13].

As pointed out above, some of the features in the dielectric behaviour observed in these systems could depend on the procedure adopted to form the gel state starting from a polymeric solution at temperatures well above that of the sol–gel transition temperature. To this end, some further experiments have been carried out in which the gel was formed by annealing a PHB solution, prepared according to the procedure described above, at a temperature of 50°C for a period of 24 h prior to measurements. This method was adopted to anneal the gel phase into more ordered domains, in analogy with standard crystallization procedures to increase regularity in the crystals. In the present case, the annealing temperature was chosen to ensure that the polymer mobility was always high enough to have an optimal packing with relatively short equilibration times.

The dielectric measurements were carried out in the low-frequency region of the interval previously investigated, from 1 kHz to 10 MHz, where the influence of the polymer clusters should be more easily shown. *Figure 8* shows the dielectric dispersions of the polymer solution at different temperatures, starting from 10°C up to 90°C. The dielectric increment of the PHB annealed samples falls abruptly as the transition temperature (at about 70°C) is reached. This feature is more clearly depicted in *Figure 9* where the low-frequency permittivity (at 1 kHz) is shown as a function of temperature. The plot shows the decrease in the permittivity at the transition temperature and moreover indicates a further decrease, at about 85°C, in analogy to the observed behaviour in the calorimetric measurements. The inset in *Figure 9* shows the corresponding results obtained in the polymer

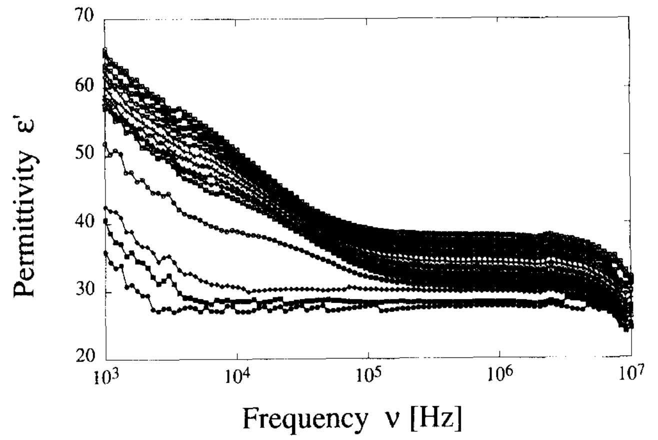

Figure 8 The permittivity ϵ' of PHB in DMF (polymer concentration: $10\,mg\,ml^{-1}$) as a function of frequency, in the low-frequency region of the dielectric spectrum. The samples were obtained after the thermal treatment described in the text. The temperature has been varied from 20°C (□) to 85°C (●) in steps of 5°C. The full lines serve to guide the eye only

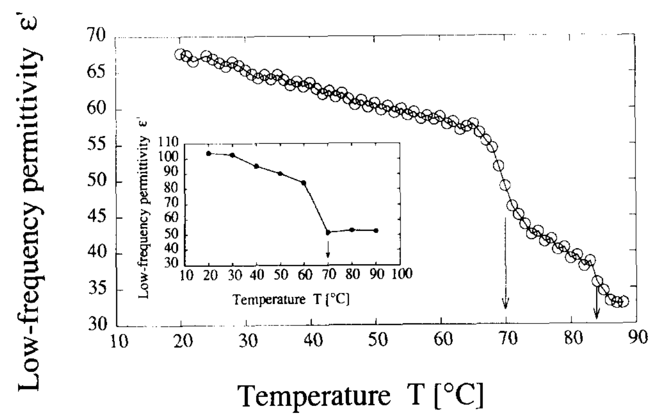

Figure 9 The low-frequency (1 kHz) permittivity ϵ' of PHB in DMF (polymer concentration: $10\,mg\,ml^{-1}$) as a function of temperature. The samples were obtained after the thermal treatment described in the text. The arrows mark the sol-gel transition temperature and the transition at higher temperature. The inset shows the corresponding low-frequency permittivity in the sample without the thermal treatment

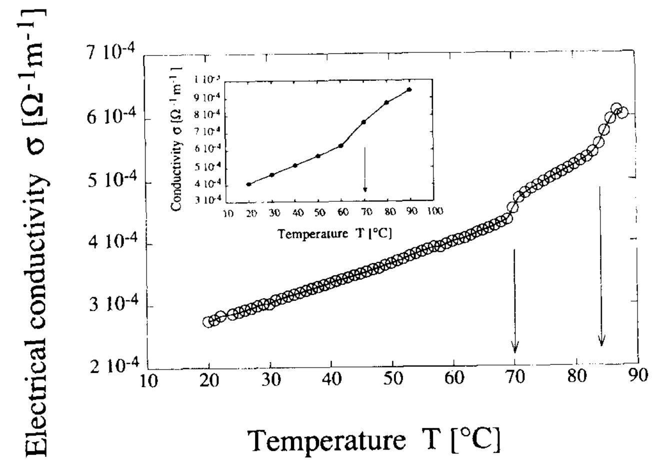

Figure 10 The low-frequency conductivity σ of PHB in DMF (polymer concentration: $10\,mg\,ml^{-1}$) as a function of temperature. The samples were obtained after the thermal treatment described in the text. The arrows mark the sol-gel transition temperature and the transition at higher temperature. The inset shows the corresponding low-frequency conductivity in the sample without the thermal treatment

solution without the thermal treatment. In this case, only one large increment of the dielectric permittivity is present, typical of systems with a higher degree of heterogeneity, while the absence of the transition at higher temperature should be noted. Similar findings are even more evident in the low-frequency conductivity behaviour shown in *Figure 10*, where the transition at high temperatures appears quantitatively more significant than the change at lower temperatures.

The results of dielectric measurements shown in *Figures 9* and *10* evidence that, in samples undergoing thermal treatment, both the low- and high-temperature transitions are detectable, although the latter is less marked in comparison to the corresponding transition observed in the d.s.c. experiment, where the peak shifts towards higher temperatures. This can be due to the different heating scan rates of the different experiments. Moreover, it must be stressed that some other small quantitative differences observed in d.s.c. and dielectric experiments with annealed and non-annealed samples are probably due to the different 'levels of structure' detected by the different methods.

The kinetics of gelation

All the reported data confirm that the gelation process of PHB in DMF consists of a local organization of macromolecular clusters with a remarkable amount of crystallinity. Isothermal kinetic studies have been carried out on the gel formation of PHB in DMF solution ($10\,g\,l^{-1}$) stored at constant temperature after rapid cooling from a higher temperature. *Figure 11* shows the low-frequency dielectric dispersion during the chain rearrangements occurring in the solution rapidly brought to a temperature of 40°C, after storage at 90°C for about an hour. The kinetics of 'crystallization' was followed by means of the time dependence of the dielectric increment of the low-frequency dispersion at a given temperature. The formation of the gel phase is clearly seen (*Figure 11*) by the progressive increase of the dielectric increment of the low-frequency dielectric dispersion. If the magnitude of the dielectric increment reflects the fraction, h, of polymer that undergoes the phase transition, then:

$$h = \frac{\epsilon(t) - \epsilon_\infty}{\epsilon_s - \epsilon_\infty} \qquad (2)$$

where $\epsilon(t)$ is the permittivity at time t, and ϵ_s and ϵ_∞ are the low- and high-frequency limits of the considered dispersion, respectively.

The kinetics of bulk crystallization processes is usually treated by the Avrami semi-empirical equation[20–22]:

$$h = 1 - \exp\left[-\left(\frac{t}{\tau}\right)^{\beta}\right] \qquad (3)$$

Although the use of this equation for a microcrystalline gel phase may be a quite drastic assumption, the qualitative support of this approach has been used to interpret the time dependence of the dielectric increment at constant temperature.

According to this equation, the crystallization process depends on two parameters, the Avrami exponent β and time constant τ, respectively. Both parameters can be determined by the slope and the intercept of the straight line obtained, for example, by plotting $\log[-\ln(1-h)]$ vs

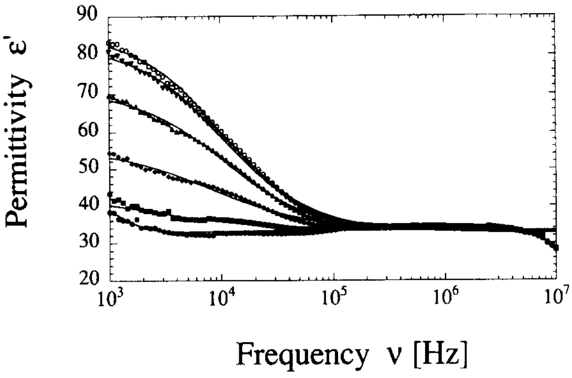

Figure 11 The permittivity ϵ' of PHB in DMF at a concentration of $10\,\mathrm{mg\,ml^{-1}}$ as a function of frequency during the time evolution of the gelling process (temperature of the measuring cell: 40°C). (●) $t = 0\,\mathrm{min}$; (□) $t = 10\,\mathrm{min}$; (◆) $t = 20\,\mathrm{min}$; (△) $t = 30\,\mathrm{min}$; (▽) $t = 40\,\mathrm{min}$; (○) $t = 50\,\mathrm{min}$

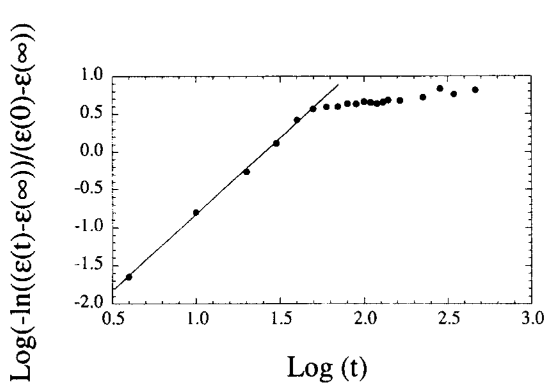

Figure 12 Avrami plot of $\log(-\ln(1-h))$ vs $\log t$ at 40°C

$\log t$. *Figure 12* shows the data plotted according to equation (3) as a function of $\log t$ for the PHB gelling process at a temperature of 40°C. The value of the exponent β, obtained in the low temperature interval, is about 4.2, slightly larger than that obtained from scattering experiments on the same system[13]. This exponent value cannot be interpreted, however, with any of the particular types of crystalline morphologies, due to the different assumptions underlying this gelling process.

CONCLUSIONS

A comparative d.s.c. and dielectric spectroscopy investigation has been carried out to study the phenomenology of the gel–sol transition of PHB in DMF ($10\,\mathrm{g\,l^{-1}}$).

A clear dependence on the thermal history of the samples is discerned from d.s.c. thermograms. Upon heating, two endothermic peaks are detected, their intensity and position being a function of the scan rate and cooling procedure. This bimodal calorimetric behaviour finds its counterpart in the temperature dependence of dielectric dispersion spectra of PHB gels prepared under similar conditions.

The behaviour of the gel permittivity and conductivity, compared with those of the solvent as well as of the solution at higher temperatures, confirms the presence of a melting process in the system upon heating. The heat evolved in this process as well as the frequency range of the permittivity and conductivity dispersions are indicative of polymeric moieties, organized in crystalline supramolecular clusters, as being responsible for the thermal and dielectric behaviour.

The magnitude of the temperature dependence of both d.s.c. and electrical conductivity is paralleled, with the major change at about 70°C and a minor change at about 85°C. This second change does not appear clearly in the dielectric measurements, unless the sample has been annealed at 50°C. Whether this is a response due to the sensitivity of the different methodologies or is evidence of another structural complexity of the system is a matter for further investigation.

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