

II. Dielectric investigation of cold crystallization of poly(3-hydroxybutyrate) and poly(3-hydroxybutyrate-co-3-hydroxyvalerate)

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Abstract

The dielectric relaxation behavior of a series of amorphous poly(3-hydroxybutyrate-co-3-hydroxyvalerate) P(3-HB-co-3-HV) having the hydroxyvalerate content: 0, 7, 14, 20 and 24 mol%, was investigated at the temperature and frequency ranges of 0°–100°C and 10³–10⁵ Hz, respectively. The dielectric spectra showed that the crystallization process starts during the temperature scan measurements at ~ 30°C regardless of the 3-HV-content. All samples of P(3-HB-co-3-HV) exhibited very similar relaxation spectra indicating the preservation of the main features of P(3-HB). However, some differences were observed in the relaxation spectra including the peak height, the onset crystallization temperature and the activation behavior. It is suggested that these differences observed in the various samples of the copolyester containing different 3-HV content are mainly controlled by: (1) the rate of crystallization, (2) the ultimate percentage of crystallinity, and; (3) the heating rate of measurements. Comparison of the onset crystallization temperature, T_{onset} , of different samples showed that the higher the 3-HV contents, the higher is onset temperature. However, measurements of T_{onset} at different heating rates showed the lower the rate, the weaker is the composition dependence of the onset temperature, so that the zero-rate onset temperature could be considered to be independent of the 3-HV content and equals that of pure P(3-HB). In addition, the study of the kinetics of cold crystallization showed that while the onset crystallization time is shortened from 14 to 4 min. by increasing the 3-HV-content from 0 to 24% HV, the offset crystallisation time is extended from 65 to 150 min. Moreover, by fitting the experimental results using Avrami equation to calculate the mechanistic exponent “*n*” the results showed surprisingly that “*n*” changes from 3.8 to ~ 2, ~ 2 and ~ 1 for samples containing 0, 7, 14, 20 and 24% HV, respectively. This change indicated the existence of mechanistic changes in the cold crystallization process. The results obtained are discussed and correlated to the literature data. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Dielectric relaxation; Poly(3-hydroxybutyrate); Poly(3-hydroxybutyrate-co-3-hydroxyvalerate)

1. Introduction

Poly(3-hydroxybutyrate), P(3-HB), is a biodegradable and bio-compatible thermoplastic crystalline polymer that possesses promising properties that qualify it for technical application, especially in areas where non-biodegradable plastic items are not allowed because of environmental pollution [2]. However, this important biodegradable polymer suffers from two main problems that limit its use in technical purposes, namely: (1) it has poor thermal stability, and; (2) it exhibits remarkable embrittlement upon storage at ambient temperatures. The earlier problem leads to a very narrow temperature window of processing, where heating for one hour at 190°C lead to a drop in the molecular weight to about half of its original value taking into account that the melting point is higher than 173°C [3]. However, the embrittlement of P(3-HB) observed at ambient temperature is

attributed to progressive crystallization process occurring upon storage of the material [4,5]. It was suggested that these drawbacks can be overcome by the development of the fermentation procedure that yields bacterial copolymers having lower melting points, like poly(3-hydroxybutyrate-co-3-hydroxyvalerate), P(3-HB and 3-HV) [6,7]. The copolyester have a statistically random distribution of 3-HB and 3-HV units [8,9]. It has been found that this copolyester exhibits the isodimorphism, i.e. the copolymer can crystallize either in P(3-HB) or P(3-HV) lattices depending on whether the 3-HV composition is lower or higher than 40 mol%, respectively [10–12]. However, the inclusion of 3-HV-units in the crystals of P(3-HB) would lead to energetically unfavourable defects. Therefore, the melting point of P(3-HB) drops considerably while the thermal stability is not affected. Consequently, processing becomes less critical with increasing the 3-HV-content, since lowering melting point widens the processing

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Table 1
Thermal properties of P(3-HB) and P(3-HB-co-3-HV)

Sample	T_g (°C)	T_{onset} (°C)	T_c (°C) ^a	T_m (°C) ^b	ΔH_f (J/g) ^b
PHB	2.5	38	47	173	87.6
PHB/7HV	1.5	46	62	162	73.6
PHB/14HV	- 1.5	50	65	146	64.8
PHB/20HV	- 2	60	82	122	46.4
PHB/24HV	- 3	-	-	108	35.6

^a T_g , T_{onset} and T_c obtained from d.s.c thermograms of quenched (amorphous) samples at a heating rate 10°C/min.

^b T_m and ΔH_f obtained from d.s.c. thermograms of cold crystallized samples at a heating rate 10°C/min.

window. In contrast, the rate of crystallization decreases with increasing the 3-HV content.

In case of P(3-HB) and P(3-HB-co-3-HV) like any other crystalline polymer, the mechanical properties and dimensional stability of the molded parts are governed by the morphology of the polymer, as formed during the molding cycle. Therefore, information concerning the temperature, time and degree of crystallization is critical in specifying the molding parameters such as molding temperature and demolding time. Accordingly, in an earlier work [1], the dielectric spectroscopy was applied to investigate the cold crystallization process of polyhydroxybutyrate, P(3-HB). The dielectric technique is an efficient tool that detects the various relaxation process as well as transformation phenomenon on a low molecular level (dipolar segments), which represents the elementary unit required for the crystal growth. Hence, some important parameters were obtained like the onset, offset crystallization temperature and the optimum crystallization temperature [1]. In addition, the bulk crystallization phenomenon could be also described by Avrami equation with an exponent ~ 3.8 [1]. This previous work is extended here to investigate the cold crystallization process of a series of P(3-HB-co-3-HV) having different contents of 3-HV, namely, 7, 14, 20 and 24 mol%. The ultimate aim of the current work is to evaluate some cold crystallization parameters that could help in understanding the cold crystallization of P(3-HB) and P(3-HB-co-3-HV) under normal storage temperature (30°C).

2. Experimental

Poly(3-hydroxybutyrate), P(3-HB), was kindly supplied by Aldrich, USA. Four poly(3-hydroxybutyrate-co-3-hydroxyvalerate) copolymers, containing 7% HV, 14% HV, 20% HV and 24% HV, were provided by ICI, Billingham, UK, as technical grade powders. These copolymers will be referred as P(3-HB)/7HV, P(3-HB)/14HV, P(3-HB)/20HV, and P(3-HB)/24HV, respectively. Prior to use, these materials were purified twice by dissolution in chloroform, filtration and precipitation into methanol. The molecular weights of the sample were determined using the viscosity method and

were found to be 110 000, 136 000, 250 000, 171 000 and 58 000 for P(3-HB) containing 0, 7, 14, 20 and 24 mol% 3-HV, respectively.

Dielectric measurements were carried out using a Polymer Laboratory DETA system, which delivers directly the dielectric constant, ϵ' , and loss, ϵ'' . The accuracy of DETA equipment is estimated to be better than 0.001 for $\tan \delta$.

Two different types of dielectric measurements were undertaken: (1) temperature scans at constant heating rate at various frequencies, the heating rate being 1 K/min, and (2) isothermal measurements over extended period of time (~ 4 h) at different frequencies.

Two types of samples were prepared for the dielectric measurements, namely amorphous (quenched) and cold crystallized. The amorphous samples were prepared by pressing the powder between two copper electrodes at 185°C for 5 min to form a condenser, which was then rapidly quenched in liquid nitrogen. Thereafter, the sample condenser under test was inserted in the measuring cell whose temperature was priorly adjusted at the required measuring temperature. The measurements were started within few seconds depending on the type of measurements. This temperature/time regime was strictly followed for all samples. The cold crystallized samples were prepared by quenching the sample condenser from 185°C (after 5 min) in liquid nitrogen. Then the samples were annealed for one week at 30°C to attain equilibrium crystallization. In order to minimise the risk of degradation, a new sample was used for each measurement.

D.s.c. thermograms were measured using a Polymer laboratories differential scanning calorimeter, PL-DSC, UK. The d.s.c was calibrated for temperature, heat and heat flow according to the method recommended by the GEEFTA, Germany [13,14]. Three to five mg of the powder samples were placed in sealed aluminium pans. In order to provide the same thermal history, each sample was heated at 200°C for 3 min. and the melt formed was quenched rapidly in liquid nitrogen. The d.s.c measurements were then carried out on the melt quenched sample once immediately, and another after the elapse of one week at room temperature, the temperature scans were carried out from -60 to 200°C with heating rate of 10 K/min. The glass-transition temperature, T_g , was taken as the inflection point of the specific heat increment and the melting point, T_m , as the peak temperature of the melting endotherms. However, when multiple endotherms were obtained, the temperature of the main peak was considered. The enthalpies of fusion (ΔH_f), were directly obtained from the areas under peaks.

3. Results and discussion

3.1. D.s.c. measurements

Prior to the dielectric investigation, d.s.c. measurements were carried out for the samples of P(3-HB-co-3-HV) with

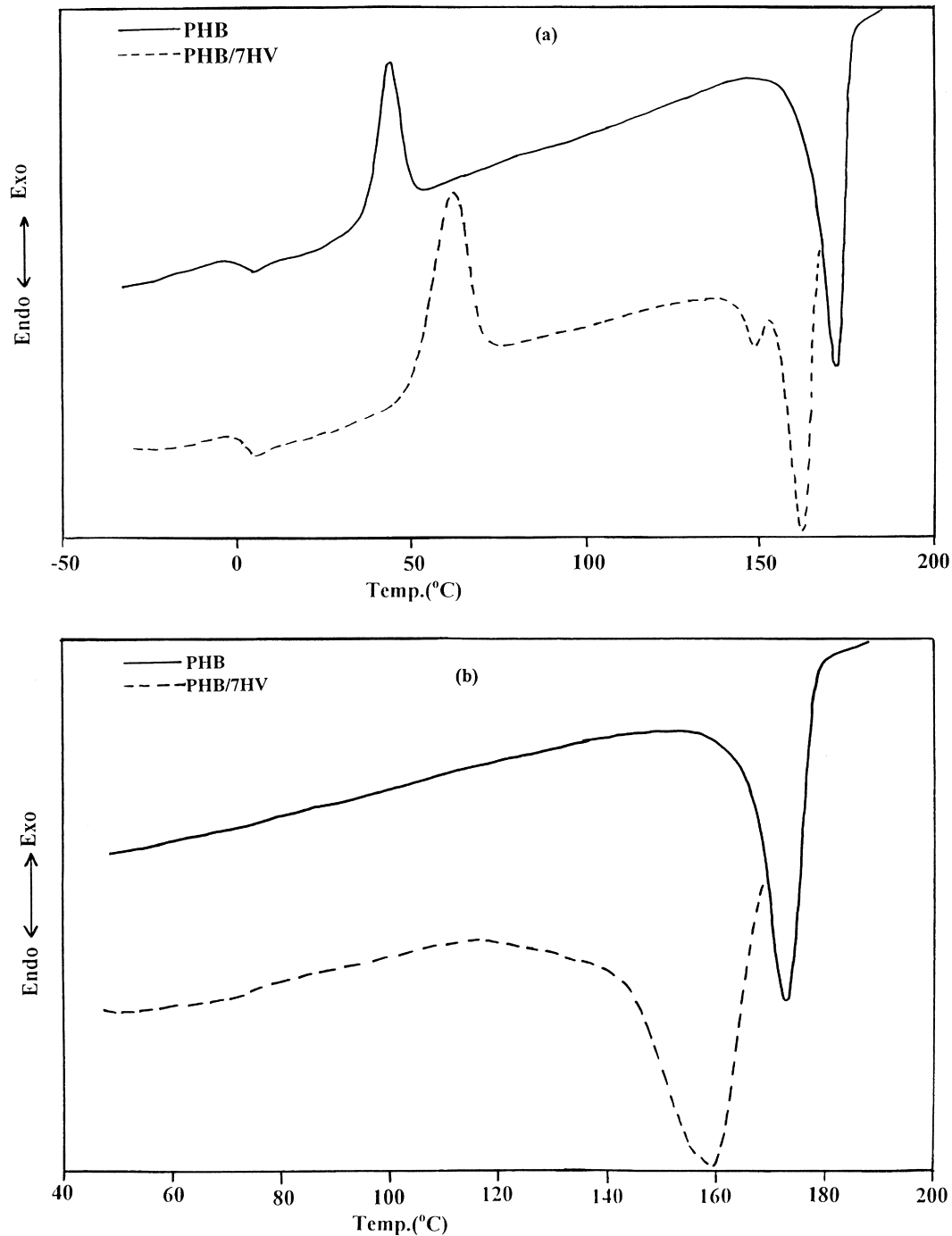


Fig. 1. D.s.c thermograms for (a) amorphous (quenched) and (b) Cold crystallized (annealed) PHB and PHB/7HV samples at a heating rate 10°C/min.

different 3-HV-content and thermal prehistories. The glass-transition temperature, T_g , onset temperature, T_{onset} , cold-crystallization peak temperature, T_c , melting temperature, T_m , and enthalpy of fusion, ΔH_f , of P(3-HB) and its co-polymer, P(3-HB-co-3-HV), containing from 7 to 24 mol% HV were determined from d.s.c. thermograms and are summarised in Table 1.

Fig. 1 shows typical d.s.c. thermograms of melt-quenched and annealed samples (cold crystallized) of P(3-HB) and P(3-HB) and P(3-HB)/7HV co-polyester,

as representative examples. When the co-polyesters are rapidly quenched in liquid nitrogen from a temperature above T_m , crystallization is inhibited and the calorimetric curves, as given in Fig. 1, show an endothermal base line shift corresponding to the glass-transition of the amorphous phase in the temperature range $-10/+10^\circ\text{C}$. Fig. 1 shows also that above T_g , a cold crystallization exothermic peak is present. Crystallization is followed by melting endotherms in P(3-HB) homopolymer as well as P(3-HB)/7HV co-polymers.

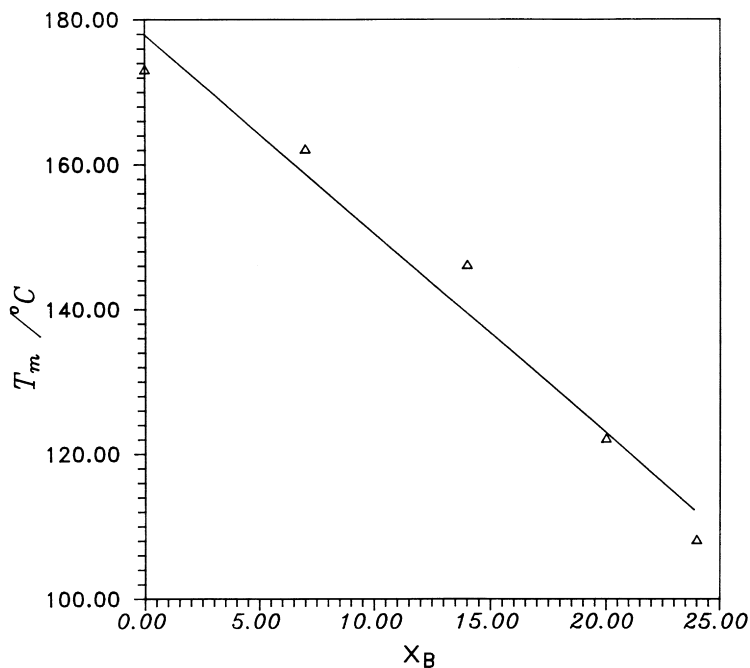


Fig. 2. Variation of T_m versus x_B for cold crystallized P(3-HB-co-3-HV) samples.

However, neither a glass transition nor an exothermic crystallization peak are observed for the annealed sample of both P(3-HB) and P(3-HB)/7HV co-polyester.

It can be seen from Table 1 that the glass transition shifts to lower temperature with increasing 3-HV fraction. Moreover, increasing amounts of 3-HV fraction disturb the crystallization process of P(3-HB), shifting the crystallization temperature to higher values and decreasing the amount of crystallising materials.

Moreover, the T_m , and ΔH_f values of cold-crystallized samples decrease with increasing 3-HV-content. This behavior is a typical of statistically random copolymers where both monomers can crystallise and the monomer units of one type are included in the crystal lattice of the other and vice versa, i.e., the behavior of an isodimorphic system.

Fig. 2 shows a plot of T_m of cold crystallised P(3-HB-co-3-HV) copolyester versus x_B which is fitted by using Sanchez-Eby equation for the melting point depression of finite crystal size in a random copolymer using the inclusion concept [15]:

$$T_m = T_m^\circ \{1 - (\epsilon x_B / \Delta H_m^\circ) - (2\sigma_e / \Delta H_m^\circ 1)\}, \quad (1)$$

where T_m° is the melting point of homopolymer P(3-HB), ΔH_m° is the enthalpy of melting of a mole of P(3-HB) units, T_m is the observed melting point of the copolymer and x_B is the mole fraction of 3-HB units in the copolymer. The melting point decrease with respect to x_B is accompanied by changes in the crystal packing energy owing to a defect free energy ϵ . σ_e is the surface free energy of the crystal surface and 1 is the lamellar thickness. The value of T_m derived from this plot, 178°C, is in a good agreement with

the literature data, below 30 mol% 3-HV [15]. Therefore, it can be concluded that, increased proportions of 3-HV units in the P(3-HB) chains will introduce some defects into the crystals and hence reduce ΔH_m and T_m .

3.2. Dielectric properties of P(3-HB-co-3-HV)

The temperature dependencies of the dielectric constant, ϵ' and the dielectric loss, ϵ'' , at various frequencies of P(3-HB-co-3-HV) copolyesters amorphous samples containing from 7 to 24 mol% 3-HV in the vicinity of the glass–rubber relaxation are represented in Figs. 3–5. These Figs. show that P(3-HB-co-3-HV) copolyesters behave in a similar way to that previously observed for P(3-HB) [1], where the value of ϵ' increase sharply with increasing temperature followed by a strong decrease in ϵ' owing to the onset of the cold crystallization process. As was discussed before the initial increase in ϵ' corresponds to the dispersion of the α -process in the mobile amorphous phase. However, when the crystallization process starts, the number of free dipoles contributing to the glass α -process will decrease and, in turn, results in a sudden drop in ϵ' . The drop in ϵ' above the onset crystallization temperatures is caused by the constrained amorphous motions. The dielectric loss, ϵ'' , shown in Figs. 3b–5b for all investigated samples regardless of 3-HV-content, is similarly affected by crystallization as P(3-HB). First the amorphous samples undergo a glass–rubber relaxation, α_b , and ϵ'' shows a strong maximum, which shifts slightly to higher temperature with increasing frequency, followed by the onset of cold crystallization (the subscript “b” indicates “before crystallization”). A second relaxation process is subsequently observed with increasing

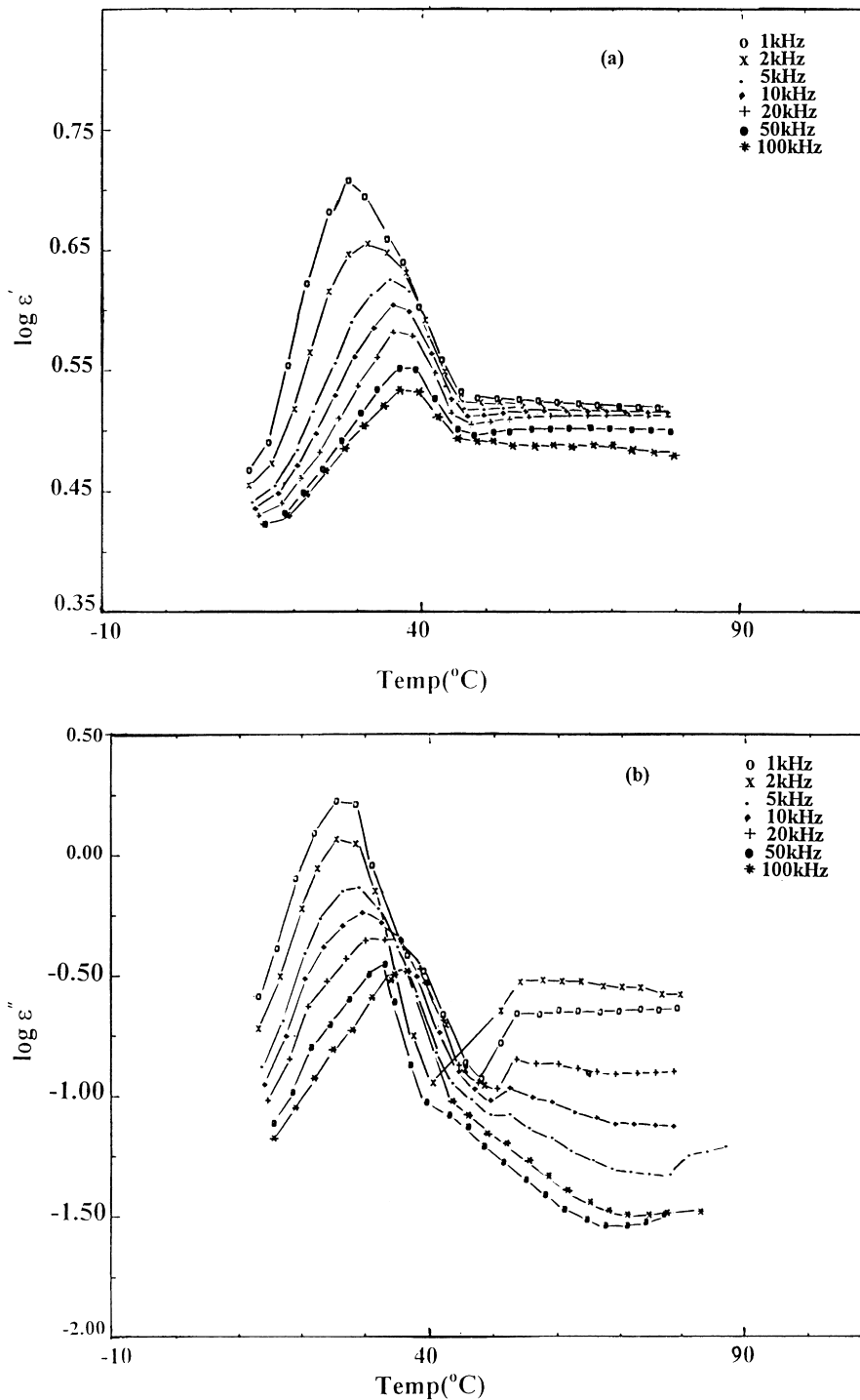


Fig. 3. Temperature dependencies of (a) dielectric constant, ϵ' and (b) dielectric loss, ϵ'' at various frequencies for amorphous PHB/7HV.

temperature, which corresponds to the glass–rubber relaxation, α_a , of amorphous chains that are now constrained by the presence of crystallinity, where the subscript “a” indicate “after crystallisation”. This second relaxation is evident as a gradual increase in ϵ' , and as a shoulder on the high temperature side of the narrow peak of ϵ'' .

In comparing the results of the P(3-HB-co-3-HV)

copolyesters containing different 3-HV content with P(3-HB), some fine differences can be observed, mainly:

1. The onset crystallization temperature, T_{onset} , increases with increasing 3-HV-content, where T_{onset} is defined as the temperature at which the decrease in the number of relaxing dipoles, as a result of crystallization, overweighs

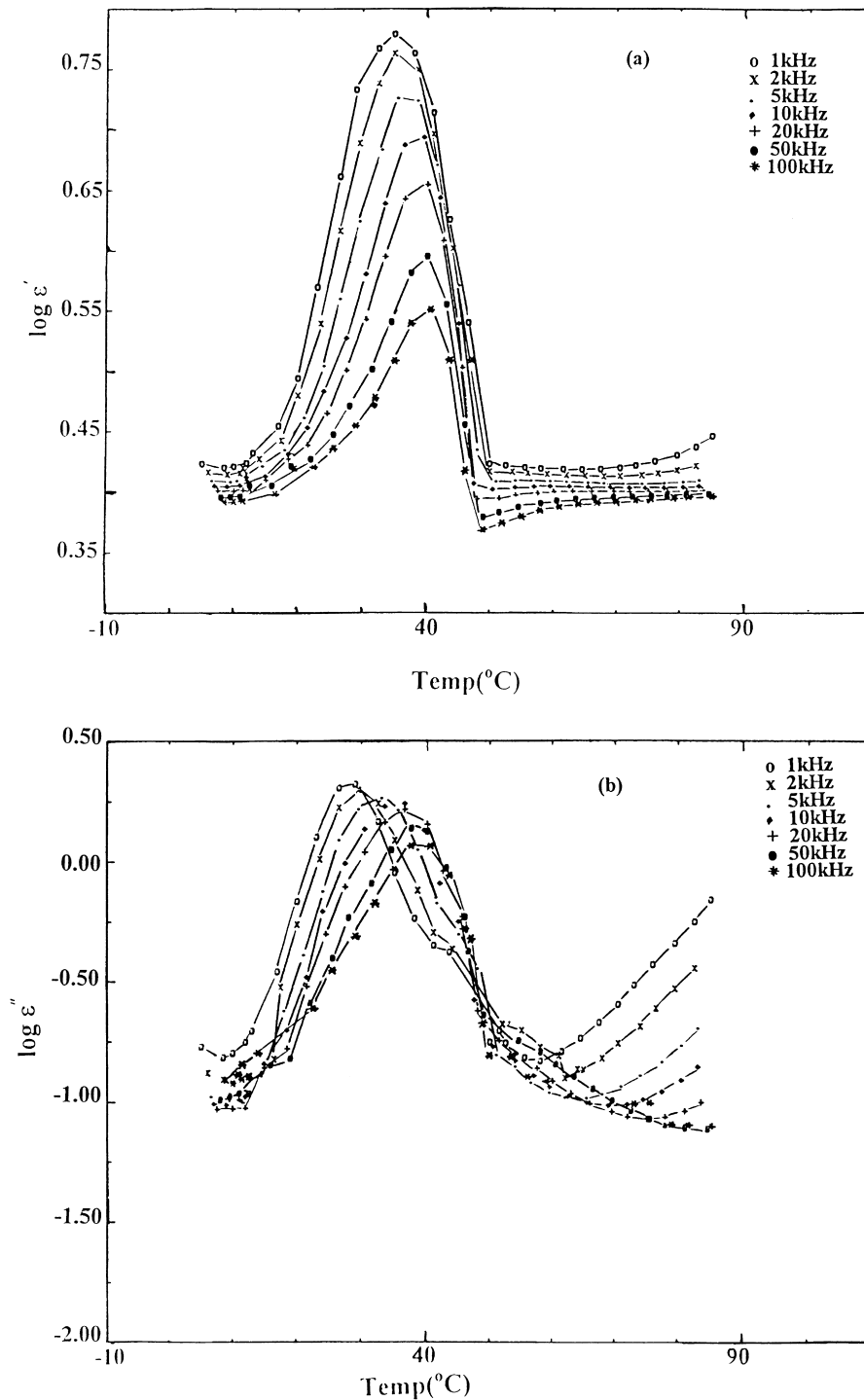


Fig. 4. Temperature dependencies of (a) dielectric constant, ϵ' and (b) dielectric loss, ϵ'' , at various frequencies for amorphous PHB/14HV.

the increase in the number of freely orienting dipoles owing to the activation of glass process.

2. The rate of initial increase in ϵ' with temperature is almost independent of the 3-HV-content, while the rate of decrease of ϵ' , after T_{onset} , is dependent on 3-HV-content; where the higher the 3-HV the lower is the rate.
3. The height α_a -process (high temperature shoulder) increases systematically with increasing 3-HV-content.

The similarity observed in all investigated samples concerning the behaviour and onset crystallization temperature can be taken as an indication of the preservation of the main features of crystallization for P(3-HB-co-3-HV) as that of P(3-HB). These results are in a good agreement with literature data, which showed that crystallization of P(3-HB-co-3-HV) copolyesters with 3-HV content less than 30 mol% is very similar to that of P(3-HB), where both

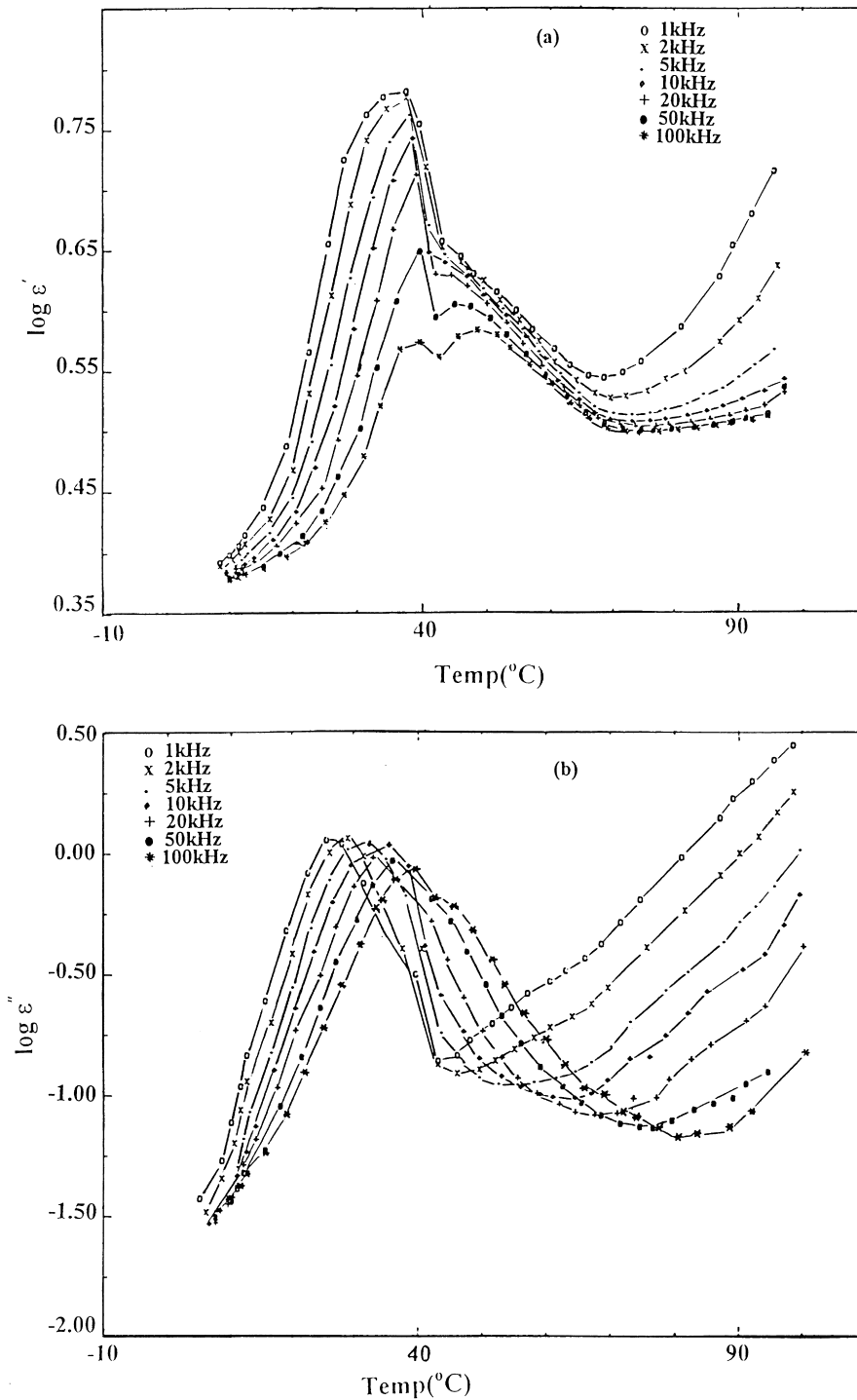


Fig. 5. Temperature dependencies of (a) dielectric constant, ϵ' and (b) dielectric loss, ϵ'' , at various frequencies for amorphous PHB/24HV.

3-HB and 3-HV monomeric units crystallise in a lattice with the geometry of P(3-HB) crystals [10–12,16].

However, the fact that T_{onset} is shifted to higher temperature with increasing 3-HV content might be attributed to the decrease in the rate of crystallization with the 3-HV-content. This property has already been established from X-ray diffraction study of the crystallization kinetics. That is, the rate of crystallization decreases steadily with increasing

3-HV-content [17]. In addition, the slower decrement in ϵ' together with the higher peak heights observed for the α_a -process upon increasing the 3-HV content can be attributed to the fact that the rate of crystallization and/or the ultimate degree of crystallization will be decreased by increasing the 3-HV-content. The latter would lead to an increase in the number of mobile dipoles contributing to α_a -process, and hence to an increase in the height of α_a

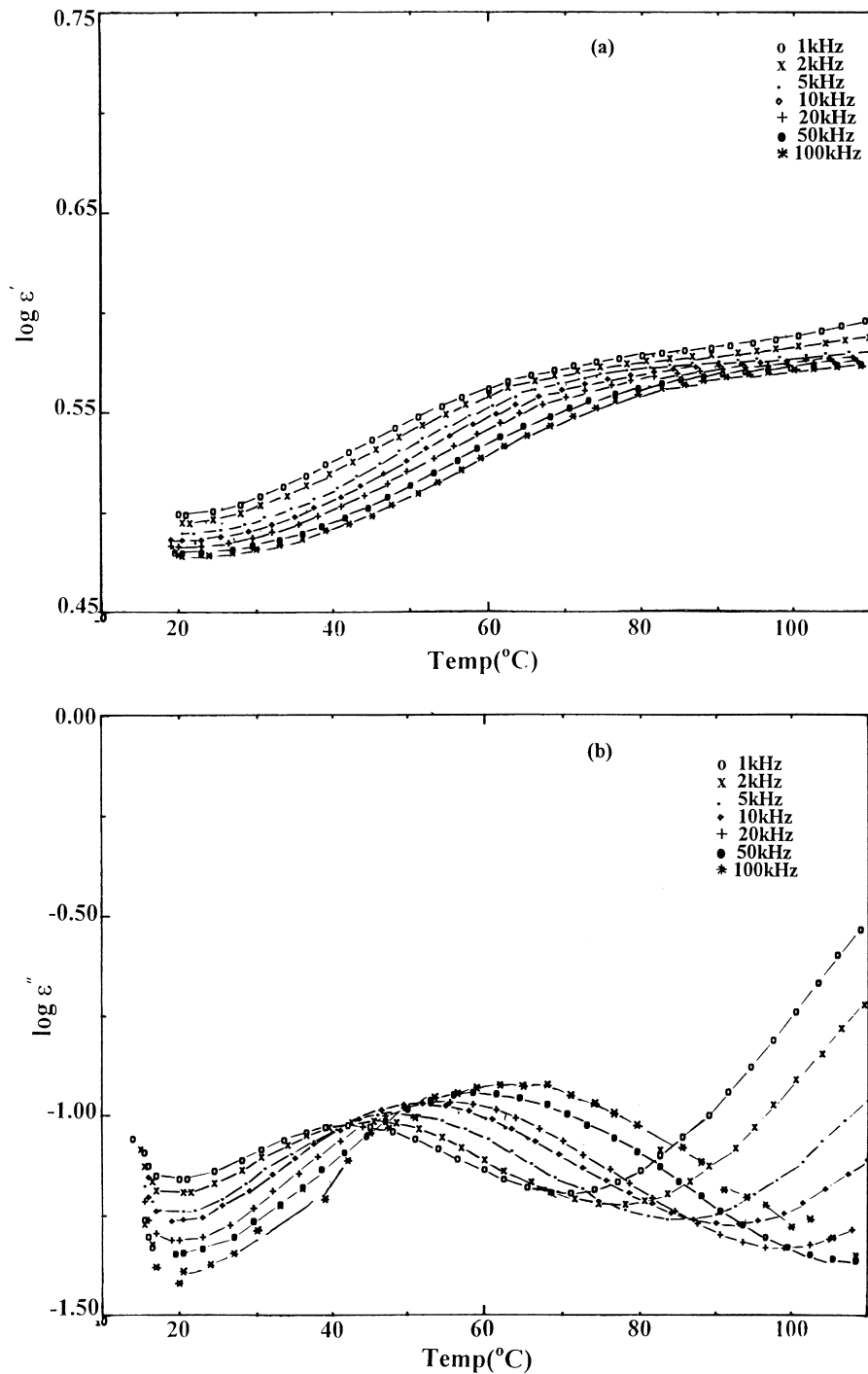


Fig. 6. Temperature dependencies of (a) dielectric constant, ϵ' and (b) dielectric loss, ϵ'' , at various frequencies for cold crystallized PHB/7HV.

peaks. This can be clearly seen in the measurements of cold crystallized samples.

Two representative examples of the cold crystallized samples (P(3-HB)/7HV and P(3-HB)/24HV) are given in Figs. 6 and 7 respectively. All samples exhibit a well defined glass process, which we call α_a -process, where the subscript "a" indicates "after crystallization". The α_a -process of all samples are very similar to that observed for P(3-HB). However, there are some differences can be observed in

these samples by comparing these two Figs., namely; (1) the higher the 3-HV-content, the higher ϵ''_{\max} of the α_a -process, (2) the higher the 3-HV-content, the lower the temperature range at which the α_a -process appears, (3) the α_a -process seems to be differently activated depending on the 3-HV-content, where the differences of T_{\max} with the different frequencies varies from sample to another.

The first finding implies that the number of freely reorienting dipoles that contribute to the α_a -process increases

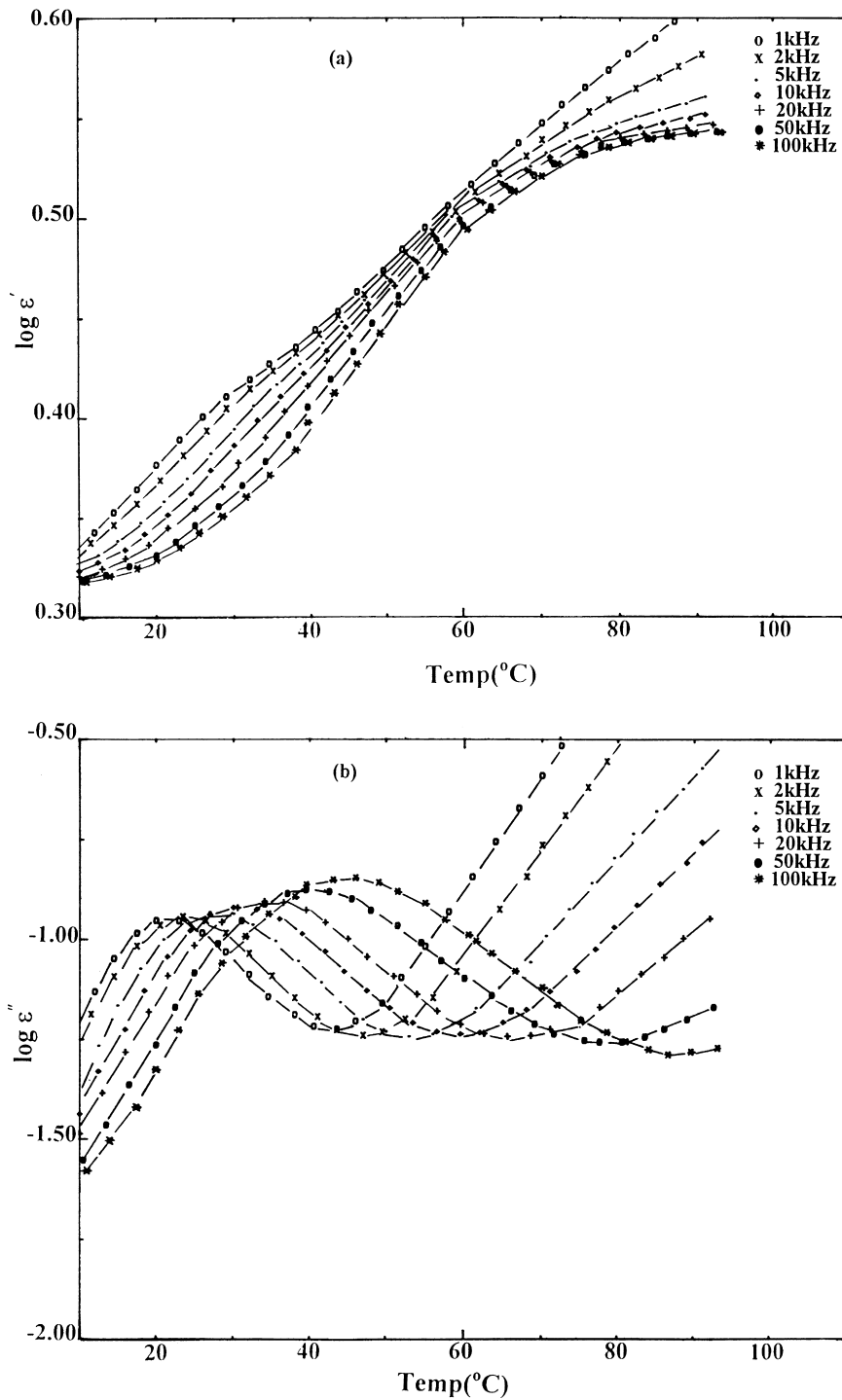


Fig. 7. Temperature dependencies of (a) dielectric constant, ϵ' and (b) dielectric loss, ϵ'' , at various frequencies for cold crystallized PHB/24HV.

with increasing the 3-HV-content. This means that the degree crystallinity decreases. This is in a good agreement with the calorimetric measurements, which show that the increase in the 3-HV-content leads to a systematic decrease in the heat of fusion, ΔH_f , as show in the Table 1. The second and the third findings can be seen in Fig. 8 that represents the activation diagram of α_a -process of the cold crystallized samples. This Fig. shows that the higher the

3-HV-content, the higher the shift of the activation curve to lower temperatures at a given frequency. This shift is an indication of the decrease of the glass temperature with increasing the 3-HV-content. This is in a good agreement with the literature data which showed that the glass temperature of amorphous samples decreases linearly as a function of 3-HV mole fraction from 4 to -170°C over the composition range p(3-HB) to P(3-HB)/95HV [18,19]. A

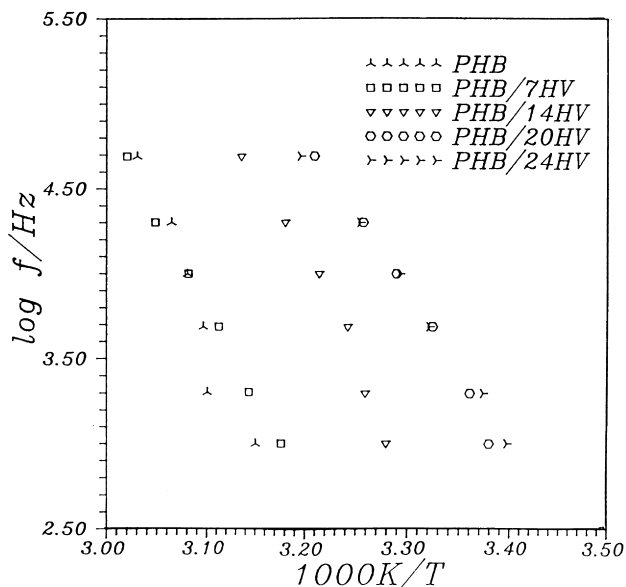


Fig. 8. Activation diagram of the glass process for cold-crystallized samples.

comparison of the glass temperature for quenched (amorphous) and cold crystallized P(3-HB-co-3-HV) samples based on calorimetric and dielectric measurements at 1 kHz are provided in Table 2. Such comparison shows that the difference between T_{\max} of P(3-HB) and P(3-HB)/24HV is about 25K for cold crystallized samples (obtained dielectrically) which is much higher than that expected for amorphous samples having the same copolyester ratio, where the estimated value equals ~ 6 K according to Fox-rule. Therefore, the shift in the activation curve observed in Fig. 8 can not be only attributed to the expected decrease in the glass temperature but also an additional factor must contribute to this effect. This factor could be the systematic decrease in the degree of crystallization with increase in the 3-HV-content, where the ΔH_f is reduced to 50% of its original value by replacing only 24% of 3-HB monomeric units with 3-HV (see Table 1).

Therefore, one can conclude that the increase in the degree of crystallinity increases synergistically the glass temperature, T_g , and therefore restricting the molecular mobility of the segments associated with α -process. In

Table 2

The glass temperature and T_g and the peak temperature of the glass process at 1kHz for cold crystallized samples

Sample	T_g for amorphous quenched samples	T_{\max} (1 kHz) for cold crystallized samples
P(3-HB)	2.5	45
PHB/7HV	1.5	42
PHB/14HV	-1.5	32
PHB/20HV	-2.0	23
PHB/24HV	-3.0	21

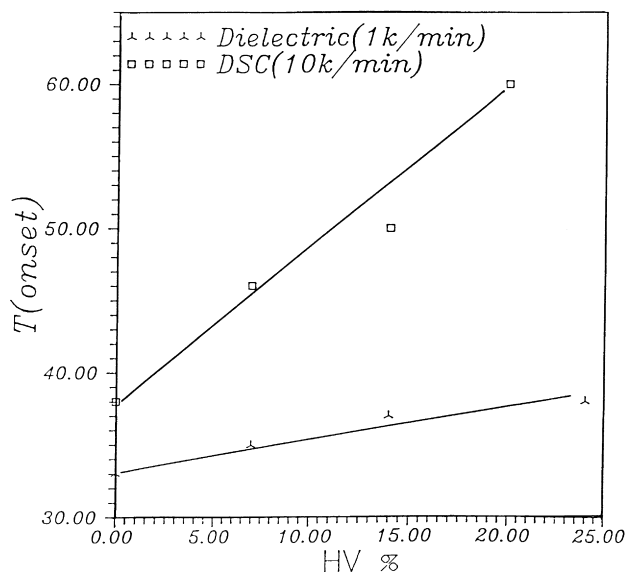


Fig. 9. The onset crystallization temperature, T_{onset} , as a function of 3-HV content.

addition, the above findings can be taken as an indication of the sensitivity of the dielectric relaxation method in detecting these fine effects.

In view of the above facts, it can be suggested that the difference in the dielectric behavior (height and shape of the peak as well as the activation curves) of the investigated samples is controlled by several factors mainly: (1) the rate of crystallization, (2) the ultimate percentage of crystallinity, and (3) the heating rate of measurements.

Therefore, it is of great importance to study the crystallization-process under controlled conditions to eliminate the effect of heating rate which plays an important role in activation of crystallization process and, in turn, the onset crystallization temperature as shown previously [1] for P(3-HB), where the lower the heating rate, the lower is the T_{onset} . Also T_{onset} reaches an equilibrium value of $\sim 47^\circ\text{C}$ at heating rates ≥ 5 K/min regardless of the method of measurements, where dielectric and calorimetric measurements were found to be in good agreement [1]. The onset crystallization temperatures obtained from non-isothermal calorimetric and dielectric measurements for different P(3-HB-co-3-HV) copolyesters at heating rates of 10 and 1 K/min., respectively are shown in Fig. 9. Both measurements show a systematic increase of T_{onset} as the 3-HV-content increases. The values obtained at higher rates are higher than those obtained at lower heating rate. This is consistent with our previous results [1]. At the same time, the measurements at low heating rate (1 K/min.) indicate that the dependence of T_{onset} on the composition of P(3-HB-co-3-HV) copolyesters of the investigated sample become weaker compared with measurements undertaken at high heating rate (10 K/min.). This finding implies that the zero-rate onset temperature, T_{onset}° (obtained by extrapolating T_{onset} to heating rate equals zero) could be considered to be

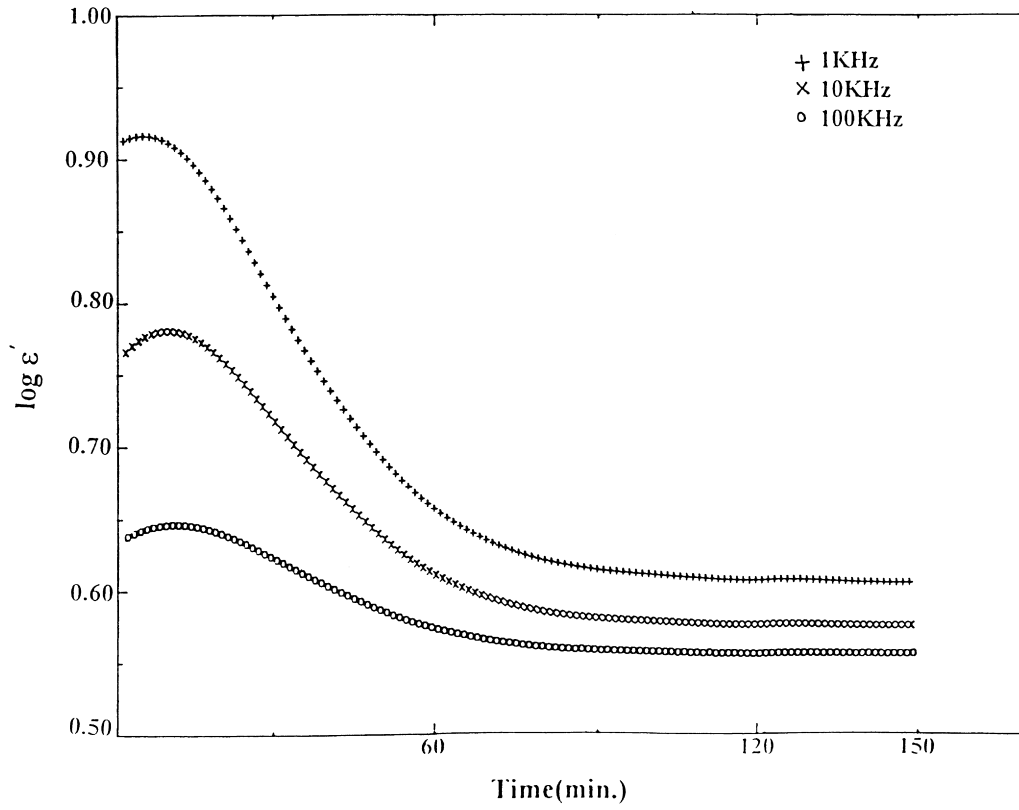


Fig. 10. Dielectric constant, ϵ' , as a function of time for amorphous PHB/7HV sample at 30°C and different frequencies.

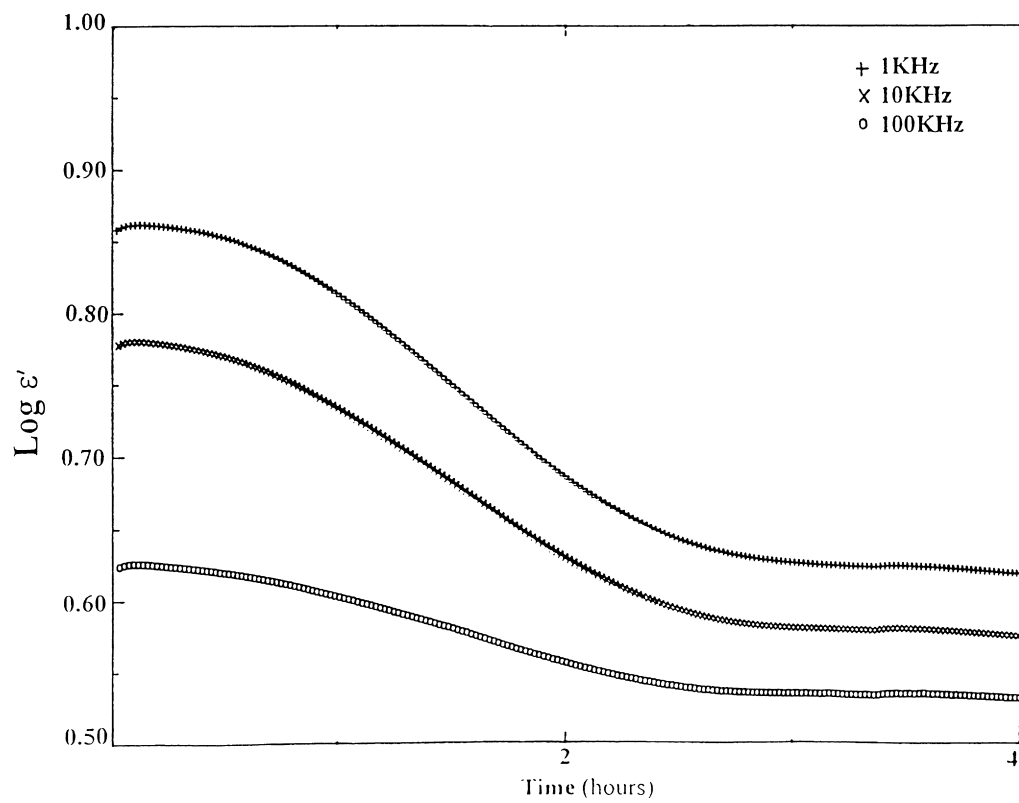


Fig. 11. Dielectric constant, ϵ' , as a function of time for amorphous PHB/20HV sample at 30°C and different frequencies.

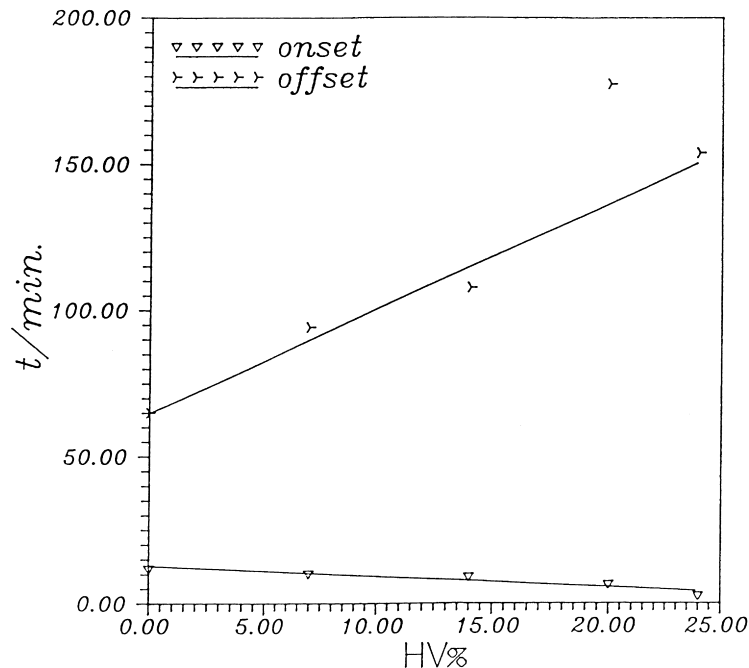


Fig. 12. The onset and offset time as a function of 3-HV content.

independent of 3-HV-content and equals to that of P(3-HB). This is reasonable because the difference in T_{onset} at low heating rate between P(3-HB) and P(3-HB)/24HV does not exceed 5 K.

Based on the above, one can conclude that reliable measurements will be obtained by tracing dielectrically the isothermal crystallization of amorphous P(3-HB-co-3-HV) over extended period of times at 30°C. The chosen temperature allows the study of crystallization process under normal storage condition, where this is one of our main aims. Also this temperature is still higher than that

of zero rate onset crystallization temperature of P(3-HB) (by ~ 5 K) as well as P(3-HB-co-3-HV) copolyesters investigated samples.

The time dependence of ϵ' for both amorphous P(3-HB)/7HV and P(3-HB)/20HV as representative examples is shown in Figs. 10 and 11 respectively. A comparison between both Figs. indicates the following:

1. P(3-HB-co-3-HV) samples followed the trend of P(3-HB), where ϵ' decreases systematically with time reaching an equilibrium value,
2. the onset crystallization time t_{onset} , decreases with increasing 3-HV-content,
3. the offset crystallization time, t_{offset} , increases with 3-HV-content, and,
4. $(d\epsilon'/dt)$ decreases with increasing 3-HV-content.

These findings can be clearly see in Figs. 12 and 13 which represent the composition dependence of t_{onset} , t_{offset} , and crystallization rate, respectively. The decrease in t_{onset} is small but still pronounced, where it decreases from 14 min. for P(3-HB) to 4 min. for P(3-HB)/24HV at 30°C. It is worth noting that the experimental error resulting from the start of measurement can not be more than 2 min. for the onset temperature. However, the t_{offset} increases rapidly with increasing 3-HV-content. The decrease of the onset time could be attributed to the fact that the incorporation of 3-HV-units leads to an increase in the molecular mobility of the whole chain due the increase of the length of side groups (internal plasticization). Therefore, one would expect that the probability of the primary nucleation would increase leading to a decrease in the induction period of crystallization. On the other side, the 3-HV units would also act as

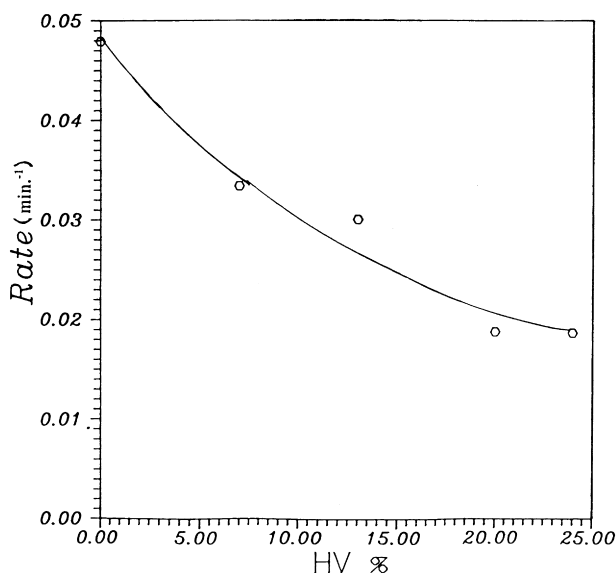


Fig. 13. The rate of crystallization as a function of 3-HV content.

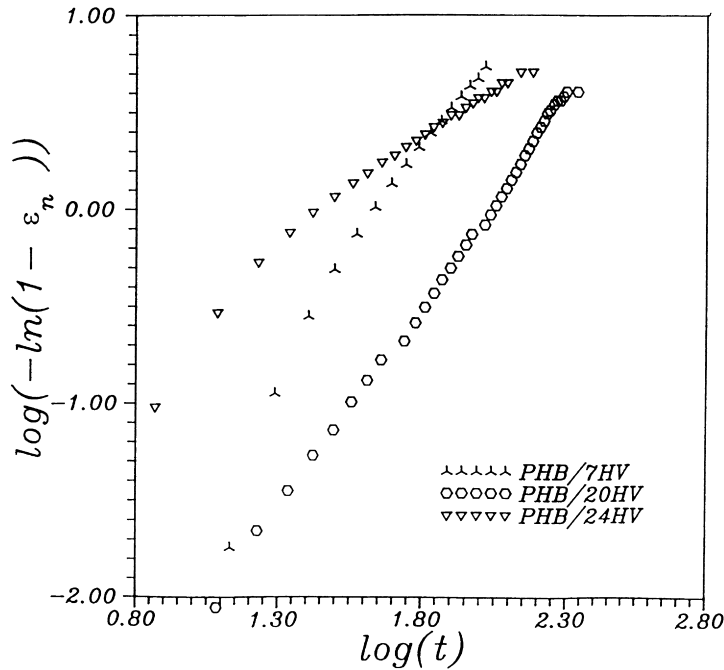


Fig. 14. Avrami plot at $T_c = 30^\circ\text{C}$ and 10^4 Hz.

structural defects that decrease not only the rate of crystallization but also the degree of crystallization, as seen from the value of ΔH_f in Table 1.

However, it must be stated that the abnormal extension of crystallization time to P(3-HB)20HV sample is intrinsic property and is still not clear, where it can not be considered as an experimental error. However, it could be attributed to some degree of heterogeneity that results from the fermentation process. In contrast, the decrease in the crystallization rate with increasing 3-HV-content, as shown in Fig. 13 is

consistent with the literature data measured at high temperatures [17]. Thus, the incorporation of 3-HV monomeric units into P(3-HB) can not lead to any technical importance. This is because although the onset crystallization time decreases with increasing 3-HV-content, the crystallization rate is reduced and therefore the offset crystallization time is extended. These facts imply that final properties of the polymer are only attained after relatively long time, i.e., lead to a longer cycle times in injection moulding. This means that not only the high cost production of (3-HB-co-3-HV) copolyesters limit its application but also the above technical reason.

Using the results obtained in Figs. 10 and 11 to calculate the normalised dielectric constant ϵ_n , as a function of the crystallization time. The normalised dielectric constant is given by [20]:

$$\epsilon_n(t) = (\epsilon_i - \epsilon_t)/(\epsilon_i - \epsilon_f), \tag{2}$$

where, ϵ_i is the dielectric constant at the start of crystallisation. ϵ_f is the long time limiting value and ϵ_t is the value at time t . The time dependence of $\epsilon_n(t)$ can be described by the Avrami equation [21,22], using the following expression:

$$\epsilon_n(t) = 1 - \exp(-kt^n), \tag{3}$$

where k and n are rate and mechanistic parameters, respectively. The exponent “ n ” parameter in Avrami equation can be obtained by the so called Avrami plot, which is a plot of the double logarithm of the $(1 - \epsilon_n)$ as a function of the logarithm of time, where “ n ” is the slope of the straight line (Fig. 14). In addition, another method called the crystallization half-time method was used to determine this parameter

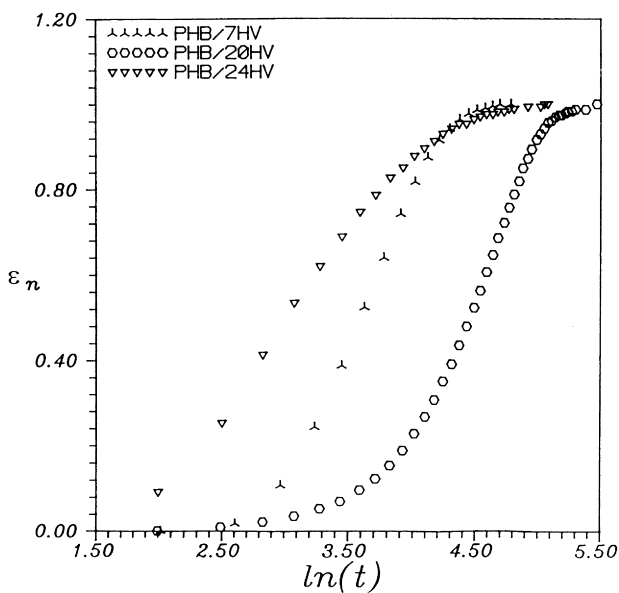


Fig. 15. The normalized dielectric constant, ϵ_n , as a function of crystallization time at $T_c = 30^\circ\text{C}$ and 10^4 Hz.

Table 3
Avrami exponent, n and characteristic nature and shape of the crystals

Sample	Avrami exponent “ n ”		Nature	Shape
	(1) ^a	(2) ^b		
PHB	3.8		sporadic	sphere
PHB/7HV	1.9	2.1	sporadic or instantaneous	rod or disc
PHB/20HV	1.9	2.2	sporadic or instantaneous	rod or disc
PHB/24HV	1.1	1.2	instantaneous	rod

^a According to Avrami plot.

^b According to crystallization half-time method.

[23]. It involves the determination of the crystallization half-time, $t_{1/2}$, from a graph of ϵ_n as a function of time, and the calculation of the slope, S , of the curve of ϵ_n as a function of logarithm of time at $t_{1/2}$ (Fig. 15). The parameter “ n ” is calculated by means of the following equation:

$$S_{1/2} = (n \ln 2)/2. \quad (4)$$

The results obtained are listed in Table 3. It is very interesting to find that the value of “ n ” decreases from 3.8 for P(3-HB) to ~ 2 , ~ 2 , and ~ 1 for P(3-HB)/7HV, P(3-HB)/20HV, and P(3-HB)/24HV, respectively. The decrease of “ n ” from 3.8 to 2 and to 1 can be taken as an indication of the change in both of the mechanism and the shape of the growing crystals. The value of “ n ” close to 4 for P(3-HB) indicates that three-dimensional sporadic spherulites are formed. For $n = 2$, the crystal can either grow sporadically as rods or instantaneously as disks, while for $n = 1$ the crystal grow instantaneously as rods. These findings are important and imply that there is serious gradual mechanistic change in the crystallization process occurring with increasing the 3-HV-content from 0 to 24%. It is worth noting that the value of “ n ” obtained for P(3-HB) is in a good agreement with the reported description of the crystallization process in the literature, where $n = 3.8$ means that there is a sporadic spherulitic growth. However, the change in the value of “ n ” with increasing the 3-HV-content was not reported before in the literature.

In order to interpret these new findings, one must recall some previous literature data. Organ and Barham [24] reported that the radial growth rate is strongly dependent not only on the temperature but also on the 3-HV-content, where the maximum growth rate of P(3-HB) was about $3.5 \mu\text{s}^{-1}$ which decreases to about $1.5 \mu\text{s}^{-1}$ for P(3-HB)/7HV and become almost temperature independent and is about $0.1 \mu\text{s}^{-1}$ for P(3-HB)/24HV. Moreover, they found that the maximum nucleation rate decreases strongly from 27 to 10 and 4 events $\text{mm}^{-3} \text{s}^{-1}$, while the maximum is shifted from 50 to 45 and 35°C for P(3-HB), P(3-HB)/7HV, P(3-HB)/24HV samples, respectively. Moreover, it is worth noting that by comparing the nucleation rate at 30°C (which is the crystallization temperature used in the current study) of the different samples, it is found that they have nearly equal values. Therefore, one would suggest that

the observed change in the mechanism according to HV-content, can be mainly attributed to a change in the balance between the rates of nucleation and growth or, in other words, to the great reduction in the growth rate where the nucleation rate is almost the same for all samples. Hoffman [25] classified the crystallization process into three regimes depending on the relative rates of nucleation and spreading along the growth front of the crystal. In regime I, the rate of spreading is much greater than the rate of nucleation, so that once the nucleus has formed, it will spread rapidly across a substrate length on the growth front. In regime II, several nuclei may form and spread across the substrate together. In regime III, the separation of nuclei is comparable with the molecular width so that no spreading occurs. This means that regime III is the most probable one for the P(3-HB)/24HV sample, while regime I is available in pure P(3-HB). This suggestion is in a good agreement with literature data.

However, Barham et al [26,27]. Suggested the presence of regime III postulated by Hoffman, where a typical lamellar thickness is observed for P(3-HB) being less than 10 nm and decreases with decreasing the temperature to 5 nm (i.e. about 6–7 repeat unit per fold stem). In addition, Scandola et al [28] found that the band spacing, S (which is proportional to lamellar thickness) is proportional to ΔT^{-n} where ΔT is the undercooling and $2 > n > 4$. They found the S decreases with increasing 3-HV-content as evidenced by the DSC and X-ray studies. Therefore, it can be concluded that at such high undercooling temperature (30°C), i.e. $\Delta T > 150^\circ\text{C}$, the crystals of P(3-HB) grows initially as thin rods. These fine crystals can undergo thickening process either by heating or with annealing for long periods of times at room temperatures. However, the thickening process is not only depending on the crystallization temperature but also on the 3-HV-content. Therefore, if this process is fast enough the value of exponent “ n ” will be close to 4 while if the rate of thickening process decreases the exponent will decrease to reach the unity. Consequently, it would be expected that the higher the 3-HV-content will lead not only to smaller initial lamellar thickness but also will largely limit the ultimate value. This conclusion is supported by some evidences in the literature that 3-HV monomeric units are excluded from the crystallization process which will limit the thickening process. This, in turn, will lead to the observed decrease in

the melting point T_m , with increasing the 3-HV-content of long annealed crystalline samples (i.e. after attaining equilibrium crystallization) where T_m is directly proportional to the lamellar thickness (see Table 1).

Based on the above, it is clear that there is a mechanistic change in the crystallization process that takes place with changing the 3-HV-content, as evidenced by the dielectric measurements and supported by the literature findings. In addition, it can be also stated that the higher the 3-HV-content leads to: (1) shorter onset crystallization time, (2) longer crystallization time, (3) smaller rate of crystallization, and; (4) smaller lamellar thickness.

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