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SYNTHESIS AND THERMAL BEHAVIOR OF POLY(2-HYDROXYETHOXYBENZOATE) AND ITS COPOLYESTERS WITH ε-CAPROLACTONE

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Abstract

Poly(2-hydroxyethoxybenzoate), poly(ε-caprolactone), and random poly(2-hydroxyethoxybenzoate/ε-caprolactone) copolymers were synthesized and characterized in terms of chemical structure and molecular mass. The thermal behavior was examined by DSC. All the samples appear as semicrystalline materials; the main effect of copolymerization was lowering in the amount of crystallinity and a decrease of melting temperature with respect to homopolymers. Flory's equation described well the T_m-composition data. Amorphous samples (in the 20–100% 2-hydroxyethoxybenzoate unit concentration range) obtained by quenching showed a monotonic decrease of the glass transition temperature T_g as the content of caprolactone units is increased. The Wood's equation described the T_g-composition data well.

Keywords: copolyesters, poly(ε-caprolactone), poly(2-hydroxyethoxybenzoate), random copolymers, thermal properties

Introduction

Poly(2-hydroxyethoxybenzoate) (PHEBA) is a polymer with a rather stiff chain, which in the past found application as fiber, being manufactured in Japan under the commercial name 'A-Tell'. The only relevant article appeared in literature about this polymer reports the results on the modification of the structure during tensile deformation of PHEBA fibers at room temperature [1]; to our knowledge, up to now no papers appeared on its thermal behavior. On the contrary, poly(ε-caprolactone) (PCL) is a well known biocompatible and biodegradable flexible aliphatic polyester, characterized by a valuable set of properties, such as non-toxicity for living organisms, re-

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sorption after an appropriate period of implantation time and good ultimate mechanical properties [2].

Copolymerization represents an easy way to modify the characteristics of a polymer in order to fit specific applications. For example, crystallinity degree and melting point can be reduced by random copolymerization and adjusted by changing the copolymer composition. In this view, we synthesized poly(2-hydroxyethoxybenzoate) and a series of random copolyesters with poly(ε-caprolactone) by direct melt polymerization, starting from 2-hydroxyethoxybenzoic acid and ε-caprolactone. The present paper reports the results of a detailed molecular and thermal characterization of the two homopolymers as well as of their copolymers, which last are formed by stiff aromatic and flexible aliphatic comonomeric units, carried out in order to study the structure-properties relationships.

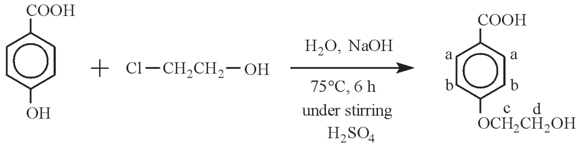
Experimental

Products

p-(2-hydroxy)benzoic acid (Aldrich) and chloroethanol (Aldrich) were used as supplied; ε-caprolactone (CL) (Aldrich) was dried over calcium hydride for 48 h at room temperature and distilled under reduced pressure just before use.

Synthesis of p-(2-hydroxyethoxy) benzoic acid (HEBA)

To a 150 mL of a water solution of NaOH (18.3 g), 30 g of *p*-(2-hydroxy)benzoic acid were dissolved and subsequently chloroethanol (19.2 g) was added dropwise at 50°C for about 45 min, giving rise to the following reaction:



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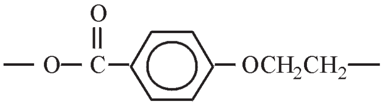
The mixture was allowed to stir at 75°C for 6 h. Then 10.5 mL of H_2SO_4 were added at 30°C, under continuous stirring, to afford 36.5 g of **1** (91%) as white powder, after filtration and water washing. After two recrystallizations from ethanol, 30 g of **1** (75%) as white crystals were obtained (*m.p.*=178–179°C).

^{1}H-NMR (DMSO): δ 7.88 (d, 1H^b), δ 7.01 (d, 1H^a), δ 4.06 (t, 2H^c), δ 3.72 (t, 2H^d).

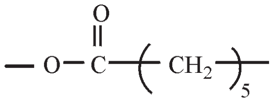
Elemental analysis calculated for $C_9H_{10}O_4$: C, 59.34; H, 5.53; O, 35.13%. Found: C, 59.23; H, 5.87; O, 34.9%.

Synthesis of polymer samples

Poly(2-hydroxyethoxybenzoate), poly(ε-caprolactone) and poly(2-hydroxyethoxybenzoate/ε-caprolactone) copolymers (PHEBA/CL) of various compositions were synthesized in bulk starting from different amounts of CL and HEBA, employing $Ti(OBu)_4$ as catalyst (about 0.2 g of $Ti(OBu)_4$/kg of polymer). In the preparation of PCL no initiator was employed. The syntheses were carried out in a 200 mL glass reactor, with a thermostatted silicon oil bath; temperature and torque were continuously recorded during the polymerization. The polymers were obtained according to the usual two-stage polymerization procedure [3]. In the first step, under pure nitrogen flow, the temperature was raised to 160–220°C (according to the initial composition of the reaction system) and maintained there for about 1 h. In the second stage the pressure was reduced, in order to facilitate the removal of water (except in the case of PCL) and the temperature was kept in the range 200–240°C until a torque constant value was measured. The copolymers obtained, because of the use of $Ti(OBu)_4$ as catalyst and the high temperature, which favour redistribution reactions [4], are statistical both in composition and molecular mass distribution. The monomeric units are the following:



(I)



$$-O-\overset{\overset{\displaystyle O}{\|}}{C}-\left(CH_2\right)_5-$$

(II)

^{1}H-NMR spectroscopy

The chain structure of PHEBA, PCL and PHEBA/CL copolyesters and the composition of these last were determined by means of ^{1}H-NMR spectroscopy. Polymer samples were dissolved (15 mg mL^{-1}) in an appropriate solvent with 0.03% (v/v) tetramethylsilane added as an internal standard. The measurements were mainly carried out using chloroform-d solutions at room temperature; in the case of copolymers rich in HEBA units, a mixture of trifluoroacetic acid/chloroform-d (20/80 v/v) was employed as solvent. Measurements were recorded on a Varian XL-300 instrument.

Gel-permeation chromatography

Molecular mass data were obtained by gel-permeation chromatography at 30°C using a 1100 Hewlett Packard system with an UV spectrophotometer (at 254 nm wavelength) as detector, equipped with PL gel 5 µ Mixed C column (300/7.5 length/i.d., in mm). A mixture of dichloromethane/chloroform/1,1,1,3,3,3-hexafluoro-2-propanol (75/20/5 mass/mass) was used as eluent with a 1.0 mL min^{-1} flow, and sample concentrations of about 10 mg mL^{-1} were employed; higher concentrations were used in the case of copolyesters containing low amount of aromatic units. A molecular mass calibration curve was obtained with several monodisperse polystyrene standards in the range of molecular mass 2 000–100 000.

Thermal analysis

Calorimetric measurements were carried out by means of a Perkin Elmer DSC7 instrument equipped with a liquid subambient accessory and calibrated with high purity standards (indium and cyclohexane). Unless otherwise indicated, weighed samples (ca. 10 mg) were encapsulated in aluminum pans and heated to about 40°C above fusion temperature at a rate of 20°C min^{-1} (first scan) and then rapidly quenched at –80°C. Finally, they were reheated from –80°C to a temperature well above the fusion temperature of the sample at a heating rate of 20°C min^{-1} (second scan). The glass-transition temperature T_g was taken as the midpoint of the heat capacity increment Δc_p associated with the glass-to-rubber transition. The melting temperature (T_m) was determined as the peak value of the endothermal phenomenon in the DSC curve; the enthalpy of fusion (ΔH_m) was determined from the area of DSC endotherm. Repeated measurements on each sample showed excellent reproducibility.

Results and discussion

At room temperature all the polymers synthesized appear as semicrystalline solids. The solubility of the samples was checked in various solvents. PHEBA and the copolymers rich in 2-hydroxyethoxybenzoate units were found to be fully soluble at room temperature only in 1,1,1,3,3,3-hexafluoro-2-propanol or in a mixture of dichloromethane/chloroform/1,1,1,3,3,3-hexafluoro-2-propanol (75/20/5 mass/mass). On the contrary, PCL and the copolymers containing high amount of ε-caprolactone units showed to be soluble in the most common organic solvents, i.e. chloroform, tetrachloroethane, methylene chloride, etc. The polymers synthesized are listed in Table 1, where the number-average molecular masses (M_n) obtained by GPC technique are also reported. In order to have an understanding into the chemical structure and copolymer composition, ^{1}H-NMR investigation on the samples was made. ^{1}H-NMR spectra of all copolyesters were found to be consistent with the expected structure. As an example, ^{1}H-NMR spectrum of the PHEBA70/CL30 copolymer is shown in Fig. 1, together with the chemical shift assignments. The peaks chosen for the determination of the composition, which is reported in Table 1, for all the samples were the one at 2.54 ppm for the ε-caprolactone unit and that at 7.03 ppm for the 2-hydroxyethoxybenzoate unit. From the data of Table 1, it can be seen that in all cases the actual composition is very close to that of the feed.

Table 1 Molecular characterization data of PHEBA/CL random copolymers

Polymer	HEBA/mol% (feed)	HEBA/mol% (NMR)	$M_n/10^3$
PHEBA	100	100	7.0
PHEBA90/CL10	90	90	6.9
PHEBA80/CL20	80	79	7.4
PHEBA70/CL30	70	69	8.2
PHEBA60/CL40	60	61	6.9
PHEBA50/CL50	50	47	7.1
PHEBA40/CL60	40	38	7.4
PHEBA30/CL70	30	28	8.1
PHEBA20/CL80	20	18	7.8
PHEBA10/CL90	10	10	8.7
PCL	0	0	9.4

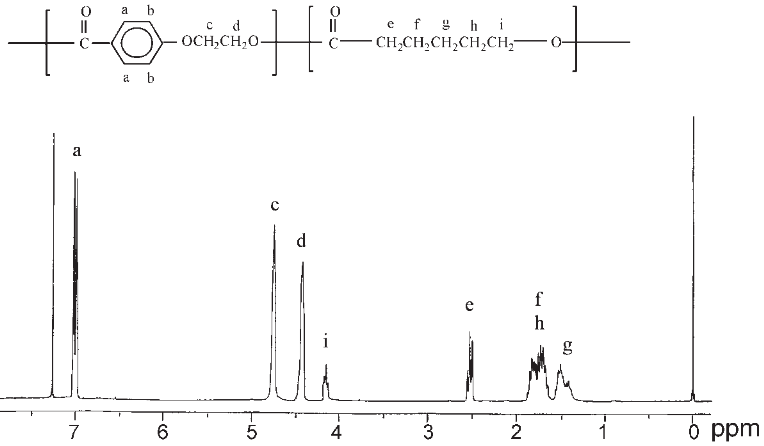


Fig. 1 ^{1}H-NMR spectrum of PHEBA70/CL30 copolymer

Thermal properties

Melting

To our knowledge, very few is reported in literature on poly(2-hydroxyethoxybenzoate); in particular, up to now no papers have appeared dealing with its thermal behavior. Therefore, the thermal properties of PHEBA have been investigated by differential scanning calorimetry, as well as those of PCL and PHEBA/CL copolymers.

Table 2 Calorimetric data of PHEBA/CL random copolymers

Polymer	1st scan				2nd scan					
	T_g/°C	Δc_p/ J g^{-1} K^{-1}	T_m/°C	ΔH_m/ J g^{-1}	T_g/°C	Δc_p/ J g^{-1} K^{-1}	T_c/°C	ΔH_c/ J g^{-1}	T_m/°C	ΔH_m/ J g^{-1}
PHEBA	71	0.175	208	80	69	0.404	106	67	208	68
PHEBA90/CL10	56	0.183	197	68	55	0.422	103	53	197	54
PHEBA80/CL20	41	0.199	172	46	40	0.420	90	36	171	37
PHEBA70/CL30	32	0.213	155	34	32	0.435	–	–	–	–
PHEBA60/CL40	19	0.202	124	33	18	0.447	–	–	–	–
PHEBA50/CL50	–1	0.222	101	22	–1	0.420	–	–	–	–
PHEBA40/CL60	–7	0.230	68	21	–8	0.424	–	–	–	–
PHEBA30/CL70	–29	0.232	38	32	–30	0.437	–	–	–	–
PHEBA20/CL80	–35	0.216	47	40	–37	0.436	–	–	–	–
PHEBA10/CL90	–43	0.087	57	77	–43	0.111	–	–	47*	60
PCL	–	–	63	97	–	–	–	–	61	75

*multiple-peak endotherm: T_m of the higher temperature peak

Being well established that the melting behavior of a polymer is affected by its previous thermal history, in order to provide the same heat treatment to all the samples investigated, PHEBA specimen has been aged for about 6 months at ambient temperature in a desiccator prior to thermal analysis. Such a thermal treatment was applied, due to the fact that some of the copolymers synthesized melt only about 10°C above room temperature.

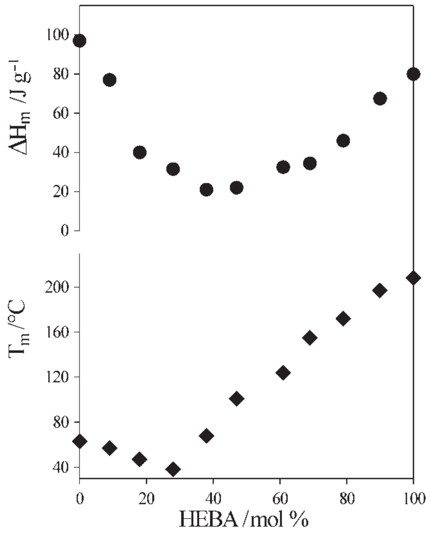


Fig. 2 Composition dependence of T_m (◆) and ΔH_m (●) for PHEBA/CL random copolymers

As far as PHEBA is concerned, from the first heating scan one can observe a glass transition (at 71°C) followed by a melting phenomenon (at 208°C). Also for the other samples synthesized, except for PCL, a glass transition and a melting endotherm are evident. In the copolymers, peak location appears to depend on composition; furthermore, the increase in the amount of comonomer added to PHEBA or to PCL leads to a marked reduction of the heat of fusion, indicating a reduced level of crystallinity in the copolymers with respect to the homopolymers. All DSC results are collected in Table 2. ΔH_m and T_m values are plotted in Fig. 2 as a function of HEBA unit content. Both the minimum in the heat of fusion and the melting point-composition dependence are typical of random copolymers, where both comonomers are able to crystallize but at each composition only the unit present in major proportion usually takes part in the crystallization process [5, 6]. According to Flory's theory [7], the T_m value corresponding to the disappearance of crystallinity in the copolymers is related to the molar fraction x_A of the crystallizing A units by the relationship:

$$1/T_m - 1/T_m^0 = -(R/\Delta H_u)\ln x_A \tag{1}$$

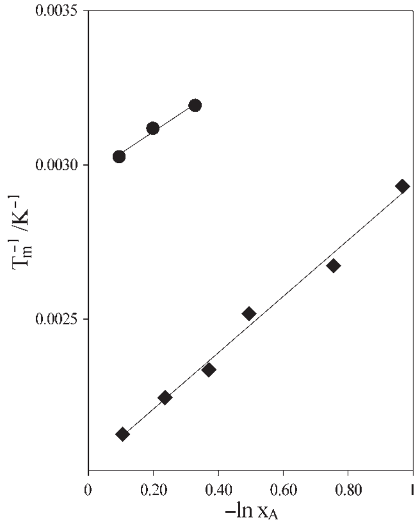


Fig. 3 $1/T_m$-composition plots according to Flory's equation for the copolymers rich in HEBA units (◆) and rich in CL units (●)

where T_m^0 and ΔH_u are the melting temperature and the heat of fusion of the completely crystalline A homopolymer, respectively. According to this theory the plot $1/T_m$ *vs.* $-\ln x_A$ should be a straight line with a slope $R/\Delta H_u$. Considering PHEBA as homopolymer A, the experimental T_m data of the copolymers rich in HEBA units fit very well onto a straight line down to HEBA mol%=40 (Fig. 3). From the slope a value of ΔH_u=63 J g^{-1} can be obtained, whereas from the intercept a T_m^0=227°C was determined. As regards the PHEBA/CL copolymers rich in ε-caprolactone, the experimental T_m data are also well correlated by Flory's equation (Fig. 3). The value of ΔH_u (115 J g^{-1}) for PCL is significantly lower than that determined by other methods [8]. The equilibrium melting temperature (T_m^0) is equal to 65°C, in good agreement with the data reported in literature [9] (where T_m^0 ranges from 58 to 76°C). The fact of obtaining lower ΔH_u is, however, a wide spread observation that has been reported for several different statistical copolymers and has been ascribed to the inability of a real random copolymer system to achieve the conditions postulated by the equilibrium theory. Theory requires a melting temperature relative to the disappearance of very long sequences of A units; on the contrary, in real conditions the amount of such sequences in random copolymers is relatively low and decreases as the co-unit content increases. As a consequence, experimental T_m values are lower than predicted. The ΔH_u of PCL is higher than that of PHEBA: similar behavior was previously found comparing other kinds of aliphatic and aromatic polymers [10].

As can be seen in Fig. 4, where the calorimetric curves of the samples after rapid quenching from the molten state are collected, a double melting peak is present in the DSC trace of PHEBA10/CL90 copolymer. It has to be emphasized that the presence of two endotherms only occurs during the second heating (after quenching from the

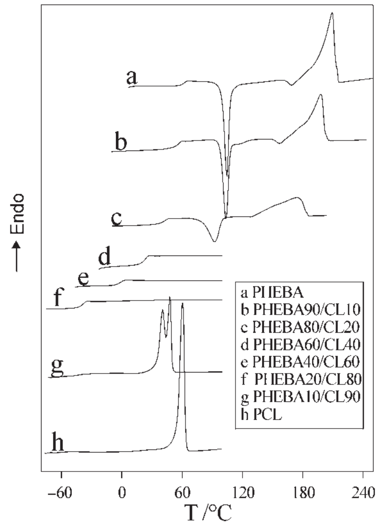


Fig. 4 Calorimetric curves of PCL, PHEBA homopolymers and their random copolymers after melt quenching

melt). As a matter of fact, the curve of the sample annealed at room temperature for several months reveals a single melting transition. It is well known that a lot of semicrystalline polymers as well as their copolymers show multiple endothermic peaks [11–19]. There has been much discussion in literature as to the possible origin of the phenomenon. Multiple endotherm peaks could be due to the presence of two or more groups of crystals with different morphologies [11–13]; alternatively, they can be ascribed to a recrystallization process occurring during the DSC scan [14–19]. In particular, the multiple endotherm behavior is typical of many polyesters, for the best-studied of which the phenomenon has always been ascribed to a reorganization processes taking place during the DSC scan [17–19]. In the case of PCL, the origin of multiple endothermic peaks is controversial. Some authors interpreted the observed double endothermic peak formation after rapid cooling from the melt as due to different crystalline morphologies of the polymer [20, 21]. Others, on the contrary, found only one crystal structure for PCL and, therefore, attributed the phenomenon to a melting-recrystallization-remelting process occurring during the heating scan [22].

In order to study the nature of these multiple endotherms, different kinds of experiments can be carried out by DSC equipment. In particular, PHEBA10/CL90 copolymer has been subjected to the two different thermal treatments described in the following:

a) heating scan well above melting temperature, keeping there for 3 min in order to cancel the previous thermal history and then rapid cooling to a chosen crystallization temperature (T_c= –15°C) up to the completion of the crystallization process. The isothermally crystallized samples were subsequently analyzed by heating directly from T_c at different heating rate (ranging from 2.5 to 40°C min^{-1});

b) cooling scan from the melt at different rates (1, 5°C min^{-1} and rapid quenching) and a subsequent heating scan at 20°C min^{-1}.

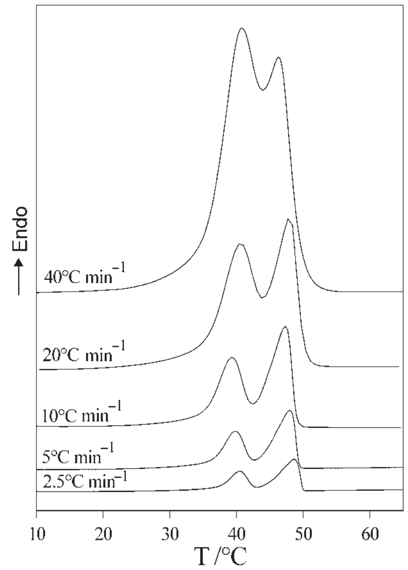


Fig. 5 DSC melting endotherms of PHEBA10/CL90 scanned at the indicated heating rate after isothermal crystallization at –15°C. The curves have not been corrected for changes in the instrumental signal with heating rate

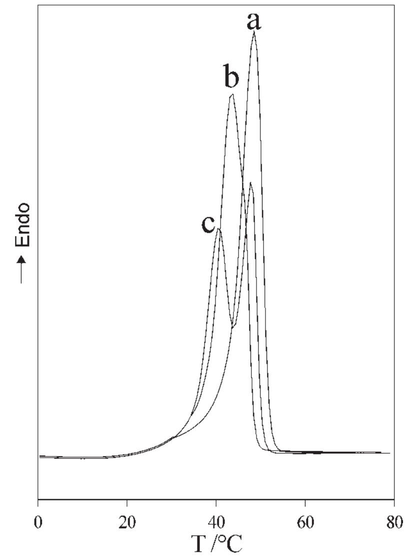


Fig. 6 Melting endotherms of PHEBA10/CL90 copolymer at a heating rate of 20°C min^{-1} after cooling from the melt at different rates: a – 1°C min^{-1}; b – 5°C min^{-1}; c – rapid quenching

The DSC heating curves of the PHEBA10/CL90 copolymer subjected to the two thermal treatments described above are reported in Figs 5 and 6 respectively. In Fig. 5 two endotherms are observed in all cases: for sake of clarity, the peak at lower temperature has been marked I whereas that at higher temperature II. It can be observed that (i) the endotherm II moves to higher temperatures as the heating rate decreases and (ii) the ratio of the area of the first melting peak to the second one increases as the heating rate is increased, confirming that the multiple melting is due to a mechanism based on melting and recrystallization of less perfect crystallites into thicker crystals, followed by a final melting process at higher temperature.

As can be seen in Fig. 6, the shape of the melting endotherm changes with the cooling rate: when the sample is rapidly cooled from the melt, two partially overlapped peaks are observed; on the contrary, the calorimetric curves of PHEBA10/CL90 obtained after cooling from the melt at the low cooling rates show only one melting peak, the width of which decreases as the cooling rate is decreased. This suggests that a reorganization process takes place during the cooling step: in fact, if the sample is allowed to crystallize slowly, the original less perfect crystallites can reorganize forming thicker crystals, which melt at higher temperatures. In addition, as the result of a progressive crystallite improvement, the melting range of the sample cooled at 1°C min^{-1} appears narrower than that of copolymer cooled at 5°C min^{-1}. In conclusion, both these DSC experiments give more value to the hypothesis that the multiple endotherms are due to the fusion process of crystallites having different degree of perfection and/or size. Moreover, when enough time is allowed for crystallization to occur (annealing for long time at room temperature), both peaks merge into one peak (calorimetric results obtained by first scan) as a consequence of the uniformity in the degree of the perfection of the crystals. Other authors, in investigating copolymers of caprolactone, came to the same conclusion [23].

Glass transition

A partially crystalline material is expected to exhibit different glass transition behavior than completely amorphous. Although some conflicting results are reported in literature [24], crystallinity usually acts like crosslinking and raises T_g through its restrictive effect on segmental motion of amorphous polymer chains. In order to study the influence of chemical structure on the glass transition of random copolymers, the phenomenon should be examined in the total absence of crystallinity. Rapid cooling (quenching) from the melt is the method commonly used to prevent crystallization and to obtain polymers in a completely amorphous condition. Some of the DSC curves obtained after rapid cooling from the melt are shown in Fig. 4: the calorimetric traces, concerning PHEBA and the PHEBA/CL copolymers rich in 2-hydroxyethoxybenzoate units (from 80 to 100 mol% of 2-hydroxyethoxybenzoate units), show an intense glass transition followed by an exothermal ‘cold crystallization’ peak and a melting endotherm at higher temperature. The enthalpy associated with the crystallization exotherm very well compares with the corresponding heat of fusion, indicating that the polymer was completely vetrified into the amorphous state by quenching and that, once T_g is exceeded, the amorphous chains acquire enough mobility to rearrange and crystallize. The glass transition temperature and the associated specific heat increment Δc_p of PHEBA were found to be 69°C and 0.404 J g^{-1} $°C^{-1}$ respectively. It is worth emphasizing that no other data of T_g and Δc_p are available in literature for this polymer.

As regards the calorimetric curves of PHEBA/CL copolymers where 2-hydroxyethoxybenzoate unit content varies from 20 to 70 mol%, only an intense endothermal baseline deviation associated with the glass transition is observed. On the contrary, the DSC traces of pure PCL and of PHEBA10/CL90 copolymer are typical of a partially crystalline polymer, being characterized by a considerable melting endotherm. As a matter of fact, PCL cannot be easily frozen in an amorphous glassy state due to its high rate of crystallization [25]. The DSC scans, obtained after rapid cooling from the molten state, indicate therefore a quite different thermal behavior of PHEBA and PCL homopolymers: the former is completely amorphous, whereas the latter is partially crystalline. Moreover, the phase behavior of PHEBA/CL copolymers depends on composition: amorphous or semicrystalline samples are obtained at high PHEBA or high PCL content respectively. As can be seen from Fig. 4 and from the data collected in Table 2, the glass transition temperature is markedly influenced by the amount of comonomeric units in the chain: the values of T_g and of the specific heat increment Δc_p associated with the glass transition are plotted in Fig. 7 as a function of HEBA unit content. The values of T_g and of Δc_p of partially crystalline PHEBA10/CL90 copolymer do not follow the same composition dependence as that of the amorphous polymers (HEBA unit content from 20 to 100 mol%). Amorphous samples show a constant Δc_p value (0.42 J g^{-1} $°C^{-1}$), whereas the magnitude

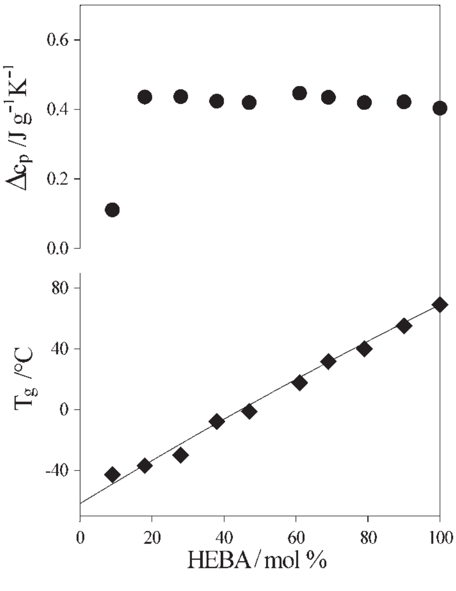


Fig. 7 Composition dependence of T_g (◆) and Δc_p (●) for PHEBA/CL random copolymers. Solid line: theoretical curve of T_g *vs.* composition calculated on the basis of Wood's equation

of the heat capacity change is considerably lower for the copolymer containing 10% HEBA units. This is an obvious consequence of the crystallinity present in this sample, which reduces the amorphous phase undergoing the transition. As far as the glass transition temperature is concerned, crystallites hinder the motion of the amorphous chains leading to T_g value higher than expected.

In amorphous random copolymers, T_g is usually a monotonic function of composition [26] and the most common relationship used to predict T_g as a function of comonomer concentration is the Fox equation [27]:

$$1/T_g = w_I / T_{gI} + w_{II} / T_{gII} \tag{2}$$

where T_{gI} and T_{gII} are the glass transition temperatures of the pure homopolymers and w_I and w_{II} the respective mass fractions.

The experimental data of PHEBA/CL polymers in the amorphous state (HEBA unit content from 20 to 100 mol%) are in general higher than the predicted values, even though they follow the same trend, i.e. T_g increases with increasing the amount of HEBA units. The Fox equation is known to have limitations, since it does not account for factors like chemical structure and polymer chain mobility.

Among the various equations proposed to describe the composition dependence of the glass transition temperature in random copolymers, the Wood one is well known [28]:

$$T_g = w_I T_{gI} + k w_{II} T_{gII} / w_I + k w_{II} \tag{3}$$

where k is a constant parameter.

The equation fits well the experimental data (with the adjustable parameter k equal to 1.3), using for PHEBA the glass transition temperature experimentally measured by us, and fixing for PCL the value of –62°C reported in literature [29].

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