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The structure of poly(ethyl acrylate-*co*-hydroxyethyl methacrylate) copolymer networks by segmental dynamics studies based on structural relaxation experiments

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Abstract

The structure of the system obtained after free radical copolymerization of ethyl acrylate and hydroxyethyl methacrylate comonomers has been studied using dynamic-mechanical and calorimetric techniques. According to the copolymerization theory it is known that the free-radical copolymerization reaction of two monomers may give rise to the formation of a copolymer having a chain composition different from the random mixture corresponding to the original solution. In our system, the dynamic-mechanical spectra suggest the existence of two main α relaxation processes in the copolymers. Conventional differential scanning calorimetry (DSC) heating scans show a single and broad glass transition located between those of the pure components. Segmental dynamics studies by subjecting the samples to isothermal annealing in the region of the glass transition and below it give information about the temperature range where conformational mobility is high enough and allow to infer conclusions about the composition distribution of the material. These results although qualitatively well correlated with the copolymerization theory, that predicts the composition of the system from the monomer feed ratios and the reactivity ratios of the monomers, provide a further insight in the final material architecture.

Keywords: Copolymers; Segmental dynamics; Structural relaxation

1. Introduction

Hydrogels stand out among synthetic materials used as biomaterials mainly due to their ability to absorb large amounts of water [1]. However, polymer hydrogels display poor mechanical properties and for many applications they are in need of reinforcement, usually with a hydrophobic component [2]. New families of polymers have been developed seeking to improve the mechanical behaviour of the corresponding hydrogels. Copolymerization with a more resistant hydrophobic group is a widespread way of getting such a goal.

The copolymerization of two monomers gives rise to the formation of a copolymer chain having a composition and a monomer sequence distribution that depend on the relative proportion of the employed monomers and their reactivities [3], and may give rise not to random copolymers but to materials with a certain degree of order in the association of the constituent monomers in the chains. Differential scanning calorimetry (DSC) is a useful technique to characterize the heterogeneity of multicomponent polymer systems at a nanometric scale [4], since the relationship between conformational mobility and the glass transition reflects the composition distribution, i.e. the copolymer structure. The conformational rearrangement of polymer chains around the glass transition temperature is a co-operative process that involves polymer segments pertaining to different chains, which must move simultaneously or sequentially. A region of the material in which a co-operative rearrangement takes place without disturbing the rest of the material is called a conformational rearranging region (CRR) [5]. The size of this region is related to the length of co-operativity and is around a few nanometers at the glass transition temperature [6]. This order of magnitude characterizes the sensitivity of the DSC technique for

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detecting phase separation in multicomponent polymer systems in the sense that if the domain of a component is larger than the size of the CRR its glass transition can be detected by DSC. Thus the study of the co-operative conformational mobility is a useful tool to characterize the miscibility in polymer blends. As an example, the broadening of the glass transition interval in a blend with respect to those of the pure components [7,8] has been explained by composition fluctuations in regions with sizes around that of the CRR [4,9–13]. This effect is also found in the copolymers studied in this work and can be analyzed in detail with the help of structural relaxation experiments.

The structural relaxation is the process of approaching an equilibrium state by a glass held at constant temperature and pressure after its formation history. During this process several physical quantities such as the specific volume, enthalpy or entropy decrease with time. The process can be studied by DSC subjecting the sample to a thermal history starting at a temperature T_0 higher than its glass transition temperature; after cooling at a controlled rate to a temperature T_a below, or in the region of the glass transition, the sample is kept isothermally for a period of time t_a. The sample is then brought at a fixed cooling rate to a temperature T_1 below T_g, and subsequently heated from T_1 to T_0. This heating thermogram shows a characteristic peak of the specific heat capacity that depends very sensitively on the previous thermal history, i.e. the annealing temperature T_a and time t_a (Fig. 1). The enthalpy loss suffered by the sample during the isothermal stage at T_a is equal to the area (from T_1 to T_0) between the heating thermogram measured after this annealing and that determined between the same temperatures in a reference scan without annealing [14]. Fig. 1 shows a sketch of the DSC thermograms (annealed and reference) and the curve obtained after subtracting them. The structural relaxation DSC peaks are the consequence of molecular mobility in the material. The temperature and the height of the peaks in heterogeneous systems depend on composition fluctuations [15] and can be used in the case of copolymer systems to investigate the structure of the material.

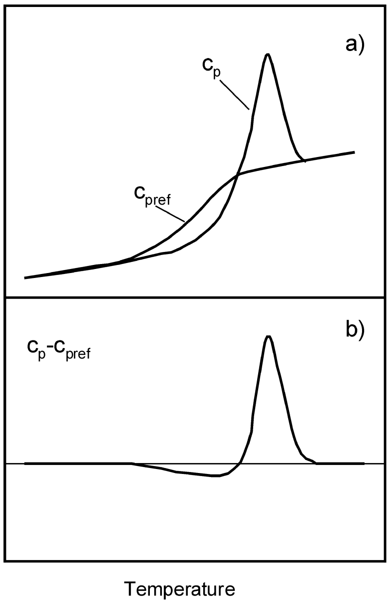

Fig. 1. (a) Sketch of the temperature dependence of the heat capacity of a material subjected to an annealing process c_p at a temperature T_a below T_g showing the characteristic peak. The unannealed reference scan, c_{pref} is also included. (b) Sketch of the $c_p - c_{pref}$ curve obtained subtracting the annealed and unannealed curves.

In this work we study copolymers based on hydrophilic and hydrophobic components first by dynamic-mechanical measurements and conventional DSC, and then we obtain a deeper insight of the system from the conformational motions that take place at different temperatures as revealed by structural relaxation experiments. These physical results are correlated with the copolymer composition predicted by the terminal model [16,17], the first and simplest model that is able to describe at least 90% of all known copolymer systems [3], which relates the copolymer composition to the monomer feed ratio and the reactivity ratios of the monomers.

2. Experimental

Copolymers were prepared from a solution of both monomers ethyl acrylate, EA, and hydroxyethyl methacrylate, HEMA, with the desired proportion, using 0.1 wt% of benzoin (Scharlau 98% pure) as photoinitiator and 2% by weight of ethyleneglycol dimethacrylate, EGDMA (Aldrich 99% pure) as crosslinking agent. The copolymerization was carried out up to limiting conversion. Three monomer feed compositions were chosen, given by the weight fractions of HEMA in the initial mixture of 0.7, 0.5 and 0.3. After polymerization took place under the ultraviolet light, low molecular weight substances were extracted from the material by boiling in ethanol for 24 h and then drying in vacuo to constant weight. Besides, pure poly(hydroxyethyl methacrylate), PHEMA, and poly(ethyl acrylate), PEA, networks were prepared in the same way. Hereafter copolymers with the aforementioned composition will be named as CH70, CH50 and CH30, respectively.

Dynamic-mechanical spectroscopy (DMS) was performed at a heating rate of 1 °C/min in a Seiko DMS210 instrument from −100 to 200 °C at a frequency of 1 Hz. Samples for DMS experiments were rectangular approximately $10 \times 2.5 \times 0.8$ mm^3.

DSC was performed in a Pyris 1 apparatus (Perkin Elmer). Dry nitrogen gas was let through the DSC cell with a flow rate of 20 ml/min. The temperature of the equipment was calibrated by using indium and benzene. The melting heat of indium was used for calibrating the heat flow. Before the heating scan, the sample was subjected to a thermal history that started at 150 °C for the copolymers and the PHEMA network and at 70 °C for the PEA network. The sample was then cooled at 40 °C/min to the annealing temperature T_a, kept isothermally for 200 min, and cooled again at 40 °C/min to -40 °C. The subsequent heating scan from this temperature to the starting one took place at 10 °C/min. Immediately after each of these experiments a reference scan was performed consisting in cooling the sample from the highest to the lowest temperature, from T_0 to T_1, at 40 °C/min. In this way the baseline of the DSC corresponding to the annealing and the reference scans are nearly identical and the position of the sample in the sample holder of the DSC is the same as well. The difference between both scans is zero with great accuracy at the start and the end of the thermogram. The normalized heat flow, which has heat capacity units, is obtained by dividing the heat flow as obtained from the apparatus by the mass and the heating rate, and was employed instead of the absolute value of the specific heat capacity.

3. Results

The dynamic-mechanical relaxation spectra of the pure PEA and PHEMA networks show a single maximum, which corresponds to the main relaxation or α process (Fig. 1). The temperatures of the maximum of the loss tangent (Fig. 2(b)) are 9 and 140 °C, respectively. A shoulder in the low-temperature side of the main peak of the PHEMA network can be ascribed to its secondary β relaxation as we will discus below. DMS experiments on copolymers show two relaxation processes of different intensity located between the temperatures of the main relaxation of the pure polymers. The bigger one is at higher temperature and its intensity is similar to that of the pure PHEMA network independently of the copolymer composition. On the contrary the second one is much smaller and occurs at a lower temperature, near the α relaxation of the PEA network; its intensity depends on composition: the higher the amount of HEMA in the copolymer the lower the magnitude of this relaxation process (Fig. 2(b)).

Fig. 3 shows the heating DSC thermograms for the pure networks and the copolymers. As expected, a single glass transition is seen both in the PEA ($T_g = -12$ °C) and PHEMA ($T_g = 93$ °C) networks. For the copolymers the situation is somewhat different. CH30 and CH70 show a single and broad glass transition between those of the pure components, and in CH50, even if it shows a single and broad glass transition, two different steps can be inferred from the thermogram.

For a detailed analysis of these systems, all the samples were subjected to structural relaxation experiments that included an isothermal annealing of 200 min at different temperatures (every 5 °C in the pure networks and every 10 °C in the copolymers). After each thermal history a heating thermogram was recorded and a reference scan followed with no change of the position of the sample and reference pans in the DSC holder. These two thermograms were used to calculate the difference between the normalized (as described in the previous section) heat flux curves for the two scans. Due to the experimental procedure this magnitude equals the difference between the heat capacity in the annealed and the reference scans ($c_p - c_{ref}$). As representative examples Fig. 4 shows ($c_p - c_{ref}$) obtained for the PHEMA and the CH50 networks. The magnitude of the peaks depends on the annealing temperature and tends to

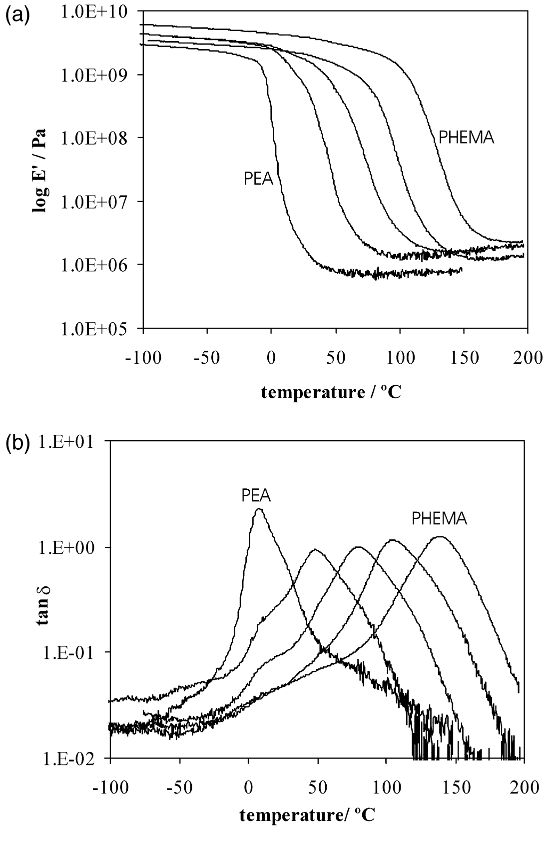

Fig. 2. Dynamic-mechanical relaxation spectra of PEA, PHEMA and the copolymers of intermediate composition (CH30, CH50, CH70) measured at 1 Hz. (a) log E'. (b) Mechanical loss tangent.

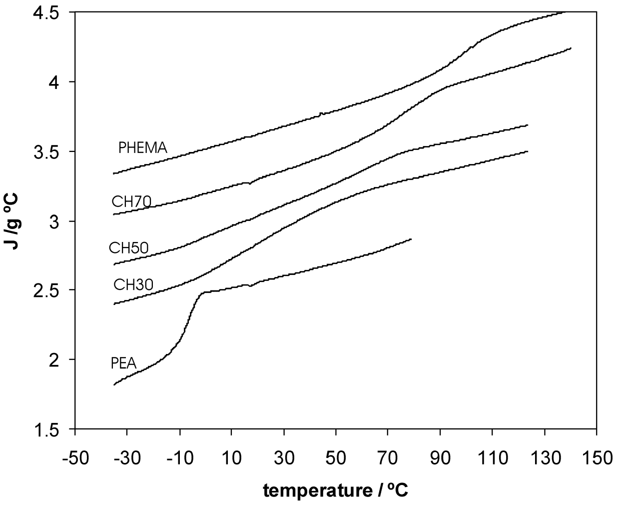

Fig. 3. DSC thermograms obtained at a heating rate of 10 °C/min for the pure PEA, PHEMA and the copolymers of intermediate compositions.

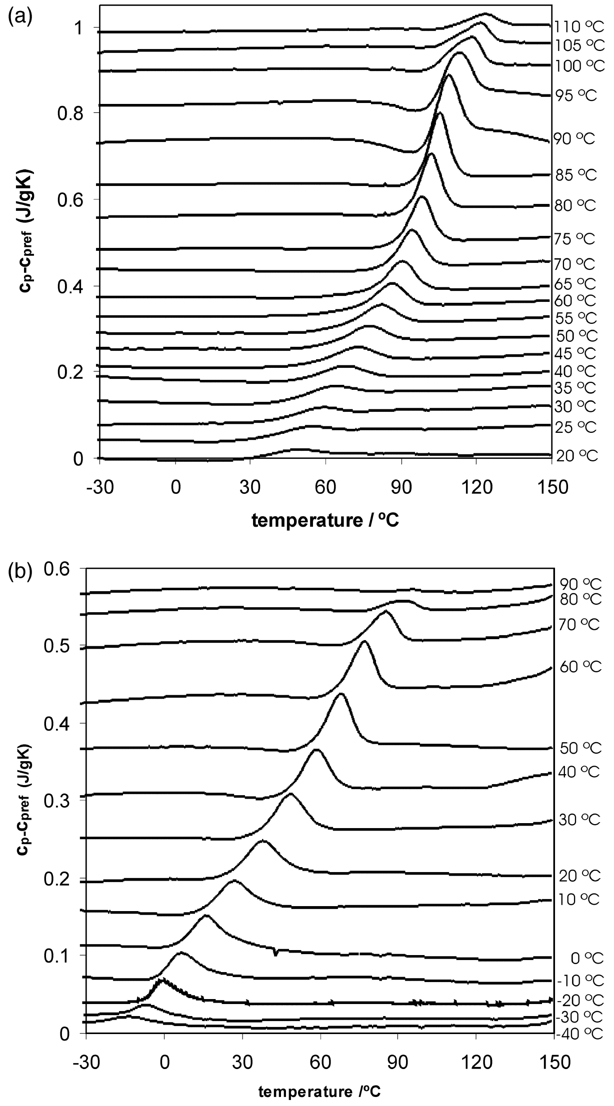

Fig. 4. Temperature dependence of $c_p - c_{pref}$ calculated for PHEMA (a) and copolymer CH50 (b) from the thermograms measured after annealing for 200 min at the temperature shown in the graph. The curves have been vertically shifted for clarity.

vanish at temperatures both sufficiently higher and lower than T_g.

4. Discussion

The copolymerization theory allows estimating, via the terminal model, the copolymer composition [16,17] once the polymerization process is finished. The monomer molar fraction F_i in the copolymer in terms of the monomer molar fraction in the reaction mixture f_i and the reactivity ratios r_i turns out to be

$$\frac{F_1}{F_2} = \frac{f_1(f_1 r_1 + f_2)}{f_2(f_2 r_2 + f_1)}, \tag{1}$$

Reactivity ratios from Ref. [18] are 0.189 and 11.21 for EA and HEMA, respectively. This enormous difference has an immediate consequence. HEMA radicals have a higher tendency to react with HEMA monomers than with the EA ones. On the other hand, the low EA reactivity ratio means that this monomer has a higher affinity towards HEMA monomers than towards the EA ones. The composition predicted by the terminal model (Eq. (1)) is shown in Fig. 5. The theoretical prediction lies above the straight line that gives the random composition of the copolymer (that is, keeping in the final copolymer the same proportion of the two components present in the original reaction mixture). The amount of EA in the copolymer chains is always lower than in the original mixture, what suggests the idea of a system formed by copolymer chains where both EA and HEMA are not randomly distributed, but where blocks of HEMA are preferentially present. Once the HEMA monomer has been completely consumed in the reacting mixture the remaining EA gives rise to pure homopolymer chains. However, the way in which the chains are spatially distributed in the final system cannot be obtained only from copolymerization theory. In this sense, if the copolymerization were carried out with 0.7 HEMA molar fraction monomer feed, the system obtained would have around 30% of PEA chains. With this in mind, one could think of two well-defined phases in the material: on the one hand the true copolymer chains and on the other hand the pure PEA chains, what should result in two well-defined glass transition process in a conventional DSC scan. Since this is not the case (Fig. 3) further research is needed if the structure of the copolymerized systems want to be clarified.

Results obtained both from DMS and structural relaxation experiments suggest the existence of composition heterogeneities in the system obtained by free radical copolymerization of EA and HEMA comonomers. Dynamic-mechanical spectra show two relaxation processes as can be seen clearly in the loss tangent (Fig. 2(b)). The

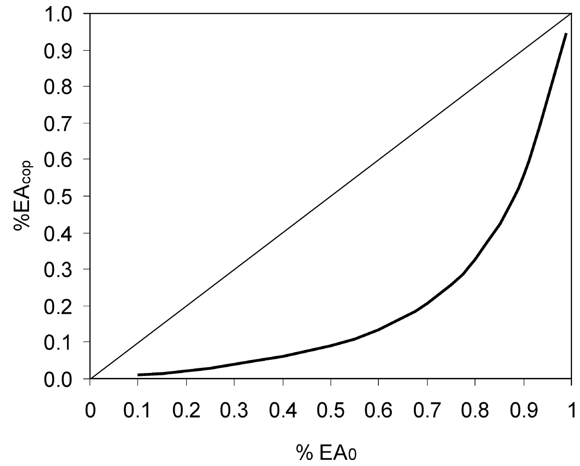

Fig. 5. Molar fraction of EA units in the copolymer as predicted by the terminal model (%EA$_{cop}$)as a function of the molar fraction of EA monomers in the reacting mixture (%EA$_0$). The straight line gives the composition of a random copolymer where the fraction of monomers of the original mixture is kept also in the polymerized material.

higher one can be ascribed to the main relaxation of the chains and its position depends on the copolymer composition, the higher the amount of HEMA the higher the temperature of the maximum. On the other hand, the mechanical spectra show a lower relaxation peak whose origin is controversial. In this sense, if one believes that the copolymer is a random system, where both of the monomers distribute statistically through the chains, the peak could be ascribed to a secondary relaxation, or β process. However, if there were some kind of phase-separation in the system, even at the nanometric scale, this lower peak could be due to a second α relaxation in the material. Although it is difficult to quantify the strength of this low-temperature relaxation due to the overlapping to the main peak, it can be accepted that the height of the low-temperature peak increases as the content of EA in the systems does. Since the secondary relaxation should be due to the HEMA units of the chain there is at least a qualitative argument to ascribe the low-temperature relaxation to the presence of EA-rich regions of the material with lower T_g than the average. With the purpose of discerning whether the relaxation in the mechanical spectrum is the consequence of an α or a β process, DSC was used, since this technique is not sensitive to the motions associated with secondary relaxations because they do not contribute to the specific heat capacity value of the material. Fig. 3 shows the calorimetric thermograms. Obviously single thermograms do not contain enough information to decide whether there are or not domains in the material that can be ascribed to different phases, i.e. whether there is some degree of phase separation.

New developments of conventional DSC which might be called calorimetric thermal sampling provides detailed information about heterogeneity in multiphase materials [4,19]. The methodology is based on structural relaxation experiments for a fixed annealing time in a broad temperature range around the glass transition. The existence of a peak in the heating thermogram after annealing for a given time at a fixed temperature is a consequence of the enthalpy approaching towards equilibrium states during the isothermal stage and, therefore, an indication that conformational motions take place in the material at the annealing temperature T_a. Fig. 4 shows that the magnitude of the peaks, which relates directly to the enthalpy relaxed isothermally, decreases as temperature moves away from T_g and this means that, since the annealing time is constant, segmental movements are quicker in the glass transition region. At higher temperatures, but still in the glass transition region, the dynamics of the process is even quicker but the magnitude of the peaks reduces dramatically since the distance from equilibrium is small. The area defined by the $(c_p - c_{ref})$ peaks (Fig. 4) allows to identify the temperature range where conformational motions take place in the material. However, the accurate determination of the enthalpy loss is difficult, especially when its magnitude is small. For this reason the height of the peak in the $(c_p - c_{pref})$ curve, $(c_p - c_{pref})_{max}$, that can be calculated much more accurately, can be preferred for characterization of the temperature interval in segmental motions on the time scale of the DSC technique take place [4]. It is interesting to note the shape of the peaks shown by PHEMA after annealing at the highest temperatures, 100 or 105 °C, as they seem to be the result of the overlapping of two peaks. This feature can be understood as a consequence of certain heterogeneity in the glass transition temperature of pure PHEMA. One may speculate with the presence of regions of higher crosslinking density than the average or regions of higher connectivity through hydrogen bonds than in the average. In both cases these regions would present a higher glass transition temperature and the structural relaxation process would produce double peaks in the thermogram [20,21]. Fig. 6 shows $(c_p - c_{pref})_{max}$ as a function of the annealing temperature for the homonetworks and the copolymers. The temperature interval where conformational motions take place in the PEA network is narrow. The well defined maximum takes place when the annealing temperature is around −20 °C, that is around 8 ° below the enthalpic T_g and it continues until around −40 °C, i.e. roughly speaking 25 ° below T_g. The phenomenology of the structural relaxation in the case of PHEMA is different, as can be seen from its $(c_p - c_{pref})_{max}$ curve. The maximum is located for an annealing temperature of 85 °C, around 15 ° below T_g, but conformational motions are detectable at temperatures even 70 ° below it, as seen from the long tail that shows the $(c_p - c_{pref})_{max}$ curve for PHEMA in Fig. 6. Besides, the height of the maximum is around 50% of that of the PEA network. The value of $(c_p - c_{pref})_{max}$ measured after annealing at a given temperature, T_a, is proportional to the number of monomeric units participating in the relaxation process at T_a. This means that the height and the width of the peak shown by the $(c_p - c_{pref})_{max}$ curve are related to each other. If the temperature interval in which the glass transition takes place is narrow, as in the case of PEA, most of the mass of the material relax at the same rate at each annealing temperature. On the contrary a broad glass transition interval reflects the presence of T_g fluctuations in the material and, as a consequence, at every annealing temperature only a part of the polymer segments participate in the structural relaxation process. Heterogeneous systems show shorter and broader peaks in the $(c_p - c_{pref})_{max}$ curve. This effect will be also shown by the copolymers as described below.

The $(c_p - c_{pref})_{max}$ curves obtained for the copolymers (Fig. 6) show that conformational rearrangements are possible in a very broad temperature range. The maximum of the curves does not follow a monotonic evolution with the composition of the samples. When the amount of HEMA in the material is higher than 50%, the position of the maximum takes place close to that of the homopolymer, around 60 °C. However, in copolymer CH30 not only is the maximum around 0 °C but also the shape of the distribution is significantly different.

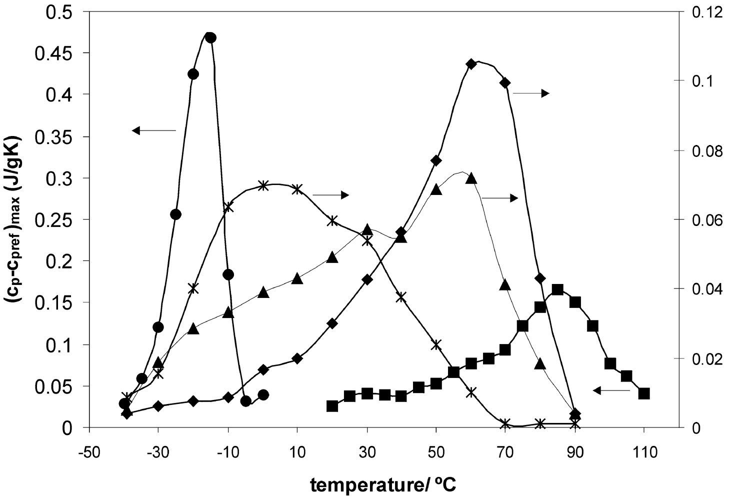

Fig. 6. Height of the maxima of the $c_p - c_{pref}$ curves for the PEA (●), PHEMA (■), and copolymers CH03 (*), CH05 (◆) and CH07 (▲). Curves between points are a guide to eye.

Copolymer CH70 shows a long tail to the left of the maximum and the greatest part of conformational motion takes place at temperatures where this motion is also present in the pure PHEMA network. In a certain way the distribution for this copolymer is that of PHEMA but displaced towards lower temperatures. This entails the existence of a temperature interval between − 10 and 20 °C where the enthalpy loss is not null for the copolymer but where the pure networks do not show conformational activity. This suggests that a significant proportion of both components are present in the co-operatively rearranging region. Besides, such a wide $(c_p - c_{pref})_{max}$ curve means a broad compositional distribution, i.e. the existence of composition hetereogeneity among the rearranging regions of this copolymer. Copolymer CH30 shows a behaviour somewhat different. The $(c_p - c_{pref})_{max}$ curve is also asymmetric but now it shows a long tail towards temperatures above the maximum. Three different temperature intervals can be distinguished. The first one, at high temperatures, where conformational motions take place both in the copolymer and in the pure PHEMA. The second one is located between − 10 and 20 °C where conformational activity takes place in the copolymer but not in the pure components. The last one covers the whole temperature range where rearranging motions take place in the pure PEA network. Again this broad temperature range suggests the heterogeneous composition of the domains in the material, but now it is important to realize that the relaxation processes at lower temperatures must be due to the existence of co-operative rearranging regions made up of PEA chains. This suggests that sample CH30 has a distribution of chains with different proportions of EA and HEMA segments in which the HEMA domains predominate, as shows the right-wing of the $(c_p - c_{pref})_{max}$ curve for this copolymer.

The $(c_p - c_{pref})_{max}$ curve for CH50 is not as asymmetric as those of the other two copolymers, but still seems to be composed of two superposed distributions. The first one, at higher temperatures, shows a maximum around 65 °C and finishes around 90 °C, the annealing temperature where the maximum for the PHEMA network appears; it can be ascribed to HEMA-rich domains. Nevertheless, there are no pure-HEMA domains in the material. If this were the case, conformational motions would take place also at higher temperatures just like it happens in the pure network. On the other hand the lower temperature distribution, due to rich EA domains, starts at − 40 °C, the same temperature where conformational motions start for the pure PEA network, and finishes around 30–40 °C. Consequently, it covers the whole temperature range of the PEA distribution and extends to the temperature interval were pure networks show no chain mobility (from − 10 to 20 °C). The existence of annealing peaks in the entire temperature interval of the PEA network suggests again the existence of pure-PEA domains, where conformational motions of PEA chains take place without disturbing the rest of the material. Then, as the amount of HEMA in a CRR increases, the position of the annealing peak moves to higher temperatures and finally there is a qualitative change, similar to the phase inversion in a blend, where HEMA rich domains plasticized by EA molecules relax following a $(c_p - c_{pref})_{max}$ distribution similar to that of copolymer CH70.

This phenomenology suggests that there is a distribution of co-operative rearranging regions in the copolymers, whose size is around a few nanometers, with a broad range of compositions. Qualitatively speaking, there are two kinds of domains: those that contain segments of both components, in which HEMA units are predominant, and those that consist of pure PEA chains. Thus copolymers CH50 and CH70 show a $(c_p - c_{pref})_{max}$ curve asymmetrically shifted towards high temperatures, where the distribution curve of the PHEMA network is located; copolymer CH30, despite the position of its peak near the PEA curve, shows a long high-temperature tail, what indicates the predominance of the HEMA component in the copolymer. This behaviour can also be explained in terms of the dependence on composition and temperature of the size of the co-operatively rearranging regions. According to the equation proposed by Donth [22], the volume of a CRR is

$$V_a(\phi) \approx \left[\frac{T_g(\phi) - c_2}{T - (T_g(\phi) - c_2)} \right]^2, \tag{2}$$

where ϕ gives composition and c_2 is the Williams–Landel–Ferry parameter [23]. The glass transition temperature of a binary mixture depends on its composition (it typically evolves monotonously from the glass transition of one of the components to that of the other), and it can be assumed that the calorimetric glass transition takes place when the volume of the CRR reaches a critical value (several nanometers). Since the higher is the HEMA amount in the domain, the higher is its glass transition, then the richer the HEMA composition of the domain, the higher the temperature at which the critical volume is obtained, what induces a distribution of T_g as a consequence of composition fluctuation.

5. Conclusions

The material obtained by free radical copolymerization of EA and HEMA monomers is not a random copolymer but a heterogeneous system as the application of copolymerization theory suggests. Besides, structural relaxation experiments reveal the existence of a composition heterogeneity in the material. DSC has shown to be a powerful tool in the analysis of nanoheterogeneities in polymer systems. The DSC technique provides a further insight in the structure of the system and is able to show whether the association or not of the monomeric units in regions at least of the size of the CRR (a few nanometers). The copolymer chains are formed by long blocks of HEMA and some EA units, and, due to the high difference between the reactivity ratios of the two comonomers, some pure PEA chains are also present in the final system but in such a way that a distribution of CRR is found in the material in a broad temperature range revealing the composition heterogeneity at the nanometric scale.

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