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Synthesis and Characterization of Functionally Gradient Materials Obtained by Frontal Polymerization

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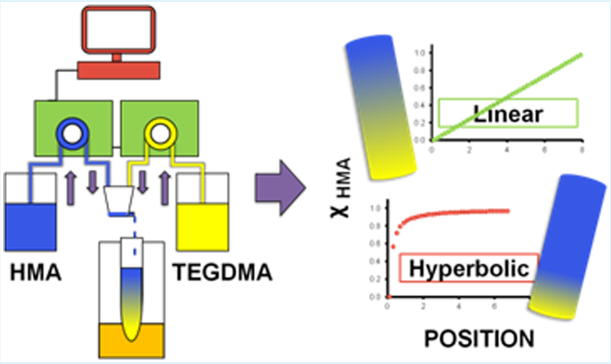

ABSTRACT: Functionally gradient materials (FGMs) with gradual and continuous changes of their properties in one or more dimensions are useful in a wide range of applications. However, obtaining such materials with accurate control of the gradient, especially when the gradient is nonlinear, is not easy. In this work, frontal polymerization (FP) was exploited to synthesize polymeric FGMs. We demonstrated that the use of ascending FP with continuous feeding of monomers with computer-controlled peristaltic pumps provided an excellent method for the preparation of functionally gradient materials with programmed gradients. To test the effectiveness of the method, copolymers made from triethylene glycol dimethacrylate/hexyl methacrylate with linear and hyperbolic gradient in composition were synthesized. Differential scanning calorimetry (DSC), Shore A hardness measurements, compression tests, and swelling studies were performed along the length of the materials to assess the relationship between the gradients and the material properties. Glass transition temperatures, determined by DSC, showed a linear dependence on the composition and were in agreement with theoretical values. The other properties showed different and specific behaviors as a function of the compositional gradient.

KEYWORDS: *functionally gradient material, frontal polymerization, mechanical properties, glass transition temperature, swelling ratio, shore A hardness, copolymer, polyacrylate*

■ INTRODUCTION

Functionally gradient materials (FGMs) are systems whose compositions, microstructures, or atomic orders progressively vary in one or more dimensions, determining a gradual change of the material properties as a function of position. One unique characteristic of FGMs is the possibility of designing materials for specific applications, in which properties are locally optimized. In addition, in FGMs the sharp interfaces typical of standard composites, where failure often occurs, are eliminated[1] and replaced by a gradient interface that produces a smooth transition from one material to the next.[2] FGMs, usually found in nature in bones, teeth, etc., have inspired technology for the design of advanced functional materials.[3]

In particular, there are two main research fields, namely, polymeric and nonpolymeric materials (metallic or ceramics), the former being the scope of interest of the present paper. Although theoretically described for the first time by Bever[4] and Shen,[5] the first successful production of a gradient material was carried out as part of a national research Japanese space program in 1984.[6,7] From then on, a major part of the research on FGMs was dedicated to the processing of these materials, and a large variety of production methods has been developed.

There are two main classes of technological processes of FGM manufacture. The first comprises methods of new material preparation by sequential addition of layers, which can be exploited in technologies such as lamination,[8] deposition,[9] or solid freeform fabrication.[10] The second category refers to the modification of initially homogeneous systems and encompasses centrifugal casting,[11] heat treatment,[12] surface treatment, or infiltration.[13] Some of the most interesting applications of FGMs include the design of aerospace materials with very high thermal gradients,[14] artificial tissues for the replacement of bones[15] or teeth,[16] materials for defense with low crack propagation,[17] materials for energy conversion devices and thermal barriers,[18] and gradient refractive index materials for optoelectronics.[19]

Gradient polymers that have been processed so far include gradient fiber composites,[20] gradient interpenetrating polymer networks,[21] polymers with a gradual composition of plasticizer,[22] gradient refractive index materials,[23] polyacrylates with nonlinear dye gradients, for which Pojman and Chekanov exploited a frontal polymerization (FP) approach.[24] It is noteworthy that with respect to the majority of the FGM production methods, FP has more potential. Indeed, while the other FGM production methods are usually limited to producing simple (linear) gradients or gradients that cannot be controlled because they are caused by diffusion or gravity, we show here that FP allows precise composition control.

Frontal polymerization allows the conversion of monomer into polymer by exploiting the heat released from the polymerization reaction to create a self-sustaining front that propagates throughout the whole reactor.[25] FP has many advantages as compared with the classical polymerization techniques: shorter reaction time, low-energy consumption, easy and simple protocols, and production of materials that often show better properties than those obtained by classical polymerization. As regards FGM production, unlike the majority of the techniques, FP does not involve multiple steps or the use of large quantities of solvents that increase cost and pollution.

Frontal polymerization was first proposed in 1972 by Chechilo and Enikolopyan, who synthesized poly(methyl methacrylate).[26] Lately, this technique was developed by Pojman's,[27−33] White's[34−36] and other groups.[37−41] Mariani et al. also exploited this technique for preparing a wide range of polymers.[42−48]

In a typical FP experiment, the hot polymerization front is generally descending; more specifically, the reactor is filled with the monomer mixture, and the front is ignited by applying heat to the upper end of the reactor, thus allowing the front to self-propagate downward. In ascending frontal polymerization (AFP), buoyancy-driven convection can negatively affect front propagation: preheated monomer immediately above the front will eventually float, and heat dissipation due to convection will overcome heat production in the reaction zone, which may cause the front to quench.[49] To overcome this problem, Pojman et al. restricted convection to a narrow layer of liquid monomer and continuously fed the top of the moving front with fresh monomer; in this way, the front was able to propagate.[24,50,51] This approach offers an excellent opportunity to create any type of gradient in a polymeric material, by simply changing the composition of the monomer feed stream while an ascending polymerization front is generated in a reaction vessel. Pumps provide monomers or resins in a controlled ratio on top of the ascending front as it propagates to maintain a nearly constant thickness of unreacted monomers. The height of unreacted monomers is finely tuned so that the front is not extinguished but progresses in a controlled manner. By varying the ratio of the monomers and/or the concentration of additives present in the mixture, functionally gradient materials can be obtained.

In this work, a gradient copolymer made of hexyl methacrylate (HMA) and triethylene glycol dimethacrylate (TEGDMA) was chosen as a model system, and the properties of the resulting materials and their variation as a function of the gradient composition are studied.

■ EXPERIMENTAL SECTION

Synthesis of Gradient Copolymers of HMA/TEGDMA. TEGDMA (MW = 286 g/mol), HMA (MW = 170 g/mol), and pararosaniline base (MW = 306 g/mol) were purchased by Sigma Aldrich and used as received. Aliquat persulfate (APS) was synthesized according to the literature.[52]

Peristaltic pumps (model NE-9000) were purchased from New Era Pump System Inc., which also supplied the software for computer control and for generating the pump program. The pumps were equipped with PERI-HEAD-KIT-YG4 for high precision dispensing, with PharMed Tubing 1/16 in. ID × 3/16 in. OD × 1/16 in. wall thickness.

The TEGDMA/initiator solution was prepared by adding 1 wt % of APS to 10 g of TEGDMA. The TEGDMA/initiator solution containing pararosaniline, used for preliminary studies, was prepared by adding 0.5 wt % of pararosaniline and 1 wt % of APS to 10 g of TEGDMA. HMA/initiator solution was prepared by adding 1 mol % of TEGDMA and 1 wt % of APS to 10 g of HMA.

As shown in Figure 1, Pump A supplies the TEGDMA/initiator solution, and pump B supplies the HMA/initiator solution. The sum of the two flow rates is kept constant at 1 mL/min, to ensure a constant feed to the top of propagating polymerization front, while the flow rate of each pump changes according to the programmed desired gradient. This value of total flow rate turned out to be sufficient for maintaining a constant layer of monomer for the propagation of the hot front: when higher flow rates were selected, the convection occurring in the liquid layer caused heat dissipation, front extinction, and poor gradient control.

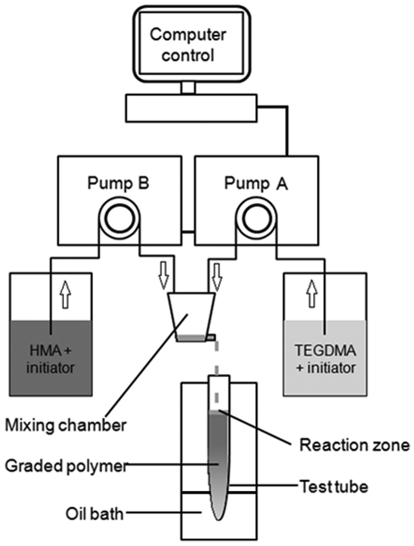

Figure 1. Schematic representation of the apparatus used for obtaining gradient polymeric materials.

The solutions from Pumps A and B flowed into a 0.5 mL mixing chamber, in which a magnetic stirrer ensured the complete mixing of the two solutions before flowing into the test tube. Before polymerization, the pumps were started to fill the tubes and the mixing chamber. A test tube (height, 100 mm, i.d. = 14 mm), already containing 1.5 mL of TEGDMA/initiator solution, was immersed to a depth of 2 cm in an oil bath at 150 °C. Immediately after the monomer started polymerizing, the selected gradient program was launched, and the reactant solutions were dropped into the tube; the monomers immediately polymerized, and the ascending front was fed with fresh monomers continuously dropping from the mixing chamber.

Differential Scanning Calorimetry Analyses. DSC measurements were performed with a Q100 Waters TA Instruments calorimeter, equipped with TA Universal Analysis 2000 software. Analyses were performed in heat−cool−heat mode at 20 °C/min in inert atmosphere (argon flow: 40 mL/min), with a first scan from 30 to 250 °C and a second scan from −80 to 250 °C. Samples were cut in small cylinders in correspondence of 0, 2, 4, 6, 8 cm for the linear gradient and at 0.1, 0.5, 1.0, 1.5, 1.9, 3.7, 5.5, 7.2 cm for the hyperbolic one.

Shore A Hardness. The surface hardness was measured according to ASTM D2240 (Shore A) at 23 ± 2 °C, directly on cylindrical samples (diameter = 14 mm) obtained after polymerization. The probe was put on the surface of cylinder, and hardness was measured every 2 mm along the vertical axis. For each gradient three samples were analyzed, five measurements were performed on different points at the same height, and the values were averaged. The standard deviation was always below 5%.

Compression Tests. Compression tests, according to ASTM D695, were performed using a Zwick-Roll Z010 apparatus, equipped with a 100 kN load cell, at 23 ± 2 °C and 50 ± 5% relative humidity. For each gradient three samples were analyzed; samples were cut in small cylinders 1 cm high, and at least five tests were repeated for each sample. The standard deviation was always below 5%.

Swelling Measurements. For swelling tests, 2 mm thick discs were cut from the cylindrical samples. The samples were put in acetone or hexane and weighed every hour until a constant weight was achieved: the swelling ratio (SR%) of copolymers was calculated by applying the following equation:

$$\mathrm{SR\%} = \frac{M_s - M_d}{M_d} \times 100 \tag{1}$$

where M_s and M_d are the sample masses in the swollen and in the dry state, respectively. For each gradient, three samples were analyzed, and average values were calculated. The standard deviation was always below 10%.

RESULTS AND DISCUSSION

A preliminary study was carried out by using a dye (pararosaniline) to have visual feedback on the gradient formation. TEGDMA was employed as the monomer, and the addition of pararosaniline in the solution fed by pump B created a variation in color along the vertical axis, as shown in Figure 1. The image of the polymer with dye gradient was analyzed to obtain a graphic of the gray level (which is related to the dye concentration) along the polymer. The dye concentration gradually varies along the polymer, as shown in Figure 2. Bubbles and cracks produced a significant variation in gray value, which appeared as noise peaks on the curve; however, a decrease of dye concentration with position is observed. Also note that, in the end parts of the material, the gray value looks almost constant, while the color saturation is reached within the last part, and further variation in dye concentration is not detectable. Notice that this visual evidence can only be considered as a first indication of the reliability of the techniques and is based on the assumption of a direct proportionality between the concentration of pararosaniline and the gray level.

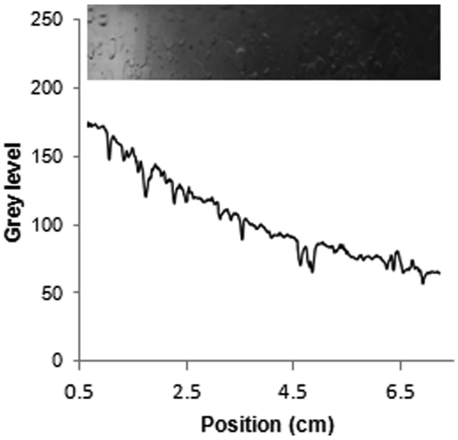

Figure 2. Gray scale image of poly(TEGDMA) with a gradient of dye and relative gray value along the position. The dye was applied to produce a linear concentration profile.

After this first confirmation of gradient creation, we decided to study a simple gradient material, that is, a copolymer material with variable macroscopic composition of two comonomers (TEGDMA and HMA) along the vertical axis. TEGDMA was used because it is known to frontally homopolymerize,[24] while HMA was chosen because of the properties of its polymer as compared with those of poly(TEGDMA) (see below). Moreover, in preliminary tests, both these monomers were found to be able to give rise to ascending frontal homopolymerization. The resulting polymers have different properties, so the change in composition along the length of the product can be easily detected. HMA is a monofunctional monomer that gives rise to a thermoplastic polymer with a glass transition temperature (T_g) at −4 °C, while poly(TEGDMA) is a cross-linked polymer exhibiting a wide $T_g \approx 135$ °C. The change in composition along the polymer material creates a variation in cross-linking density, swelling behavior and, more generally, of the thermal and mechanical properties.

By using the optimized conditions, two types of copolymer materials of TEGDMA were synthesized, namely, a copolymer with a linear increase in concentration of HMA and a copolymer with a hyperbolic increase in concentration of HMA. In Figure 3, the programmed gradients are described as molar fractions of HMA versus position.

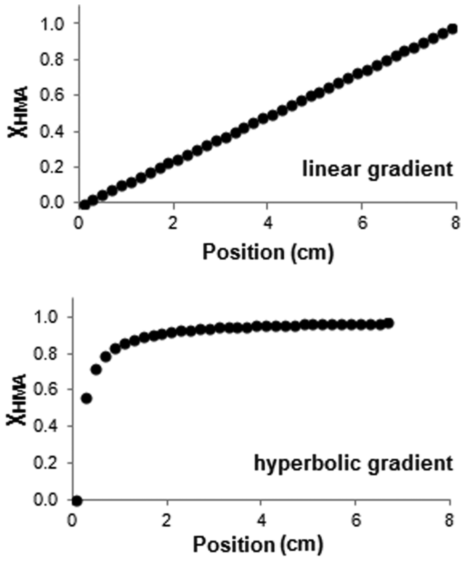

Figure 3. Theoretical molar fraction of HMA as a function of the position.

With the purpose of investigating the properties of the material and their changes with gradient composition, glass transition temperature, hardness, mechanical properties, and swelling behavior of copolymers were investigated.

DSC measurements were performed to assess the T_g of gradient copolymers and to study the variation of T_g with composition. First of all, the absence of any exotherm in the DSC traces during the first heating cycle confirmed the complete conversion of the monomers for all samples.

The T_g values are listed in Figure 4 as a function of position for the two gradients. For comparison, T_g trends calculated by the Fox eq 2 are also shown,

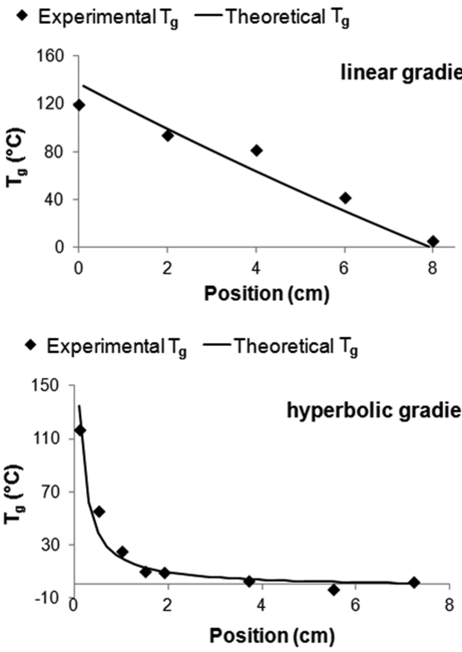

Figure 4. Experimental glass transition temperature as a function of position and theoretical T_g trend determined by the Fox equation for the two types of gradient.

$$\frac{1}{T_g} = \frac{w_{\mathrm{HMA}}}{T_{g,\mathrm{HMA}}} + \frac{w_{\mathrm{TEGDMA}}}{T_{g,\mathrm{TEGDMA}}} \tag{2}$$

where T_g is the glass transition temperature of the copolymer, w_{HMA} and w_{TEGDMA} are the weight fractions of HMA and TEGDMA, and $T_{g,\mathrm{HMA}}$ and $T_{g,\mathrm{TEGDMA}}$ are the glass transition temperatures of poly(HMA) and poly(TEGDMA).

A clear dependence of glass transition temperature on composition of the copolymer can be observed; the T_g values linearly decrease with the molar fraction of hexyl methacrylate. This is due to the different values of T_g of the HMA and TEGDMA homopolymers (−4 °C, and ~135 °C, respectively). Moving from $\chi_{\mathrm{HMA}} = 0.99$ to $\chi_{\mathrm{HMA}} = 0$, the T_g value increases and becomes broader and less evident, because poly(TEGDMA) is characterized by a heterogeneous network with a broad distribution of relaxation times and motions.[53] Because of the linear dependence of T_g on composition, this parameter follows χ_{HMA} variations along the vertical axis, and the theoretical values of T_g calculated by Fox equation fit very well the experimental values.

Shore A hardness measurements showed that the composition influences the hardness of the copolymers (Figure 5). However, the hardness of the sample with a linear gradient is significantly affected by the copolymer composition only when χ_{HMA} is higher than 0.8. The corresponding graph shows that, for molar fractions lower than 0.8 (zone I of the graph), the hardness is only slightly influenced and continuously decreases from 80 to 70 (averaged values). Above 0.8, the influence of HMA concentration becomes much more significant, as hardness dramatically decreases from 70 to 20 (zone II of the graph). Because of the linear composition gradient, hardness versus position plot follows an identical trend; indeed, the hardness is almost constant until 6 cm and then dramatically decreases. However, it should be emphasized that, even if the formation of the gradient is evident, the relationship between hardness and composition is complex and does not follow the same linear trend that characterizes the relationship between composition and position.

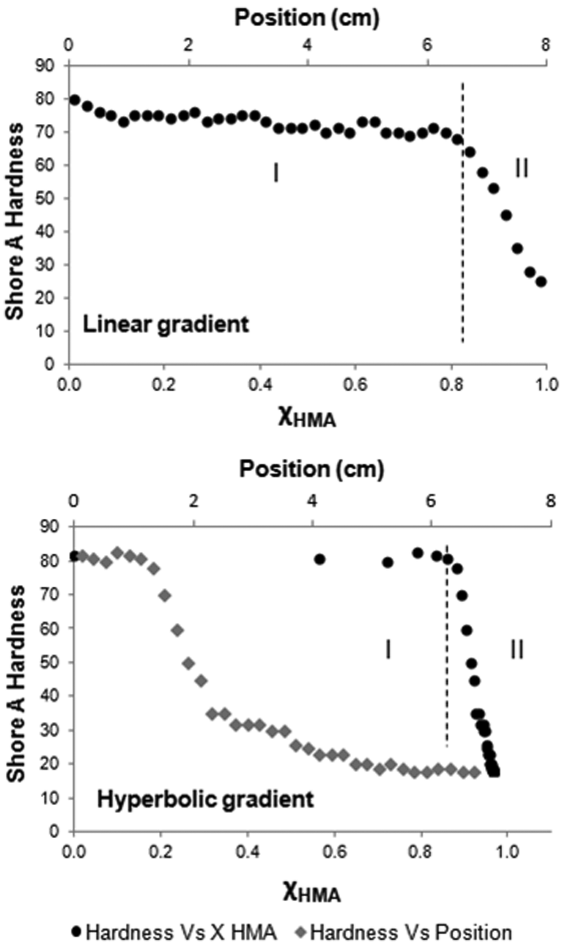

Figure 5. Shore A hardness as a function of χ_{HMA} and position for the two gradient samples.

The hardness behavior for the sample with a hyperbolic gradient of χ_{HMA} confirms that a significant variation of hardness occurs when χ_{HMA} is beyond 0.8 (zone II). The dependence of position shows that, after the first centimeter (where $\chi_{\mathrm{HMA}} < 0.8$, zone I) along which hardness is practically constant, it starts to decrease.

Figure 6a,b shows the elastic moduli of the two different gradient materials, determined by compression tests, as a function of the position and molar fraction of HMA. For this last graph, χ_{HMA} and E obtained for linear and hyperbolic samples were considered. The trend of E values can be referred to the composition of the gradient material, as already found and discussed for hardness. However, unlike hardness measurements, which involve a very limited portion of the surface of the sample, the profiles of elastic modulus versus position are less equivalent to the selected gradient.

Despite this, linear gradient and hyperbolic gradient samples showed a decrease in modulus due to the change of composition. Indeed, also in this case the relationship between compression modulus and composition is not linear (eq 3).

In particular, for χ_{HMA} values lower than 0.5 and higher than 0.8, E did not change significantly and had a value very similar to that of the poly(TEGDMA) and poly(HMA), respectively. On the contrary, in the zone between $\chi_{\mathrm{HMA}} = 0.5$ and $\chi_{\mathrm{HMA}} = 0.8$ the elastic modulus was strongly affected by composition, and E

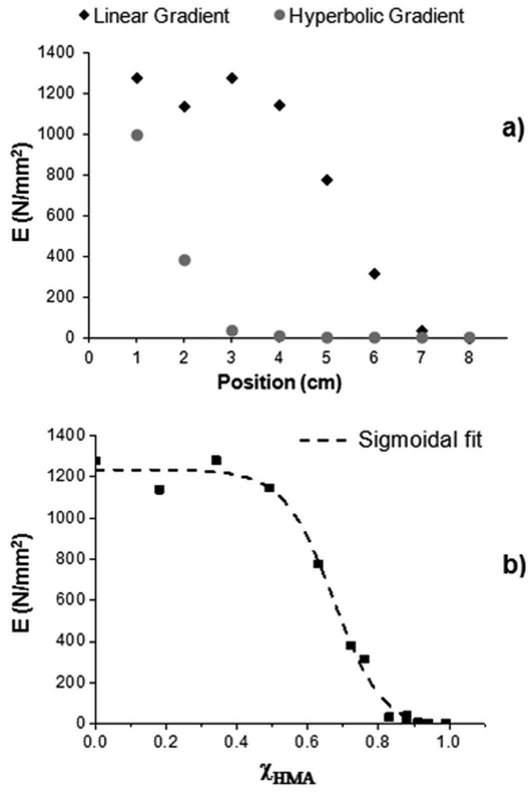

Figure 6. Elastic modulus as a function of position (a) and χ_{HMA} (b). This last graphic also shows the fitting of the data from which eq 3 was carried out.

rapidly decreased by increasing the amount of HMA. The trend of these data was well-fitted by a sigmoidal function (eq 3) that describes the actual relationship that links the modulus E and composition for our copolymer system:

$$E = -33.32 + \left(\frac{1269.25}{1 + 10^{((0.67-\chi_{HMA})\cdot(-6.17))}}\right) \tag{3}$$

Swelling tests in organic solvents were performed. Since the gradient polymers can be considered as materials with an increasing cross-link density due to the variation of TEGDMA concentration, the swelling behavior should be strictly related to the chosen gradient.

As expected, the swelling of copolymers increases by increasing the amount of HMA because of the different affinity of this monomer toward the swelling solvents and to the decreasing cross-linking degree in the polymer matrix as the content of TEGDMA decreases.

The swelling ratio of HMA/TEGDMA copolymers is higher in acetone than in hexane, thus indicating that the polymer matrix has more affinity for solvents with medium polarity ($p_{acetone} = 5.1$, $p_{hexane} = 0.1$). In addition, these polymers do not swell in highly polar solvents like water ($p_{water} = 10.2$).

Figure 7 shows the swelling behavior of gradient copolymers in acetone and hexane. The global trend is roughly exponential for the SR% as a function of χ_{HMA} (Figure 7a), for both solvents. The SR% for samples immersed in acetone gradually increases with increasing χ_{HMA}. When the composition exceeds 0.8 in mole fraction of HMA, the SR% sharply increases, and this point can be viewed as a threshold value, after which the cross-linking degree is low enough to result in large swelling increases as the composition of HMA increases. In other words, beyond this composition value, the material could be better defined as poly(HMA) cross-linked with TEGDMA instead of a copolymer of HMA/TEGDMA.

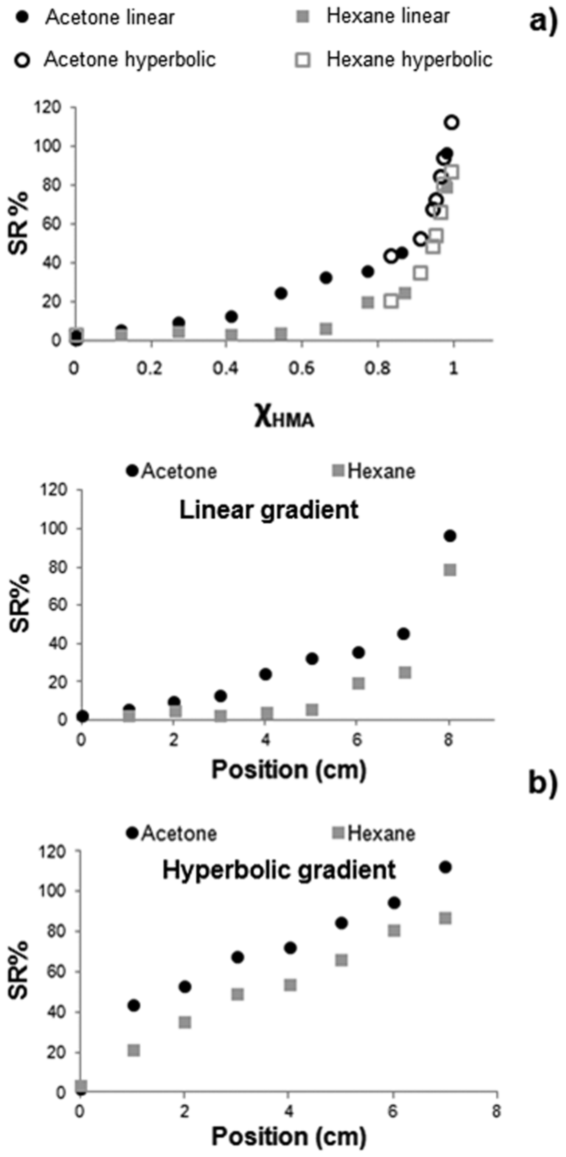

Figure 7. Swelling ratio as a function of χ_{HMA} for the two gradient samples (a) and SR% as a function of position for linear gradient and hyperbolic gradient (b).

The threshold value of 0.8 was also observed for the Shore A hardness measurements. Because of the poor affinity with hexane, the SR% is lower in this solvent than with acetone. Furthermore, the swelling is negligible for χ_{HMA} below 0.66, which can be considered as the SR% threshold value in this solvent. We fit the data of SR% versus molar fraction (not shown), and we found the best exponential equations describing the swelling behavior of copolymers in acetone (eq 4) and hexane (eq 5) as a function of χ_{HMA} was

$$\mathrm{SR\%}_{acetone} = e^{(2.17+(-0.77\cdot\chi_{HMA})+(3.28\cdot\chi_{HMA}{}^{2}))} \tag{4}$$

$$\mathrm{SR\%}_{hexane} = e^{(1.49+(-5.07\cdot\chi_{HMA})+(8.18\cdot\chi_{HMA}{}^{2}))} \tag{5}$$

Also in this case, a nonlinear dependence of swelling to composition was found; however, the presence of the gradient is absolutely demonstrated.

As regards SR% as a function of position for hyperbolic gradient sample, the plot shows a very interesting behavior: the hyperbolic gradient in composition of HMA leads to a material with a nearly linear dependence on the position of SR%, for both solvents.

CONCLUSIONS

The use of FP to obtain FGMs was investigated. Gradient materials were successfully obtained by using two computer-controlled peristaltic pumps feeding monomers onto ascending polymerization fronts. This approach ensures the continuous change in composition of the monomer feed stream thus allowing the preparation of any type of gradient in polymer materials that can be prepared by FP.

This great versatility is a unique advantage of this technique that other FGM production methods do not offer. Indeed, they are usually limited to creating simple (linear) gradients or gradients that cannot be actually controlled, being the consequence of diffusion or gravity, which are properties that cannot be tuned to get the desired composition variation.

The effectiveness of the technique was demonstrated by producing two different copolymers with a gradient in composition: linear and hyperbolic. The T_g values, carried out by DSC analyses, showed a linear dependence on the composition and were in agreement with values calculated by the Fox equation for copolymers.

As regards the other properties investigated, we found that there was no linear dependence on composition because these properties are not directly proportional to the programmed gradient. However, the formation of the latter was confirmed. Interestingly, each property was influenced by the composition change in a specific manner. It was found that hardness was affected by composition only above a threshold value ($\chi_{\mathrm{HMA}} \approx 0.8$), beyond which it decreases with increasing χ_{HMA}; on the contrary, compression tests showed that E modulus varied in a sigmoidal way with respect to composition. Finally, as regards swelling test, an exponential dependence on the composition was found. We also proved that the synthesis of copolymers with a gradient in composition could be useful to investigate the effect of this parameter on material properties, without the need to synthesize different samples with specific compositions.

Finally, the continuous supplying of fresh monomer solution on the top of the polymerization front permitted an ascending self-sustaining front without the buoyancy-driven convection, which is often responsible for front quenching. In addition, if compared with the other methods, FP is very convenient in terms of time and, unlike the others FGM production techniques, does not involve multiple steps or complicated apparatus.

In conclusion, we demonstrated that programmed polymeric gradient materials can be obtained using ascending FP. This approach could be applied for the synthesis of various polymeric gradient materials in the fields of electronic optoelectronic, optic, aerospace, defense, automotive, and tissue engineering, in which accurate and special gradients are required.

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Notes

The authors declare no competing financial interest.

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