

# Thermal Characterization of “Comb-Like” Block Copolymers Based on PCL Obtained by Combining ROP and RAFT Polymerizations

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**Summary:** In this work we report the synthesis of poly(hydroxyethyl-methacrylate-graft-polycaprolactone)-*block*-poly(caprolactone) copolymers, P(HEMA-*g*-PCL)-*b*-PCL, by combining ring-opening polymerization (ROP) and reversible addition-fragmentation chain-transfer polymerization (RAFT). The successful synthesis of the targeted “comb-like” block copolymers obtained was confirmed by <sup>1</sup>H-Nuclear Magnetic Resonance, Fourier Transform Infrared Spectroscopy and Size Exclusion Chromatography. Thermal behavior of the copolymers was studied by Differential Scanning Calorimetry, and their thermal stability was investigated by modulated thermogravimetric analysis. In this sense, the “comb-like” block copolymers exhibited controlled molar masses between 6,000 g/mol and 45,000 g/mol, and polydispersity indexes lower than 1.3. Besides, thermal analysis evidenced a noticeable reduction in the melting temperature compared with linear PCL homopolymer, as well as, in the activation energy for the degradation process.

**Keywords:** reversible addition fragmentation chain transfer (RAFT); ring-opening polymerization; poly( $\epsilon$ -caprolactone); thermal properties

## Introduction

The combination of two or more blocks of structurally different polymers can be used to obtain materials with specific properties, such as chemical resistance, impact strength, flexibility or weather ability, among others.<sup>[1,2]</sup> Grafted copolymers represent a special kind of structures where each molecule has more than two chain ends. This particularity imparts changes on their dynamics, bulk morphologies and nanoscale order.<sup>[3,4]</sup> Thus, branched polymers and particularly “comb-like” copolymers correspond to a special class of materials where

some chains are distributed in an specific segment of the backbone.<sup>[5,6]</sup> These macromolecular architectures are important from a scientific perspective because they exhibit properties that reflect the combined effects of the thermodynamic incompatibility of the polymer segments and the architectural constraints of the branched architecture.<sup>[7,8]</sup> In this sense, branched and linear copolymers with similar molar mass exhibit different physicochemical properties, such as a significant entanglement in solid state, high solubility in various solvents and low melt viscosity.<sup>[9,10]</sup> For example, Choi and Kwak<sup>[3]</sup> studied the thermal properties of hyperbranched PCL polymers, and stressed that melting temperature of branched polymers resulted lower than that of linear ones and gradually decreased with an increase in the degree of branching. This behavior is expected because the presence of branches in a given polymeric molecule may render more difficult the crystallization process

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compared to linear ones. Besides, the understanding of the physicochemical behavior of “comb-like” copolymers can be justified if it is considered that commercially synthesized copolymers frequently display some degree of branching. Thus, many industrial polymer processing techniques (such as extrusion, molding, and melt spinning of synthetic fibers) involve polymer melts, and the presence of branches must be taken into account in order to make real predictions concerning their behavior.

Nowadays, the scientific literature provides many synthetic methods to produce complex macromolecular structures with good control over their final properties. Among these methods, the reversible addition-fragmentation chain-transfer polymerization (RAFT) is a living radical polymerization process that provides excellent control over the molar mass, molar mass distribution, architecture and composition.<sup>[11,12]</sup> It is a robust strategy under a wide range of reaction conditions (bulk, solution, suspension, emulsion, miniemulsion); it does not require complex equipment; it is suitable for a great variety of monomers (including (meth)acrylates, styrene, (meth)acrylamides); and it is tolerant to a large variety of functional groups such as hydroxyl (–OH), carboxyl (–COOH), amine (–NR<sub>2</sub>), and amide (–CONR<sub>2</sub>).<sup>[13]</sup> Consequently, RAFT is a facile route to obtain polymers with distinct topology, composition, and functionality.<sup>[14,15]</sup>

The fundamental feature of RAFT mechanism is an addition-fragmentation sequential equilibrium between active and dormant species. Thus, living radical polymerization only becomes possible in the presence of a chain transfer agent (CTA), commonly a thiocarbonyl compound that reacts with the propagating radicals by reversible deactivation or reversible chain transfer so that the majority of chains are maintained in a dormant form. The rapid equilibration between active and dormant species ensures that all chains possess an equal chance for grow and that all chains will grow. Thus, under these conditions, the molar mass increases linearly with

conversion and molar mass distribution can be very narrow.<sup>[11,16]</sup>

Ring-opening polymerization (ROP) of cyclic esters is another potential method to prepare polymers with controlled properties.<sup>[17]</sup> Under optimized experimental conditions, ROP is an important alternative to synthesize homopolymers with well-defined structures or functional end-groups, as well as copolymers with different architectures (such as block, graft, or star-shaped).<sup>[18,19]</sup> Ring-opening is generally initiated by active hydrogen atoms from amines or alcohols in the presence of a catalyst, resulting in polymer chains with an ester and an alkoxy end group.<sup>[20–22]</sup> In the last years, ROP have been combined with other polymerization processes in order to obtain polymers with specific properties. For example, RAFT and ROP have been employed in a one-step route to synthesize well-defined copolymers.<sup>[23–27]</sup> The reaction is mediated by a bifunctional compound (i.e. the CTA agent of the RAFT process) with an alcohol function able to initiate simultaneously the ROP process.<sup>[24,28]</sup>

In this work, well-defined “comb-like” block copolymers were obtained by a combination of ring-opening polymerization (ROP) and reversible addition-fragmentation chain-transfer polymerization (RAFT) of 2-hydroxyethylmethacrylate (HEMA) and  $\epsilon$ -caprolactone (CL) monomers. The targeted macromolecules were obtained by designing two synthetic strategies and employing an easier experimental procedure compared to a previous published method.<sup>[3]</sup> Copolymers obtained were chemically characterized by <sup>1</sup>H-Nuclear Magnetic Resonance (<sup>1</sup>H-NMR), Fourier Transform Infrared Spectroscopy (FTIR) and Size Exclusion Chromatography (SEC). Their thermal transitions were obtained by Differential Scanning Calorimetry (DSC) and thermal stability was studied by Thermogravimetric Analysis (TGA). In this sense, Modulated Thermogravimetry tests (MTGA) were employed to obtain kinetic information for the decomposition and volatilization reactions. Obtained results were compared

with linear PCL in order to determine the influence of branching on the thermal behavior of the resulting copolymers.

## Materials and Methods

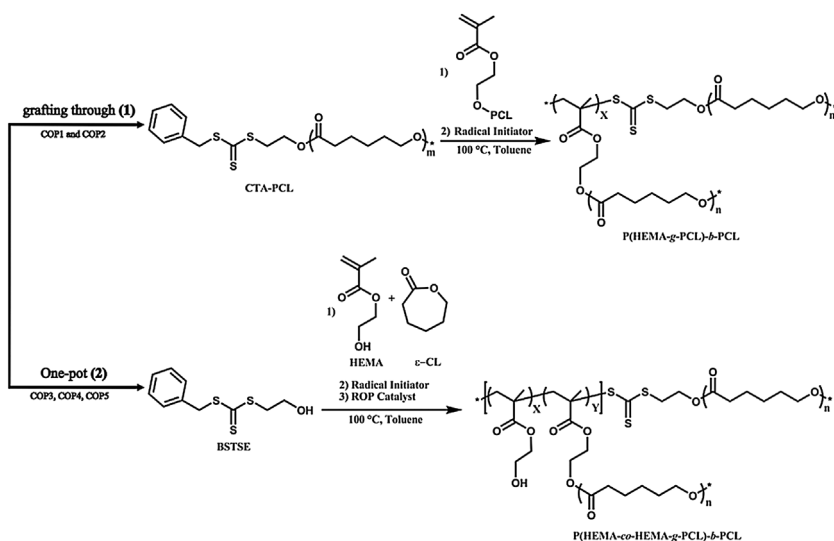
$\epsilon$ -caprolactone ( $\epsilon$ -CL, Aldrich, 99%), 2-hydroxyethylmethacrylate (HEMA, Aldrich, 97%), diphenyl phosphate (DPP, Aldrich, 99%), 1,1'-azobis(cyclohexanecarbonitrile) (VAZO catalyst 88, Aldrich, 98%), toluene (Aldrich), methanol (Química Industrial), dimethylformamide (DMF, 99%), chloroform ( $\text{CDCl}_3$ ), and petroleum ether were used as solvents without any further purification. (Benzylsulfanylthiocarbonylsulfanyl) ethanol (BSTSE), the chain transfer agent (CTA) employed for RAFT polymerizations, was prepared following a one-pot procedure previously described.<sup>[4,24,29]</sup>

## Copolymers Synthesis

Scheme 1 shows the polymerization pathways employed in this work. Block copolymers COP1 and COP2 (Scheme 1, route 1) were obtained by RAFT polymerization employing the *grafting through*

methodology, the CTA-PCL<sup>[24]</sup> and a methacryloyl-terminated PCL macromonomer (mPCL).<sup>[30]</sup> Regarding to this methodology, mPCL, CTA-PCL, VAZO catalyst 88 and toluene as reaction solvent were introduced into a Schlenk reactor. The reaction was performed during 24 h by immersing the reactor in an oil bath settled at 100 °C under continuous stirring. Finally, the resulting product was precipitated in cold methanol and dried until constant weight. It is important to note that all materials were dissolved in toluene and successive precipitated in cold methanol in order to remove the unreacted mPCL, in accordance with the methodology reported by Le Hellaye et al.<sup>[25]</sup> In this sense, the removal of free mPCL was confirmed by SEC analysis.

One-pot, simultaneous RAFT and ROP polymerization was employed for the synthesis of COP3, COP4 and COP5 copolymers (Scheme 1, route 2). In this sense, the co-initiator agent BSTSE, HEMA and  $\epsilon$ -CL monomers, VAZO catalyst 88, DMF (0.2 mL, as internal reference for NMR spectroscopy conversion analysis) and toluene as solvent were placed in a Schlenk apparatus. Then, the



**Scheme 1.**

Synthetic pathways employed. (1) Grafting through; and (2) One-pot reaction.

ring-opening polymerization catalyst DPP was added and the reactor was immersed in an oil bath at 100 °C under vigorous stirring. Samples were precipitated in cold methanol, filtered and dried until constant weight.

Finally, a linear PCL homopolymer was synthesized following classical anionic polymerization procedures.<sup>[2,31,32]</sup> This homopolymer was synthesized by using this technique in order to have a perfect control of its molar mass and polydispersity, with the purpose of having a true model PCL homopolymer. Briefly, a conventional whole-sealed glass reactor, a high-vacuum line, sealed-glass ampoules of reagents, and glass-blowing techniques were employed to perform the polymerization. More details for these procedures have been previously reported in the scientific literature.<sup>[2,33,34]</sup>

#### Fourier Transform Infrared Spectroscopy (FTIR)

FTIR spectra of the synthesized copolymers were obtained on a Nicolet<sup>®</sup> FTIR 520 spectrometer. Cast films from samples solutions (1% w/w in chloroform) were obtained onto NaCl windows. FTIR spectra were recorded at 4 cm<sup>-1</sup> resolution over the 4,000–400 cm<sup>-1</sup> range, using an accumulation of 64 scans and air as background.

#### Size Exclusion Chromatography (SEC)

Obtained samples were characterized by SEC on a system built equipped with a Waters 515 HPLC pump and a Waters model 410 differential refractometer detector, equipped with three mixed bed Phenogel linear (2) columns and a pre-column with 5 μm bead size (Phenomenex). The solvent employed was toluene, flowing at a rate of 1 mL/min. The injection volume was 200 μL, and polystyrene (PS) standards were used for calibration.

#### Nuclear Magnetic Resonance (<sup>1</sup>H-NMR)

<sup>1</sup>H-NMR spectra of block copolymers were obtained using an Avance DPX 400 spectrometer (400 MHz for <sup>1</sup>H) by dissolving a

small quantity of the polymer at room temperature, using CDCl<sub>3</sub> as solvent.

#### Differential Scanning Calorimetry (DSC)

DSC tests were performed on a Perkin-Elmer<sup>®</sup> Pyris 1 apparatus. All experiments were carried out under nitrogen atmosphere. Approximately 10 mg of each sample was analyzed from 30 °C to 90 °C and kept at this temperature for 5 min. After cooling at 10 °C/min, samples were heated from 30 °C to 90 °C at a rate of 10 °C/min to obtain thermal properties such as melting temperature (*T*<sub>m</sub>), and heat of fusion ( $\Delta H_f$ ). The percentage of crystallinity (*X* [%]) was estimated by comparing the melting enthalpy ( $\Delta H_f$ ) of the samples and the theoretical melting enthalpy for a 100% crystalline PCL, ( $\Delta H_{ref} = 136.1 \text{ J g}^{-1}$ <sup>[35]</sup>) according to the equation proposed by Liu et al.<sup>[36]</sup>

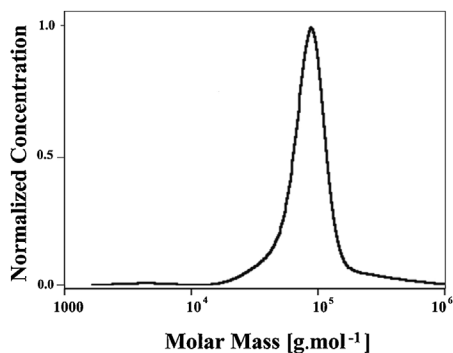
$$X[\%] = \frac{\Delta H_f}{\Delta H_{ref}} \times 100 \quad (1)$$

#### Thermogravimetric Analysis (TGA)

Thermal degradation behavior was studied in a TA Instrument Discovery Series thermogravimetric balance. Samples were heated from 30 °C to 700 °C at 10 °C/min, employing a flux of air (25 mL/min). Weight loss curves as a function of temperature were registered. Besides, modulated thermogravimetry assay (MTGA) were performed to obtain continuous kinetic information regarding decomposition and volatilization reactions. MTGA tests were made using an oscillatory temperature program. The experimental conditions employed were: an amplitude of ±5 °C; a period of 200 s; and an undelaying heating of 5 °C/min.

## Results and Discussion

Figure 1 shows the SEC chromatogram of COP5. A unimodal peak and a narrow molar mass distribution are observed, confirming that the reaction pathway proposed truly provides homogeneous polymeric samples.



**Figure 1.**

SEC chromatogram for COP5 obtained by simultaneous RAFT and ROP polymerizations.  $M_n = 45,100$  g/mol,  $M_w/M_n = 1.14$ .

Table 1 summarizes the molecular characterization of the synthesized block copolymers. Molar mass ranged from 6,000 to 45,000 g/mol, and all samples exhibit narrow molar mass distributions ( $M_w/M_n$  between 1.1 and 1.28). These results clearly show that synthetic pathways employed allow obtaining block copolymers with a good control of their molecular characteristics. The synthetic strategies employed in this paper provides an easier methodology for synthesizing “comb-like” PCL copolymers since a one-pot procedure by combining RAFT and ROP is feasible. In this sense, compared to previous work reported

by Choi and Kwak,<sup>[3]</sup> this last fact represents a great advantage: it provides less synthetic reactions and chemical workup. In addition, the degree of polymerization and the degree of branching in the resulting copolymers were confirmed by  $^1\text{H-NMR}$  analysis.<sup>[30]</sup>

Figure 2 shows the characteristics absorption bands in the FTIR spectra of PCL and COP1. For PCL, typical absorption bands can be observed at  $2,960\text{ cm}^{-1}$  and  $2,865\text{ cm}^{-1}$ , that corresponds to the vibration bands of methylene groups ( $-\text{CH}_2-$ ). In  $1,724\text{ cm}^{-1}$  appears a strong and acute band due to stretching vibrations of carbonyl groups ( $>\text{C}=\text{O}$ ).<sup>[38]</sup> At  $1,260$  and  $1,191\text{ cm}^{-1}$  appear the bands corresponding to the absorption of  $\text{O}-\text{C}=\text{O}$  bonds. Block copolymers present the existence of C-H bond in methylene groups due to an increase in the signal at  $2,920$  and  $2,850\text{ cm}^{-1}$ , and the typical vibrations at  $3,440\text{ cm}^{-1}$  for hydroxyl groups ( $\text{O}-\text{H}$  stretching).<sup>[39]</sup> Besides, an increase in the signals at  $1,447\text{ cm}^{-1}$  and  $740\text{ cm}^{-1}$  could be associated to the vibration of  $-\text{CH}_2-$  bonds in methacrylic polymers.<sup>[40]</sup> In addition, absorption bands corresponding to the  $>\text{C}=\text{O}$  group in PHEMA and PCL segment (observed at  $1,728$ ,  $1,240$  and  $1,174\text{ cm}^{-1}$ ), and the absorption band assigned to the  $>\text{C}=\text{S}$  bond in the CTA

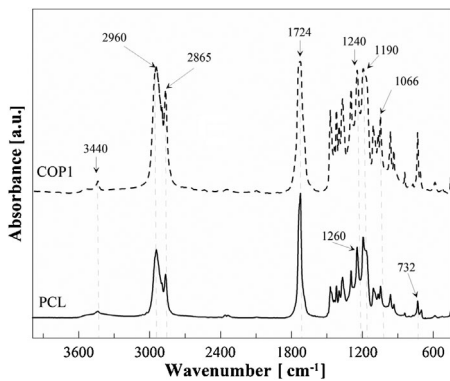
**Table 1.**

Chemical and thermal characterization for PCL homopolymer and synthesized block copolymers.

Sample	Copolymer	$M_n(\text{target})$ [g mol <sup>-1</sup> ]	$M_n(\text{theo})^{\text{a}}$ [g mol <sup>-1</sup> ]	$M_n(\text{GPC})^{\text{b}}$ [g mol <sup>-1</sup> ]	$M_w/M_n^{\text{b}}$	$T_m^{\text{c}}$ [°C]	$X^{\text{c}}$ [%]	$E^{\text{d}}$ [KJ mol <sup>-1</sup> ]
PCL*	PCL <sub>10</sub> *	12,500	nd	12,500	1.14	56.9	44.7	159
COP1	P(HEMA <sub>10</sub> -g-PCL <sub>3</sub> )-b-PCL <sub>10</sub>	6,400	nd	6,000	1.10	53.6	38.2	151
COP2	P(HEMA <sub>12</sub> -g-PCL <sub>5</sub> )-b-PCL <sub>15</sub>	10,400	nd	9,300	1.28	50.5	39.1	156
COP3	P(HEMA <sub>4</sub> -co-HEMA <sub>38</sub> -g-PCL <sub>8</sub> )-b-PCL <sub>8</sub>	65,000	34,600	38,800	1.20	44.9	38.7	153
COP4	P(HEMA <sub>4</sub> -co-HEMA <sub>25</sub> -g-PCL <sub>12</sub> )-b-PCL <sub>12</sub>	57,200	39,600	43,600	1.13	41.1	31.9	132
COP5	P(HEMA <sub>2</sub> -co-HEMA <sub>27</sub> -g-PCL <sub>14</sub> )-b-PCL <sub>14</sub>	57,200	48,800	41,200	1.14	38.2	36.2	134

\* Obtained by anionic polymerization.<sup>[2]</sup> <sup>a</sup>Determined by  $^1\text{H-NMR}$  analysis. <sup>b</sup>Determined by SEC (THF) analysis using the appropriate Mark-Houwink parameters ( $K = 13.95 \cdot 10^{-5} \text{ dL g}^{-1}$  and  $\alpha = 0.786$  for PCL).<sup>[37]</sup>

<sup>c</sup>Determined by DSC analysis. <sup>d</sup>Determined by TGA modulated analysis.



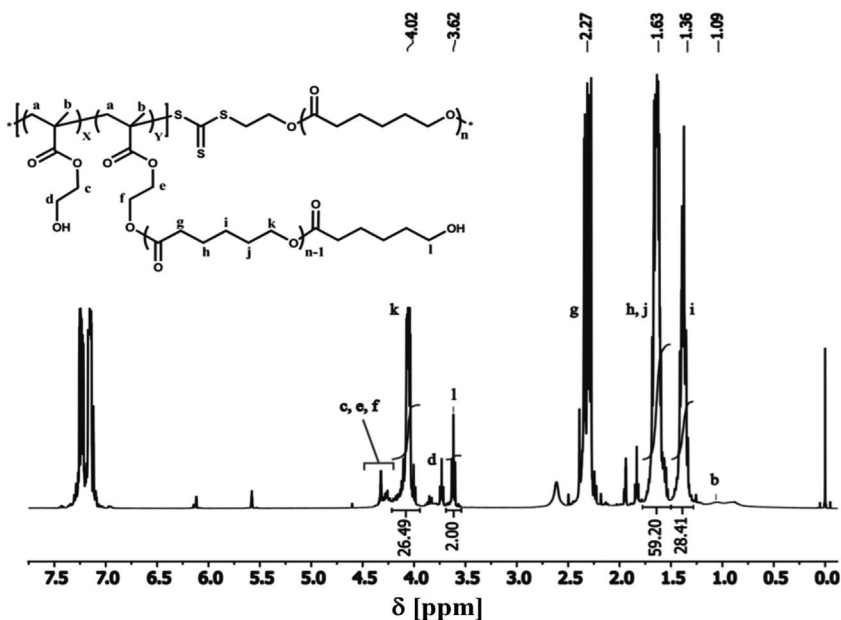
**Figure 2.** FTIR spectra of PCL homopolymer (black bottom) and (COP1) copolymer (up, black dash line).

end group (at  $1,066\text{ cm}^{-1}$ ) are also distinguishable.<sup>[30]</sup>

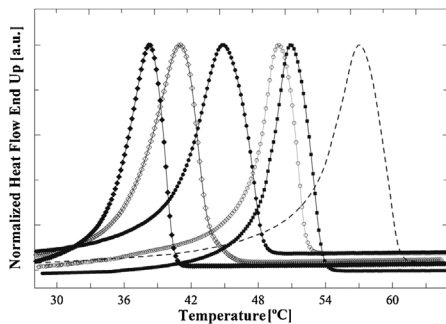
Figure 3 shows the  $^1\text{H-NMR}$  spectrum of COP5. The major resonance signals *a-d* are attributed to PCL. In addition, the signals assigned to the two pendent methylene groups of the HEMA units linked to PCL chains (signals *e* and *f*) are observed. In this sense, Yuan et al.<sup>[4]</sup> reported similar

results for the synthesis of brush copolymers based on PCL. Regarding to the degree of polymerization of PCL in the block copolymers (*n* values in Figure 1), values were calculated from the integral ratio between PCL main chain signals at 2.27 ppm (peak denoted as *g*) relative to methylene end-groups of the same chain at 3.62 ppm (peak denoted as *l*).

DSC measurements were performed in order to evaluate the influence of branching on thermal properties of comb-like copolymers. All samples were heated from  $30^\circ\text{C}$  to  $90^\circ\text{C}$  to obtain  $T_m$  and [%] values of each sample. DSC thermograms of PCL and comb-like copolymers are shown in Figure 4. As it can be seen, a synergistic effect of the length and the number of branches in the copolymers produces a significant decrease in  $T_m$  and X [%] values. Concerning to  $T_m$ , a reduction of  $\sim 20^\circ\text{C}$  was obtained; and for X [%], a reduction of  $\sim 28\%$  was observed. These results clearly show that presence of branches in block copolymers affect the crystallization process.<sup>[41]</sup> Similar results



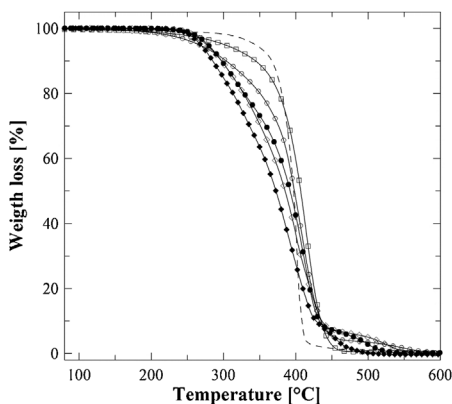
**Figure 3.**  $^1\text{H}$  NMR spectrum of COP5.



**Figure 4.** DSC thermograms of PCL and comb-like copolymers. Symbols: (---) PCL, (■) COP1, (○) COP2, (●) COP3, (◇) COP 4, and (◆) COP5.

were reported by Choi and Kwak.<sup>[3]</sup> These authors stressed that  $T_m$  values of hyper-branched PCL were lower than the linear homopolymer, and gradually decreased with an increase in the degree of branching. Authors mentioned that branching turns difficult the crystallization compared to linear polymers and this fact could be ascribed to the architectural feature, noticeably affected by the absence or the presence of branches into the main chain.

Thermogravimetric measurements were used to evaluate the degradation processes of the comb-like copolymers as function of temperature. Figure 5 shows TGA curves

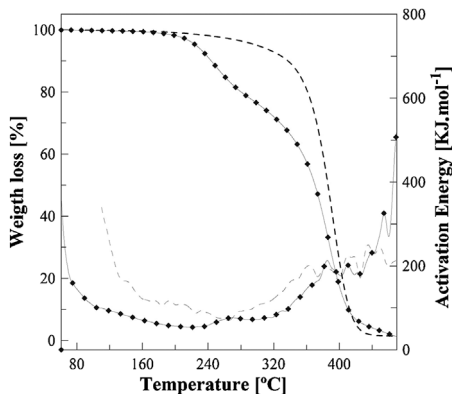


**Figure 5.** TGA curves of PCL and PCL and comb-like copolymers. Symbols: (---) PCL, (□) COP1, (○) COP2, (●) COP3, (◇) COP 4, and (◆) COP5.

corresponding to PCL and COP1 to COP5, respectively. As it can be appreciated, PCL presents mainly two typical weight loss steps. The first one is associated to PCL decomposition at  $\sim 407^\circ\text{C}$ , and the other event at  $\sim 550^\circ\text{C}$  is associated to the glowing combustion process.<sup>[34,42,43]</sup> Regarding the PHEMA homopolymer, Figueiredo et al.<sup>[40]</sup> reported three degradation steps. The first one, at  $\sim 120^\circ\text{C}$ , is associated to the volatilization of absorbed water; the second one, between  $230^\circ\text{C}$  and  $290^\circ\text{C}$ , is related to the degradation of HEMA bonds; and finally, the third one at  $\sim 600^\circ\text{C}$  is assigned to the glowing combustion of the residual components.

All the copolymers obtained in this work showed the thermal degradation events associated to both, PCL and PHEMA homopolymers. They evidenced a reduction in the maximum degradation temperature (compared to linear PCL), and seemed to be less thermally stable in the range of  $200\text{--}400^\circ\text{C}$ . These results are in good agreement to those reported by Goiti et al.<sup>[44]</sup> regarding to the thermal degradation of branched and cross-linked PHEMA hydrogels.

In order to obtain qualitative information about decomposition and volatilization reactions, MTGA were performed. Mass changes as a function of temperature (dynamic method) were analyzed. The continuous activation energy curve resulting from the linear heating rate is showed in Figure 6 for PCL and COP5. PCL homopolymer presented an average activation energy value of  $\sim 159\text{ kJ mol}^{-1}$ , which is similar to values reported in the literature.<sup>[2,45]</sup> Rázga & Petránek and Çekingen et al. reported values of activation energy for the degradation process of PHEMA homopolymer of  $\sim 129\text{ kJ mol}^{-1}$ .<sup>[46,47]</sup> In this sense, “comb-like” copolymers with shorter branches (COP1, COP2, and COP3) exhibited similar  $E$  values than linear PCL. However, a reduction in  $E$  values was observed for COP4 and COP5 that could be associated to a higher presence of HEMA in the PCL backbone (Table 1).



**Figure 6.**

MTGA and activation energy (E) curves. Symbols: (---) linear PCL and (◆) COP5.

## Conclusion

*Comb-like* copolymers from  $\epsilon$ -caprolactone (CL) and 2-hydroxyethylmethacrylate (HEMA) were obtained by combining ROP and RAFT polymerizations. All samples exhibited controlled molar mass and polydispersity indexes lower than 1.3. Complementary techniques such as FTIR,  $^1\text{H-NMR}$ , and SEC confirmed the presence of PCL and PHEMA in the synthesized materials. DSC and TGA measurements were used to study the thermal behavior of *comb-like* copolymers, and the results obtained were compared to a linear PCL homopolymer synthesized by conventional anionic polymerization. The presence of a higher branching degree led to a decrease of  $\sim 20^\circ\text{C}$  in  $T_m$  values. This phenomena can be ascribed to the architectural features of *comb-like* copolymers, noticeable affected by the length and the absence/presence of branches into the main chain. Obtained results for TGA and MTGA analysis showed that all copolymers studied exhibited the typical degradation steps for PCL and PHEMA, and a reduction in the values of activation energy for the degradation process.

- [1] D. Uhrig, J. Mays, *Polym. Chem.* **2011**, 2, 69.  
 [2] M. D. Ninago, A. J. Satti, A. E. Ciolino, M. A. Villar, *J. Therm. Anal. Calorim.* **2013**, 112, 1277.  
 [3] J. Choi, S. Kwak, *Macromolecular* **2003**, 36, 8630.

- [4] W. Yuan, J. Yuan, F. Zhang, X. Xie, C. Pan, *Macromolecular* **2007**, 40, 9094.  
 [5] D. Lanson, F. Ariura, M. Schappacher, R. Borsali, A. Deffieux, *Macromolecular* **2009**, 42, 3942.  
 [6] S. Christodoulou, H. Iatrou, D. J. Lohse, N. Hadjichristidis, *J. Polym. Sci. Part A Polym. Chem.* **2005**, 43, 4030.  
 [7] V. V. Palyulin, I. I. Potemkin, *Polym. Sci. Ser. A* **2007**, 49, 473.  
 [8] M. B. Runge, S. Dutta, N. B. Bowden, *Macromolecular* **2006**, 39, 498.  
 [9] Y. F. Chen, E. M. Woo, *Colloid Polym. Sci.* **2008**, 286, 917.  
 [10] J. Zhang, C. P. Hu, *Eur. Polym. J.* **2008**, 44, 3708.  
 [11] G. Moad, E. Rizzardo, S. H. Thang, *Aust. J. Chem.* **2009**, 62, 1402.  
 [12] J. Chiefari, Y. K. B. Chong, F. Ercole, J. Kristina, J. Jeffery, T. P. T. Le, R. T. A. Mayadunne, G. F. Meijjs, C. L. Moad, G. Moad, E. Rizzardo, S. H. Thang, C. South, *Macromolecular* **1998**, 31, 5559.  
 [13] G. Moad, E. Rizzardo, S. H. Thang, *Aust. J. Chem.* **2005**, 58, 379.  
 [14] M. Benaglia, J. Chiefari, Y. K. Chong, G. Moad, E. Rizzardo, S. H. Thang, *J. Am. Chem. Soc.* **2009**, 131, 6914.  
 [15] G. Moad, E. Rizzardo, S. H. Thang, *Acc. Chem. Res.* **2008**, 41, 1133.  
 [16] A. Favier, M. T. Charreyre, *Macromol. Rapid Commun.* **2006**, 27, 653.  
 [17] S. M. Guillaume, *Eur. Polym. J.* **2013**, 49, 768.  
 [18] A. C. Albertsson, I. K. Varma, *Biomacromolecules* **2003**, 4, 1466.  
 [19] M. Labet, W. Thielemans, *Chem. Soc. Rev.* **2009**, 38, 3484.  
 [20] M. Möller, R. Kånge, J. L. Hedrick, *J. Polym. Sci. Part A Polym. Chem.* **2000**, 38, 2067.  
 [21] D. Delcroix, B. Martín-Vaca, D. Bourissou, C. Navarro, *Macromolecular* **2010**, 43, 8828.  
 [22] Y. C. Wang, L. Y. Tang, T. M. Sun, C. H. Li, M. H. Xiong, J. Wang, *Biomacromolecules* **2008**, 9, 388.  
 [23] M. Hales, C. Barner-Kowollik, T. P. Davis, M. H. Stenzel, *Langmuir* **2004**, 20, 10809.  
 [24] A. G. O. de Freitas, S. G. Trindade, P. I. R. Muraro, V. Schmidt, A. J. Satti, M. A. Villar, A. E. Ciolino, C. Giacomelli, *Macromol. Chem. Phys.* **2013**, 214, 2336.  
 [25] M. Le Hellaye, C. Lefay, T. P. Davis, M. H. Stenzel, *J. Polym. Sci. Part A Polym. Chem.* **2008**, 46, 3058.  
 [26] K. J. Thurecht, A. M. Gregory, S. Villarroya, J. Zhou, A. Heise, S. M. Howdle, *Chem. Commun.* **2006**, 4383.  
 [27] T. Öztürk, M. N. Atalar, M. Göktas, B. Hazer, *J. Polym. Sci. Part A Polym. Chem.* **2013**, 51, 2651.  
 [28] M. Seo, C. J. Murphy, M. A. Hillmyer, *ACS Macro Lett.* **2013**, 2, 617.  
 [29] J. Skey, R. K. O. Reilly, *Polym. Chem.* **2008**, 46, 3690.  
 [30] M. D. Ninago, A. G. O. De Freitas, V. Hanazumi, P. I. R. Muraro, V. Schmidt, C. Giacomelli, A. E. Ciolino, M. A. Villar, *Macromol. Chem. Phys.* **2015**, 216, 2331.



- [31] M. L. Arnal, V. Balsamo, F. Lo, J. Contreras, M. Carrillo, *Macromolecular* **2001**, *34*, 79732.
- [32] V. Balsamo, G. Gil, C. U. De Navarro, I. W. Hamley, F. Von Gyldenfeldt, V. Abetz, E. Can, *Macromolecular* **2003**, *36*, 4515.
- [33] J. Contreras Ramirez, M. Carrillo, V. Balsamo, C. Torres, F. L. Carrasquero, *Rev. Latinam. Metal. Mater.* **2007**, *27*, 41.
- [34] M. D. Ninago, O. V. López, M. M. S. Lencina, M. A. García, N. A. Andreucetti, A. E. Ciolino, M. A. Villar, *Carbohydr. Polym.* **2015**, *134*, 205.
- [35] F. B. Khambatta, F. Warner, T. Russell, R. S. Stein, *J. Polym. Sci. Part B Polym. Phys.* **1976**, *14*, 1391.
- [36] W. Liu, C. M. Dong, *Macromolecular* **2010**, *43*, 8447.
- [37] C. Strazielle, H. Benoit, O. Vogl, *Eur. Polym. J.* **1978**, *14*, 331.
- [38] S. H. Murphy, G. A. Leeke, M. J. Jenkins, *J. Therm. Anal. Calorim.* **2011**, *107*, 669.
- [39] Y. Kodama, M. Barsbay, O. Güven, *Radiat. Phys. Chem.* **2014**, *105*, 31.
- [40] A. G. R. P. Figueiredo, A. R. P. Figueiredo, A. Alonso-Varona, S. C. M. Fernandes, T. Palomares, E. Rubio-Azpeitia, A. Barros-Timmons, A. J. D. Silvestre, C. P. Neto, C. S. R. Freire, *Biomed. Res. Int.* **2013**, 2013, 1.
- [41] J. Choi, S. W. Chun, S. Y. Kwak, *Macromol. Chem. Phys.* **2006**, *207*, 1166.
- [42] J. Cai, Z. Xiong, M. Zhou, J. Tan, F. Zeng, MeiHuma, S. Lin, H. Xiong, *Carbohydr. Polym.* **2014**, *102*, 746.
- [43] J. Hubackova, M. Dvorackova, P. Svoboda, P. Mokrejs, J. Kupec, I. Pozarova, P. Alexy, P. Bugaj, M. Machovsky, M. Koutny, *Polym. Test.* **2013**, *32*, 1011.
- [44] E. Goiti, M. M. Salinas, G. Arias, D. Puglia, J. M. Kenny, C. Mijangos, *Polym. Degrad. Stab.* **2007**, *92*, 2198.
- [45] G. B. Abdellatif Mohamed, S. H. Gordon, *Polym. Degrad. Stab.* **2007**, *92*, 1177.
- [46] J. Rázga, J. Petránek, *Eur. Polym. J.* **1975**, *11*, 805.
- [47] S. K. Çekingen, F. Saltan, Y. Yildirim, H. Akat, *Thermochim. Acta* **2012**, *546*, 87.