SYNTHESIS AND CHARACTERIZATION OF THREE-ARMED [P(HEMA-G-PCL)]$_3$ GRAFT COPOLYMERS OBTAINED BY ONE-POT RAFT AND ROP

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Abstract
Branched copolymers are a special class of polymeric materials in which are reflected the combined effects of polymer segments and architectural constraints of the branched architecture. In this work, three-armed graft copolymers, poly(hydroxyethyl methacrylate-*graft*-poly(caprolactone), [P(HEMA-*g*-PCL)]$_3$, were synthesized by combination of reversible addition-fragmentation chain-transfer (RAFT) and ring opening polymerization (ROP) mechanisms in a one-pot/one-step protocol. The resulting macromolecules were characterized by ^{1}H nuclear magnetic ressonance (NMR), size exclusion chromatography (SEC), differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The preliminary results indicate the success of the methodology and are in agreement with literature reports.

Keywords: *synthesis one-pot, simultaneous RAFT and ROP, graft copolymers, polycaprolactone, thermal analysis.*

Introduction

Graft copolymers constitute a special class of polymeric materials.[1] Unlike linear diblock or triblock copolymers, graft copolymers constitute a distinct kind of macromolecular architecture in which each molecule have more than two chain ends.[2] Multiphase materials, such as block copolymers, segmented or grafted, have been the subject of numerous studies in macromolecular chemistry in recent years.[3-5]

Branched macromolecular architectures are important from a scientific perspective because they exhibit properties that reflect the combined effects of thermodynamic incompatibility of the polymer segments and the architectural constraints of the branched architecture.[6] Poly(ε-caprolactone) (PCL) is an aliphatic and hydrophobic polyester with good biodegradable and mechanical properties. This semicrystalline polymer has a relative low melting temperature (T_m ~ 60 °C) and an appropriate glass-transition temperature for technical applications (Tg ~ − 60 °C). On the other hand, poly(2-hydryoxyethyl methacrylate) (PHEMA) is another biocompatible polymer that has been used to produce ocular devices and soft contact lens, among other applications.[7]

In this work the one-pot synthesis of three-armed graft copolymers with the backbones composed of PHEMA and the branches constituted by PCL, is reported. This approach is made possible by the application of a three-arms CTA agent and simultaneous RAFT and ROP processes.

Experimental

Materials

Reactants and solvents used in this work were purchased from Sigma-Aldrich (St. Louis, MO, USA). The methanol used in purification process were purchased from Neon Comercial (Suzano, SP, Brazil). All chemical products were of high-grade purity and used without further purification.

Synthesis of [P(HEMA-g-PCL)]$_3$ Three-armed block copolymers

In a dry Schlenk flask equipped with a magnetic bar, HEMA, ε-CL, CTA agent, DPP catalyst and the radical initiator VAZO™-88 were dissolved in toluene. The tube was closed and the solution was purged with nitrogen by 30 minutes. Then, the flask was immediately immersed in an oil bath at 100 °C to start the polymerization. The resulting polymers were precipitated in an excess of methanol, filtered, and dried in vacuum for 24 h.

Chemical characterization

Nuclear magnetic resonance

^{1}H NMR spectra were acquired by using an Avance DPX 400 spectrometer (400 MHz for ^{1}H) at 25 °C, using $CDCl_3$ as solvent.

Size Exclusion Chromatography

Polymer samples were characterized by SEC on a system built with a Shimadzu Prominence HPLC, equipped with a CBM-20A controller, Shim-pak Gel 80M column and Shim-pak GPC-800P precolumn, SPD-20A UV detector, RID-20A differential refractive index detector and a LC-20AD pump. The solvent employed was THF at a flow rate of 1 mL·min^{-1} and polystyrene (PS) standards were used for calibration.

Differential Scanning Calorimetry

Thermal transitions were determined using a MDSC Q2000 (TA Instruments Inc., New Castle, DE, USA). The samples were weighted on hermetic pans using a Sartorius scale (M 500 P) to an accuracy of 0.001 mg. Each sample was submitted to two heating and cooling cycles in a temperature range from -80 °C to 100 °C. The heating rate and N_2 flow rate was 283.15 K min^{-1} and 50 mL min^{-1}, respectively.

Results and Discussion

The synthesis process was carried out by a one-pot protocol with simultaneous RAFT and ROP mechanisms, without any intermediary purification step. Figure 1 summarize the methodology applied in this work. The general procedure was performed based on our similar investigations reported in the literature.[5,8] Before starting the reaction, all the reactants were completely solubilized resulting in a translucent monophasic solution. The reactions conditions and the copolymers properties are shown in Table 1.

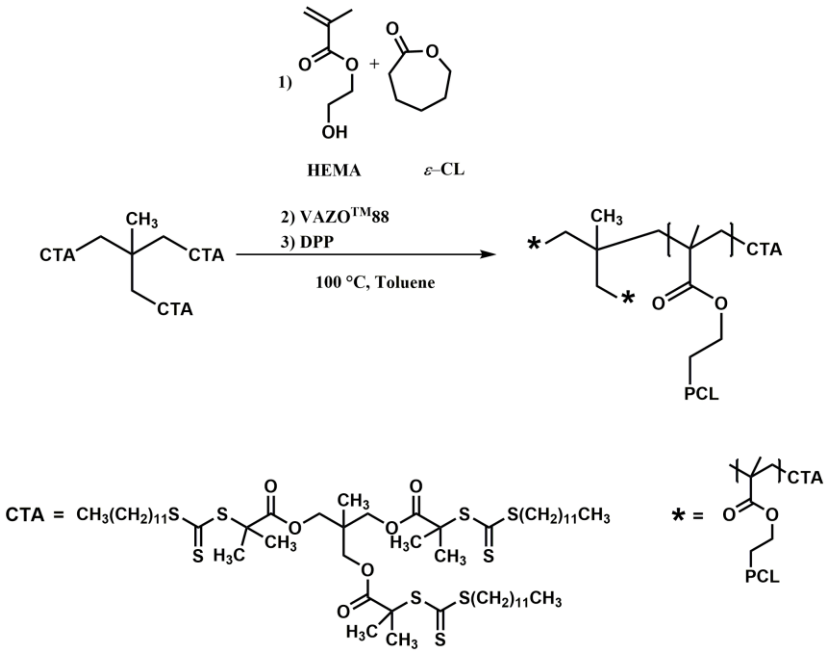

Figure 1: Synthesis of [P(HEMA-*g*-PCL)]$_3$ three-armed block copolymers by one-pot protocol.

Similar to previous reports, [5,8] we were able to produce a grafted block copolymer by the combination of RAFT and ROP mechanisms. In this case, the hydroxyl group from HEMA monomer act as a nucleophilic species and attack the activated carbonyl of the ε-CL ring, allowing the initiation of the ROP. At the same time that HEMA acts as initiator of ROP, it can be incorporated into the backbone by the RAFT mechanism, resulting in a grafted topology. The most impactful aspect of this approach is the three arm of the CTA agent that allows the preparation of a three-armed grafted copolymer, with controlled architecture, without any intermediary purification step. A careful search in the specialized literature reveals that there is not similar reports to this approach, with respect to the production of a three-armed graft copolymer by one-pot protocol with simultaneous RAFT and ROP.

The monomer conversion was determined by ^{1}H NMR, using DMF as an internal reference. For detailed information about this calculation, see reference.[5] Figure 2 shown a representative ^{1}H NMR spectrum of three-armed block copolymer with all peak attributions.

Table 1. Experimental conditions for one-pot reactions and physicochemical properties of the three-armed grafted copolymers.

Entry	time (h)	DP(target) PHEMA:PCL	DP(theo)[a] PHEMA:PCL	M_n(target)[b] (g.mol^{-1})	M_n(theo)[c] (g.mol^{-1})	M_n[d] (g.mol^{-1})	PDI
01	2	20:05	14:07	43200	40200	37600	1.07
02	2	20:10	18:09	74500	63600	51800	1.32
03	5	50:10	44:10	191900	169000	60100	1.31
04	8	100:10	68:07	382600	260500	33000	1.50
05	8	100:20	60:10	725000	230000	-	-

[a] = determined by ^{1}H NMR.
[b] = {[([HEMA]$_0$/[RAFT]$_0$) * 130,14] + [([CL]$_0$/[RAFT]$_0$) * 114.14)]}*3 + 1200
[c] = {[DP$_{theo}$ (PHEMA) * 130,14] +[DP$_{theo}$ (PCL) * 114.14]}*3 + 1200.
[d] = determined by SEC

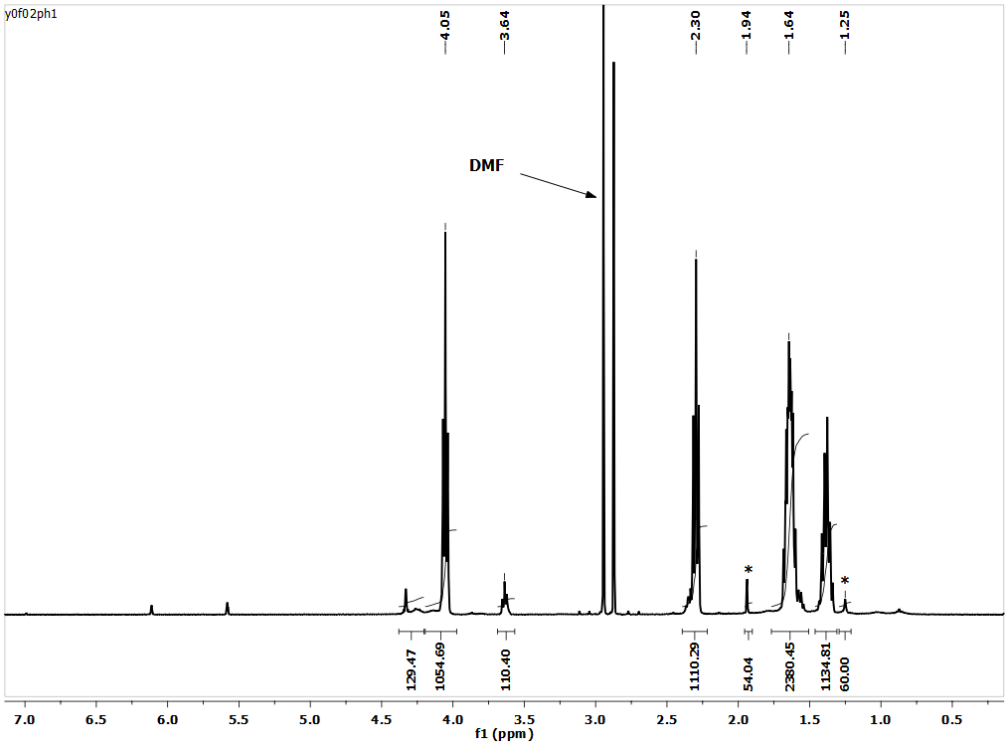

Figure 2: ^{1}H NMR spectrum of [P(HEMA-*g*-PCL)]$_3$ three-armed block copolymer, entry 2. (*) relative to CTA peaks.

Preliminaries SEC analysis (Figure 3) confirms the grown of polymer chains, as demonstrated by NMR. The SEC traces, relative to a final sample of copolymer 2, reveals the presence of two populations with different molar mass. The population of lower molar mass is relative to HEMA-PCL homopolymer, while the population of higher molar mass could be attributed to the three-armed block copolymer.[5] In cases in which the viscosity allow higher reaction times the HEMA-PCL homopolymer population disappear, indicating high conversions of the RAFT process.

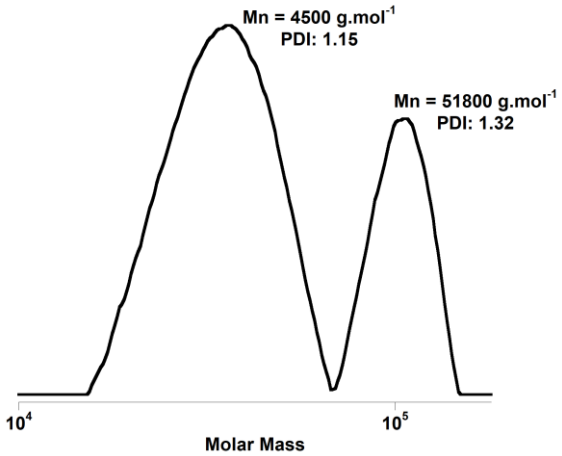

Figure 3: SEC chromatogram of COP 2.

Figure 4 shows representative DSC curves of heat flow as a function of temperature for the copolymers 1 and 3. Essentially the same profile is observed for other copolymer samples. The values of crystallization temperature (*T*c), correspond to the temperature in the maximum of the exothermic peak, and the melting temperature (T_m), shows the effect of the grafted architecture. The T_m of 36,59 and 40,29 °C relative to COP 1 and COP 3, respectively, are lower than the values of linear PCL. The reduction of the crystallization temperatures in both samples can also be attributed

to the complex grafted architecture.[5,8] Further analysis will be performed to elucidate the effects of branches in the thermal properties of the materials.

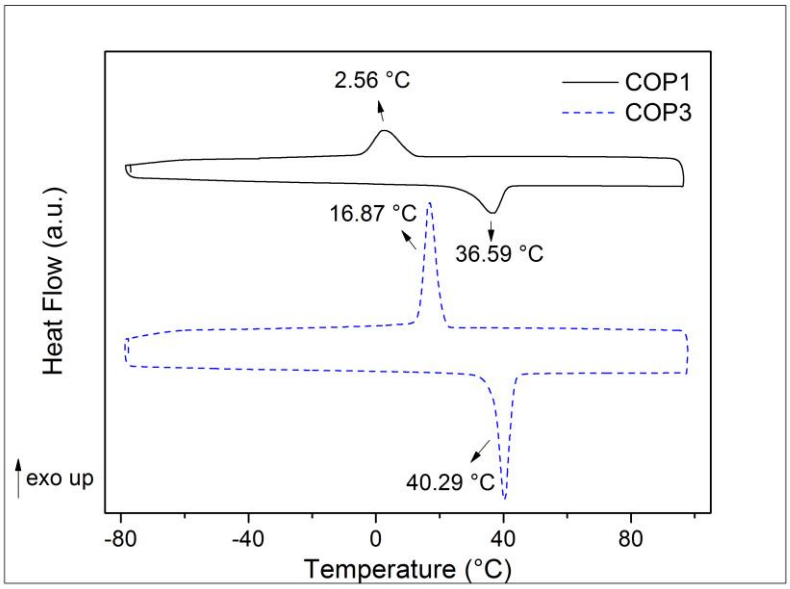

Figure 4: DSC exothermic curves for copolymers 1 and 3.

Conclusions

Three-armed graft copolymers were obtained by simultaneous RAFT and ROP in a one-pot protocol. Preliminary analysis of NMR, DSC, TGA and SEC confirm the presence of this graft copolymer in the material. The SEC analysis indicates that the reaction time and the viscosity should be adjusted to ensure highest fractions of the three-armed graft copolymer at the end of reaction process. The values of T_m and T_c are typical of graft copolymer with PCL branches and, therefore, are clear evidence of the synthesis of the target copolymers.

Acknowledgements

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