

Article

Synthesis and Characterization of a Core-Shell Copolymer with Different Glass Transition Temperatures

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Abstract: The aim of this study is to synthesize an organic core-shell co-polymer with a different glass transition temperature (T_g) between the core and the shell that can be used for several applications such as the selective debonding of coatings or the release of encapsulated materials. The co-polymer was synthesized using free radical polymerization and was characterized with respect to its morphology, composition and thermal behavior. The obtained results confirmed the successful synthesis of the co-polymer copolymer poly(methyl methacrylate)@poly(methacrylic acid-co-ethylene glycol dimethacrylate), *PMMA@P(MAA-co-EGDMA)*, which can be used along with water-based solvents. Furthermore, the T_g of the polymer's core *PMMA* was 104 °C, while the T_g of the shell *P(MAA-co-EGDMA)* was 228 °C, making it appropriate for a wide variety of applications. It is worth mentioning that by following this specific experimental procedure, methacrylic acid was copolymerized in water, as the shell of the copolymer, without forming a gel-like structure (hydrogel), as happens when a monomer is polymerized in aqueous media, such as in the case of super-absorbent polymers. Moreover, the addition and subsequent polymerization of the monomer methyl methacrylate (*MAA*) into the mixture of the already polymerized *PMMA* resulted in a material that was uniform in size, without any agglomerations or sediments.

Keywords: core-shell; polymers; glass temperature; SEM; TEM

1. Introduction

In recent years, the need to synthesize new core-shell polymers has increased as chemical procedures have required accuracy and effectiveness more than ever. Micro- and nanostructured core-shell copolymers solve many problems of materials industry, medicine and infrastructure, while remaining practically easy to synthesize and apply [1].

Core-shell polymers can be manufactured through a vast number of experimental means, including various methods such as electrospinning [2] and solvent-free and large scale processes [3], as well as ultrasound-assisted methods [4]. Furthermore, material properties have been studied under several circumstances and environmental conditions, such as laser fields, mini-emulsions, pre-emulsions and acid media [5,6].

Many attempts have been made to synthesize a novel core-shell in the last five years. In order to cover the continuously increasing number of modern needs for core-shells, scientists have tried many new chemistry-based approaches, while attempting to keep the total cost relatively low. A few novel approaches from the literature include Hu et al., who wrote a review about a single-component

core-shell [7]; Han et al., who developed a core-shell magnetic material with applications in food chemistry [8]; Gul et al., who managed to imprint a polymer onto a core-shell material with magnetic properties [9]; and Farboudi et al., who synthesized core-shell nanofibers grafted with chitosan for the controlled release of drugs [10]. Furthermore, several studies were conducted by our group based on the production of core-shell particles and microcapsules that can be used either for the removal of chlorides from water or as additives into coatings that can protect metal alloys from corrosion [11].

In recent years, research focusing on this type of polymer has increased. Core-shell polymers have been used for numerous biological and medical applications, such as controlled calcium and drug delivery, antibacterial applications, stem cells, wound healing, virus chromatography, cancer and hyperthermia therapy and glaucoma treatment [12–14]. They have also been used for electronics and energy applications such as solar cells, energy storage, batteries, photovoltaics, fuel cells and sensors, as they enhance electrical conductivity and electrical properties in general [15–20]. However, the majority of core-shell materials concern engineering applications such as mechanical reinforcements, where they are used as fillers for their high strength and tensile performance [21] as well as for their high interfacial strength between the cell and the core [22]. They are also used for toughening epoxy resins [23].

Additionally, lots of synthetic processes and characterization techniques have been deployed in order to investigate core-shell materials more accurately and fully understand their effects on other compounds. Various methods are already known, with in situ synthesis, emulsion polymerization, catalysis, use of particles as sacrificial templates, and use of reactive surfactants being some of the most popular among them research in this field remains ongoing [24–27]. Moreover, acidic media, transmission electron microscopy (TEM) and other numerous techniques have shed light on the structure, morphology and characteristics of these materials [28–31].

In this study, the concept was to synthesize core-shell polymers that could be triggered by heat. Therefore, the shell can be selectively weakened by an external trigger (heat), while leaving the core exposed, to release its encapsulations at a specific moment in a given targeted area. For this to happen, it is necessary that the polymers that form the core and the cell have different glass transition temperatures (T_g), meaning that the T_g of the shell should be higher than the T_g of the core [32]. According to this idea, a core-shell polymer (core@shell) was produced—poly(methyl methacrylate)@poly(methacrylic acid), $PMMA@P(MAA-co-EGDMA)$ —in which the T_g of the core and the shell were 104 and 228 °C, respectively. This organic polymer was characterized via scanning electron microscopy (SEM), Fourier-transform infrared spectroscopy (FT-IR), TEM, thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). It should be mentioned, that, following this experimental path, MAA was polymerized via classic radical polymerization using water as solvent, without forming a hydrogel. The produced material was uniform in size, without any agglomerations or sediments.

Finally, it may be remarked that the added value of our work resides in the fact that this copolymer combined hydrophilic and lipophilic parts and different glass transition temperatures, while it was synthesized in a one-pot synthetic process.

2. Materials and Methods

2.1. Materials

Analytical reagent grade chemicals were used. Methacrylic acid (MAA, Fisher Chemicals, Waltham, MA, USA), methyl methacrylate (MMA, Sigma Aldrich, St. Louis, Missouri, USA), ethylene glycol dimethacrylate (EGDMA, Sigma Aldrich, St. Louis, MO, USA) and potassium peroxodisulphate (KPS, Acros Organics, Geel, Belgium) were used as received without further purification. Also, distilled water was used. Methacrylic acid and methyl methacrylate were distilled under vacuum prior to use.

2.2. Synthesis of Core-Shell Copolymer

Radical polymerization was performed for the synthesis of the thermo-responsive core-shell co-polymer $PMMA@P(MAA-co-EGDMA)$. First, 20 mL of methyl methacrylate was dissolved in 500 mL of water and nitrogen gas was flushed into a round, three-neck, 1 L glass reaction flask. Then, 0.2 g potassium persulfate (KPS-initiator) was added and the temperature was adjusted to 90 °C for the initiation of the polymerization. A glass reflux condenser was used to recycle the solvent during the polymerization reaction. After 4 h, when the polymerization of methyl methacrylate was completed, 20 mL of distilled methacrylic acid was added to the flask together with 2 mL of crosslinker (EGDMA) and 0.2 g of initiator (KPS). The reaction was left to react for 4 h under vigorous stirring at 90 °C. After this, the contents of the flask were centrifuged and gently dried in an oven at 40 °C for 24 h. Figure 1 illustrates the schema of the produced core-shell copolymer $PMMA@P(MAA-co-EGDMA)$. The produced thermo-responsive core-shell nanostructured co-polymer was characterized in respect to its morphology, composition and structure.

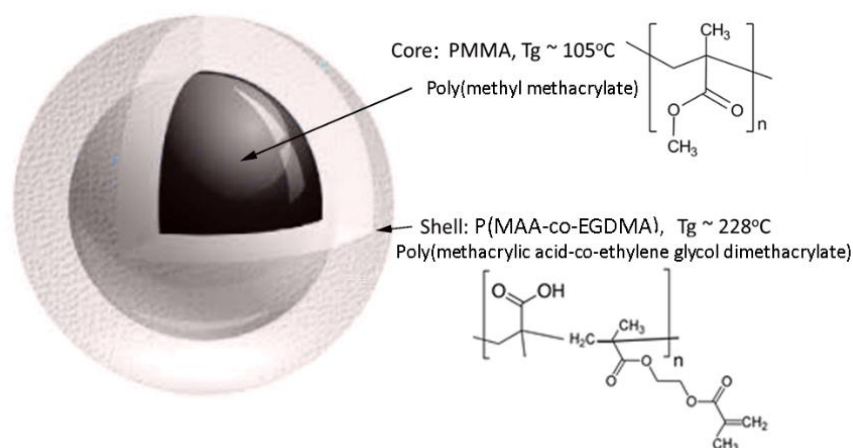


Figure 1. Schematic representation of the produced core-shell copolymer $PMMA@P(MAA-co-EGDMA)$.

2.3. Characterization

The morphology and composition of the produced materials were estimated with an ultra-high resolution scanning electron microscope (UHR-SEM) using NOVA NANOSEM 230 (FEI Company) coupled with a Hitachi electron microscope TM3030 and an energy dispersive X-ray spectrophotometer (EDS) (QUANTAX 70) [33]. In addition, the morphology of the core-shell copolymers was also characterized by TEM (model FEI CM20), operated at an accelerating voltage of 200 kV [34–36].

The FT-IR spectra of the produced polymers was analyzed via an attenuated total reflectance FT-IR instrument, the Cary 630 spectrometer (Agilent), with a resolution of 4 cm^{-1} and an operating wavelength range of 4000–400 cm^{-1} [34]. Thermal analysis of the produced polymers was conducted via a TGA/DSC instrument, the STA 449 F5 Jupiter. The system consists of an SiC furnace with an operation temperature varying between 25 and 1550 °C. The gas used was nitrogen at a volumetric rate of 50 mL/min and at a heating rate of 20 °C/min [34]. The size distribution of the produced polymers was estimated via dynamic light scattering (DLS) measurements using a Zetasizer Nano ZS.

Gel permeated chromatography (GPC) analysis was performed using a modular instrument consisting of a waters model 510 pump, a U6K sample injector, a 401 refractometer and a set of four 1 μm -Styragel columns with a continuous porosity range of 10^6 – 10^3 Å. The carrier solvent was CHCl_3 at a flow rate of 1 mL/min. The system was calibrated with seven polystyrene (PS) standards having molecular weights (MWs) between 1000 and 900,000 g/mol. The system was operated at 25 °C.

3. Results and Discussion

3.1. Morphological Characterization (SEM and TEM)

Figure 2a illustrates the SEM image of the produced core-shell copolymer $PMMA@P(MAA-co-EGDMA)$. It can be seen that the synthetic process of producing the material resulted in a copolymer with a spherical morphology. Taking into account Figure 2b, which depicts a corresponding particle size distribution histogram with values from 63 core-shell copolymer particles, it can be seen that the diameter of these spheres was in the nanoscale, ranging from approximately 160 to 210 nm [37]. These properties indicate that this material's volume was appropriate for its use in several applications that would require the capsules to take up as little space as possible (e.g., incorporation into coatings or layers). It can be seen from the transmission electron microscopy images (Figure 3) that there was a thin shell on the outside of the polymeric core [38,39].

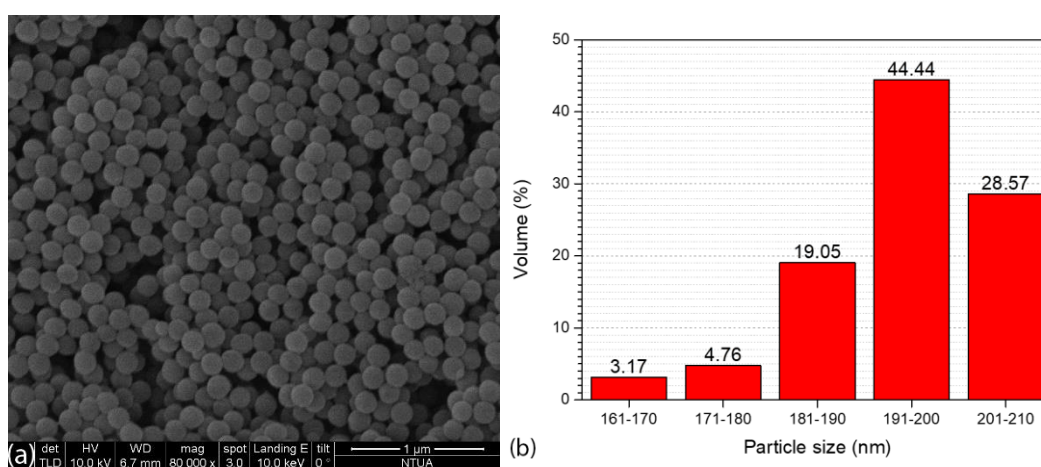


Figure 2. SEM image (a) and particle size distribution histogram (b) of the $PMMA@P(MAA-co-EGDMA)$ core-shell copolymer.

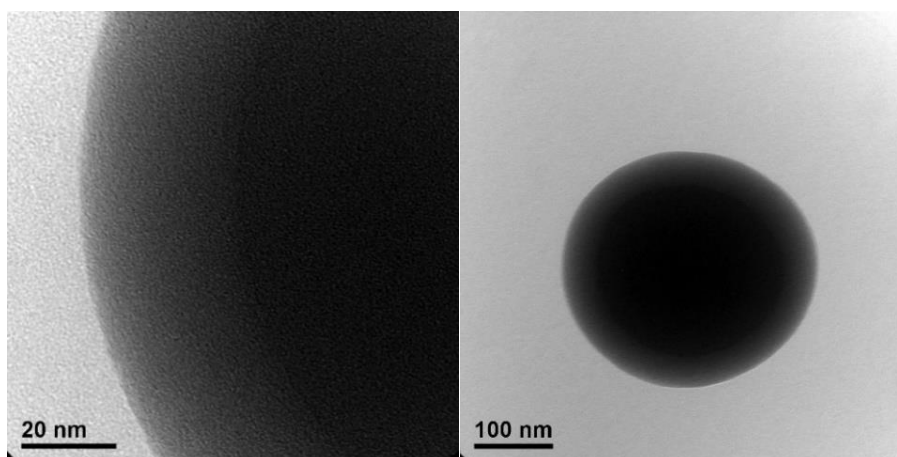


Figure 3. TEM images of the core-shell copolymer $PMMA@P(MAA-co-EGDMA)$.

The thin shell of $P(MAA-co-EGDMA)$ around the core of $PMMA$ protects and surrounds the core, while on the other hand it can easily be weakened and removed without the use of a great amount of energy, if an application requires the core to be exposed relatively easy for the selective release of ingredients encapsulated in the core (e.g., targeted delivery or coatings).

3.2. Thermal Analysis (TGA and DSC)

Thermogravimetric Analysis was performed in inert atmosphere with a gas flow of 50 mL/min and a heating rate of 5 °C/min. Figure 4 illustrates the TGA/DSC graphs of the produced (a) *PMMA* core and (b) *PMMA@P(MAA-co-EGDMA)* core-shell copolymer. From the TGA curve of Figure 4a, it can be seen that the weight loss of the *PMMA* (core) was much more abrupt than in the case of the core-shell copolymer. This was expected, because the presence of the shell in the second case allowed a slower degradation, which was also smoother. The slight increase in mass at the start of the measurement is attributable to the scale drift of the instrument. This effect occurs when the measurement starts after the temperature has been increased from room temperature to 100 °C at an accelerating rate.

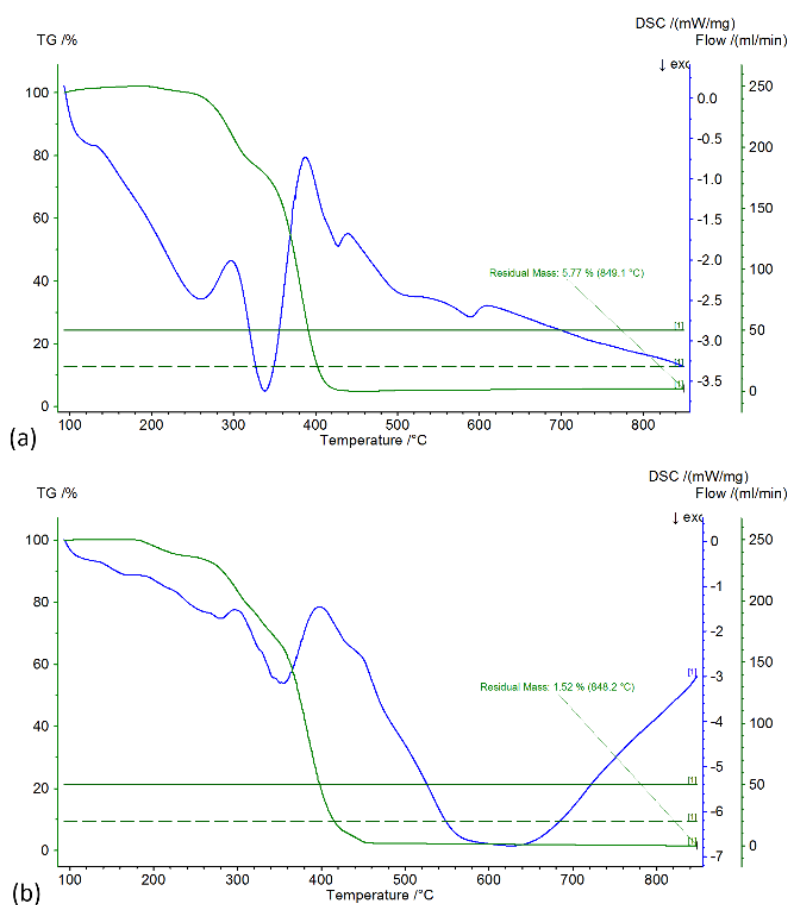


Figure 4. TGA/DSC graphs of the produced *PMMA* core (a) and *PMMA@P(MAA-co-EGDMA)* core-shell copolymer (b).

The DSC endothermic curve at 400 °C on the same graph corresponds to the polymer's degradation. The exothermic curve at 340 °C can be attributed to the C-OCH₃ bond rupture, which enriched the nitrogen atmosphere with oxygen and led to partial oxidation of the polymer [40]. From the TGA curve of the Figure 4b, it can be readily observed that there was a first weight loss between 200 and 290 °C that can be attributed to the degradation of *PMMA*, and the second sharp weight loss between 290 and 440 °C can be attributed to the degradation of *P(MAA-co-EGDMA)*. Furthermore, the DSC curve (blue) demonstrates two endothermic curves, the first small one at 280 °C and the second big one at 360 °C, which correspond to the two thermal decompositions of *PMMA* and *P(MAA-co-EGDMA)*, respectively. The residual mass at 850 °C is the remaining carbon, approximately 1.5% of the initial mass [41].

Finally, it should be mentioned that an exothermic DSC curve can be observed in the TGA/DSC graphs of Figure 4a at about 105 °C, where the *T_g* of the *PMMA* is 104 °C. Additionally, in the TGA/DSC

graphs of Figure 4b, there is an exothermic DSC curve at about 230 °C where the T_g of the PMAA is 228 °C. These two curves correspond to the respective T_g of the two polymers, although their intensity was low, due to the slight decrease in bond strength after the T_g point. On the other hand, the DSC exothermic curves corresponding to the decomposition had high intensity.

3.3. Attenuated Total Reflectance Fourier-Transform Infrared Spectroscopy (FT-IR)

The FT-IR graphs concerning the PMMA core as well as the PMMA@P(MAA-co-EGDMA) core-shell copolymer are illustrated in Figure 5 and the corresponding peaks are tabulated in Table 1. The peak at 1156 cm^{-1} corresponds to the $-\text{CH}_2-$ bond wagging of the aliphatic chains of both PMMA and PMAA. Moreover, the peak at 475 cm^{-1} corresponds to the $\text{C}=\text{C}=\text{O}$ in the plane deformation vibration of the carboxyls of the two polymers, while the peaks at 747 and 840 cm^{-1} can be ascribed to the C-H deformation vibration and the peak at 963 cm^{-1} is related to the C-O stretching vibration. The peak at 1187 cm^{-1} can be attributed to the $-\text{OCH}_3$ vibration (methyl methacrylate) [42]. Furthermore, the peaks at 1237, 1384 and 1435 cm^{-1} can be ascribed to the $-\text{CH}-$ bending of the methyl groups, which were present in both compounds, as well as to the $-\text{CH}_3$ deformation of the branches of the main polymer chain [43]. A C-H scissor vibration can be seen at 1474 cm^{-1} , while the C=C stretching vibration can be observed at 1636 cm^{-1} . Additionally, the $-\text{C}=\text{O}$ stretch can be noticed at 1716 cm^{-1} . The stretching of $-\text{CH}_3$ is visible at 2925 cm^{-1} , while the stretching of $-\text{CH}_2$ can be seen at 2996 cm^{-1} [44]. Finally, the $-\text{O}-\text{H}$ stretches of methacrylic acid can be seen in the region of 3400 cm^{-1} [45].

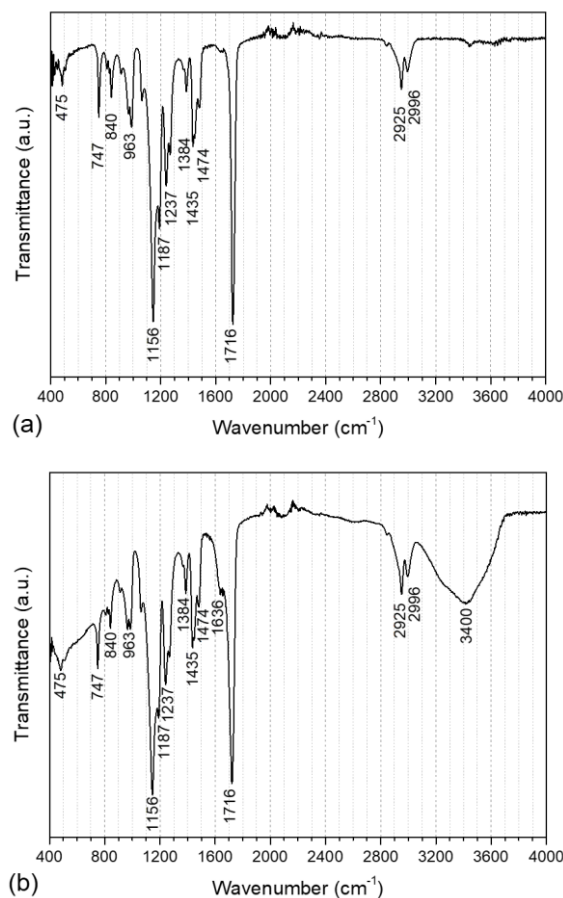


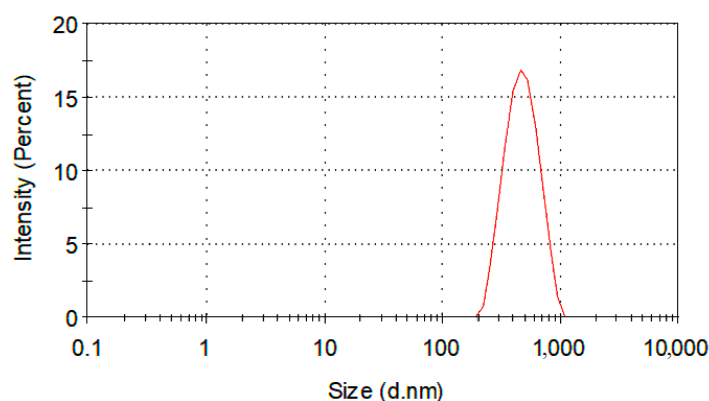
Figure 5. FT-IR spectra of the PMMA core polymer (a) and PMMA@P(MAA-co-EGDMA) core-shell copolymer (b).

Table 1. FT-IR peak analysis.

Wavenumber (cm ⁻¹)	Corresponding Bond
475	C-C=O in plane deformation vibration
747, 840	C-H deformation vibration
963	C-O stretching vibration
1156	-CH ₂ - wagging and C-O phenol stretch
1187	-OCH ₃ vibration (methyl methacrylate)
1237, 1384, 1435	C-H and O-H deformation vibration
1474	C-H scissor vibration
1636	C=C stretching vibration (EGDMA)
1716	-C=O stretch
2925	-CH ₃ stretching
2996	-CH ₂ stretching
3400	-O-H stretch (methacrylic acid)

3.4. Dynamic Light Scattering (DLS)

Dynamic light scattering (DLS) analysis is very useful for polymer characterization, because it can offer important information about organic compounds. DLS can be used to monitor polymer formation processes, in diffusion analysis and to characterize polymer solutions and surfactants, as well as to investigate natural polymers [46]. Moreover, a lot of properties can be determined via DLS analysis such as viscosity, polymerization mechanisms, molecular weight and molecular size, even particle size and particle size distribution. The study of reaction kinetics during polymerization and the detection of polymeric structures in emulsions are also feasible using DLS [47]. In our case, about 10 mg of the solid polymer was dispersed in 5 mL of water in a small vial. The vial was left under supersonic vibrations for 10 min so that the polymer would be sufficiently dispersed for DLS characterization. The Z-Average diameter was 446 nm, while the polydispersity index (PDI) was 0.077 (Figure 6). These facts denote that the sample was uniform in size distribution, without any agglomerations or sediments [48]. It should be mentioned that the average diameter of the produced *PMMA@P(MAA-co-EGDMA)* core-shell copolymer determined by DLS was higher than the values illustrated in the particle size distribution histogram of Figure 2b. The reason for this is that the hydrodynamic volume of the materials was measured as part of the DLS method. In our case, the produced *PMMA@P(MAA-co-EGDMA)* core-shell copolymer interacted with the solvent that was used for the measurement (water), resulting in an expansion of its hydrodynamic volume.

**Figure 6.** Particle size distribution by intensity of *PMMA@P(MAA-co-EGDMA)* core-shell copolymer.

3.5. Gel Permeated Chromatography

GPC was used to estimate the molecular weights of the produced materials. Unfortunately, it was not feasible to determine the molecular weight of the *PMMA@P(MAA-co-EGDMA)* core-shell

copolymer due to solubility difficulties. In detail, GPC measurements were conducted using four different chromatography solvents including water with acetonitrile, chloroform, tetrahydrofuran, and dimethylformamide (DMF). The *PMMA* (core) was fully soluble in DMF, allowing a GPC graph to be obtained. On the other hand, the *PMMA@P(MAA-co-EGDMA)* core-shell copolymer was not soluble in any of these four solvents because it formed a gel-like two-phase structure that looked like an emulsion or suspension in the solvents. It should be mentioned that this final remark underlines the successful synthesis of the core-shell copolymer between the lipophilic *PMMA* and the hydrophilic *PMAA*, although it was not possible to obtain a molecular weight measurement. The distinctive ability of the instrument was up to a million Daltons. Judging from the GPC graph (Figure 7), it can be observed that the polydispersity index of the *PMMA* was relatively high, as there was a very wide distribution of molecular weights after the elution of the polymer (Table 2). The molecular weight ranged from one million to a few thousand Daltons. It should be noted that the first inverse peak (at an approximate elution time of 5 min) is attributable to the solvent and was not taken under consideration.

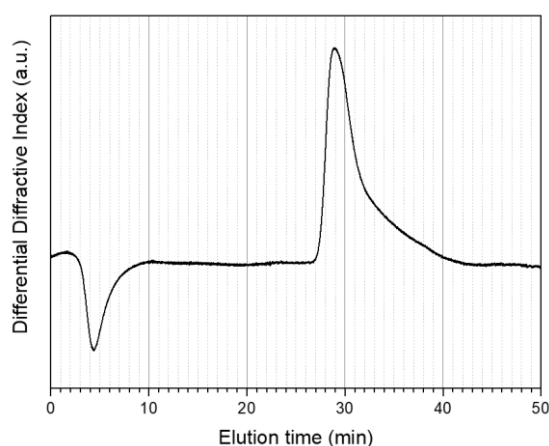


Figure 7. Gel permeated chromatography (GPC) traces of the *PMMA* (core) polymer.

Table 2. Tabulated values of the *PMMA* core polymer GPC measurement.

Retention Time (min)	Evolution Volume (mL)	Mol Wt (Daltons)	Calculated Weight (Daltons)
28.811	28.811	900,000	872,947
29.628	29.628	520,000	547,317
30.184	30.184	410,000	408,730
30.264	30.264	390,000	392,540
32.189	32.189	170,000	164,923
35.754	35.754	50,000	47,892
36.994	36.994	30,000	32,768
40.176	40.176	12,500	11,728
43.049	43.049	3350	3569
43.821	43.821	2500	2412

3.6. Outcome Analysis

The *Yield*(%) of the polymerization reaction for the synthesis of *PMMA@P(MAA-co-EGDMA)* core-shell copolymer can be calculated from the following Equations (1)–(3):

$$m_{MMA} = d_{MMA} \times V_{MMA} = 0.94 \text{ g/mL} \times 20 \text{ mL} = 18.8 \text{ g} \quad (1)$$

$$m_{MAA} = d_{MAA} \times V_{MAA} = 1.015 \text{ g/mL} \times 20 \text{ mL} = 20.3 \text{ g} \quad (2)$$

$$Yield(\%) = \frac{m_{expe}}{m_{MMA} + m_{MAA}} \times 100(\%) = \frac{32.1 \text{ g}}{18.8 \text{ g} + 20.3 \text{ g}} \times 100(\%) = 78.1(\%) \quad (3)$$

where m_{MMA} is the theoretical mass of the MMA, m_{MAA} is the theoretical mass of the MAA, d_{MMA} is the density of the MMA, d_{MAA} is the density of the MAA, V_{MMA} is the volume of the MMA, V_{MAA} is the volume of the MAA, and m_{expe} is the mass of the copolymer after the termination of the experiment.

We considered the initiator and crosslinker to have no contribution to the yield of the reaction. After drying, we obtained $m_{expe} = 32.1$ g of the $PMMA@P(MAA-co-EGDMA)$ core-shell copolymer. Theoretically, 18.8 g of MMA and 20.3 g of MAA react, resulting in 39.1 g of product. The surplus amount of MAA ($20.3 \text{ g} - 18.8 \text{ g} = 1.5 \text{ g}$) was added just to make sure that there would be enough MAA to form the $P(MAA-co-EGDMA)$ shell. According to Equation (3), the $Yield(\%)$ of the polymerization reaction for the synthesis of the $PMMA@P(MAA-co-EGDMA)$ core-shell copolymer was 78.1(%). Concerning the kinetics of the reaction, free radical polymerization started at a slow rate, but quickly accelerated, forming the polymer. Temperature plays a significant role in the polymerization reaction, as the initiator is activated at about 90 °C, producing the free radicals that polymerize the monomers [49–52].

Judging from the results of the different characterization techniques, it can be concluded that the product had a spherical shape at a nanoscale, with a very thin shell of $P(MAA-co-EGDMA)$ around the core of the $PMMA$. FT-IR analysis showed peaks in the polymer's graph corresponding both to $PMMA$ and $PMAA$ bonds, while the SEM and TEM images confirmed its morphological properties. The morphological characterization also provided information about the composition of the product in regards to the two polymers, which was further demonstrated by the thermal analysis. The larger size of the core and the thinness of the shell exhibit advantages for potential applications, as the core could encapsulate larger amounts of other nanocompounds while the shell breaks smoothly to release the encapsulations. This is the case of delivery of antioxidants and other substances as well as adsorption and catalysis [53,54].

Recent literature on this subject by Peralta et al. [55] demonstrated the grafting of thermo-responsive polymers on inorganic compounds. However, these materials were activated at a temperature of 40 °C for drug delivery, while the copolymer in this study had a shell with a T_g of 228 °C, enabling its use at elevated temperatures for different applications such as incorporation in coatings. To that end, Wang et al. [56] synthesized lipophilic core-shell microspheres with inorganic shells. Nonetheless, the goal in the present research was to have both a polymeric core and a polymeric shell, and preferably for them to be hydrophilic. This aim was achieved using the PMAA as a compound of the shell. While Huang et al. have shown that the size of a core-shell copolymer can be tuned by following a specific method [37], that method requires an emulsion polymerization that is substantially more complex than the conventional radical polymerization proposed in the present work. Additionally, other researchers have synthesized core-shell compounds using specialized laboratory equipment and elaborate experimental paths [57–60] using catalysts [24] or by performing in situ processes [61].

Core-shell copolymers, both organic and inorganic, are very promising materials for several applications in the near future. Specifically, they can enhance the stability of crystal structures [62] and the responsiveness of sensors [63]. In addition, they increase the reaction activity of composite catalysts [64], have contributed to greener syntheses using natural plant products [65] and can also be very useful in magnetic applications [66]. It should be mentioned that core-shell polymers could play a significant role in effectively designing new multifunctional active materials for battery cells [67].

These applications notwithstanding, the simple synthesis discussed in this study was designed to be able to be performed in vitro, employing common experimental techniques and laboratory instruments without using intricate means for the production of the final product. Most importantly, the use of distilled water as the solvent/medium of the polymerization reaction is worth mentioning, due to the fact that most chemical routes nowadays continue to use expensive organic solvents to produce these or similar types of materials.

4. Conclusions

Following a simple experimental process of a two-step radical polymerization, a novel core-shell polymer was formed with a uniform size distribution, homogeneous spherical shape and thin shell

around the polymeric core, without any admixtures. The novelty of this study is the relatively easy experimental setup and the fact that the copolymer exhibited different glass transition temperatures between the core and the shell, rendering the compound suitable for several applications. In addition, methacrylic acid was successfully polymerized as the shell in water, without forming a gel. This phenomenon was possible due to the already polymerized methyl methacrylate in the mixtures, which allowed the second monomer to be polymerized around the core. The produced core-shell copolymer was thoroughly characterized in respect of its morphology, structure, composition and thermal behavior. The results confirmed the successful synthesis of the material.

Author Contributions: Conceptualization, P.G. and I.A.K.; methodology, P.G. and I.A.K.; software, P.G. and I.A.K.; validation, P.G., I.A.K. and C.A.C.; formal analysis, P.G. and I.A.K.; investigation, P.G. and I.A.K.; resources, P.G. and I.A.K.; data curation, P.G.; writing—original draft preparation, P.G. and I.A.K.; writing—review and editing, I.A.K. and C.A.C.; visualization, P.G. and I.A.K.; supervision, C.A.C.; project administration, C.A.C.; funding acquisition, C.A.C. All authors have read and agreed to the published version of the manuscript.

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