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## ARTICLE

# Facile Synthesis of Well-controlled Poly(glycidyl methacrylate) and its Block Copolymers via SARA ATRP at Room Temperature

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The detailed synthesis of poly(glycidyl methacrylate) (PGMA) by atom transfer radical polymerization (ATRP) using a catalytic system of Fe(0)/Cu(II)Br<sub>2</sub> at room temperature is reported. The reaction system was optimized regarding the ligand structure, solvent mixture and temperature. The kinetic data confirmed the controlled character of the ATRP of GMA revealing a linear increase of the molecular weight with the conversion, very low dispersity ( $\mathcal{D} < 1.1$ ) and the complete retention of the chain end functionality. The molecular structure of the PGMA was confirmed by <sup>1</sup>H NMR. As proof-of-concept, hybrid block copolymers of poly(dimethyl siloxane)-*b*-PGMA were prepared using ppm concentrations of soluble copper and a mixture of solvents. The results presented in this manuscript demonstrated the robustness of the catalytic system to afford PGMA and its block copolymers with controlled structures that can be further functionalized exploring the portfolio of chemistries involving the oxirane ring.

The developments achieved on the area of reversible-deactivation radical polymerization (RDRP) methods over the last decades are absolutely remarkable<sup>1</sup>. These new methods opened a myriad of opportunities regarding the synthesis of tailor-made polymers. Among the most popular RDRP methods, atom transfer radical polymerization (ATRP) is particularly used at the academia and industrial levels due to several intrinsic advantages, such as: simplicity, tolerance to a wide range of functionalities, and commercial availability of most compounds<sup>2,3</sup>. The ATRP mechanism is based on a metal-complex mediated fast equilibrium between dormant and active species<sup>4</sup>. Different transition-metals as Cu, Ru, Fe, Ni, Os<sup>5,6</sup> have been used for ATRP typically in combination with different types of nitrogen-based ligands. Recently, our group and Matyjaszewski's research group reported the use of mixed-transition-metal catalyst involving the use of zero valent metals (Fe(0), Zn(0) and Mg(0))<sup>2,7</sup> in combination with small amounts of Cu(II)Br<sub>2</sub>/(tris(2-dimethylamino)amine) (Me<sub>6</sub>TREN) or Cu(II)Br<sub>2</sub>/N,N,N',N'',N'''-pentamethyldiethylenetriamine (PMDETA)<sup>7</sup> for ATRP of methyl acrylate<sup>2</sup> (MA), methyl methacrylate (MMA)<sup>7</sup> and styrene (St)<sup>7</sup> in DMSO at room temperature. The catalytic system, Fe(0)/Cu(II)Br<sub>2</sub>/Me<sub>6</sub>TREN proved to be suitable for the control over the Mn,  $\mathcal{D}$  and chain ends functionalities in polar solvents<sup>2</sup>. The zero valent metals

act as supplemental activators and reducing agents (SARA) during the polymerization<sup>4</sup>.

Glycidyl methacrylate (GMA) is a very valuable monomer due to its epoxy group that can undergo ring-opening reactions with several nucleophiles<sup>8-10</sup>. PGMA has a wide range of commercial applications, involving coatings, printing inks, semiconductors, resins and adhesives<sup>11-14</sup>. Also, photopolymerizable acrylic based polymers can be prepared from polymers based on PGMA by reacting the oxirane ring with (meth)acrylic acid<sup>15</sup>. Therefore, the development of suitable and robust RDRP methods to afford tailor-made macromolecules based on PGMA is of particular interest. The ATRP of glycidyl acrylate (GA) was firstly reported using catalytic system of CuBr/4'-bis(5-nonyl)-2,2 bipyridine (dNbipy) at 90°C in bulk<sup>16</sup>. Srinivasan<sup>17</sup> synthesized PGMA using Cu(I)Br/*N*-(*n*-propyl)-2-pyridylmethanimine in bulk and in various solvents (diphenyl ether, anisole, ethyl methyl ketone and methanol) with  $\mathcal{D}$  ranging from 1.25 to 1.49. Fernandez-Garcia<sup>18</sup> proposed the synthesis of this polymer using a catalytic system of Cu(I)Cl/PMDETA in toluene and diphenyl ether at temperatures ranging from 30°C to 50°C. Tsarevsky prepared well-defined copolymers of GMA and MMA in acetone at 50°C using a catalytic system of CuBr/CuBr<sub>2</sub>/N,N,N',N'',N'''-N''''-hexamethyldiethylene triamine (HMTETA)<sup>19</sup>. Goyal<sup>20</sup> have proposed the synthesis of

copolymers P(GMA-co-St) using a Cu(II)Br/PMDETA system. Recently, it was demonstrated that the activators regenerated by electron transfer (ARGET) ATRP of GMA using Sn<sup>II</sup> based reducing agents is accompanied by side reactions<sup>21</sup>. The controlled polymerization of GMA was achieved by initiators for continuous activator (ICAR) ATRP using CuBr<sub>2</sub>/TPMA in anisole at 60°C and azobisisobutyronitrile (AIBN) as conventional initiator<sup>21</sup>. Herein we report, for the first time, the synthesis of PGMA and its block copolymers using a catalytic system of Fe(0)/Cu(II)Br<sub>2</sub> via SARA ATRP at room temperature in toluene/dimethylformamide (DMF) mixtures. The polymerization was carried out in the presence of three different ligands Me<sub>6</sub>TREN, PMDETA and tris(2-pyridylmethyl)-amine (TPMA). The influence of the solvent mixtures and reaction temperature were also evaluated. Different ATRP initiators such as EBiB, an alkyne terminated initiator (PgBiB) and a 4-arm star initiator (4f-BiB) were applied to confirm the robustness of the method in the polymerization of different functional polymers.

## Experimental

### Materials

GMA (Sigma-Aldrich, 97% stabilized) was passed through a sand/alumina column before use to remove the radical inhibitor. Copper (II) Bromide (Cu(II)Br<sub>2</sub>) (Acros, 99+% extra pure, anhydrous), zerovalent iron powder (Fe(0)) (Acros, 99%, ~70 mesh), dimethylformamide (DMF) (Sigma-Aldrich, 99.8%), chloroform (Fisher Chemical, 99.9%), hexane (Fisher Chemical, 99.05%), diphenyl ether (Sigma-Aldrich, 99.9%), ethyl 2-bromoisobutyrate (EBiB) (Sigma-Aldrich, 98%), pentaerythritol tetrakis(2-bromoisobutyrate) (4f-BiB) (Sigma-Aldrich, 97%), N,N,N',N''-Pentamethyldiethylenetriamine (PMDETA) (Sigma-Aldrich, 99%), deuterated chloroform (CDCl<sub>3</sub>) (Euriso-top, +1% TMS) were used as received. Toluene was dried over sodium and benzophenone and distilled prior to use. Tris[2-(dimethylamino)ethyl]amine (Me<sub>6</sub>TREN)<sup>22</sup>, tris(2-pyridylmethyl)amine (TPMA)<sup>23</sup>, propargyl-2-bromoisobutyrate (PgBiB)<sup>24</sup> and -Br terminated PDMS macroinitiator<sup>25</sup> were synthesized according to the literature.

### Methods

The chromatographic parameters of the homopolymer samples were determined by gel permeation chromatography (GPC), carried out using high performance size-exclusion chromatography (HPSEC), with refractive index (RI) (Knauer K-2301) detection. The column set consisted of a PL 10-μL guard column (50 x 7.5mm<sup>2</sup>), followed by two MIXED-B PL gel columns (300 x 7.5mm<sup>2</sup>, 10 μL). The HPLC pump was set with a flow rate of 1 mL/min and the analyses were carried out at 60°C using an Elder CH-150 heater. The eluent was DMF, containing 0.3% of LiBr. Before injection (100 μL), the samples were filtered through a polytetrafluoroethylene (PTFE) membrane with 0.2 μm pore size. The system was calibrated against PMMA standards.

For the copolymers, the chromatographic parameters of the samples were determined using high performance gel permeation chromatography (GPC); Viscotek (Viscotek TDAmix) with a differential viscometer (DV); right-angle laser-light scattering (RALLS) (Viscotek); low-angle laserlight scattering (LALLS) (Viscotek) and refractive index (RI) detectors. The column consisted of a PL 10 mm guard column (50 × 7.5 mm<sup>2</sup>) followed by one Viscotek T200 column (6 μm), one MIXED-E PLgel column (3 μm) and one MIXED-C PLgel column (5μm). A HPLC dual piston pump was set at a flow rate of 1 mL/min. The eluent, THF, was previously filtered through a 0.2 μm filter. The system was also equipped with an on-line degasser. The tests were done at 30 °C using an Elder CH-150 heater. Before the injection (100 μL), the samples were filtered through a polytetrafluoroethylene (PTFE) membrane with 0.2 μm pore. The system was calibrated with narrow PS standards. The software used for the analysed of the data obtained was Omnisec, version 4.6.1.354.

The conversion of the monomer was determined by integration of the monomer and the polymer <sup>1</sup>H-NMR peaks. 400 MHz <sup>1</sup>H NMR spectra of the polymers, were recorded on a Bruker Avance III 400 MHz spectrometer, with a 5 mm TIX triple resonance detection probe, in CDCl<sub>3</sub> with TMS as an internal standard. The software used for the analysis of the spectra obtained was MestRenova, version 6.0.2-5475.

The UV/Vis studies were performed with a Jasco V-530 spectrophotometer. The analyses were carried out in the 400–1500 nm range at 30°C with N<sub>2</sub> atmosphere.

### Procedures

**Typical procedure for the SARA ATRP of GMA ([Fe(0)]<sub>0</sub>/[Cu(II)Br<sub>2</sub>]<sub>0</sub>/[TPMA]<sub>0</sub>=1/0.1/1.1, DP=200).** Toluene and DMF were bubbled separately with nitrogen for about 30 minutes. A mixture of Cu(II)Br<sub>2</sub> (2.52 mg, 0.01 mmol), Fe(0) powder (6.30 mg, 0.11 mmol) and TPMA (36.06 mg, 0.12 mmol) in DMF (0.6 mL) was placed in a Schlenk tube reactor. GMA (3.00 mL, 22.58 mmol) was added to the reactor followed by a mixture of EBiB (22.02mg, 0.11 mmol) in toluene (2.4 mL). The reactor was sealed and the mixture was frozen in liquid nitrogen. The reaction mixture was deoxygenated by three freeze-pump thaw cycles and purged with nitrogen. The Schlenk tube reactor was placed in a water bath at 30°C with magnetic stirring. Small samples were periodically withdrawn from the reaction mixture and analyzed by <sup>1</sup>H NMR spectroscopy to determine the monomer conversion and by GPC to determine the M<sub>n, GPC</sub> and Đ of the polymers.

At the end of the reaction, the polymer was precipitated in cold hexane, dissolved in chloroform and passed over a neutral sand/alumina column to remove the copper catalyst. The solution was reprecipitated in an excess of cold hexane. PGMA was dried under vacuum until constant weight was achieved.

**Chain extension experiment:** A mixture of Cu(II)Br<sub>2</sub> (5.04 mg, 0.023 mmol), Fe(0) (12.16 mg, 0.23 mmol), TPMA (72.12 mg, 0.25 mmol) and DMF (0.3 mL) (previously bubbled with

nitrogen) was placed in a Schlenk tube reactor. GMA (1.50 mL, 11.29 mmol) and a mixture of EBiB (44.04 mg, 0.23 mmol) in toluene (1.2 mL) (previously bubbled with nitrogen) were added to the reactor that was sealed and frozen in liquid nitrogen. The Schlenk tube reactor containing the reaction mixture was deoxygenated with several freeze-vacuum thaw cycles and purged with nitrogen and then placed in a water bath at 30°C with magnetic stirring. The reaction proceeded for 3 hours (91% conversion,  $M_{n,th} = 7082 \text{ g mol}^{-1}$ ,  $M_{n,GPC} = 9329 \text{ g mol}^{-1}$ ,  $D=1.2$ ). After that, a degassed solution of GMA (3.00 mL, 23 mmol) in toluene/DMF (4.8 mL/1.2 mL) was added and the reaction proceeded for 24 hours.

**Synthesis of a PDMS-*b*-PGMA block copolymer:** A mixture of Cu(II)Br<sub>2</sub> (1.01 mg, 0.005 mmol), Fe(0) (2.52 mg, 0.05 mmol), TPMA (14.43 mg, 0.05 mmol) and DMF (0.15 mL) (previously bubbled with nitrogen) was placed in a Schlenk tube reactor. GMA (3 mL, 22.58 mmol) and a mixture of -Br terminated PDMS macroinitiator ( $M_{n,GPC} = 6300 \text{ g mol}^{-1}$ ,  $D = 1.1$ ) (300 mg, 0.05 mmol) in a mixture of toluene (2.85 mL) and DMF (0.15 mL) (95/5 (v/v)) (previously bubbled with nitrogen) were added to the reactor that was sealed and frozen in liquid nitrogen. The Schlenk tube reactor containing the reaction mixture was deoxygenated with several freeze-vacuum thaw cycles and purged with nitrogen and then placed in a water bath at 30°C with magnetic stirring. The reaction proceeded for 11 hours.

**Typical UV/Vis experiment of [Fe(0)]/[Cu(II)Br<sub>2</sub>]/[PMDETA]:** The Fe(0) was placed in a quartz UV/Vis cell and purged with nitrogen. The complex Cu(II)Br<sub>2</sub> and PMDETA were dissolved in a mixture of toluene/DMF (80/20 (v/v)) in a vial and bubbled with nitrogen for about 15 min to remove oxygen. This solution was then transferred to a UV/Vis cell, which was sealed under nitrogen. The cell was placed in a water bath at 30°C under magnetic stirring. At different times, the cell was placed in the spectrophotometer for spectra acquisition and the absorbance measured in the 200–1100 nm range.

## Results and Discussion

The controlled polymerization of GMA through ATRP methods has been already reported for the homopolymerization and copolymerization<sup>21, 18, 20, 26-29</sup>. Nevertheless, most of the literature describes the preparation of PGMA for specific applications, and scarce information is provided regarding kinetic data.<sup>26-37</sup> Furthermore, in order to achieve control over the polymerization, most of the available synthetic methods report high concentrations of copper catalysts like Cu(I)Br or Cu(I)Cl chelated with various nitrogen based ligands such as PMDETA, 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA), *tris*[2-aminoethyl]amine (TREN) or 2,2'-bipyridine (Bpy)<sup>17, 26, 28, 32</sup>.

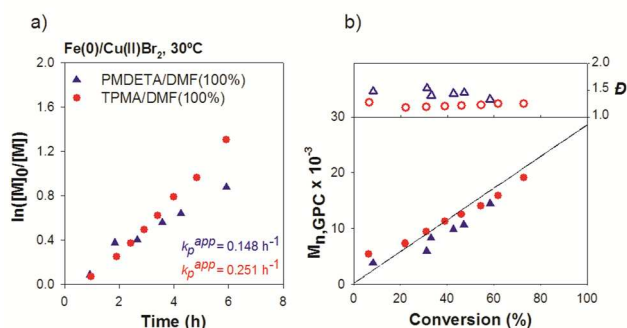
Fe(0)-mediated SARA-ATRP using Cu(II)Br<sub>2</sub>/Me<sub>6</sub>TREN as a deactivator complex was recently reported by our research

group for the controlled polymerization of St<sup>24</sup> and poly(2-(dimethylamino)ethylmethacrylate) (PDMAEMA)<sup>38</sup>. This catalytic system allows a good control over the polymer  $M_n$  and  $D$  with small amounts of copper/ligand complex<sup>2, 3, 24, 38</sup>.

SARA ATRP of GMA was carried out using a ratio  $[GMA]_0/\text{solvent} = 1/1$  (v/v) and a molar ratio of  $[Fe(0)]_0/[Cu(II)Br_2]_0/[ligand]_0 = 1/0.1/1.1$ .

### Influence of the solvent mixture and ligand structure

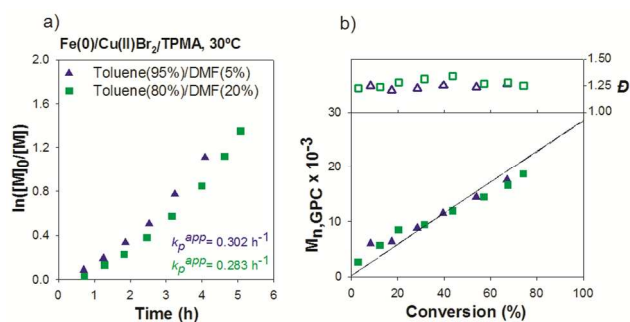
The effect of the solvent mixture in the SARA-ATRP of GMA is a very important parameter of the system aiming to afford a robust system for the synthesis of well-defined PGMA and its block copolymers. Canãmero et al.<sup>28</sup> reported the normal ATRP synthesis of PGMA in toluene using Cu(I) based catalytic complexes. The same solvent and monomer/solvent ratio was applied for the SARA ATRP of GMA using a catalytic system of Fe(0)/Cu(II)Br<sub>2</sub>/PMDETA. However, no polymer was obtained in these conditions, due to the lack of catalyst solubility in toluene. Solvents with high polarity such as DMF have also been reported for the homopolymerization and copolymerization of GMA<sup>20, 28</sup>. Due to solubility of the copper (II) /ligand complex in DMF, the SARA ATRP of GMA was conducted in this solvent. Fig. 1 presents the kinetic plots of SARA ATRP of GMA in DMF using either PMDETA or *tris*(2-pyridylmethyl)amine (TPMA) as ligand at 30°C. The TPMA is a stronger binding ligand and its use in this system was envisaged considering previous results published by Matyjaszewski<sup>39</sup> and our research group<sup>40, 41</sup>.



**Fig. 1** Influence of different ligand structure in SARA ATRP of GMA in DMF at 30°C. (a) First-order kinetic plot, (b) evolution of MWs and  $D$  with conversion (the dashed line represents the theoretical MW at a given conversion). Reaction conditions:  $[GMA]_0/[EBiB]_0/[Fe(0)]_0/[CuBr_2]_0/[ligand]_0 = 200/1/1/0.1/1.1$  (molar).

Fig. 1a indicates that the catalytic system Fe(0)/Cu(II)Br<sub>2</sub> allows the synthesis of PGMA in DMF using either PMDETA or TPMA as ligands. The polymerization proceeds following a first order kinetics relative to the monomer, reaching 60% conversion in 6 hours, with low  $D$  values around 1.5. Interestingly, the use TPMA led to faster reaction and at the same time a tighter control over  $D$  (~1.24). This result is in perfect accordance with previous reports from our research groups revealing the suitability of this ligand for ARGET<sup>41</sup> and SARA-ATRP<sup>40</sup>. Indeed, TPMA has found to allow a significant decrease of the amount of soluble copper required to achieve control over the polymerization in comparison with other

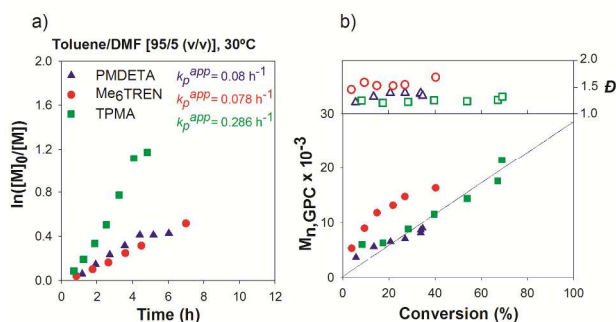
ligands<sup>40</sup>. In spite of the preliminary results showing that a SARA ATRP of GMA proceeded in a controlled manner in DMF, the use of toluene can be particularly relevant in order to afford a polymerization system able to copolymerize GMA with a wide number of other monomers with different functionalities (e.g. acrylates<sup>42</sup>, styrene<sup>43</sup>, siloxanes, etc). Aiming to understand the effect of the ratio of toluene/DMF in the SARA-ATRP of GMA, two different ratios have been studied (Fig. 2). The kinetic plots for the homopolymerization of GMA presented in Fig. 2 show a linear first order kinetics and very similar polymerization rates for both solvent mixtures. The evolution of the  $M_n$  is linear with monomer conversion, with a good agreement between the  $M_{n,th}$  and  $M_{n,GPC}$ . The  $\bar{D}$  values are close to 1.25 during the entire course of the polymerization. These results suggest that only 5% of DMF in the reaction mixture is enough to achieve a well-controlled polymerization of GMA, with high monomer conversion (about 70%) in less than 5 hours.



**Fig. 2** Influence of solvent mixture, toluene/DMF, 95/5 (v/v) and 80/20 (v/v) in SARA ATRP of GMA. (a) First-order kinetic plots, (b) evolution of MWs and  $\bar{D}$  with conversion (the dashed line represents the theoretical MW at a given conversion). Reaction conditions  $[GMA]_0/[initiator]_0/[Fe(0)]_0/[Cu(II)Br_2]_0/[TPMA]_0=200/1/1/0.1/1.1$  (molar).

### Influence of ligand structure in the toluene/DMF solvent mixtures

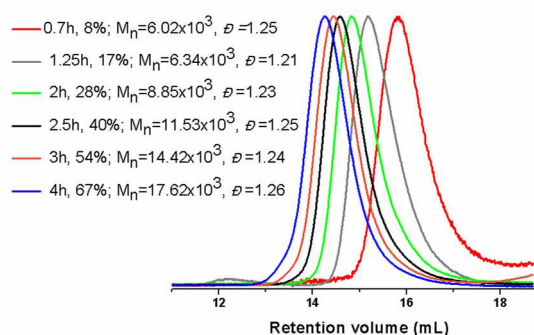
It is known that, in ATRP, the nature, activity and stability of the catalyst plays a decisive role in the dynamic equilibrium between the active and dormant species<sup>39</sup>. On this matter, a key parameter for the success of the catalytic system is the ligand structure<sup>44</sup>. Using the toluene/DMF [95/5 (v/v)] solvent mixture, three different copper-ligand complexes, *tris*(2-dimethylaminoethyl)-amine ( $Me_6TREN$ )<sup>4</sup>, PMDETA and TPMA were evaluated for the SARA ATRP of GMA at 30°C (Fig. 3).



**Fig. 3** Influence of different ligand structure in SARA ATRP of GMA in toluene-DMF=95/5 (v/v) at 30°C. (a) First-order kinetic plot, (b) evolution of MWs and  $\bar{D}$  with conversion (the dashed line represents the theoretical MW at a given conversion). Reaction conditions:  $[GMA]_0/[EBiB]_0/[Fe(0)]_0/[Cu(II)Br_2]_0/[ligand]_0=200/1/1/0.1/1.1$  (molar).

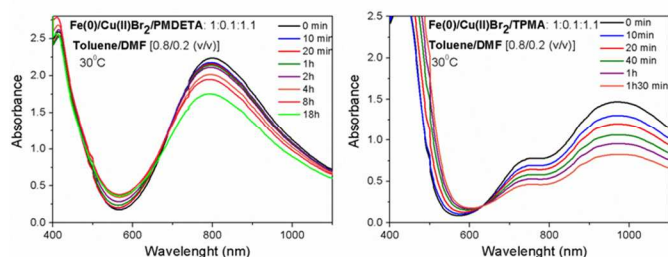
The kinetic data presented in Fig. 3 indicate that a stronger binding ligand as TPMA<sup>40, 45, 46</sup> provides a faster polymerization compared to PMDETA and  $Me_6TREN$ . The polymerization reaches 60% of conversion in less than 4 hours, while for PMDETA and  $Me_6TREN$  the conversion obtained for the same time is 34% and 40%, respectively. For the different ligands, it is observed a linear increase of  $M_n$  with conversion. Nevertheless, PMDETA and  $Me_6TREN$  lead to polymers with higher  $\bar{D}$  (~1.4 - 1.6), whereas the  $\bar{D}$  obtained for TPMA was around 1.2. These results suggest that TPMA is the most suitable ligand for the catalytic system proposed here, regardless the polarity of the solvent mixture.

The GPC data from polymerization with TPMA presented in Fig. 3 obtained for the different kinetic points, reveal that this ligand provides a high control over the  $M_n$  and  $\bar{D}$  values, with good agreement between theoretical and experimental  $M_{n,th}$  and  $M_{n,GPC}$  (~1.25). Fig. 4 demonstrates that the control over the  $\bar{D}$  is maintained throughout the polymerization.



**Fig. 4** GPC traces with conversion for SARA ATRP of PGMA in toluene/DMF =95/5 (v/v) at 30°C. Reaction conditions:  $[GMA]_0/[EBiB]_0/[Fe(0)]_0/[Cu(II)Br_2]_0/[TPMA]_0=200/1/1/0.1/1.1$  (molar).

In order to explore the effect of the ligand structure in the reduction of  $Cu(II)Br_2$  by  $Fe(0)$  in the toluene/DMF [0.8/0.2 (v/v)] mixture at 30°C, UV-vis experiments were performed (Fig. 5).



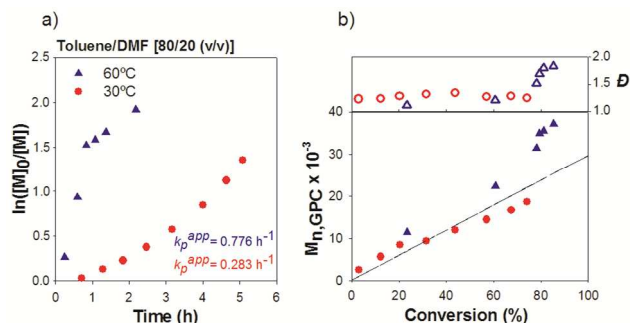
**Fig. 5** UV-vis spectrum of  $[\text{Fe}(0)]/[\text{Cu}(\text{II})\text{Br}_2]/[\text{TPMA}] = 1/0.1/1.1$  (left) and  $[\text{Fe}(0)]/[\text{CuBr}_2]/[\text{PMDETA}] = 1/0.1/1.1$  (right) in a mixture of toluene/DMF (0.8/0.2 (v/v)) during time. Conditions:  $V_{\text{total}} = 1.6 \text{ mL}$ ,  $T = 30^\circ\text{C}$ ,  $\text{N}_2$  atmosphere.

Both UV-vis spectra shown in Fig. 5 indicate the continuous reduction  $\text{Cu}(\text{II})\text{Br}_2$  over time. For the  $\text{Cu}(\text{II})\text{Br}_2/\text{TPMA}$  system the metal reduction is faster, about 50% in less than 40 minutes, contrarily to  $\text{Cu}(\text{II})\text{Br}_2/\text{PMDETA}$  system that requires 8 hours to reach the same reduction. The UV-vis data for the  $\text{Cu}(\text{II})$  reduction supports the conclusion drawn based on the kinetic data (Fig. 2 and Fig. 3) indicating that TPMA is the most suitable ligand for SARA-ATRP of GMA.

The polarity of the solvent mixture is a key factor in the SARA ATRP of GMA mainly due to the ability to dissolve the copper/ligand complex. The versatility of the present catalytic system in the polymerization of GMA was also evidenced by the success synthesis of well-defined PGMA in a reverse solvent mixture, composed by toluene/DMF [90/10 (v/v)] (Fig. S1). This result is particular relevant since it opens the possibility of changing the ratio of solvents to achieve an optimum values for specific monomers.

### Influence of the polymerization temperature

In order to evaluate the effect of temperature, the polymerization was conducted at  $30^\circ\text{C}$  and  $60^\circ\text{C}$  (Fig. 6).

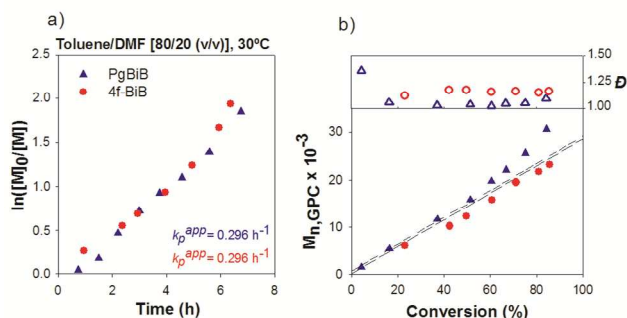


**Fig. 6** Effect of the reaction temperature in SARA ATRP of GMA in toluene/DMF = 80/20 (v/v). (a) First-order kinetic plots, (b) evolution of MWs and  $\bar{D}$  with conversion (the dashed line represents the theoretical MW at a given conversion). Reaction conditions  $[\text{GMA}]_0/[\text{EBiB}]_0/[\text{Fe}(0)]_0/[\text{Cu}(\text{II})\text{Br}_2]_0/[\text{TPMA}]_0 = 200/1/1/0.1/1.1$  (molar).

Despite a notorious increase of polymerization rate at  $60^\circ\text{C}$  (Fig. 6), the control over the  $\bar{D}$  is very poor (near 2.0). This lack of polymerization control with the temperature may be due to the appearance of side reactions, like chain transfer or termination reactions<sup>20</sup>.

### Influence of the use of different initiators

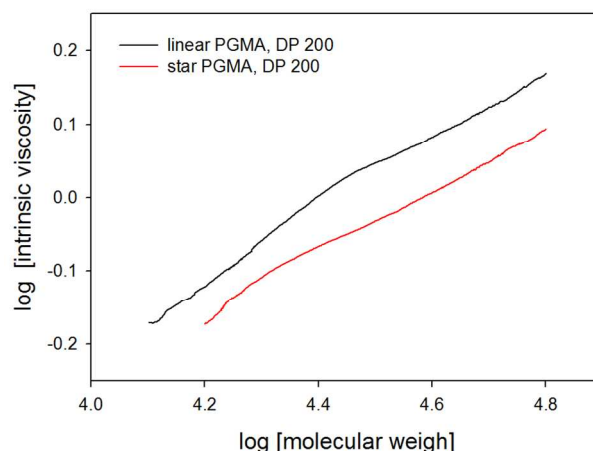
The influence of the initiator structure on the kinetics data was evaluated using two different initiators: alkyne based initiator (PgBiB) to afford PGMA macroinitiators that can be further functionalized by copper-catalyzed azide-alkyne cycloaddition ( $\text{CuAAC}$ )<sup>24, 47</sup>; and 4 arm-shaped initiator (4f-BiB) as proof-of-concept to allow the synthesis of star-shaped PGMA structures (Fig. 7).



**Fig. 7** Effect of the initiator in SARA ATRP of GMA in toluene/DMF = 80/20 (v/v). (a) First-order kinetic plots, (b) evolution of MWs and  $\bar{D}$  with conversion (the dashed line represents the theoretical MW at a given conversion). Reaction conditions  $[\text{GMA}]_0/[\text{initiator}]_0/[\text{Fe}(0)]_0/[\text{Cu}(\text{II})\text{Br}_2]_0/[\text{TPMA}]_0 = 200/1/1/0.1/1.1$  (molar).

As can be seen from Fig. 7, the polymerization rate for both initiators is very similar. The values are also close to the ones obtained for EBiB.  $M_{n,\text{GPC}}$  is in good agreement with  $M_{n,\text{th}}$  for both initiators. The results suggest the possibility of synthesizing PGMA with controlled features using different initiators. The use of these initiators is particularly relevant for Macromolecular Engineering<sup>48</sup> aiming to achieve complex structures with GMA that can be further modified.

The GPC results from last kinetic point of Fig. 7 for the reaction with EBiB and the 4-fBiB were analyzed in detail (Fig. 8). Those two polymers were synthesized using the same catalytic system,  $\text{Fe}(0)/\text{Cu}(\text{II})\text{Br}_2/\text{TPMA}$  in toluene/DMF [80/20 (v/v)] at  $30^\circ\text{C}$  and a target DP of 200.

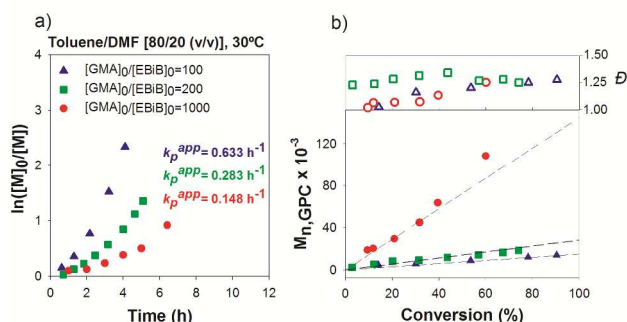


**Fig. 8** Log-log plot of intrinsic viscosities against MW for linear and 4-arm PGMA.

The star polymer always shows a lower intrinsic viscosity when compared to its linear analogue. The dependence of the intrinsic viscosity with the polymer MW is given by the equation,  $[\eta]=kM^\alpha$ , being  $[\eta]$  the intrinsic viscosity,  $M$  the molecular weight and  $k$ ,  $\alpha$  the Mark-Houwink constants. The Mark-Houwink exponent (slope of the curves), as expected, is lower for the 4-arm PGMA ( $\alpha=0.417$ ) in comparison to the linear analogue ( $\alpha=0.489$ ), indicating that the solution configuration of the star polymer is more dense and compact than the linear one. The  $k$  value observed for star and linear polymer was  $1.24 \times 10^{-2}$  and  $0.69 \times 10^{-2}$ , respectively.

### Study of different degrees of polymerization

Fig. 9 presents the influence of the target DP on the SARA ATRP of GMA. As expected, the polymerization rate decreases for higher target DP. The decrease of rate can be ascribed to the lower concentration of radicals in the polymerization.



**Fig. 9** Effect of the target DP in SARA ATRP of GMA in toluene/DMF = 80/20 (v/v). (a) First-order kinetic plots, (b) evolution of MWs and  $\bar{D}$  with conversion (the dashed line represents the theoretical MW at a given conversion). Reaction conditions  $[GMA]_0/[EBiB]_0/[Fe(0)]_0/[Cu(II)Br_2]_0/[TPMA]_0=DP/1/1/0.1/1.1$  (molar).

For the lower target DP (100), the kinetic data shows the expected profile for a RDRP method with a linear increase of  $M_n$  with the conversion.

From the kinetic data of Fig. 9, it can also be seen that lower conversions are obtained for high target DPs. This fact can be related with the increase of the solution viscosity for higher polymerization conversions that reduces radical mobility and therefore precludes the addition of new monomer units to the active chain ends.

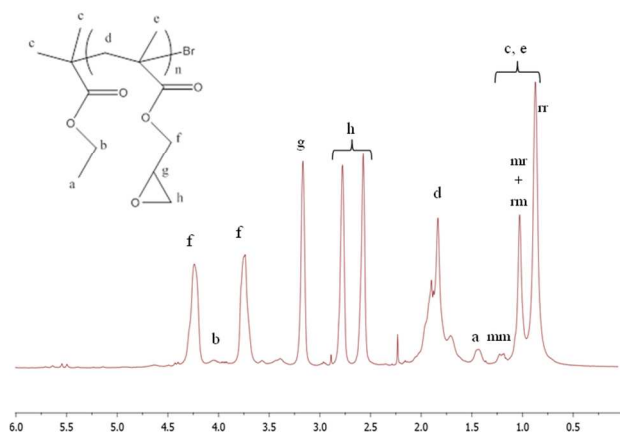
**Table 1 - SARA ATRP of GMA in the presence of Fe(0) and Cu(II)Br<sub>2</sub>/ligand at 30°C in different toluene/DMF mixtures (monomer/solvent ratio = 1/1 (v/v)).**

Entry	[tol.]/[DMF] (v/v)	$[GMA]_0/[EBiB]_0/[Fe(0)]_0/[Cu(II)Br_2]_0/[ligand]_0$	Ligand	Time <sup>a</sup> , h	Conv <sup>a</sup> , %	$M_{n,th}^a \times 10^{-3}$	$M_{n,GPC}^a \times 10^{-3}$	$\bar{D}^a$	$k_p^{app}$ , h <sup>-1</sup>
1	95/5	200/1/1/0.1/1.1	TPMA	5.0	74.2	20.90	18.60	1.20	0.286
2	95/5	200/1/1/0.1/1.1	Me <sub>6</sub> TREN	7.0	40.3	10.10	16.30	1.50	0.078
3	95/5	200/1/1/0.1/1.1	PMDETA	6.0	66.7	18.80	17.80	1.30	0.08
4	10/90	200/1/1/0.1/1.1	TPMA	7.0	87.9	24.50	30.30	1.30	0.323
5	0/100	200/1/1/0.1/1.1	TPMA	6.0	72.9	20.90	19.10	1.20	0.251
6	0/100	200/1/1/0.1/1.1	PMDETA	19.0	84.8	20.90	28.30	1.40	0.094
7	90/10	200/1/1/0.1/1.1	TPMA	6.0	76.3	21.20	20.60	1.30	0.283
8	80/20	200/1/1/0.1/1.1	TPMA	5.0	74.2	20.70	18.70	1.25	0.283
9 <sup>b</sup>	80/20	200/1/1/0.1/1.1	TPMA	2.0	85.3	25.20	37.20	1.80	0.776
10 <sup>c</sup>	80/20	200/1/1/0.1/1.1 (PgBiB)	TPMA	7.0	84.2	21.80	30.60	1.10	0.296
11 <sup>d</sup>	80/20	200/1/1/0.1/1.1 (4f-BiB)	TPMA	6.0	85.5	22.00	23.20	1.16	0.296
12	80/20	100/1/1/0.1/1.1	TPMA	4.0	90.4	13.50	14.20	1.27	0.633
13	80/20	1000/1/1/0.1/1.1	TPMA	6.0	60.1	108.50	86.80	1.25	0.148
14	80/20	11000/1/1/0.1/1.1	TPMA	64.0	26.7	251.10	185.30	1.58	-

<sup>a</sup> values obtained from the last sample from the kinetic study. <sup>b</sup>Reaction temperature was 60°C. <sup>c</sup>PgBiB was used as the initiator. <sup>d</sup>4f-BiB was used as the initiator.

**<sup>1</sup>H NMR analysis**

The chemical structure of the PGMA obtained via SARA ATRP, using the catalytic system [Fe(0)]/[Cu(II)Br<sub>2</sub>]/[TPMA], was determined by <sup>1</sup>H NMR spectroscopy (Fig. 10).



**Fig. 10** <sup>1</sup>H NMR spectrum of PGMA-Br obtained at high conversion ( $M_{n,GPC}=8700$  g mol<sup>-1</sup>;  $\bar{D}=1.15$ ;  $M_{n,NMR}=6800$  g mol<sup>-1</sup>); in CDCl<sub>3</sub>. PGMA is mainly syndiotactic: [rr]=0.66; [mr+rm]=0.30 and [mm]=0.04.

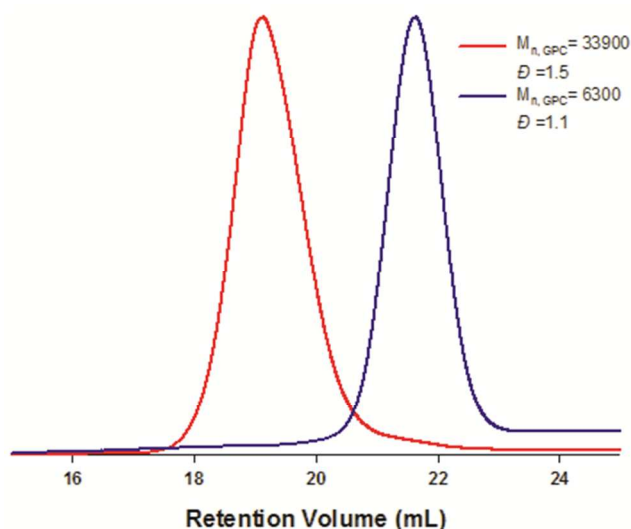
Fig. 10 presents the <sup>1</sup>H NMR spectrum of PGMA-Br. The peaks observed at 2.63–2.84 ppm (h, –CHCH<sub>2</sub>O–), 3.23 ppm (g, –CH<sub>2</sub>CHO–), 3.81 and 4.30 ppm (f, COOCH<sub>2</sub>CH–) are in agreement with the PGMA chemical structure<sup>28</sup>. The ethyl group (CH<sub>3</sub>CH<sub>2</sub>O–) corresponding to the initiator fragment, references (a) and (b) respectively. Regarding tacticity, the analysis of the proton resonances found at 0.93, 1.09 and 1.24 ppm (e, –CCH<sub>3</sub>Br) correspond to the isotactic (mm), heterotactic (mr+rm) and syndiotactic (rr) segments, respectively, in which this signal is split. The difference in chemical shifts between the signals (mm–(mr+rm))= 0.15 ppm and ((mr+rm)–rr)= 0.16 ppm as well as the isotacticity parameter obtained  $\sigma=0.2$  are in close agreement with the reported tacticity data<sup>28, 49–51</sup> for PGMA. From the integral ratio from the polymer (f) and initiator (b) <sup>1</sup>H NMR peaks it is possible the calculation of the  $M_{n,NMR}=6800$  g mol<sup>-1</sup>.

**Chain Extension Experiment**

To prove the “living” character of the PGMA obtained via SARA ATRP, a chain extension experiment was carried out. Fig. S2 shows the shift of the GPC trace of PGMA towards lower values of retention volume due to the addition of fresh monomer. The  $M_n$  of the macroinitiator obtained at 91% conversion ( $M_{n,th}=7082$ ,  $M_{n,GPC}=9329$ ,  $\bar{D}=1.2$ ) more than doubled ( $M_{n,th}=14029$ ,  $M_{n,GPC}=29500$ ,  $\bar{D}=1.6$ ). These results indicate the “living” character of the PGMA obtained using the reported catalytic system and therefore its ability to be applied in the synthesis of block copolymers with this catalytic system.

**Synthesis of well-defined GMA based block copolymers via SARA ATRP**

In order to explore the potential of using a mixture of solvents, in PGMA copolymerization, a PDMS-*b*-PGMA hybrid block copolymer was prepared via SARA ATRP of GMA ([GMA]<sub>0</sub>/[PDMS-Br]<sub>0</sub>/[Fe(0)]<sub>0</sub>/[Cu(II)Br<sub>2</sub>]<sub>0</sub>/[TPMA]<sub>0</sub>=500/1/1/0.1/1.1) at 30°C in Toluene/DMF [95/5(v/v)]. Bromide functionalized PDMS was used as macroinitiator. The PDMS segments have been focus of particular attention in the scientific community due to their interesting properties like: hydrophobicity, low irritation potential, low glass-transition temperatures and melting point, low surface tension, low toxicity and good environmental compatibility<sup>25, 52</sup>.



**Fig. 11** GPC traces of the PDMS-Br macroinitiator (right curve) and the PDMS-*b*-PGMA block copolymer (left curve) prepared by SARA ATRP macroinitiation.

Fig. 11 shows the complete shift of the GPC trace of PDMS-*b*-PGMA ( $M_{n,th}=25800$ ,  $M_{n,GPC}=33900$ ,  $\bar{D}=1.5$ ) towards lower values of retention volume in comparison with the GPC trace of PDMS-Br ( $M_{n,th}=5000$ ,  $M_{n,GPC}=6300$ ,  $\bar{D}=1.1$ ).

These results confirm the success of the synthesis of controlled hybrid block copolymers from PDMS based macroinitiators using the reported catalytic system.

The structure of the PDMS-*b*-PGMA block copolymers was evaluated by <sup>1</sup>H-NMR (Fig. S3). It can be observed that the relative intensities of the peaks at 0.94–1.28 ppm (o), 2.63–2.84 ppm (r), 3.23 ppm (q), 3.80 and 4.30 ppm (p) are in agreement with the expected chemical structure of PGMA<sup>28</sup>. A sharp peak at 0.06 ppm (e) is ascribed to the siloxane segment. The ratio of the integration of peaks (d, f) and (r), segments from PDMS-Br and PGMA respectively, allows the calculation of the  $M_{n,NMR}=27500$ .

Table 1 summarizes the kinetic data obtained using different reaction conditions for SARA-ATRP of GMA.

The results presented in Table 1 show that the Fe(0)/Cu(II)Br<sub>2</sub> mediated catalytic system allows the SARA ATRP of GMA using various ligands as well as various reaction conditions, affording PGMA with high conversions and low  $\bar{D}$  values.



Nonetheless the kinetic data suggest that TPMA is the most suitable ligand regarding polymerization control, rate and conversion. Regarding the solvent mixture there is no significant difference in the kinetic data to stress a specific mixture for the polymerization of GMA. However, different solvent ratios can be used taking into account solubility parameters of other polymer segments that will be copolymerized with PGMA.

## Conclusions

To sum up, this manuscript reports a convenient method based on SARA-ATRP to afford the synthesis of controlled PGMA and related block copolymers at room temperature. The polarity of the solvent mixture is a key factor in the SARA ATRP of GMA due to its ability to dissolve the copper/ligand complex. The results presented herein are extremely relevant for researchers aiming to prepare PGMA based macromolecules using residual amounts of soluble copper.

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## Notes and references

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