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Polymerization

Group-Transfer Polymerization-Induced Self-Assembly (GTPISA) in Non-polar Media: An Organocatalyzed Route to Block Copolymer Nanoparticles at Room Temperature

Assia Stiti, Ana Maria Cenacchi Pereira, Sébastien Lecommandoux, and Daniel Taton*

Abstract: Polymerization-induced self-assembly (PISA) enables the synthesis at large scale of a wide variety of functional nanoparticles. However, a large number of works are related to controlled radical polymerization (CRP) methods and are generally undertaken at elevated temperatures ($>50^{\circ}\text{C}$). Here is the first report on methacrylate-based nanoparticles fabricated by group transfer polymerization-induced self-assembly (GTPISA) in non-polar media (*n*-heptane). This GTPISA process is achieved at room temperature (RT) using 1-methoxy-1-(trimethylsilyloxy)-2-methylprop-1-ene (MTS) and tetrabutylammonium bis-benzoate (TBABB) as initiator and organic catalyst, respectively. Under these conditions, well-defined metal-free and colorless diblock copolymers are produced with efficient crossover from the non-polar stabilizing poly(lauryl methacrylate) (PLMA) block to the non-soluble poly(benzyl methacrylate) (PBzMA) segment. The resulting PLMA-*b*-PBzMA block copolymers simultaneously self-assemble into nanostructures of various sizes and morphologies. GTPISA in non-polar solvent proceeds rapidly at RT and avoids the use of sulfur or halogenated compounds or metallic catalysts associated with the implementation of CRP methods, thus expanding the potential of PISA formulations for applications in non-polar environments.

Polymerization-induced self-assembly (PISA) has emerged as a facile, rapid and robust route to in situ engineering polymeric nanoparticles of various sizes and morphologies over the last decade.^[1–19] A PISA process advantageously avoids the sequential steps of synthesis followed by self-

assembly of amphiphilic block copolymers in different reaction vessels. Moreover, PISA can be achieved at relatively high solid contents, namely, at 10–50 % w/w, within short reaction times, and in absence of exogenous surfactants for colloidal stabilization of the nanoparticles, due to the steric stabilization provided by peripheral blocks. Typically, a controlled/living polymerization is used to prepare a precursor block. Crossover from this first block to a second growing block, which becomes insoluble in the reaction mixture once it reaches a critical molar mass, is then ensured by selecting a second monomer and an appropriate solvent. Micellar nucleation thus takes place simultaneously during copolymer synthesis, enabling the formation of sterically stabilized block copolymer nanoparticles.^[12,20] To date, PISA has been essentially developed by controlled radical polymerization processes, most notably by reversible addition fragmentation chain transfer (RAFT) polymerization, in either dispersion or emulsion.^[5,21–24] RAFT-mediated PISA is indeed well adapted to many monomers, and a wide range of nanostructures have thus been achieved, including spheres, vesicles, worms, lamellae or octopus-like structures.^[25–27] Examples of PISA formulations by tellurium-mediated radical polymerization (TERP) have also been reported.^[28] Implementation of PISA by non-CRP methods is scarcer. For instance, PISA has been adapted to the ring-opening metathesis polymerization (ROMP) of norbornenyl derivatives,^[29–34] and more recently to the ring-opening polymerization (ROP) of *N*-carboxy-anhydrides.^[35–37] There are also some examples of PISA carried out by coordination polymerization.^[38,39] In addition, a large majority of PISA processes have been developed for a use in aqueous or alcoholic formulations.^[40–42] Much fewer PISA-derived block copolymers in non-polar media have been reported.^[12,36–39] PISA carried out by living anionic polymerization (LAP) requiring the use of butyl lithium as initiator and diene and styrenic derivatives as monomers, has also already been reported.^[43–46] Non-polar dispersion media, such as mineral^[47,48] or silicone oils^[49,50] or *n*-alkanes^[51,52] have allowed achieving hydrophobic diblock copolymer nanoparticles by PISA. Such nanoparticles dispersed in non-polar media may be suited for specific applications, for instance, as viscosity modifiers or as lubricants for automotive engine oils.^[53,54]

Another constraint of CRP-mediated PISA, in particular by RAFT, is that these reactions are often undertaken at elevated temperatures, i.e., usually $>50^{\circ}\text{C}$ by thermal

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initiation. Recently, non-thermally initiated RAFT PISA processes have been developed though, including by photo-, redox/oscillatory reaction-, enzyme- and ultrasound wave-initiation.^[55] Lastly, CRP methods, such as RAFT or TERP, use an organosulfur or organotelluric controlling agent, which can cause color and/or toxicity and/or odor problems in certain applications (e.g. cosmetics, packaging, coatings). A chemical post-treatment step may therefore be necessary, for example to eliminate the chain ends resulting from RAFT polymerizations.^[56] Therefore, new methodologies for PISA are still needed to overcome the inherent limitations of CRP methods, and in order to achieve specific nanoparticles in a variety of dispersion solvents under mild conditions. Here we report on the design of hydrophobic methacrylate-based nanoparticles in non-polar media by an unprecedented PISA process, coined group transfer polymerization-induced self-assembly, and abbreviated as GTPISA (Figure 1). Specifically, *n*-alkanes have been selected as non-polar solvents, as they are preferred for fundamental studies—as those described here—over more complex mineral oils.

Disclosed by the Webster group at Dupont® in the mid 1980's, group-transfer polymerization (GTP) was acknowledged as a major breakthrough in polymer synthesis. GTP indeed described a living polymerization method for essentially methacrylic monomers operating at room temperature (RT), not requiring stringent conditions like in anionic polymerization.^[57–59] Based on the reiteration of the C–C bond forming Mukaiyama-Michael reaction,^[60] GTP is initiated and propagates by the conjugate addition of a silyl ketene acetal serving as initiator to the incoming (meth)acrylic monomers, followed by transfer of the trimethylsilyl group to chain end.^[61,62] GTP remains a method of choice in industry to produce tailor-made colorless (meth)acrylate-based (co)polymers, for instance, for a

use as pigment dispersants for paints.^[63] Advantageously, GTP-derived polymer chains are terminated with a silylketene-acetal (SKA) end group, which rapidly hydrolyzes during workup into an enol and trimethylsilanol as by-product. The enol in turn is rearranged into an ester, while trimethylsilanol evolves into hexamethyl disiloxane, that can be readily removed. Therefore, polymer chain ends simply consist of C–H bonds after workup. Over the last 15 years, the scope of GTP has been broadened through the use of a variety of organic catalysts, such as *N*-heterocyclic carbenes (NHCs) or super strong Brønsted phosphazene bases, or strong Brønsted acids (e.g., bis(trifluoromethanesulfonyl)imide).^[64–74] Synthesis of non-aqueous dispersions of poly(methyl methacrylate) (PMMA)-based nanoparticles by GTP was reported since 1995. This was achieved by GTP of MMA or MMA and ethyleneglycol dimethacrylate (EDMA) in dispersion in *n*-heptane using polystyrene-*b*-poly(ethene-*alt*-propene) as dispersing agent, 1-methoxy-1-(trimethylsilyloxy)-2-methylprop-1-ene (MTS) as initiator and tetrabutylammonium fluoride (TBAF) or tetrabutylammonium cyanide (TBAC) as catalyst.^[75] However, significant increase in both molar masses and particle size distributions with monomer conversion was noted. Better control was achieved using cross-linked free radical polymerization-derived PMMA seeds.

Here we report for the first time in situ methacrylate-based nanoparticles formation by GTPISA in *n*-heptane. We thus extend the PISA strategy to the GTP method proceeding at RT in non-polar media, in absence of sulfur, metal or halogen atom, so that GTPISA clearly distinguishes from other PISA processes described so far. The stabilizing block, namely, poly(lauryl methacrylate) (PLMA) is first synthesized by GTP in solution in *n*-heptane, using MTS as initiator and tetrabutylammonium bibenzoate (TBABB) as organic catalyst (Scheme 1). Highly efficient crossover from

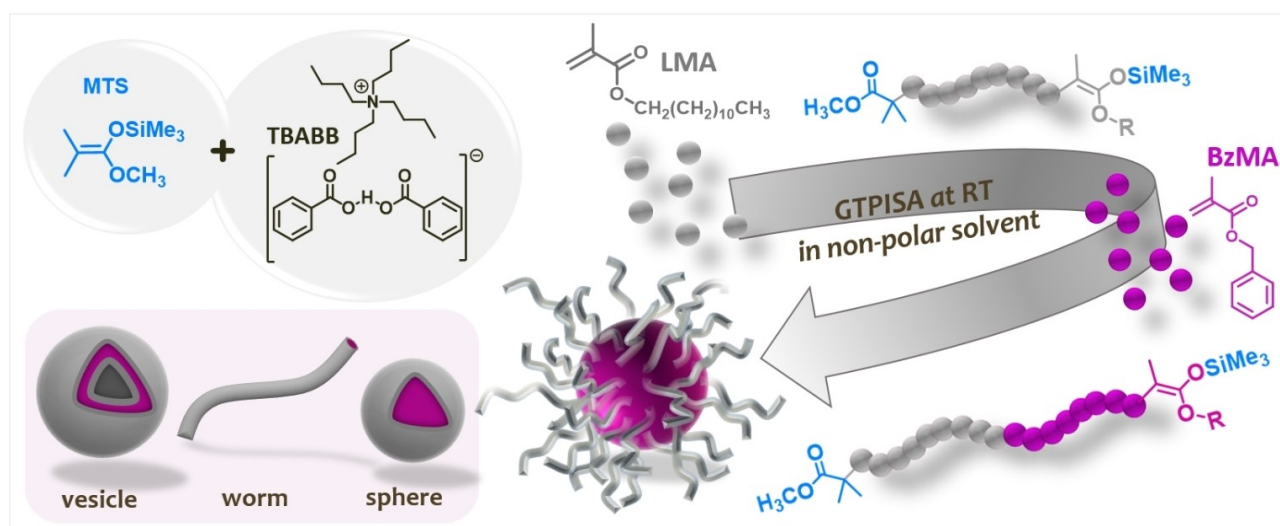
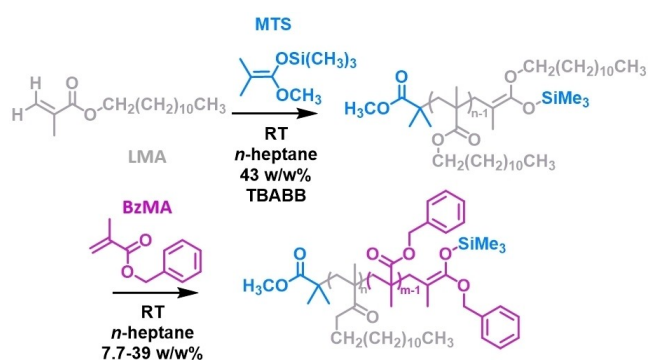


Figure 1. Group transfer polymerization induced self-assembly (GTPISA) of (meth)acrylate monomers at RT in non-polar solvent as an organocatalyzed route to block copolymer nanoparticles (spheres, worms and vesicles).



Scheme 1. Synthesis of PLMA-*b*-PBzMA block copolymers via sequential GTPISA in *n*-heptane at room temperature. The solid content has been calculated using the following formula: % solids = (net weight of the dry specimen/Net weight of the original specimen) × 100.

the parent PLMA block to the non-soluble poly(benzyl methacrylate) (PBzMA) segment thus yields stable colloidal dispersions based on PLMA-*b*-PBzMA diblock copolymers of various sizes and morphologies by GTPISA in *n*-heptane (Figure 1).

PLMA precursors were synthesized by GTP in *n*-heptane. As our objective was to directly prepare the nanoparticles in non-polar medium, thus avoiding the prior synthesis of the block precursors in a specific solvent, each constitutive block of the PLMA-*b*-PBzMA block copolymers was elaborated in a single solvent, in this case *n*-heptane. To the best of our knowledge, GTP of (meth)acrylic monomers in solution in *n*-heptane has never

been reported. PLMA blocks of different molar masses were successfully synthesized by GTP of LMA at RT in *n*-heptane at [LMA] = 2 mol/L, using MTS as initiator and TBABB as organic catalyst, under the following conditions: [LMA]/[MTS]/[TBABB] = 15-30/1/0.1 (Table S1). Near quantitative yields were achieved within 150 minutes, according to ¹H NMR analysis. A typical ¹H NMR spectrum in CDCl₃ of a GTP-derived precursor is provided in Figure 2.C. Comparing the methyl signals assigned to the PLMA end-group at 3.65 ppm with those of the oxymethylene protons due to LMA units at 3.7 ppm allows the determination of the average degree of polymerization of PLMA block (DP_{PLMA} = 27). Several observations led to the conclusion of excellent control of the GTP process, including i) the production of PLMA's of controlled molar masses and of narrow dispersity ($\mathcal{D} < 1.17$), as determined by SEC. In addition, ii) the MALDI-ToF spectrum of a PLMA₁₂ precursor showed an isotopic single distribution of peaks, with the expected structure including a peak-to-peak mass increment of 254 g/mol corresponding to the molar mass of a LMA unit (Figure 2.A). On the other hand, iii) successful chain extension experiment confirmed the controlled character of the polymerization (Figure 2.B). After synthesis of a PLMA₂₇ by GTP in *n*-heptane, addition of 27 eq. of LMA yielded a PLMA₅₄ after 115 minutes, while maintaining a low dispersity ($\mathcal{D} = 1.16$) indicating quantitative re-initiation of GTP from PLMA₂₇ parent chains. Finally, iv) GTP of LMA in *n*-heptane, targeting DP = 27, indicated first-order kinetics confirming a linear evolution of both molar masses with LMA conversion and $\ln([LMA]_0/[LMA])$ with time (Figure 2.D). Of particular interest, these kinetic studies

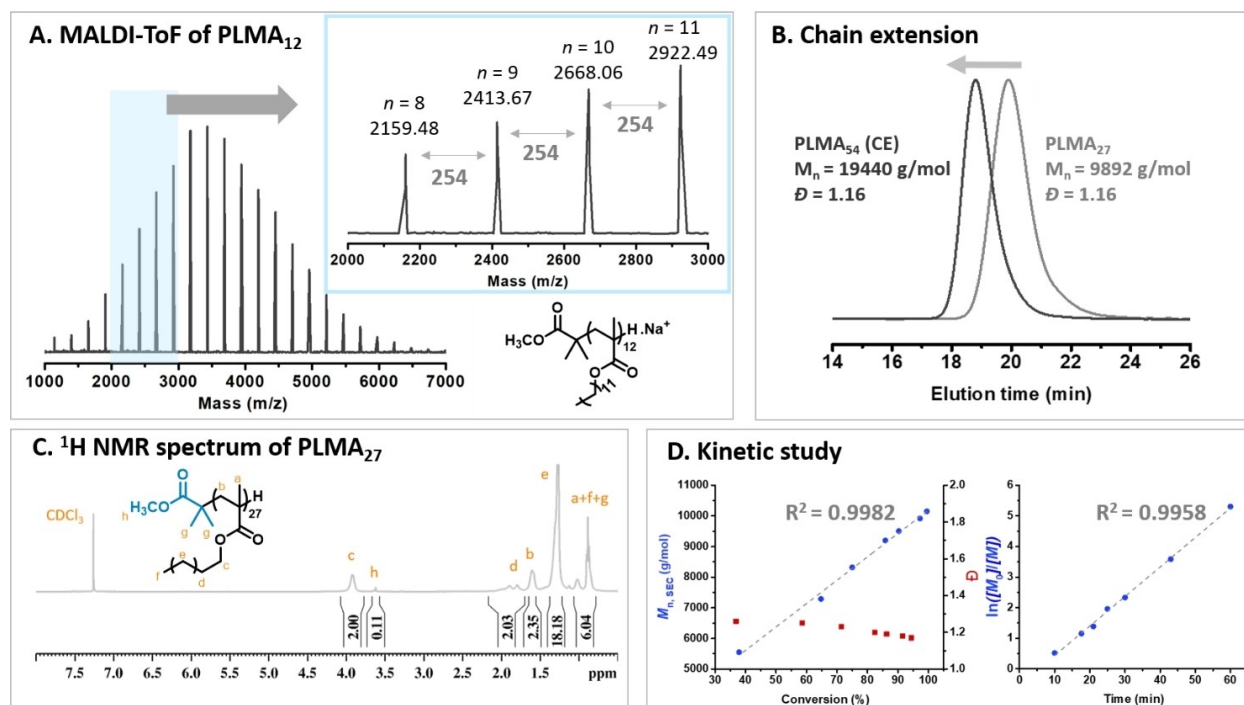


Figure 2. A. MALDI-ToF MS spectrum of PLMA₁₂. B. Chain extension of PLMA₂₇ to PLMA₅₄. C. ¹H NMR spectrum of PLMA₂₇. D. M_n and \mathcal{D} versus conversions of LMA at [M] = 2 mol/L; Plot of $\ln([M]_0/[M])$ with time.

show that GTP of LMA in *n*-heptane is free of termination reaction until full monomer conversion, which contrasts with what is generally observed during CRP processes. There was thus no need to purify the PLMA precursors before the growth of the structuring block, greatly simplifying the synthesis procedure. Ultimately, these results attest that GTP of MTS-initiated and TBABB-catalyzed LMA can be achieved under controlled/living conditions in *n*-heptane. The sequential GTPISA was optimized to achieve well-defined PLMA-*b*-PBzMA block copolymers. Synthesis of methacrylic-type block copolymers by RAFT dispersion polymerization in non-polar media has already been reported. This is typically achieved at 90 °C.^[22,76,77] Herein, the GTPISA of BzMA was conducted at final 7.7–39 % w/w solids in *n*-heptane at RT, depending on the targeted DP, utilizing the PLMA precursor blocks described above (Scheme 1). Based on literature background on PISA formulations,^[78–80] we hypothesized that the mode of BzMA addition would have a decisive effect on the quality of GTPISA control, and consequently on the final structure of the PLMA-*b*-PBzMA block copolymers. Thus, GTP of BzMA was either carried out using a rather rapid monomer addition process at 0.07 mL/min, or following a much slower monomer addition at different flow rates (Figure S1). In all cases, the reaction mixture turned turbid after a few minutes of reaction, suggesting the onset of micellar nucleation (see photographs in Figure S2). When targeting the synthesis of PLMA₂₇-*b*-PBzMA₄₀ from the rapid monomer addition protocol, BzMA was completely converted after 100 minutes. SEC traces of the resulting compounds systematically showed a shift toward higher molar masses, compared to the SEC trace of the parent PLMA. However, adding the monomer using a flow rate of 0.07 mL/min invariably revealed the presence of a low molar masse shoulder by dRI detection (Figure 3), which was not observed by UV because the UV response was ascribed to the absorbance of BzMA units only. This shoulder thus indicated the presence of unreacted PLMA precursor, due to nonoptimal re-initiation

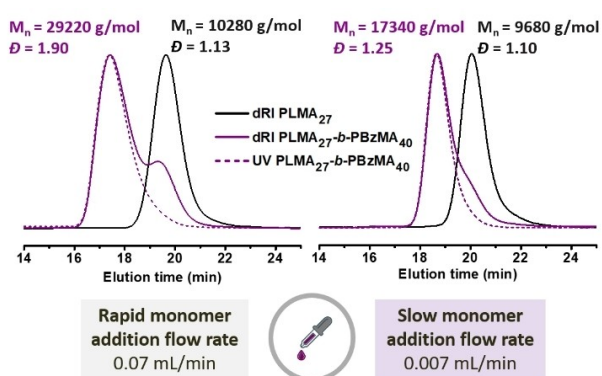


Figure 3. Effect of slow monomer addition on the control over the polymerization illustrated by SEC traces of PLMA₂₇-*b*-PBzMA₄₀ synthesized with a rapid monomer addition of 0.07 mL/min (left) and at slow addition flow rate of 0.007 mL/min (right) at [M] = 2 mol/L in *n*-heptane. The UV signal is represented by a dashed line and the dRI by a solid line.

of BzMA from the PLMA block precursor under the rather rapid monomer addition protocol. A control experiment performed by GTP in solution in THF led to structurally very well-defined block copolymers (Figure S3). This strongly suggested that the bimodal distribution observed for GTPISA experiments conducted at 0.07 mL/min was related to the self-assembly process taking place in *n*-heptane, as already reported, including by Armes et al.^[4,81–84] and by Zhang et al.^[85,86] in the context of RAFT-PISA formulations. In another study, Sakurai et al. reported that the kinetics of an aqueous PISA reaction can be decoupled from the structuring of the forming micelle.^[87] By monitoring the whole PISA process using both in situ small-angle X-ray scattering and NMR spectroscopy, it was shown that the formation/growth of micelles was much faster than the polymerization. This difference in kinetics between the two key stages of the PISA process may explain that, in some cases, re-initiation from the first block is not quantitative, thus showing a shoulder in SEC due to this residual block. We found that by decreasing the monomer addition rate, using an optimal flow rate of 0.007 mL/min, we significantly improved the control of the GTPISA, reducing the molar mass distribution of the PLMA₂₇-*b*-PBzMA₄₀ block copolymers (\bar{D} = 1.90 at 0.07 mL/min vs. 1.25 at 0.007 mL/min; Figure 3) and minimizing the shouldering in the low molar masse region by dRI detection. Details of a more systematic investigation of the semi-continuous BzMA addition process, including the addition rates used, are provided in the ESI (Figure S1). Improved polymerization control was also demonstrated by DOSY NMR analysis (see details in Figure S4). We indeed observed that the difference between the diffusion coefficients of each block was significantly reduced by slowly adding the BzMA monomer. Alternatively, formation of a small intermediate block before the growth of the structuring PBzMA block proved to be another advantageous option. Such a transient block was thus generated from the mixture of the two monomers (LMA + BzMA), forming a P(LMA-*co*-BzMA) statistical copolymer. Figure S5 shows the beneficial effect of such a procedure, through the formation of the GTPISA-derived PLMA₁₅-*b*-P(LMA₂₀-*co*-BzMA₂₀)-*b*-PBzMA₂₅ and PLMA₁₅-*b*-P(LMA₂₀-*co*-PBzMA₂₀)-*b*-PBzMA₅₀ block copolymers. In both cases, the shoulder due to the parent PLMA precursor has almost disappeared. Therefore, both the slow monomer addition process and formation of an intermediate statistical copolymer between the stabilizing and the structuring blocks represent efficient strategies for improving the crossover from one block to the other during GTPISA.

Apparent molar masses of PLMA-*b*-PBzMA block copolymer were determined by SEC and by ¹H NMR as well (Table S1). A typical ¹H NMR spectrum of a PLMA-*b*-PBzMA block copolymer is shown in Figure S6. The composition in each monomer unit could be estimated from the relative integrations of characteristic signals at around 3.9 ppm and at 4.9 ppm for PLMA and PBzMA blocks, respectively. Knowing the molar mass of the PLMA precursor, the \overline{Mn} value of the PLMA-*b*-PBzMA could thus be determined (Table S1). For instance, a $\overline{Mn}_{\text{NMR}}$ value of 16365 g/mol was calculated, corresponding to a molar mass

of 9033 and 7332 g/mol for the PLMA and PBzMA block, respectively (Table S1, run 3). The differences observed between experimental and theoretical values were attributed to the use of polystyrene standards to calibrate SEC columns. It is established that the GTP method is well suited to possibly obtain methacrylic polymers with high molar masses ($> 300,000 \text{ g}\cdot\text{mol}^{-1}$).^[65–66] In the present study, block copolymers of moderate molar masses (DP between 15 and 30 for the PLMA block and DP between 25 and 150 for the PBzMA block) were purposely synthesized to self-assemble and form nanoparticles stable in *n*-heptane. The possibility of accessing compounds of higher molar masses was not considered here, but could be the subject of further studies.

In principle, PISA-derived block copolymers of asymmetric composition should lead to the formation of spheres, worms and vesicles.^[10,12] In practice, however, specific parameters can lead to morphological constraints, i.e. preventing the formation of higher order morphologies. For instance, a too long steric stabilizer can lead to kinetically trapped spheres.^[4] Herein, GTPISA allowed accessing the three main morphologies, provided structural parameters and experimental conditions were properly selected. By thus targeting PLMA₃₀-*b*-PBzMA_x block copolymers synthesized by GTPISA in *n*-heptane (Figure 4.A), only spherical nanoparticles were observed by TEM. As shown in Figure 4.B, sizes obtained by TEM were found in good agreement with intensity-average diameters determined by DLS. The increase in size of the nanoparticles, from 33 nm to 54 nm, were correlated to the length of the core-forming PBzMA block. These results are consistent with a restricted morphology to a spherical shape observed for RAFT-PISA experiments in non-polar medium involving rather long block stabilizers,^[4] precluding the fusion of spheres and the formation of worms and vesicles. In contrast, targeting a shorter PLMA stabilizing block, i.e., DP_{PLMA} = 15, higher

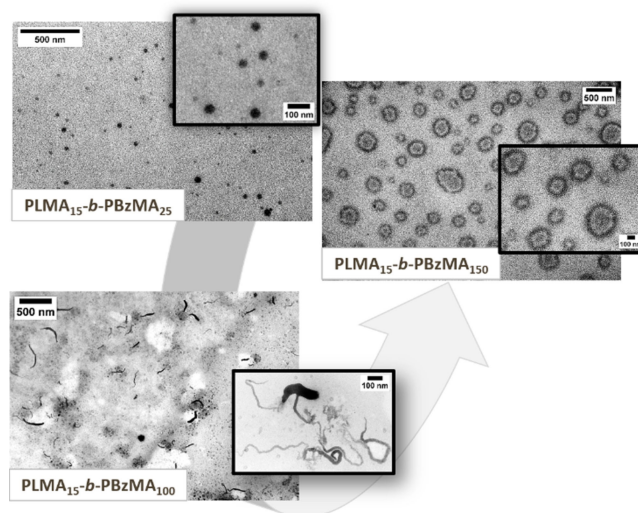


Figure 5. TEM images obtained for PLMA₁₅-*b*-PBzMA_x nanoparticles synthesized by organocatalyzed GTPISA in *n*-heptane at room temperature. Morphologies such as spheres, worms and vesicles are accessible depending on the PBzMA block targeted DP.

order morphologies could be observed by TEM from the resulting PLMA₁₅-*b*-PBzMA_x block copolymers made by GTPISA in *n*-heptane (Figure 5). Thus, spheres with a mean size diameter of 28 nm were obtained upon targeting a DP_{PBzMA} of 25. A predominant morphology of worms was observed for copolymers with DP_{PBzMA} varying from 75 to 100, but coexisting with a population of spheres. Finally, vesicles are predominantly present for copolymers with DP_{PBzMA} > 100 (e.g., for the PLMA₁₅-*b*-PBzMA₁₅₀ sample shown in Figure 5). The exemplification of the GTPISA method unveiled in this communication to other methacrylic

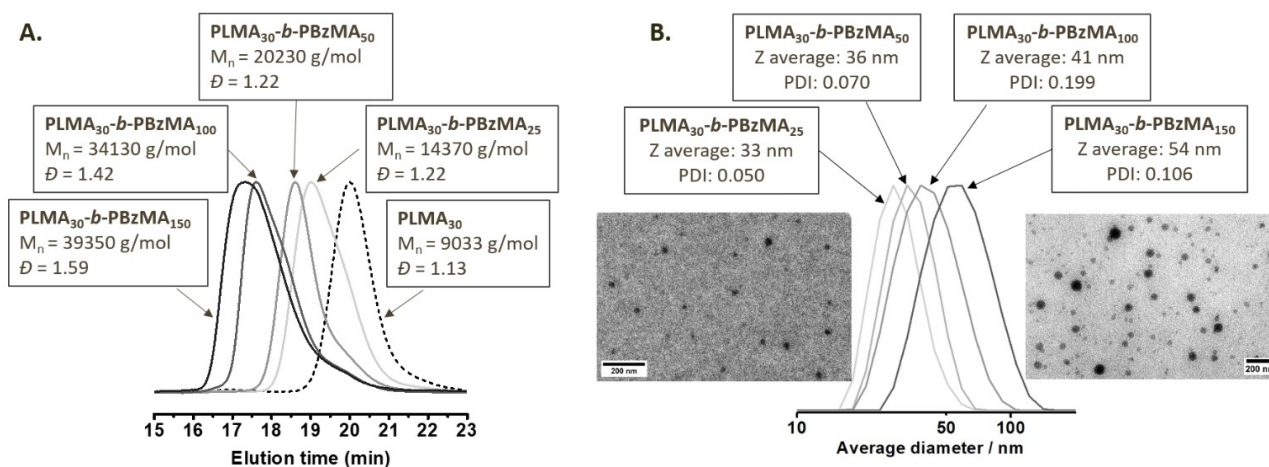


Figure 4. A. THF gel permeation chromatograms (polystyrene standards) obtained for a series of PLMA₃₀-*b*-PBzMA_x diblock copolymers synthesized via GTP in *n*-heptane at room temperature. The corresponding PLMA₃₀ first block prepared in *n*-heptane is also shown as a reference. B. Dynamic light scattering particle size distributions obtained for a series of PLMA₃₀-*b*-PBzMA_x nanoparticles prepared by GTP in *n*-heptane at room temperature are represented. The mean diameter of these spherical diblock copolymer nanoparticles can be systematically increased simply by targeting a higher degree of polymerization (x) for the core-forming PBzMA block; transmission electron microscopy images are shown for PLMA₃₀-PBzMA₂₅ and PLMA₃₀-PBzMA₁₅₀ diblock copolymers.

monomers, and indeed its diversification to other types of block copolymers, will be the subject of subsequent publications.

In summary, we report an original and facile synthetic route to self-stabilized methacrylic-based polymeric nanoparticles in non-polar media. These findings break ground for a novel concept, namely, group transfer polymerization-induced self-assembly (GTPISA), to control polymerization and self-assembly pathways in non-aqueous media at RT. GTPISA can be conducted in the same solvent for the growth of the PLMA stabilizing block and the core-structuring PBzMA block. It also avoids the use of metal, sulfur and halogen atom, which is of prime importance for potential applications of the resulting compounds as specialty additives, notably in motor oils and/or fuels. The slow addition of the monomer forming the core-structuring blocks represents a decisive lever to optimize the GTPISA process and thus obtain well-defined diblock copolymer structures. By targeting a relatively short stabilizing block—here PLMA— and by varying the size of the core-forming block—PbzMA—, the three main morphologies of PISA formulations can be obtained, namely, spheres, worms and vesicles. In contrast, longer stabilizing PLMA blocks restrict the morphology to spherical shapes, though of varied sizes depending on the length of the PBzMA block. As GTPISA employs an organic catalyst, it further expands the scope of organocatalyzed polymerization reactions for engineering block copolymers in non-aqueous dispersed media. Work is in progress in our group to investigate the scope of GTPISA and diversify the structure and/or functionalize both the stabilizing and the core-forming segments of the as-derived nanoparticles.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords: Block Copolymers · Group Transfer Polymerization · Nanoparticles · PISA · Tunable Morphologies

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