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Ring-Opening Metathesis Polymerization in Aqueous Media using a Macroinitiator Approach

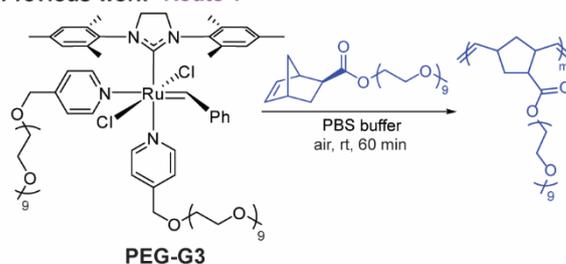
Jeffrey C. Foster, Spyridon Varlas, Lewis D. Blackman, Lucy A. Arkinstall, and Rachel K. O'Reilly*

Abstract: Water-soluble and amphiphilic polymers are of great interest to industry and academia, as they can be used in applications such as biomaterials and drug delivery. Whilst ring-opening metathesis polymerization (ROMP) is a fast and functional group tolerant methodology for the synthesis of a wide range of polymers, its full potential for the synthesis of water-soluble polymers has yet to be realized. To address this we report a general strategy for the synthesis of block copolymers in aqueous milieu using a commercially available ROMP catalyst and a macroinitiator approach. This allows for excellent control in the preparation of block copolymers in water. If the second monomer is chosen such that it forms a water-insoluble polymer, polymerization-induced self-assembly (PISA) occurs and a variety of self-assembled nano-object morphologies can be accessed.

Ring-opening metathesis polymerization (ROMP) has emerged as a versatile technology, providing easy access to polymers with a variety of topologies (i.e., statistical copolymers and block or graft copolymers) and functionalities under a wide range of reaction conditions.^[1] The broad application of this technique stems from the high tolerance of Ru-based metathesis catalysts toward a range of functional groups, air, and moisture.^[2] Because of this tolerance, interest has grown in the use of these Ru-based metathesis catalysts in aqueous media as an environmentally friendly solvent alternative for the preparation of polymers,^[3] as well as for applications in biological media^[4] or in aqueous dispersion polymerization.

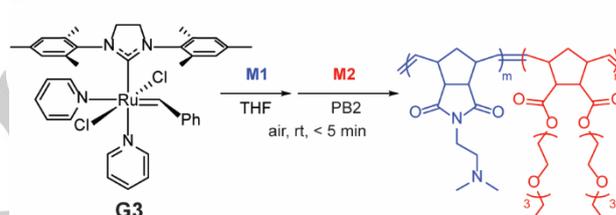
To the best of our knowledge, all existing reports on homogenous ROMP in H₂O are mediated by a catalyst that has been made water-soluble through the incorporation of hydrophilic ligands (i.e., though PEGylation or the addition of charged groups).^[4-5] In addition to their often difficult preparation and low yields, these catalysts are typically poor at controlling the molecular weight (MW) and dispersity of the resulting polymers. This is most often attributed to the low initiation rate and efficiency of these catalysts in H₂O, leading to a loss of living character.^[6d] To improve MW control, we sought a new method for carrying out aqueous ROMP. We hypothesized that a commercially available catalyst, (H₂IMes)(py)₂(Cl)₂Ru=CHPh (**G3**), could be initiated in a water-miscible organic solvent *via* ring-opening of a few hydrophilic monomers. This macroinitiator, rendered water-soluble through the covalent attachment of a hydrophilic polymer chain, could then be transferred to H₂O, whereupon chain extension would proceed in the presence of additional water-soluble monomer. The

A. Previous work - Route 1



Modified catalyst, aqueous milieu

B. This work - Route 2



Traditional catalyst, aqueous milieu, excellent MW control

Figure 1. Strategies to conduct aqueous ROMP. A) Polymerization initiated by a water-soluble catalyst. B) Preparation of a water-soluble macroinitiator in organic solvent which mediates living ROMP in aqueous milieu.

proposed strategy differs from other approaches in the fact that the water-solubilizing moiety is fitted through the propagating alkylidene as opposed to a pre-installed ligand.

An improved capability to conduct ROMP in H₂O would facilitate applications in polymerization in biological media (i.e., for conjugation of polymers to proteins or DNA) and in the preparation of nano-objects *via* aqueous dispersion polymerization. Recent developments in polymerization-induced self-assembly (PISA) have enabled facile preparation of self-assembled nanoparticles of diverse morphologies in aqueous media.^[6] PISA has been most often conducted using reversible addition-fragmentation chain transfer (RAFT) polymerization, with self-assembly induced upon crossing a solubility transition in the growing polymer chain.^[7] To the best of our knowledge, the first report of PISA using non-radical methods was reported by Gianneschi in 2017.^[8] In this seminal work, ring-opening metathesis polymerization induced self-assembly (ROMPISA) was conducted in organic solvent mixtures with excellent polymerization and morphology control. However, due to limitations in catalyst activity in an aqueous environment, ROMPISA in H₂O remains a challenge.^[9] We aim to broaden the scope of aqueous PISA, which to date has been primarily limited to radical polymerization mechanisms,^[10] through the development of a generalized strategy for successful ROMP in aqueous media using a commercially available catalyst.

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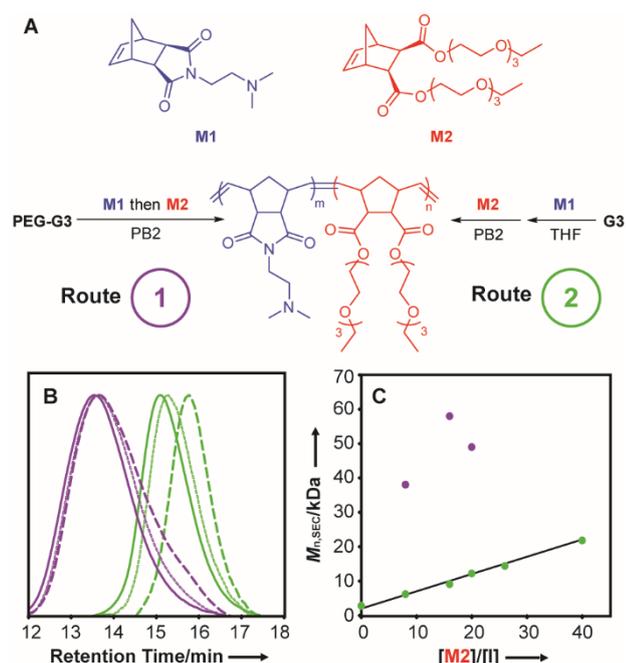


Figure 2. Preparation of block copolymers *via* ROMP in aqueous milieu. A) Schematic representation of two different strategies to conduct aqueous ROMP. B) Normalized SEC RI traces in THF of polymerizations targeting $DP_{M2} = 8$ (purple dashed trace), 16 (purple dotted trace), and 20 (purple trace) using route 1 compared against those targeting $DP_{M2} = 8$ (green dashed trace), 16 (green dotted trace), and 20 (green trace) using route 2. C) M_n as a function of targeted DP using route 1 (purple circles) and route 2 (green circles). The black line represents expected MW values for both routes. All polymerizations were conducted at 1 wt% solids under air at rt for 5 min.

In contrast to previous reports on aqueous ROMP in which a water-soluble catalyst was developed and utilized (Fig. 1A),^[4-5] we describe a generalized synthetic strategy for conducting ROMP in H_2O using a traditional Grubbs' catalyst which facilitates excellent MW control over the resulting polymers (Fig. 1B). With this strategy, we prepare diblock copolymers using ROMP through chain extension of a hydrophilic polymer with various water miscible monomers. In addition, we also report PISA using ROMP in aqueous milieu to allow for ready access to well-defined polymers which can form higher-order nanostructures in aqueous media at high solids content. By varying the degree of polymerization of the core-forming block during ROMPISA, we access common self-assembled morphologies expected in a PISA process.

To carry out ROMP in aqueous media, monomers **M1-M3** were selected based on previous reports.^[5b, 5e, 11] Polymerization of **M1** yields water-soluble polymers stabilized *via* ionization of the pendant tertiary amines. **M2** was first reported by Slugovc and coworkers, who studied the lower critical solution temperature (LCST) behavior of polymers prepared from a series of PEGylated norbornene monomers.^[11] We opted to utilize **M2** (Fig. 2A) due to its good water solubility and the interesting LCST behavior of the resulting polymer. We also chose to evaluate the polymerization of *exo*-5-norbornenecarboxylic acid (**M3**), which is soluble in acidic media at elevated temperatures, but produces polymers that are insoluble in H_2O .

Our initial attempts at block copolymer synthesis in H_2O were conducted using the water-soluble catalyst **PEG-G3** (see Fig. 1A).

Similar to a previous report,^[4] polymerizations were first attempted in PBS buffer (pH = 7); however, under these conditions, very low conversions were obtained. It is hypothesized that the rate of ligand dissociation, which has been recently demonstrated to influence catalyst turn-over rate,^[12] occurs slowly in H_2O .^[5a] As such, acid (i.e., HCl or TFA) is often utilized as an additive during aqueous ROMP to protonate phosphine or pyridyl ligands, facilitating ligand dissociation.^[5c] To evaluate the effect of an acid additive in our system, polymerization of **M1** followed by chain extensions with **M2**, initiated by **PEG-G3**, were repeated in acidic phosphate buffer (pH = 2) (PB2), (Fig. 2 - Route 1, Table 1). A series of polymerizations were conducted using this procedure and varying the $[M2]/[PEG-G3]$ ratio to target different MWs for the core forming block. Full conversion of norbornene olefins was confirmed by 1H NMR spectroscopy for all polymerizations. However, the SEC traces of the resulting polymers were broad (Fig. 2B) and the corresponding MW values were significantly higher than expected (based on the $[M2]/[PEG-G3]$ feed ratio, Fig. 2C). We attributed this discrepancy to slow initiation of the catalyst in aqueous milieu, as has been previously reported.^[5d]

Table 1. Comparison of block copolymer synthesis (**M1-M2**) by aqueous ROMP using Routes 1 and 2.

$[M2]/[G3]$	$M_{n,exp.}$ (kDa) ^[a]	Route 1		Route 2	
		$M_{n,SEC}$ (kDa) ^[b]	D_M ^[b]	$M_{n,SEC}$ (kDa) ^[b]	D_M ^[b]
8	6.8	38.1	2.35	6.2	1.31
16	10.8	58.0	2.03	9.1	1.34
20	12.9	49.0	2.05	12.2	1.33
26	15.9	--- ^c	--- ^c	14.4	1.33
40	22.9	--- ^c	--- ^c	21.8	1.35

[a]Expected M_n values for both routes calculated from conversion. [b]Calculated by SEC in THF against PMMA standards. [c]Polymers insoluble in SEC mobile phase.

To circumvent the issue of slow initiation in H_2O , we opted to initiate the catalyst in organic solvent by polymerizing a few units of hydrophilic monomer. We then transferred the resulting macroinitiator to acidic media, where chain extension could occur in the presence of additional monomer. We evaluated our proposed two-step strategy by conducting a series of polymerizations using monomers **M1-M3** and catalyst **G3** according to Fig. 2A, Route 2. First, a solution of **G3** in THF was added to **M1**, then polymerization was allowed to proceed for 2 min, yielding a water-soluble macroinitiator ($M_n = 2.8$ kDa, $D_M = 1.21$, Fig. S1). A series of chain extensions were then carried out using either **M1**, **M2**, or **M3** by adding an aliquot of the macroinitiator solution in THF directly to a solution of the second monomer in PB2. When chain-extending with **M1**, water-soluble polymers were obtained with narrow molecular weight distributions and MWs that were in excellent agreement with expected values (Fig. 3A-B and Table S1). To expand the scope of this method, five chain extensions were conducted with both **M2** and **M3** targeting increasing DPs.

As shown in Fig. 3, chain extensions using **M2** (Fig. 3C-D, Table 1, and Fig. S2-S3) or **M3** (Fig. 3E-F and Tables S2 and S3) were also successful. It is important to note that chain extensions using **M2**

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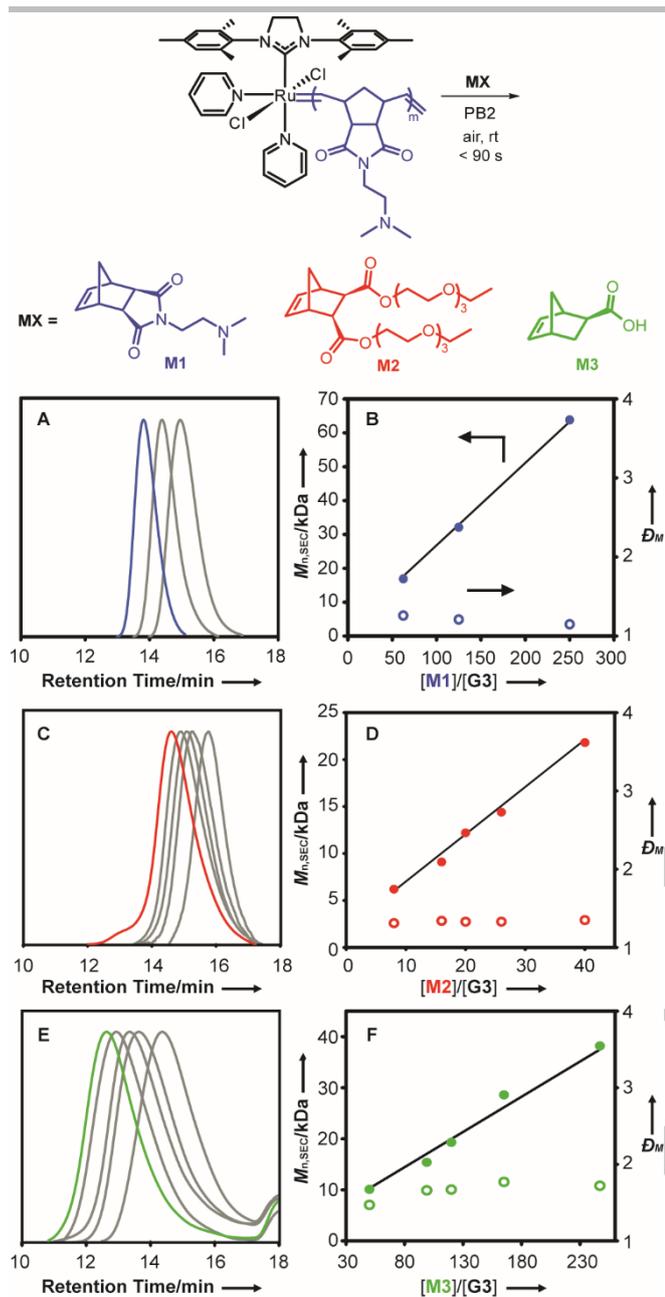


Figure 3. Chain extension of ROMP macroinitiator using 3 different monomers. A) Normalized SEC RI traces in THF for chain extensions with **M1**. B) M_n and \bar{D}_M as a function of targeted DP using **M1**. C) Normalized SEC RI traces in THF for chain extensions with **M2**. D) M_n and \bar{D}_M as a function of targeted DP using **M2**. E) Normalized SEC RI traces in DMF for chain extensions with **M3**. F) M_n and \bar{D}_M as a function of targeted DP using **M3**. Polymerizations conducted using Route 2. The solid lines represent expected M_n values calculated using the monomer feed ratio. All polymerizations were conducted at 1 wt% solids under air at rt for 5 min.

or **M3** operate under a dispersion mechanism at 1 wt% since the macroinitiator and monomer(s) are completely soluble under the polymerization conditions. If the results of this approach (Route 2) are compared to our previous attempts which used conventional approaches using catalyst **PEG-G3** in H_2O (Route 1), two observations are of particular significance: (1) the molecular weight distributions of the SEC traces obtained using Route 2 were significantly narrower compared to Route 1; (2) M_n s

determined by SEC were in far better agreement with expected values when using Route 2. These linear relationships between observed and expected M_n values confirmed the living nature of the polymerizations, in accordance with previous reports.^[13] We also attempted chain extensions using **M2** at higher solids concentrations (5, 10, and 20 wt%). These polymerizations operated according to an emulsion mechanism due to the immiscibility of **M2** at these concentrations. As shown in Fig. S7 and Table S4, ROMPISA using Route 2 was successful at concentrations up to 20 wt%, achieving full conversions and producing block copolymers with narrow molecular weight distributions. Importantly, the M_n values obtained from these polymerizations at higher concentrations agreed well with the M_n from the 1 wt% sample. From these data, it is clear that better control is achieved using a two solvent approach. By initiating the polymerizations in THF and then transferring to H_2O , block copolymers could be prepared using a commercially available catalyst under air in < 90 s. Based on the excellent control achieved *via* Route 2 using 3 different monomers, we envisioned that this method could be broadly applied to the synthesis of a variety of multi-block copolymers.

During polymerization of **M3** using Route 2, the polymerization solutions became turbid rapidly, especially as the targeted degree of polymerization increased, indicating an onset of aggregation and a PISA process. To gain insight into the morphology of the self-assembled structures that arose during ROMPISA, transmission electron microscopy (TEM) was conducted on samples produced using Route 2. As shown in Fig. 4, TEM indicated that the predominate morphology evolved from spheres to worms to vesicles as the DP of the hydrophobic **M3** block increased from 14 to 97 as confirmed by dry-state and cryo-TEM. Chain-extensions using **M2** also led to turbid solutions. Polymers of **M2** possess an LCST transition below rt (Fig. S4, ca. 22 °C), thus, as polymerizations of **M2** in H_2O progressed, the core block became increasingly insoluble in H_2O due to this LCST transition. Under PISA conditions, sphere, worm, and vesicle morphologies were also obtained for polymerizations using **M2** as the core-forming monomer (Fig. S5). We refer to this phenomenon as ring-opening metathesis polymerization-induced thermal self-assembly (ROMPITSA), analogous to RAFT PITSA which was recently reported by the Sumerlin group.^[7a] TEM also confirmed that chain extension using **M2** at higher solids contents (5-20 wt%) produced nano-objects, as shown in Fig. S8.

In addition to mediating the facile preparation of higher-order morphologies during polymerization, PISA should also exhibit faster polymerization kinetics relative to chain extension in organic solvent.^[14] Typically, the kinetic plot for a PISA shows a sharp transition, with the critical point assigned to the onset of aggregation. To confirm that the morphologies observed in Fig. 4 originated from a PISA process, a kinetic experiment was carried out using the general procedure described above. Aliquots of the polymerization solution were removed at various time points and quenched *via* addition of diethylene glycol vinyl ether. 1H NMR spectroscopy was then utilized to determine conversion and kinetic plots were then constructed using these data (Fig. S6). The polymerization occurred rapidly, reaching full conversion in < 90 s, however no critical point in the kinetic plot was observed. It is likely the case that, due to the rapid polymerization rate, the critical point originating from the onset of self-assembly was encountered very early in the polymerization and could not be detected. Instead, we compared the rate of polymerization

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obtained using Route 2 to a similar polymerization conducted entirely in THF. Indeed, polymerization conducted using Route 2 occurred more rapidly than in THF, with a >4 fold increase in k_p (Fig. S6). Given that recent ROMP work of macromonomers suggests that polymerization rate does not vary dramatically as a function of solvent,^[15] it is likely the case that the observed increase in k_p is due to the high local concentration of monomer within the self-assembled structures as a result of a PISA process. In summary, we report a general strategy for the synthesis of block copolymers prepared by ROMP, using a commercially available catalyst in aqueous milieu. By initiating polymerization in organic solvent, a water-soluble macroinitiator was readily obtained that was capable of mediating living ROMP in H₂O. The

resulting polymers were well-defined and possessed narrow molecular weight distributions. As the monomers chosen for the second block produced polymers that were insoluble in H₂O, PISA was observed, allowing access to common self-assembled morphologies (i.e., spheres, worms, and vesicles). The novel approach described herein circumvents the issue of slow initiation that is typically observed in reports on, aqueous ROMP and we anticipate that this strategy can be broadly applied in PISA/PITSA using ROMP and also in the synthesis of fully soluble polymers in aqueous milieu. Overall, given the speed and functional group tolerance of ROMP and the versatility and scalable nature of PISA, this approach offers exciting new opportunities in functional nanostructure synthesis.

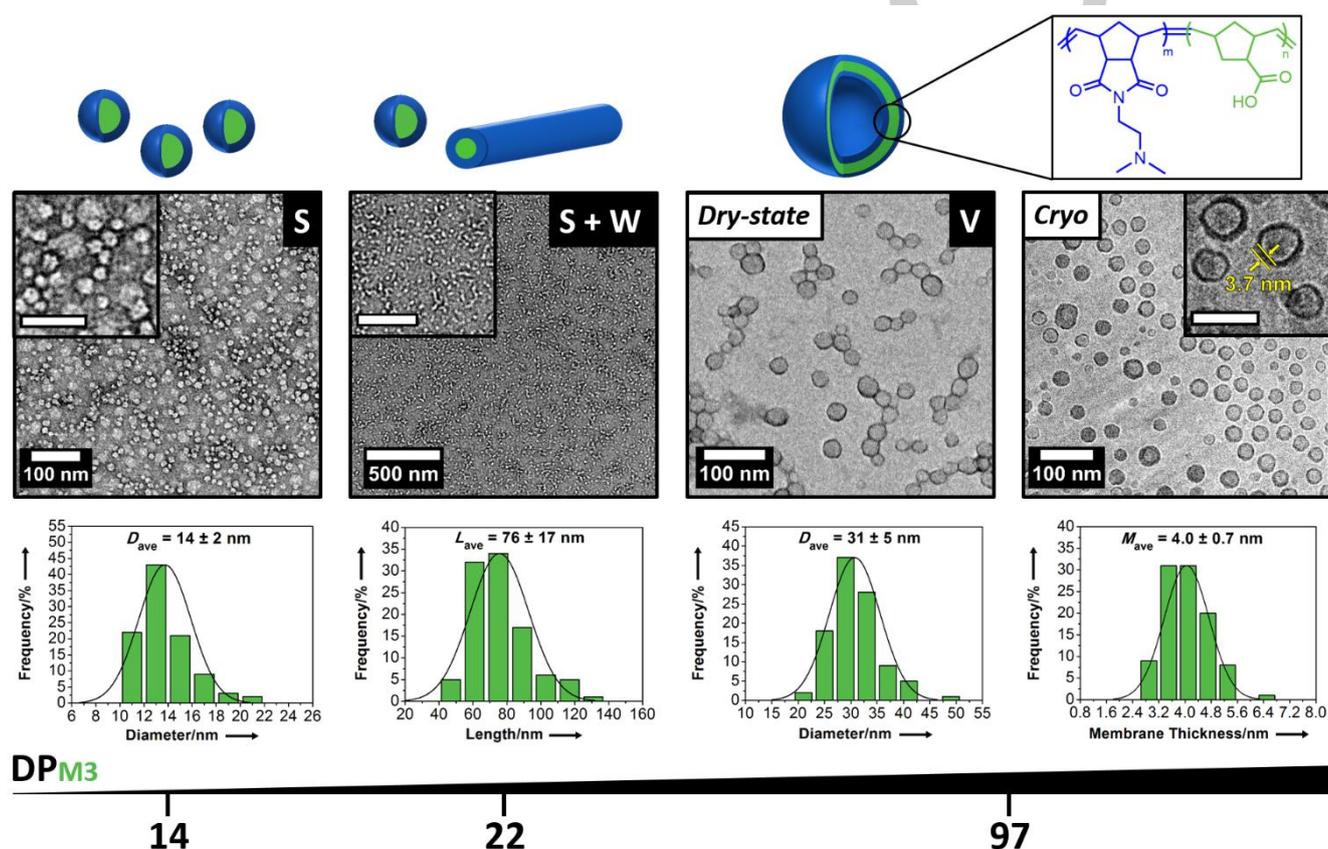


Figure 4. Representative TEM images of various morphologies obtained from ROMPISA upon increasing DP_{M3} , along with corresponding histograms for average size or membrane thickness (in case of vesicles) determination. For TEM insets of spheres and vesicles the scale bar represents 50 nm, while for worms' inset the scale bar represents 250 nm. Dry-state samples were stained using 1 w/v% uranyl acetate solution.

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Conflict of interest

The authors declare no conflict of interest.

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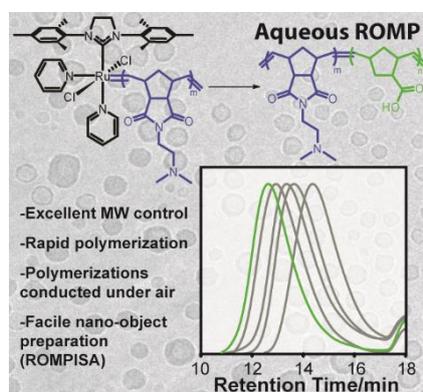
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We report a general strategy for the synthesis of block copolymers in aqueous milieu *via* ROMP involving synthesis of a water-soluble macroinitiator in organic solvent. Using this strategy, we readily access common self-assembled nano-object morphologies (spheres, worms, and vesicles) *via* polymerization-induced self-assembly (PISA).



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Keywords – ROMP, PISA, aqueous polymerization, block copolymers, Grubbs catalyst