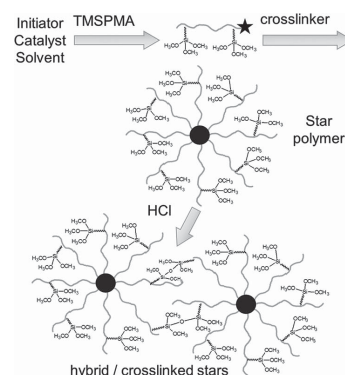


Toward Hybrid Materials: Group Transfer Polymerization of 3-(Trimethoxysilyl)propyl Methacrylate

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In this study, the group transfer polymerization (GTP) of the functional monomer 3-(trimethoxysilyl)propyl methacrylate (TMSPMA) is reported to produce polymers of different architectures and topologies. TMSPMA is successfully polymerized and copolymerized with GTP to produce well-defined (co)polymers that can be used to fabricate functional hybrid materials like hydrogels and films.



1. Introduction

The polymerization of alkoxy silane-based monomers leads to the production of functional polymers that can later be used to produce advanced materials such as hybrid hydrogels, films, and particles.^[1–4] Thus, it is not surprising that, in the last two decades with the development of controlled free-radical polymerization methods several studies report the polymerization of alkoxy silane-based monomers like 3-(trimethoxysilyl)propyl methacrylate (TMSPMA). However, the first report on TMSPMA polymerization was with living anionic polymerization where a polymer of 8.2 kg mol^{-1} and a molecular weight dispersity (D), $M_w/M_n = 1.05$ was reported.^[5] Since then no other study has been able to produce a TMSPMA-based homo- or copolymer of such narrow polydispersity.

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Particularly in 2004, a systematic study of TMSPMA polymerization with atom transfer radical polymerization (ATRP) was reported. Interestingly, it was observed that when a poly(ethylene oxide) macroinitiator was used, instead of the ethyl 2-bromoisobutyrate initiator, polymers with narrower D s ranging from 1.10 to 1.39 were produced.^[6] Consequently, several PEO-*b*-TMSPMA diblocks were reported with ATRP with similar D s^[7–10] as well as a stearyl methacrylate TMSPMA diblock copolymer with a $M_w/M_n = 1.14$.^[11] In 2008, TMSPMA was polymerized using 1,2-bis(bromoisobutyryloxy)ethane as an initiator and a homopolymer with a $M_w/M_n = 1.13$ was produced, which was then used as a precursor for the formation of an ABA triblock with a $M_w/M_n = 1.34$.^[12] Later on, more triblock^[13,14] as well as pentablock^[15,16] copolymers containing TMSPMA were synthesized by ATRP with D s ranging from 1.16 to 1.46.

Reversible Addition-Fragmentation chain-Transfer (RAFT) polymerization has also been used to produce TMSPMA-based polymers with relatively broad D s ranging from 1.22 to 1.49.^[17–19] Only one study reported such polymers with narrow D s (1.06 and 1.15) but the blocks consisted of no more than seven repeating units of TMSPMA.^[20]

It should be noted that all the studies, where block copolymers were fabricated, used multipot and time-consuming procedures. In this study we report the

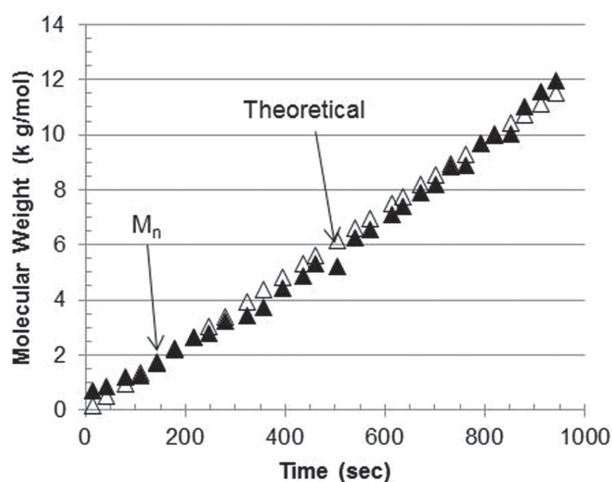


Figure 1. GTP kinetics of TMSPMA. The theoretically calculated molecular weight and the M_n are shown as white and black triangles, respectively.

one-pot synthesis of diblock copolymers. Specifically TMSPMA was homo- and copolymerized by group transfer polymerization (GTP),^[21–24] a living polymerization method to produce linear and star (co)polymers. GTP is performed at room temperature which is a major, cost-effective, advantage compared to conventional living anionic polymerization where methacrylate monomers have to be polymerized at -78 °C.^[5,22,25] In addition, compared to RAFT and ATRP, GTP produces polymers with narrower D_s ^[24] and is a much faster polymerization method. The possibility of TMSPMA being polymerized with GTP was first demonstrated in 2005,^[26] however the copolymers had broad D_s (1.15 to 1.5) from the TMSPMA crosslinking with the amino containing groups during the polymerization. Here, we report the first systematic study of

polymerizing TMSPMA by GTP to demonstrate that well-defined copolymers with narrow D_s of different architectures and topologies can be produced. A monofunctional 1-methoxy-1(trimethylsiloxy)-2-methyl propene initiator was used for all the polymerizations.

2. Results and Discussion

A TMSPMA homopolymer was first produced to confirm that it can be successfully polymerized with GTP to produce well-defined polymers. As can be observed in Figure 1, unlike any controlled free-radical polymerization techniques, TMSPMA homopolymerization of 10 kg mol^{-1} with a $D = 1.06$ took less than 15 min using GTP. In addition, the TMSPMA GTP kinetics was similar to that of the most commonly used methacrylate monomer, methyl methacrylate (MMA).^[27]

In order to prove that TMSPMA can easily be homo- and copolymerized with GTP, several polymers were synthesized. The polymers were synthesized similarly to previous GTP studies on linear block copolymers^[28–33] and star polymers.^[34–36] The polymerization catalyst, solvent, and initiator were added in a round-bottom flask and then the monomer(s) were syringed sequentially. No polymerization took longer than 30 min. More details are provided in the Supporting Information while all the synthesized polymers are listed in Table 1. In the same table the gel permeation chromatography (GPC) and proton nuclear magnetic resonance ($^1\text{H NMR}$) spectroscopy data of all the polymers as well as their precursors are given.

The first polymer was a TMSPMA chain growth polymer (GPC traces shown in Figure 2a) that had a number average molecular weight (M_n) close to the

Table 1. Molecular weights and compositions of the TMSPMA-based (co)polymers and their precursors.

No.	Polymer structure	Theor. MW ^{a)} [g mol ⁻¹]	M_n ^{b)} [g mol ⁻¹]	M_w/M_n ^{b)}	% mol TMSPMA	
					Theor.	By NMR
1	TMSPMA ₁₅	3825	4380	1.08	100	100
	TMSPMA ₁₅ - <i>b</i> -TMSPMA ₁₅	7550	7640	1.07	100	100
2	MMA ₂₀	2102	3140	1.09	0	0
	MMA ₂₀ - <i>b</i> -TMSPMA ₂₀	7069	9030	1.05	50	45
3	TMSPMA ₂₀	5067	5600	1.06	100	100
	TMSPMA ₂₀ - <i>b</i> -MMA ₂₀	7069	8400	1.05	50	51
4	TMSPMA ₂₀	5067	5870	1.06	100	100
	TMSPMA ₂₀ - <i>star</i>	^{c)}	54100	1.19	N/A	N/A

^{a)}Calculated as $MW_{\text{polymer}} = MW_{\text{monomer}} \times DP_{\text{monomer}} + 100 \text{ g mol}^{-1}$ (for the initiator fragment, an MMA group, that is attached at the end of the chain); ^{b)}Determined using gel permeation chromatography with an RI detector which was calibrated using poly(methyl methacrylate) (PMMA) standards; ^{c)}Cannot be theoretically calculated because the number of arms is not known and cannot be predicted.

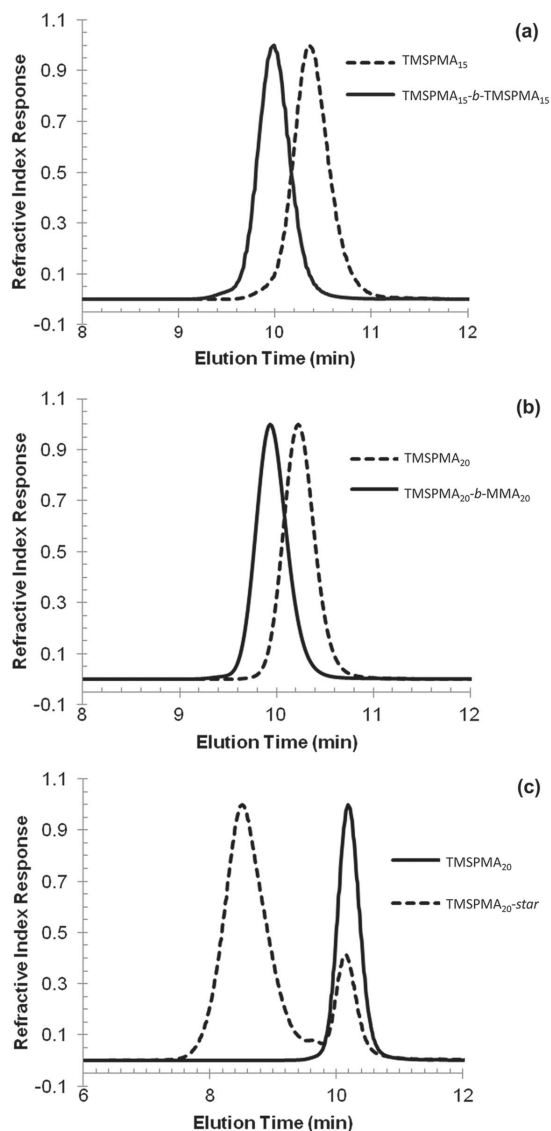


Figure 2. GPC traces a) of the TMSPPMA₁₅-*b*-TMSPPMA₁₅ chain growth polymer, b) of the TMSPPMA₂₀-*b*-MMA₂₀ diblock copolymer, c) of the TMSPPMA₂₀-*star* homopolymer, and their corresponding precursors.

theoretically expected molecular weight (MW) and a narrow $M_w/M_n = 1.07$. The second and third polymers, diblock copolymers of TMSPPMA and MMA, were synthesized successfully, again proving that TMSPPMA can easily be polymerized with GTP as the first or the second block. From the GPC traces (Figure 2b), it can be confirmed that there is no termination after the formation of the first block and the block polymers can be synthesized without any difficulties. Also the D s of the polymers decreased as the MW increased, as expected for a living polymerization method. This is shown in Table 1, where the D s of the second blocks were always lower than that of the first blocks, the precursors to the copolymers. To

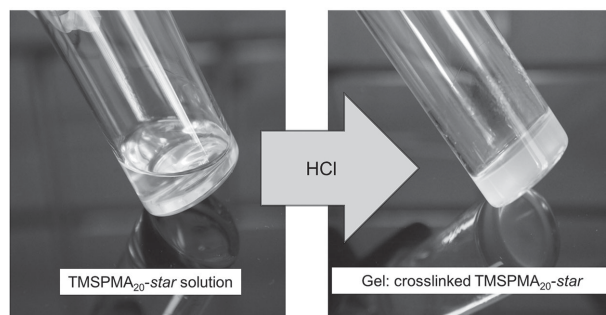


Figure 3. Gel formation in seconds after the addition of HCl in a TMSPPMA₂₀-*star* solution.

this end, it should be pointed out that the D s of the two diblock copolymers were very narrow ($M_w/M_n = 1.05$) and matched the first study^[5] on TMSPPMA polymer synthesis with living anionic polymerization.

The NMR results confirmed that the % mol composition of the MMA-*b*-TMSPPMA and the TMSPPMA-*b*-MMA diblock copolymers were close to the targeted compositions (an NMR spectrum is given in the Supporting Information).

In addition to the linear TMSPPMA-based homo- and copolymers, a star polymer was also synthesized using the “arm-first” approach. In particular, a linear TMSPPMA homopolymer was synthesized first and then a bifunctional monomer (a crosslinker), ethylene glycol dimethacrylate, was added last to interconnect the linear homopolymer to form a star polymer. The M_n of the synthesized star homopolymer was about ten times higher than that of the corresponding linear precursor and the D was equal to 1.19, which was acceptably narrow for a star polymer. The GPC traces of the star polymer and its precursor are shown in Figure 2c. The peak on the left (of higher MWs) corresponds to the star polymer while the peak on the right represents the linear precursor that was not interconnected to the star polymer. This was expected for an “arm-first” star polymer synthesis and it has been observed before.^[34–43] At this point we would like to point out that, to the best of our knowledge, this is the first time that a TMSPPMA containing star polymer has been synthesized with the TMSPPMA units being intact.

Finally, in order to confirm that the trimethoxysilyl-functional group was unaffected by the polymerization, the star polymer was crosslinked to produce a gel with the addition of hydrochloric acid. The gel was formed instantly as can be seen in Figure 3. This demonstrated the possibility of producing hybrids by GTP in a one-pot synthesis.

3. Conclusions

TMSPPMA (co)polymers were successfully synthesized using GTP method to produce well-defined (co)polymers. Both

linear and star polymers were synthesized with D_s lower than 1.09 and 1.20, respectively. This opens up possibilities to produce more well-defined organic/inorganic hybrids.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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