Photoinduced Sequence-Controlled Copper-Mediated Polymerization: Synthesis of Decablock Copolymers

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S *Supporting Information*

ABSTRACT: Photoinitiated copper-mediated radical polymerization offers an one-pot and time efficient method of preparing a decablock copolymer PMA-PtBA-PMA-PDEGA-PMA-PtBA-PMA-PDEGA-PnBA-PDEGA with an overall molecular weight of 8500 g·mol^{-1}. The molecular weight is in close agreement with theoretical expectations and significantly narrow dispersities ($Đ$ = 1.1−1.17) are achieved for the various block extensions. The *tert*-butyl group of the decadeblock was deprotected to form PMA-PAA-PMA-PDEGA-PMA-PAA-PMA-PDEGA-PnBA-PDEGA. The deprotection is confirmed by the disappearance of *tert*-butyl signal and the loss of molecular weight investigated by ^{1}H NMR and SEC, respectively. The carboxylic group of PAA is protonated in acidic solution (water insoluble) and deprotonated in basic solution (water-soluble). This enables a conformational change of PMA-PAA-PMA-PDEGA-PMA-PAA-PMA-PDEGA-PnBA-PDEGA in water/ethanol mixture (80/20%v/v), as is demonstrated by a turbid solution at pH 2 and transparent solutions at pH 10.
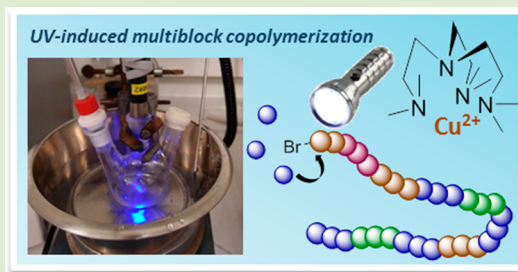
Reversible deactivation radical polymerization (RDRP), often referred to as controlled living radical polymerization (CRP), provides a versatile synthetic pathway toward an almost endless variety of polymers with defined average molecular weight, narrow molecular weight distribution, and precisely engineered functionality. In this sense, CRP opens unprecedented opportunities for molecular structure design and this enhances the potential of polymers to be applied in biological and biomedical fields, such as medical imaging,[1] drug delivery,[2] and adhesives for tissue engineering,[3] to name just a few examples.

Generally, CRP operates via establishment of an equilibrium between a actively propagating and a dormant, deactivated polymeric species.[4] Next to reversible addition−fragmentation radical transfer (RAFT) polymerization[5−7] and nitroxide-mediated polymerization (NMP),[8] atom-transfer radical polymerization (ATRP)[4,9,10] is one of the most applied control methodologies. In ATRP, interchange between active and dormant macrospecies is achieved via exchange of a halide using a transition metal complex (e.g., copper). Traditional ATRP requires a rather high concentration of copper to maintain a reasonable reaction rate and to achieve good results for the polymerization. High copper content, however, is uneconomical from an industrial prospective[11] and raises concerns of copper toxicity to environments.[11,12] Significant efforts have been made to produce greener and less toxic versions of ATRP. For example, ARGET-ATRP or ICAR have been developed in order to reduce the required amount of catalyst.[13,14] SET-LRP utilizes elemental copper as an activating

species in place of copper salts as in ATRP.[15,16] SET-LRP (or SARA-ATRP for that instance)[17,18] provides high polymerization rates when carried out at room temperature, with the interesting feature that bimolecular termination appears to not affect the structural fidelity of the resulting polymers even at very high monomer conversions. This feature is particularly interesting, since it allows to synthesize (multi)block copolymers with high efficiency and without the need to remove residual monomer between polymerization steps.[19] Multiblock copolymers, and hereby particularly sequence controlled multiblocks, have recently attracted significant interest. Via various techniques, copolymers, often based on polyacrylates or polyacrylamides, carrying a significant number of individual blocks have been obtained using refined synthesis conditions to allow for such precise control over molecular weight and functionality.[20−22] Such materials hold great promise for future endeavors since they allow for encoding of information by the choice of the followed sequence, as well as having potentially very complex behavior. This may in the future be used to create synthetic polymer materials that are able to form tertiary structures, hence, mimicking the structure and function of proteins. Nevertheless, the field of sequence control multiblock copolymerization is still in an early stage, and while synthesis protocols based on CRP are thoroughly

explored, not many examples have yet been demonstrated in which the properties of such multiblocks had been investigated.

To reach a high level of control in polymerization, mild reaction conditions are generally advantageous. When polymerizations are carried out at low temperatures, potential interference of side reactions, for example, backbiting in acrylate polymerization,[23] can be diminished, thus, increasing the structural control of the respective method. While SET-LRP generally allows to work at room temperature, also photoinduced reactions are interesting. Compared to SET-LRP, photoreactions have the additional advantage that they allow for a temporal control, thus, a switch-on/switch-off of the reaction simply by turning on or off the light source. Recently, photoinduced ATRP has in fact been demonstrated by a couple of different research groups. Yagci reported on the UV-activated ATRP in the presence and absence of conventional photoinitiators.[24−26] Hawker and co-workers showed that an ATRP process can be induced by visible light with a photoactive iridium complex.[27] Mosnáček et al. reported on direct activation of a copper/PMDETA complex by UV light, which lead to well-controlled ATRP.[28] At the same time, also Matyjaszewski demonstrated a photoATRP process.[29] While the direct activation of copper-ligand species processes were found to be relatively slow, faster polymerization was observed by Haddleton, who used $CuBr_2$ in the presence of an excess of the ligand Me_6Tren successfully.[19] When carried out in a flow process, almost complete conversion can be achieved for an acrylate polymerization at room temperature within 20 min under retention of pristine end group fidelity.[30]

Here, we combine the $CuBr_2$/Me_6Tren photoactivation methodology with the concept of sequence controlled polymerization. Photo-copper-mediated polymerization (photoCMP) is ideal to target multiblock copolymer synthesis. Reaction rates are very high, while reaction conditions are comparatively mild, giving less rise to side reactions that can potentially disturb the structural integrity of materials. Also, polymerizations can be carried out essentially up to full monomer conversion without loss of the required bromine end group, thus, allowing to synthesize high-quality block copolymers in one-pot without the need to isolate materials in between chain extension steps. Using photoCMP, we thus prepared decablock copolymers in one-pot by simple sequential addition of monomers. To avoid overreaction (that is, radical coupling after all monomer was consumed), reactions were monitored by online FT-IR measurements. In this way, PMA-PtBA-PMA-PDEGA-PMA-PtBA-PMA-PDEGA-PnBA-PDEGA (where PMA is poly(methyl acrylate), PtBA is poly(*tert*-butyl acrylate), PDEGA is poly(di(ethylene glycol) ethyl ether acrylate), and PnBA is poly(*n*-butyl acrylate)) has been synthesized. Based on this example, the efficiency of the polymerization methodology is described. To study the properties of the decablock material, the pendant *tert*-butyl groups in the structure were deprotected. Due to the anionic property of residual poly(acrylic acid) in water, the multiblock copolymer exhibits pH responsive character in a THF/water mixture, leading to formation of self-assembled nanoaggregates at low pH. The self-assembly structure is further characterized by dynamic light scattering (DLS). The highlights of the work presented in this paper are the simplicity of multiblock synthesis, relatively short time of synthesis (2−7 h per block with increasing reaction times with increasing number of blocks), and the potential of producing complex self-assembling nanostructures via sequence-controlled polymer materials.

Block-copolymer synthesis via photoCMP had been demonstrated before.[30] From these previous experiments, it is evident that photoCMP proceeds not only very efficiently, but also allows synthesizing materials to almost full conversion without significant loss of end group functionality. This feature, in combination with the ability to perform reactions at low temperatures to avoid side reactions, makes the process ideal to target higher multiblock copolymer structures. In order to achieve such a synthesis, several considerations have to be taken into account. The $CuBr_2$/Me_6TREN combination only allows polymerizing acrylates and acrylamides efficiently. Methacrylate or styrene polymerizations are comparatively very slow and necessitate other ligand combinations.[28,31] Thus, to obtain multiblock copolymers by sequential addition of monomers without purification of intermediate reaction steps is only possible if all monomers belong to the same family. While this does limit the choice, it is, however, not a fundamental problem. A broad variety of hydrophilic, hydrophilic of ionic acrylate monomers (or precursors thereof) exist, hence, giving rise to a similar choice of chemical functionalities as found in amino acids. Polyacrylate chains can thus be constructed that mimic this exact variety.

Another limitation with respect to photoCMP is that products are prone to side reactions when high conversions are reached. If no monomer is available for consumption, radical interchange between active and dormant radical states will inevitably lead at a certain point to radical coupling, both under ATRP as well as SET conditions.[32] Thus, if reactions are carried out for too long, loss of bromine functionality might occur, which needs to be prevented when targeting multiblock copolymers from sequential addition of monomers. For this reason, we employed online-FT-IR monitoring to determine when monomer batches are consumed in the reaction. To avoid unwanted coupling reactions, monomer conversions of typically close to 95% were targeted. Remaining traces of monomer thus lead in principle to small gradients in the polymer structure. This was deemed the "lesser evil" when compared to coupling reactions and, hence, loss of end group fidelity. Figure 1 depicts the characteristic IR profile for a sequential photoCMP. The double bond vibration of the acrylate monomers can be observed at around 1640 cm^{-1}, regardless of the ester side chain. With each addition of monomer a sudden rise in peak intensity is observed, which then depletes over the course of the reaction. In the depicted case, fast polymerization was achieved,
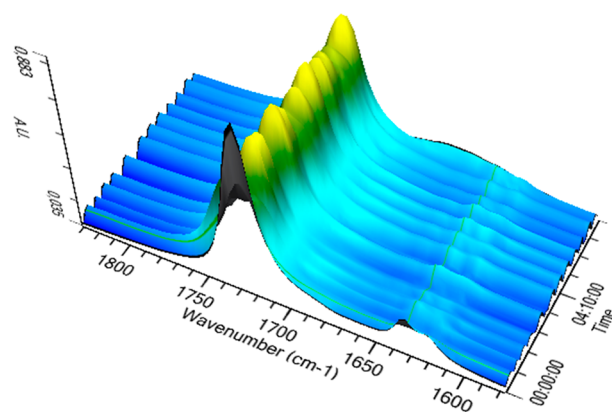

Figure 1. FT-IR profiles of the sequential copolymerization of quasi-block copolymers from consecutive addition of monomers in a UV-induced copper-mediated radical polymerization.

Scheme 1. Sequential Copolymerization of Decablock Copolymers via UV-Induced Copper-Mediated Radical Polymerization
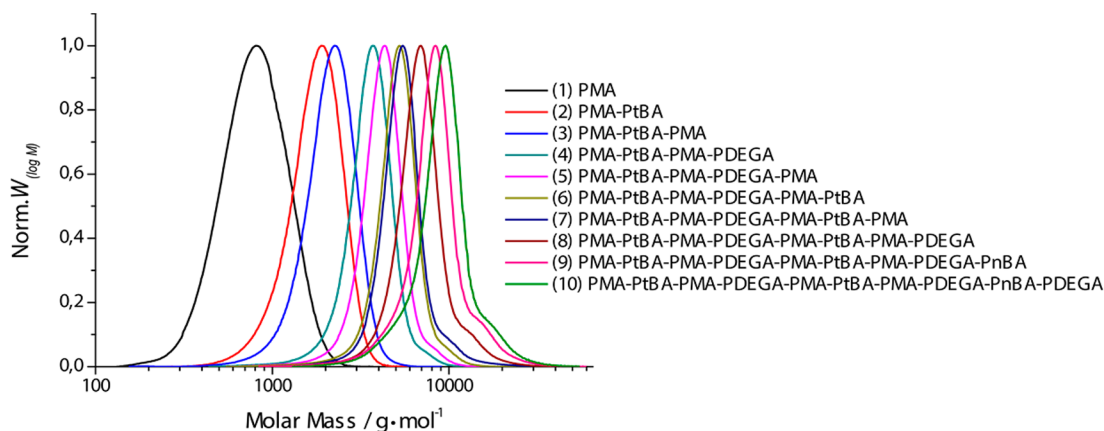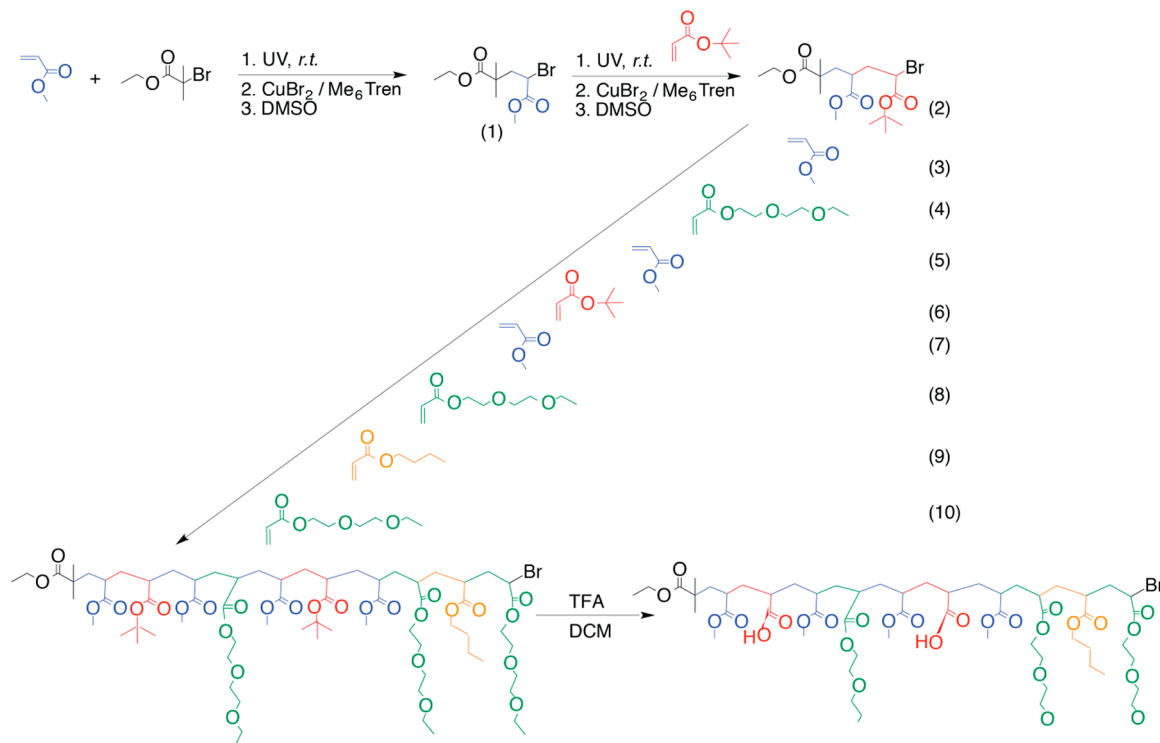

Figure 2. Molecular weight distributions of the intermediate block copolymer products in the synthesis of decablock copolymers from sequential monomer addition.

with typical reaction times being around 30 min per added monomer batch. In this way, a polymer with a sequence of 15 alternating blocks was obtained: [PMA-PtBA-PMA]₅. Yet, despite the seemingly large success of the reaction, closer analysis revealed that in place of multiblock copolymers gradient if not statistical copolymer were synthesized. Despite the depletion of IR signals, no high conversions could surprisingly be obtained as was indicated by NMR analysis. This can in all likelihood be attributed to the reaction setup that was used for these reactions. For the sake of simplicity, reactions were carried out in a flask with illumination by a 100 W UV lamp from the side. Thereby, the volume of the reaction solution was small, while the free volume above the solution was large. Due to the constant UV irradiation, and due to the exothermicity of the reaction, the solution heated up which probably caused a significant amount of monomer to evaporate, hence, giving a wrong picture when analyzing IR

intensities. This discrepancy demonstrated that the choice of reactor setup is crucial and that flask and lamp design need to be carefully considered in order to achieve good UV-initiated reaction conditions. To avoid overheating and evaporation, cooling of the reaction setup is required, which was for the following reactions consequently implemented by changing the reactions setup. Regardless, already these experiments demonstrate the potential of the technique. Despite the gradient nature of the materials (gradients often also display interesting self-assembly behavior),[33,34] 15 blocks were synthesized within 1 day reaction time, which gives access to production of such materials on significant scale in short time scales.

The setup that was employed in all following reactions is shown in Figure S1. Reactions were carried out in a water bath to provide cooling to room temperature. Via a three-neck flask, the IR probe was inserted as well as the UV source (transmitted via a light guide). The third neck could be used for degassing

Table 1. Results for the Sequential Block Copolymerization of the Obtained Decablock Copolymers

	sample	conversion (%)	time (hours)	M_n (theo; g/mol)	M_n (exp; g/mol)	Đ
1	PMA	94	2.3	1060	710	1.20
2[a]	PMA-PtBA	97	4.7	1660	1610	1.13
3	PMA-PtBA-PMA	92	4.0	2070	1960	1.13
4	PMA-PtBA-PMA-PDEGA	93	3.6	2890	3340	1.11
5[a]	PMA-PtBA-PMA-PDEGA-PMA	93	4.7	3280	3940	1.10
6	PMA-PtBA-PMA-PDEGA-PMA-PtBA	95	5.6	3980	4810	1.10
7[b]	PMA-PtBA-PMA-PDEGA-PMA-PtBA-PMA	87	3.5	4300	5160	1.11
8[a]	PMA-PtBA-PMA-PDEGA-PMA-PtBA-PMA-PDEGA	89	4.7	5320	6500	1.13
9[a]	PMA-PtBA-PMA-PDEGA-PMA-PtBA-PMA-PDEGA-PnBA	96	7.3	5900	7600	1.17
10[c]	PMA-PtBA-PMA-PDEGA-PMA-PtBA-PMA-PDEGA-PnBA-PDEGA	37	4	6370	8450	1.16

[a]The polymerization of the sample was completed on the day and was stored in the freezer for the subsequent monomer addition on the next day.
[b]The polymerization was not completed and was stored in the fridge overnight. The polymerization was continued the following day, and its final monomer conversion was recorded as shown in the table here. [c]The reaction was finished and no further monomer was added.

and addition of fresh monomer. With this setup, photoCMP could indeed be carried out to high conversion, whereby results from online FT-IR and NMR yielded conversions in good agreement with each other.

First, homopolymerizations of MA were performed for initial testing, which was followed by multiblock copolymerization. The target monomer sequence is given in Scheme 1. The molecular weight distributions (MWDs) after each reaction step are given in Figure 2. Reaction times, conversions, and SEC results are given in Table 1. The MWDs are monomodal and show a clear shift to higher molecular weights after each monomer addition. It is important to stress that the polymer was at no stage isolated from the solution or from the copper/ligand mixture. Reactions were carried out as a true one-pot, whereby only fresh monomer is added, always using the initial catalyst system. The experimental molecular weight was close to the theoretical value in the initial chain extension but was gradually exceeding the theoretical molecular weight as the number of blocks increases. Theoretical molecular weights were calculated taking the loss of active bromine end groups due to sample extraction after each reaction step into account. Calculations are based on the molar amounts employed in the first polymerization. The exact amount of bromine-terminated macroinitiator in the solution is then calculated based on the weight of sample extracted after the polymerization, assuming ideal mixing of all components. With the amount of monomer added, the theoretically reachable M_n is then derived from the ratio of macroinitiator to monomer. The small difference in molecular weight of theory and experiment could be due to (i) the extraction of sample for NMR and SEC study after each chain extension. As the viscosity of reaction mixture increases, the error in the estimation of the amount of macroinitiator left in the reaction vessel increases, hence, the theoretical M_n could be underestimated or (ii) due to the change of the Mark−Houwink relation. K and a of methyl acrylate was used for the determination of M_n, which is a good approximation but certainly is associated with a distinct systematic error. Nevertheless, agreement between theoretical end experimental molecular weight is satisfactory (see also Figure S2) and the measured dispersity Đ can be seen as accurate. It is also noteworthy that the extension of each block took only 2−7 h. The rate of polymerizations of the employed monomers decrease in the order of DEGA > MA > tBA > nBA, which is somewhat surprising since nBA is associated with faster propagation compared to the methyl ester.[35] On the other side, a general increase in reaction time is observed with

increasing number of blocks so that the effect of nBA may be distorted since it is only added as the ninth block. It may hence rather be concluded that the reactions slow down with the addition of monomers. It may be speculated that since after each block extension samples are taken for SEC and NMR analysis that the copper and ligand concentration decreases with each consecutive step, which may exert such influence on the reaction. Also, viscosity effects and starting self-aggregation of the growing polymer chains may play a role for this effect.

Block 3 (MA) reaches 92% monomer conversion in 4 h, while when DEGA is added, the reaction time decreases slightly to 3.6 h to reach to 93% monomer conversion. Upon addition of tBA, the reaction time increased to 4.7 h to reach to the same monomer conversion. Conversions, as determined by IR, were confirmed by NMR analysis, which, however, becomes less straightforward after the first addition of DEGA due to unavoidable peak overlaps. Overall, despite the variation in reaction time per block, overall relatively fast reactions were generally observed, especially regarding that reactions were carried out strictly at low temperatures. The monomer conversion of each cycle was well above 90% as targeted, except for blocks 7 and 8. Interestingly, the polymerization of block 7 was stopped before completion of reaction and was stored in the freezer for 3 days before continuing the polymerization. The polymerization ceased at only 86% with the exact reason being unknown. It should thereby be noted that IR determination of conversions is hampered when the sample is stored in the between as the reference spectrum might not be valid anymore after restart of polymerization. Nevertheless, reactions were further carried out, since a small gradient is (even if not favorable), in principle, no contradiction to the multiblock copolymer concept.

Interesting to note is also that the dispersity of the polymers remained narrow throughout the whole reaction sequence. Dispersities well below 1.2 are consistently obtained with no significant broadening with the number of blocks being added. This demonstrates that reactions could in all likelihood also be continued, since the livingness of the process seems to be still excellent in the last reaction step, even if reactions may become slow due to the observed decrease in reaction rate with further addition of monomers. Noteworthy is, however, that the distributions from block 4 on feature a high molecular weight shoulder that appears to increase with proceeding reactions. In principle, such high-molecular weight shoulder can be induced by irreversible termination taking place. This is, however, in contradiction to the seemingly very high livingness of the

process as well with considering the fact that acrylates tend to terminate via disproportion rather than combination. Yet, the source of the shoulder lies currently in the dark and requires further investigation.

After synthesis of the decablock, the *tert*-butyl functional group of the multiblock copolymer is hydrolyzed to acrylic acid (AA) under acidic condition. The hydrolysis of tBA to AA is confirmed by the disappearance of the characteristic tBA peak in ¹H NMR and by the decrease in overall molecular weight (see Supporting Information for details). Interestingly, the high-molecular weight shoulder observed in the initial distributions (see discussion above) almost quantitatively disappears after deprotection. The hydrolyzed copolymer, PMA-PAA-PMA-PDEGA-PMA-PAA-PMA-PDEGA-PnBA-PDEGA, is dissolved in a water/ethanol solution (80/20% v/v). The blocks, MA and nBA, serve as hydrophobic block (i.e., insoluble in water), and the PAA and PDEGA are switchable in hydrophobic–hydrophilic properties. PAA has carboxylic group moiety and is known to protonate in acidic condition and deprotonate in basic condition. When the multiblock copolymer dissolves in a solution at pH 2, the PAA chains are protonated (no charge) and tends to swell in THF.[36] As the pH value increases to 5, acrylic acid is partially deprotonated (negatively charged), and this anionic block becomes hydrophilic.[36] In a pH 10 environment, PAA segments are fully charged and the material becomes soluble in water (see Supporting Information). The change of ionized state has induced certain structural formation as the solution has changed from cloudiness to clear appearance when pH increases from 2 to 10 (see Figure 3). PDEGA on the other
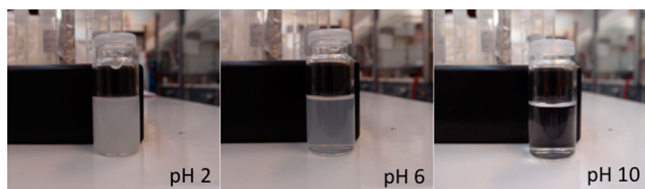

Figure 3. Turbidity of the decablock copolymer solution in water at different pH.

hand is known to have distinct LCST characteristics. Indeed, the decablock shows self-assembly behavior in basic conditions. Also, the size of particle structures change due to the thermoresponsive character of the PEG-acrylate with temperature (see Supporting Information). It must be noted that the data described here are only preliminary experiments to demonstrate the potential of multiblock copolymer in self-assembly applications. Due to the interplay of the various groups, very complex multiresponsive behavior is expected and the study of the specific properties of such polymer will constitute a study in its own right. A study on self-assembly of such multiblocks under variation of the respective monomer sequence is currently underway in our laboratories.

Photoinitiated copper-mediated radical polymerization provides a one-pot and a less time-consuming method to synthesize decablock copolymers with high structural definition. Polymerizations require reaction times between 2 and 7 h, with increasing reaction times with consecutive addition of monomer. The optimization of the polymerization has been demonstrated, and a decablock copolymer (PMA-PtBA-PMA-PDEGA-PMA-PtBA-PMA-PDEGA-PnBA-PDEGA) with a molecular weight close to theoretical values with remarkable

narrow dispersity ($Đ \sim 1.11-1.17$) has been obtained. Followed by the deprotection of tBA of decablock copolymer, the functional modification is confirmed by ¹H NMR and SEC. The anionic property of residual PAA in water enables the decablock material to exhibit a pH switch character. The solution changes from cloudy to transparent when the pH increases from 2 to 10. Also, the PDEGA blocks induce a thermoresponsive behavior.

■ ASSOCIATED CONTENT

ⓢ Supporting Information
Experimental details, information on the deprotection step, and DLS measurements. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

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