Polymerization of Free Secondary Amine Bearing Monomers by RAFT Polymerization and Other Controlled Radical Techniques

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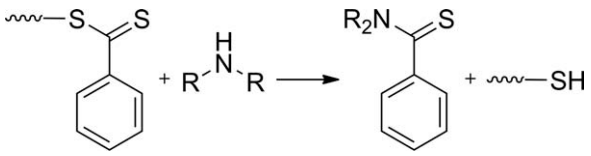
ABSTRACT: This work describes the polymerization of the free secondary amine bearing monomer 2,2,6,6-tetramethylpiperidin-4-yl methacrylate (TMPMA) by means of different controlled radical polymerization techniques (ATRP, RAFT, NMP). In particular, reversible addition-fragmentation chain transfer (RAFT) polymerization enabled a good control at high conversions and a polydispersity index below 1.3, thereby enabling the preparation of well-defined polymers. Remarkably, the polymerization of the secondary amine bearing methacrylate monomer was not hindered by the presence of the free amine that commonly induces degradation of the RAFT reagent. Subsequent oxidation of the polymer yielded the polyradical poly(2,2,6,6-tetramethylpiperidinyloxy-4-yl methacrylate), which represents a valuable material used in catalysis as well as for modern batteries. The obtained polymers having a molar mass (M_n) of 10,000–20,000 g/mol were used to fabricate well-defined, radical-bearing polymer films by inkjet-printing. © 2012 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 50: 1394–1407, 2012

KEYWORDS: atom transfer radical polymerization (ATRP); battery material; nitroxide mediated polymerization (NMP); organic radical battery; radical polymerization; reversible addition fragmentation chain transfer polymerization (RAFT); secondary amine; TEMPO polymer

INTRODUCTION Controlled radical polymerization (CRP) of free amine bearing monomers is a demanding task. Although reversible addition-fragmentation chain transfer (RAFT) polymerization excels in versatility with respect to the choice of monomer, functional group tolerance as well as the required experimental conditions, the RAFT polymerization of amines has usually to be carried out with protected amine functionalities. This is necessary to omit the aminolysis of the thiocarbonylthio chain transfer agents (Scheme 1) that commonly occurs with free primary and secondary amines. Aminolysis not only renders the polymerization of free amines impossible, it is even used to intentionally cleave thiocarbonylthio end groups. While the polymerization of tertiary amines such as 2-(dimethylamino)ethyl methacrylate is possible, monomers with primary and secondary amine functionalities may only be polymerized in a controlled manner with the amine being protected as an ammonium salt. Common examples include 2-aminoethyl methacrylate hydrochloride and *N*-(2-aminoethyl)-methacrylamide hydrochloride.[1–3]

Additional obstacles hinder the successful polymerization of amine bearing monomers by atom transfer radical polymerization (ATRP). The growing polymer chain may displace the ligand of the copper catalyst complex bringing the reaction to a premature halt. Monomers that were successfully polymerized by ATRP, for example, supported by the use of polydentate ligands, include the tertiary amine 2-(dimethylamino)ethyl methacrylate as well as the hydrochloride of the primary amine 2-aminoethyl methacrylate.[4,5]

The polymerization of the secondary amine bearing monomer 2,2,6,6-tetramethylpiperidin-4-yl methacrylate (TMPMA) is of special interest as its polymers can be further processed to obtain polyradical bearing polymers.[6] Up to now, such polymers have been prepared in several different ways: (i) polymer-analogous reactions, for example, transesterification of poly(methyl methacrylate) (PMMA) with 2,2,6,6-tetramethyl-4-aminopiperidinyloxyl)[7] or poly(pentafluorophenyl acrylate) with 4-amino-2,2,6,6-tetramethyl-1-oxyl-piperidine,[8] (ii) free radical polymerization (FRP) with a subsequent oxidation of the formed amine bearing precursor polymer[9] as well as (iii) direct anionic polymerization of a free radical bearing monomer.[10] While the transesterification route (i) is marked by only a low degree of functionalization (<25%)



SCHEME 1 Schematic representation of the aminolysis of thiocarbonylthio chain transfer agents by secondary amines.

that can be achieved, anionic polymerization (iii) permits good functionalization but requests stringent reaction conditions. As radical polymerizations are uncomplicated in their general handling they are to be preferred over ionic procedures. Nevertheless, an intrinsic drawback of free radical polymerization is the lack of control over the molar mass and the broad polydispersity index (PDI) value of the polymers formed.

Our goal was to use the polyradical bearing polymers for inkjet printing. For this advanced processing technique it is essential to have well-defined polymers at hand. As the solubility of the polymer and its solution's viscosity have a significant influence on the printability of an ink-formulation the molar mass needs to be adjusted accordingly. For this reason, the preparation of the PTMA-NO precursor polymer from TMPMA by CRP techniques such as ATRP, RAFT, and nitroxide mediated polymerization (NMP) was evaluated. When the limitations of the polymers prepared by free radical polymerization—like high viscosity and undefined molar mass distribution—are overcome, inkjet printing can be used to process the polymers. Inkjet printing is a noncontact and drop-on-demand film preparation technique, which requires only small amounts of solutions and serves over a high reproducibility.[11–13] Furthermore, inkjet printing is a noncontact patterning technique that does not need expensive masks, showing clear advantages in comparison to other solution deposition or film formation methods like doctor blading, spin-coating or gravure printing. This advanced processing technique is able to bridge the gap between polymer synthesis and solid-state property characterization, since this particular technique opens the way for an automated preparation of thin-film libraries, with a systematic variation of parameters, such as the chemical composition or the film thickness.[14]

To our best knowledge, there have only been two previous reports using CRP techniques for the preparation of TEMPO radical bearing polymers.[15] Surface-initiated ATRP was used to fabricate patterned thin-film electrodes, whereas RAFT was used in the preparation of the second block of an amphiphilic copolymer subsequently used as ESR probe in bioimaging. Even though the latter polymerization is the first example of a polymerization of a free amine bearing monomer by the RAFT process, no explanation for this noteworthy exception is given. As the authors of the previously published reports on CRP of piperidine bearing monomers peruse an application-focused approach we herein investigate the preparation by the most versatile CRP techniques in detail from a synthetic point of view as to create a valid foundation for future applications of this resourceful material. Special emphasis is focused on the optimization of the reaction conditions to obtain polymers that exhibit good printability as to permit a flexible and fast processing of radical bearing polymers by means of inkjet printing.

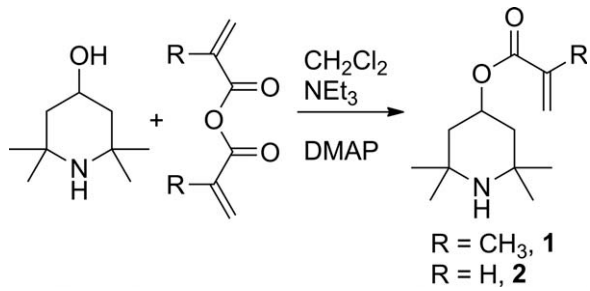
RESULTS AND DISCUSSION

Monomer Synthesis

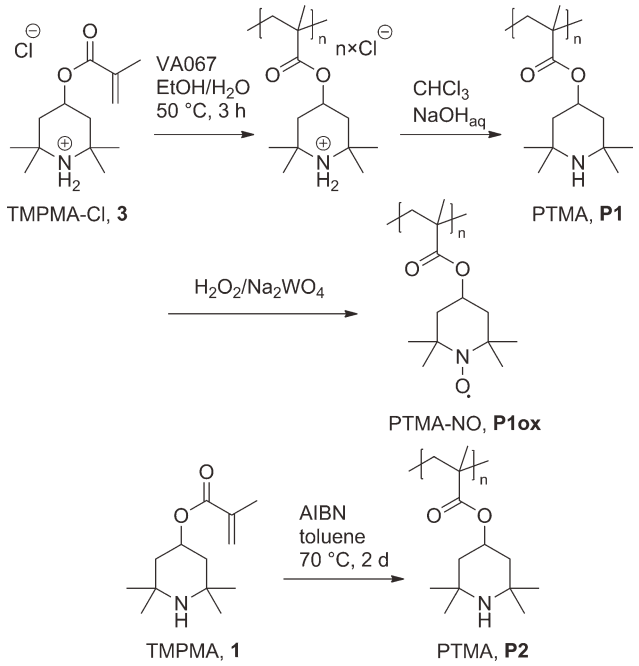
Numerous industrial polymers are prepared by a radical polymerization process. Because this technique is robust and cost effective its use in the synthesis of radical-bearing polymers is desirable. Although the radical polymerization technique is compatible with many monomers and versatile with respect to the reaction conditions, the polymerization of free radical (TEMPO) bearing monomers is not possible. For this reason, a precursor polymer has to be prepared. Based on the inexpensive and commercially available 2,2,6,6-tetramethylpiperidin-4-ol the synthesis of a poly(methacrylate) represents an useful approach.

The preparation of the required methacrylate monomer TMPMA, **1** by esterification is complicated by the simultaneous presence of, both, a hydroxyl and an amino group, since both functionalities show similar reactivity towards carboxylic acid derivatives. Previous publications have used methacryloyl chloride without providing detailed information of the synthetic protocol or the obtained yields.[16,17] Our experiments indicate that methacryloyl chloride is not a suitable reagent because it shows no significant OH-selectivity. The desired TMPMA is only obtained in low yields (<15%) with the *bis*-substituted 2,2,6,6-tetramethylpiperidin-4-ol **1a** being the main product, as could be proven by mass spectrometry (MS) and nuclear magnetic resonance (NMR) spectroscopy.

Using the less reactive methacrylic anhydride in combination with 1 mol-% of a nucleophilic catalyst, 4-dimethylaminopyridine (DMAP), results in improved yields up to 60% (Scheme 2); the formation of **1a** was minimized. By using the anhydride and catalytic amounts of DMAP the concentration of the active electrophilic reagent was constantly kept at a low level, self-controlled by the reaction rate of the esterification. Since no excess of the active electrophilic reagent was present and the reaction with the sterically less hindered hydroxyl group was kinetically favored, the formation of a bis-substituted product is suppressed.



SCHEME 2 Schematic representation of the synthesis of the free secondary amine bearing monomers **1** (TMPMA) and **2** (TMPA) by DMAP catalyzed esterification.



SCHEME 3 Schematic representation of the preparation of PTMA (**P1** and **P2**) via the polymerization of TMPMA hydrochloride (top) and of the free amine (bottom) as well as of the oxidation of PTMA to **P1ox** (middle).

The corresponding acrylate monomer 2,2,6,6-tetramethylpiperidin-4-yl acrylate (TMPA, **2**) was prepared in a similar manner in moderate yield. Therefore acrylic anhydride was prepared by the reaction of acrylic acid with sodium hydride and acryloyl chloride before use.[18]

Free radical Polymerization

Methacrylates can be polymerized by conventional free radical polymerization using standard initiators. TMPMA was polymerized in toluene at 70 °C initiated by 2,2′-azobis(2-methylpropionitrile) (AIBN) to obtain poly(2,2,6,6-tetramethylpiperidin-4-yl methacrylate), PTMA (Scheme 3, bottom). The polymer obtained can easily be isolated and purified by precipitation making this a robust and reliable method. Nevertheless, the technique has to be marked rather inefficient, since the polymerization proceeds slowly resulting in only 40% conversion after 48 hours of reaction time. The reason for this slow reaction lies in the nature of the monomer: As known from literature reports amines can function as retarders in free radical polymerizations.[19,20]

When TMPMA is reacted with hydrochloric acid, the retarding amine-functionality is protonated and rendered innocuous. Polymerization of the ionic TMPMA-Cl **3** can be carried out in a mixture of water and ethanol (1:1) using the water-soluble 2,2′-azobis(2-methyl-propionamidine) dihydrochloride (VA067) as initiator at 50 °C (Scheme 3, top). The use of this system reduces the reaction time to 3 hours while doubling the yield of the polymer. The slow addition of a solution of the protonated polymer in water/ethanol to a vigorously stirred mixture of aqueous sodium hydroxide and chloroform was established as the most suitable procedure for conducting the deprotonation of the prepolymer in homogeneous phases. PTMA **P1** is finally isolated from the chloroform layer in good yields. Its molar mass exceeds $M_n > 300{,}000$ g/mol as determined by size exclusion chromatography (SEC) using dimethylacetamide (DMAc) as mobile phase and poly(styrene) as standard. An absolute molar mass of $M_n = 60{,}000$ g/mol was obtained by universal calibration using tetrahydrofuran/triethylamine (96:4) as mobile phase. This result indicates an overestimation of the molar mass with respect to a poly(styrene) standard on the dimethylacetamide based SEC system, which one needs to keep in mind upon interpreting further results on this class of polymers.

The precursor polymer obtained by free radical polymerization was subsequently oxidized with hydrogen peroxide and sodium tungstate as catalyst to form the nitroxide radical bearing polymer.[21] The orange colored, oxidized polymer precipitates from the aqueous methanol solution, permitting a simple separation of the oxidized polymer from the reaction mixture and excellent yields.

The formation of the free nitroxide radical is indicated by the typical orange color with absorption maxima at 251 nm (π-π^*) and 451 nm (n-π^*). Further prove is provided by infrared (IR) and electron spin resonance (ESR) spectroscopy (Fig. 1). The IR spectrum exhibits a dominant signal at 1364 cm^{-1} attributed to N—O stretching vibrations. This signal superimposes the much weaker symmetric C—H deformation vibrations of the CH_3 groups at 1366/1377 cm^{-1}. These observations contrast with the precursor polymer's IR spectrum, where the $\delta_s(CH_3)$ at 1366/1377 cm^{-1} is the only signal present in this region.

Quantitative ESR spectroscopy (internal standard: copper sulfate), elemental analysis, and determination of the spin concentration using a superconducting quantum interference device (SQUID) indicate complete functionalization of the polymer. The ESR spectrum (Fig. 1) of the polymer is dominated by a broad signal at $g = 2.0064$, which is

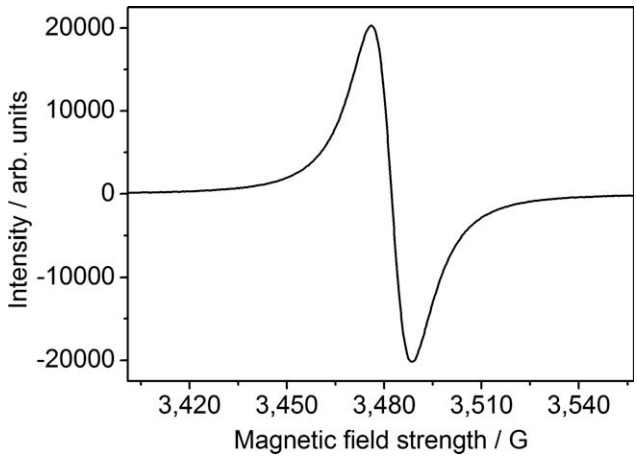


FIGURE 1 ESR spectrum (X-Band) of PTMA-NO (**P1**) with $g = 2.0064$.

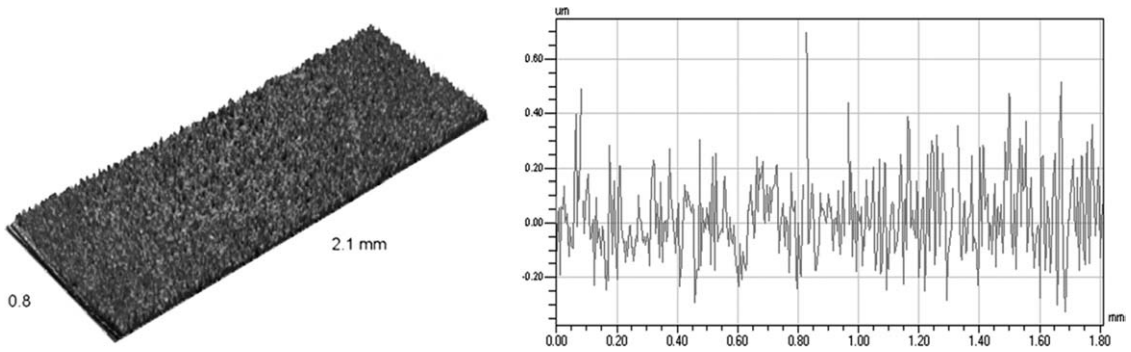


FIGURE 2 Optical profiler image (left) and 2D profile (right) of an inkjet printed film of the radical bearing polymer **P1ox** prepared by free radical polymerization and subsequent oxidation. The film was inkjet-printed on glass from *N*-methylpyrrolidone at a polymer concentration of 4 mg/mL.

characteristic for organic radical polymers. Radical-radical interaction, due to close spatial proximity of the TEMPO moieties, broadens the signal. Therefore, no hyperfine structure is visible.

As a consequence of the oxidation process the high molar mass polymer is partially cross-linked, decreasing its solubility in common organic solvents. For inkjet printing the only suitable solvent was 1-methyl-2-pyrrolidone (NMP). However, even in NMP the polymer is only partially soluble (<4 mg/mL). This makes the processing of **P1ox** via inkjet printing difficult, but is inevitable when using high molar mass PTMA as produced by free radical polymerization. The topography of the printed films was studied with an optical interferometric profiler and the results are summarized in Figure 2. As a consequence of the polymer's low solubility, **P1ox** exhibits poor film formation properties and a very rough film surface as can be seen from the 2D profile of the film. The use of the high boiling solvent NMP (b.p. = 202 °C) resulted in a long drying time of the processed films, that is, characteristic for the formation of rough surfaces. In addition, agglomeration occurs upon drying at elevated temperatures. An optimization of the film formation by varying either the concentration or the solvent could not be performed due to the low solubility of the polymer. For these reasons inkjet printing is no suitable technique to process this kind of polymer prepared by free radical polymerization and subsequent oxidation.

As the polymers prepared by FRP cannot be inkjet printed properly, CRP techniques were used subsequently to obtain more defined PTMA of a lower molar mass. To acquire a complete picture the three most versatile techniques were evaluated.

Nitroxide Mediated Polymerization

The high amount of propagating radicals, that is, caused by a high activation–deactivation equilibrium constant complicates the controlled homopolymerization of methacrylates since it leads to irreversible termination reactions. This can, theoretically, be overcome by (co)polymerization with styrene that exhibits a low activation–deactivation equilibrium constant leading to a strong reduction of the overall equilibrium constant and, thereby, improving the control.[22]

The (co)polymerization of TMPMA was studied, using SG1-based alkoxyamine BlocBuilder™. In addition, the homopolymerization of the corresponding acrylate monomer TMPA, that was expected to show better compatibility with the NMP technique, was examined under similar conditions.

At a reaction temperature of 120 °C reference values for the homopolymerization of TMPMA (conversion, molar mass, PDI) were obtained. The polymer revealed a molar mass of M_n = 5,800 g/mol after 6 hours reaction time (21% conversion) with a PDI value of 1.8, indicating loss of the control over the polymerization kinetics. Decreasing the temperature to 90 °C did not improve the control but raised the molar mass due to a lowered initial radical concentration at this temperature (**P3**). In comparison to the reference homopolymerization the addition of 10 mol % styrene enabled an improved PDI value of 1.4 suggesting a better control of the polymerization. In accordance with the previous observations a lowered temperature caused no significant improvement. All results are summarized in Table 1 showing that the values do not meet the requirements.

In comparison with TMPMA the homopolymerization rate of the corresponding acrylate monomer TMPA is much higher, reaching 91% of monomer conversion after 6 hours (Table 2). Expectedly, the reaction control is improved as indicated by a significant decrease of the PDI to 1.51.

Another parameter that was changed to decrease the overall reaction rate is the dynamic equilibrium between the dormant and the active species. By adding an excess of the free nitroxide radical SG-1 or by releasing free SG-1 radicals *in situ* by means of preheating BlocBuilder™ the equilibrium is pushed towards the dormant species.[23] Before the addition of TMPA a BlocBuilder™ solution was heated at 60 °C for 40 minutes. The free nitroxide radical formed has a strong influence on the reaction kinetics, slowing down the reaction by factor 10 with respect to a procedure without additional SG-1. After 16 hours of reaction the monomer conversion amounted to merely 28%. On the other hand, adding 0.1 mol-% of free SG-1 to the standard reaction

TABLE 1 Selected Polymerization Conditions and Characterization Data of PTMA and PTMA-*co*-PS Prepared by NMP

[TMPMA]: [styrene]	T (°C)	Conv. (%)[a]	t (h)	M_n (g/mol)[b]	M_w (g/mol)[b]	PDI
1:0	120	21	6	5,800	10,400	1.78
9:1	120	12	6	6,500	17,500	1.45
1:0	90	17	6	9,600	9,500	1.81
9:1	90	13	6	11,100	15,900	1.43

[a] Conversions determined by GC.
[b] Molar mass determined by SEC ($CHCl_3$, PS calibration).

TABLE 2 Selected Polymerization Conditions and Characterization Data of PTMA and PTA Prepared by NMP

Monomer	Conv. (%)[a]	t (h)	M_n (g/mol)[b]	M_w (g/mol)[b]	PDI
TMPMA	22	6	5,900	10,600	1.80
TMPA	91	6	3,900	5,900	1.51
TMPA[c]	5	4	3,700	4,600	1.24
TMPA[c]	28	16	13,900	21,500	1.55
TMPA[d]	92%	16	3,800	6,400	1.69

[a] Conversion determined by GC.
[b] Molar mass determined by SEC ($CHCl_3$, PS calibration).
[c] Preheating of the initiator.
[d] Addition of free SG-1.

mixture did not slow down the reaction, concluding that a higher amount of the free nitroxide is formed during the preheating step. To obtain results that can be compared with the preheating procedure, the reaction was not quenched before 16 hours of reaction time. The polymer formed exhibits a molar mass and a monomer conversion similar to the polymer prepared without additional SG-1.

Considering the results of the NMP polymerization of TMPMA and TMPA as a whole, it appears that this radical polymerization technique is not suitable to prepare the precursor polymers in a controlled manner. In view of the general restraints of the NMP of (meth)acrylates the choice of another polymerization technique was required.

Atom Transfer Radical Polymerization

N,N,N′,N″,N″-Pentamethyldiethylenetriamine (PMDETA) was chosen for the polymerization of TMPMA in combination with copper(I) bromide and the initiator ethyl 2-bromoisobutyrate. First experiments were conducted in anisole at 130 °C. The polymer obtained revealed a molar mass of M_n = 3,500 g/mol and a PDI value of 1.51 (SEC, DMAc, PS calibration), indicating poor control over the polymerization process. The ideal reaction temperature, which was consequently used for all additional experiments, was found to be 90 °C. The resulting polymer **P4** exhibits a molar mass of M_n = 33,900 g/mol while having a PDI value of 1.14 (20% yield).

For further investigations of the living character kinetic studies were conducted (Figs. 3 and 4). When using PMDETA as ligand, the reaction stopped after about 3 hours of reaction time and a monomer conversion of 15% (GC). All samples taken after this point of time revealed no significant change of the molar mass of polymers and the monomer conversion, respectively. To ensure that no contamination occurred when sampling the reaction mixture the polymerization of a monomer stock-solution was carried out in five separate microwave vials and each vial was only probed once. As a consequence, any disturbance of the reaction can be ruled out as origin of the early termination.

From literature it is known that the use of highly active ligands, such as Me_6TREN, entail equilibrium constants too high to achieve a controlled ATRP polymerization of methacrylates.[24] With the intention to rule out the catalyst system as possible source of the polymerization's termination two less reactive ligands, *N*-(pyridin-2-ylmethylene)ethanamine (PMEA) and 2,2′-bipyridine (bpy), were tested. Using bpy resulted in similar values as the use of PMDETA does. When

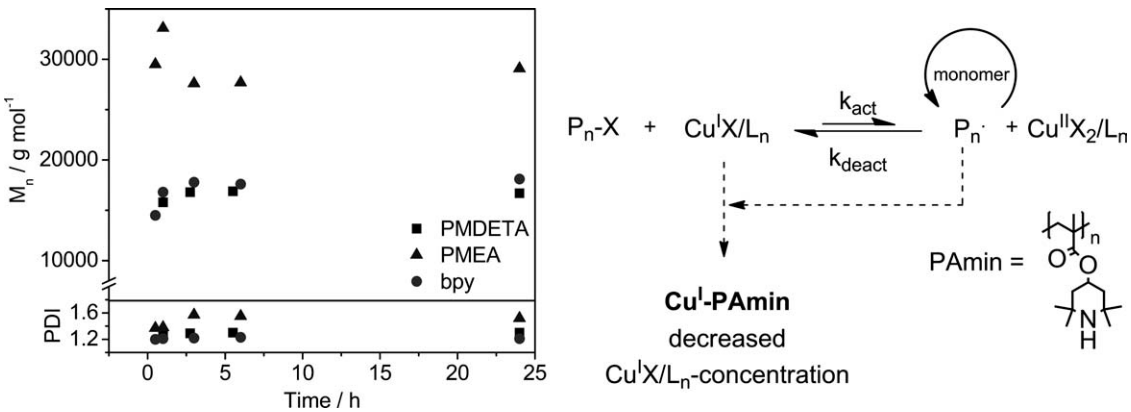


FIGURE 3 Molar masses and PDI values (SEC in DMAc, PS calibration) of the amine bearing precursor polymer PTMA, which was prepared by ATRP using three different ligands, as a function of reaction time (left). Schematic representation of the proposed deactivation mechanism of the polymerization of the amine bearing monomer TMPMA by ATRP (right). The complexation of copper by the growing polymer chain inhibits the activation of the dormant species.

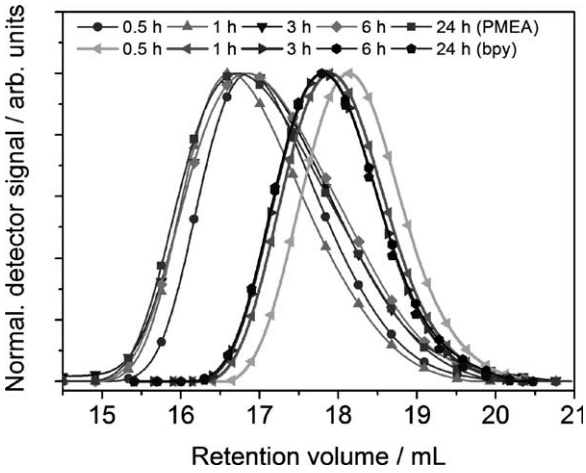


FIGURE 4 SEC traces (DMAc) of the kinetic study of the polymerization of the monomer TMPMA by the ATRP technique using *N*-(pyridin-2-yl-methylene) ethanamine (PMEA) and 2,2′-bipyridine (bpy) as ligand for the catalyst system.

using PMEA as ligand, the reaction terminated after 3 hours and 18% conversion. Furthermore, the PDI value increased to 1.5 and the molar mass decreased to $M_n = 27{,}600$ g/mol after it had already reached 31,100 g/mol. These observations indicate poor control over the polymerization kinetics when PMEA is used since side reactions occur, for example, chain transfer.

Because the use of three different catalysts showed comparable results, the catalyst system can be eliminated as possible reason for the termination of the polymerization after 15 to 20% of monomer conversion. It is more reasonable to assume that the growing polymer chain itself inhibits the reaction as illustrated in Figure 3: The polymer formed exhibits an amine functionality in every single repeating unit and may also act as chelating agent forming a complex with the copper ions of the catalyst system (Cu^I-PAmin). Thereby, the active catalyst is removed from the equilibrium resulting in a decrease of the activation rate of the dormant species and a decrease of the overall reaction rate. When no free catalyst is present anymore, the reaction eventually terminates.

This mechanism may also enhance the persistent radical effect. If the total amount of the activating catalyst is lower than the concentration of the chains that terminate, for example, because it formed a complex with the growing polymer chain, the polymerization will stop at low conversion since all of the catalyst is present as a persistent radical.[25]

In an additional reaction step polymer **P4** was oxidized with hydrogen peroxide/sodium tungstate according to the procedure explained before. Thereby the molar mass, as determined by SEC measurement (DMAc, PS calibration), decreased from $M_n = 33{,}900$ g/mol to 26,300 g/mol while the PDI value increased from 1.14 to 1.31 for the oxidized polymer **P4ox** (Fig. 5, left). This change is an indicator for degradation reactions taking place during oxidation of PTMA. Nevertheless, the polymer obtained was soluble in toluene, dichloromethane, tetrahydrofuran, *N*-methylpyrrolidone, and chlorobenzene, making it processable by inkjet printing. Cross-linking phenomena, which hindered the proper processing of the polymer prepared by free radical polymerization, had no significant influence due to the lower molar mass of the polymers.

The precursor polymer **P4** and the radical bearing **P4ox** revealed a good solubility in printable solvents and readily formed films when printed from toluene/*ortho*-dichlorobenzene 90/10 (5 mg/mL). By using toluene as main solvent that has a lower boiling point (111 °C) than NMP a smoother film could be obtained, even though some agglomeration occurred upon drying (Fig. 5, right). It is known that by using a solvent mixture which contains a few percentages of a higher boiling solvent, the coffee-drop-effect, which describes the phenomenon of material accumulation at the rim of a dried feature, can be reduced.[26] For this

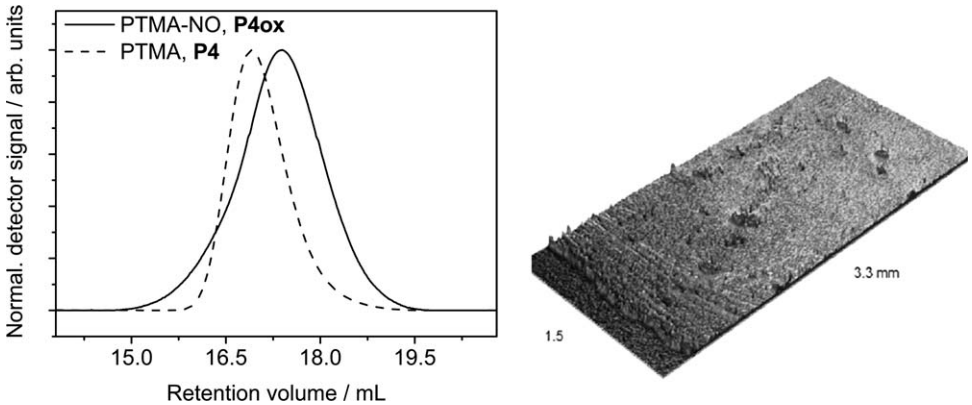


FIGURE 5 SEC trace (DMAc) of the secondary amine bearing precursor polymer **P4** prepared by ATRP and of its oxidized form **P4ox** (left). A shift in the elution volume is clearly visible. Optical profiler image of an inkjet printed film of the stable radical bearing polymer **P4ox** on glass (right). The film was inkjet-printed from toluene/*ortho*-dichlorobenzene (ratio 90/10) at a polymer concentration of 5 mg/mL.

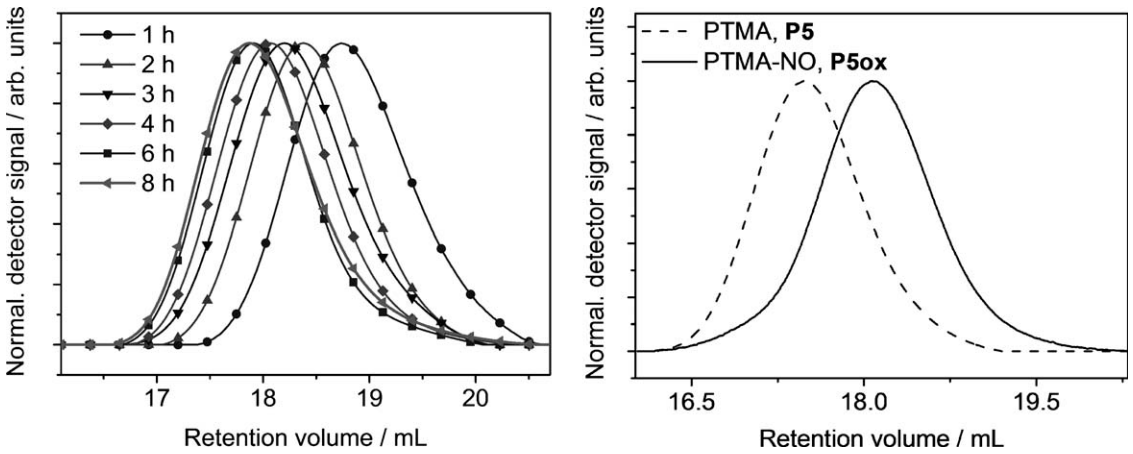


FIGURE 6 SEC traces (DMAc) of the kinetic study of the polymerization of the monomer TMPMA-Cl exhibiting a amine functionality protected by formation of its hydrochloride (left). Comparison of SEC traces (DMAc) of polymer P5 prepared from the protected monomer and of its oxidized polymer **P5ox** (right).

purpose, *ortho*-dichlorobenzene (179 °C) was used to decrease the coffee-drop-effect and, subsequently, to improve the film formation, but Figure 5 shows that still more material is located at the edge of the film. These results confirm that an enhanced film formation can be obtained from **P4** and **P4ox** in comparison to **P1ox**, but further investigations need to be done to identify a solvent or solvent system that leads to a film formation without agglomeration and the reduction of a coffee-ring. Although this represents an improvement in comparison to the FRP prepared polymers, a consolidated view of the experimental results indicates that polymerization of TMPMA cannot be the method of choice, since the conversion of the monomer does not exceed 20%.

RAFT Polymerization

Aminolysis of thiocarbonylthio chain transfer agents by primary and secondary amines commonly renders the polymerization of amines impossible. Therefore the polymerization of TMPMA, which bears a secondary amine functionality, appears to be a challenging task. Nevertheless, RAFT polymerization of the hydrochloride TMPMA-Cl **3** and even of the free amine bearing TMPMA **1** is possible.

Polymerization of the Hydrochloride TMPMA-Cl

Hydrolysis of the chain transfer agent represents a known problem of RAFT polymerization in aqueous media. In particular basic conditions facilitate the hydrolysis of thiocarbonylthio compounds, while they are rather stable in an acidic environment.[27] To take advantage of the only moderately decreased stability in acidic media a polymerization of TMPMA in water/ethanol (1:3) adjusted to pH = 2 with hydrochloric acid was performed, generating the desired TMPMA-Cl hydrochloride *in situ*. The reaction was carried out at 50 °C using 2-cyano-2-butyl dithiobenzoate (CBDB) as chain transfer agent (CTA 1) and VA067 as initiator. Nevertheless, only 5% monomer conversion were observed after 22 hours of reaction time (M_n = 13,100 g/mol, PDI = 1.35). This is an indication of termination reactions, most likely hydrolysis of the chain transfer agent due to the low pH value.

Since a polymerization at a low pH value with *in situ* generation of the hydrochloride resulted in hydrolysis, TMPMA-Cl was prepared in advance and the polymerization was conducted at an increased pH value of 5.5 in phosphate buffer/ethanol (3:1). After 23 hours reaction time a well-defined polymer (M_n = 5,400 g/mol, PDI = 1.17) with a yield of 60% was obtained. This proofs that polymerization of TMPMA-Cl hydrochloride is possible in slightly acidic environments using CBDB as chain transfer agent.

A mixture of water and ethanol is required to ensure the solubility of all reactants. When using phosphate buffer as aqueous component the ethanol fraction has to be kept low to ensure the stability of the buffer. This is prejudicial to the other reactant's solubility. For this reason polymerization in water/ethanol (1:3) is desirable. When polymerizing TMPMA-Cl in unbuffered water/ethanol the pH ranges between six and three, enabling smooth polymerization of the monomer. The well-defined polymer **P5** (M_n = 24,500 g/mol, PDI = 1.18) was obtained in 90% yield after deprotonation and oxidized according the procedure described earlier. As for ATRP the molar mass of the oxidized polymer **P5ox** decreases upon oxidation to 16,100 g/mol, this may be attributed to degradation reactions or a change in the polymer's hydrodynamic volume (Fig. 6). In contrast to the ATRP polymer **P4ox** the polymer **P5ox** did not show an increase of the PDI upon oxidation. The polymer obtained is soluble in dichloromethane, tetrahydrofuran, *N*-methylpyrrolidone, and chlorobenzene making it processable by inkjet printing (*vide infra*).

The polymerization of TMPMA-Cl in water/ethanol (1:3) with CBDB and VA067 as well as subsequent deprotonation can be established as standard procedure for the preparation of PTMA by the RAFT technique. To gain further understanding of the reaction a kinetic study was carried out (Figs. 6 and 7).

Following pseudo first order kinetics the data revealed a linear behavior in the semilogarithmic kinetic plot (Fig. 7, left). This

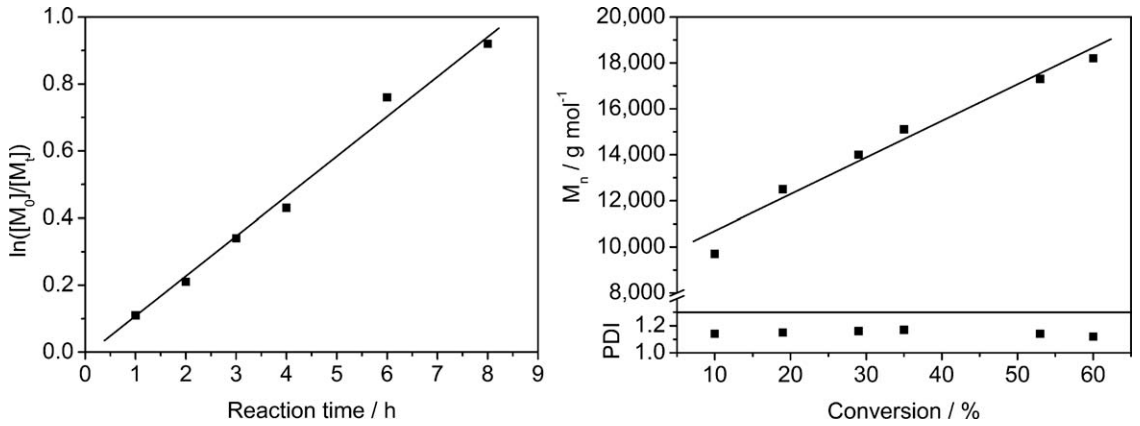


FIGURE 7 Kinetics plots of the RAFT polymerization of the monomer TMPMA-Cl exhibiting an amine functionality protected by formation of its hydrochloride. Monomer concentration determined by ^{1}H NMR spectroscopy (DMSO-d6; 300 MHz); M_n and PDI values determined by SEC in DMAc, PS calibration.

indicates a constant radical concentration throughout the reaction due to the absence of termination processes. Moreover, the molar mass of the polymer increases linearly with increasing monomer conversion as illustrated in Figure 7, right. Concluding from the *y*-intercept being at $M_n = 8{,}900$ g/mol and not at zero, the initializing radicals add several monomers before the main equilibrium is established. In summary one can state that the RAFT polymerization of TMPMA-Cl can be performed in a controlled manner.

Polymerization of the Free Amine Bearing TMPMA

Aminolysis of the chain transfer agent represents a fundamental problem. Nevertheless, RAFT polymerization of TMPMA, which is bearing a secondary amine functionality, is possible. This exceptional property of TMPMA can be attributed to the steric hindrance of the amine functionality as well as solvent effects: The basicity of a nucleophile is generally raised while its nucleophilicity decreases upon increased steric hindrance, on the one hand. On the other hand, the nucleophile TMPMA is further stabilized by a polar solvent, resulting in decreased reactivity. While the polymerization in apolar aprotic solvents like toluene is not successful, the use of water/ethanol (1:3) enables the polymerization, because the amine is stabilized through the formation of hydrogen bonds.

Nevertheless, polymerization is only possible if the initiator concentration is raised in comparison to standard RAFT conditions. While the experiments presented before were carried out at a monomer to chain transfer agent to initiator ratio of 80:1:0.33, the polymerization of free amine bearing TMPMA had to be performed at ratios of 80:1:0.5 to even 80:1:1. At lower initiator concentration proper and reproducible initiation of the polymerization is not ensured.

Although the initiator concentration of the latter reaction was twice the concentration of the chain transfer agent, it proceeded in a controlled manner up to conversions of 85%, as proven by a kinetic study (**P6**; Figs. 8 and 9). At higher conversions termination reactions occurred and the reaction did not follow pseudo first order kinetics anymore. As a consequence, the semilogarithmic kinetic plot exhibited no linear behavior after 2 hours of reaction time (equates 85%

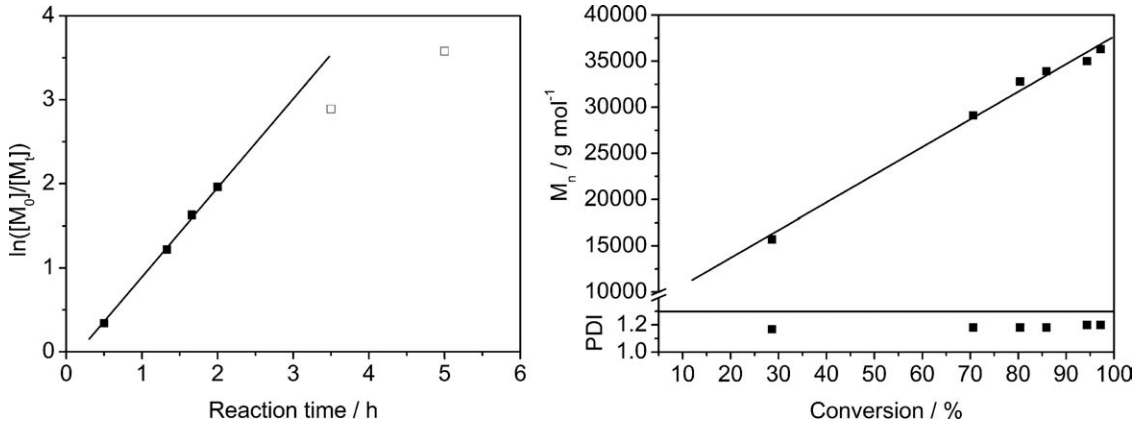


FIGURE 8 Kinetics plots of the polymerization of the free amine bearing monomer TMPMA by the RAFT technique using a dithiobenzoate-type chain transfer agent (CTA 1). Monomer concentration determined by ^{1}H NMR spectroscopy (DMSO-d6; 300 MHz); M_n and PDI values determined by SEC in DMAc, PS calibration.

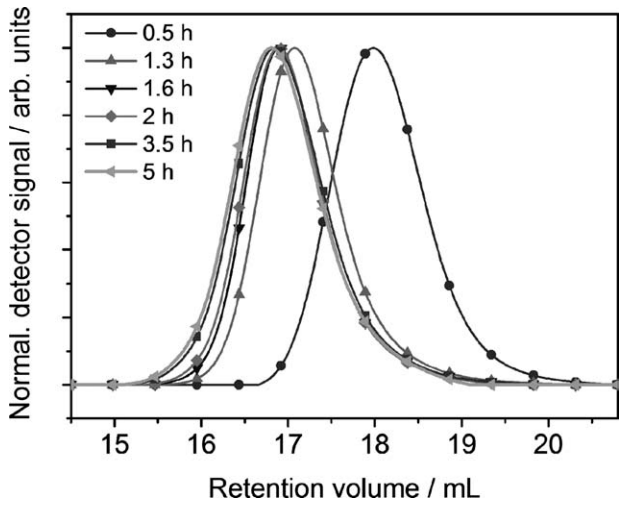


FIGURE 9 SEC traces (DMAc) of the kinetic study of the polymerization of the monomer TMPMA exhibiting an amine functionality via the RAFT technique using a dithiobenzoate-type chain transfer agent (CTA 1).

conversion). Nonetheless, full conversion could be reached in 5 hours yielding a well-defined, low-PDI polymer **P6**.

To reference the results of the SEC measurement, a mere relative method for molar mass determination, the absolute molar mass of the polymer **P6** was determined by vapor pressure osmometry in chloroform revealing a value of M_n = 5,700 g/mol. This result indicates an overestimation of the material's molar mass determined by SEC (M_n = 24,500 g/mol). The same holds true for the corresponding radical polymer **P6ox** that was obtained by oxidation of **P6** with hydrogen peroxide/$Na_2WO_4 \times 2H_2O$. Although SEC indicated a shift in the molar mass from M_n = 24,500 to 16,100 g/mol, vapor pressure osmometry measurements prove this to be a only an effect attributed to a change in the materials hydrodynamic volume, as the molar mass is, as expected, slightly increased upon oxidation (M_n = 5,900 g/mol). Further verification by absolute SEC techniques, for example, using a multiangle laser light scattering (MALS) detector, were not successful due to the low molar mass of these polymers.

The cyclic voltammogram of the oxidized polymer **P6ox** revealed a distinct and reversible redox reaction at 0.38 V (vs. Fc/Fc^-) that has been absent in the corresponding monomer TMPMA and the precursor polymer **P6**, respectively (Fig. 11). The reaction can be attributed to the oxidation of the free radical units to the related oxammonium cations. This highly reversible and fast redox reaction is of special interest in the development of organic radical batteries.[28]

Applying the developed technique well-defined polymers with varying molar masses (M_n) covering the area from 3,000 to 25,000 g/mol could be prepared (Table 3). While increased temperatures lead to lower reaction times the disadvantage of obtaining less well-defined polymers becomes obvious.

A MALDI-TOF mass spectrum of the low molar mass polymer revealed the expected variations of the desired distributions (Fig. 10). Cleavage of the dithiobenzoate-type CTA occurs during the measurement which is known in literature for this type of end group. In addition partial cleavage of the side group can be observed.

The precursor polymer **P6** and the radical bearing **P6ox** show a good solubility and form homogeneous films with a thickness of 200 nm when inkjet printed from toluene/*ortho*-dichlorobenzene 90/10 (5 mg/mL). No agglomeration was observed yielding much improved results in comparison to the polymers prepared by the other polymerization techniques (Fig. 11). The polymer films, readily usable in a variety of applications, can be prepared with various film thicknesses and shapes by changing the concentration of the printed solutions or varying the drop-to-drop distance of the deposited droplets.

Besides the described dithiobenzoate CTA a trithiocarbonate RAFT agent was applied for the polymerization of TMPMA. Using 4-cyano-4-(dodecylsulfanylthiocarbonyl)sulfanyl pentanoic acid (CTA 2) increased the control over the polymerization. While preparation of low molar mass polymers (M_n = 3,800 g/mol; PDI = 1.13) enabled the analysis via MALDI-TOF mass spectrometry, the synthesis of polymers with higher molar mass (M_n = 15,400 g/mol; PDI = 1.17) was possible as well without losing control over the polymerization. A kinetic study indicating the controlled character of the polymerization is depicted in Figures 12 and 13.

The MALDI-TOF mass spectrum of the polymers prepared by RAFT polymerization using the trithiocarbonate type CTA 2 shows several distributions, which, however, can be assigned to the desired structure with an increasing loss of the TMP-side groups (Fig. 14). This is probably caused by the MALDI-TOF MS measurement process itself due to the higher laser energy which is necessary to desorb the polymer.

EXPERIMENTAL

Materials and Preparation

All chemicals and solvents were received from Aldrich, Fluka and Acros. Unless otherwise stated, the chemicals and solvents were used without further purifications.

2,2,6,6-Tetramethylpiperidin-4-yl methacrylate (1)

To 2,2,6,6-Tetramethylpiperidin-4-ol (100 g, 0.64 mol) in dry dichloromethane (500 mL) were added *N,N*-dimethylpyridin-

TABLE 3 Characterizing Data of PTMA Prepared via RAFT Polymerization

[TMPMA]/[CTA]	T (°C)	t (h)	M_n (g/mol)[a]	PDI
25	50	24	3,100	1.18
100	50	13	11,000	1.21
100	70	4	25,200	1.31

[a] Molar mass determined by SEC (DMAc, PS calibration).

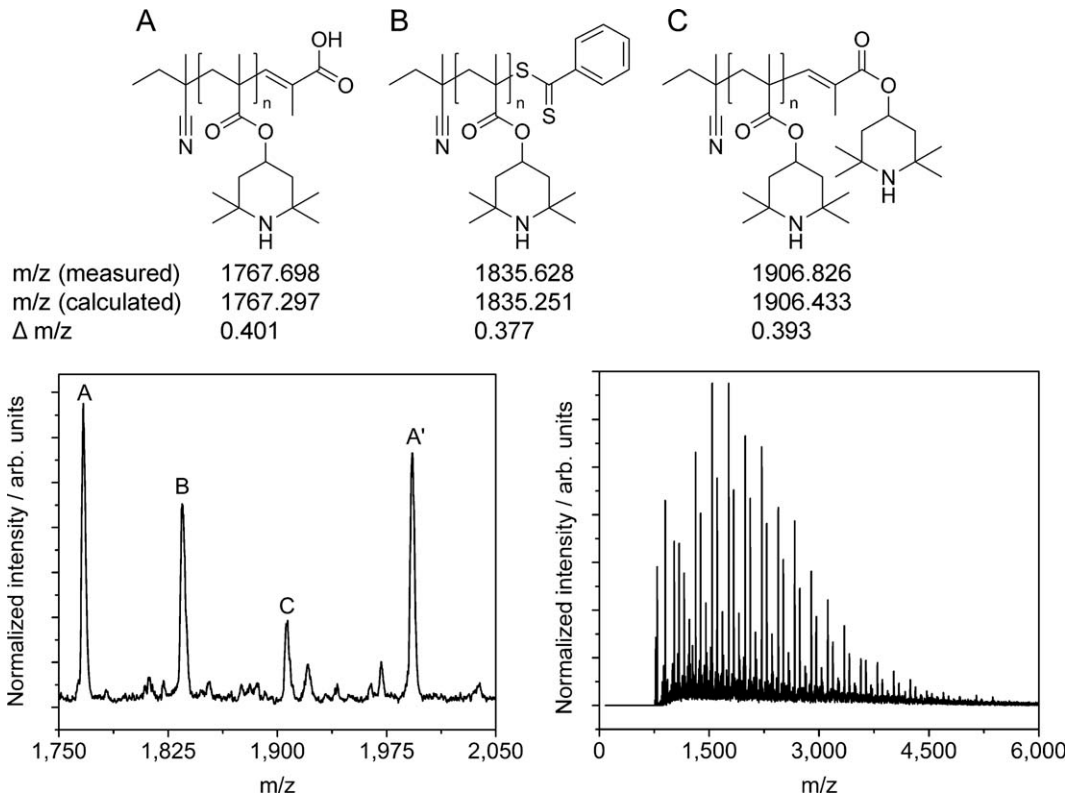


FIGURE 10 MALDI-TOF mass spectrum of the free secondary amine bearing polymer PTMA prepared via RAFT polymerization using a dithiobenzoate type chain transfer agent; matrix: *trans*-3-indoleacrylic acid; reflector mode (bottom) and assigned structures as well as *m/z* values for the exemplary structure $n = 7 + Na^+$ (top).

4-amine (7.8 g, 64 mmol) and dry triethylamine (180 mL) under argon atmosphere. Methacrylic anhydride (98 g, 0.64 mol), dissolved in dry dichloromethane (150 mL), was added dropwise under stirring. After stirring the mixture for 40 hours at room temperature the solution was washed twice with saturated aqueous sodium carbonate solution (250 mL) and brine (250 mL). The organic layer was dried over magnesium sulfate, filtered, and evaporated. Recrystallization from cyclohexane gave **1** (83 g, 58% yield) as a white powder (alternative purification: flash silica gel column chromatography using hexane and ethyl acetate with 3% of methanol as eluent).

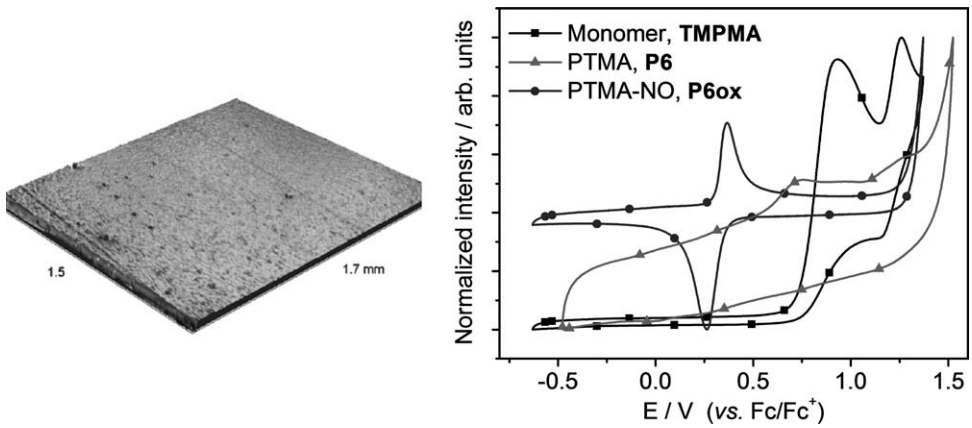


FIGURE 11 Optical profiler image of an inkjet printed film of the radical bearing polymer **P6ox** prepared from an amine precursor polymer **P6** by the RAFT technique and subsequent oxidation (left). The film was inkjet-printed on glass from toluene/*ortho*-dichlorobenzene (ratio 90/10) at a polymer concentration of 5 mg/mL. Cyclic voltammograms of the amine bearing polymer PTMA (**P6**), the stable radical bearing polymer PTMA-NO (**P6ox**), and the corresponding monomer (TMPMA) in CH_2Cl_2, 200 mV/s, 0.1 mol/L $TBAPF_6$ (right).

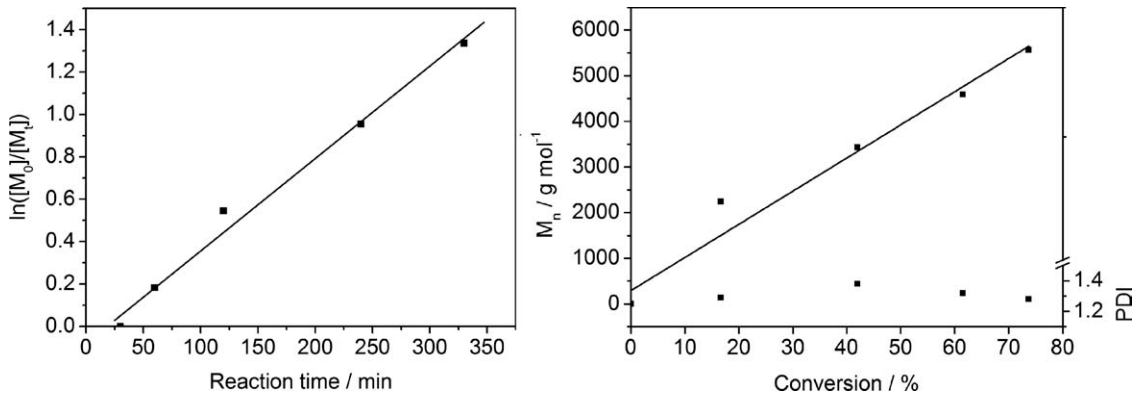


FIGURE 12 Kinetics plots of the polymerization of TMPMA by RAFT using a trithiocarbonate type chain transfer agent (CTA 2). Monomer concentration determined by ^{1}H NMR spectroscopy (300 MHz); M_n and PDI determined by SEC in DMAc, PS calibration.

^{1}H NMR (250 MHz, $CDCl_3$, δ, ppm): 1.19 (m, 14H; 4×CH_3, CH_2), 1.96 (m, 5H; CH_2=C—C**H**$_3$, CH_2), 5.24 (m, 1H; CH—O), 5.53 (s, 1H; C=CH_2), 6.07 (s, 1H; C=CH_2). ^{13}C NMR (63 MHz, $CDCl_3$, δ, ppm): 18.2 (CH_2=C—**C**H_3), 29.1 (2×CH_3), 34.7 (2×CH_3), 43.8 (2×C_q), 51.4 (2×CH_2), 69.1 (CH—O), 124.9 (C=**C**H_2), 136.8 (ROOC—**C**=C), 166.9 (COOR). FTIR (ATR, cm^{-1}): 752 (s), 945 (s), 972 (s), 1165 (vs, ν_{as}(O-CC=O)), 1300 (s, ν_{as}(CC=OO)), 1365 (m, δ_s(CH_3)), 1456 (w, δ(CH_2)), 1633 (m, ν(C=CH_2)), 1701 (vs, ν(C=O)), 2970 (m, ν(CH)), 2999 (w, ν(CH)), 3300 (w, ν(NH)). MS (EI, 70 eV) *m/z*: 107 (9), 124 (100), 410 (3), 210 (6), 225 (0.3, M^+). Anal. calcd. for $C_{13}H_{23}NO_2$: C, 69.29; H, 10.29; N, 6.22; found: C, 69.22; H, 10.53; N, 5.93.

2,2,6,6-Tetramethylpiperidin-4-yl acrylate (2)

Acrylic anhydride was freshly prepared following a literature procedure by the reaction of acrylic acid with sodium hydride and acryloyl chlorid.[18]

To 2,2,6,6-tetramethylpiperidin-4-ol (5.0 g, 31.8 mmol) in dry dichloromethane (50 mL) and dry triethylamine (10 mL) *N,N*-dimethylpyridin-4-amine (390 mg, 3.18 mmol) was added. The mixture was stirred at room temperature while acrylic anhydride (4.0 g, 31.8 mmol), dissolved in dry dichloromethane (10 mL), were added dropwise. Subsequently, the reaction was quenched after 20 hours by the addition of saturated aqueous sodium carbonate solution (30 mL). The organic layer was washed twice with aqueous sodium carbonate solution (50 mL) and brine (50 mL), dried over calcium sulfate, and evaporated to dryness. The crude product was purified by flash silica gel column chromatography using hexane and ethyl acetate with 3% of methanol as eluent to give **2** (1.96 g, 30% yield).

^{1}H NMR (250 MHz, $CDCl_3$, δ, ppm): 1.21 (m, 14H; 4×CH_3, CH_2), 1.96 (m, 2H; CH_2), 5.27 (m, 1H; CH—O), 5.80 (dd, ^2J(H,H) = 1.6 Hz, ^3J(H,H) = 10.3 Hz, 1H; CH=C**H**$_2$), 6.11 (dd, ^3J(H,H) = 10.3 Hz, 17.3 Hz, 1H; CH_2=C**H**), 6.39 (dd, ^2J(H,H) = 1.6 Hz, ^3J(H,H) = 10.3 Hz, 1H; CH=C**H**$_2$). ^{13}C NMR (63 MHz, $CDCl_3$, δ, ppm): 29.0 (2×CH_3), 34.8 (2×CH_3), 43.9 (2×CH_2), 51.4 (2×C_q), 69.0 (CH—O), 129.0 (CH_2=**C**H), 130.3 (**C**H_2=CH), 165.7 (COOR). FTIR (ATR, cm^{-1}): 719 (m), 813 (s, γ(C=CH_2)), 981 (s), 972 (s), 1055 (vs, ν_{as}(OCC=O)), 1190 (m), 1278 (s, ν_{as}(CC=OO)), 1366 (m, δ_s(CH_3)), 1452 (w, δ(CH_2)), 1616 (m, ν(C=CH_2)), 1701 (vs, ν(C=O)), 2972 (m, ν(CH)), 3005 (m, ν(CH)), 3315 (w, ν(NH)). MS (EI, 70 eV) *m/z*: 107 (10), 124 (100), 196 (6), 211 (0.2, M^+). Anal. calcd. for $C_{12}H_{21}NO_2$: C, 68.21; H, 10.02; N, 6.63, found: C, 68.21; H, 10.16; N, 6.27.

4-(Methacryloyloxy)-2,2,6,6-tetramethylpiperidinium chloride (3)

To TMPMA (50 g, 0.22 mol) dissolved in ethanol (250 mL) hydrochloric acid (4.1 mol/L, 65 mL, 0.27 mol) were slowly added at room temperature. The solution was stirred for 1 hour, evaporated to dryness, and the product was dried at 80 °C (20 mbar) to give **3** (58 g, 99% yield).

^{1}H NMR (250 MHz, DMSO-d_6, δ, ppm): 1.45 (m, 12H; CH_3), 1.71 (m, 2H; CH_2), 1.86 (s, 3H; CH_2=C—C**H**$_3$), 2.02 (m, 2H; CH_2), 5.16 (m, 1H; CH—O), 5.70 (s, 1H; C=CH_2), 6.01 (s, 1H; C=CH_2), 8.55 (d, ^2J(H,H) = 11 Hz, 1H; NH_2), 9.35 (d, ^2J(H,H) = 11 Hz, 1H; NH_2). ^{13}C NMR (63 MHz, DMSO-d_6, δ, ppm): 18.3 (CH_2=C—**C**H_3), 25.7 (2×CH_3), 29.4 (2×CH_3), 39.5

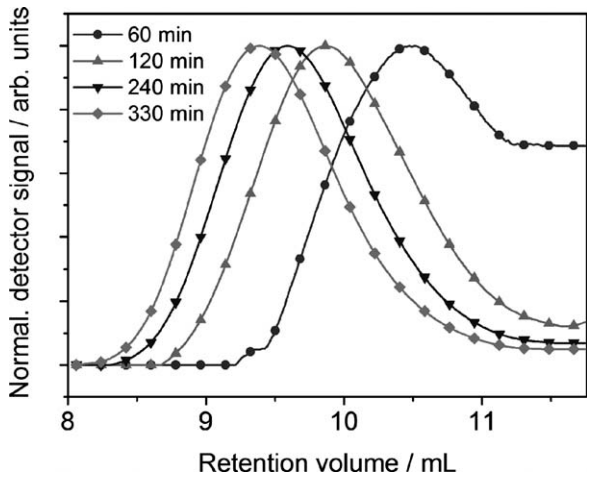


FIGURE 13 SEC traces (DMAc) of the kinetic study of the polymerization of the monomer TMPMA exhibiting an amine functionality via the RAFT technique using a trithiocarbonate type chain transfer agent (CTA 2).

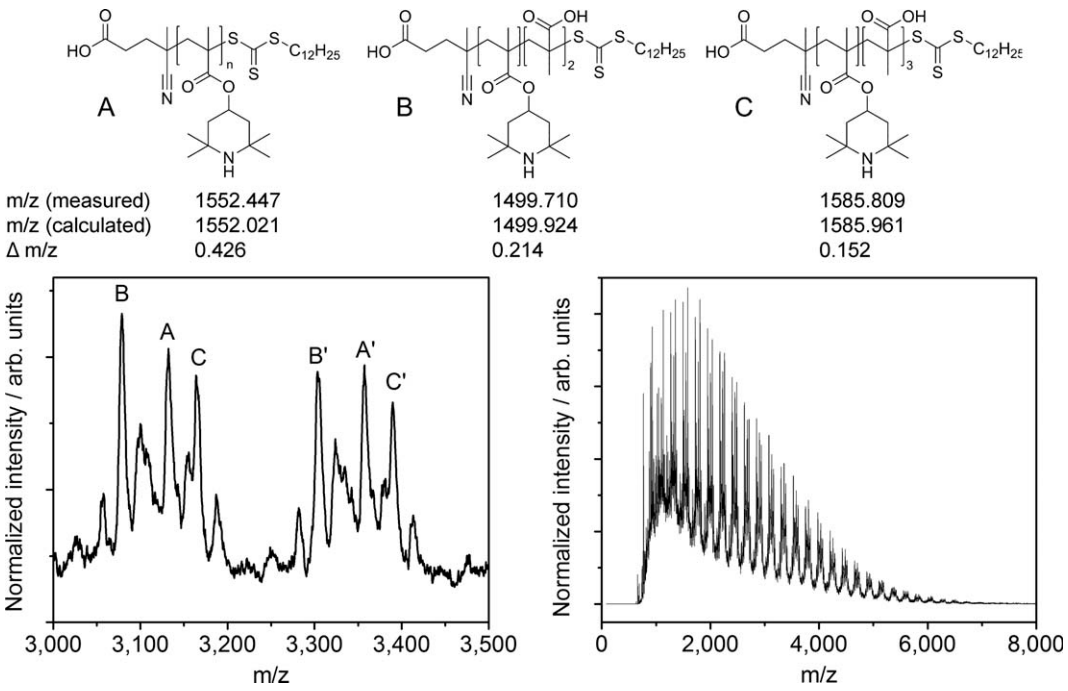


FIGURE 14 MALDI-TOF mass spectrum of the free secondary amine bearing polymer PTMA prepared via RAFT polymerization using a trithiocarbonate type chain transfer agent (CTA2); matrix: *trans*-3-indoleacrylic acid; linear mode (bottom) and assigned structures as well as *m/z* values for the exemplary structure $n = 5 + Na^+$ (top).

($2\times C_q$), 56.9 ($2\times CH_2$), 66.23 (CH—O), 126.6 (C=$\mathbf{C}H_2$), 136.2 (ROOC—**C**=C), 166.2 (COOR). FTIR (ATR, cm^{-1}): 661 (s), 929 (m), 1016 (s), 1047 (s, $\gamma(C{=}CH_2)$), 1170 (vs, ν_{as}(O-CC=O)), 1219 (s, ν_{as}(CC=OO)), 1390 (m, $\delta_s(CH_3)$), 1442 (w, $\delta(CH_2)$), 1587 (m, $\nu(C{=}CH_2)$), 1705 (vs, $\nu(C{=}O)$), 2465 (m), 2592 (m), 2738 (bs), 2943 (bs, $\nu(CH)$), 3020 (m, $\nu(CH)$), 3171 (m, $\nu(NH)$). Anal. calcd. for $C_{13}H_{24}ClNO_2$: C, 59.64; H, 9.24; N, 5.35; Cl, 13.54; found: C, 59.33; H, 9.28; N, 5.24; Cl, 13.76.

Polymerization

The polymerizations were carried out in sealed microwave vials under nitrogen atmosphere. Solutions were degassed by bubbling with nitrogen for 30 minutes. Samples for ^{1}H-NMR spectroscopy, GC, and SEC measurements were taken under inert conditions via a microliter syringe. Oxidation of the precursor polymer **PTMA** was generally carried out in methanol with hydrogen peroxide catalyzed by Na_2WO_4.

Free Radical Polymerization

4-(Methacryloyloxy)-2,2,6,6-tetramethylpiperidinium chloride (58.0 g, 0.22 mol) were dissolved in a mixture of ethanol (90 mL) and water (90 mL). After degassing the solution with argon 2,2′-azobis(2-methyl-propionamidine) dihydrochloride (2.0 g, 7.3 mmol) were added and the mixture was stirred for 3 hours at 50 °C. The viscous solution was diluted with ethanol (300 mL) and added dropwise to a vigorously stirred mixture of chloroform (500 mL) and aqueous sodium hydroxide (500 mL, 1.25 mol/L). The mixture was stirred for 15 hours, the organic layer was subsequently separated and washed with water (500 mL) as well as brine (500 mL). Precipitation in hexane (2000 mL) yielded 49.7 g PTMA (**P1**) as white powder, which was dried at 40 °C (20 mbar).

Oxidation. PTMA **P1** (25.0 g), disodium ethylenediamine tetraacetate (0.7 g, 1 mmol), and $Na_2WO_4\times 2H_2O$ (0.4 g, 1.5 mmol) were dissolved in methanol (250 mL). Hydrogen peroxide (150 mL) were added portion wise (40 mL) every 10 hours and the mixture was stirred at room temparatur for a total of 48 hours. A red precipitate formed, which was separated and washed thoroughly with water (300 mL) and methanol (300 mL). Upon drying at 40 °C (20 mbar) 24.0 g PTMA-NO (**P1ox**) were obtained.

ATRP. The required amount of copper(I)-bromide, ligand, and half of the required amount of toluene were placed in a microwave vial. In a second vial, **(1)** and the initiator ethyl 2-bromoisobutyrate were dissolved in the other half amount of toluene, required to reach the desired concentration of 1 mol/L. After transferring the degassed monomer/initiator solution to the catalyst solution, the reaction mixture was placed in an oil bath (90 °C).

RAFT. Two stock solutions, one of the chain transfer agent 2-cyano-2-butyl dithiobenzoate (CTA 1) or 4-cyano-4-(dodecylsulfanylthiocarbonyl)sulfanyl pentanoic acid (CTA 2) and the other one of the initiator 2,2′-azobis(2-methyl-propionamidine) dihydrochloride, were prepared in 1 mL ethanol/water (3:1). To **(1)** an ethanol/water (3:1) mixture was added in a microwave vial to reach the desired concentration of 1 mol/L. After the addition of the required amount of initiator and CTA solution (momomer/initator/CTA ratio 80:1:4), the vial was salad, degassed, and placed in an oil bath (60 °C).

NMP. Procedure I: 0.15 g of **(1)** or **(2)** and BlocBuilder™ (ratio 100:1) were placed in a microwave vial. After the addition of anisole (1 mol/L), the vial was sealed, degassed, and placed in an oil bath (90 or 120 °C). Procedure II: 0.15 g of **(1)** or **(2)**, BlocBuilder™ (ratio 100:1), and SG-1 free radical (0.1% related to BlocBuilder™) were placed in a microwave vial. After the addition of anisole (1 mol/L), the vial was sealed, degassed, and placed in an oil bath pre-heated at 120 °C. Procedure III: BlocBuilder™ (ratio 100:1) was dissolved in anisole and placed in a sealed microwave vial. In a second microwave vial, 0.15 g of **(2)** was dissolved in anisole (1 mol/L). Subsequently, the degassed BlocBuilder™ solution was placed in an oil bath preheated to 60 °C. After 40 minutes the temperature was raised to 120 °C and the degassed solution of **(2)** was transferred to the pre-heated BlocBuilder™ solution.

Analytical Data of the Printed Polymers. P1: SEC (DMAc, PS-standard): $M_n > 300{,}000$ g/mol (exclusion limit of the SEC column). SEC (THF/NEt_3, univ. calibration): $M_n = 60{,}000$ g/mol. ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 0.65–1.55 (17H), 1.60–2.40 (4H), 5.06 (1H). FTIR (ATR, cm^{-1}): 970 (m), 1152 (vs, ν_{as}(OCC=O)), 1236 (s, ν_{as}(CC=OO)), 1377 (m, $\delta_s(CH_3)$), 1456 (m, $\delta(CH_2)$), 1718 (vs, ν(C=O)), 2960 (m, ν(CH)), 3332 (m), 3427 (m, ν(NH)). Anal. calcd. for repeating unit: C, 69.29; H, 10.29; N, 6.22; found: C, 68.17; H, 10.36; N, 6.33. $T_g = 143$ °C.

P1ox: SEC (DMAc, PS-standard): $M_n > 300{,}000$ g/mol (exclusion limit of the SEC column; only soluble portion of polymer tested). FTIR (ATR, cm^{-1}): = 966 (w), 1141 (vs, ν_{as}(O-CC=O)), 1238 (m, ν_{as}(CC=OO)), 1364 (m, ν(N—O)), 1463 (m, $\delta(CH_2)$), 1724 (s, ν(C=O)), 2974 (m, ν(CH)). Anal. calcd. for repeating unit: C, 64.97; H, 9.23; N, 5.83; found: C, 64.62; H, 9.49; N, 5.51. ESR: $g = 2.0062$, $N_s = 4.02 \times 10^{21}$ g^{-1}. $T_g = 168$ °C.

P4: ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 0.65-1.55 (17H), 1.60-2.40 (4H), 5.06 (1H). SEC (DMAc, PS-standard): $M_n = 33{,}900$ g/mol; $M_w = 38{,}800$ g/mol; PDI = 1.14. FR-IR (ATR, cm^{-1}): 970 (m), 1148 (vs, ν_{as}(OCC=O)), 1238 (s, ν_{as}(CC=OO)), 1377 (m, $\delta_s(CH_3)$), 1460 (m, $\delta(CH_2)$), 1720 (vs, ν(C=O)), 2956 (m, ν(CH)). Anal. calcd. for repeating unit and bromine end-group: C, 67.93; H, 10.08; N, 6.09; Br, 1.56; found: C, 67.74; H, 10.08; N, 6.06; Br, 1.51. $T_g = 113$ °C.

P4ox: SEC (DMAc, PS-standard): $M_n = 26{,}300$ g/mol; $M_w = 34{,}700$ g/mol; PDI = 1.31. FTIR (ATR, cm^{-1}): 964 (w), 1144 (vs, ν_{as}(OCC=O)), 1232 (m, ν_{as}(CC=OO)), 1364 (m, ν(N—O)), 1464 (m, $\delta(CH_2)$), 1724 (s, ν(C=O)), 2974 (m, ν(CH)). Anal. calcd. for repeating unit and bromine end-group: C, 57.75; H, 8.20; N, 5.18; found: C, 57.36; H, 8.51; N, 5.10. ESR: $g = 2.0064$, $N_s = 1.09 \times 10^{21}$ g^{-1}. $T_g = 162$ °C.

P6: SEC (DMAc, PS-standard): $M_n = 24{,}500$ g/mol; $M_w = 29{,}100$ g/mol; PDI = 1.18. Vapor pressure osmometry ($CHCl_3$): $M_n = 5720$ g/mol. ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 0.65-1.55 (17H), 1.60-2.30 (4H), 5.06 (1H). FTIR (ATR, cm^{-1}): 970 (m), 1147 (vs, ν_{as}(OCC=O)), 1238 (s, ν_{as}(CC=OO)), 1377 (m, $\delta_s(CH_3)$), 1460 (m, $\delta(CH_2)$), 1720 (vs, ν(C=O)), 2956 (m, ν(CH)). Anal. Calcd. for repeating unit without endgroups: C, 69.29; H, 10.29; N, 6.22; found: C, 69.06; H, 10.47; N, 6.16. $T_g = 128$ °C.

P6ox: SEC (DMAc, PS-standard): $M_n = 16{,}100$ g/mol; $M_w = 18{,}400$ g/mol; PDI = 1.15. Vapor pressure osmometry ($CHCl_3$): $M_n = 5960$ g/mol. FTIR (ATR, cm^{-1}): 966 (w), 1145 (vs, ν_{as}(OCC=O)), 1232 (m, ν_{as}(CC=OO)), 1364 (m, ν(N—O)), 1463 (m, $\delta(CH_2)$), 1724 (s, ν(C=O)), 2970 (m, ν(CH)). Anal. Calcd. for for repeating unit without endgroups: C, 64.97; H, 9.23; N, 5.83; found: C, 64.03; H, 8.42; N, 5.49. ESR: $g = 2.0064$, $N_s = 1.61 \times 10^{21}$ g^{-1}. $T_g = 160$ °C.

Instrumentation

Size exclusion chromatography (SEC) was used to determine the molar masses and polydispersity indices of the polymer samples with respect to polystyrene standards. Either an Agilent 1200 series system (degasser: Polymer Standard Service Mainz, pump: G1310A, auto sampler: G1329A, oven: Techlab, diode array detector: G1315D, RI detector: G1362A) using a pC/PSS GRAM 1000/30 Å column and dimethylacetamide (+0.21% lithium chloride) as eluent at a flow rate of 1 mL/min (40 °C) or a Shimadzu system (controller: SCL-10A VP, degasser: DGU-14A, pump: LC-10AD VP, auto sampler: SIL-10AD VP, oven: Techlab, UV detector: SPD-10AD VP, RI detector: RID-10A) using a PSS SDV pre/lin S column and chloroform/*iso*-propanol/triethyl-amine [94:2:4] as eluent at a flow rate of 1 mL/min (40 °C). Absolute molar masses were determined on a Shimadzu system (controller: SCL-10A VP, degasser: DGU-14A, pump: LC-10AD VP, auto sampler: SIL-10AD VP, oven: CTO-10A VP, detectors: UVD: SPD-10AD VP, RID: RID-10A, Visco: PSS ETA-2010, MALS: PSS SLD 7000 (BIC) at $\lambda = 635$ nm) using a PSS SDV pre/10^4/10^2 Å column and tetrahydrofurane as eluent at a flow rate of 1 mL/min (40 °C). Vapor pressure osmometry was measured on a Knauer vapor pressure osmometer (K 7000) using chloroform solutions (temperature: 30 °C). Conversion was determined by gas chromatography on a Shimadzu GC-2010 (carrier gas helium; flame ionization detector with hydrogen and air as detector gases; Restek Rtx-5 column, 30 m length, 0.25 mm ID, 0.25 μm film thickness, 5% diphenyl polysiloxane 95% dimethyl polysiloxane). NMR spectra were obtained on a Bruker AC 300 spectrometer. The MALDI-TOF MS spectra were measured on an Ultraflex III TOF/TOF (Bruker Daltonics GmbH) equipped with a Nd:YAG laser and a collision cell. All spectra were measured in the positive reflector or linear mode using 2,5-dihydroxy benzoic acid (DHB) or α-cyano-4-hydroxycinnamic acid (CHCA) as matrix. Elementary analysis was performed using a λ EuroVector EuroEA3000 instrument. The inkjet printing experiments were carried out on an Autodrop system (Microdrop Technologies). The printer was equipped with a piezo-based printhead (micropipette system AD-K-501). The inner diameter of the used nozzle was 70 μm. Voltages between 60 and 70 V and pulse lengths between 40 and 50 μs were found as typical print settings to create stable droplets for all tested polymers. Surface topography as well as film thicknesses were measured using an optical interferometric profiler Wyko NT9100 (Veeco, Mannheim, Germany). Electrochemical measurements were performed on an Autolab PGSTAT30 model potentiostat. For

cyclic voltammetry a standard three-electrode configuration, using a platinum-disk working electrode, a platinum-rod auxiliary electrode, and an Ag/AgCl reference electrode. The experiments were carried out in acetonitrile and dichloromethane containing tetra-*n*-butylammonium hexafluorophosphate (0.1 mol/L) and using several scan rates. At the end of each measurement ferrocene was added as an internal standard. Spin concentrations were determined on a X-Band ESR spectrometer (Bruker) using copper bromide as internal standard.

CONCLUSIONS

RAFT polymerization represents the most suitable technique to prepare well-defined, PTMA. Both, the hydrochloride of the monomer TMPMA and even the free secondary amine bearing monomer itself can be polymerized in a controlled manner. Aminolysis of the chain transfer agent, which commonly renders the RAFT polymerization of primary and secondary amines impossible, is no issue in the polymerization of TMPMA. This extraordinary behavior can be attributed to the steric hindrance of the amine functionality as well as stabilizing solvent effects. Opposite to ATRP and NMP, which both show major drawbacks, the RAFT technique enables a practical and fast access to precursor polymers required to produce TEMPO free radical bearing polymers of excellent solubility. This readily allows the preparation of tailor-made polymer-films of defined thickness and shape by means of inkjet printing. Considering the electrochemical and catalytic properties of TEMPO functionalized polymers, the use of these films as printed electrodes for organic radical batteries or as catalytically active layer in a chemical reactor represents promising potential application.

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