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RAFT Polymerization of 1-Ethoxyethyl Acrylate: A Novel Route toward Near-Monodisperse Poly(acrylic acid) and Derived Block Copolymer Structures

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ABSTRACT: The reversible addition fragmentation chain transfer (RAFT) polymerization of 1-ethoxyethyl acrylate (EEA) was demonstrated. Temperature optimization revealed an optimum polymerization temperature of 70 °C. Deprotection of the p(EEA) could be performed by a simple heating step, under mild conditions leading to well-defined poly(acrylic acid) (p(AA)) and under more severe conditions resulting in cross-linked networks of p(AA). In addition, block copolymers with a poly(methyl acrylate), a poly(*n*-butyl acrylate), a poly(methyl methacrylate), or a poly(*N,N*-(dimethylamino)ethyl methacrylate) first block and a p(EEA) second block were successfully synthesized by RAFT polymerization in toluene as was demonstrated by GPC and ^{1}H NMR characterization. For all these experiments, a high-throughput workflow procedure was used. Deprotection of the p(EEA) containing block copolymers was also performed, resulting in well-defined p(AA) containing materials as evidenced by both GPC and ^{1}H NMR spectroscopy.

Introduction

Block copolymers are of main scientific interest due to their phase separation[1−3] and solution aggregation[4−7] behavior. To obtain significant phase separation, the combined polymer segments need to have different properties. Therefore, amphiphilic block copolymers are often used since the difference between the hydrophobic and hydrophilic blocks leads to demixing of the polymer chains and thus to a nanoscopic phase separation. Moreover, amphiphilic block copolymers are known to self-assemble in water to form a variety of micellar structures.[4−8] Poly(acrylic acid) (p(AA)) is a frequently used hydrophilic polymer in these amphiphilic block copolymers. To incorporate p(AA) in well-defined (block) copolymers, it has to be synthesized via a controlled polymerization technique.[9] So far, unprotected acrylic acid (AA) has been polymerized successfully utilizing reversible addition fragmentation chain transfer (RAFT) polymerization[10,11] and nitroxide mediated polymerization (NMP)[12,13] techniques. In addition, the sodium salt of acrylic acid has been polymerized with atom transfer radical polymerization (ATRP).[14] Even though it is possible to directly polymerize acrylic acid, the applied polymerization solvents need to be polar implying that block copolymers with a variety of apolar monomers cannot be synthesized in a straightforward manner. To overcome this solvent incompatibility, the protected analogues *tert*-butyl acrylate[15,16] and benzyl acrylate[17] are often used followed by a deprotection step.[9] However, these strategies include postpolymerization deprotection and subsequent purification of the p(AA). To avoid these steps, ATRP of 1-ethoxyethyl acrylate (EEA) was recently reported.[18] The applied protecting 1-ethoxyethyl group could be easily removed by thermolysis preventing the need of an additional purification step after deprotection. However, the applied copper(I) mediated ATRP is quite sensitive to residual acrylic acid that is able to coordinate the copper(I) ions and protonate the nitrogen ligands, leading to an uncontrolled polymerization.[19] Therefore, the EEA has to be stringently purified and the polymerization process has to be performed at moderate temperatures to prevent deprotection of the monomer during the polymerization reaction.

In this contribution, RAFT polymerization of EEA is described for the first time. RAFT polymerizations are insensitive to acid groups making the monomer purification less critical. Moreover, partial deprotection of the monomer does not influence the RAFT polymerization allowing higher polymerization temperatures when compared to ATRP. The current investigations were performed utilizing a high-throughput workflow that was previously applied for the temperature optimization of RAFT polymerization processes[20] (for recent reviews on combinatorial and high-throughput experimentation in polymer science see, e.g., refs 21−23). In addition, different deprotection methods of the resulting p(EEA) will be discussed leading to well-defined p(AA)s or to cross-linked p(AA)s. To end with, the possibility of synthesizing block copolymers containing a p(EEA) segment via RAFT polymerizations in an apolar solvent will be demonstrated for a variety of structures.

Experimental Part

Materials. Methyl acrylate (MA), *n*-butyl acrylate (*n*-BA), methyl methacrylate (MMA), and *N,N*-(dimethylamino)ethyl methacylate (DMAEMA, all obtained from Aldrich) were purified by passing over a basic aluminum oxide filtration

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column. 1-Ethoxyethyl acrylate (EEA) was prepared as described in the literature.[18] Azobis(isobutyronitrile) (AIBN, Aldrich) was recrystallized from methanol. 2-Cyano-2-butyl dithiobenzoate (CBDB) was prepared according to a literature procedure for a related compound.[24] Analytical grade solvents were purchased from Biosolve Ltd. All solutions were deoxygenated by purging with argon gas prior to use.

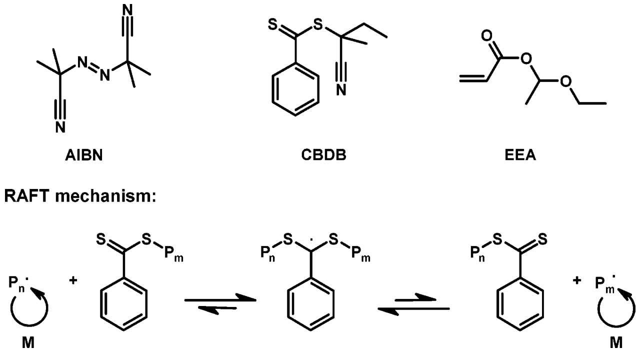
Instrumentation. Polymerizations were performed on a Chemspeed Accelerator SLT100 automated synthesizer. This synthesis robot was equipped with a four needle head, a solid dosing unit, and an array of 16 parallel 13 mL glass reactors. The reactors could be heated by a Huber Unistat Tango (heating range: −40 to +145 °C) via their double jackets. The temperature optimization was performed with an array of individually heatable reactors. In this array, each reactor has a separate ceramic heating mantle and an internal temperature sensor providing the possibility to perform 16 parallel reactions at 16 different temperatures (ambient temperature to 230 °C). Moreover, the reactors were equipped with a coldfinger reflux condenser that could be cooled or heated from −5 up to +50 °C. An inert atmosphere was maintained by applying a 1.1 bar flow over the reactors and a 1.5 bar argon flow through the hood of the Accelerator.[25]

Gel permeation chromatography (GPC) of p(EEA) and the copolymers was measured on a Shimadzu system equipped with a SCK-10A system controller, a LC-10AD pump, a RID-10A refractive index detector and a PL gel 5 μm Mixed-D column at 50 °C utilizing a chloroform/triethylamine/2-propanol (94/4/2) mixture as eluent at a flow rate of 1 mL·min^{-1}. GPC characterization of the p(AA) samples was performed on a Waters system with a 1515 pump, a 2414 refractive index detector and a Waters Styragel HT4 column utilizing *N*,*N*-dimethylformamide with 5×10^{-3} M NH_4PF_6 as eluent at a flow rate of 0.5 mL·min^{-1} at 50 °C. The molecular weights were calculated on the basis of poly(methyl methacrylate) standards. ^{1}H NMR spectra were recorded on a Varian Mercury 400 spectrometer or a Varian Gemini 300 spectrometer. Chemical shifts are given in ppm relative to TMS or solvent signals. Thermogravimetric analyses were performed utilizing a Netsch TG 209 F1 Iris apparatus.

Parallel Temperature Optimization. To obtain an inert atmosphere, the hood of the Accelerator was flushed for at least 90 min with argon before starting the polymerization procedure. An inert atmosphere was created inside the individually heatable reaction vessels by performing three cycles of heating (120 °C) under vacuum (15 min at ~ 25 mbar) followed by argon flushing (1 min). During the polymerizations, the temperature of the coldfinger reflux condensers was set to −5 °C. 1-Ethoxyethyl acrylate (1.360 g; 9.34 mmol) and stock solutions of AIBN (1.450 mL; 0.016 M) and CBDB in toluene (1.450 mL; 0.065 M) were dispensed into the reaction vessels resulting in 4.2 mL reaction mixtures with EEA/RAFT/initiator = 100/1/0.25 and 2.2 M monomer concentration. The mixtures were heated (50, 60, 70, 80, 90, 100 °C; each temperature twice) and vortexed at 600 rpm for 15 h, whereby samples (100 μL aliquots) were taken from each reactor to 2.0 mL vials prefilled with GPC eluent (1.0 mL; chloroform/triethylamine/2-propanol) at 2, 4, 6, 8, 10, and 15 h polymerization time. These samples were used for GPC analysis.

Block Copolymerizations. The block copolymerizations were performed in a similar manner utilizing an array of 16 parallel 13 mL reactors with a double jacket for heating. After creating an inert atmosphere in the hood and the reaction vessels, the monomers (MA, *n*-BA, MMA, and DMAEMA), stock solutions of AIBN and CBDB in toluene and toluene were dispensed into the reactors resulting in 1.5 mL polymerization mixtures with a monomer/RAFT/initiator ratio of 25/1/0.25 and a monomer concentration of 2.2 M. Four separate polymerizations were performed for each monomer. After 3 h polymerization time, samples (100 μL aliquots) were taken from each reactor to 2.0 mL vials prefilled with GPC eluent (1.0 mL; chloroform/triethylamine/2-propanol). Subsequently, the second monomer (EEA) was added to the reaction vessels. For each first monomer, four different amounts of EEA (470, 940, 1410, or 1880 μL) were added to the four separate reactions resulting in a theoretical amount for full conversion of 25, 50, 75, or 100 units EEA and the polymerizations were continued for 12 h.

Scheme 1. Reagents (Top) and Mechanism (Bottom) for the Investigated RAFT Polymerization of 1-Ethoxyethyl Acrylate (EEA) with Azobis(isobutyronitrile) (AIBN) as Initiator and 2-Cyano-2-butyl Dithiobenzoate (CBDB) as RAFT Agent



Results and Discussion

The reversible addition fragmentation chain transfer (RAFT) polymerization of 1-ethoxyethyl acrylate (EEA) with azoisobutyronitrile (AIBN) as initiator and 2-cyano-2-butyl dithiobenzoate (CBDB) as RAFT agent (see Scheme 1, top) was investigated in toluene. The control over the radical polymerization is achieved by establishing an equilibrium between a dormant polymeric RAFT agent and the free polymeric radicals as depicted in Scheme 1 (bottom). This equilibrium controls the amount of free radicals present and thus determines the polymerization speed and, even more important, it determines the probability of chain termination and chain transfer reactions. When appropriate reaction conditions are applied, chain termination is reduced to a minimum resulting in a controlled radical polymerization in which all polymer chains have a (dormant) radical chain end. As a result, all polymer chains will grow with similar rates resulting in a narrow molecular weight distribution. Moreover, the controlled polymerization method allows the synthesis of well-defined random, gradient, and block copolymers.[26–28]

Recent investigations revealed an optimal RAFT to initiator ratio of 1:0.25 for the polymerization of methyl methacrylate (MMA) utilizing CBDB as RAFT agent and AIBN as initiator in toluene.[20] This ratio was found to be the optimum regarding both control and speed of the polymerization. Therefore, the current investigations on the RAFT polymerization of EEA with CBDB and AIBN in toluene were all conducted at this optimal RAFT to initiator ratio of 1:0.25 aiming for a degree of polymerization of 100 units. The polymerizations were performed in parallel utilizing a Chemspeed Accelerator SLT100 synthesis robot equipped with an array of individually heatable reactors. During the polymerization run, six polymerization temperatures (50, 60, 70, 80, 90, and 100 °C) were investigated. In addition, for each temperature, two experiments were performed to verify the reproducibility of the polymerization reactions. During the polymerization processes, samples were taken at 2, 4, 6, 8, 10, and 15 h to investigate the development of the molecular weight as a function of time by gel permeation chromatography (GPC). The conversion as a function of time was not investigated during this screening since the objective was to inves-

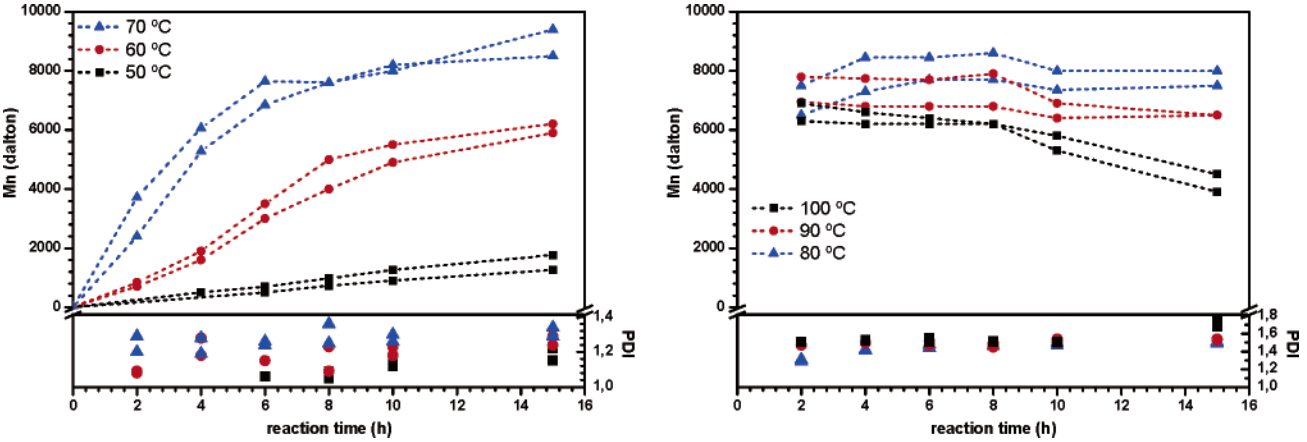


Figure 1. Development of the number-average molecular weight (M_n) and molecular weight distribution (PDI) as a function of time for the RAFT polymerizations of EEA at 50, 60, and 70 °C (left) and 80, 90, and 100 °C (right). The results of two experiments are shown for each polymerization temperature. GPC eluent: $CHCl_3$:NEt_3:*i*-PrOH.

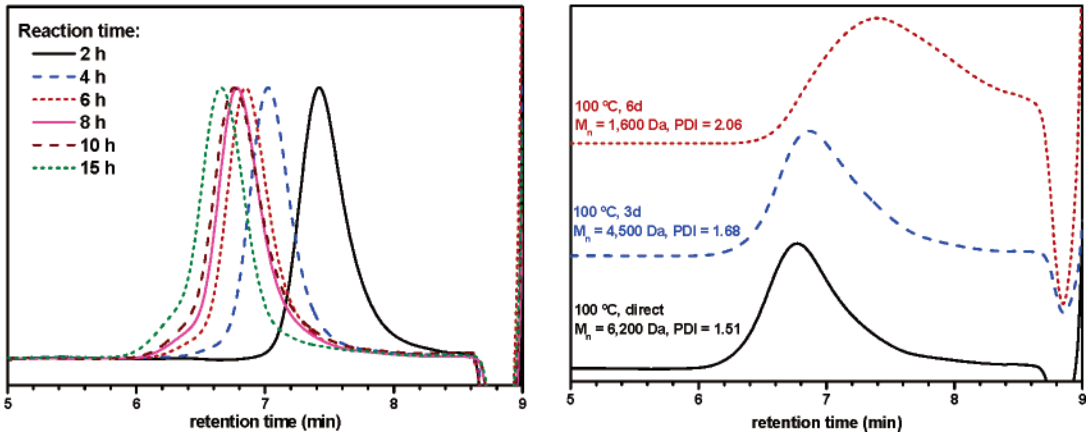


Figure 2. Left: GPC traces of the RAFT polymerization of EEA at 70 °C. Right: GPC traces of the end-sample obtained from the EEA polymerization at 100 °C demonstrating the broadening of the signal upon deprotection in time in the GPC eluent. GPC eluent: $CHCl_3$:NEt_3:*i*-PrOH.

tigate the feasibility of the RAFT polymerization to obtain well-defined p(EEA). Moreover, measuring the conversion by gas chromatography (GC) or by gravimetrical analysis would lead to misleading results due to the thermal degradation of both monomer and polymer while conversion determination by ^{1}H NMR spectroscopy would result in a serious bottleneck in the present high-throughput workflow. The plots of the number-average molecular weight (M_n) as a function of time demonstrate the good reproducibility of the RAFT polymerizations of EEA (Figure 1). The polymerizations at 50, 60, and 70 °C showed a clear increase of M_n against time, whereby the polydispersity indices (PDI's) remained at values below 1.3. Figure 2, left, depicts the GPC-traces obtained for one of the polymerizations at 70 °C demonstrating the increase of molecular weight as a function of time. Note that a small shoulder at the higher molecular weight side appears with higher conversion suggesting the occurrence of chain termination by radical coupling. In contrast to the polymerizations at 50, 60, and 70 °C, the polymerizations at 80, 90, and 100 °C did not reveal an increase of molecular weight as a function of polymerization time, because relatively high conversions were already reached within the first 2 h.

All obtained final M_n's are lower than the theoretical values ($M_{n,th}$ = 14 700 for 100% monomer conversion), which might be partially due to the p(MMA) standards used for calibrating the GPC system and which is also due to incomplete conversion, as determined by ^{1}H NMR spectroscopy for the final samples (reaction time = 15 h): T = 50 °C, 19%; T = 60 °C, 55%; T = 70 °C, 82%; T = 80 °C, 94%; T = 90 °C, 94%; T = 100 °C, 83%. Moreover, both molecular weight and PDI values are influenced by (partial) deprotection of the p(EEA). This deprotection can not only occur during synthesis but also in the GPC eluent. Interactions of the acid with the column material cannot be avoided (utilizing chloroform as eluent) resulting in longer retention times, lower apparent molecular weights, and tailing of the signals. This effect is clearly demonstrated in Figure 2 (right), showing the GPC traces of the final polymer obtained at 100 °C directly after synthesis, after 3 days and after 6 days storage in the GPC eluent. As a result, the decrease of M_n in time for the polymerizations performed at 80, 90, and 100 °C can be attributed to partial deprotection (see Figure 1, right). From this temperature screening, it can be concluded that 70 °C is the optimal temperature for the RAFT polymerization of EEA, providing a good balance between reaction speed and control over the polymerization without significant deprotection during the polymerization reaction.

Deprotection of p(EEA) can be performed to obtain near-monodisperse poly(acrylic acid) (p(AA)). Different ways of deprotection resulting in linear or, if so desired, cross-linked p(AA) were investigated. The first method of deprotection was already shortly mentioned in the

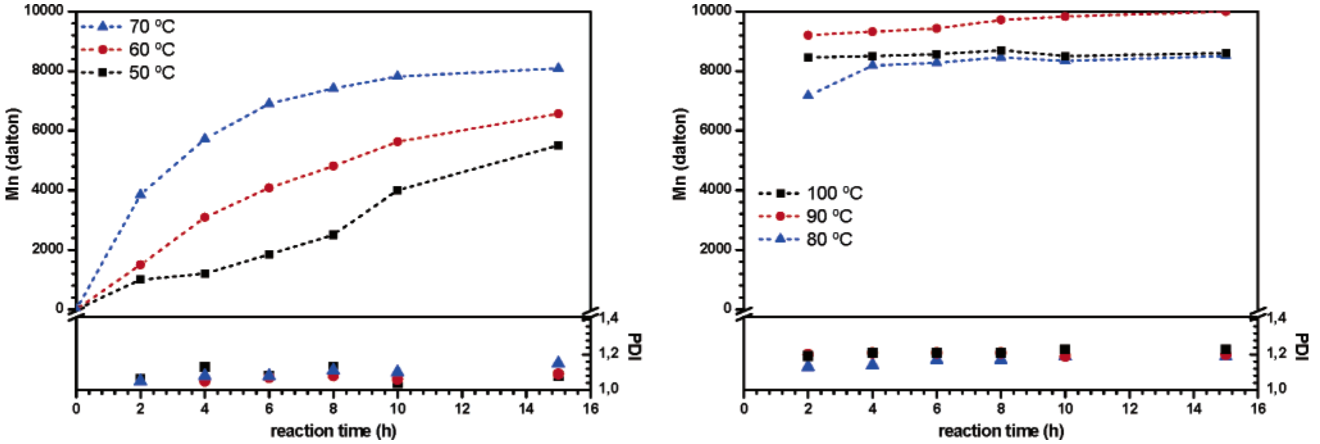


Figure 3. Number-average molecular weights (M_n) and molecular weight distributions (PDI) of p(AA) obtained after deprotection of the samples taken during the RAFT polymerizations of EEA at 50, 60, and 70 °C (left) and 80, 90, and 100 °C (right). GPC eluent: DMF.

previous section by the change in GPC traces over time (Figure 2, right). All GPC samples (in the $CHCl_3$/NEt_3/*i*-PrOH eluent) from the temperature screening were kept at ambient temperature for 2 weeks during which the polymers precipitate, indicating that p(AA) was formed. The samples were more than 90% deprotected as determined by ^{1}H NMR spectroscopy for a few randomly chosen samples. GPC analysis of these p(AA) samples was performed utilizing DMF as eluent to suppress the interactions between the acid groups and the column material. The resulting plots of M_n as a function of time are depicted in Figure 3.

For all investigated temperatures an increase of M_n as a function of conversion is observed for the PAA samples, in contrary to the M_n's obtained with $CHCl_3$ as eluent. Moreover, narrow molecular weight distributions (PDI < 1.20) were obtained for all investigated samples proving the possibility of creating near-monodisperse p(AA) via RAFT polymerization of the protected EEA monomer. In addition, these results proof that the RAFT polymerizations at 80, 90, and 100 °C were also controlled, despite the fact that partial deprotection already took place during the polymerizations. The second method of deprotection, by a heating process or thermolysis, was previously demonstrated for poly(1-ethoxyethyl methacrylate) synthesized by ATRP.[18] Note that the results of the thermolysis strongly depend on the thermolysis conditions. At lower temperature, under conditions where anhydride formation of the p(AA) is prevented during the thermolysis, near-monodisperse p(AA) is formed, just as described above. At higher temperature and/or during longer periods of heating, anhydride formation occurs, resulting in cross-linked p(AA), as explained hereunder. The p(EEA) samples synthesized by RAFT were also deprotected by thermolysis at 160 °C for 3 h in a thermal gravimetrical analyzer under both oxygen and argon atmosphere. ^{1}H NMR spectroscopy revealed complete deprotection of the soluble part of the polymer and GPC characterization (Figure 4; GPC system with DMF as eluent) exposed a signal at 11 min corresponding to the exclusion limit of the utilized column representing a molecular weight exceeding 1 MDa. This high-molecular weight fraction can be interpreted as cross-linked p(AA) and the signal at 19.5 min, which is broadened due to partial cross-linking, corresponds with the p(EEA) obtained after mild deprotection. The thermolysis under oxygen atmosphere resulted in a higher content of cross-linked p(AA) than the thermolysis under nitrogen atmosphere. The cross-linking mechanism is believed to be anhydride formation with the loss of a water molecule as it was proposed earlier.[18,29] However, the cross-linking can be undone by stirring the cross-linked p(AA) in water.[29]

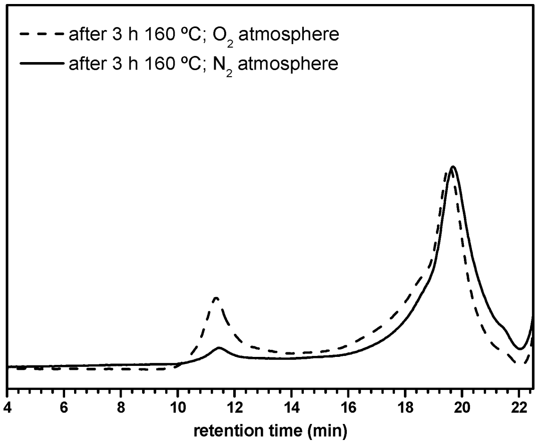


Figure 4. GPC traces after thermolysis (3 h at 160 °C) of p(EEA) indicating cross-linking of the resulting p(AA) by the signal at the exclusion limit of the GPC column (11 min; M_n > 1 MDa). GPC eluent: DMF.

In the previous sections, we have demonstrated the possibility to polymerize EEA in a controlled way utilizing the RAFT mechanism. The subsequent deprotection to well-defined p(AA) or cross-linked p(AA) was discussed as well. In a next step, the controlled synthesis of block copolymers containing a p(EEA) segment was investigated in an apolar solvent (toluene). In this way, block copolymers containing a p(AA) segment can be obtained via synthesis in an apolar solvent, which would be unattainable by the direct polymerization of AA. The block copolymerizations were performed at the optimal temperature of 70 °C. The synthesis robot was applied for the synthesis of 16 block copolymers consisting of 25 units of the first block composed of poly(methyl acrylate) (p(MA); experiments 1–4), poly(*n*-butyl acrylate) (p(*n*-BA); experiments 5–8), poly(methyl methacrylate) (p(MMA); experiments 9–12), or poly(*N*,*N*-(dimethylamino)ethyl methacrylate) (p(DMAEMA); experiments 13–16) and a second block of p(EEA) consisting of 25, 50, 75, or 100 units. The first blocks were polymerized for 3 h after which a sample was taken for GPC analysis. Subsequently, EEA was added and the polymerizations were continued for 12 h. The

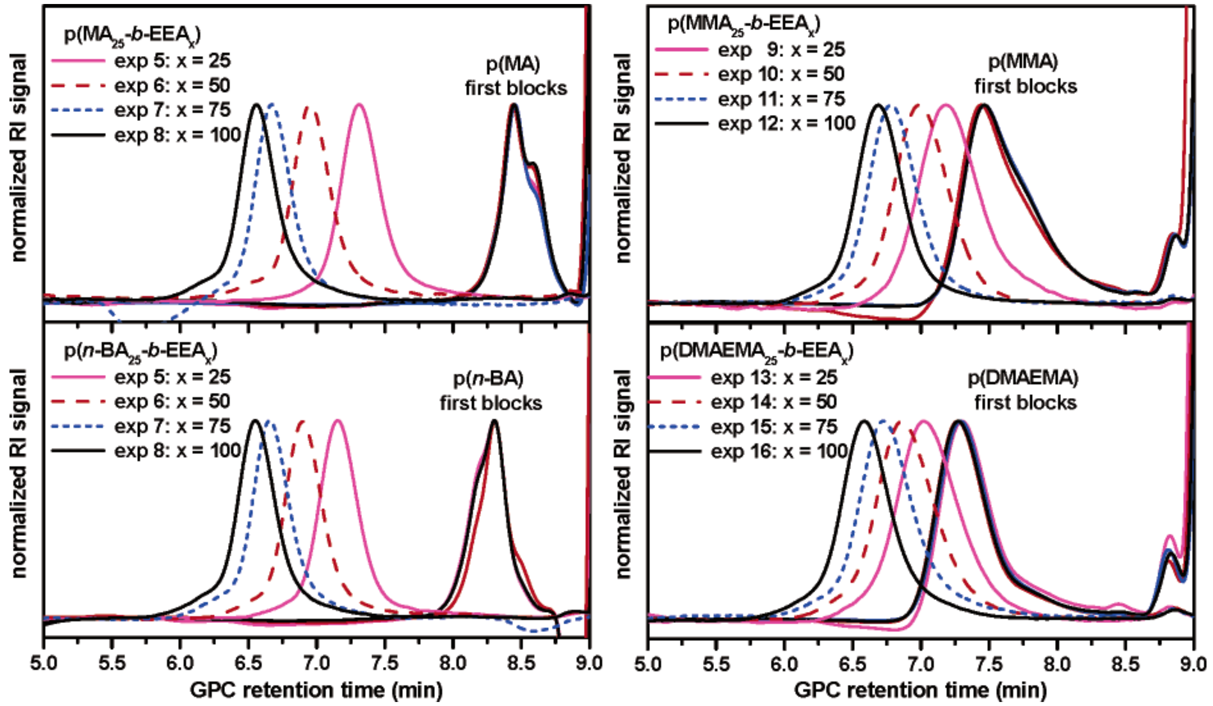


Figure 5. GPC traces of the first blocks and the final block copolymers consisting of a pMA (left top), p(n-BA) (bottom left), p(MMA) (top right) or p(DMAEMA) (bottom right) first block (25 units) and a p(EEA) (25, 50, 75, and 100 units for 100% conversion) second block. GPC eluent: $CHCl_3$:NEt_3:i-PrOH.

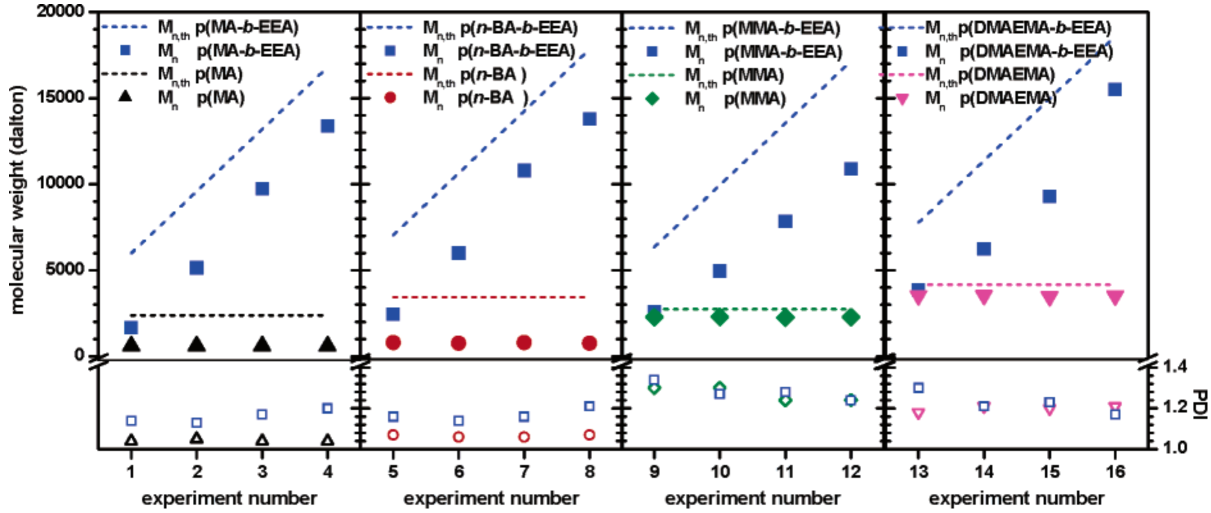


Figure 6. Number-average molecular weights (M_n) and molecular weight distributions (PDI) obtained for the first blocks and for the final block copolymers of p(MA), p(n-BA), p(MMA) or p(DMAEMA) (25 units) with p(EEA) (25, 50, 75, and 100 units for 100% conversion). All M_n values are calculated against p(MMA) standards. GPC eluent: $CHCl_3$:NEt_3:i-PrOH.

obtained GPC traces of both the first blocks and the final block copolymers are depicted in Figure 5.

The overlap of the first blocks demonstrates the good reproducibility of the RAFT polymerizations in the synthesis robots. Moreover, the final block copolymers show the expected shift toward higher molecular weights (lower retention times) with increasing number of EEA units. The GPC traces of the first blocks of p(MA) and p(n-BA) clearly reveal the existence of shoulders in the GPC traces. These shoulders are most likely due to the low conversions (~5 monomer units) resulting in incomplete equilibration between polymeric RAFT-agent and the free polymeric radicals. Figure 6 plots the M_n's and PDI values that were calculated (p(MMA) calibration) from the GPC traces of the first blocks and the resulting block copolymers, clearly demonstrating the ability to synthesize p(EEA) containing block copolymers.

The polymerizations with an acrylate monomer (MA or n-BA) as first block showed M_n's lower than the $M_{n,th}$ for the first block indicating insufficient reaction times. This is in agreement with recent investigations that showed incomplete (50%) conversion for the polymerization of MA utilizing similar conditions with a monomer to RAFT ratio of 100.[30] After addition of the EEA to the active centers of the first block, the polymerization was continued resulting in copolymers with a short first block of MA or n-BA and a random/gradient second block of MA and EEA or n-BA and EEA. The molecular weights of the resulting copolymers largely exceeded the $M_{n,th}$ of the first block demonstrating that indeed both the first monomer (MA or n-BA) and EEA were copo-

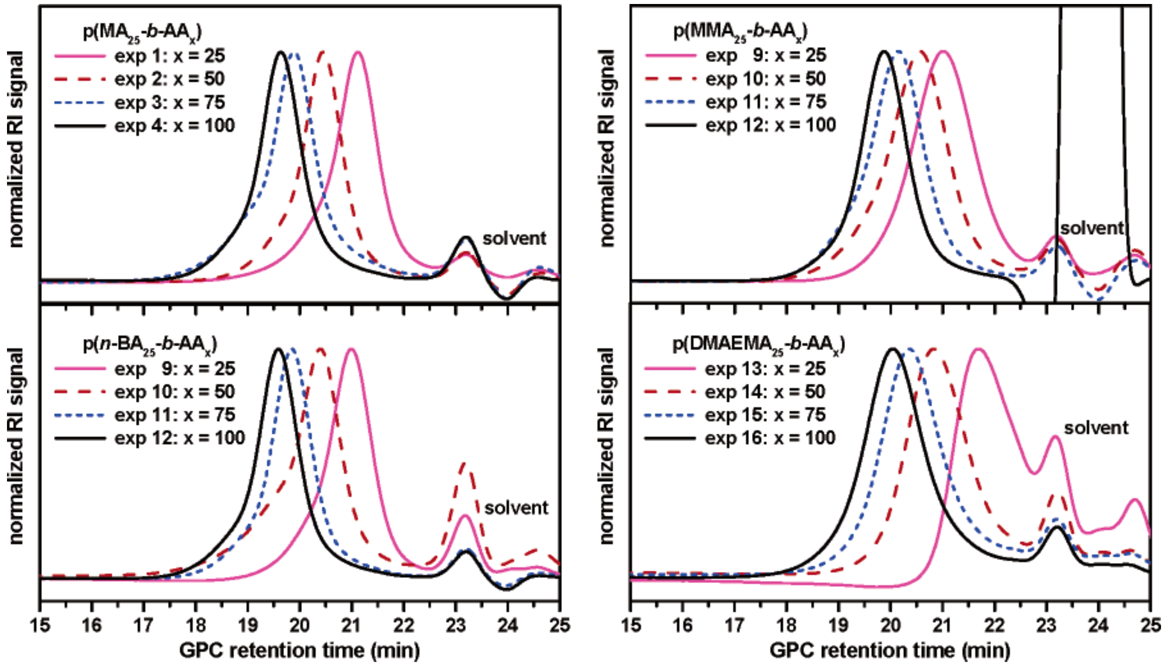


Figure 7. GPC traces of the p(MA-*b*-AA) (top left), p(*n*-BAA-*b*-AA) (bottom left), p(MMA-*b*-AA) (top right) and p(DMAEMA-*b*-AA) (bottom right) obtained by deprotection of the corresponding p(EEA) containing block copolymers. GPC eluent: DMF.

Table 1. Compositions of the Synthesized Block Copolymers As Determined by ^{1}H NMR Spectroscopy

expt no.	monomer A	$DP_{A,th}$	$DP_{EEA,th}$	$f_{EEA,th}$	$DP_{A,NMR}$	$DP_{EEA,NMR}$	$f_{EEA,NMR}$
1	MA	25	25	0.5	19	9	0.32
2	MA	25	50	0.67	17	22	0.56
3	MA	25	75	0.75	18	35	0.66
4	MA	25	100	0.8	20	52	0.72
5	*n*-BA	25	25	0.5	18	20	0.53
6	*n*-BA	25	50	0.67	18	44	0.71
7	*n*-BA	25	75	0.75	19	73	0.79
8	*n*-BA	25	100	0.8	22	87	0.80
9	MMA	25	25	0.5	23	6	0.21
10	MMA	25	50	0.67	23	12	0.34
11	MMA	25	75	0.75	23	20	0.47
12	MMA	25	100	0.8	23	32	0.58
13	DMAEMA	25	25	0.5	22	8	0.27
14	DMAEMA	25	50	0.67	22	20	0.48
15	DMAEMA	25	75	0.75	22	35	0.61
16	DMAEMA	25	100	0.8	22	51	0.70

lymerized. The molecular weights obtained for the methacrylate (MMA or DMAEMA) first blocks revealed a monomer conversion close to 100% as can be seen by the close resemblance with the theoretical molecular weights.[31] After addition of the second monomer EEA, the block copolymers were successfully synthesized as can be concluded from the GPC analysis. Also for these copolymerizations, the reaction times for the second blocks were insufficient resulting in lower molecular weights than theoretical, whereby it is noteworthy to mention that also the applied p(MMA) calibration could lead to lower observed molecular weights for the p(EEA) block. For all synthesized EEA containing copolymers, the molecular weight distributions were relatively narrow (PDI < 1.30) indicating good control over the block copolymerizations.

The composition of the resulting block copolymers was further determined by ^{1}H NMR spectroscopy (Table 1). The integral ratios of the CH_2 and/or CH_3 resonances next to the ester groups (MA, *n*-BA, MMA, DMAEMA: 3.65, 4.05, 3.60, or 4.10 ppm, respectively) or the ether bond (EEA: 3.50 and 3.72 ppm) in the polymers were used to determine the ratio of the two present monomers. For the p(MA) and p(MMA) containing copolymers, the integral of the CH resonance of EEA (5.90 ppm) was also used to calculate the monomer ratios, because the CH_3 resonances of MA and MMA overlapped with the CH_2 signals of EEA. Moreover, the integrals of the aromatic resonances of the RAFT agent were applied to calculate the number-average degree of polymerization (DP_n) for the monomers present in the block copolymers.

The ^{1}H NMR spectroscopy proved the successful incorporation of the EEA monomer in the block copolymers. Moreover, the NMR data confirmed the incomplete polymerization of the EEA second blocks as was already indicated by GPC characterization. The block copolymerizations with an acrylate monomer as first block seem to have a higher reactivity to the EEA, which is also an acrylate, than the polymerizations with a methacrylate first block. In addition, the p(*n*-BA) and p(DMAEMA) first blocks resulted in a higher degree of polymerization of EEA compared to the polymerizations with p(MA) and p(MMA) first blocks. The rationality behind these observations is not fully understood at this moment.

Deprotection of the p(EEA) containing block copolymers was performed by heating the $CDCl_3$ ^{1}H NMR solutions under pressure for 3 h to 80 °C in closed 2 mL vials. After 3 h, the block copolymer solutions with a high EEA content became cloudy indicating deprotection of the acrylic acid. ^{1}H NMR spectroscopy in DMSO-d_6 revealed 85−100% deprotection for a few randomly selected block copolymers. The GPC traces for the p(MA-*b*-AA), p(*n*-BA-*b*-AA), p(MMA-*b*-AA) and p(DMAEMA-*b*-AA) are depicted in Figure 7. The GPC analysis revealed monomodal distributions and low polydispersity indices (PDI < 1.20) for all block copolymers demonstrating successful deprotection resulting in well-defined p(AA) containing block copolymers. However, some of the GPC traces show slight shoulders at lower retention times (higher molecular weight) indicative of minor cross-linking reactions.

Conclusions

The successful polymerization of 1-ethoxyethyl acrylate via a RAFT polymerization process was demonstrated. Temperature optimization revealed an optimum polymerization temperature of 70 °C providing an optimal balance between control over the polymerization and reaction speed without significant deprotection. At lower temperatures, the polymerization proceeded very slowly, whereas deprotection was observed at higher temperatures. Deprotection of the p(EEA) was performed at ambient temperature by keeping it in chloroform solution for 2 weeks resulting in well-defined p(AA), as an alternative for thermolysis under mild conditions. Moreover, thermolysis under severe conditions (at 160 °C during 3 h) proved to be useful for the formation of cross-linked networks of p(AA), whereby thermolysis under oxygen atmosphere resulted in more cross-links than thermolysis under nitrogen atmosphere. In addition, the direct synthesis in toluene of block copolymer structures with an p(EEA) second block, without purification of the first block, was demonstrated. Block copolymerizations with acrylate (MA or *n*-BA) first blocks revealed very short first blocks (insufficient reaction times) and thus random/gradient type second blocks. When methacrylates (MMA or DMAEMA) were applied as monomers for the synthesis of the first blocks, the block copolymers were successfully synthesized without significant incorporation of the first monomer in the EEA block. Thermal deprotection of these block copolymers was performed at 80 °C resulting in the corresponding well-defined p(AA) containing block copolymers. The successful (co)polymerizations of EEA utilizing RAFT offer many possibilities for the straightforward synthesis of p(AA) containing copolymers without the need for polar solvents or labor-intensive deprotection steps.

The discussed investigations were all performed utilizing a high-throughput workflow equipped with synthesis robots and fast analysis equipment demonstrating the added value of such approaches in polymer research.

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