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Atom Transfer Radical Polymerization of 1-Ethoxyethyl (Meth)acrylate: Facile Route toward Near-Monodisperse Poly((meth)acrylic acid)

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Poly((meth)acrylic acid) polymers are of vast interest for a wide range of applications because of their pH-responsive nature and hydrophilic characteristics and for their interaction with metal ions.[1,2] Therefore, the ability to synthesize polymers containing (meth)acrylic acid units with control of chain architecture and molar mass is of great importance.

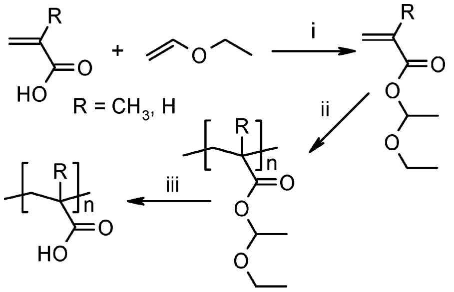
Traditional polymerization routes toward such polymers include living anionic[3] and group-transfer[4] polymerization techniques, both operating using protected analogues of the (meth)acrylic acid monomers.

More recently, living and controlled radical polymerization techniques have shown to be routes toward these materials.[2] Charleux et al. reported the first nitroxide-mediated controlled free-radical polymerization (NMP) of acrylic acid (AA).[5] Rizzardo was the first to describe the controlled polymerization of AA via reversible addition−fragmentation transfer (RAFT).[6] These two polymerization techniques, however, are from a synthetic point of view, not the most practical ones when it comes to the design of more complex polymer architectures, such as star, graft, and brush copolymers.

Atom transfer radical polymerization (ATRP), developed and refined by several research groups including the ones of Sawamoto,[7] Matyjaszewski,[8] Haddleton,[9] and others,[10,11] shows its advantage here. A great variety of initiators for more complex polymer chain architectures are accessible via relative simple synthetic routes.[12]

ATRP is commonly not able to polymerize acidic monomers due to a side reaction of the monomer with the metal complex and quaternization of the nitrogen ligands.[13] One strategy to overcome these complications, as reported by Armes et al. in 1999, is the ATRP synthesis of methacrylic acid (MAA) (co)polymers in aqueous media, using the sodium salt analogue of MAA.[14] However, no details were given on the control of the polymerization, and although it was claimed as a facile route to obtain poly(methacrylic acid) polymers, further results have not been published until now. Moreover, with this method, only water-soluble copolymers can be synthesized, which limits the variety of copolymers that can be prepared. Alternative strategies include the use of protected derivatives of the acidic monomers, such as benzyl (meth)acrylate and *tert*-butyl (meth)acrylate.[15] In all these cases, a postpolymerization deprotection and purification step is required to generate the desired polyacid. However, this procedure is not always straightforward; e.g., (benzyl methacrylate)-rich copolymers cannot be debenzylated completely, and catalyst residues limit the utility.[16]

Scheme 1. Reagents and Conditions for the Synthesis of PEE(M)A[a]



[a] i, phosphoric acid catalyst, 25 °C, 48 h; ii, ATRP reaction (see Table 1 for details); iii, heat.

In this communication we report the synthesis of poly(1-ethoxyethyl methacrylate) (PEEMA) and poly(1-ethoxyethyl acrylate) (PEEA) by ATRP, giving polymers with a good control of average molar mass (M_n) and narrow polydispersity (<1.2). These polymers are precursors for poly(methacrylic acid) and poly(acrylic acid), respectively. Moreover, block copolymers are prepared to illustrate the versatility of our approach in the synthesis of more complex pH-responsive polymer architectures. Deprotection is easily carried out by thermolysis, thus without the need for a second time-consuming purification step (see Scheme 1).

Note that the deprotection step can alternatively be carried out at lower temperatures under acid-catalyzed conditions, e.g., using a photo acid generator.[17] This simple deprotection step without the need for further purification adds new prospects for the use of these polymers in thermoresponsive systems and in applications where a change from hydrophobic to hydrophilic properties is needed, for instance in photoresist technology.[17] Even reversible systems are possible.[18]

The monomers, 1-ethoxyethyl methacrylate (EEMA) and 1-ethoxyethyl acrylate (EEA), were synthesized by the acid-catalyzed addition reaction of (meth)acrylic acid to ethyl vinyl ether,[19] as previously described[20] (see Scheme 1).

Our ATRP formulations are based on the ones originally described by both Haddleton and Matyjaszewski.[8,9] Initiators, catalysts, ligands, and solvents were varied to optimize polymerization conditions (see Table 1).

In the ATRP of 1-ethoxyethyl methacrylate (EEMA)[21] the choice of initiator and ligand is important to obtain good control over the polymerization (entries 1−3, Table 1). With Haddleton's *N*-octyl-2-pyridylmethanimine ligand[22] (**1**), the rate of polymerization is slow, and a 5-fold excess of CuBr was used to obtain a reasonable polymerization rate. Because of the high CuBr concentration and the absence of Cu(II)Br in the beginning of the reaction, the system tries to attain equilibrium on

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Table 1. Summary of the Data and Results of the Polymerizations of 1-Ethoxyethyl (Meth)acrylates Using ATRP

entry	initiator[a]	ligand[a]	monomer	$[M]_0/[In]_0/[Cu]_0/[ligand]$[b]	temp (°C)	time (min)	conv (%)[c]	$M_{n,th}$ (g mol^{-1})	$M_{n,exp}$ (g mol^{-1})	M_w/M_n
1[d]	**4**	**1**	EEMA	50/1/5/10	50	135	78	6400	11650[e]	1.40[e]
2[f]	**4**	**2**	EEMA	50/1/0.5/0.75	50	60	50	4150	4630[g]	1.23[g]
3[h]	**3**	**2**	EEMA	80/1/0.5/0.75	90	180	53	7000	6290[g]	1.16[g]
4[i]	**5**	**2**	EEA	50/1/1/1	50	270	68	5050	4960[g]	1.10[g]
5[j]	**5**	**6**	EEA	200/1/1/1	30	120	47	13700	11 500[g]	1.35[g]
6[d]	PMMA[k]	**1**	EEMA	65/1/5/10	50	80	14	9400	10 550[e]	1.08[e,l]
7[m]	PMMA[n]	**2**	EEMA	150/1/0.5/1	50	120	34	17000	18 600[g]	1.19[g]
8[o]	PS[p]	**2**	EEA	50/1/1/1	50	240	71	7200	6350[g]	1.28[g]

[a] **1** = *N*-octyl-2-pyridylmethanimine, **2** = *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine (PMDETA), **3** = 2,2,2-trichloroethanol, **4** = ethyl 2-bromoisobutyrate, **5** = methyl 2-bromopropionate, **6** = tris[2-(dimethylamino)ethyl]amine (Me_6TREN). [b] $[M]_0$, $[In]_0$, $[Cu]_0$, and [ligand] = initial concentration of monomer, initiator, copper catalyst, and ligand, respectively. [c] Calculated from ^1H NMR. [d] 50 vol % toluene; CuBr catalyst. [e] SEC with THF as eluent and PMMA standards. [f] 50 vol % anisole, CuCl catalyst, 20 mol % $CuCl_2$ added. [g] SEC with $CHCl_3$ as eluent and polystyrene (PS) standards. [h] 55 vol % anisole, CuCl catalyst, 20 mol % $CuCl_2$ added. [i] 25 vol % acetone, CuBr catalyst. [j] 25 vol % anisole, CuBr catalyst. [k] PMMA macroinitiator $M_n = 7950^e$, $M_w/M_n = 1.11$. [l] After precipitation in hexane. [m] 50 vol % anisole, CuBr catalyst. [n] PMMA macroinitiator $M_n = 8950^g$, $M_w/M_n = 1.10^g$. [o] Bulk polymerization, CuBr catalyst. [p] PS macroinitiator, $M_n = 2100^g$, $M_w/M_n = 1.11^g$.

its own by radical termination. Because of this, the observed molecular weight is higher than expected as the initiator efficiency is reduced. In addition, a large excess of Cu needs to be avoided because of its difficult removal and the risk for Cu-catalyzed hydrolysis of the EEMA. Polymerizations carried out using *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine (**2**, PMDETA) as ligand resulted in faster overall rates of polymerization. Good control of chain growth throughout the polymerization was obtained upon addition of 20 mol % Cu(II)Cl_2 (with respect to overall Cu concentration) prior to reaction. This control was further optimized with the use of 2,2,2-trichloroethanol (**3**) as initiator instead of ethyl-2-bromoisobutyrate (**4**). This can be explained by the lower back strain effect of the latter.[23] The first-order kinetic plot of the polymerization of EEMA shows a deviation from linearity (see Figure 1).

A similar deviation from linearity in the first-order kinetic plot of the polymerization of other bulky methacrylates was observed earlier.[22] The plot of the average molar mass (M_n) as a function of conversion shows a linear behavior (Figure 1).

The corresponding acrylate, 1-ethoxyethyl acrylate (EEA), was also polymerized (entries 4 and 5, Table 1). In this case, a common initiator for acrylates, methyl 2-bromopropionate (**5**), was used. Using PMDETA as ligand resulted in a near-monodisperse polymer (PDI = 1.10). The first-order kinetic plot of the polymerization and the average molar mass as a function of conversion both show the expected linear behavior (see Figure 1). When tris[2-(dimethylamino)ethyl]amine (**6**, Me_6TREN) was used as a ligand, a polymer with higher molecular weight (11 500 g mol^{-1}) but broader molecular weight distribution was obtained. The research toward higher molecular weight polymers of EE(M)A is still in progress.

A few block copolymers with PEEMA as the second block, starting from a poly(methyl methacrylate) (PMMA) macroinitiator, were also synthesized successfully (entries 6 and 7, Table 1) as well as a block copolymer of EEA with a polystyrene (PS) macroinitiator (entry 8, Table 1). Although block copolymers with PEE(M)A as the first block can also be synthesized, it is more convenient to prepare block copolymers with PEE(M)A as the second block. Because of the rather high temperatures that are needed for the polymerization of some monomers, there is always the risk of deprotection of the PEE(M)A, which would destroy the catalyst during the synthesis of the second block.

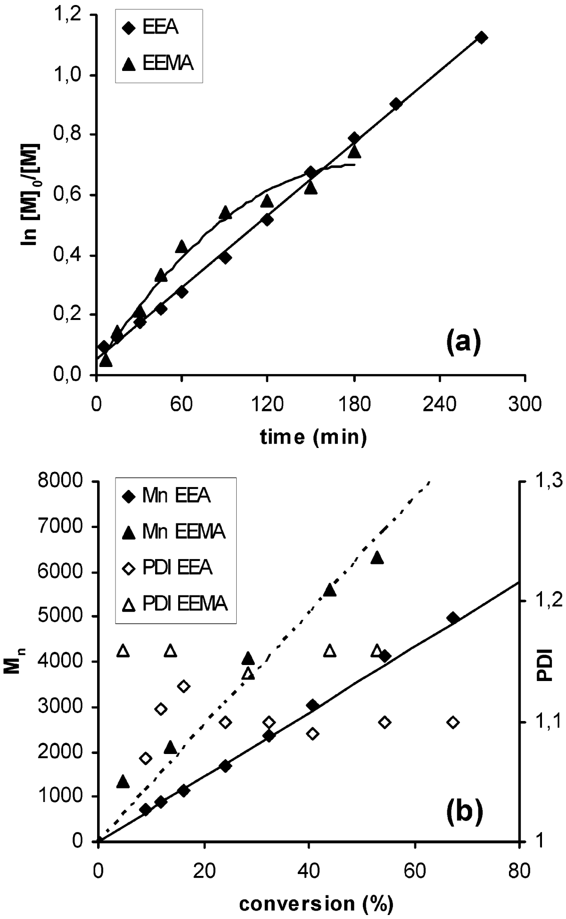

Figure 1. (a) First-order kinetic plot of the polymerization of EEMA (entry 3, Table 1) (▲) and EEA (entry 4, Table 1) (◆). (b) Average molar mass (M_n) and polydispersity (PDI) as a function of conversion of the polymerization of EEMA (entry 3, Table 1) (▲) and EEA (entry 4, Table 1) (◆). The dotted and the solid line show the theoretical M_n for the polymerization of EEMA and EEA, respectively.

The results of thermogravimetric analysis (TGA) of a purified sample of PEEMA are shown in Figure 2.

After about 30 min at 160 °C, about 90% of the deprotection is complete. For entry 1, with a theoretical $DP_n = 50$ and a conversion of 78% the experimental DP_n is 39 for complete initiation; the theoretical weight loss for 100% deprotection is thus 39 times the molecular weight (MW) of ethyl vinyl ether, which corresponds to

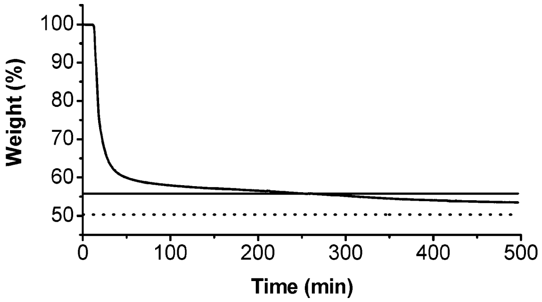

Figure 2. Isothermal TGA at 160 °C under a N_2 atmosphere (heating 20−160 °C at 10 °C/min) of PEEMA (entry 1, Table 1). The horizontal solid line corresponds to 100% deprotection to PMAA and the dotted one to 100% anhydride formation.

a weight loss of 44.2% (taking into account the MW of the initiator). Further decrease in weight is explained by anhydride formation with loss of water (total weight loss: 49.7%).

Contact angle measurements show a significant change in hydrophilicity before and after thermolysis, confirming that deprotection has occurred (for figure, see Supporting Information). A thin polymer film was made by spin-coating on a glass plate (from a 15 wt % solution in toluene), and a drop of H_2O was added before and after heating the film at 160 °C for 30 min. On the glass plate with the unheated polymer film, the water drop does not spread. When the same experiment is repeated with a previously heated polymer film, the water drop starts spreading out quickly over the surface.

^{1}H NMR experiments confirm that the deprotection is quantitative by disappearance of two characteristic peaks for poly(1-ethoxyethyl methacrylate) at 3.4−3.9 and 5.6−5.8 ppm (in $CDCl_3$), which are assigned to the hemiacetal ester moieties in the side chain, and the appearance of a methacrylic acid peak at 12.4 ppm (in DMSO-d_6, see Supporting Information).

In summary, we have demonstrated that ATRP is a suitable technique for the polymerization of 1-ethoxyethyl(meth)acrylate. Well-defined homopolymers and block copolymers can be prepared, which can be deprotected to give the corresponding polyacids or polyacid segments by simple heating, without the need for an additional purification step, offering possibilities for the use of these polymers in a broad range of end-use applications.

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Supporting Information Available: Experimental section, spectral data of EEA and EEMA, typical experimental procedure for a block copolymerization, figure of water droplets on a thin polymer film of PEEMA, ^{1}H NMR spectra of deprotection of PEEMA to PMAA, and SEC traces of the macroinitiators and block copolymers of entries 6−8 of Table 1. This material is available free of charge via the Internet at http://pubs.acs.org.

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(19) Procedure for the synthesis of 1-ethoxyethyl (meth)acrylate: Under a nitrogen atmosphere, 1.0 mol (68.6 mL) of acrylic acid or 1.0 mol (85.2 mL) of methacrylic acid was added slowly at 0 °C to a mixture of 1.2 mol (114.9 mL) of ethyl vinyl ether and 0.002 mol (0.2 g) of phosphoric acid as a catalyst. The mixture was stirred at room temperature for 48 h. The catalyst was then absorbed on $Mg_6Al_2(OH)_{16}CO_3{\cdot}4H_2O$. After filtration the excess vinyl ether was evaporated. The product was distilled at reduced pressure with phenothiazine as inhibitor. The boiling point was 32 °C (6 mbar) for 1-ethoxyethyl methacrylate (EEMA) and 47 °C (18 mbar) for 1-ethoxyethyl acrylate (EEA). Yields are about 90%. Spectral data: see Supporting Information.

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(21) Typical polymerization procedure: First, the monomer was passed through a small column of basic Al_2O_3 to remove traces of residual acid. A mixture of 0.120 mol (20 mL) of 1-ethoxyethyl methacrylate, 20 mL of toluene as a solvent (50 vol %), and 0.024 mol (5.60 mL) of *N*-octyl-2-pyridylmethanimine as a ligand was degassed by several freeze−pump−thaw cycles. Cu(I)Br (0.012 mol, 1.72 g) was added, and the reaction flask was placed in an oil bath at 50 °C. When the reaction mixture reached the desired reaction temperature, the polymerization was started by adding 0.0024 mol (0.352 mL) of ethyl 2-bromoisobutyrate as initiator. The reaction was ended by cooling the reaction mixture in liquid nitrogen. The resulting polymer was purified by passing the diluted reaction mixture over a column of neutral Al_2O_3 to remove the copper catalyst. After evaporating the excess solvent, the polymer was precipitated in cold methanol.

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