Supporting Information for

Mild and efficient bromination of Poly(hydroxyethyl)acrylate and its use towards lonic-Liquid containing polymers

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ABBREVIATION LIST

HEA (M)	: 2-Hydroxyethyl acrylate	
EBiB (I)	: Ethyl 2-bromoisobutyrate	
Вру	: Bipyridine	
PHEA (P1)	: Poly(2-hydroxyl)ethylacrylate	
PBEA (P2)	: Poly(2-bromo)ethylacrylate	
PAEPy-Br (P3)	: Poly(2-acryloxy)ethyl-pyridinium bromide	
PAETBP-Br (P4)	: Poly(2-acryloxy)ethyl-tributylphosphonium bromide	
PAEMIm-Br(P5)	: Poly(2-acryloxy)ethyl-3-methylimidazolium bromide	

MATERIAL AND METHODS

General procedures. All reactions were performed under an argon atmosphere using schlenk techniques. CH_2Cl_2 and THF were dried and degassed on a solvent station by passage through an activated alumina column followed by argon flush. Other solvents were used without further purification. HEA purchased from Alfa Aesar was purified according to the reported procedures.¹ All other chemicals were obtained from Sigma Aldrich, Acros or Alfa Aesar and were used as received. 1H NMR spectra (500.1MHz) and 13C NMR spectra (126.3 MHz) were recorded at 298K on a BRUKER® Avance I spectrometer. Data are listed in parts per million (ppm) and are reported relative to tetramethylsilane (¹H, ¹³C), residual solvent peaks being used as internal standard (DMSO ¹H: 2.54 ppm, ¹³C: 40.45 ppm).

FTIR spectra (ATR) were performed on solid samples using a JASCO FT/IR 4100 spectrometer equipped with a JASCO ATR PRO450-S ATR module.

GPC analyses were carried on *ca* 4mg/mL solutions of each polymer in DMF LiBr (0.05M), using a Viscotek MM system equipped with a Rheodyne 7725i injector three Styragel HR 4E (WAT044241) columns set in series at 70°C, coupled to a Viscotek VE3580 differential refractive index detector (at 55°C) and a Viscotek T60A viscosimetrer. The polydispersity indexes (PDI = M_w/M_n) of the samples were derived from the RI signal by a calibration curve based on polystyrene standards. The number-average molar mass (M_n) were calculated from RI signals with the OmniSEC 4.6 software.

1D-1H and 2D-DOSY experiments were carried out at 298 K on a 500 MHz Bruker Avance I NMR spectrometeremploying a 5 mm TXI probe equipped with z-gradients. 2D-DOSY experiments were acquired using a LED experimentwith bipolar pulses. Gradients were linearly sampled in 50 points. 16 scans were acquired on 8192 data points. The gradient pulse length was d/2 = 1.5 ms and the D diffusion delay was adapted to the sample for values in the 150- 250 ms range. The DOSY spectra were obtained by applying an Inverse Laplace Transform (ILT) along the diffusion axis, using the Gifa algorithm embedded into the commercial software NMRnotebook (NMRTEC, Illkirch). Careful spline polynomial correction was applied along the F2 dimension before the ILT processing.

EXPERIMENTAL

Polymerization of HEA.



Polymerization was conducted with a reactant ratio of M:I:Cu:Bpy = 100:1:1:2. All the reactants, initiator EBiB (I, 0.185 g, 0.95 mmol), HEA (M, 11.0 g, 94.73 mmol), 2,2'-bipyridine ligand (Bpy, 0.296 g, 1.90 mmol)and CuBr catalyst (Cu, 0.136 g, 0.95mmol), were mixed and three freeze thaw cycles were performed. Polymerization of the resulting dark brown solution was initiated by stirring the mixture at 85 °C. Polymerization started immediately, leading to an increase in viscosity of the solution. The polymerization was quenched by adding CuBr₂ (0.22 g) after 40 min. The solution was cooled rapidly in liq. N₂, diluted with deionized water, transferred into a dialysis membrane (spectra/por membrane, MWCO=1000), and dialized against a large volume of deonized water. The external water was regularly replaced at 6H intervals with fresh water during dialysis (2 days). Finally, the dialysis bag content was filtered and lyophilized to yield 3.4 g of the expected polymer (**P**1), $M_n = 5000$ (NMR), PDI = 1.12 (GPC). For other characterizations: see below

Synthesis of PBEA(P2) by bromination of PHEA(P1).



To a 1.45 g of polymer suspension in CH₂Cl₂ (15mL) at 0 °C, excess amount of trimethylsilyl bromide (4.94 mL, 37.5 mmol) (3 equiv. with respect to –OH group of the **PHEA**) was added drop-wise and the solution was slowly allowed to warm to room temperature. After 24 h stirring the brominated polymer, which became completely soluble in CH₂Cl₂ in the course of the reaction, was precipitated in cold methanol (100 mL). The polymer was extensively washed with methanol (50mL x 2) and dried under vacuum at 50 °C. Yield = 2.16 g (96.6%), $M_n = 7800$ (NMR), PDI = 1.15 (GPC) For other characterizations: see below

Synthesis of poly ionic liquids by quarternization reactions of PBEA(P2).



In a typical reaction, a solution of polymer in THF and amine/phosphine (5 equiv. for each –Br group in the polymer chain) was refluxed at 85 °C for 48 h under argon atmosphere. The reactor was then cooled to room temperature, and precipitation of the corresponding functionalized polymer is completed by adding diethyl ether. After removal of the solvents, the resulting precipitate was washed with diethyl ether. The final purification procedures were slightly different for each polymers based on their solubility. In the case of **P3** and **P5**, the polymer was dissolved in methanol and re-precipitated in ether and the process was repeated two times to remove excess reagent. But for **P4**, the same procedure was repeated using CH_2Cl_2 as solvent and ether as anti-solvent. Polymers were then dried under vacuum and their yield is shown in table S1.

Polymer	Amount of P2 used	Yield of Polymer
	(g)	(g)
P3	0.288	0.44
P4	0.235	0.35
P5	0.376	0.46

Table S1 Yield of poly ionic liquids

For all NMR (including DOSY) and IR characterizations, see below

ANALYSES



Figure S1. ¹H and ¹³C NMR of PHEA(P1) in DMSO-d6



Figure S2. ¹H and ¹³C NMR of PBEA(P2) in DMSO-d6



Figure S3. ¹H and ¹³C NMR of PAEMIm-Br(P5) in DMSO-d6 ($* = -O-CH_2-CH_2-OH$ peaks)



Figure S4. ¹H and ¹³C NMR of PAEPy-Br(**P3**) in DMSO-d6(* = -O-CH₂-CH₂-Br peaks)



Figure S5. ¹H NMR of PAETBP-Br(P4) in DMSO-d6 and ¹³C in CDCl₃ (* = -O-CH₂-CH₂-Br peaks)





S7 DOSY Spectra of P₁₋₅











Figure S8. FTIR spectra of polymers

References

 Coca, S., Jaseieczek, C.B., Beers, K.L., Matyjaszewski K., J Polym. Sci., Part A: Polym. Chem. 1998, 36, 1417-1424.