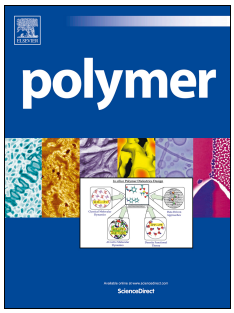
# Accepted Manuscript

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PII: S0032-3861(17)30845-5

DOI: 10.1016/j.polymer.2017.08.058

Reference: JPOL 19960

To appear in: *Polymer*

Received Date: 8 June 2017

Revised Date: 25 August 2017

Accepted Date: 26 August 2017

Please cite this article as: Rössel C, Billing M, Görls H, Festag G, Grube M, Bellstedt P, Nischang I, Schacher FH, Synthesis and modification of Poly(ethyl 2-(imidazol-1-yl)acrylate) (PEImA), *Polymer* (2017), doi: 10.1016/j.polymer.2017.08.058.

# Synthesis and Modification of Poly(ethyl 2-(imidazol-1-yl)acrylate) (PEImA)

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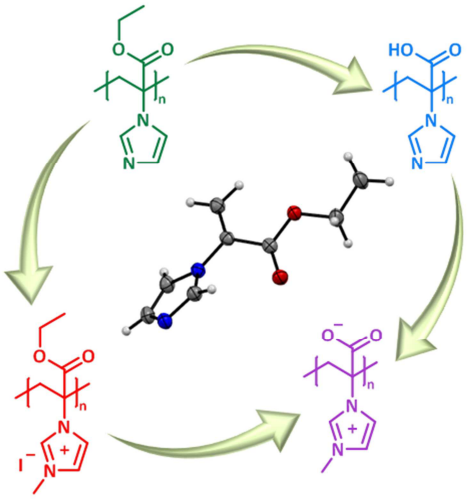
*Dedicated to Prof. Axel H. E. Müller on the occasion of his 70th birthday*

# Abstract

We present the synthesis and characterization of poly(ethyl 2-(imidazol-1-yl)acrylate) (PEImA) using free radical polymerization in various solvents with and without acids as additive. In addition, PEImA was also prepared using anionic polymerization with KO*t*Bu as initiator in DMF and in THF at different M:I ratios. The resulting polymers of moderate dispersity were characterized by $^{1}$H-NMR, solid state $^{13}$C-NMR, and size exclusion chromatography (SEC) both in water and DMAc. PEImA is an interesting highly substituted polymer as it can be modified by methylation to poly(ethyl 2-(methyl imidazolium-1-yl iodide)acrylate) PEMeImA, *via* ester cleavage into the polyzwitterion poly(2-(imidazol-1-yl)acrylic acid) (PImAA), and – finally - to poly(2-(methyl imidazolium-1-yl)acrylic acid) (PMeImAA) if both modification steps are carried out. We also investigated structure and solubility of these different polyelectrolytes using potentiometric titration in aqueous media.

Table of contents graphic:



# Introduction

Polyelectrolytes are macromolecules containing ionizable groups along the polymer backbone or within the side chain.[1,2] Depending on the nature of the functional group, such material can be further subdivided into weak or strong polycations or polyanions. In contrary to strong polyelectrolytes which are completely ionized over the full range of commonly accessible pH values, the charge density of weak polyelectrolytes depends on the solution pH.[3] Typical examples are poly(methacrylic acid) (PMAA)[4], poly(2-(dimethylamino)ethyl methacrylate) (PDMAEMA)[5], poly(ethylenimine) (PEI)[6] and poly(vinylimidazole) (PVIm)[7]. There are many possible applications of polyelectrolytes such as oil recovery, mineral processing, as stabilizers in emulsion polymerizations and as flocculation or coagulation agents and this explains the constant and broad interest in both the synthesis as well as modification of such materials.[8,9] In addition, especially cationic polyelectrolytes are of interest as potential non-viral gene transfection agents due to their ability to reversibly bind and release DNA or RNA.[10]

If both cationic and anionic charges are present within a macromolecule, such materials are termed polyampholytes and these examples are of interest for sewage treatment, metals binders (*e.g.* Ni, Cu or Cd), water purification, paper reinforcement, as antifouling coatings or in cosmetic formulations.[11,12] If both charges are located within the same monomer unit, polyzwitterions as subclass of polyampholytes are formed and can further be subdivided into poly(sulfobetaine)s, poly(phosphobetaine)s and poly(carboxybetaine)s – depending on the nature of the negatively charged group. Especially in the latter case, the overall ratio of positive and negative charges can further be adjusted by variation of the pH value.[11,13] One further example for a polyzwitterion with tunable charge is poly(dehydroalanine) (PDha), which exhibits varying charge and rather high charge density depending on the pH of the surrounding solution.[12,14] Another interesting functionality for the construction of polyampholytes or polyzwitterions is the imidazole moiety. In most cases, imidazole-based polyzwitterions feature a betaine structure with the imidazole moiety being turned into a permanently charged group by alkylation.[15,16,17] One possible application field for these polymers is as poly(ionic liquid)s, like other polyimidazoles as electrolytes in fuel cells and batteries, as solid ionic conductors, or in the field of gas separation.[18,19] In contrast to low molar mass ionic liquids, the polymeric examples often exhibit enhanced mechanical stability and durability, but at the cost of higher melting points.[20] These properties in turn can be influenced by variation of the corresponding counterions and the moiety used for alkylation.[21]

Possible starting materials for the preparation of polyampholytic materials based on imidazole are shown in Scheme 1, with urocanic acid as example for a natural product, which is enzymatically prepared from histidine on human skin and acts as sunscreen to protect DNA from UV induced damage.[22] Hence, urocanic acid was already of interest for cosmetic applications *via* copolymerization with acrylic acid.[23] However, only a few β-substituted acrylates have so far been successfully polymerized using radical techniques.[24] An isomer of urocanic acid, 2-(imidazol-1-yl)acrylic acid, was synthesized by *Yavari et al.* both as methyl (MeImA) and ethyl ester (EImA, Scheme 1).[25] In that regard, the free radical copolymerization of MeImA with acrylonitrile has been described by *Batchelor et al.* as low molecular weight plasticizers in poly(acrylonitrile) fibers to prepare carbon fibers.[26]

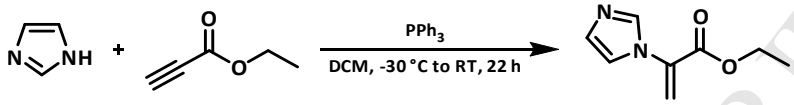

**Urocanic acid** **Ethyl 2-(imidazol-1-yl)acrylate (EImA)**

**Scheme 1:** Monomers of potential interest for radical polymerization based on urocanic acid.

Herein, we present the preparation and modification of poly(ethyl 2-(imidazol-1yl)acrylate) (PEImA), both using conventional free radical polymerization and anionic techniques. The resulting PEImA is a weak polyelectrolyte and can be converted into a strong polycation by alkylation of the imidazole group. Furthermore, the cleavage of the ester moiety results in the formation of a polyzwitterion, where the charge density depends on the pH of the solution. The resulting materials are characterized by size exclusion chromatography (SEC, SEC-MALLS), solution and solid state nuclear magnetic resonance spectroscopy (NMR), and thermogravimetric analysis (TGA). Additionally, we use potentiometric titration to access the pH-dependant charge density of different modifications of PEImA.

# Results and Discussion

Herein, we report on the synthesis and polymerization of EImA, both using free radical and anionic polymerization techniques. Our main motivation is that the resulting PEImA can be multiply functionalized: it can either be converted into a poly(ionic liquid) using alkylation of the imidazole moiety or turned into a polyampholyte/polyzwitterion *via* hydrolysis of the ester moiety. At first, the described synthesis of EImA from *Yavari et al.* was optimized for a larger scale by adding the triphenylphosphine solution at -30 °C (Scheme 2).[25]




**Scheme 2:** Optimized synthesis of ethyl 2-(imidazol-1-yl)acrylate (EImA).

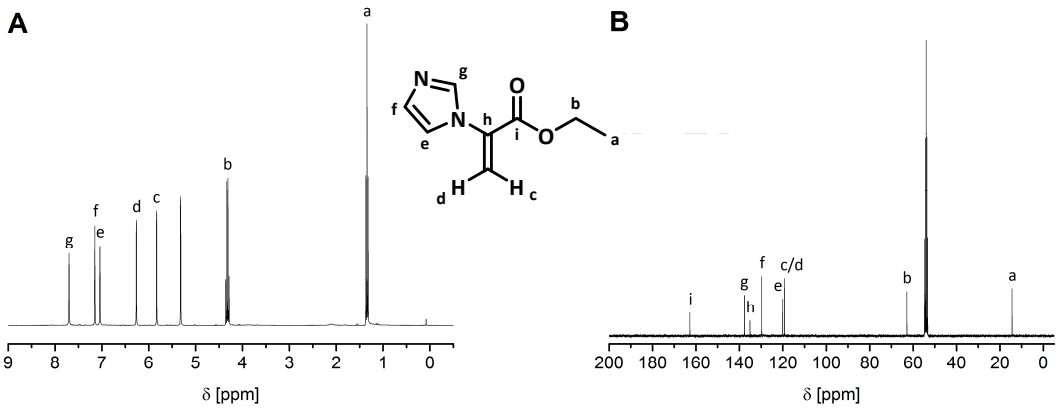



**Figure 1:** $^{1}$H-NMR spectrum (**A**) and $^{13}$C-NMR spectrum (**B**) of ethyl 2-(imidazol-1-yl)acrylate (EImA) in $CD_2Cl_2$.

After purification of the crude product EImA was yielded as yellowish oil, which crystallized at -25 °C overnight. The crystals were analyzed by solution NMR spectroscopy (Figure 1), which showed all expected signals, and X-ray analysis (Figure 2) to verify both the structure and purity. The molecular structure exhibits a conjugation between the carbonyl group and the double bond as expected, but the imidazole ring is out of plane with a torsion angle C5C4N2C1 of 37.0(3)°. Therefore, the imidazole group acts only as electron donating group and does not influence the double bond by conjugation. This means that the monomer can be regarded as an activated acrylate with the carbonyl as electron withdrawing and the imidazole moiety as electron donating group.

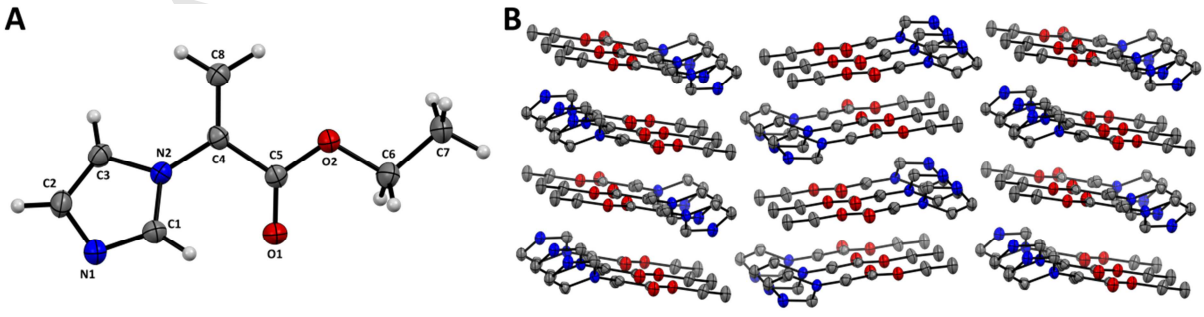



**Figure 2:** Molecular structure and numbering scheme (**A**) and crystal structure (**B**) of ethyl 2-(imidazol-1-yl)acrylate (EImA). The ellipsoids represent a probability of 50%.

At first, PEImA was synthesized *via* free radical polymerization at 65 °C in various solvents with and without the addition of different acids. In the literature, the homopolymerization of vinylimidazoles and imidazole containing acrylates has been reported either after protonation or alkylation of the imidazole group.[27,28,29,30] *Santanakrishnan* and *Hutchinson* studied the polymerization of *N*-vinylimidazole and quarternized vinylimidazole in aqueous solution depending on the pH value.[31] They reported a degradative addition of radicals to the imidazole group and on the possibility to suppress this side reaction by protonation. Only few examples of imidazole containing monomers have been reported so far where the polymerization was carried out without protonation or quaternization like in case of 2-[(1-imidazolyl)formyloxy]ethyl methacrylate and 2-(1-imidazolyl)ethyl methacrylate.[32,33] Furthermore, it was reported that a direct copolymerization of such monomers and MeImA with acrylonitrile was possible due to the formation of a charge transfer complex between the nitrile and imidazole group.[26,27,34]


**Scheme 3:** Free radical polymerization of ethyl 2-(imidazol-1-yl)acrylate (EImA).

Based on these facts, EImA was polymerized with 0.5 mol% AIBN and 5 equivalents of acetic acid in various solvents like water, methanol, hexafluoroisopropanol, 2,2,2-trifluoroethanol or 2-methoxyethanol, which so far afforded only oligomers in low yields between 20% and 40%. The polymerizations were repeated with 1.1 equivalents of concentrated hydrochloric acid instead of acetic acid and also oligomers were observed, but the overall yield increased up to 99% (Table 1). Additionally, EImA was polymerized without the addition of acid and an increase in molar mass to a range of 2,000 - 13,000 g·mol$^{-1}$ and with moderate dispersities of approximately 1.5 according to SEC in water was observed (Figure 3, Table 1).

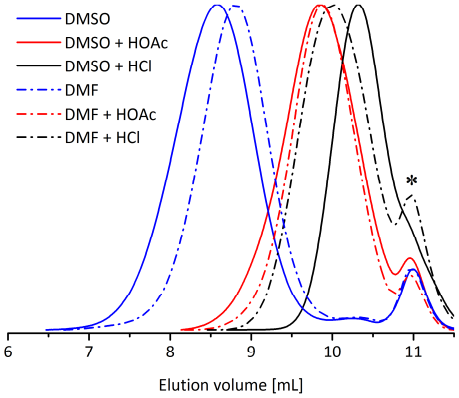



**Figure 3:** SEC elugrams (water with 0.1 M NaCl and 0.3% TFA, P2VP calibration, * system peak) of PEImA prepared by free radical polymerization in DMSO and DMF with added acids and without.

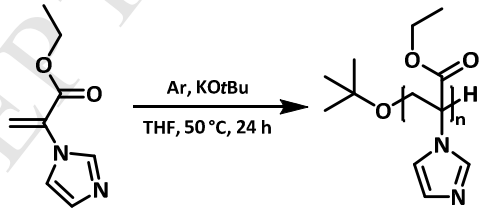
**Table 1:** Free radical polymerization of EImA in different solvents with 0.5 mol% AIBN.

| Entry | Solvent | Additive | Yield [%] | $M_n$ [g·mol$^{-1}$]$^{a)}$ | PDI$^{a)}$ | $M_n$ [g·mol$^{-1}$]$^{b)}$ | PDI$^{b)}$ |
|---|---|---|---|---|---|---|---|
| 1 | DMSO | - | 50 | 13,300 | 1.45 | 30,200 | 1.45 |
| 2 | DMSO | HOAc | 22 | 2,700 | 1.53 | - | - |
| 3 | DMSO | Conc. HCl | 99 | 1,000 | 1.52 | - | - |
| 4 | DMF | - | 52 | 10,000 | 1,54 | 20,600 | 1.45 |
| 5 | DMF | HOAc | 38 | 2,700 | 1.39 | - | - |
| 6 | DMF | Conc. HCl | 99 | 2,100 | 1.37 | - | - |
| 7 | Anisole | - | 44 | 11,500 | 1.65 | 23,800 | 1.53 |
| 8 | Benzol | - | 40 | 13,400 | 1.59 | 29,400 | 1.51 |
| 9 | MeCN | - | 29 | 8,600 | 1.48 | 17,000 | 1.42 |
| 10 | THF | - | 42 | 8,700 | 1.49 | 16,500 | 1.56 |

[a)] Determined by SEC (Water, 0.1 M NaCl, 0.3% TFA). P2VP calibration. [b)] Determined by SEC (DMAc + 0.21% LiCl). PMMA calibration.

The combination of an increased overall polymer yield and decreasing molar mass for PEImA obtained using free radical polymerization in the presence of HCl in comparison to HOAc or without any acid suggests transfer (*e.g.* to monomer) occurring as side reaction. Besides an increased molar mass without protonation of EImA, the solubility of PEImA is improved in organic solvents like DMAc, DMF, DCM and chloroform. The free radical polymerization of EImA was therefore repeated without any acid in various solvents and the resulting materials were further analyzed by SEC in DMAc with 0.21% LiCl using PMMA calibration (Table 1, Figure S1). Here, approximately the doubled molar masses with similar dispersities was detected in comparison to SEC data acquired in water.

Moreover, we also investigated the anionic polymerization of EImA using KO*t*Bu (0.1 M in THF) as initiator in THF and DMF at 50 °C (Scheme 4). In comparison to *N*-vinylimidazole, anionic polymerization so far is not described in the literature, probably due to the acidity of the proton at the 2 position of the imidazole ring. A proton exchange study with deuterium oxide *via* NMR spectroscopy of *N*-vinylimidazole at 40 °C was reported by *Green et al.* and a half-life time of approximately 2.6 hours was reported.[35]




**Scheme 4:** Anionic polymerization of ethyl 2-(imidazol-1-yl)acrylate (EImA).

We carried out a comparable proton exchange experiment with EImA in $D_2O$ at the polymerization temperature of 50 °C by $^1$H-NMR spectroscopy. In our case, an even faster exchange rate was observed (Figure 4) and after approximately 2 hours the deuteration is completed according to NMR, which might turn anionic polymerization attempts problematic. On the other hand, 1-tritylimidazole-4-ethylene oxide could be successfully polymerized *via* anionic ring-opening polymerization initiated with KO*t*Bu by *Ramirez et al.* which indicates that KO*t*Bu as base is probably not strong enough to deprotonate the imidazole group.[36]

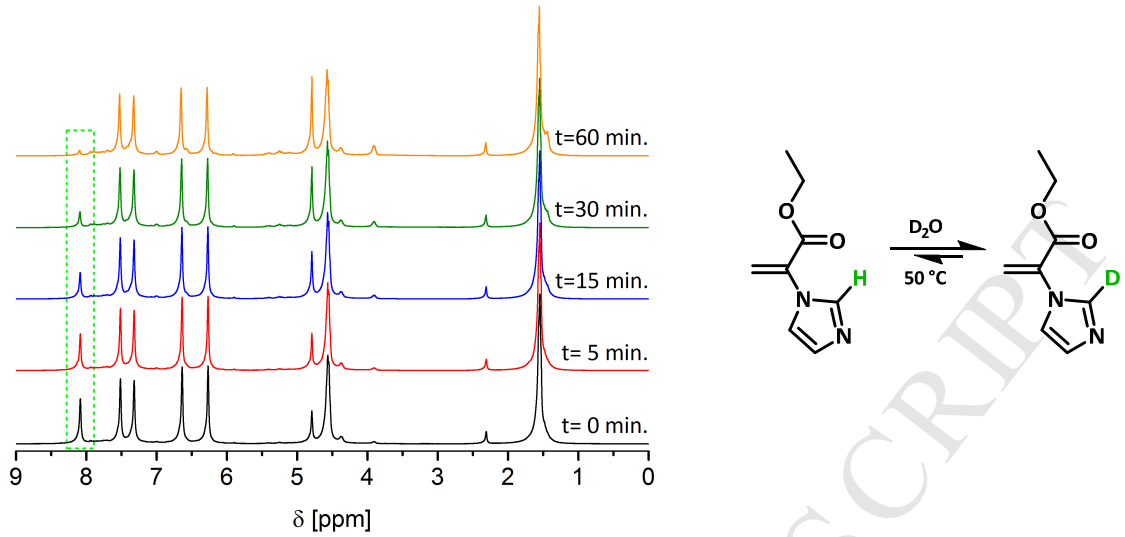



**Figure 4:** Proton exchange of EImA in $D_2O$ at 50 °C monitored *via* $^1$H-NMR.

At first, anionic polymerization was attempted at 50 °C for 24 hours in bulk, and in DMF or THF as solvent with a 0.1 M KO*t*Bu solution as initiator in THF (Figure 5). Here, the bulk polymerization afforded the polymer with the highest molar mass and a rather broad molar mass distribution. However, performing the anionic polymerization in DMF and THF afforded PEImA of lower dispersity. In DMF, we observe an improved solubility of PEImA if compared to THF, which seems to affect the degree of polymerization, leading to a distinctly higher molar mass (Table 2). Possibly caused by the more polar solvent DMF, a faster polymerization with less control is observed, leading to a moderately broad dispersity of 1.4-1.7. In comparison, anionic polymerization of EImA in THF results in a dispersity of approx. 1.3.

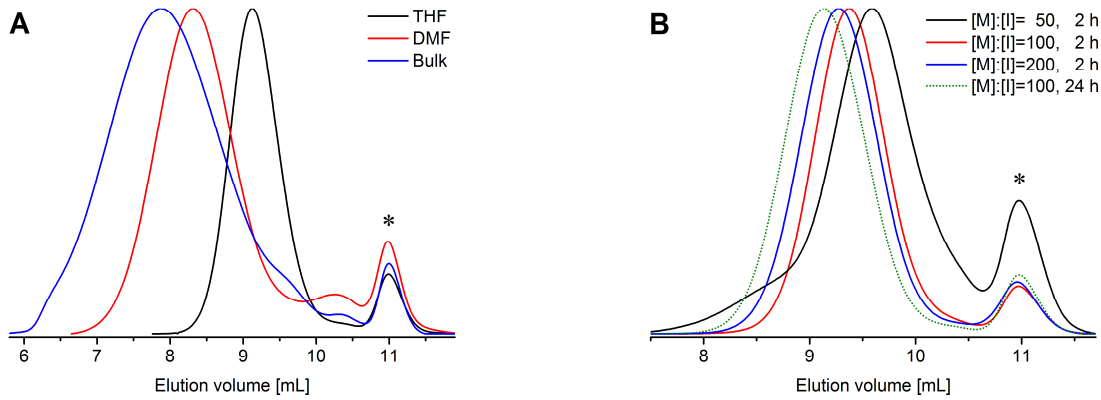



**Figure 5:** SEC elugrams (water with 0.1 M NaCl and 0.3% TFA, P2VP calibration, * system peak) of PEImA prepared by anionic polymerization with [M]:[I]=100 in different solvents (**A**) and different [M]:[I] ratios as well as different reaction times in THF (**B**).

In order to access the possibility to control the molar mass of the resulting PEImA using anionic polymerization we carried out different reactions at varying M:I ratios and a reduced polymerization time of 2 hours (Figure 5, Table 2). As can be seen, increasing molar masses are obtained for M:I ratios of 50:1 (3,700 g·mol$^{-1}$), 100:1 (5,000 g·mol$^{-1}$), and 200:1 (5,800 g·mol$^{-1}$) at moderate dispersities

down to 1.28 (according to SEC in water). We are aware that this does not exclude that side reactions are occurring, but at least indicates a certain level of control. In addition, the fact that a comparable reaction after 24 hours afforded an increased molar mass of 7,000 g·mol$^{-1}$ at a dispersity of 1.28 (M:I was 100:1) further supports this observation.

**Table 2:** Anionic polymerization of EImA with KOtBu at 50 °C.

| Entry | Solvent | [M]:[I] | Time [h] | $M_n$ [g·mol$^{-1}$]$^{a)}$ | PDI$^{a)}$ | $M_n$ [g·mol$^{-1}$]$^{b)}$ | PDI$^{b)}$ | Yield [%] |
|---|---|---|---|---|---|---|---|---|
| 11 | THF | 50 | 2 | 3,700 | 1.76 | 5,400 | 2.00 | 13 |
| 12 | THF | 100 | 2 | 5,000 | 1.28 | 8,000 | 1.42 | 31 |
| 13 | THF | 200 | 2 | 5,800 | 1.29 | 9,600 g | 1.44 | 38 |
| 14 | THF | 100 | 24 | 7,000 | 1.28 | 13,000 | 1.32 | 30 |
| 15 | DMF | 100 | 24 | 17,800 | 1.71 | 43,500 | 1.42 | 10 |
| 16 | - | 100 | 4 | 22,300 | 3.74 | 47,100 | 2.23 | 53 |

$^{a)}$ Determined by SEC (Water, 0.1 M NaCl, 0.3% TFA). P2VP calibration. $^{b)}$ Determined by SEC (DMAc + 0.21% LiCl). PMMA calibration.

In comparison with the anionic polymerization in THF, PEImA prepared by free radical polymerization reaches a higher molar masses but with broader dispersities. The $^{1}$H-NMR spectra and solid state $^{13}$C-NMR spectra of both, radically or anionically synthesized PEImA are mostly identical (Figure S2), although no fine splitting for the imidazole protons occurs in case of PEImA prepared by free radical polymerization. To determine the absolute molar mass of suitable samples of PEImA, we additionally carried out SEC-MALLS measurements in water containing 0.1 M NaCl and 0.3 % TFA (Table 3, Table S1, Figure S3).

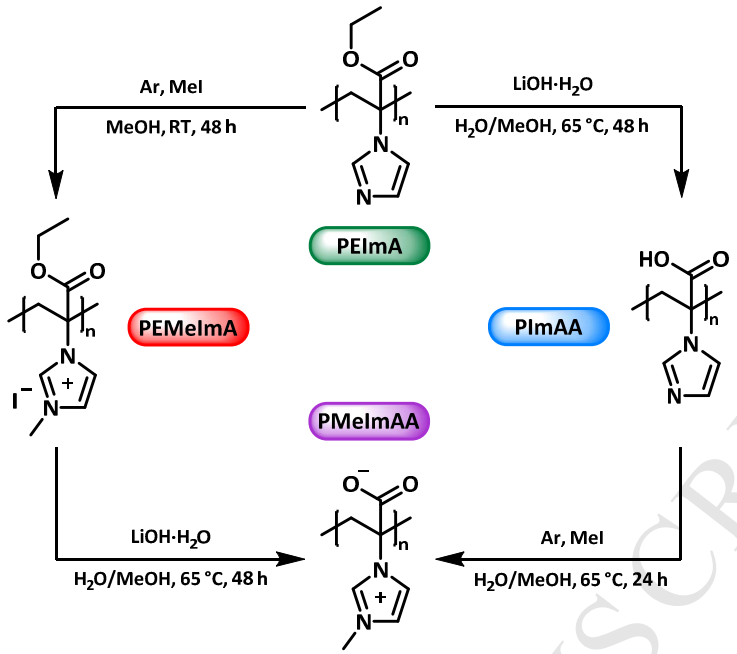
**Table 3:** Comparison of molar masses of PEImA obtained by SEC and SEC-MALLS.

| Entry | $M_n$ [g·mol$^{-1}$]$^{a)}$ | PDI$^{a)}$ | $M_n$ [g·mol$^{-1}$]$^{b)}$ | PDI$^{b)}$ | $M_n$ [g·mol$^{-1}$]$^{c)}$ | $M_w$ [g·mol$^{-1}$]$^{c)}$ |
|---|---|---|---|---|---|---|
| 4 | 10,000 | 1,54 | 20,600 | 1.45 | 34,400 | 36,300 |
| 14 | 7,000 | 1.28 | 13,000 | 1.32 | 16,900 | 17,800 |

$^{a)}$ Determined by SEC (Water, 0.1 M NaCl, 0.3% TFA), P2VP calibration. $^{b)}$ Determined by SEC (DMAc + 0.21% LiCl), PMMA calibration. $^{c)}$ Determined by SEC-MALLS (Water, 0.1 M NaCl, 0.3% TFA).

These data show that both aqueous SEC and SEC in DMAc with the respective calibration underestimate molar masses of PEIma as distinctly higher values are obtained using SEC-MALLS for both samples investigated.

We were further interested in the modification of PEImA by either alkylation of the imidazole moiety or hydrolysis of the ethyl ester. By this, the material will be changed from a weak polyelectrolyte into a polyzwitterion poly(2-(imidazol-1-yl)acrylic acid) (PImAA) or poly(2-(3-methylimidazolium-1-yl)acrylic acid) (PMeImAA) or a poly(ionic liquid) poly(ethyl 2-(3-methylimidazolium-1-yl iodide)acrylate) (PEMeImA) (Scheme 5) and the corresponding materials might be of interest as carrier material for catalysts, water purification, or as pH-responsive materials in future applications.[37]




**Scheme 5:** Conversion of PEImA into strong polyelectrolyte and polyzwitterion.

The transformation of PEImA into a polyzwitterion and strong polycation was carried out by either cleavage of the ester moiety with lithium hydroxide and alkylation with methyl iodide starting from anionically polymerized PEImA (for details see Table 4). In case of the alkylation, methyl iodide can easily be exchanged by other alkyl halides similar to poly(ionic liquids) based on PVIm.[28] The conversion of PEImA into poly(ethyl 2-(3-methylimidazolium-1-yl iodide)acrylate) (PEMeImA) with methyl iodide succeeded with a degree of alkylation over 90%. A new signal at 4.37 ppm appears in the $^{1}$H-NMR spectrum with nearly the same intensity as the methyl group of the ester moiety at 1.64 ppm and the solid state $^{13}$C-NMR shows the signal of the introduced methyl group at 33.87 ppm (Figure 6, B and C). However, the SEC in water showed a decrease in apparent molar mass for PEImA if compared to the used PEImA (Table 4, Figure 7). Additionally, PEMeImA was converted into the polyzwitterion poly(2-(3-methylimidazolium-1-yl)acrylic acid) (PMeImAA) *via* hydrolysis of the ethyl ester. PMeImAA was purified by dialysis against water and a small decrease of the molar mass was observed by SEC in water. One explanation could be that methylation (if compared to protonation) results in a slightly less hydrophilic polycation and, thus, a slightly reduced hydrodynamic volume in solution. In addition, changes in the apparent hydrodynamic volume might also originate from the presence of iodide and tri-iodide counterions. Additionally, PEMeImA was converted into the polyzwitterion poly(2-(3-methylimidazolium-1-yl)acrylic acid) (PMeImAA) *via* hydrolysis of the ethyl ester. PMeImAA was purified by dialysis against water and a small decrease of the molar mass was observed by the SEC in water. The integration of the $^{1}$H-NMR spectrum confirms that about 94% of the ester moiety were successfully cleaved, which can be seen by the disappearance of the $CH_3$-group of the ethyl ester at 1.37 ppm and in the solid state $^{13}$C-NMR spectrum at 8-9 ppm.

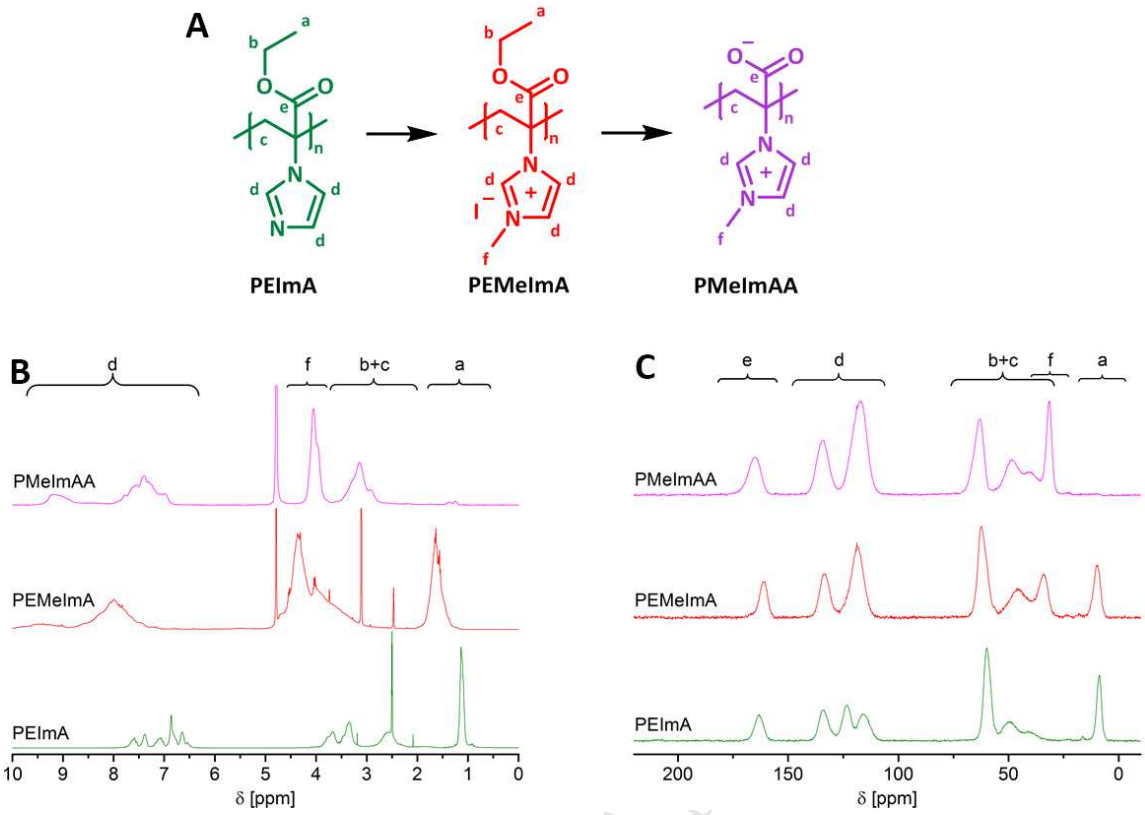



**Figure 6:** Structure (A), $^{1}$H-NMR spectra (B) and solid state $^{13}$C-NMR spectra (C) of PEImA, PEMeImA and PMeImAA.

As an alternative pathway, first the ester moiety of PEImA was hydrolyzed with lithium hydroxide to afford poly(2-(imidazol-1-yl)acrylic acid) (PImAA) as polyzwitterion with a tunable charge and, depending on the pH value, a polyanion, polyzwitterion, or polycation could result. Based on calculations by $^{1}$H-NMR spectroscopy of PImAA (Figure 8) approximately 5% of the ethyl ester remain and a shift of the distribution to higher elution volumes and apparent lower molar masses is visible in SEC in water (Figure 7).

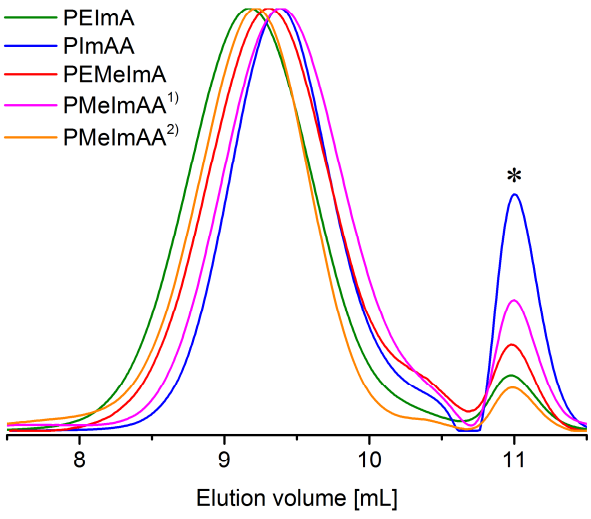


**Figure 7:** SEC elugram (water with 0.1 M NaCl and 0.3% TFA, P2VP calibration, * system peak) of PEImA and its modifications. [1)] Prepared by ester cleavage. [2)] Prepared by methylation.

**Table 4:** Modification of PEImA *via* ester cleavage and methylation.

| Polymer | $M_n$ [g·mol$^{-1}$][a)] | PDI [a)] |
|---|---|---|
| PEImA | 6,500 | 1.40 |
| PImAA | 4,900 | 1.31 |
| PEMeImA | 5,100 | 1.46 |
| PMeImAA[1)] | 4,800 | 1.57 |
| PMeImAA[2)] | 6,800 | 1.45 |

[a)] Determined by SEC (Water, 0.1 M NaCl, 0.3% TFA). P2VP calibration. [1)] Prepared by ester cleavage. [2)] Prepared by methylation.

Afterwards, alkylation of PImAA using methyl iodide was used to prepare PMeImAA following the second pathway. Therefore, PImAA was dissolved in methanol/water (v/v 1/1) under Ar atmosphere and methyl iodide was added. The biphasic mixture was heated up to 65 °C and merged to a single-phase reaction mixture. The degree of alkylation of 83% was determined by $^1$H-NMR integration of the introduced methyl group at 4.07 ppm and the molar mass increased from 4,900 g·mol$^{-1}$ to 6,800 g·mol$^{-1}$ according to SEC in water.

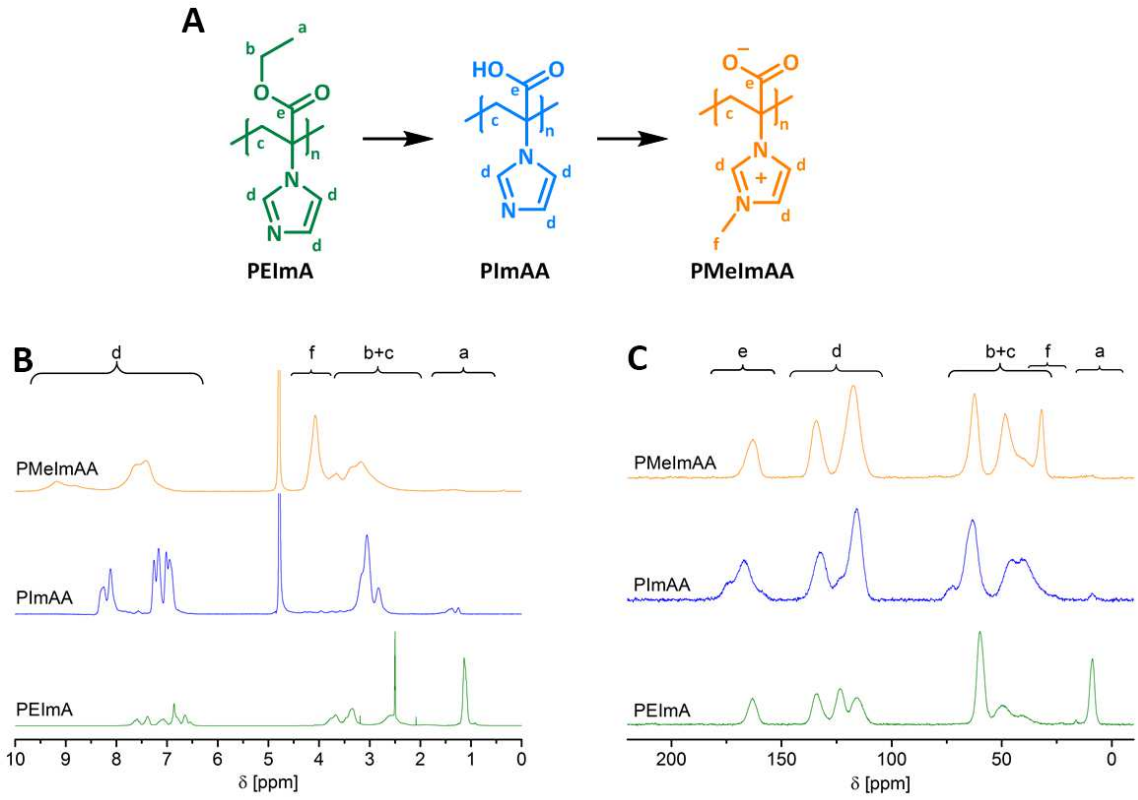



**Figure 8:** Structure (A), $^{1}$H-NMR spectra (B) and solid state $^{13}$C-NMR spectra (C) of PEImA, PImAA and PMeImAA.

After successful modification of PEImA, we also investigated the resulting polyelectrolytes and polyzwitterions using potentiometric titration in aqueous solution. Whereas PImAA and PMeImAA were titrated with 0.1 M HCl starting at high pH. Both PEImA and EImA were titrated with 0.1 M NaOH starting under acidic conditions to prevent ester hydrolysis occurring already during the measurement (Table 5). The monomer EImA features a $pK_a$ value of 9.13, which is higher if compared to other *N*-substituted imidazole compounds with a $pK_a$ of 6.9 to 7.5, presumably due to the presence of the electron withdrawing carbonyl functionality.[38] An increased basicity was also observed for PEImA and the modified polymers (Table 5, Figure 9, S4-S8). For PImAA the $pK_a$ value of the carboxylic acid is difficult to specify, due to partial precipitation and, hence, a heterogeneous mixture from pH 6.8 to 2.2. PImAA was completely redissolved at pH of 2.2, but the carboxylic acid has presumably a $pK_a$ value between 4 and 5 similar to PMeImAA. For both PMeImAA a $pK_a$ of approximately 9.3 was determined, which in our opinion results from the 10-17% of non-alkylated imidazole groups present in the material.

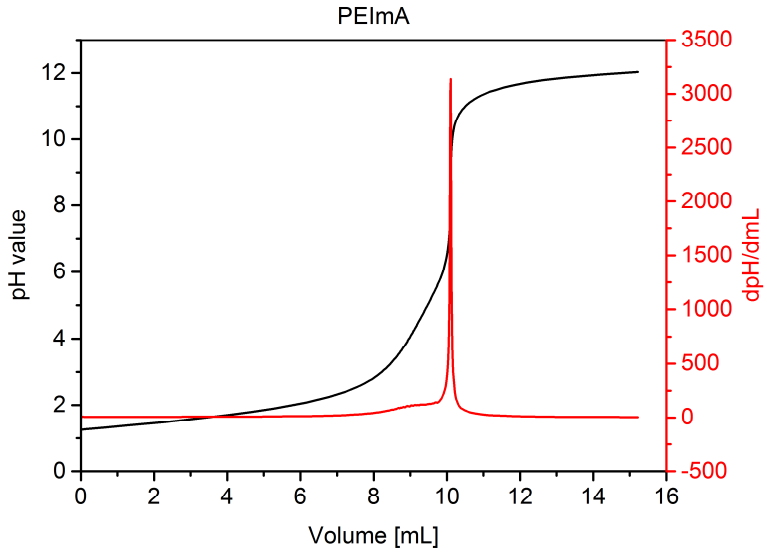


**Figure 9:** Titration curve of PEImA (5 g/L in 0.1 M HCl) with 0.1 M NaOH (black) and the first derivative (red).

**Table 5:** Determined pKa values for EImA, PEImA and the modified polymers.

| Polymer | $pK_a$ 1 | $pK_a$ 2 |
|---|---|---|
| EImA | 9.13 | - |
| PEImA | 9.17 | - |
| PImAA | 10.78 | - |
| PMeImAA[1)] | 9.38[a)] | 5.10 |
| PMeImAA[2)] | 9.23 [a)] | 4.24 |

[a)] Presumably due to non-alkylated imidazole groups. [1)] Prepared by ester cleavage. [2)] Prepared by methylation.

The thermogravimetric analysis of PEImA and its derivatives shows the release of water and in case of PEMeImA probably methanol up to temperatures of 120 °C (Figure S9). The decomposition of PEImA starts around 150 °C and the mass loss over 80% at 800 °C indicates the degradation of both the ethyl ester and the imidazole ring. Furthermore, PEMeImA seems to decompose at lower temperatures and PImAA seems to feature significantly increased thermal stability as degradation starts around 250 °C.

# Conclusion

We describe the homopolymerization of PEImA *via* free radical and anionic techniques as well as the modification into permanently charge polyelectrolytes or polyzwitterions through either alkylation of the imidazole ring or hydrolysis of the ester moiety. The materials were characterized by SEC, SEC-MALLS (for selected examples), NMR spectroscopy, titration, and TGA. Whereas anionic polymerization of EImA seems to produce polymers of lower dispersity, higher molar masses so far can be reached using free radical polymerization in various solvents. We think that the resulting materials, especially the polyzwitterions PImAA or PMeImAA are interesting candidates as materials with tunable charge and charge density and further studies regarding the pH- and salinity-dependent solubility will follow. In addition, such materials might be of interest in the context of protein-repellant coatings (for nanoparticles) or as potential biocompatible polymers. Also, imidazole-based polymeric materials can act as carrier system for metal catalysts and, in our case, both the imidazole and the carboxylic acid can act as ligands.[39]

# Experimental Section

Ethyl propiolate (99%), triphenyl phosphine (ReagentPlus®, 99%), 2,2'-azobis(2-methylpropionitril) (AIBN) recrystallized in methanol and iodomethane (99%) were purchased from Sigma Aldrich. Potassium *tert*-butoxide (Fluorochem Ltd., 99%), imidazole (AppliChem GmbH, 99%), DMF (Acros Organics, 99.8%, Extra Dry, AcroSeal®) and lithium hydroxide monohydrate (Acros Organics, extra pure, 56% LiOH) were used without further purification. Tetrahydrofuran (VWR International, HiPerSolv CHROMANORM® for HPLC) was dried by refluxing over sodium with benzophenone and stored under Ar. All deuterated solvents were obtained from Deutero GmbH (Kastellaun, Germany). For dialysis, a regenerated cellulose membrane (Spectrum, Inc., Spectra/Por® 6 pre-wetted dialysis tubing) with a nominal molecular weight cut-off of 1 kDa was used.

**Size-exclusion chromatography (SEC)**

SEC measurements in DMAc were performed on an Agilent (Santa Clara, CA, USA) system equipped with G1310A pump, a G1362A refractive index detector, and both a PSS GRAM 30 Å and a PSS GRAM 1000 Å column in series (PSS Polymer Standards Service, Mainz, Germany). *N*,*N*-Dimethylacetamide with 2.1 $g \cdot L^{-1}$ of lithium chloride was applied as eluent at 1 $mL \cdot min^{-1}$ flow rate and the column oven was set to 40 °C. The system was calibrated with PMMA (505-981,000 $g \cdot mol^{-1}$) standards.

SEC measurements in water were performed on a Jasco (Groß-Umstadt, Germany) system equipped with a PU-980 pump and a RI-930 refractive index detector. Water with 0.3% trifluoroacetic acid and 0.1 M sodium chloride was used as solvent at a flow rate of 1 $mL \cdot min^{-1}$ on an PSS SUPREMA-MAX 300 Å column at 30 °C. The system was calibrated with P2VP (1,300-81,900 $g \cdot mol^{-1}$) standards (Polymer Source, Dorval, Quebec, Canada).

**Size-exclusion chromatography with multi-angle light scattering (SEC-MALLS)**

SEC measurements (PSS, NOVEMA Max column) were performed on an adapted AF2000 MT System from Postnova Analytics GmbH (Landsberg, Germany), equipped with a tip pump used to control the mobile phase flow rate (PN1130), an autosampler (PN5300), and a column oven unit (PN4020). The column was coupled to a multi-angle laser light scattering (MALLS) detector (PN3621) equipped with a 532 nm laser. A mobile phase of 0.1 M NaCl + 0.3% TFA was used as sample and run solvent. The oven temperature was set to T=25 °C and the injection volume was 50 µL. The polymer was dissolved in the running mobile phase at a concentration of 2.5 mg $mL^{-1}$. A refractive index (RI) detector was used as a concentration sensitive detector and the elutions further detailed *via* MALLS. Values for the recovery were found close to 100%. Example elugrams are shown in Figure S3 with the weight-average molar mass trace against elution time shown in blue.

Values of the refractive index increment *dn/dc*, necessary to estimate appropriate values of the molar mass, were determined with an Optilab rEX system (Wyatt, Germany) by manual delivery of six known concentrations of the polymer in respective mobile phases used in SEC-MALLS experiments *via* a plastic syringe at a temperature of T = 25 °C. The *dn/dc* was calculated by the slope of the plot from the refractive index against the concentration. Values for the *dn/dc* of 0.1557±0.0003 mL $g^{-1}$ for entry 14 of Table 3 and 0.1594±0.0008 mL $g^{-1}$ for entry 4 of Table 3 were determined.

**Nuclear magnetic resonance spectroscopy (NMR)**

$^{1}$H-NMR and $^{13}$C-NMR spectra of the monomer were recorded in $CD_2Cl_2$ on a Bruker Fourier spectrometer equipped with a direct observe probehead operating at a proton frequency of

300 MHz. Sample temperature was set to 298 K. Chemical shifts are given in parts per million (ppm, [δ]) and were referenced by using the residual signal of the deuterated solvent.

$^1$H-NMR spectra of the polymers were recorded in $d_6$-DMSO or $D_2O$ on a Bruker Avance III spectrometer equipped with a direct observe probehead operating at a proton frequency of 400 MHz. Sample temperature was set to 333 K. Chemical shifts are given in parts per million (ppm, [δ]) and were referenced by using the residual signal of the deuterated solvent.

**Solid state NMR**

Proton decoupled $^{13}$C solid-state magic angle spinning (ssMAS) NMR spectra were acquired utilizing cross polarization with a contact time of 2 ms and a spinning frequency of 15 kHz. All data were collected on a Bruker Avance III HD 400 MHz spectrometer equipped with a 4 mm dual channel probe. Sample temperature was set to 300 K. The carbon chemical shifts were referenced externally, setting the high-frequency (methylene) signal of adamantane to 38.5 ppm.

**Thermogravimetric analysis (TGA)**

TGA measurements were carried out from 30 °C up to 800 °C under nitrogen atmosphere with a heating range of 10 K·min$^{-1}$ on a Perkin Elmer TGA8000 device.

**Crystal Structure Determination**

The intensity data were collected on a Nonius KappaCCD diffractometer, using graphite-monochromated Mo-$K_\alpha$ radiation. Data were corrected for Lorentz and polarization effects; absorption was taken into account on a semi-empirical basis using multiple-scans.[40][41][42]
he structure was solved by direct methods (SHELX[43]) and refined by full-matrix least squares techniques against $Fo^2$ (SHELXL-97[43]). All hydrogen atoms were located by difference Fourier synthesis and refined isotropically. MERCURY[44] was used for structure representations.
**Supporting Information Available:** Crystallographic data deposited at the Cambridge Crystallographic Data Centre under CCDC-1554466 for **EImA** contain the supplementary crystallographic data excluding structure factors; this data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

**Potentiometric titration**

The Titrations were done with a titrator TitroLine® 7000 with WA 20 exchangeable unit and magnetic stirrer TM 235 equipped ScienceLine pH combination electrodes with temperature sensor A162 from SI Analytics GmbH (Mainz, Germany). Therefore, a 5 g·L$^{-1}$ solution of PImAA or PMeImAA was prepared with 0.1 M NaOH and titrated against 0.1 M HCl by automatic dynamic pH titration method. Additionally, EImA and PEImA were dissolved in 0.1 M HCl and titrated with 0.1 M NaOH using the same method.

**Lyophilisation**

An Alpha 1-2 LDplus from Martin Christ Gefriertrocknungsanlagen GmbH (Osterode am Harz, Germany) were used for freeze-drying of aqueous solutions.

**Centrifugation**

The precipitated polymer was centrifuged with a Thermo Scientific Heraeus Megafuge 8 Centrifuge at 8,000 rpm for 5 minutes.

**Synthesis of ethyl 2-(imidazol-1-yl)acrylate (EImA)**

To a solution of imidazole (10.093 g; 148.25 mmol) in DCM (350 mL) ethyl propiolate (15 mL; 148.01 mmol) was added at -15 °C and cooled to -30 °C. A solution of triphenylphosphine (38.701 g; 147.55 mmol) in DCM (80 mL) was added dropwise and the reaction mixture was allowed to warm up to room temperature over 2 hours. After 20 hours the mixture was concentrated and purified by column chromatography (DCM, followed by EtOAc) to afford 18.706 g ethyl 2-(imidazol-1-yl)acrylate (75%) as yellow oil, which crystallized at -25 °C.

*$^{1}$H-NMR* (300 MHz, $CD_2Cl_2$, 25 °C): δ = 1.34 (t, *J*=7.1, -$CH_2$-C*H*$_3$), 4.32 (q, *J*=7.1, -C*H*$_2$-$CH_3$), 5.83 (d, *J*=1.1, -C=C*H*$_2$), 6.26 (d, *J*=1.1, -C=C*H*$_2$), 7.04 (dd, *J*=1.4, 1.0 Hz, -N-CH=C*H*-), 7.15 (t, *J*=1.4, -N-C*H*=CH-), 7.70 (t, *J*=1.1 Hz, -N=C*H*-N-) ppm.

*$^{13}$C-NMR* (75 MHz, $CD_2Cl_2$, 25 °C): δ = 14.42 (-$CH_2$-*C*$H_3$), 62.87 (-*C*$H_2$-$CH_3$), 119.26 (-C=*C*$H_2$), 120.03 (-N-CH=*C*H-), 129.70 (-N-*C*H=CH-), 135.11 (-*C*=$CH_2$), 137.66 (-N=*C*H-N-), 162.78 (-*C*=O) ppm.

*Crystal Data for EImA*: $C_8H_{10}N_2O_2$, Mr = 166.18 g·mol$^{-1}$, colourless prism, size 0.088 x 0.080 x 0.064 mm$^3$, monoclinic, space group P $2_1$/c, a = 6.4082(7), b = 20.135(3), c = 6.8450(8) Å, β = 110.585(7)°, V = 826.83(18) Å$^3$ , T= -140 °C, Z = 4, $\rho_{calcd.}$ = 1.335 g·cm$^{-3}$, μ (Mo-$K_\alpha$) = 0.98 cm$^{-1}$, multi-scan, transmin: 0.4553, transmax: 0.7456, F(000) = 352, 8634 reflections in h(-8/7), k(-24/25), l(-8/8), measured in the range 3.34° ≤ Θ ≤ 26.36°, completeness $\Theta_{max}$ = 99.9%, 1691 independent reflections, $R_{int}$ = 0.1018, 1263 reflections with $F_o > 4\sigma(F_o)$, 149 parameters, 0 restraints, $R1_{obs}$ = 0.0617, $wR^2_{obs}$ = 0.1222, $R1_{all}$ = 0.0939, $wR^2_{all}$ = 0.1368, GOOF = 1.176, largest difference peak and hole: 0.248 / -0.286 e Å$^{-3}$.

**General procedure for free radical polymerization of EImA**

To a flask charged with EImA under Ar atmosphere were added solvent (1.75 M EImA) and AIBN (0.5 mol%). The mixture was degassed by three cycles of freeze-pump-thaw and heated up to 65 °C for 48 hours. The polymer was precipitated in EtOAc (45 mL), centrifuged and dried under vacuum.

*$^{1}$H-NMR* (400 MHz, $d_6$-DMSO, 60 °C): δ = 0.7-1.5 (-$CH_2$-C*H*$_3$), 1.6-3.1 (back bone), 3.5-4.4 (-C*H*$_2$-$CH_3$), 6.4-7.9 (Imidazole group) ppm.

*Solid state $^{13}$C-NMR*: δ = 5-12 (-$CH_2$-*C*$H_3$), 30-54 (back bone), 54-77 (-*C*$H_2$-$CH_3$, back bone), 109-141 (Imidazole group), 159-172 (-*C*=O) ppm.

**General procedure for the anionic polymerization of EImA**

A microwave vial was charged with EImA under Ar atmosphere was introduced into a glove box and dry solvent was added. The monomer solution was added to a second microwave vial with solvent and KO*t*Bu (0.1 M in THF) and stirred for 24 hours. Methanol was added to the reaction mixture and the polymer was precipitated in EtOAc, centrifuged and dried under vacuum.

*$^{1}$H-NMR* (400 MHz, $d_6$-DMSO, 60 °C): δ = 0.7-1.4 (-$CH_2$-C*H*$_3$), 1.5-3.0 (back bone), 3.1-4.0 (-C*H*$_2$-$CH_3$), 6.4-7.9 (Imidazole group) ppm.

*Solid state $^{13}$C-NMR*: δ = 5-13 (-$CH_2$-*C*$H_3$), 29-54 (back bone), 54-65 (-*C*$H_2$-$CH_3$, back bone), 107-140 (Imidazole group), 157-171 (-*C*=O) ppm.

**Synthesis of PEMeImA**

In a microwave vial PEImA (299.5 mg) was dissolved in methanol (5 mL) and purged with Ar for 5 minutes. Methyl iodide (0.56 mL; 9.0 mmol; 5 eq. per monomer unit) was added to the polymer solution and stirred at room temperature for 48 hours. The polymer was precipitated in EtOAc (175 mL), centrifuged and dried under vacuum to afford 456.4 mg PEMeImA as yellowish solid.

*$^{1}$H-NMR* (400 MHz, $D_2O$, 60 °C): δ = 1.2-2.1 (-$CH_2$-C*H*$_3$), 3.2-4.8 (back bone, -C*H*$_2$-$CH_3$, -N-C*H*$_3$), 7.0-10.1 (Imidazole group) ppm.

*Solid state* $^{13}$*C-NMR*: δ = 5-15 (-$CH_2$-*C*$H_3$), 26-54 (-N-*C*$H_3$, back bone), 54-69 (-*C*$H_2$-$CH_3$, back bone), 110-140 (Imidazole group), 156-169 (-*C*=O) ppm.

**Synthesis of PImAA**

In a microwave vial PEImA (101.7 mg) was dissolved in methanol (2 mL) and a solution of lithium hydroxide monohydrate (162.3 mg; 3.87 mmol; 5 eq. per monomer unit) in water (2 mL) was added. The reaction mixture was heated up to 65 °C for 48 hours and dialyzed against water. The aqueous solution of the polymer was freeze-dried and afforded 75.7 mg PImAA as white solid.

$^1$*H-NMR* (400 MHz, $D_2O$, 60 °C): δ = 2.5-3.5 (back bone), 6.5-8.5 (Imidazole group) ppm.

*Solid state* $^{13}$*C-NMR*: δ = 22-54 (backbone), 55-77 (back bone), 108-142 (Imidazole group), 152-181 (-*C*=O) ppm.

**Synthesis of PMeImAA**

**Preparation by ester cleavage of PEMeImA**

In a microwave vial PEMeImA (250.5 mg) was dissolved in methanol (2.5 mL) and a solution of lithium hydroxide monohydrate (178.8 mg; 4.26 mmol; 5 eq. per monomer unit) in water (2.5 mL) was added. The reaction mixture was heated up to 65 °C for 48 hours and dialyzed against water. The aqueous solution of the polymer was freeze-dried and afforded 142.2 mg PMeImAA as yellowish solid.

$^1$*H-NMR* (400 MHz, $D_2O$, 60 °C): δ = 2.6-3.6 (back bone), 3.7-4.3 (-N-C*H*$_3$), 6.8-9.6 (Imidazole group) ppm.

*Solid state* $^{13}$*C-NMR*: δ = 27-35 (-N-*C*$H_3$), 35-57 (back bone), 58-72 (back bone), 106-142 (Imidazole group), 157-176 (-*C*=O) ppm.

**Preparation by methylation of PImAA**

In a microwave vial PImAA (97.6 mg) was dissolved in methanol (2 mL) and water (2 mL). The solution was purged with Ar for 5 minutes and methyl iodide (0.25 mL; 4.02 mmol; 5 eq per monomer unit). The biphasic mixture was heated up to 65 °C for 24 hours and the yellow solution was dialyzed against water, 50% methanol and water again. After freeze-drying 83.4 mg PMeImAA was yielded as white solid.

$^1$*H-NMR* (400 MHz, $D_2O$, 60 °C): δ = 2.4-3.8 (back bone), 3.8-4.4 (-N-C*H*$_3$), 6.7-9.8 (Imidazole group) ppm.

*Solid state* $^{13}$*C-NMR*: δ = 28-36 ((-N-*C*$H_3$), 36-56 (back bone), 57-71 (backbone), 107-141 (Imidazole group), 157-172 (-*C*=O) ppm.

# Acknowledgements

We would like to acknowledge the NMR-platform at the Friedrich-Schiller-University Jena for support in NMR spectroscopy and Steffen Weidner (Federal Ministry for Economic Affairs and Energy, BAM) and Jan Steinkönig (Karlsruhe Institute of Technology, KIT) for attempted MALDI-MS or ESI-MS measurements of PEIMA or the corresponding oligomers. Further support of this study was obtained from the Thüringer Ministerium für Wirtschaft, Wissenschaft und Digitale Gesellschaft (TMWWDG, ProExzellenz II, NanoPolar) for funding the Solution Characterization Group (SCG) at the Jena Center for Soft Matter (JCSM). We are further grateful to Moritz von der Lühe for TGA analysis.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**Highlights:**

- We report on the synthesis of Poly(ethyl 2-(imidazol-1-yl)acrylate) (PEImA)
- PEImA can be prepared using either free radical or anionic polymerization
- PEImA can further be transformed into different polyampholytes or polyzwitterions