NANO-COMPARTMENTALIZED POLYMERIC IONIC LIQUIDS AS A NEW MATERIAL PLATFORM FOR TAILORING RESPONSIVE MACROMOLECULAR SYSTEMS

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ERA-CHEMISTRY COLLABORATIVE PROJECT

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1. Introduction

The participants of this collaborative project have targeted a highly challenging fundamental research task: synthesis of multi-component nano-compartmentalized polymeric ionic liquid (NCPIL) structures by combining incompatible macromolecular building blocks containing chemically bonded hydrophobic and responsive (smart, intelligent, adaptive) hydrophilic polymer chains, and in addition ionic liquid moieties. Nanostructured polymer assemblies with stimuli-responsive behavior are in the focus of current research worldwide, as they are expected to find applications in a broad spectrum of advanced and specialty areas. Key issues in the development of such advanced new macromolecular materials are precise tailoring of their polymeric building blocks, utilization of responsive polymers, and controlled micelle formation. In the framework of this project, novel functional polymeric ionic liquids (PILs) compartmentalized in the nanoscale, which have not existed before, are planned to be synthesized by combining hydrophobic liquid polymers, such as polyisobutylene (PIB) and poly(tetrahydrofuran) (PTHF), with hydrophilic thermoresponsive poly(2alkyl-2-oxazoline)s (POXs) and ionic liquid (IL) moieties, followed by the fundamental structural and property characterizations. The creation of micellar structures was hypothesized to be achieved by incorporation of highly branched macromolecules as well as by the design of self-assembling amphiphilic block copolymers. The resulting nano-compartmentalized polymeric ionic liquids (NCPILs), which are assumed to be endowed with lower critical solution temperature (LCST) behavior owing to the presence of the POX segments, were planned to be thoroughly characterized and investigated with respect to structure-property relationships. Special emphasis was placed upon nanostructure and micelle formation, phase behavior, and thermoresponse. In addition, the synthesis and characterization of nanoconfined PILs on the basis of the chemical derivatization of nanophase separated amphiphilic polymer conetworks were also attempted. Finally, application perspectives of NCPILs as smart materials were also planned to be examined, e.g. for thermally switchable shuttling of nanoparticles, in the course of this project.

2. Molecular toolbox of end-functionalized PIBs

The synthesis of the envisioned NCPILs necessitates a molecular toolbox of endfunctionalized PIB intermediates. As starting materials, both well-defined allylterminated PIB with narrow molecular weight distribution, produced via quasiliving cationic isobutylene polymerization^[1], as well as a commercial PIB (Glissopal[®]1000 from BASF SE) bearing an olefinic chain end of mostly vinylidene-type have been used. Both types were of rather low molar mass (M_n of approx. 1000 g/mol), and thus, viscous liquids. By means of consecutive chain end modification reactions, first PIBs with hydroxyl (PIB-OH), then tosylate (PIB-OTs) and nosylate (PIB-ONs) chain ends were synthesized as presented in Figure 1.





Figure 2 shows the ¹H NMR spectra of the derivatized PIBs. In this Figure, the spectrum of the chlorine-ended PIB is also shown which may form in a side reaction through the involvement of tosyl or nosyl chloride. Subsequent to tosylation, PIBs with piperidine (PIB-Pip) and imidazole (PIB-Im) end groups have been prepared. The synthesis and endfunctionalization of well-defined allyl-ended PIB was carried out in Hungary, while derivatization of Glissopal was mostly examined by the German team. To the best of our knowledge, among these materials, PIB derivatives with nosylate and piperidine end groups have not been described so far. Special emphasis was put on achieving quantitative chain end functionality, which is crucial for further use of the PIB intermediates as building blocks in NCPIL design. This goal was accomplished by elaborate screening and improvement of reaction conditions or, if quantitative end group modification could not be reached, by the development of sophisticated purification procedures based on column chromatography. Thorough characterization by means of NMR spectroscopy and SEC analysis clearly confirmed the structure of the aforementioned PIB derivatives. Thus, significant progress has been made with respect to the preparation of perfectly endfunctionalized PIBs, and a molecular PIB toolbox was successfully created, albeit it took more time than

expected. The synthetic investigations on the tosylation and nosylation of PIB-OH will the topic of a manuscript which will be submitted for publication soon.

It has to be mentioned that due to the lack of time, and since another strategy for coupling of PIB with POXs turned out to be very promising (see Section 8), we refrained from launching trials to synthesize oxazoline- and oxazolinium-terminated PIBs, as originally planned. It has also to be commented that because of the original focus on PIB-OTs and the lack of time exploitation of the more electrophilic PIB-ONs for creation of NCPIL structures was limited only to few trials.



Figure 2. ¹H NMR spectra of endfunctional PIBs derived from allyl-ended PIB: PIB-OH (bottom), PIB-OTs (lower middle), PIB-ONs (upper middle), PIB-CI (top).

3. Oxazoline polymerization in benzotrifluoride and IL-terminated polyoxazolines

Well-defined polyoxazolines (POXs) are usually produced by quasiliving cationic ringopening polymerization (CROP) of 2-alkyl-2-oxazolines. For coupling of hydrophobic PIB and hydrophilic POXs, a reaction medium capable of dissolving both components is needed. However, the solvents usually employed in the CROP of polar 2-alkyl-2oxazolines, such as acetonitrile or dimethylacetamide, do not fulfill this task, since they do not dissolve PIB. Benzotrifluoride (BTF), an environmentally benign solvent, which has never been used for oxazoline polymerization before, was found by us to be a well-suited alternative solvent for quasiliving CROP of oxazolines. Thus, these conditions developed by us enables the design of well-defined poly(2-ethyl-2oxazoline) (PEtOx) building blocks and is compatible with PIB. Kinetics of the methyl tosylate initiated CROP of 2-ethyl-2-oxazoline (EtOx) in BTF were studied in details. These investigations proved that well-defined PEtOx with predetermined molar mass and low polydispersity can be obtained. Reference experiments even revealed superiority of BTF over conventional solvents concerning propagation rate. Moreover, in the frame of these investigations, 1-methylimidazole and piperidine were tested as terminating agents for the EtOx polymerization, and these were found to be effective nucleophiles for opening the terminal oxazolinium ring of the active chains, thus giving access to novel types of PEtOx species containing an ionic liquid (IL) type methylimidazolium tosylate or piperidinium tosylate end groups (see Figures 3 and 4). It should be mentioned that the successful end-capping with methylimidazole also led to inspiring us, and these new findings served as model for the preparation of PIB-IL-PEtOx block copolymers, which are described later in this report (see Section 8). The study of CROP of EtOx in BTF and synthesis of the novel PEtOx-IL will be published in the very near future.



Figure 3. CROP of EtOx in BTF and termination by 1-methylimidazole (R = methyl) or 1-vinylimidazole (R = vinyl).

It is worth mentioning that termination of EtOx polymerization works also with 1-vinylimidazole as well, yielding PEtOx macromonomers bearing a vinylimidazolium cation chain end. Radical polymerization produces novel types of thermoresponsive graft PILs with PEtOx side chains. Thus, the readily available PEtOx-IL macromonomers are more interesting and feasible than the originally envisioned dual functional IL-oxazoline monomers, whose synthesis would require more tedious procedures. Ongoing research concentrates on preparation and characterization of homopolymers, copolymers, and networks on the basis of ionic POX macromonomers as well as investigation of possible applications of the respective macromolecular systems.



Figure 4. ¹H NMR spectra of endfunctional poly(ethyloxazoline)s prepared in BTF bearing oxazolinium, hydroxyl, piperidine and methylimidazolium moieties.

4. Poly(2-ethyl-2-oxazoline)s with hydrophobic chain ends

In order to investigate the effect of hydrophobic chain segments attached to PEtOx chains on the thermo-responsive behavior of POEtOx, a series of well-defined thermoresponsive PEtOx homopolymers bearing alkyl chains (*n*-dodecyl, *n*-octadecyl) at one terminus or both termini has been prepared by using 1-iodooctadecane as initiator for EtOx polymerization in BTF and/or 1-dodecylamine as terminating agent. The synthetic procedures are displayed in Figure 5.



Figure 5. Synthetic routes for the preparation of poly(ethyloxazoline)s bearing hydroxyl or hydrophobic alkyl terminal segments.

Three series of PEtOx were prepared with varying the molecular weight of the PEtOx sequences. The resulting terminally modified PEtOx samples were thoroughly characterized with respect to micelle formation in water and LCST-type behavior. These results are presented in Table 1. As the data in this table indicate, both the critical micelle concentration (cmc) and cloud points (T_{CP}) were found to strongly depend on the type of terminal groups and molecular weight. A manuscript for publication on these new results is expected to be submitted soon.

Polymer	M _n (g/mol) ¹	D ¹	$T_g (°C)^2$	$T_{CP} (°C)^3$	cmc (mg/ml) ⁴
C1-PEtOx-OH 1	7550	1.25	55.2	-	-
C1-PEtOX-C12 1	7380	1.26	54.6	-	0.20
C18-PEtOx-OH 1	10560	1.28	53.9	74.6	0.02
C18-PEtOx-C12 1	10440	1.26	51.0	82.5	0.02
C1-PEtOx-OH 2	11820	1.30	58.7	89.0	-
C1-PEtOX-C12 2	11330	1.34	57.5	87.8	1.00
C18-PEtOx-OH 2	15390	1.28	57.5	70.1	0.05
C18-PEtOx-C12 2	15110	1.29	56.5	74.6	0.10
C1-PEtOx-OH 3	16110	1.29	59.0	81.0	-
C1-PEtOX-C12 3	15440	1.34	61.5	82.0	2.92
C18-PEtOx-OH 3	19780	1.32	60.7	66.8	0.08
C18-PEtOx-C12 3	19700	1.33	59.4	70.5	0.10

Table 1. Number average molecular weight (M_n) , polydispersity (D), glass transition temperature (T_g) , cloud point (T_{CP}) and critical micelle concentration (cmc) of PEtOx samples with different terminal groups.

¹determined by gelpermeation chromatography (GPC); ²T_g: glass transition temperature, determined by differential scanning calorimetry (DSC); ³T_{CP}: cloud point temperature, determined by turbidimetry measurements, 10 mg/ml polymer concentration, inflection point of the first heating curve; ⁴cmc: critical micelle concentration, determined by pyrene fluorescence probe at room temperature.

5. Nanostructured ionic liquid functionalized polyisobutylenes (PIB-ILs)

Though not explicitly mentioned in the project proposal, we identified piperidineended polyisobutylene (PIB-Pip) and imidazole-terminated polyisobutylene (PIB-Im) as ideal intermediates for the preparation of IL-terminated PIBs. In fact, simple alkylation with methyl iodide afforded the corresponding PIB-ILs, *i.e.* PIBmethylpiperidinium iodide (PIB-MePipI) and PIB-methylimidazolium iodide (PIB-MeImI), with 100% chain end functionality (see Figure 6 left). This reaction was described for PIB-Im before,^[2] whereas in the case of PIB-Pip the resulting PILs are completely novel.



Figure 6. Synthesis of PIB-MePipI and PIB-MeImI (left) and schematic illustration of hexagonally packed cylinders in these nanostructured PIB-ILs (right).

Inspired by a recent report on the temperature-dependent formation of hierarchical morphologies with ionic clusters in the case of similar IL-functionalized PIBs,^[3] PIB-MePipI and PIB-MeImI were thoroughly analyzed by means of variabletemperature SAXS measurements. In addition, in collaboration with Prof. Christian Friedrich (FMF, University of Freiburg), comprehensive rheological examinations of PIB-MePipI and PIB-MeImI have resulted in more in-depth findings than those reported earlier. Our PIB-ILs displayed temperature-dependent nanostructural organization. For all the investigated PIB-ILs, SAXS measurements indicated the presence of hexagonally arranged cylindrical nanostructures (see Figure 6 right). This finding is somewhat surprising, since Binder et al. earlier described a simple cubic lattice for a similar methylimidazolium bromide terminated PIB.^[3] Presumably. the different morphology is a consequence of significantly shorter PIB chains and maybe the larger iodide anion in the case of our PILs. Depending on the type of cation end group and uniformity of the PIB chains, pronounced differences with respect to stability and regularity of the structures, long-range ordering, flow behavior, and temperature-induced order-disorder transitions were observed by us. The results of our detailed studies on the morphology of PIB-MePipI and PIB-MeImI significantly broaden existing knowledge about micro- and nanostructural self-assembly in PIB-IL materials and are planned to be published in an international scientific journal in the near future.

6. NCPILs with micelle-like topologies on the basis of terminally functionalized hyperbranched poly(3-ethyl-3-hydroxymethyloxetane)

Compartmentalized PILs with onion- and micelle-like topology based on a hyperbranched poly(3-ethyl-3-hydroxymethyloxetane) (PEHO) core were reported few years ago.^[4] These PILs were produced by converting the hydroxyl groups of PEHO into tosylate functions (PEHO-OTs) and subsequent nucleophilic substitution by 1-alkylimidazoles. In an alternative route, PEHO is functionalized with imidazole groups (PEHO-Im) and subsequently reacted with electrophiles, *e.g.* alkyl tosylates or alkyl bromides.^[5] Due to expected advantages of polyisobutylene (PIB) shell for such NCPILs, intensive experimental research was carried out by us to develop successful conditions to prepare NCPILs composition of PEHO-IL-PIB. Both reported routes were explored for the creation of unimolecular NCPIL micelles with an outer shell of PIB instead of alkyl chains (see Figure 7).



Figure 7. Routes explored for creation of hyperbranched PEHO-based PIB NCPILs and illustration of the micelle-like topology.

PEHO-OTs and PEHO-Im were synthesized by CROP of 3-ethyl-3hydroxymethyl oxetane and subsequent post-modification of PEHO as illustrated in Figure 4 according to previously developed procedures.^[4,5] The number average molecular weights of the PEHO cores produced were around 2500 g/mol with polydispersity of 1.7 and a degree of branching of around 50%. PEHO-OTs and PEHO-Im were obtained with a high degree of functionalization of >90% and ca. 85%, respectively.

First, the synthesis of NCPILs decorated with PIB chains was explored by following the second route, *i.e.* by reacting PEHO-Im with PIB-OTs, since PIB-Im was not on hand at this stage of the project and since we knew that this approach works well with low molecular weight alkylating agents under mild conditions.^[5] However, this was not the case for PIB-OTs. General problems were poor miscibility of the polymers (bulk reaction) and impossibility to use a polar solvent. In principal, coupling could be achieved to some extent, but rather high temperatures (at least 90 °C) and long reaction times (several days) were found to be required, which resulted in side reactions, such as elimination of toluenesulfonic acid from PIB-OTs under formation of olefin-terminated PIB chains as well as partial formation of insoluble material. Moreover, even when using PIB-OTs in sub-stoichiometric amount, reaction of PIB-OTs with the imidazole functions of PEHO-Im was incomplete. In spite of thorough variation of conditions (reaction time, temperature, solvent, reaction in bulk, stoichiometry), always mixtures were obtained which were difficult to analyze by NMR spectroscopy but apparently consisted of only moderately PIB-functionalized NCPILs and significant amounts of non-reacted PIB-OTs and side products (see Figure 5). Efforts were made to isolate the NCPILs from the raw mixtures by different purification methods, such as precipitation, liquid-liquid extraction, and column chromatography. Unfortunately, all of the procedures tried turned out to be ineffective and the NCPILs could not be isolated.

Later, the inverse route, *i.e.* coupling of PEHO-OTs and PIB-Im, was examined as well, although it was regarded to be less promising, since it was known that this route requires harsh conditions and large excess of the nucleophile even in case of low molecular weight alkylimidazoles.^[4] Several reactions, carried out either in bulk or solution at different temperatures, did not yield the desired NCPILs. Coupling of the components might have taken place to a little extent, but the coupling efficiency was much worse compared to the former route.



Figure 8. Representative ¹H NMR spectrum of a reaction product obtained by reacting PEHO-Im with PIB-OTs (conditions: 0.7 eq. PIB-OTs, 48 h, 120 °C, reaction in bulk).

Another approach to micelle-like NCPILs with a PIB-*b*-POX outer shell was also explored by the use of a PIB macroinitiator for oxazoline polymerization and termination of the polymerization by PEHO-Im. Thus, PIB-OTs was examined as potential macroinitiator in the CROP of EtOx. However, very slow initiation and severe elimination reactions, impeding controlled diblock copolymer formation, were observed, which is why this plan was not investigated further. These findings also imply that synthesis of PIB-oxazolinium cations from PIB-OTs is not possible, in contrast to expectations. Finally, when PIB-nosylates were on hand, few trials indicated that they show significantly better performance as macroinitiator than the tosylates. Thus, utilization of PIB-ONs for initiation of oxazoline polymerization and subsequent coupling with PEHO-Im might be a viable route for NCPIL design, but could not be explored any more within this project due to a lack of time.

Another option for preparation of NCPILs is based on alkylation of hyperbranched poly(ethyleneimine) (PEI) with PIB-OTs. We tried to couple these polymers, but did not find a successful way. The main problem was that no solvent capable of dissolving both components could be found. Synthesis of NCPILs with PEI core and PIB-*b*-POX shell was not tried, because the prerequisite macroinitiator approach for preparation of the block copolymer shell failed, as explained above.

In spite of our intensive experimental work, none of the investigated approaches resulted in sufficiently coupled PEHO and PIB. We came to the conclusion that the planned PEHO-PIB coupling requires conditions, such as high temperature and/or highly polar solvents, which cannot be fulfilled with known procedures at the moment. However, it should be mentioned here, that not only this but several other directions have been planned to be investigated simultaneously from the start of this project.

7. Nanoconfined poly(ionic liquid) (PIL) conetworks

The synthesis of completely new nanoconfined PILs were attempted by alkylating poly(*N*-vinylimidazole) with methyl iodide in poly(*N*-vinylimidazole)-*I*-poly(tetrahydrofuran) (PVIm-*I*-PTHF) (*"I"* stands for *linked by*) nanophasic amphiphilic conetworks composed of chemically cross-linked, separate PVIm and PTHF nanophases in the ~10 nm range. The reaction route for obtaining the PVIm-*I*-PTHF conetworks and the subsequent alkylation reaction is depicted in Figure 9.



Figure 9. Synthesis of poly(N-vinylimidazole)-*I*-poly(tetrahydrofuran) conetworks by free radical copolymerization and formation of PIL conetworks by subsequent alkylation with methyl iodide.

For the alkylation reaction, the conetworks were swollen without the addition of any solvent directly in methyl iodide and let the swollen conetworks react at room temperature. It was found by solid state NMR that near to complete alkylation occurs under this simple condition. The conetworks keep their nanophase separated structure even after alkylation with minor alteration in the d-spacing (q values at the maxima of the SAXS curves) as shown in Figure 10. AFM images confirmed these findings (see Figure 11). This means that the poly(*N*-vinylimidazolium) PIL nanophases are confined in the nanophasic PTHF matrix.



Figure 10. SAXS curves of the PVIm-/-PTHF-57 (*A*) and PVIm-/-PTHF-76 (*B*) conetworks (dashed line) and their methylated derivatives, PVImMe-/-PTHF-57 (*A*) and PVImMe-/-PTHF-76 (*B*) (solid line)



Figure 11. AFM images of PVIm-*I*-PTHF-57 (*A*), PVIm-*I*-PTHF-76 (*B*), PVImMe-*I*-PTHF-57 (*C*) and PVImMe-*I*-PTHF-76 (*D*) conetworks (PTHF domains are presented by darker, PVIm and PVImMe domains with lighter color).



Figure 12. Equilibrium swelling degree (Q_e) of PVIm-/-PTHF-57 and PVImMe-/-PTHF-57 in different solvents (A), the ratio of the equilibrium swelling degrees of the starting conetworks (APCN) and the poly(ionic liquid) conetworks (PIL) in the investigated solvents (B) the ratio of the equilibrium swelling degree of the PIL and the initial conetworks as a function of the dipole moment and dielectric constant of the solvents (C), and the ratio of the equilibrium swelling degrees versus the polarity index of the solvents (D)

The equilibrium swelling degree was determined for a variety of solvents. Surprisingly, the observed data indicate that conetworks with the nanoconfined PIL change their swelling behavior dramatically in comparison to the PVIm-*I*-PTHF by increasing their swelling capacity for certain solvents, such as DMF, DMSO and NMP, but not for a variety of other polar solvents, including water. These observations are summarized in Figure 12. To reveal the relationship between the effect of the PIL functionalization of the PVIm-*I*-PTHF conetworks and the quality of the solvent, the ratio of the equilibrium swelling degree of the PIL conetwork and the starting network was plotted as a function of the dipole moment and the dielectric

constant (see Figure 12C) and the polarity index of the solvents (see Figure 12D). As these Figures show, the swelling is increased only in a small dielectric constantdipole moment region. Namely, when the dipole moment of the applied solvent is higher than 3.8 and the dielectric constant is between 30-50, the swelling degree increases by 2 to 6 times, but otherwise the swelling decreases. The same tendency can be seen in the case of the polarity index. Between zero and 6 polarity index, only a low extent of decrease can be seen, namely from 0.2 to 0.5. Above the polarity index of 6, there is a small increment in which the ratio of the swelling change significantly increases, but this ratio is low again in the case of water. Moreover, it was found by us that that Gauss equilibrium fits best on the experimental points. From these results, it can be supposed that the maximum swelling increase can be obtained by a solvent with polarity index of 7.8, but this type of solvent was not found in the literature for testing this observation.

This unique swelling behavior of the new nanoconfined PILs can be utilized for a variety of applications, such as selective solvent absorbers, nanocatalysis, transporter, nanoreactor, ion conducting materials etc. In general, our results on the synthesis and unexpected structural features and behavior of the new nanocompartmentalized poly(ionic liquid) containing polymer conetworks are expected to inspire a variety of new research directions. A manuscript about these novel PIL conetworks is in preparation.

8. Thermoresponsive NCPIL micelles on the basis of PIB-*b*-PEtOx diblock copolymers

The design of amphiphilic block copolymers by combining hydrophobic PIB and hydrophilic polyoxazoline segments holds a lot of promise with respect to the creation of self-assembled micellar nanostructures with thermo-responsive features. However, only few examples of PIB-*b*-POX diblock copolymers have been reported,^[6-9] and surprisingly neither micellar self-assembly nor possible LCST behavior of such block copolymers have been studied so far. Moreover, PIB-*b*-POX copolymers comprising ionic moieties have not been reported at all yet.



Figure 13. Synthesis of amphiphilic PIB-IL-PEtOx diblock copolymers by termination of quasiliving EtOx polymerization with PIB-Im.

Based on the knowledge gained by us during our investigations on EtOx polymerization in BTF and the termination reaction with 1-methylimidazole (see Section 3), we developed a subtle route for the synthesis of unique PIB-b-PEtOx diblock copolymers in which the PIB block is coupled with the PEtOx block via just one imidazolium cation (with tosylate counter anion) as ionic liquid (IL) group. In our synthetic approach, these PIB-IL-PEtOx copolymers are produced by employing methyl tosylate initiated quasiliving CROP of EtOx in BTF or BTF:DMF solvent mixture and utilization of imidazole-ended polyisobutylene (PIB-Im) (see Section 5) as macromolecular terminating agent, as depicted in Figure 13. By simple variation of the molar ratio of oxazoline monomer and PIB-Im, a series of PIB₂₃-IL-PEtOx_m block copolymers with constant PIB chain length (23 isobutylene repeating units) and variable degree of polymerization (DP) of the PEtOx block (m = 10, 20, 30, and 40) were synthesized. Efficient purification of the raw products, accomplished by liquidliquid extraction or hot filtration, yielded the PIB-IL-PEtOx copolymers in excellent purity. As revealed by NMR analysis, block lengths were in good accordance with the expected values, and SEC measurements indicated very low polydispersities (<1.2). Moreover, the imidazolium cation provides not only chemically but also thermally highly stable covalent linkage of the blocks. Thus, the developed synthetic approach qualifies, in an ideal way, for the design of novel well-defined and robust amphiphilic PIL systems.

Designed alteration of the length of the PEtOx block and thus hydrophilic/hydrophobic balance turned out to be a viable tool for adjustment of the properties of PIB-IL-PEtOx copolymers, such as solubility behavior both in organic solvents and in water. Notably, PIB₂₃-IL-PEtOx_m with $m \ge 20$ readily dissolves in water under formation of low-viscosity solutions, whereas the more hydrophobic PIB₂₃-IL-PEtOx₁₀ was found to form slowly flowing hydrogels already at moderate concentrations. Investigation of CMC as well as TEM analysis of aqueous PIB-IL-

PEtOx solutions revealed self-assembly of the amphiphilic block copolymers into micellar nanostructures. However, distinct differences were observed as a function of composition. Reducing the chain length of the PEtOx block from 40 to 20 caused a gradual change of the morphology of the micelles from spherical (Figure 14a) to elongated, as visualized by TEM. Finally, in case of PIB₂₃-IL-PEtOx₁₀, extremely long worm-like nanostructures were observed, which are capable of entangling and thus account for hydrogel formation (Figure 14d and 14e).



Figure 14. TEM image of $PIB_{23}IL$ -PEtOx₄₀ micelles (a); aqueous $PIB_{23}IL$ -PEtOx₄₀ solution (c = 50 mg/mL) at room temperature (b) and above the cloud point (c). PIB_{23} -IL-PEtOx₁₀ hydrogel (c = 150 mg/mL) in inverted tube (d); TEM image of PIB_{23} -IL-PEtOx₁₀ micelles (e).

The water-soluble PIB-IL-PEtOx copolymers display thermoresponsive LCSTtype behavior. Upon heating aqueous PIB-IL-PEtOx solutions, turbid dispersions are formed, which are transformed into the original clear solutions when cooling down again (Figure 14b and 14c). as shown in Figure 15, turbidimetry measurements revealed sharp transitions with cloud points varying between 72 °C and approx. 90 °C, depending on the PEtOx block length. Cooling curves prove reversibility of the phase transitions. Only in the case of PIB₂₃-IL-PEtOx₂₀, significant hysteresis was detected. Interestingly, the PIB₂₃-IL-PEtOx₁₀ hydrogels show thermoresponsive features as well. Upon heating, separation into a clear water phase and a white lump is observed, which occurs over a broad temperature range. This peculiar transition from gel-like state to macrophase separated system, which is not fully understood yet, was found to be reversible or irreversible, depending on the time of heating, and will be subject of further examinations.



Figure 15. Transmittance–temperature curves of aqueous solutions of PIB_{23} -IL-PEtOx_m copolymers with m = 20, 30 and 40 in the range from 60 °C to 85 °C (polymer concentration: 50 mg/mL each; heating/cooling rate: 1 K/min).

Finally, first trials aiming at unveiling possible applications of the PIB-IL-PEtOx copolymers have been performed. The water-soluble PIL micelles were found to be capable of encapsulating hydrophobic molecules and temperature-triggered solubilization in aqueous media, as demonstrated by experiments with hydrophobic dye Sudan Red III. The resulting colored solutions are reversibly changed into dispersions of aggregated dye-loaded micelles, which slowly precipitate by heating above the cloud point of PIB-IL-PEtOx. Furthermore, the block copolymers qualify as effective dispersing agents for nanomaterials such as functionalized graphene (FG). In the presence of the amphiphilic PIB-IL-PEtOx, highly stable aqueous graphene dispersions are obtained, which can be reversibly transformed into a biphasic system (water – FG/polymer/water) by increasing the temperature.

In conclusion, a novel class of PIB-*b*-PEtOx diblock copolymers possessing an ionic liquid moiety between the blocks has been developed, which self-assemble into thermoresponsive NCPIL micelles, exhibit temperature-induced polarity switching, and bear great potential to be applied for thermally controlled transportation and shuttling of molecules and nanomaterials. Thus, they enable the realization of the envisioned concepts and functions. These new achievements and results have been published in one of the leading journals of polymer science (B. Kerscher, T. M. Trötschler, B. Pásztói, S. Gröer, Á. Szabó, B. Iván, R. Mülhaupt: Thermoresponsive Polymer Ionic Liquids and Nanostructured Hydrogels Based upon Amphiphilic Polyisobutylene-b-poly(2-ethyl-2-oxazoline) Diblock Copolymers, *Macromolecules*, 2019, 52, 3306-3318).^[10]

9. Manuscripts under preparation for publication in international scientific journals

Due mainly to time consuming experimental work, and especially to required additional instrumental analyses and measurements, results for various segments sufficient for publications in leading international journals have become available only very recently. As a result, after some further necessary minor measurements, the following manuscripts are planned to be finalized and submitted for publication in the near future.

Balázs Pásztói, Tobias M. Trötschler, Ákos Szabó, Györgyi Szarka, Benjamin Kerscher, Rolf Mülhaupt, Béla Iván: Synthesis of tosyl- and nosyl-ended polyisobutylenes with high efficiency: the effect of reaction conditions on tosylation and nosylation

Finalization of the manuscript is in progress.

Balázs Pásztói, Tobias M. Trötschler, Ákos Szabó, Benjamin Kerscher, Heikki Tenhu, Rolf Mülhaupt, Béla Iván: Quasiliving ring-opening polymerization of 2-ethyl-2oxazoline in benzotrifluoride, an environmentally benign solvent Finalization of the manuscript is in progress.

Balázs Pásztói, Tobias M. Trötschler, Ákos Szabó, Gergő Gyulai, Benjamin Kerscher, Heikki Tenhu, Rolf Mülhaupt, Béla Iván: Synthesis, characterization and thermoresponsive behavior of poly(2-ethyl-2-oxazoline)s with hydrophobic chain ends Finalization of the manuscript is in progress.

Tobias M. Trötschler, Balázs Pásztói, Benjamin Kerscher, Ákos Szabó, Györgyi Szarka, Barbara Heck, Valentin A. Bernauer, Levente Szántó, Christian Friedrich, Rolf Mülhaupt, Béla Iván: Self-assembling polyisobutylene-piperidinium and polyisobutylene-imidazolium nanoconfined poly(ionic liquid)s Manuscript is in preparation.

Tímea Stumphauser, György Kasza, Balázs Pásztói, Attila Domján, András Wacha, Zoltán Varga, Yi Thomann, Ralf Thomann, Tobias M. Trötschler, Benjamin Kerscher, Rolf Mülhaupt, Béla Iván: Nanoconfined poly(ionic liquid) with unique selective swelling properties from poly(*N*-vinylimidazole)-*I*-poly(tetrahydrofuran) nanophasic conetworks

Finalization of the manuscript is in progress.

10. Summary

In this highly challenging collaborative research project, with the cooperation between the Polymer Chemistry Research Group of the Institute of Materials and Environmental Chemistry, Research Centre for Natural Sciences of the Hungarian Academy of Sciences (principal investigator: Prof. Béla Iván) and Freiburger Materialforschungszentrum (FMF) und Institut für Makromolekulare Chemie, Albert-Ludwigs-Universität Freiburg (principal investigator: Prof. Rolf Mülhaupt), intensive investigations have been carried out to synthesize and explore the structure-property relations of new classes of nanocompartmentalized polymeric ionic liquids (NCPILs) which have not existed before. Tailoring of novel functional and responsive macromolecular systems has been achieved by creation of nano-compartmentalized polymeric ionic liquid (NCPIL) micelles, which combine polyisobutylene (PIB), poly(2alkyl-2-oxazoline) (POX), and ionic liquid (IL) groups. Aiming at intermediates for NCPIL creation, robust procedures have been developed that allow for the synthesis of various perfectly end-functionalized PIBs. Benzotrifluoride (BTF), which is also compatible with the non-polar PIB, was identified as suited solvent for quasiliving cationic ring-opening polymerization (CROP) of 2-ethyl-2-oxazoline (EtOx) and enables the production of well-defined poly(2-ethyl-2-oxazoline) (PEtOx) chains. Termination with alkylimidazoles yielded novel IL-terminated PEtOx species and ionic macromonomers which can be readily polymerized, thus opening ways to thermoresponsive PILs with graft architectures, unexplored so far. By using 1iodooctadecane as initiator for EtOx polymerization and/or 1-dodecylamine as terminating agent, hydrophobically modified PEtOx have been prepared, whose critical micelle concentration and cloud points were found to strongly depend on substitution pattern and molecular weight. Concerning nanostructured PIL materials, IL-terminated PIBs were synthesized by endfunctionalization procedures developed by us in the course of this project followed by simple methylation reactions. Rheological investigations and SAXS analyses revealed temperature-dependent nanostructural self-assembly, which has expanded our knowledge about PIBs with ionic liquid terminus. Moreover, new nanocompartmentalized PILs were prepared from poly(N-vinylimidazole)-I-poly(tetrahydrofuran) conetworks by alkylation of the imidazole rings in the nanophasic conetwork structure. Owing to their unique swelling behavior, these PILs can be used for applications such as nanocatalysis or ion conducting materials. Several attempts were made to synthesize NCPILs as

unimolecular micelles by coupling PIB derivatives with hyperbranched poly(3-ethyl-3hydroxymethyloxetane) (PEHO) or poly(ethyleneimine) cores but failed due to miscibility problems and side reactions. As a proof of principle, coupling of imidazolefunctionalized PEHO and PIB-tosylate worked to some extent, but coupling efficiency was low and the NCPILs could not be isolated. Generation of NCPILs with PIB-b-POX block copolymer shells failed as well, since the PIB-tosylates turned out to be inefficient initiators for EtOx polymerization, contrary to expectations. However, another strategy for NCPIL design was successful. By termination of the quasiliving CROP of EtOx in BTF or BTF:DMF mixture with imidazole-terminated PIB, a series of highly defined amphiphilic PIB-b-PEtOx diblock copolymers bearing an imidazolium cation as single IL moiety, which covalently couples both blocks, were synthesized. Hydrophilic/hydrophobic balance and thus properties of these PIB-IL-PEtOx copolymers are easily adjusted by variation of the block length ratio. As a function of the PEtOx block length, self-assembly of the copolymers results either in watersoluble spherical and elongated PIL micelles or in hydrogel-forming worm-like nanostructures as proved by a variety of techniques, such as TEM and SAXS. The water-soluble PIB-IL-PEtOx micelles possess thermoresponsive LCST-type behavior with composition-dependent cloud points. The PIB-IL-PEtOx hydrogels exhibit thermoresponsive features as well. Finally, these novel unique PIB-IL-PEtOx diblock copolymers were found to enable thermally switchable solubilization, dispersion and shuttling of molecules and nanomaterials, such as functionalized graphenes, and thus, offer new opportunities in the creation of a variety of advanced functional NCPIL systems.

11. References

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