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Programmable thermoresponsive micelle-inspired polymer ionic liquids as molecular shuttles for anionic payloads

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ABSTRACT. To enable the programmable thermoresponsive transport of anions between two phases, multifunctional hyperbranched polymer ionic liquids (hyperPILs) exhibiting micelle-inspired architectures are tailored as molecular shuttles. These polyelectrolytes consist of a hyperbranched poly(3-ethyl-3-hydroxymethyloxetane) (PEHO) core, an inner polyionic imidazolium (Im^+) and an outer thermoresponsive polyoxazoline (POx) shell, which exhibits lower critical solution temperature (LCST) behavior in aqueous medium. Key step of the hyperPIL synthesis is the efficient chain termination of the cationic ring-opening 2-oxazoline polymerization by addition of polyfunctional imidazole-terminated PEHO. The resulting covalent attachment of the LCST-polyoxazoline shell renders hyperPIL polyelectrolytes thermoresponsive. As a function of the polyoxazoline chain length and the oxazoline monomer type, the hyperPIL cloud points (T_{CP}) vary over a wide temperature range. The inner imidazolium shell enables the immobilization and transport of various anionically charged organic and inorganic payloads *via* anion exchange. Due to the thermal switching of the hydrophilicity/hydrophobicity balance, hyperPILs function as programmable molecular shuttles for anionic payloads transported back and forth between the phases of ethyl acetate and water. Thus, switchable hyperPILs qualify for manifold potential applications like catalytic processes with facile recycling of homogeneous catalysts *via* phase transfer.

INTRODUCTION

Micelles and micellar nanostructures play an outstanding role in biological and industrial processes.^{1–5} Therefore, the exploration of micelle-inspired polymer structures represents a fascinating field in polymer chemistry, since they can be used as functional nanocompartments and transporters. Typically, such micellar polymer systems are based on self-assembly of amphiphilic block copolymers. However, many of the resulting supramolecular assemblies are highly sensitive to shear and changes of pH or temperature, which frequently account for disintegration of the micelles accompanied by loss of their function. This risk is avoided by creating robust nanostructured core/shell polymers resembling unimolecular micelles.⁶

Polymers containing either repeat units or functional groups similar to ionic liquids (ILs) – often referred to as polymer ionic liquids (PILs) – have established themselves in the group of polyelectrolytes as an intriguing subclass of materials exhibiting exceptional characteristics.⁷ Recently, owing to their unique combination of properties and related expected applications, the number of studies on thermoresponsive PILs, in particular ones with lower critical solution temperature (LCST) behavior in water, has increased rapidly.⁷ One strategy towards thermoresponsive PILs is homopolymerization of already thermoresponsive IL monomers. This strategy, pioneered by the groups of Ohno and Yuan,^{8,9} was exploited for the synthesis of a variety of LCST PILs with polycationic or polyanionic backbone.^{10–13} The second approach is the design of random or block copolymers of an IL monomer and a non-ionic monomer with at least one of them showing thermoresponsive behavior in polymerized form. Most prominent examples are copolymers of different imidazolium-type IL monomers and *N*-isopropylacrylamide (NIPAM).^{14–19} Similar to thermoresponsive PILs, stimulus-responsive hyperbranched macromolecules are attracting great attention.²⁰ In a recent advance and as a rare

example of thermoresponsive PILs with highly branched architecture, Tsukruk *et al.* tailored core/shell polymers composed of hyperbranched carboxylate-functionalized polyester cores and ammonium-terminated poly(*N*-isopropylacrylamide) (PNIPAM) chains bonded to the core molecules as thermoresponsive corona by ionic interactions.²¹

In the past, hyperbranched polymer ionic liquids (hyperPILs) with onion-like compartmentalized topology have been developed in our group, which combine the features of PIL materials with the benefits of unimolecular micellar architecture.²² They are composed of a hyperbranched poly(3-ethyl-3-hydroxymethyloxetane) (PEHO) core, an inner ionic shell of covalently attached imidazolium cations with tosylate counter anions, and a non-polar outer shell of alkyl chains. These micelle-inspired polyelectrolytes function as highly effective molecular transporters in two-phase systems and enable phase transfer of molecules and nanomaterials from water into immiscible non-polar organic solvents.²³ However, they only allow for the unidirectional and irreversible transport and do not enable shuttling of payloads back and forth between two phases. The programmable thermal switching of the transport between two phases is highly desirable for many applications including catalyst recycling. Hence, aiming at making this phase transfer reversible and switchable we have developed stimulus-responsive micellar core/shell hyperPILs as molecular shuttles. This is achieved by equipping the hyperPILs with an outer shell of thermoresponsive polyoxazoline segments exhibiting LCST behavior in aqueous media. Whereas this outer LCST-polyoxazoline shell enables thermal switching of the hydrophilicity/hydrophobicity balance, the cationic imidazolium coupling groups as inner shell account for the immobilization of anionic payloads *via* anion exchange.

During recent years, non-ionic thermoresponsive polymer systems have been tailored as molecular shuttles for the reversible transport of payloads back and forth between two liquid

phases in a controlled manner. Most of them exploit self-assembly and the formation of block copolymer micelles. For example, since 2006, the Lodge group has pioneered such systems based on micelle-forming poly((1,2-butadien)-*b*-ethylene oxide), poly(*N*-isopropylacrylamide-*b*-ethylene oxide), and poly(ethylene oxide-*b*-propylene oxide-*b*-ethylene oxide) block copolymers, which can reversibly transport dye molecules as payloads back and forth between water and a water-immiscible IL. This shuttling process is controlled by temperature changes.^{24–28} Schubert's group demonstrated that also polyoxazoline block copolymers function as thermoreversibly switchable transporters in the two-phase systems used by Lodge.^{29,30} Apart from block copolymers, appropriately designed polymer brush-grafted “hairy particles” were shown to reversibly travel back and forth between two phases not only in water/IL systems,^{31,32} but also in two-phase systems consisting of water and an organic solvent.^{33,34} For example, in octane/water, thermoresponsive hairy particles, like poly(methoxytri(ethylene glycol) methacrylate) grafted on a cross-linked poly(acrylic acid) core, were used as carriers for palladium nanoparticles, which catalyzed hydrogenation reactions and were easily recycled.³⁵ However, to the best of our knowledge, the use of polyionic micelle-inspired macromolecules as thermoresponsive shuttles in two-phase systems has not been reported to date.

The novel hyperPILs presented herein are readily obtained by termination of the cationic ring-opening 2-oxazoline polymerization with polyfunctional imidazole-terminated hyperbranched PEHO to covalently attach LCST-polyoxazolines to the PEHO core *via* cationic imidazolium groups as IL moieties. By the facile variations of the size and composition of the polyoxazoline segments, the cloud point (T_{CP}) of the core/shell polyelectrolytes in aqueous solution is readily adjusted. Special attention is paid to temperature-induced transport in two-phase water/organic solvent systems using various payloads to unveil the transport mechanism and to demonstrate the

concept of switchable hyperPILs as thermoresponsive molecular shuttles operating in two-phase systems.

RESULTS AND DISCUSSION

The synthetic route for the preparation of the thermoresponsive hyperPILs with micelle-inspired core/shell architectures is shown in Scheme 1. The hyperPIL unimolecular micelles are readily obtained *via* a “grafting-to” process in which the cationic ring-opening polymerization of 2-oxazolines is terminated with polyfunctional imidazole-terminated hyperbranched poly(3-ethyl-3-hydroxymethyloxetane) (PEHO-Im), which is prepared in a three step synthesis following previously reported procedures.^{22,36} This chain termination reaction affords coupling of PEHO-Im and poly(2-oxazoline)s *via* the nucleophilic attack of the imidazole groups at the terminal oxazolinium rings to produce the inner shell consisting of imidazolium cations with tosylate counter anions. This strategy of using imidazole-functionalized polymers as macro-terminating agents for living polyoxazoline chains is very versatile and has been presented as an efficient method for the synthesis of ionic polyisobutylene-*b*-poly(2-ethyl-2-oxazoline) diblock copolymers.³⁷

Scheme 1: Synthesis and molecular architectures of thermoresponsive hyperPILs.

Synthesis of the hyperPILs. The synthesis of PEHO-OH was performed by cationic ring-opening polymerization of 3-ethyl-3-hydroxymethyloxetane (EHO) using $\text{BF}_3 \cdot \text{OEt}_2$ as initiator, following a published procedure.³⁸ The obtained hyperbranched PEHO-OH was identified by ^1H and ^{13}C NMR spectroscopy (for Figures of NMR spectra, SEC, TGA, and DSC curves of PEHO-OH and its derivatives see SI). Direct investigation of the molecular weight distribution using size exclusion chromatography (SEC) failed due to its poor solubility in the solvents commonly used for this purpose. The degree of branching of the PEHO-OH is 46 % as determined by ^{13}C inverse-gated NMR spectroscopy of the trifluoroacetylated derivative (PEHO-TFA).

In order to enable the substitution of the hydroxy groups by imidazole, the PEHO-OH was subsequently treated with tosyl chloride to form the tosylate derivative PEHO-OTs, as previously described by our group.²² According to ^1H NMR spectroscopy, a high degree of functionalization (DF) of 90 % was achieved. SEC analysis revealed a number-average molecular weight (M_n) of 3800 g mol^{-1} and, as a result of chain transfer occurring as side reaction during EHO polymerization,³⁹ a dispersity (D) of 2.0. However, since calibration of SEC with linear standards usually underestimates the molecular weight as well as the dispersity of hyperbranched polymers, these numbers have to be considered with appropriate care. From M_n of PEHO-OTs, the degree of polymerization (DP) of the PEHO core was calculated to be 15, which corresponds to a molar mass of the original PEHO-OH of 1700 g mol^{-1} . Finally, the tosyl groups were substituted by imidazole,³⁶ thereby obtaining PEHO-Im with a high DF of 82 %. SEC measurement failed due to interactions of the imidazole groups with the stationary phase. However, based on DP of PEHO-OTs and taking into account DF, M_n of PEHO-Im was calculated to be 2500 g mol^{-1} .

The yields of the polymerization and the polymer-analogous reactions were very high and amounted to at least 90 % each, which resulted in a total yield of remarkable 78 % over all the three steps. As expected, thermal analysis showed that all PEHO derivatives were amorphous substances with strongly end group-dependent glass transition (T_g) and onset decomposition temperatures (T_o). Generally, the T_g values of hyperbranched macromolecules increase with higher end group polarity, i.e. stronger end group interaction, which is reflected in the higher values for PEHO-OH (40 °C) and PEHO-Im (52 °C) compared to PEHO-OTs (23 °C). It is worth to mention the extraordinary thermal stability of the PEHO-Im, which does not show significant mass loss up to temperatures of almost 400 °C, even under air. The substantially lower decomposition temperature of PEHO-OTs is explained, in analogy to the structurally related neopentyltosylate,⁴⁰ by rearrangement of the end groups followed by elimination of *p*-toluene sulfonic acid. The most important characteristics of PEHO-OH and its derivatives are summarized in Table 1.

Table 1: Properties of PEHO-OH and its derivatives.

Sample code	DF ^a [%]	M_n [g mol ⁻¹]	Yield [%]	T_g^d [°C]	T_o^e (air) [°C]	T_o^e (N ₂) [°C]
PEHO-OH	100	1700 ^c	90	40	340	401
PEHO-OTs	90	3800 ^b	91	23	235	299
PEHO-Im	82	2500 ^c	95	52	402	404

^aEnd group fraction of the name-giving functional groups, according to ¹H NMR spectroscopy; ^bdetermined by SEC ($D = 2.0$; calculated from M_n : DP = 15); ^ccalculated from DP and average molar mass of the respective linear repeat unit (for further explanations see SI); ^ddetermined by DSC; ^edetermined by TGA.

To synthesize the thermoresponsive hyperPILs, poly(2-alkyl-2-oxazoline)s were grafted onto PEHO-Im core molecules in a “grafting-to” process. The oxazoline polymerization was

performed by means of a cationic ring-opening process with methyl tosylate (MeOTs) as initiator. After complete consumption of the monomer, PEHO-Im was added to the solution as terminating agent of the cationic oxazoline polymerization in which most chains contained cationic oxazolinium rings as end groups. Dimethylformamide (DMF) was chosen as solvent, which, due to its polar aprotic nature, enables both the cationic ring-opening oxazoline polymerization and the dissolution of PEHO-Im. The monomers used were 2-ethyl-2-oxazoline (EtOx), 2-*n*-propyl-2-oxazoline (*n*PrOx), and a 1:1 molar mixture of the two monomers (EtOx/*n*PrOx) producing random copolymers. In addition, the DP of the polyoxazoline segments was varied by the molar ratio of monomer to initiator (10:1 or 20:1). A ratio of 1.1:1 was chosen as the molar ratio of initiator to imidazole groups of the PEHO-Im to achieve complete functionalization of the imidazole groups. Six hyperPILs with different polyoxazoline shells were synthesized, which are abbreviated as PEHO-IL-POX_m (*m* = theoretical DP of the polyoxazoline shell according to monomer:initiator ratio).

The thermoresponsive hyperPILs were isolated by precipitation of the reaction mixture in Et₂O, which in the case of the two PEHO-IL-*Pn*PrOx samples and PEHO-IL-P(EtOx/*n*PrOx)₁₀ afforded core/shell polymers with acceptable purity (max. 4 wt.% low-molecular-weight components, which correspond to the fraction below 5 kg mol⁻¹ for *m* = 10 and below 10 kg mol⁻¹ for *m* = 20 in the SEC curves; see Table S2 + S3 and Figure S14). For the other samples, no satisfactory purity was achieved in this process due to poor solubility of the respective free polyoxazolines in Et₂O. To separate the oxazoline homopolymer byproducts, the two PEHO-IL-PEtOx samples and PEHO-IL-P(EtOx/*n*PrOx)₂₀ were therefore subjected to a further purification step. For this purpose, highly concentrated aqueous solutions (*c* = 100 g L⁻¹) of the polymers were heated a few degrees above their *T*_{CP}, which led to a macroscopic

temperature-induced phase separation (TIPS). At temperatures only slightly above T_{CP} of the respective hyperPIL, the free polyoxazoline chains were still well soluble in water and, thus, remained in the water-rich upper phase, while the purified hyperPILs were isolated from the polymer-rich bottom phase. In this way, the amount of non-attached polyoxazoline chains was significantly reduced, as indicated by the decrease of the low-molecular-weight fraction to maximally 7 wt.%. However, the TIPS purification process was accompanied by a massive loss of product, resulting in moderate total yields of the respective PEHO-IL-POx samples of only 24 – 56 %, whereas the PEHO-IL-*Pn*PrOx samples and PEHO-IL-P(EtOx/*n*PrOx)₁₀ were obtained in much higher yields ranging between 74 and 85 % (see Table 2).

Table 2: Properties of the hyperPILs.

Sample code	Polyoxazoline chain length		M_n [g mol ⁻¹]		$\bar{D}$	Yield [%]
	[M] ₀ /[I] ₀	¹ H NMR	¹ H NMR	SEC ^a	SEC ^a	
PEHO-IL-PEtOx ₁₀	10	10.6	18 000	19 000	1.7	56
PEHO-IL-PEtOx ₂₀	20	22.8	33 000	34 000	2.0	24
PEHO-IL-P(EtOx/ <i>n</i> PrOx) ₁₀	10	10.8	19 000	20 000	1.6	85
PEHO-IL-P(EtOx/ <i>n</i> PrOx) ₂₀	20	26.5	40 000	37 000	1.7	36
PEHO-IL- <i>Pn</i> PrOx ₁₀	10	11.4	21 000	22 000	1.6	74
PEHO-IL- <i>Pn</i> PrOx ₂₀	20	22.1	36 000	32 000	1.6	80

^aTo determine M_n and $\bar{D}$ of the hyperPILs from the SEC curves, the corresponding high-molecular signal was used without taking into account any low-molecular-weight impurities.

The ¹H NMR analysis of the hyperPILs (Figure 1 exemplarily shows the ¹H NMR spectrum of PEHO-IL-*Pn*PrOx₁₀, for ¹H NMR spectra of the other hyperPILs see SI) revealed almost quantitative functionalization of the imidazole groups, as reflected by disappearance of the

imidazole signals. Only the NMR spectrum of PEHO-IL-P(EtOx/*n*PrOx)₂₀ showed clearly recognizable signals of unreacted imidazole groups, but reliable quantification was prevented by overlapping of the signals. By comparing the signal intensities of the polyoxazoline repeat unit directly bound to the imidazolium cation with the remaining polyoxazoline backbone, the DP of the attached polyoxazoline chains was determined. In accordance with the SEC analysis, the remaining traces of free polyoxazoline chains were neglected in this calculation. The chain lengths calculated in this way are always slightly larger than the monomer:initiator ratio, but the deviation was usually less than 15 %. Only the sample PEHO-IL-P(EtOx/*n*PrOx)₂₀ showed a higher deviation of 33 %.

Figure 1: ¹H NMR spectrum of PEHO-IL-PnPrOx₁₀ (top) and magnification of the spectrum (bottom).

The M_n values of the hyperPILs calculated from the ^1H NMR spectra varied between 18 000 and 21 000 g mol^{-1} for the PEHO-IL-POx₁₀ samples and between 33 000 and 40 000 g mol^{-1} for the PEHO-IL-POx₂₀ samples. Of course, as SEC results of the PEHO-OTs intermediate are included in these calculations, these molar masses are afflicted with some uncertainty. However, even though SEC analysis of the hyperPILs is similarly problematic due to the hyperbranched core/shell architecture, the M_n values measured by SEC matched very well those ones determined by ^1H NMR spectroscopy and, depending on the polyoxazoline shell, fell in the range of 19 000 g mol^{-1} (PEHO-IL-PEtOx₁₀) to 37 000 g mol^{-1} (PEHO-IL-P(EtOx/*n*PrOx)₂₀). Thus, these numbers at least illustrate the magnitude of the molar masses of the hyperPILs. The dispersities varied from 1.6 to 2.0, however, due to the calibration with linear PMMA standards, SEC tends to underestimate these values. Table 2 summarizes the polyoxazoline chain lengths and the M_n and D values of the hyperPILs.

The thermal analysis of the hyperPILs by DSC revealed T_g values varying between 24 and 45 °C. As expected due to the longer alkyl side-chains in *n*PrOx,^{41,42} the PEHO-IL-*n*PrOx samples had slightly lower T_g values as compared to the PEHO-IL-PEtOx or PEHO-IL-P(EtOx/*n*PrOx) samples (see Table 3). The T_O values determined by TGA under air ranged between 340 and 360 °C, whereas under nitrogen atmosphere slightly higher T_O values between 350 and 370 °C were detected. In general, the differences in the decomposition temperatures of the hyperPILs are very small and a rational relation to their structure is not evident. Under air, no mass loss was detectable up to at least 200 °C, under nitrogen even up to at least 300 °C. Hence, the novel thermoresponsive hyperPILs exhibited the same high thermal stability as their alkyl-modified predecessors.²²

Table 3: Thermal properties of the hyperPILs.

Sample code	T_g^a [°C]	T_O^b (air) [°C]	T_O^b (N ₂) [°C]
PEHO-IL-PEtOx ₁₀	44	349	353
PEHO-IL-PEtOx ₂₀	31	356	367
PEHO-IL-P(EtOx/ <i>n</i> PrOx) ₁₀	32	346	355
PEHO-IL-P(EtOx/ <i>n</i> PrOx) ₂₀	45	358	365
PEHO-IL-P <i>n</i> PrOx ₁₀	24	339	353
PEHO-IL-P <i>n</i> PrOx ₂₀	25	359	366

^aDetermined by DSC; ^bdetermined by TGA.

Thermoresponsive behavior of the hyperPILs. Special attention was payed to the investigation of the thermoresponsive properties of the micellar polyelectrolytes in aqueous solution. Due to the covalent attachment of the LCST-polyoxazoline shell, all six hyperPIL polyelectrolytes exhibited LCST behavior when exceeding sufficiently high concentrations. Upon heating above a concentration-dependent and material-specific temperature, clouding of the solution was observed. By subsequent cooling, the solution cleared again. This behavior, which is typical for LCST-polyoxazolines, can be explained by phase separation into a polymer-rich and a water-rich phase at higher temperatures. Below T_{CP} the polyoxazoline chains are well dissolved due to the hydrogen bond formation between water and the polymer. Above T_{CP} intra- and intermolecular hydrogen bonds between polyoxazoline chains are favored.⁴³ This results in aggregation of the hyperPILs and produces polymer droplets of sufficient size to scatter light, resulting in the observed turbidity (see Scheme 2).

Scheme 2: Clouding/clearing of an aqueous PEHO-IL-P(EtOx/*n*PrOx)₂₀ solution by heating/cooling and schematic illustration of the aggregation of the hyperPILs leading to phase separation.

For a more detailed investigation of the thermoresponsive phase transitions and determination of T_{CP} , temperature-dependent photometric transmission measurements were performed at different concentrations. As an example, Figure 2 shows the transmission-temperature curves of PEHO-IL-*Pn*PrOx₁₀ at concentrations of 5, 15, and 25 g L⁻¹ (see Figure S17 for the other hyperPILs). It can easily be seen that with increasing concentration the clouding occurs at lower temperatures and the temperature range of the phase transition becomes narrower.

Figure 2: Transmission-temperature curves of aqueous solutions of PEHO-IL-*Pn*PrOx₁₀.

The T_{CP} of all hyperPILs at the investigated concentrations are graphically displayed in Figure 3 (the T_{CP} values are listed in Table S3). The hyperPILs equipped with a PEtOx shell (PEHO-IL-

PEtOx₁₀ and PEHO-IL-PEtOx₂₀) showed thermoresponsive behavior only at relatively high concentrations of 75 g L⁻¹ and 25 g L⁻¹, respectively, whereas for the other hyperPILs, phase transitions were detected already at much lower concentrations of 5 g L⁻¹. Hence, the turbidimetric characterization of these PILs therefore focused on low concentrations (5 – 25 g L⁻¹), while the PEHO-IL-PEtOx samples were examined up to a concentration of 100 g L⁻¹.

Figure 3: T_{CP} of aqueous hyperPIL solutions of different concentrations.

In summary, the T_{CP} values detected varied between 21 and 93 °C. The chemical structure of the polyoxazoline shell had the strongest influence on T_{CP} . Therefore, the values for T_{CP} of the PEHO-IL-PEtOx solutions (76 – 93 °C) were clearly above those of the PEHO-IL-P(EtOx/nPrOx) solutions (43 – 60 °C), which in turn became cloudy at considerably higher temperatures with respect to the PEHO-IL-PnPrOx solutions (21 – 32 °C). The second key parameter influencing the thermoresponsive behavior was the concentration. For all samples, T_{CP} decreased with increasing concentration. For example, T_{CP} of PEHO-IL-PEtOx₂₀ decreased by 16 °C when increasing the concentration from 25 to 100 g L⁻¹. As a third parameter, for the same chemical composition and concentration increasing the polyoxazoline chain length accounted for lowering T_{CP} . Especially the T_{CP} values of PEHO-IL-PEtOx solutions were found to be strongly

dependent on the size of the shell. The same trend was observed for the other hyperPILs, but the differences were less pronounced and significant changes only occurred at the lowest concentration of 5 g L⁻¹. The effect of longer alkyl side-chain substituents on T_{CP} is in accord with linear polyoxazolines and can be explained by the resulting decrease of hydrophilicity. In fact, the observed influences of concentration and molar mass on T_{CP} were very similar to those observed for polyoxazoline homo- and copolymers.⁴⁴ As a result of the turbidimetric investigations, it can be concluded that by appropriately selecting the ratio of the oxazoline monomers and the DP of the polyoxazoline chains, the thermoresponsive behavior can be readily adjusted to tailor hyperPILs with programmable T_{CP} .

TEM. The representative TEM images of PEHO-IL-P(EtOx/*n*PrOx)₁₀ and PEHO-IL-(PEtOx/*n*PrOx)₂₀ displayed in Figure 4 show single circular particles with an average diameters with standard deviation of 20.7 ± 4.3 nm and 22.4 ± 4.8 nm respectively. Surprisingly, the length of the polyoxazoline segments has no substantial influence on the particle size. Therefore, the particles seem to represent aggregates of a small number of core-shell macromolecules, A single hyperPIL molecule has an average diameter not larger than 6 or 9 nm respectively, depending on the length of the polyoxazoline segments, as estimated by distance measurements on simulated 3D models. Samples prepared from more diluted solutions showed empty grids instead of the expected single macromolecules, probably because the small amount of deposited material was removed by the staining procedure with uranyl acetate solution. However, the size distribution of the particles is rather homogeneous, suggesting an energetic minimum at the observed diameter of about 20 nm. Images obtained from the other hyperPILs show particles with diameters around 20 nm aswell, yet the contrast is too low for a solid evaluation of the average size (see Figure S19). In general, the results obtained from TEM can only give an idea about the micellar

morphology of the dissolved hyperPILs as upon drying previously individually dissolved macromolecules might fuse together to the observed larger structures. Cryo-TEM measurements, which would give a more accurate picture of the conditions in solutions, unfortunately showed no material.

Figure 4: TEM images of PEHO-IL-P(EtOx/*n*PrOx)₁₀ (left) and PEHO-IL-P(EtOx/*n*PrOx)₂₀ (right); scale bar = 200 nm.

HyperPILs as thermoresponsive transporters. The thermal switching of the polarity and the hydrophilicity/hydrophobicity balance of the polyoxazoline shell accounted for a temperature-dependent phase change of the hyperPILs in two-phase systems consisting of water and an immiscible organic solvent. At temperatures below T_{CP} , the hyperPILs were soluble in the aqueous phase, provided that water is the better solvent as compared to the organic phase. Above T_{CP} , the hyperPILs became less polar and were rendered insoluble in water, prompting them to migrate into the organic phase. Thus, the hyperPILs can travel back and forth between aqueous and organic medium, depending on the temperature. This holds great prospects for the controlled and reversible shuttling of payloads between the two phases.

In order to investigate the temperature-induced phase change and to evaluate potential applications of the hyperPILs as programmable shuttles, the water-soluble anionic dye Congo red was used as model substance to be transported. The PEHO-IL-PEtOx samples were excluded

from these transport experiments, since they showed thermoresponsive behavior only at relatively high concentrations and because their T_{CP} values were above the boiling points of many common organic solvents. Depending on the selection of the organic solvent, different observations were made. In case of relatively polar solvents such as chloroform, an immediate phase transfer of hyperPIL and dye into the organic phase occurred already at room temperature. When an aqueous Congo red/hyperPIL solution was added to chloroform, discoloration of the aqueous phase and coloration of the organic phase was observed. This state was maintained regardless of temperature. Thus, chloroform was always a better solvent for the hyperPILs than water, which prevented shuttling in this two-phase system. On the other hand, highly non-polar solvents such as *n*-hexane did not dissolve the hyperPILs, irrespective of the temperature, which impeded any phase transfer of the dye in such systems.

In the ethyl acetate/water system, however, the hyperPILs showed a temperature-dependent phase change and enabled the desired switchable shuttling of Congo red. The best results regarding reversibility and completeness of the phase transfer were achieved with PEHO-IL-*PnPrOx*₁₀. Figure 5 illustrates this hyperPIL-mediated Congo red transport. At temperatures below the T_{CP} of the hyperPIL, the dye was dissolved in the aqueous phase. Upon heating to 60 °C, the hyperPIL transported the dye into the organic medium. Cooling to 4 °C induced shuttling *via* the reversed transport of both hyperPIL and dye into the aqueous phase. The employed PEHO-IL-*PnPrOx*₁₀ carrier contains about 0.6 mmol g⁻¹ of cations and shuttled 0.8 g of Congo red anions per 1 g of hyperPIL. Although maximal transport capacity was not studied, this illustrates the substantial shuttling capability of the hyperPILs. This shuttling process was repeated several times without encountering noticeable differences.

Figure 5: Temperature-controlled shuttling of Congo red in ethyl acetate/water using PEHO-IL- $PnPrOx_{10}$ as molecular shuttle.

For elucidation of the transport mechanism, identical experiments were performed with a water-soluble cationic dye (methylene blue) and a water-insoluble non-ionic dye (Sudan IV) (see Figure S18 for structures of the investigated dyes). In both cases, a temperature-induced hyperPIL-mediated shuttling could not be observed. The polar methylene blue always remained in the aqueous phase, whereas the non-polar Sudan IV always stayed in the ethyl acetate phase. In view of these results, it is apparent that shuttling only worked with anionic dye payloads as they were immobilized on hyperPILs *via* anion exchange for the tosylate counter ions of imidazolium cations in the inner ionic hyperPIL shell.

Going beyond the shuttling of anionic organic dyes, the switchable hyperPILs also turned out to be effective with respect to shuttling anionic palladium complexes (see Figure 6). The water-soluble palladium complex used was formed from the dipotassium salt of the triphenylphosphine ligand bis(*p*-sulfonatophenyl)phenylphosphine and disodium tetrachloropalladate (see Figure S20 for proposed structure of the complex). Similar to the transport of Congo red, PEHO-IL- $PnPrOx_{10}$ was used as thermoresponsive shuttle. At 0 °C, the Pd complex was dissolved in the aqueous phase. Upon heating to 70 °C, the hyperPIL migrated into the ethyl acetate phase

together with the palladium complex payload. By cooling to 0 °C, the complex was transported back from the ethyl acetate phase to the aqueous phase. Just like the Congo red transport, this process was repeated several times without impairing shuttling. Hence, PEHO-IL- $PnPrOx_{10}$ serves as shuttle for both organic and inorganic anions.

Figure 6: PEHO-IL- $PnPrOx_{10}$ as thermoresponsive shuttle for an anionic water-soluble Pd-phosphine complex in the ethyl acetate/water two-phase system.

CONCLUSION

Polyfunctional polyelectrolyte carriers and molecular shuttles for anionic organic and inorganic payloads are readily tailored *via* the chain termination of the cationic 2-oxazoline ring-opening polymerization with imidazole-terminated hyperbranched poly(3-ethyl-3-hydroxymethyloxetane) (PEHO-Im). In this efficient “grafting-to” process, the cationic oxazolinium end groups of the poly(2-alkyl-2-oxazoline)s alkylate the imidazole groups of PEHO-Im to produce cationic alkyl imidazolium coupling groups as IL moieties incorporated within the hyperbranched polyelectrolyte backbone. The resulting hyperbranched polymer ionic liquids (hyperPILs) exhibit nanostructures resembling micelles but are much more robust with respect to their thermal and chemical stabilities as well as their low shear and pH sensitivity. The covalent attachment of LCST-polyoxazolines derived from 2-ethyl- and 2-*n*-propyl-2-oxazoline renders hyperPILs thermoresponsive and enables the programmable thermal switching of the

hyperPIL polarity and its hydrophilicity/hydrophobicity balance. The monomer type, the polyoxazoline chain length and copolymer compositions govern the cloud point (T_{CP}) of hyperPILs in water, which varies from 21 to 93 °C. As verified by the addition of an anionic organic dye (Congo red), both hyperPILs and dye molecules are shuttled back and forth between water and ethyl acetate phases at temperatures below and above the corresponding T_{CP} . In contrast, substitution of LCST-polyoxazolines by long-chain alkyl groups exclusively permits irreversible temperature-independent dye transport in one direction from water to the organic phase. Since shuttling in water/ethyl acetate is achieved only by using *anionic* dyes, it appears highly likely that anionic dyes are immobilized on hyperPILs *via* anion exchange for tosylate counter ions of the imidazolium moieties. Successful shuttling in water/ethyl acetate in the presence of hyperPILs is also demonstrated for inorganic anions such as palladium complexes containing bis(*p*-sulfonatophenyl)phenylphosphine as a ligand. In principle, this thermal switching process using programmable thermoresponsive hyperPILs as polyfunctional carriers for anionic payloads holds great prospects with respect to the facile recovery of homogeneous catalysts. Upon completing the catalytic reaction in an organic medium at a temperature above T_{CP} , the temperature is lowered to recover the catalyst by extracting it with water. It is then reused by the subsequent shuttling back into an organic phase at elevated temperature.

EXPERIMENTAL SECTION

Materials. 3-Ethyl-3-hydroxymethyloxetane (EHO) was kindly provided by Perstorp Polyols. $\text{BF}_3 \cdot \text{OEt}_2$ and 2-ethyl-2-oxazoline (99 %) were purchased from Alfa Aesar. Trifluoroacetic anhydride (99 %), tosyl chloride (98 %), methyl tosylate (98 %), and Congo red were obtained from Merck. Imidazole (99 %), Na_2PdCl_4 (98 %), and bis(*p*-sulfonatophenyl)phenylphosphine dihydrate dipotassium salt (97 %) were purchased from Sigma-Aldrich. 2-*n*-Propyl-2-oxazoline was synthesized according to a literature procedure.⁴² Solvents were of analytical grade and purchased from different suppliers. DMF, 2-ethyl-2-oxazoline and 2-*n*-propyl-2-oxazoline were distilled and stored over molecular sieves (4 Å) prior to use. All other chemicals were used as received.

General remarks. All syntheses were performed in dry conditions and under a nitrogen atmosphere using standard Schlenk techniques. In the calculation of the end group equivalents of the PEHO derivatives, the degrees of functionalization determined from the respective ^1H NMR spectra were considered.

Synthesis of PEHO-OH. To a solution of $\text{BF}_3 \cdot \text{OEt}_2$ (5.5 mL, 6.2 g, 44 mmol, 1.0 equiv.) in dry CH_2Cl_2 (100 mL) 3-ethyl-3-hydroxymethyloxetane (50 mL, 51 g, 0.44 mol, 10 equiv.) was added dropwise under cooling in a water bath over a period of 2 h. Then, the reaction mixture was stirred at room temperature for 48 h. Afterwards, the reaction was stopped by addition of ethanol (10 mL) and the mixture was concentrated under reduced pressure until it became highly viscous but was still pourable. Subsequently, the mixture was precipitated in cyclohexane. The precipitate was dissolved in ethanol (75 mL) under gentle heating and the resulting polymer solution was precipitated in water (300 mL). The solid part was first dried at 60 °C in an oven

and then at 80 °C under high vacuum. The product was obtained as a colorless solid (48.4 g; 95 %).

Synthesis of PEHO-TFA. A solution of PEHO-OH (474 mg, 4.08 mmol OH groups, 1.0 equiv.) in trifluoroacetic anhydride (10 mL, 15 g, 71 mmol, 17 equiv.) was stirred under reflux for 4 h. Excess trifluoroacetic anhydride and formed trifluoroacetic acid were distilled off and the remaining highly viscous liquid was dried at 70 °C under high vacuum. A colorless liquid (872 mg; 100 %) was obtained.

Synthesis of PEHO-OTs. To a solution of PEHO-OH (25.0 g, 215 mmol OH groups, 1.0 equiv.) in pyridine (125 mL), a solution of *p*-tosyl chloride (82.0 g, 430 mmol, 2.0 equiv.) in pyridine (63 mL) was added at 0 °C over a period of 30 min. The reaction mixture was then stirred at room temperature for 7 d. Toluene (63 mL) was added to the reaction solution and the resulting precipitates were filtered off. Then, saturated aqueous K₂CO₃ (63 mL) was added portion wise to the filtrate. The aqueous phase was separated and the organic phase was concentrated under reduced pressure. The residue was taken up in CHCl₃ (200 mL) and washed with water (2 × 200 mL), aqueous HCl (10 %, 2 × 200 mL), water (2 × 200 mL), and saturated aqueous NaCl (200 mL). The organic phase was dried over Na₂SO₄ and concentrated under reduced pressure. The residue was dried at 80 °C under high vacuum. PEHO-OTs was obtained as a slightly yellow solid (52.8 g; 91 %).

Synthesis of PEHO-Im. A mixture of PEHO-OTs (10.6 g, 37.4 mmol OTs groups, 1.0 equiv.) and imidazole (55.3 g, 826 mmol, 22 equiv.) was heated to 120 °C, causing the imidazole to melt. The mixture was stirred at 120 °C for 24 h. After cooling, the solidified mixture was dissolved in CH₂Cl₂ (200 mL) and the resulting solution was washed with aqueous NaOH (2M, 2 × 200 mL), water (200 mL), and saturated aqueous NaCl (200 mL). The organic phase was

dried over MgSO_4 and concentrated under reduced pressure. The residue was dried at $100\text{ }^\circ\text{C}$ under high vacuum to yield PEHO-Im as a slightly brown solid (6.38 g; 90 %).

Synthesis of the hyperPILs. The syntheses of the hyperPILs were performed according to the following general procedure (weights, volumes and durations of polymerizations are listed in Table S1). To a solution of MeOTs (1.0 equiv.) in DMF the oxazoline monomer (10 or 20 equiv.) was added and the reaction solution was stirred in a preheated oil bath at $90\text{ }^\circ\text{C}$ until the monomer was fully consumed. A solution of PEHO-Im (0.9 equiv. imidazole groups) in DMF was then added and stirred at $90\text{ }^\circ\text{C}$ for another 20 h. After cooling, the solution was precipitated in Et_2O (3 times the volume of the reaction mixture). The precipitate was dissolved in CH_2Cl_2 (3 mL per gram of precipitate) and again precipitated in Et_2O (10 times the volume of the CH_2Cl_2 solution). The precipitation was performed one more time. The obtained precipitate was filtered off and dried under high vacuum. In the case of PEHO-IL-PEtOx₁₀, PEHO-IL-PEtOx₂₀, and PEHO-IL-P(EtOx/*n*PrOx)₂₀, after precipitation in Et_2O the hyperPILs, according to SEC analysis, still contained a considerable amount of low-molecular-weight free polyoxazolines. Therefore, a temperature-induced phase separation (TIPS) procedure was performed for further purification. For this purpose, the polymer to be purified was dissolved in water ($c = 100\text{ g L}^{-1}$) and heated in a closed vessel slightly above T_{CP} for 24 h (see Table S2 and S3). As a result two phases formed. The upper phase contained the main part of the free polyoxazolines, the lower phase the hyperPIL in purified form. The upper phase was pipetted off and the solvent was removed from both phases by freeze-drying. Yields and purities of the hyperPILs, which were obtained as white or yellow solids, are listed in Table S4.

HyperPIL-mediated temperature-switchable phase transfer of Congo red. Solutions of Congo red in water ($c = 0.3\text{ g L}^{-1}$) and of PEHO-IL-*Pn*PrOx₁₀ in EtOAc ($c = 0.35\text{ g L}^{-1}$) were

prepared. 2 mL of each of the solutions were mixed, resulting in a two-phase system consisting of a colorless upper EtOAc phase and a red lower aqueous phase. In a closed vessel, the two-phase system was then kept at 60 °C for 23 h in an oven. As a result, the upper EtOAc phase was colored red, whereas the lower aqueous phase was almost completely colorless. The two-phase system was then kept in a refrigerator at 4 °C for 18 h, whereupon the pattern was reversed. The EtOAc phase was almost colorless and the aqueous phase was colored red. This process was repeated several times with the same observation.

HyperPIL-mediated temperature-switchable phase transfer of a Pd complex. A solution of bis(*p*-sulfonatophenyl)phenylphosphine dihydrate dipotassium salt (13 mg, 0.036 mmol, 3.0 equiv.) and disodium tetrachloropalladate (3.5 mg, 0.012 mmol, 1.0 equiv.) in degassed water (3 mL) was prepared under nitrogen atmosphere. This solution was let to stand at room temperature for 8 d to ensure complete complex formation. In addition, a solution of PEHO-IL-*Pn*PrOx₁₀ in degassed water ($c = 1.5 \text{ g L}^{-1}$) was prepared. A part of the Pd complex solution (0.25 mL) and a part of the polymer solution (2.25 mL) were mixed and degassed EtOAc (2.5 mL) was added. At this stage, the EtOAc phase was clear and colorless, while the aqueous phase was orange. The mixture was heated at 70 °C in an oil bath for 100 min under vigorous stirring. After letting the mixture rest for a short time for phase separation, a completely decolorized aqueous phase and an orange colored EtOAc phase were obtained. Then, the mixture was cooled to 0 °C in an ice bath, stirred vigorously for 30 min and let to rest for 35 min without stirring for phase separation. By this means, the state before heating was restored. The aqueous phase was colored orange and the EtOAc phase was colorless. This heating-cooling cycle was repeated several times with the same observation.

ANALYSIS AND CHARACTERIZATION

NMR. NMR spectra were generally recorded in deuterated DMSO at 110 °C on a Bruker Avance III HD 500 MHz spectrometer (for ^1H) or at 27 °C on a Bruker Avance II 300 MHz spectrometer (for ^{13}C). As an exception, PEHO-TFA was measured in deuterated chloroform at 27 °C on a Bruker Avance II 300 MHz spectrometer (^1H and ^{13}C IG). The chemical shifts were referenced by the solvent signal.

SEC. SEC measurement of PEHO-OTs was performed on an Agilent 1260 Infinity System with RI detector and chloroform as eluent at a flow rate of 1 mL min^{-1} and a temperature of 22 °C. The injection volume was 100 μL . SDV columns (5 μm) by PSS were used: 1 x precolumn (8 * 50 mm), 1 x 1000 Å, 1 x 10 000 Å, 1 x 100 000 Å and 1 x 1 000 000 Å (each 8 * 300 mm). For calibration, narrow PS standards (from PSS) in the mass range 162 – 1 800 000 g mol^{-1} were used. Toluene was used as internal standard.

SEC measurements of the hyperPILs were performed on an Agilent 1260 Infinity System with RI detector and DMAc/LiBr(0.5 wt.%) as eluent at a flow rate of 1 mL min^{-1} and a temperature of 50 °C. The injection volume was 50 μL . GRAM columns (10 μm) by PSS were used: 1 x precolumn (8 * 80 mm), 1 x 30 Å und 2 x 1000 Å (each 8 * 300 mm). For calibration, narrow PMMA standards (from PSS) in the mass range 410 – 988 000 g mol^{-1} were used. To determine the average molecular weights and dispersities of the hyperPILs, the high-molecular weight peak was evaluated, in case of the presence of minor low-molecular-weight impurities (the lower integration limit was chosen from the minimum between the two peaks).

TGA. TGA curves were recorded on a STA 409 or a STA 449F5 from Netzsch with a heating rate of 10 K min^{-1} . To characterize the mass loss curves, the onset temperatures (T_o) were determined.

DSC. DSC curves were recorded on a DSC Seiko 6200 with heating and cooling rates of 10 K min^{-1} . The glass transition temperatures (T_g) were determined from the second heating curve using the inflection point of the transition.

Determination of T_{CP} . The transmission measurements were performed on photometers with Peltier element from Analytik Jena (S 300 VIS; for $T_{CP} < 60\text{ }^{\circ}\text{C}$) or ThermoFisher Scientific (Evolution 201; for $T_{CP} > 60\text{ }^{\circ}\text{C}$) at a wavelength of 500 nm and a heating/cooling rate of 1 K min^{-1} . The reference was demineralized water at $20\text{ }^{\circ}\text{C}$. The inflection point of the transmission-temperature curve was used to determine T_{CP} .⁴⁵

TEM. TEM images were captured with a FEI Talos L120C transmission electron microscope. The samples were prepared at room temperature by dropcasting of clear 1 wt.% aqueous hyperPIL solutions on a 200 mesh carbon-coated copper grid (Science Services, Munich, Germany) and were stained with aqueous uranyl acetate solution.

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Supporting Information

Programmable Thermoresponsive Micelle-Inspired Polymer Ionic Liquids as Molecular Shuttles for Anionic Payloads

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1. PEHO-OH and its derivatives

1.1. General remarks

For the sake of convenience, the structural formulas in the following NMR spectra only show the linear repeat unit of PEHO-OH and its derivatives despite the hyperbranched architecture. To calculate the average molecular mass of a repeat unit of PEHO-OH and its derivatives, the molecular masses of the linear repeat units were used in good approximation. In case of different end groups being present, weighting was based on the corresponding degree of functionalization (DF). This is demonstrated exemplary in the following equation for a PEHO derivative PEHO-B, which was obtained from PEHO-A by polymer analogous reaction and contains not just B groups, but also still a certain amount of non-reacted A groups.

$$\overline{M}_{rep} (PEHO-B) = [1 - DF (PEHO-B)] * M (PEHO-A) + DF (PEHO-B) * M (PEHO-B)$$

To calculate the equivalents of the functional end group B, the molar mass $M (B)$ was used, which indicates the mass of PEHO-B that contains one mole of B groups:

$$M (B) = \frac{\overline{M}_{rep} (PEHO-B)}{DF (PEHO-B)}$$

1.2. Structural characterization by NMR and SEC

1.2.1. PEHO-OH

Figure S1: ^1H (top) and ^{13}C NMR spectrum (bottom) of PEHO-OH.

^1H NMR (500 MHz, DMSO-d_6 , 383 K): δ = 0.75 – 0.92 (3H, H^1), 1.26 – 1.43 (2H, H^2), 3.13 – 3.33 (4H, $\text{H}^4 + \text{H}^5$), 3.33 – 3.42 (2H, H^6), 3.44 – 3.75 (1H, H^7) ppm.

^{13}C NMR (75 MHz, DMSO-d_6 , 300 K): δ = 7.66 (C^1), 22.07, 22.65 (C^2), 43.46 (C^3), 62.11 (C^6), 71.68 ($\text{C}^4 + \text{C}^5$) ppm.

Since SEC measurements of PEHO-OH were not possible due to its limited solubility in the solvents commonly used for this purpose, M_n was determined by multiplying the degree of polymerization (DP) determined for PEHO-OTs (see Section 1.2.3) with the molecular weight of a linear repeat unit of PEHO-OH.

$$M_n(\text{PEHO-OH}) = \text{DP} * M_{\text{rep}}(\text{PEHO-OH}) = 15 * 116 \frac{\text{g}}{\text{mol}} = 1700 \frac{\text{g}}{\text{mol}}$$

1.2.2. PEHO-TFA

Figure S2: ^1H (top) and ^{13}C IG NMR spectrum (bottom, with magnification of signal 3) of PEHO-TFA. Assignment of the different structural units to the respective signals of C^3 is according to Bednarek et al.¹

^1H NMR (300 MHz, CDCl_3 , 300 K): δ = 0.65 – 1.00 (3H, H^1), 1.18 – 1.61 (2H, H^2), 3.00 – 3.49 (4H, $\text{H}^4 + \text{H}^5$), 4.11 – 4.47 (2H, H^6) ppm.

^{13}C IG-NMR (75 MHz, CDCl_3 , 300 K): δ = 7.11 (C^1), 22.72 (C^2), 41.89 ($\text{C}^{3\text{t}}$), 42.60 ($\text{C}^{3\text{l}}$), 43.35 ($\text{C}^{3\text{d}}$), 67.17 – 72.56 ($\text{C}^4 + \text{C}^5 + \text{C}^6$), 114.42 (qd, $^1J_{\text{C,F}} = 286$ Hz, 11 Hz, C^8), 156.99 (q, $^2J_{\text{C,F}} = 43$ Hz, C^7) ppm.

Complete disappearance of the signal H^6 of PEHO-OH in the ^1H NMR spectrum of PEHO-TFA proves quantitative functionalization.

The proportion of the respective structural units (d = dendritic, l = linear, t = terminal) was calculated from the integrals of the associated signals of 3d (43.0 – 43.7 ppm), 3l (42.2 – 43.0 ppm), 3t (41.5 – 42.2 ppm), and the total integral of all signals associated to C^3 (41.5 – 43.7 ppm) in the ^{13}C inverse-gated (IG) NMR spectrum. Signal assignment is according to Bednarek et al.¹

This results in the following proportions of the structural units:

d = 23 %; l = 53 %; t = 24 %.

The degree of branching (DB) was calculated from the proportions of the structural units according to the equation of Frey et al.²:

$$DB = \frac{2d}{2d + l} = 0.46$$

1.2.3. PEHO-OTs

Figure S3: ^1H (top) and ^{13}C NMR spectrum (bottom) of PEHO-OTs.

^1H NMR (500 MHz, DMSO-d_6 , 383 K): δ = 0.60 – 0.89 (3H, H^1), 1.10 – 1.39 (2H, H^2), 2.30 – 2.44 (3H, H^{11}), 2.96 – 3.27 (4H, $\text{H}^4 + \text{H}^5$), 3.76 – 3.97 (2H, H^6), 7.30 – 7.48 (2H, H^9), 7.64 – 7.76 (2H, H^8) ppm.

^{13}C NMR (75 MHz, DMSO-d_6 , 300 K): δ = 6.64, 7.06, 7.49 (C^1), 21.10 (C^{11}), 21.57, 22.14 (C^2), 68.92, 69.91 ($\text{C}^4 + \text{C}^5 + \text{C}^6$), 127.63 (C^9), 130.14 (C^8), 131.82, 132.20 (C^7), 145.07 (C^{10}) ppm.

The DF was determined from the ^1H NMR spectrum by comparing the integrals of the methyl groups of the PEHO core (H^1) with one of the two aromatic signals of the tosyl groups (H^8) according to the following equation.

$$DF (\text{PEHO-OTs}) = \frac{\left(\frac{I(\text{H}^8)}{2}\right)}{\left(\frac{I(\text{H}^1)}{3}\right)} = 0.90$$

Based on DF and, thus, the proportions of tosyl and hydroxy end groups, the average molar mass of a linear repeat unit of PEHO-OTs was calculated from the molar masses of the respective linear repeat units by weighting according to the following equation.

$$M_{\text{rep}} (\text{PEHO-OH}) = 116 \text{ g mol}^{-1}, M_{\text{rep}} (\text{PEHO-OTs}) = 270 \text{ g mol}^{-1}, \text{DF} = 0.90$$

$$\begin{aligned} \overline{M}_{\text{rep}} (\text{PEHO-OTs}) &= (1 - \text{DF} (\text{PEHO-OTs})) * M_{\text{rep}} (\text{PEHO-OH}) \\ &+ \text{DF} (\text{PEHO-OTs}) * M_{\text{rep}} (\text{PEHO-OTs}) \\ &= 0.10 * 116 \frac{\text{g}}{\text{mol}} + 0.90 * 270 \frac{\text{g}}{\text{mol}} = 255 \frac{\text{g}}{\text{mol}} \end{aligned}$$

The DP can be calculated from M_n determined by SEC through dividing it by the average molecular weight of a linear repeat unit.

$$\text{SEC (CHCl}_3\text{): } M_n = 3800 \text{ g mol}^{-1}, M_w = 7600 \text{ g mol}^{-1}, \bar{D} = 2.0$$

$$DP = \frac{M_n (\text{SEC})}{\overline{M}_{\text{rep}}} = \frac{3800 \frac{\text{g}}{\text{mol}}}{255 \frac{\text{g}}{\text{mol}}} = 15$$

Figure S4: SEC curve of PEHO-OTs.

1.2.4. PEHO-Im

Figure S5: ^1H (top) and ^{13}C NMR spectrum (bottom) of PEHO-Im. The signals marked with # originate from unreacted OTs groups that are still bonded to the PEHO. The signals marked with ^-OTs , whose integral values are negligibly small, originate from free tosylate ions present as counterions to PEHO-bonded imidazolium units, which are formed to a small extent by presumably intramolecular dialkylation of imidazole groups.

^1H NMR (500 MHz, DMSO-d_6 , 383 K): δ = 0.62 – 1.03 (3H, H^1), 1.04 – 1.59 (2H, H^2), 2.99 – 3.54 (3H, $\text{H}^4 + \text{H}^5$), 3.76 – 4.06 (4H, H^6), 6.76 – 7.04 (2H, $\text{H}^8 + \text{H}^9$), 7.33 – 7.50 (1H, H^7) ppm.

^{13}C NMR (75 MHz, DMSO-d_6 , 300 K): δ = 7.46 (C^1), 23.27 (C^2), 43.01 (C^3), 48.44 (C^6), 71.18 ($\text{C}^4 + \text{C}^5$), 120.83 (C^8), 128.14 (C^9), 138.48 (C^7) ppm.

The DF was determined from the ^1H NMR spectrum by comparing the integrals of the methyl groups of the PEHO core (H^1) with one of the three aromatic signals of the imidazole groups (H^7) according to the following equation.

$$DF (\text{PEHO-Im}) = \frac{(I (\text{H}^7))}{\left(\frac{I (\text{H}^1)}{3}\right)} = 0.82$$

Based on proportions of hydroxy, tosyl, and imidazole end groups, the average molar mass of a linear repeat unit of PEHO-Im was calculated from the molar masses of the respective linear repeat units by weighting according to the following equation.

$$M_{rep} (PEHO-Im) = 166 \text{ g mol}^{-1}$$

$$\begin{aligned} \overline{M}_{rep} (PEHO-Im) &= (1 - DF (PEHO-OTs)) * M_{rep} (PEHO-OH) \\ &+ (DF (PEHO-Im) - DF (PEHO-OTs)) * M_{rep} (PEHO-OTs) \\ &+ DF (PEHO-Im) * M_{rep} (PEHO-Im) \\ &= 0.10 * 116 \frac{\text{g}}{\text{mol}} + 0.08 * 270 \frac{\text{g}}{\text{mol}} + 0.82 * 166 \frac{\text{g}}{\text{mol}} = 170 \frac{\text{g}}{\text{mol}} \end{aligned}$$

Since SEC measurements of PEHO-Im were not possible, M_n was determined by multiplying DP (obtained from the analysis of PEHO-OTs) with the average molecular weight of a repeat unit.

$$M_n (PEHO-Im) = DP * \overline{M}_{rep} (PEHO - Im) = 15 * 170 \frac{\text{g}}{\text{mol}} = 2500 \frac{\text{g}}{\text{mol}}$$

1.3. Thermal characterization by TGA and DSC

Figure S6: DSC thermograms (2nd heating curve) of PEHO-OH and its derivatives.

Figure S7: TGA curves of PEHO-OH and its derivatives measured under air (left) and nitrogen atmosphere (right).

2. hyperPILs

2.1. Listing of amounts and reaction times employed in syntheses

Table S1: Weights, solvent volumes, and reaction times in hyperPIL syntheses.

Sample code	MeOTs [mg mmol equiv.]	2-Ethyl-2-oxazoline [mL g mmol equiv.]	2- <i>n</i> -Propyl-2-oxazoline [mL g mmol equiv.]	DMF ^a [mL]	t [h]	PEHO-Im ^c [mg mmol equiv.]	DMF ^d [mL]
PEHO-IL-PEtOx ₁₀	373 2.00 1.0	2.02 1.99 20.0 10	-	5.0	2	383 1.76 0.9	4.0
PEHO-IL-PEtOx ₂₀	148 0.80 1.0	1.61 1.58 15.9 20	-	4.0	4	152 0.73 0.9	1.5
PEHO-IL-P(EtOx/ <i>n</i> PrOx) ₁₀	220 1.18 1.0	0.60 0.59 5.91 5	0.66 0.67 5.91 5	3.0	2	226 1.09 0.9	3.0
PEHO-IL-P(EtOx/ <i>n</i> PrOx) ₂₀	164 0.88 1.0	0.89 0.87 8.80 10	1.00 1.02 8.80 10	2.5	4	168 0.81 0.9	1.5
PEHO-IL-P <i>n</i> PrOx ₁₀	360 1.94 1.0	-	2.15 2.19 19.4 10	5.0	2	374 1.81 0.9	4.0
PEHO-IL-P <i>n</i> PrOx ₂₀	238 1.28 1.0	-	2.83 2.89 25.5 20	6.5	4	245 1.18 0.9	3.0

^aSolvent volume for oxazoline polymerization; ^bduration of oxazoline polymerization before addition of PEHO-Im; ^cequivalents refer to imidazole groups; ^dsolvent volume of PEHO-Im solution.

2.2. ^1H NMR spectra

Figure S8: ^1H NMR spectrum of PEHO-IL-PEtOx₁₀ with magnification below.

Figure S9: ^1H NMR spectrum of PEHO-IL-PEtOx₂₀ with magnification below.

Figure S10: ^1H NMR spectrum of PEHO-IL-P(EtOx/*n*PrOx)₁₀ with magnification below.

Figure S11: ^1H NMR spectrum of PEHO-IL-P(EtOx/*n*PrOx)₂₀ with magnification below.

Figure S12: ¹H NMR spectrum of PEHO-IL-PnPrOx₁₀ with magnification below.

Figure S13: ¹H NMR spectrum of PEHO-IL-PnPrOx₂₀ with magnification below.

2.3. SEC curves

Figure S14: SEC curves of the hyperPILs after the respective purification steps (TIPS = temperature-induced phase separation, for details see experimental section).

2.4. Listings of low-molecular-weight fractions, yields and purities

Table S2: Percentage of low-molecular-weight impurities in PEHO-IL-POx₁₀ samples after precipitation in Et₂O and, if applied, subsequent TIPS.

Sample code	Purification procedure	Weight fraction < 5 kg mol ⁻¹ [wt.%] ^b
PEHO-IL-PEtOx ₁₀	precipitation in Et ₂ O	12
	precipitation in Et ₂ O + TIPS (95 °C) ^a	5
PEHO-IL-P(EtOx/ <i>n</i> PrOx) ₁₀	precipitation in Et ₂ O	3
PEHO-IL-P <i>n</i> PrOx ₁₀	precipitation in Et ₂ O	<1

^aPhase separation was induced by heating to the temperature indicated in brackets;

^bdetermined by SEC.

Table S3: Percentage of low-molecular-weight impurities in PEHO-IL-POx₂₀ samples after precipitation in Et₂O and, if applied, subsequent TIPS.

Sample code	Purification procedure	Weight fraction < 10 kg mol ⁻¹ [wt.%] ^b
PEHO-IL-PEtOx ₂₀	precipitation in Et ₂ O	18
	precipitation in Et ₂ O + TIPS (80 °C) ^a	4
PEHO-IL-P(EtOx/ <i>n</i> PrOx) ₂₀	precipitation in Et ₂ O	29
	precipitation in Et ₂ O + TIPS (40 °C) ^a	7
PEHO-IL-P <i>n</i> PrOx ₂₀	precipitation in Et ₂ O	4

^aPhase separation was induced by heating to the temperature indicated in brackets;

^bdetermined by SEC.

Table S4: Yields and purities of the hyperPIIs after precipitation in Et₂O and, if applied, subsequent TIPS.

Sample code	Purification procedure ^a	Purity ^b [wt.%]	Yield [g %]
PEHO-IL-PEtOx ₁₀	precipitation in Et ₂ O + TIPS (95 °C)	95	0.62 ^c 56
PEHO-IL-PEtOx ₂₀	precipitation in Et ₂ O + TIPS (80 °C)	96	0.27 ^c 24
PEHO-IL-P(EtOx/ <i>n</i> PrOx) ₁₀	precipitation in Et ₂ O	97	1.33 85
PEHO-IL-P(EtOx/ <i>n</i> PrOx) ₂₀	precipitation in Et ₂ O + TIPS (40 °C)	93	0.37 ^c 36
PEHO-IL-P <i>n</i> PrOx ₁₀	precipitation in Et ₂ O	99	1.98 74
PEHO-IL-P <i>n</i> PrOx ₂₀	precipitation in Et ₂ O	96	2.45 80

^aPhase separation was induced by heating to the temperature indicated in brackets; ^bpurity is defined as the percentage by weight of the fraction with molar masses larger than 5 kg mol⁻¹ (for PEHO-IL-POx₁₀ samples) or 10 kg mol⁻¹ (for PEHO-IL-POx₂₀ samples), as determined by SEC analysis; ^cfor the purification by TIPS only a part of the crude product obtained after Et₂O precipitation was used (1.0 g for each sample).

2.5. Procedure for calculating M_n from the ^1H NMR spectra

In the ^1H NMR spectra of the hyperPILs, the signals of the imidazole groups either completely disappeared or are at least of such low intensity that a meaningful quantitative analysis by integration is not possible. Therefore, in good approximation, a quantitative alkylation of the imidazole groups with polyoxazoline chains can be assumed for estimation of the molecular weights. Accordingly, the integral of a proton of the imidazolium rings and the polyoxazoline chains corresponds to 0.82 times ($\text{DF (PEHO-Im)} = 0.82$) the integral of a proton of a repeat unit of the PEHO core. To normalize the integrals, the signal of the CH_2 group (H^{11}) of the polyoxazoline repeat unit directly bonded to the imidazolium cation was selected and its integral was set to 1.64.

The DP of the attached polyoxazoline chains can now be determined from the signal of the polyoxazoline backbone or from the signals of the CH_2 - and CH_3 - units of the side chains. The expected contributions of any overlapping signals are subtracted from the integral value of the respective signal. The remaining integral value is then divided by the product of DF (PEHO-Im) and the number of protons per repeat unit that contribute to the signal, which gives DP of the polyoxazoline chains. In case of using the polyoxazoline backbone signal, the obtained value must be increased by 1, since the signals of the repeat unit directly bonded to the imidazolium cation do not overlap with those of the remaining repeat units. If several signals are suitable for determining DP, the arithmetic mean of the calculated DP values based on different signals is given.

To calculate the M_n of the hyperPILs, DP of the polyoxazoline chains is first multiplied with the molar mass of the respective monomer and the molar mass of the initiator (MeOTs) is added to obtain the M_n of a single polyoxazoline chain. This value is multiplied with the number of imidazole units per PEHO-Im molecule, which is calculated by multiplying DF (PEHO-Im) (0.82) with DP of the PEHO core (15). Finally, to the M_n of the polyoxazoline shell obtained in this way, the M_n of PEHO-Im (2500 g mol^{-1}) is added to obtain M_n of the hyperPILs.

This calculation is shown below by the example of PEHO-IL-*Pn*PrOx₁₀. DP_1 , DP_2 etc. denote the degrees of polymerization determined from different signals. From these values, the arithmetic mean is formed.

$$DP_1 = \frac{I(H^1 + H^{17} + H^{20}) - 3}{3 * DF} = 11.6$$

$$DP_2 = \frac{I(H^2 + H^{16} + H^{19}) - 2}{2 * DF} = 11.7$$

$$DP_3 = \frac{I(H^{15} + H^{18} + H^{21}) - \frac{3}{2} * I(H^{22})}{2 * DF} = 11.3$$

$$DP_4 = \frac{I(H^4 + H^5 + H^{12} + H^{13}) - 4}{4 * DF} + 1 = 11.2$$

$$\overline{DP} = \frac{DP_1 + DP_2 + DP_3 + DP_4}{4} = 11.4$$

$$M_n (PEHO-IL-PnPrOx_{10})$$

$$= \left(\left(\left(\overline{DP} (PnPrOx) * M (nPrOx) \right) + M (MeOTs) \right) \right.$$

$$* DF (PEHO-Im) * DP (PEHO-Im) \left. \right) + M_n (PEHO-Im)$$

$$= \left(\left(\left(11.4 * 113 \frac{g}{mol} \right) + 186 \frac{g}{mol} \right) * 0.82 * 15 \right) + 2500 \frac{g}{mol}$$

$$= 21\,000 \frac{g}{mol}$$

2.6. Thermal characterization by TGA and DSC

Figure S15: DSC thermograms (2nd heating curve) of the hyperPILs.

Figure S16: TGA curves of the hyperPILs under air (left) and nitrogen atmosphere (right).

2.7. Transmission-temperature curves

Figure S17: Transmission-temperature curves of aqueous hyperPIL solutions (heating/cooling rate = 1 K min⁻¹).

2.8. Listing of cloud points (T_{CP})

Table S5: T_{CP} values of hyperPILs at various concentrations.

Sample code	T_{CP} [°C] ^a					
	5 g L ⁻¹	15 g L ⁻¹	25 g L ⁻¹	50 g L ⁻¹	75 g L ⁻¹	100 g L ⁻¹
PEHO-IL-PEtOx ₁₀	-	-	-	-	93	89
PEHO-IL-PEtOx ₂₀	-	-	91	82	79	76
PEHO-IL-P(EtOx/ <i>n</i> PrOx) ₁₀	60	48	44	nd	nd	nd
PEHO-IL-P(EtOx/ <i>n</i> PrOx) ₂₀	52	45	43	nd	nd	nd
PEHO-IL- <i>Pn</i> PrOx ₁₀	32	25	23	nd	nd	nd
PEHO-IL- <i>Pn</i> PrOx ₂₀	26	22	21	nd	nd	nd

^aDetermined from the inflection point of the transmission-temperature curve during heating ($\lambda = 500$ nm; heating rate = 1 K min⁻¹); - = no clouding detected, nd = not determined.

2.9. TEM images

Figure S18: TEM images of PEHO-IL-PEtOx₁₀ (A), PEHO-IL-PEtOx₂₀ (B), PEHO-IL-*Pn*PrOx₁₀ (C), and PEHO-IL-*Pn*PrOx₂₀ (D); scale bar = 100 nm.

2.10. Chemical structures of the molecules used for the transport experiments

Figure S19: Chemical structures of Congo red, Methylene blue, and Sudan IV.

Figure S20: Proposed complex forming reaction and structure of the Pd-phosphine complex.

3. References

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