

Thermoresponsive Polymeric Ionic Liquids and Nanostructured Hydrogels based upon Amphiphilic Polyisobutylene-*b*-Poly(2-ethyl-2-oxazoline) Diblock Copolymers

Benjamin Kerscher,^{*,1,2} Tobias M. Trötschler,^{1,2,5} Balázs Pásztói,^{3,4} Saskia Gröer,^{1,2,5} Ákos Szabó,³ Béla Iván,³ and Rolf Mülhaupt^{*,1,2,5}

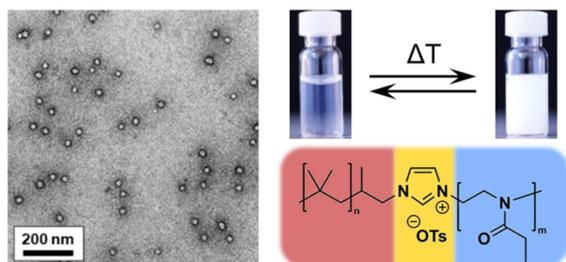
¹Institute for Macromolecular Chemistry, University of Freiburg, Stefan-Meier-Str. 31, D-79104 Freiburg, Germany

²Freiburg Materials Research Center (FMF), University of Freiburg, Stefan-Meier-Str. 21, D-79104 Freiburg, Germany

³Polymer Chemistry Research Group, Institute of Materials and Environmental Chemistry, Research Centre for Natural Sciences, Hungarian Academy of Sciences, H-1117 Budapest, Magyar tudósok krt. 2, Hungary

⁴George Hevesy PhD School of Chemistry, Institute of Chemistry, Faculty of Science, Eötvös Loránd University, H-1117 Budapest, Pázmány Péter sétány 2, Hungary

⁵Freiburg Center for Interactive Materials and Bioinspired Technologies (FIT), University of Freiburg, Georges-Köhler-Allee 105, D-79110 Freiburg, Germany



for Table of Contents use only

ABSTRACT

The precise molecular engineering of amphiphilic diblock copolymers as thermoresponsive polymeric ionic liquids (PILs) couples polyisobutylene (PIB) and poly(2-ethyl-2-oxazoline) (PEtOx) blocks via an imidazolium cation. It enables thermal switching of micellar self-assembly and yields nanostructured hydrogels. Just one ionic liquid (IL)-type imidazolium cation is readily incorporated into the backbone of the PIB-IL-PEtOx block copolymers by terminating the cationic 2-ethyl-2-oxazoline (EtOx) ring-opening polymerization by alkylation of an imidazole-terminated PIB. The PEtOx block length varies as a function of the PIB-imidazole/EtOx molar ratio and governs solubility, hydrophilic/hydrophobic balance, and nanophase separation. In spite of the presence of highly hydrophobic PIB segments, PIB-IL-PEtOx are rendered water soluble with increasing PEtOx block length and form spherical and elongated micelles as well as hydrogels exhibiting worm-like nanostructures. Furthermore, the lower critical solution temperature (LCST) of PEtOx segments is the key to thermoresponsive behavior of both water-soluble copolymers and copolymer hydrogels. Owing to low glass temperature and high stability of PIB, these PIB-PILs represent attractive macromolecular nanosystems enabling thermal switching of solubilization, dispersion, transport, and shuttling of molecules and nanoparticles.

INTRODUCTION

Among polymeric materials, polyisobutylene (PIB) is outstanding with respect to its very low glass transition temperature (T_g) combined with excellent chemical and thermal stability, low permeability, and biocompatibility. However, owing to its hydrocarbon nature, PIB is highly water insoluble. In the past, improved conventional as well as living isobutylene polymerization techniques have been developed,¹⁻⁵ and several synthetic methods have been introduced to functionalize PIB with varying end groups.⁶⁻¹¹ PIB succinimides have gained major technical relevance as ashless dispersants in fuel and engine oil.^{4,12} Recent and ongoing investigations mainly concentrate on the synthesis and use of telechelic, star, arborescent, and in-chain functionalized PIBs as intermediates in the production of novel biomaterials for implantable medical devices.¹³⁻²²

Monodisperse poly(2-oxazoline)s are readily tailored by cationic ring-opening polymerization (CROP) of 2-oxazolines, which proceeds in a highly controlled fashion. This paves the way towards well-defined macromolecules with adjustable composition, different pendant moieties, variable functional end groups, controllable molar mass, and low polydispersity.²³⁻²⁶ Depending on the substituent at the C₂-atom of the oxazoline monomer, water-soluble polymers displaying lower critical solution temperature (LCST) phase behavior can be obtained. By means of facile variation of the polymer structure and composition, *e.g.* side chain substitution, molar mass, and end groups, the LCST can be fine-tuned in a broad temperature range,²⁷⁻³⁰ which renders thermoresponsive poly(2-oxazoline)s promising candidates for advanced areas of application such as thermoreversible phase transfer,³¹ optical temperature sensors,^{32,33} and molecular logic gates.^{34,35} Owing to the biocompatibility typical for many poly(2-oxazoline)s³⁶⁻³⁹ and the stealth behavior of poly(2-methyl-2-oxazoline) (PMeOx) and poly(2-ethyl-2-oxazoline) (PEtOx),^{40,41} this class of polymers bears great potential to be used in diverse biomedical and biotechnological applications.⁴²⁻⁵⁰ Meanwhile, a great variety of different oxazoline homopolymers, random and gradient copolymers, block

copolymers, poly(2-oxazoline) based networks and hydrogels, and more complex structures, including sophisticated poly(2-oxazoline) biohybrids and heteropolymer architectures, have been designed.^{25,30,43,45,47,51-57}

Today, the development of intelligent functional materials is in the focus of scientific and industrial research. The precise design of tailor-made polymers, utilization of stimuli-responsive building blocks, and controlled nanostructure formation are key issues in the generation of such systems. Without any doubt, the combination of non-polar liquid PIB and thermoresponsive poly(2-oxazoline)s holds great promise with respect to the creation of well-defined amphiphilic macromolecules and their controlled self-assembly into smart micelles. In literature, few examples of copolymers composed of poly(2-oxazoline) and PIB segments can be found. PIBs equipped with electrophilic end groups have been used as macroinitiators in the CROP of 2-oxazolines, especially 2-methyl-2-oxazoline (MeOx) or 2-ethyl-2-oxazoline (EtOx), to afford the corresponding PIB-*b*-poly(2-oxazoline) diblock copolymers.⁵⁸⁻⁶¹ This strategy has been expanded to telechelic and three arm star PIB macroinitiators as well as isobutylene-chloromethylstyrene copolymers, which led to triblock, star, and graft copolymers, respectively.⁶²⁻⁶⁸ However, in case of initiator groups with insufficient reactivity, the macroinitiator approach bears the risk of producing rather broad molecular weight distributions. Alternative strategies are based on coupling preformed PIB and poly(2-oxazoline) building blocks.^{58,61} Surprisingly, micellar self-assembly of amphiphilic PIB-poly(2-oxazoline) copolymers has not been studied in detail. Only in case of poly(isobutylene-*co*-chloromethylstyrene)-*graft*-PMeOx, viscosimetry and light scattering have been performed and indicate aggregate formation.^{65,68} Remarkably enough, possible LCST behavior of PIB-poly(2-oxazoline) copolymers has not been addressed so far.

Due to the unique physico-chemical properties of ionic liquids (ILs), it is very attractive to incorporate IL moieties into polymers, and a plethora of polymeric ionic liquids (PILs) with

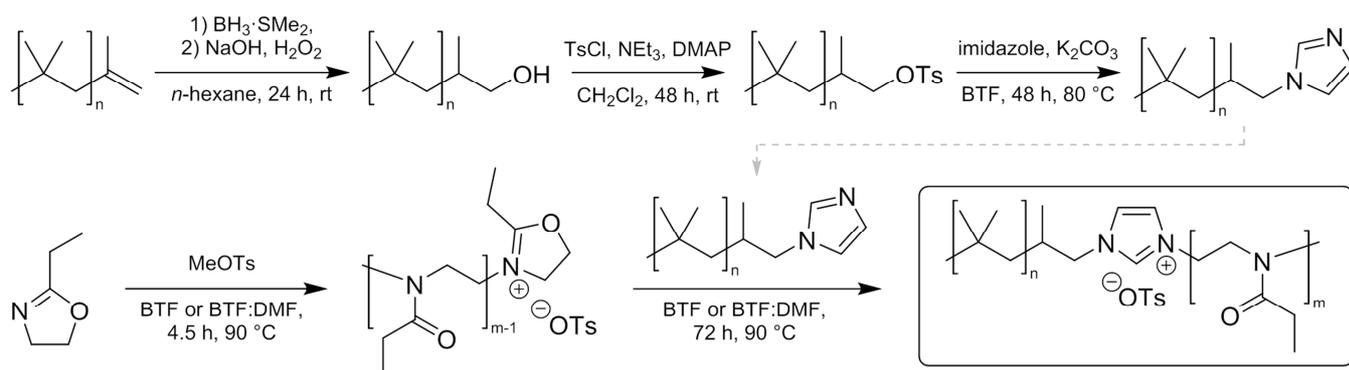
various chemical structures and topologies has been prepared.^{69–73} The development of thermoresponsive PILs, as reviewed by Kohno *et al.*,⁷⁴ represents an intriguing field of research. There are some examples of poly(2-oxazoline)s bearing IL cation end groups such as trialkylammonium^{75,76} or pyridinium.^{76,77} Moreover, ionic poly(2-phenyl-2-oxazoline) macromonomers and corresponding comb-like polyelectrolytes have been prepared.⁷⁵ Concerning PIB, end-functionalized polymers having IL-type termini^{78–84} and imidazolium salts bearing two pendant PIB chains^{78,85} have been reported. However, to the best of our knowledge, ionic PIB-poly(2-oxazoline) copolymer structures have not been described yet.

Herein, we report on the molecular engineering of PIB-*b*-PEtOx diblock copolymers as PIB-PILs in which the hydrophobic PIB block is covalently coupled with the hydrophilic PEtOx block via just one imidazolium cation as IL moiety. These novel PIB-IL-PEtOx diblock copolymers are readily produced by employing a straightforward synthetic approach utilizing a commercially available PIB as intermediate. Special emphasis is placed upon the influence of the PEtOx segment length on solubility, nanostructure formation, and thermoresponsive behavior of the amphiphilic copolymers.

RESULTS AND DISCUSSION

The synthetic route for the preparation of the amphiphilic PIB-IL-PEtOx diblock copolymers is illustrated in Scheme 1. Imidazole-terminated PIB (PIB-Im) serves as macro terminating agent in the CROP of EtOx. PIB-Im is easily obtained by means of a series of consecutive end group modification reactions starting from a PIB with an olefinic chain end. First, the hydroboration/oxidation/hydrolysis sequence yields hydroxyl-terminated PIB (PIB-OH). Subsequently, the hydroxyl functions are converted into toluene sulfonic ester groups to yield tosylate-terminated PIB (PIB-OTs). Finally, nucleophilic substitution of the tosylate groups by imidazole affords PIB-Im. To build up the PEtOx block, methyl tosylate initiated EtOx

polymerization is employed, which produces PEtOx chains bearing cationic oxazolinium termini. Upon addition of PIB-Im, the oxazolinium ring is opened by nucleophilic attack of the imidazole group, which is alkylated to produce PIB-IL-PEtOx copolymers in which the PIB and PEtOx blocks are covalently coupled by the resulting imidazolium cation (with tosylate as counter anion) as IL moiety.



Scheme 1. Synthetic route towards PIB-IL-PEtOx diblock copolymers (for simplification, only the vinylidene-type PIB chain end and structures derived therefrom are shown)

As starting material, Glissopal[®] 1000 from BASF SE was used, which possesses an olefinic double bond at one chain terminus as reactive functional group. As revealed by ¹H NMR analysis, the vast majority (77%) of the isomeric olefinic end groups is of the vinylidene type (see Figure S1 and S2). SEC measurement indicates a number-average molar mass (M_n) of approximately 1200 g/mol, which is in good accordance with the value calculated from the NMR spectrum (1100 g/mol).

On the basis of a synthesis protocol reported by Bergbreiter's group,^{9,86} the Glissopal was reacted with $\text{BH}_3 \cdot \text{SMe}_2$, followed by oxidation and hydrolysis using H_2O_2 and NaOH , to yield hydroxyl-functionalized PIB chains. ¹H NMR investigation of the product indicated complete disappearance of any signals of the olefinic protons. Thus, all types of olefinic groups, *i.e.* both the highly reactive vinylidenic double bonds and the less reactive isomers, were

successfully converted. In order to transform the hydroxyl functions into toluenesulfonic ester end groups, PIB-OH was reacted with *p*-toluenesulfonyl chloride in presence of 4-dimethylaminopyridine and triethylamine. In this reaction, the majority of approximately 83% of the hydroxyl groups could be tosylated and no attempts were made to remove the fraction of non-reacted PIB-OH at this stage. The final chain end transformation was performed by reacting the PIB-OTs with a large excess of imidazole in presence of potassium carbonate. By this means, near to quantitative replacement of the tosylate groups by the desired imidazole functions was achieved and formation of side products such as 1,3-di(polyisobutylene)imidazolium tosylate was almost completely suppressed. Isolation of the PIB-Im, *i.e.* separation from the significant amount of PIB-OH chains and traces of other PIB derivatives present in the raw mixture, was accomplished by means of column chromatography. As a result, a perfectly pure material with 100% imidazole functionality was obtained. The ^1H NMR spectrum of PIB-Im is shown in Figure 1 (^1H NMR spectra of PIB-OH and PIB-OTs can be found in the Supporting Information). Properties and features of PIB-Im and the other end-functionalized PIBs, which are all viscous liquids at room temperature, are summarized in Table 1. Compared to the parent Glissopal, the M_n of PIB-Im is noticeably higher. NMR analysis reveals the presence of approximately 23 isobutylene repeating units, which corresponds to a M_n of ca. 1450 g/mol. This increase in molar mass is mainly a consequence of the loss of low-molecular-weight chains during purification of the PIB-OTs intermediate by precipitation, as also reflected by the narrowing of the molar mass distribution.

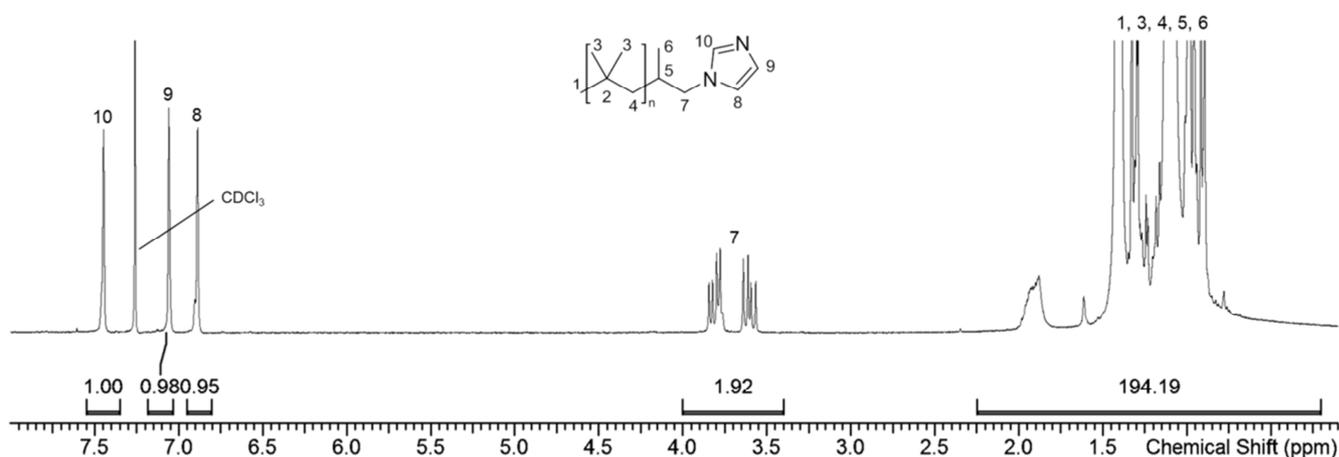


Figure 1. ^1H NMR spectrum of PIB-Im.

Table 1. Properties and features of end-functionalized PIBs

polymer	M_n^a	M_n^b	M_w/M_n^b	DF ^c	yield	T_g^d	T_d^e	T_d^e
	(NMR)	(SEC)	(SEC)				(air)	(N ₂)
	[g/mol]	[g/mol]		[%]	[%]	[°C]	[°C]	[°C]
Glissopal	1100	1200	1.70	100	–	-81	224	257
PIB-OH	1200	1250	1.65	100	100	-70	251	230
PIB-OTs	1800	1650	1.51	83	78	-70	238	256
PIB-Im	1450	nd ^f	nd ^f	100	53	-68	316	332

^aCalculated via ^1H NMR end group analysis. ^bDetermined by SEC with CHCl_3 eluent. ^cDegree of functionality, determined by ^1H NMR spectroscopy. ^dDetermined by DSC. ^eDecomposition temperature, determined by TGA under air and N₂ atmosphere, respectively. ^fNot determined (SEC analysis of imidazole-terminated PIB failed).

Methyl tosylate initiated CROP of EtOx and the in-situ end-capping reaction were performed in benzotrifluoride (BTF) or BTF:DMF mixture, which are capable of dissolving both the PEtOx homopolymer initially produced and the non-polar PIB-Im macro terminating agent added after formation of the PEtOx block. The molar ratio of initiator (and thus, the active

PEtOx chains formed) and PIB-Im was adjusted to 2:1, and a rather long reaction time of three days was chosen for coupling of the polymers. By this means, complete reaction of the PIB-Im is ensured, *i.e.* all PIB chains are incorporated into the desired PIB-IL-PEtOx diblock copolymer structures. This greatly facilitates purification, since there is no non-reacted PIB-Im present in the raw product and the PIB-IL-PEtOx needs just to be separated from the non-coupled excess PEtOx homopolymer. By systematic variation of the oxazoline/initiator ratio, a series of four copolymers with constant length of the PIB block and variable degree of polymerization (DP) of the PEtOx block was prepared. The syntheses of the PILs, which are abbreviated as PIB₂₃-IL-PEtOx_m (23 = theoretical number of isobutylene repeating units of the PIB block, m = theoretical DP of the PEtOx block), are listed in Table 2.

Table 2. Synthesis and purification of PIB-IL-PEtOx diblock copolymers

block copolymer	EtOx	MeOTs ^a	PIB-Im	solvent ^b	purification method
	[eq.]	[eq.]	[eq.]		
PIB ₂₃ -IL-PEtOx ₁₀	10	1.0	0.49	BTF	liquid-liquid extraction
PIB ₂₃ -IL-PEtOx ₂₀	20	1.0	0.50	BTF:DMF	hot filtration
PIB ₂₃ -IL-PEtOx ₃₀	30	1.0	0.50	BTF:DMF	hot filtration
PIB ₂₃ -IL-PEtOx ₄₀	40	1.0	0.49	BTF:DMF	hot filtration

^aMeOTs = methyl tosylate. ^bSolvent for EtOx polymerization (in case of BTF:DMF, a 4:1 v/v mixture was employed).

^1H NMR analysis clearly confirmed successful formation of the diblock copolymers. This can already be concluded from the NMR spectra of the raw products. As an example, in Figure 2 (bottom), the ^1H NMR spectrum of the unpurified $\text{PIB}_{23}\text{-IL-PEtOx}_{30}$ is shown. In addition to peaks stemming from the PIB backbone, very intense signals arise which are typical for PEtOx chains. A closer inspection of the spectrum reveals that there are no signals any more that can be attributed to imidazole moieties of PIB-Im, proving complete reaction of the macro terminating agent. Instead, characteristic new signals are observed, which can be assigned to the cationic imidazolium ring of the PIB-IL-PEtOx. As a consequence of the substoichiometric use of PIB-Im, there is a substantial amount of non-coupled PEtOx homopolymer present in the raw mixture. This is, *e.g.*, reflected by the appearance of small signals at 4.1-4.4 ppm and 8.8-9.7 ppm, probably caused by ammoniumethyl propionate-terminated PEtOx species most likely formed upon hydrolysis of oxazolinium chain ends by moisture after opening the reaction vessel,^{87,88} and the fact that the integral values of the imidazolium cation peaks are far too small as compared to those of the tosylate anion signals. For separation of the PEtOx homopolymer, two different procedures were applied. In case of $\text{PIB}_{23}\text{-IL-PEtOx}_{10}$, which does not readily dissolve in water, the non-coupled hydrophilic PEtOx was removed by liquid-liquid extraction. The other block copolymers possessing longer PEtOx segments turned out to be highly soluble in water at room temperature but to precipitate upon heating to 90 °C, which does not happen in the case of the PEtOx homopolymers at such relatively low molecular weights. Thus, removal of the PEtOx and isolation of the PILs was performed by applying a hot filtration procedure. Both methods enabled very efficient purification of the respective block copolymers. In Figure 2 (top), the ^1H NMR spectrum of $\text{PIB}_{23}\text{-IL-PEtOx}_{30}$ after hot filtration is depicted. The signals of PEtOx homopolymer chain ends completely disappeared and the integral values of the imidazolium

peaks now agree well with those of the tosylate anion signals. NMR spectra of the other purified PIB-IL-PEtOx copolymers also confirm the absence of residual homopolymer impurities (see Figures S6, S7, S9). From SEC analysis, removal of non-coupled PEtOx is reflected as well. This is illustrated in Figure 3a, where the SEC profiles of the raw and purified PIB₂₃-IL-PEtOx₃₀ are compared. After purification, a significant narrowing of the distribution is observed. The SEC elugrams of the whole PIB-IL-PEtOx series, which nicely indicate the differences in molar masses, are shown in Figure 3b.

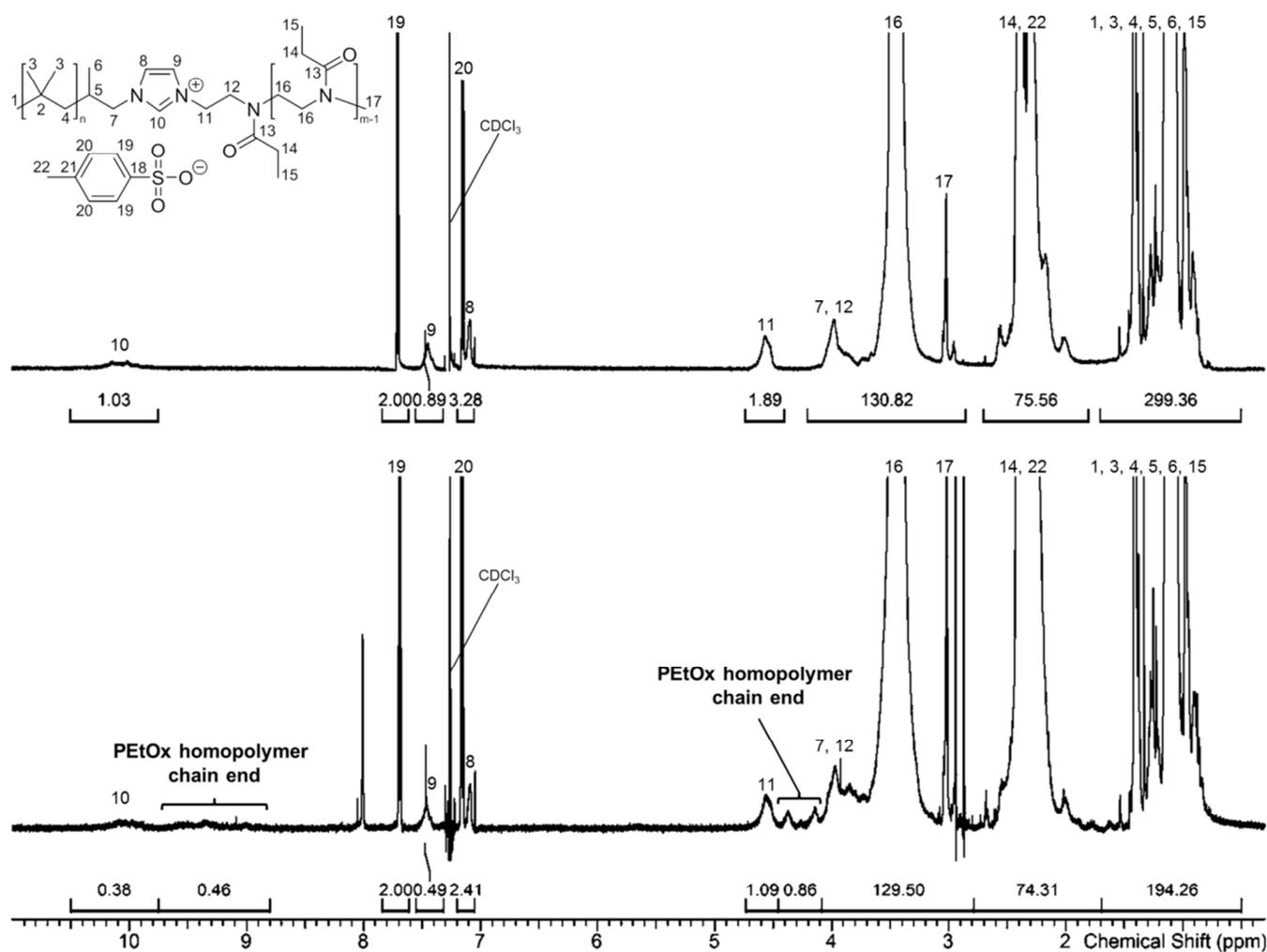


Figure 2. ¹H NMR spectra of PIB₂₃-IL-PEtOx₃₀ (top) and unpurified PIB₂₃-IL-PEtOx₃₀ prior to hot filtration (bottom). Singlets at 2.87, 2.94, and 8.01 ppm in the spectrum of the raw product are attributed to traces of DMF.

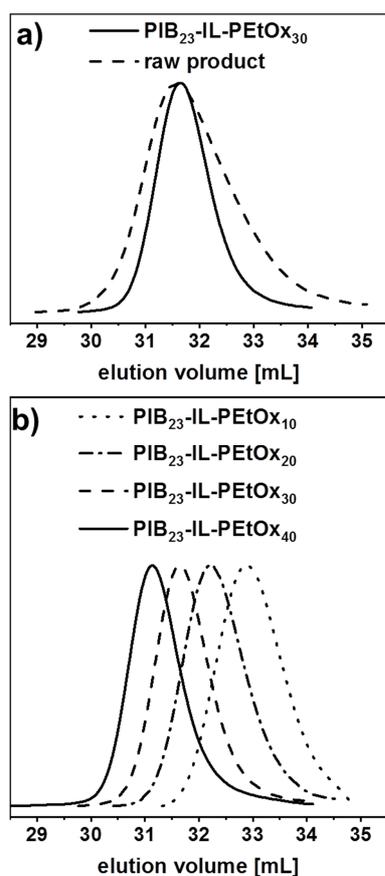


Figure 3. SEC traces of raw and purified $\text{PIB}_{23}\text{-IL-PEtOx}_{30}$ (a). SEC elugrams of the whole series of PIB-IL-PEtOx block copolymers (b).

In Table 3, the results of structural characterization and molar mass determination of the PIB-IL-PEtOx block copolymers are summarized. The block lengths, calculated from the ^1H NMR spectra, are in good accordance with the expected values, especially when taking into account that the calculation is based on comparing the integral value of a fairly small tosylate anion signal of the IL group with the huge signals of the PIB and PEtOx segments. Consequently, the molar masses derived from the NMR integrals, ranging from 2800 g/mol ($\text{PIB}_{23}\text{-IL-PEtOx}_{10}$) to 5800 g/mol ($\text{PIB}_{23}\text{-IL-PEtOx}_{40}$), agree well with the theoretical molecular weights. SEC measurements against PMMA standards reveal conclusive M_n values for the two lower-molecular-weight copolymers, whereas values somewhat larger than plausible

were measured for PIB₂₃-IL-PEtOx₃₀ and PIB₂₃-IL-PEtOx₄₀. Notably, very low polydispersities <1.2 were detected, which emphasizes the feasibility of the synthetic approach to produce well-defined macromolecules with tailored structure in a highly controlled fashion. All of the diblock copolymers could easily be prepared in several gram quantities and were obtained in good to excellent yields as waxy substance (PIB₂₃-IL-PEtOx₁₀) or powdery solids (PIB₂₃-IL-PEtOx_m with m = 20, 30, 40).

Table 3. Characteristics of PIB-IL-PEtOx diblock copolymers

block copolymer	n	n	m	m	M _n ^c	M _n ^d	M _n ^e	M _w /M _n ^e	yield
	PIB ^a	PIB ^b	PEtOx ^a	PEtOx ^b	(theo.)	(NMR)	(SEC)	(SEC)	
	(theo.)	(NMR)	(theo.)	(NMR)	[g/mol]	[g/mol]	[g/mol]		[%]
PIB ₂₃ -IL-PEtOx ₁₀	23	24	10	11	2650	2800	2550	1.18	100
PIB ₂₃ -IL-PEtOx ₂₀	23	26	20	22	3600	4000	3800	1.17	80
PIB ₂₃ -IL-PEtOx ₃₀	23	25	30	32	4600	4850	5450	1.12	95
PIB ₂₃ -IL-PEtOx ₄₀	23	24	40	41	5600	5800	7000	1.14	72

^aTheoretical number of repeating units of the PIB block and the PEtOx block, respectively. ^bNumber of repeating units of the PIB block and the PEtOx block, respectively, calculated from the ¹H NMR spectra. ^cTheoretical molecular weight. ^dCalculated from the ¹H NMR spectra. ^eDetermined by SEC with *N,N*-dimethylacetamide/LiBr eluent.

In order to evaluate the properties of the amphiphilic PILs and the influence of the block length ratio, first their solubility in several common organic solvents was examined (polymer concentration: 50 mg/mL; see Table S1). The polymers comprising 20, 30, and 40 EtOx units turned out to behave very similar. They dissolve in a great variety of protic and aprotic organic solvents covering a wide range of different polarities, *e.g.*, methanol, ethanol, acetone, dimethylformamide, tetrahydrofuran, and toluene. However, they do not mix with diethyl

ether or *n*-hexane, which are good solvents for PIB, reflecting the strong influence of the PEtOx block in these three copolymers. In contrast, PIB₂₃-IL-PEtOx₁₀ containing the shortest PEtOx block in the series of PIB-IL-PEtOx PILs mostly dissolves in these two solvents, which is a clear consequence of a much more pronounced contribution of the non-polar PIB segment.

Special emphasis was placed on the solubility behavior in water. PIB₂₃-IL-PEtOx₄₀, PIB₂₃-IL-PEtOx₃₀, and even PIB₂₃-IL-PEtOx₂₀ readily dissolve, which means that already approximately 20 hydrophilic *N*-propionylethylenimine units in PIB₂₃-IL-PEtOx_m are sufficient to render the highly hydrophobic PIB water soluble. However, when mixing 50 mg of PIB₂₃-IL-PEtOx₁₀ with 1 mL of water, the polymer does not dissolve under formation of a transparent low-viscosity solution like the other PILs. Instead, slow formation of an opaque highly viscous mixture with gel-like consistency is observed, which does not flow instantaneously upon tube inversion and exhibits distinct shear-thinning behavior. Further solubility tests revealed that this peculiarity is a clear consequence of the specific block length ratio in PIB₂₃-IL-PEtOx₁₀ and not just an effect of different molar concentrations (see Table S2). When employing molar amounts that are equivalent to 50 mg of PIB₂₃-IL-PEtOx₁₀, the PIB₂₃-IL-PEtOx_m copolymers with *m* = 20, 30, and 40 again gave low-viscosity solutions. Increasing the content of PIB₂₃-IL-PEtOx₁₀ to concentrations as few as 100 mg/mL or 150 mg/mL effects a significant gain in strength and results in the formation of quite stable hydrogels that flow extremely slowly, as illustrated in Figure 4. Gelation upon mixing amphiphilic molecules with water is a well-known phenomenon which, depending on the chemical structure of the amphiphile, can already occur at low to moderate concentrations as seen here for PIB₂₃-IL-PEtOx₁₀. Such behavior has been reported for both low-molecular-weight surfactants and amphiphilic (co)polymers and is attributed to specific types of

colloidal self-assembly, *e.g.* dense packing of micelles or vesicles that can bind a large volume of water or the formation of long worm-like micelles capable of entangling.^{89,90}



Figure 4. PIB₂₃-IL-PEtOx₁₀ hydrogel before (a) and immediately (b), 2.5 hours (c), and 24 hours (d) after tube inversion. Comparison of PIB₂₃-IL-PEtOx₁₀ hydrogel (e) and low-viscosity aqueous solution of PIB₂₃-IL-PEtOx₃₀ (f). Polymer concentration is 150 mg/mL.

In order to gain deeper insight into the anticipated formation of self-assembled PIB-IL-PEtOx nanostructures, aqueous solutions of the amphiphilic PILs were investigated by means of transmission electron microscopy (TEM; see Figure 5). For PIB₂₃-IL-PEtOx₄₀, TEM images indicate self-assembly of the copolymer chains into individual micelles of spherical shape. However, decreasing the DP of the PEtOx block to 30 and 20 induces a gradual change in the morphology of the copolymer nano-objects. Beside spherical ones, slightly elongated or rod-like assemblies as well as aggregates consisting of several individual micelles arise. Finally, further reduction of the PEtOx chain length in PIB₂₃-IL-PEtOx₁₀ results in the formation of extremely long worm-like micelles. Occasionally, even some vesicle-like structures can be found (see Figure S10). The changes in the type of micellar morphology can be explained by the variation of the hydrophilic/hydrophobic balance of the copolymers. Shortening of the

PEtOx block at constant PIB chain length decreases the length of the hydrophilic segment, which forms the micellar corona, while the length of the hydrophobic segment forming the core of the micelles is not affected. Obviously, this variation of the block length ratio changes the geometric constraints for micellar packing in a way that results in the observed transition from spherical to cylindrical micelles.⁹¹ Thus, TEM analysis elucidates the distinctly different behavior of aqueous mixtures of PIB₂₃-IL-PEtOx₁₀ as compared to the other PILs of the series. Most likely, worm-worm interactions and entanglements of the nano-worms account for the emergence of colloidal network structures accompanied by the formation of highly viscous solutions or even hydrogel-like materials.

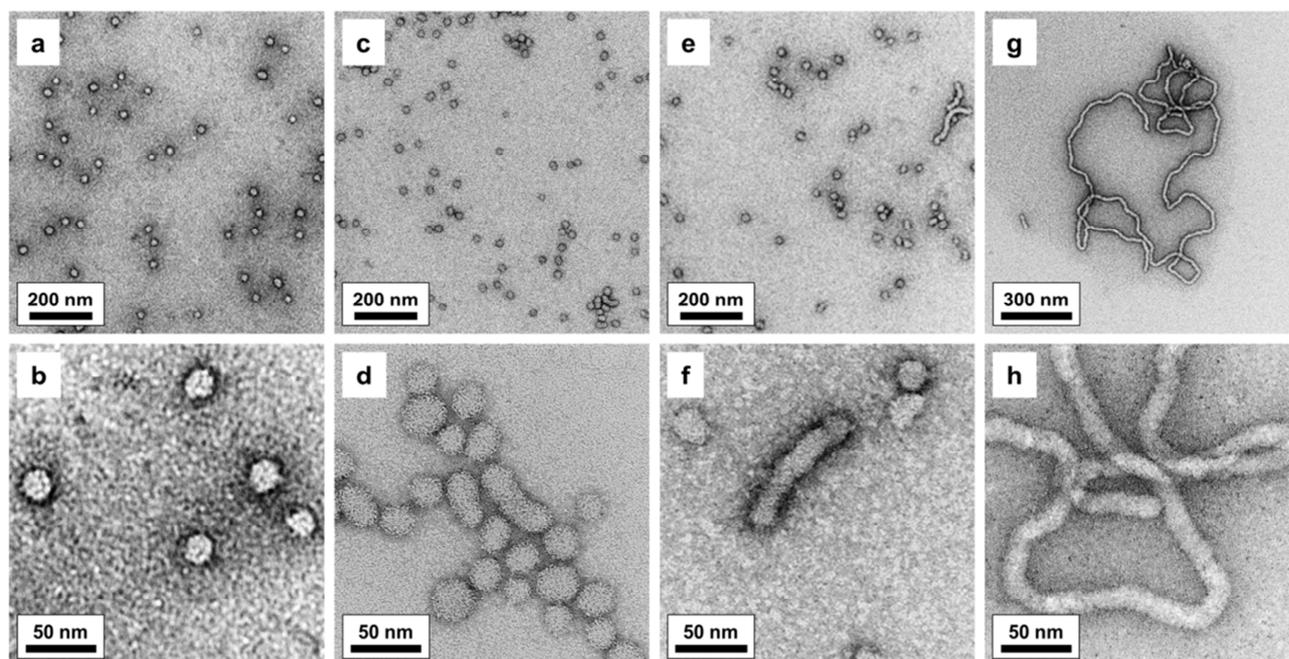


Figure 5. TEM images of copolymer micelles formed by self-assembly in water: PIB₂₃-IL-PEtOx₄₀ (a, b), PIB₂₃-IL-PEtOx₃₀ (c, d), PIB₂₃-IL-PEtOx₂₀ (e, f), PIB₂₃-IL-PEtOx₁₀ (g, h).

The critical micelle concentration (CMC) of the amphiphilic PIB-IL-PEtOx copolymers was determined by a dye absorption method utilizing Sudan Red III. It is detected from the strong increase in light absorption due to encapsulation of the non-polar dye in the hydrophobic interior of the PIL micelles formed when reaching sufficient concentrations (see Figure S11). The CMC values were found to be in the order of magnitude of several 10^{-4} mol/L and, surprisingly, decrease with increasing length of the hydrophilic block (see Table 4). This unexpected trend possibly might be explained by the different morphologies of the copolymer micelles. However, since the CMCs are quite similar and small inaccuracies during measurement can have a relatively strong impact on the results, we refrain from a definite interpretation here. Interestingly, despite the large hydrophobic PIB block, the molar CMC values seem to be significantly higher than those ones reported for ordinary hydrophobically modified PMeOx, PEtOx, and poly(2-isopropyl-2-oxazoline) homopolymers possessing a comparably short *n*-octadecyl chain end.^{92,93} It can be assumed that this difference is

attributed to the presence of the ionic imidazolium tosylate group, which is expected to enhance unimer solubility. This assumption is supported by the CMCs of ionic dimethyldodecylammonium-terminated PEtOx,⁷⁶ which are in the same magnitude as those of the PIB-IL-PEtOx diblock copolymers. However, different DPs and CMC determination methods impede conclusive comparisons.

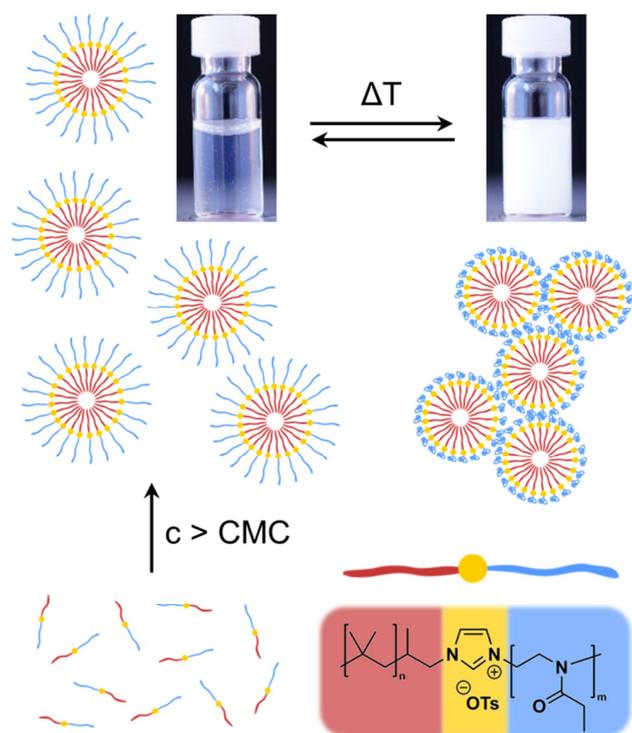
Table 4. Important properties of PIB-IL-PEtOx diblock copolymers

block copolymer	micelle morphology ^a	CMC ^b		T _{CP} (mg/mL) ^c			T _g ^d	T _d ^e	T _d ^e
		[g/L]	[mol/L]	(10)	(20)	(50)		(air)	(N ₂)
				[°C]	[°C]	[°C]	[°C]	[°C]	[°C]
PIB ₂₃ -IL-PEtOx ₁₀	worm-like	2.3	8.2 × 10 ⁻⁴	–	~90	40-90	-77 31	318	305
PIB ₂₃ -IL-PEtOx ₂₀	elongated	2.2	5.5 × 10 ⁻⁴	–	–	81	-78 40	309	324
PIB ₂₃ -IL-PEtOx ₃₀	spherical	2.1	4.3 × 10 ⁻⁴	–	~90	75	-77 49	311	320
PIB ₂₃ -IL-PEtOx ₄₀	spherical	1.7	2.9 × 10 ⁻⁴	–	83	72	-76 47	322	332

^aPredominant morphology of self-assembled copolymer micelles in water. ^bDetermined by dye absorption method. ^cDetermined by turbidimetry or, in case of PIB₂₃-IL-PEtOx₁₀, by visual observation (values in brackets specify the concentration in mg/mL). ^dDetermined by DSC. ^eDecomposition temperature, determined by TGA under air and N₂ atmosphere, respectively.

As already mentioned, the diblock copolymers comprising PEtOx segments with a DP of 20, 30, and 40 were found to precipitate from aqueous solution upon heating, resulting in the formation of turbid dispersions. Most probably, this phenomenon is attributed to temperature-induced aggregation of copolymer micelles and the dehydration of the PEtOx chains (see Scheme 2), as demonstrated by Winnik and co-workers for hydrophobically end-capped poly(2-oxazoline)s.^{93,94} For thorough investigation of the LCST behavior and accurate cloud point (T_{CP}) determination, solutions of the amphiphilic PILs were examined by turbidimetry

in the temperature range from 30 °C to 90 °C (see Figure 6, Figure S12, and Table 4). The T_{CP} values, detected from the inflection point of the transmittance–temperature curves,⁹⁵ noticeably decrease with increasing length of the PEtOx block and increase with decreasing concentration. For a concentration of 50 mg/mL, sharp transitions with cloud points of 81 °C, 75 °C, and 72 °C were found for PIB₂₃-IL-PEtOx_m with $m = 20, 30,$ and $40,$ respectively. For a concentration of 20 mg/mL, only PIB₂₃-IL-PEtOx₄₀ having the longest PEtOx chain exhibits a T_{CP} (83 °C) in the temperature range studied. Though, from the shape of the transmittance–temperature curve of PIB₂₃-IL-PEtOx₃₀, a cloud point just slightly above 90 °C can be surmised, whereas there is no indication for any temperature-induced phase transition in case of PIB₂₃-IL-PEtOx₂₀ at this concentration. Finally, at 10 mg/mL, none of the block copolymers showed a thermal transition below 90 °C any more. The pronounced decrease of T_{CP} with increasing DP and increasing concentration is a typical feature of PEtOx chains.²⁸ However, the occurrence of cloud points well below 90 °C is clearly attributed to the presence of the hydrophobic PIB block, as ordinary PEtOx homopolymers with comparably short chain lengths show much higher thermal transition temperatures or even no LCST behavior at all. Cooling curves of the copolymer solutions prove the reversibility of the phase transitions, albeit in case of PIB₂₃-IL-PEtOx₂₀ significant hysteresis and incomplete transmittance recovery are observed.



Scheme 2. Illustration of colloidal self-assembly of PIB-IL-PEtOx as well as temperature-induced dehydration/collapse of PEtOx segments and aggregation of copolymer micelles. The photographs show an aqueous solution of PIB₂₃-IL-PEtOx₄₀ (polymer concentration: 50 mg/mL) at room temperature (left picture) and on a heating plate set to 100 °C (right picture)

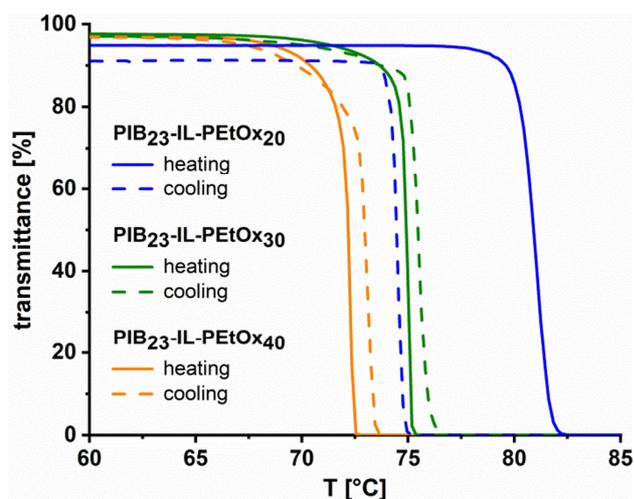


Figure 6. Transmittance–temperature curves of aqueous solutions of $\text{PIB}_{23}\text{-IL-PEtOx}_m$ copolymers with $m = 20, 30,$ and 40 in the range from $60\text{ }^\circ\text{C}$ to $85\text{ }^\circ\text{C}$ (polymer concentration: 50 mg/mL each; heating/cooling rate: 1 K/min). Full curves are depicted in Figure S12.

The aqueous mixtures of worm-forming $\text{PIB}_{23}\text{-IL-PEtOx}_{10}$ were found to display thermoresponsive properties as well. However, turbidimetry measurements did not give conclusive results (see Figure S13), presumably due to opacity and peculiar phase separation effects. Hence, the viscous and gel-like solutions, respectively, were examined by heating them in an oil bath without stirring. Unexpectedly, for a concentration of 20 mg/mL , blurring of the solution at ca. $90\text{ }^\circ\text{C}$ was observed. Even more surprising, the opaque gelatinous mixture at 50 mg/mL concentration exhibited a strange phase transition over a broad temperature range from approximately $40\text{ }^\circ\text{C}$ to $90\text{ }^\circ\text{C}$, which starts with blurring accompanied by a drastic decrease in viscosity and ends with separation into a clear water phase and a white lump floating to the top. The more stable hydrogels formed at 100 mg/mL and 150 mg/mL essentially behaved in the same way (see Figure 7). It is obvious that this behavior, which is distinctly different from those of the other amphiphilic PILs, is a consequence of the dominant PIB block in $\text{PIB}_{23}\text{-IL-PEtOx}_{10}$, though we do not have detailed insights into the phase separation process yet. Probably, temperature-induced dehydration of

the PEtOx segments causes morphological changes and severe aggregation of the worm-like nanostructures. Apparently, time plays a crucial role as well. When heating the PIB₂₃-IL-PEtOx₁₀/water mixtures for only a short period of time (1 hour), the original gel-like state is reconstituted after letting to stand at room temperature for some days. In contrast, when having applied heat for several hours, the more dense lump formed disintegrates after cooling under formation of a low-viscous polymer dispersion and no hydrogel reconstitution is observed even after several weeks.

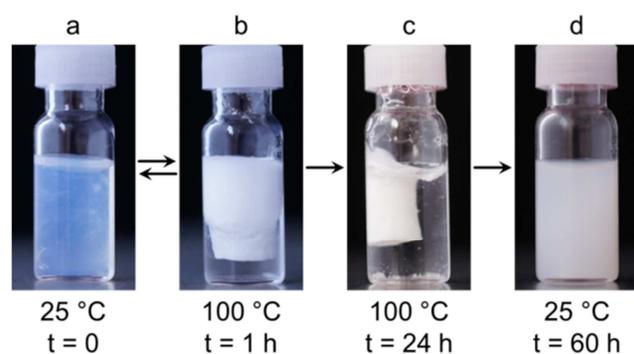


Figure 7: PIB₂₃-IL-PEtOx₁₀ hydrogel at room temperature (a), situation at 100 °C after heating for 1 hour (b), situation at 100 °C after heating for 24 hours (c), and low-viscosity polymer dispersion obtained after heating at 100 °C for 24 hours and subsequently letting to stand at room temperature for 36 hours (d). Polymer concentration is 150 mg/mL.

Finally, the PIB-IL-PEtOx copolymers were analyzed by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). DSC measurements indicated two distinct glass transitions: a first one at around -77 °C, which is attributed to the PIB segment, and a second one varying between 31 °C and 49 °C, which is in a temperature range typical for low-molecular-weight PEtOx chains (see Table 4). By tendency and within experimental error, the T_g of the PEtOx segment increases with increasing chain length, as expected. In TGA, no significant mass loss was detected up to temperatures of approximately 300 °C, indicative for

an outstanding thermal stability. Accompanied by the chemical robustness of the stable imidazolium tosylate linkage, this feature represents another highly advantageous property of the PIB-IL-PEtOx based PILs.

First trials emphasize the perspective of the PIB-IL-PEtOx amphiphiles in view of possible applications. On the one hand, the water soluble PIL micelles qualify as vehicles for transporting hydrophobic guest molecules by encapsulation in the PIB core and solubilization in aqueous media. This is demonstrated with the aid of water-insoluble Sudan Red III, which has been utilized for CMC determination. In presence of the amphiphilic PILs, intensively colored solutions are obtained. When heating above the cloud point of the copolymer, however, the dye-loaded micelles precipitate and slowly settle down, as shown in Figure 8a. Upon cooling to room temperature, the PILs quickly dissolve again, resulting in formation of the same colored solution as before. Several heating-cooling cycles confirm full repeatability of the process. Ongoing experiments are focused on exploiting this LCST-mediated precipitation for separation of the polymer/dye from the aqueous phase by hot filtration, followed by isolation and redissolution of the residue as well as quantification of the separation efficiency. Furthermore, the diblock copolymers turned out to be efficient dispersing agents for nanomaterials such as functionalized graphene (FG) nanosheets, which have been obtained by thermal reduction of graphite oxide.⁹⁶ In fact, PIB₂₃-IL-PEtOx₃₀ provides aqueous FG dispersions that are stable for more than six months, whereas in pure water at pH 7 no dispersion is obtained at all. It is well-known that poly(2-oxazoline)s can act as dispersing agents,^{97,98} but it can be strongly assumed that in PIB-IL-PEtOx this capability is further enhanced by the ionic imidazolium group. Interestingly, heating PIB₂₃-IL-PEtOx₃₀/FG dispersions above T_{CP} induces slow formation of an upper water phase and a lower water/polymer/FG phase (see Figure 8b). When cooling down again, the FG sheets are immediately redispersed in the whole volume of liquid, and this phase switching can be

readily repeated without any problems. Without any doubt, these simple experiments clearly underline the potential of the amphiphilic PIB-IL-PEtOx diblock copolymers as thermoresponsive PILs to be used as thermally switchable solubilizing agents and dispersants in highly diversified applications such as advanced catalytic processes, reversible transportation, and temperature-controlled separation.

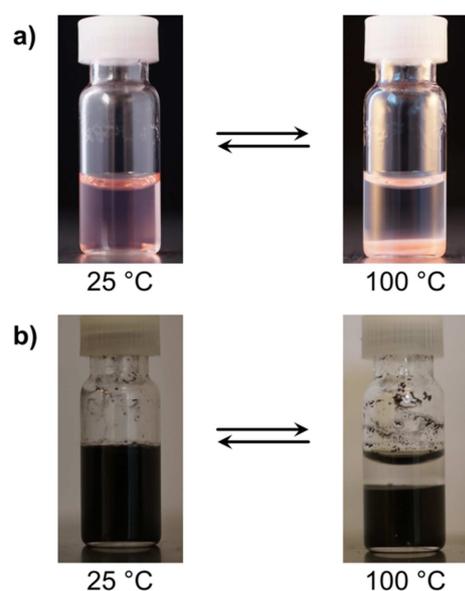


Figure 8: Temperature-triggered solubilization of Sudan Red III in water by PIB₂₃-IL-PEtOx₃₀ (a): polymer/dye solution at room temperature (left photograph) and situation after letting to stand at 100 °C for 14 days (right photograph). Temperature-switchable aqueous dispersion of FG nanosheets stabilized by PIB₂₃-IL-PEtOx₃₀ (b): dispersion at room temperature (left photograph) and situation after letting to stand at 100 °C for 10 days (right photograph). Polymer concentration is 50 mg/mL.

CONCLUSION

Aiming at the development of stimuli-responsive macromolecular nanosystems, a series of amphiphilic PIB-IL-PEtOx diblock copolymers have been tailored. Key feature is the covalent coupling of the hydrophobic PIB block with the hydrophilic PEtOx block via an

imidazolium group as a single IL moiety incorporated in the PIL backbone. This coupling reaction is achieved by means of chain termination of PEtOx bearing a cationic oxazolinium end group which alkylates the imidazole end group of PIB-Im. This straightforward synthetic approach allows for the production of PIB-IL-PEtOx macromolecules with high purity, well-defined molecular architecture, and narrow molecular weight distribution. By systematic and controlled alteration of the DP of the polar PEtOx block at invariable length of the non-polar PIB segment, the hydrophilic/hydrophobic balance, which governs solubility behavior both in organic solvents and in aqueous medium, is easily manipulated. Thus, the morphology of the supra-molecular assemblies formed in water can be varied from spherical and elongated micelles to ultra-long worm-like aggregates, as visualized by TEM. The former types of diblock copolymer micelles give low-viscosity colloidal solutions. Owing to the thermoresponsive features of the PEtOx block, they are endowed with LCST-type phase behavior and show sharp transitions at composition-dependent cloud points. In contrast, the worm-like micelles form highly viscous solutions or even hydrogels due to entanglements of the copolymer nano-worms. These gels show thermally induced phase transitions as well. Upon heating, they are transformed from a hydrogel-like material to a macrophase separated state, which occurs over a broad temperature range and turned out to be reversible or irreversible, depending on the conditions applied.

Exceptional chemical composition, thermoresponsive properties, and the precise control over polymer structure and, thus, nanostructure formation render the novel family of amphiphilic PIB-IL-PEtOx copolymers promising candidates for smart functional macromolecular systems useful in a wide variety of applications. This has been outlined by first simple experiments, which illustrate the capability of the PIB-IL-PEtOx diblock copolymers to be applied as thermally switchable solubilization and dispersing agents, respectively, for transportation and shuttling of hydrophobic molecules and nanomaterials. Ongoing research

will concentrate on further elucidation of such application perspectives, a more detailed investigation of the thermoresponsive worm-hydrogels by means of rheology, and variation of the 2-oxazoline monomer employed in the block copolymer synthesis in order to shift the cloud point to lower temperatures.

EXPERIMENTAL SECTION

Materials. Glissopal[®]1000 (BASF SE), borane-dimethyl sulfide complex (2 M in THF; Sigma-Aldrich), 4-dimethylaminopyridine (Sigma-Aldrich, $\geq 99.5\%$), aqueous hydrogen peroxide (30%; Roth), imidazole (Sigma-Aldrich, 99.8%), *p*-toluenesulfonyl chloride (Merck, 98%), potassium carbonate (Sigma-Aldrich, 99%), Sudan Red III (Sigma-Aldrich, technical grade), cyclohexane (Fisher scientific, 99.9%), ethanol (VWR Chemicals, 99.96%), *n*-hexane (Fisher scientific, 98.62%), and methanol (VWR Chemicals, 100%) were used as received. Benzotrifluoride (abcr GmbH, 99%), *N,N*-dimethylformamide (Fisher scientific, 99.9%), 2-ethyl-2-oxazoline (Alfa Aesar, 99%), and triethylamine (Roth, 99.5%) were distilled and stored over molecular sieve 3 Å for 24 h prior to use. Dichloromethane (Fisher scientific, 99.9%) was dried using a double column solvent filtration system from MBraun (MB-SPS-800) equipped with two columns (MB-KOL-A) and stored over molecular sieve 3 Å. Methyl *p*-toluenesulfonate (Sigma-Aldrich, 98%) was dried under vacuum for 2 h at 40 °C directly in the reaction flask prior to addition of solvent and monomer. All other chemicals were from different companies and used without purification. Functionalized graphene was synthesized by thermal reduction of graphite oxide at 700 °C according to Tölle *et al.*⁹⁶

General Remarks. All reactions were performed under dry conditions and under nitrogen atmosphere applying standard Schlenk techniques, except the synthesis of PIB-Im, which was carried out under air. In case of PIB derivatization, the molar masses determined via SEC have been used for calculation of the equivalents. Calculation of the equivalents of PIB-Im in

the synthesis of the PIB-IL-PEtOx diblock copolymers is based on the molar mass of PIB-Im determined from the ^1H NMR spectrum.

Synthesis of PIB-OH. Synthesis of PIB-OH was performed on the basis of a literature procedure.^{9,86} $\text{BH}_3 \cdot \text{SMe}_2$ (2 M in THF; 36 mL, 72 mmol, 1.4 eq.) was mixed with *n*-hexane (260 mL). Under cooling in an ice-water bath, a solution of Glissopal[®]1000 (61.3 g, 51.1 mmol) in *n*-hexane (260 mL) was added slowly. After that, the solution was allowed to warm to room temperature and stirred for 24 h. Then, EtOH (220 mL), a solution of NaOH (11 g, 0.28 mol, 5.4 eq.) in water (100 mL), and finally aqueous H_2O_2 (30%; 32 mL, 35 g, 0.31 mol, 6.1 eq.) were added dropwise. The resulting mixture was stirred at room temperature for 2 h, heated to 80 °C, and stirred at 80 °C for additional 2 h. After cooling to room temperature, the organic phase was separated from the aqueous phase, washed with H_2O (3×100 mL) and brine (200 mL), dried over MgSO_4 , and filtered. Removal of the solvent under reduced pressure and drying under vacuum at 90 °C yielded PIB-OH as colourless viscous liquid (yield: 62.1 g, 100%). ^1H NMR (300 MHz, CDCl_3 , 23 °C): $\delta = 0.20\text{-}2.25$ (m, 165H), 3.20-4.30 (m, 2H) ppm.

Synthesis of PIB-OTs. PIB-OH (42.1 g, 34.7 mmol) was dried at 60 °C under reduced pressure for 2 h, followed by cooling down to room temperature and dissolving it together with DMAP (8.6 g, 70 mmol, 2.1 eq.) and NEt_3 (49 mL, 35 g, 0.35 mol, 10 eq.) in CH_2Cl_2 (300 mL). Then, a solution of *p*-toluenesulfonyl chloride (17 g, 91 mmol, 2.7 eq.) in CH_2Cl_2 (136 mL) was added dropwise. The solution was stirred at room temperature for 48 h. After that, CH_2Cl_2 was removed under reduced pressure. The crude product was taken up in *n*-hexane (60 mL) and precipitated in MeOH (600 mL). Precipitation was repeated two times. After drying under vacuum at 60 °C, the product was obtained as colourless viscous liquid (yield: 36.0 g, 78%). ^1H NMR (300 MHz, CDCl_3 , 23 °C): $\delta = 0.20\text{-}2.25$ (m, 238H), 2.45 (s, 3H), 3.20-4.30 (m, 2H), 7.34 (d, $J = 7.93$ Hz, 2H), 7.79 (d, $J = 8.40$ Hz, 2H) ppm.

Synthesis of PIB-Im. PIB-OTs (34.6 g, 21.0 mmol), imidazole (34 g, 0.50 mol, 29 eq.), K_2CO_3 (8.3 g, 60 mmol, 3.5 eq.), and BTF (500 mL) were put into a flask together and stirred at room temperature until the PIB-OTs was completely dissolved. The resulting mixture was heated to 80 °C and stirred for 48 h. After cooling down to room temperature, the solution was concentrated under reduced pressure. The crude product was taken up in CH_2Cl_2 (40 mL) and precipitated in MeOH:H₂O (8:2 v/v; 400 mL). The precipitate was dried at 90 °C under reduced pressure and purified by column chromatography using cyclohexane: CH_2Cl_2 (1:1 v/v; 400 mL), then CH_2Cl_2 (700 mL), and finally CH_2Cl_2 :EtOH (8:2 v/v; 500 mL; 1:1 v/v; 1 L) as eluent. Volatiles of the product fraction were removed and the residue was dried at 90 °C under vacuum. For final purification, the product was dissolved in CH_2Cl_2 (15 mL) and precipitated in MeOH:H₂O (8:2 v/v; 200 mL). Precipitation was repeated once again. Drying in vacuum at 90 °C afforded PIB-Im as colourless viscous liquid (yield: 14.5 g, 53%). ¹H NMR (300 MHz, $CDCl_3$, 23 °C): δ = 0.20-2.25 (m, 194H), 3.40-4.00 (m, 2H), 6.89 (s, 1H), 7.06 (s, 1H), 7.45 (s, 1H) ppm.

Synthesis of PIB-IL-PEtOx Diblock Copolymers. Block copolymer syntheses were performed according to the following general procedure (amounts of chemicals employed and yields are specified in Table 5). Methyl *p*-toluenesulfonate was dried at 40 °C for 2 h under reduced pressure. After cooling to room temperature, either BTF or BTF:DMF mixture (4:1 v/v) and 2-ethyl-2-oxazoline were added (see Table 5). The flask was immersed in an oil bath preheated to 90 °C and the solution was stirred at 90 °C for 4.5 h. Then, a solution of PIB-Im (PIB-Im has been pre-dried in vacuum at 90 °C for 2 h) in BTF (6 mL) was added. The solution was stirred at 90 °C for 72 h. After cooling down to room temperature and removal of solvent under reduced pressure, different methods were applied for purification of the raw product (*i.e.*, removal of non-coupled excess PEtOx homopolymer), depending on the PEtOx block length.

PIB₂₃-IL-PEtOx₁₀: The raw product was dissolved in CH₂Cl₂ (10 mL) and washed with water (6 × 10 mL). The organic phase was dried over MgSO₄ and filtered. After removal of the solvent under reduced pressure and drying at 60 °C in high vacuum, PIB₂₃-IL-PEtOx₁₀ was obtained as slightly yellowish waxy substance. ¹H NMR (500 MHz, CDCl₃, 40 °C): δ = 0.50-1.70 (m, 233H), 1.80-2.70 (m, 30H), 2.85-4.20 (m, 48H), 4.40-4.73 (m, 2H), 7.05-7.20 (m, 3H), 7.36-7.59 (m, 1H), 7.61-7.84 (m, 2H), 9.75-10.50 (m, 1H) ppm.

PIB₂₃-IL-PEtOx_{20/30/40}: The respective raw product was dissolved in water to obtain a solution with a concentration of 50 mg/mL. The solution was put in an oven heated to 90 °C and kept at 90 °C for 24 h. The precipitated diblock copolymer was isolated by filtration in the hot oven using a preheated glass frit. The product was taken up in water, isolated by freeze-drying, and dissolved in water again to obtain a solution with a concentration of 100 mg/mL. Temperature-induced precipitation and hot filtration were repeated as described before. Dissolving in water and freeze-drying yielded PIB₂₃-IL-PEtOx₂₀, PIB₂₃-IL-PEtOx₃₀, and PIB₂₃-IL-PEtOx₄₀ as white powdery solids. PIB₂₃-IL-PEtOx₂₀: ¹H NMR (500 MHz, CDCl₃, 40 °C): δ = 0.50-1.70 (m, 279H), 1.80-2.70 (m, 59H), 2.85-4.20 (m, 93H), 4.40-4.73 (m, 3H), 7.05-7.20 (m, 3H), 7.36-7.59 (m, 1H), 7.61-7.84 (m, 2H), 9.77-10.54 (m, 1 H) ppm. PIB₂₃-IL-PEtOx₃₀: ¹H NMR (500 MHz, CDCl₃, 40 °C): δ = 0.50-1.70 (m, 299H), 1.80-2.70 (m, 76H), 2.85-4.20 (m, 131H), 4.40-4.73 (m, 2H), 7.05-7.20 (m, 3H), 7.36-7.59 (m, 1H), 7.61-7.84 (m, 2H), 9.75-10.50 (m, 1H) ppm. PIB₂₃-IL-PEtOx₄₀: ¹H NMR (500 MHz, CDCl₃, 40 °C): δ = 0.50-1.70 (m, 326H), 1.80-2.70 (m, 94H), 2.85-4.20 (m, 169H), 4.40-4.73 (m, 2H), 7.05-7.20 (m, 3H), 7.36-7.59 (m, 1H), 7.61-7.84 (m, 2 H), 9.75-10.50 (m, 1H) ppm.

Table 5. Synthesis and yield of PIB-IL-PEtOx diblock copolymers

block copolymer	MeOTs	EtOx	PIB-Im	BTF ^a	DMF ^a	yield
	[g mmol eq.]	[mL g mmol eq.]	[g mmol eq.]	[mL]	[mL]	[g %]

PIB ₂₃ -IL-PEtOx ₁₀	0.77 4.1 1.0	4.2 4.1 42 10	2.96 2.04 0.49	12.0	–	5.37 100
PIB ₂₃ -IL-PEtOx ₂₀	0.54 2.9 1.0	5.9 5.8 58 20	2.11 1.46 0.50	14.4	3.6	4.24 80
PIB ₂₃ -IL-PEtOx ₃₀	0.42 2.3 1.0	6.9 6.8 68 30	1.63 1.12 0.50	16.8	4.2	4.95 95
PIB ₂₃ -IL-PEtOx ₄₀	0.35 1.9 1.0	7.5 7.4 74 40	1.33 0.92 0.49	18.4	4.6	3.67 72

^aVolume of solvent used for EtOx polymerization.

Application of PIB-IL-PEtOx for Thermally Switchable Solubilization and

Dispersion. 100 mg of PIB₂₃-IL-PEtOx₃₀ was mixed with 2 mL of water and placed in an ultrasonic bath for 10 min. 1 mL of the solution was added to 5 mg Sudan Red III. Another 1 mL was added to 3 mg of functionalized graphene. Both mixtures were placed in an ultrasonic bath for 10 min, shaken overnight, and sonicated for 10 min once again. The Sudan Red III mixture was filtrated with a syringe filter (PTFE 0.46 μm) in order to remove the portion of excessive dye not being dissolved in the copolymer micelles. Thermal switching of dye solubilization and graphene dispersion was examined by placing the samples in an oven set to 100 °C.

Analysis and Characterization. ¹H NMR spectra of end-functionalized PIBs and raw PIB-IL-PEtOx block copolymers were recorded on a Bruker Avance II 300 MHz NMR spectrometer. ¹H NMR spectra of purified PIB-IL-PEtOx block copolymers were recorded on a Bruker Avance III HD 500 MHz NMR spectrometer. SEC measurements of end-functionalized PIBs were performed on an Agilent Technologies 1200/1260 with chloroform eluent. SEC measurements of raw and purified PIB-IL-PEtOx block copolymers were performed on an Agilent 1260 Infinity with *N,N*-dimethylacetamide/LiBr (0.5%) eluent. Molecular weights were determined against polystyrene and PMMA standards, respectively. DSC measurements were conducted on a DSC 204 F1 from Netzsch. Glass transition temperatures were determined from the second heating curve (heating rate: 20 K/min). TGA

was performed on a STA 409 C from Netzsch with a heating rate of 10 K/min. For TEM imaging of PIB-IL-PEtOx micelles, diluted aqueous solutions of the diblock copolymers were placed on plasma-treated carbon-coated copper grids and excess liquid was removed with filter paper. Staining of the nanostructures was performed with an aqueous uranyl acetate solution. TEM imaging was realized with a FEI Talos L120C transmission electron microscope. The CMC of PIB-IL-PEtOx diblock copolymers was determined by a dye absorption method using Sudan Red III. The absorbance at 506 nm of aqueous dye solutions with varying concentration of PIB-IL-PEtOx was measured on a SHIMADZU UV-1800 UV-Vis spectrophotometer. The CMC was detected by plotting the absorbance values against polymer concentration. Turbidimetry measurements were conducted on a Jasco V-650 spectrophotometer at 488 nm wavelength with a heating/cooling rate of 1 K/min. Aqueous mixtures of PIB₂₃-IL-PEtOx₁₀ were examined by heating them in an oil bath, on a heating plate, or in an oven. Changes of the samples were registered by visual observation.

ASSOCIATED CONTENT

Supporting Information. Additional Tables and Figures as well as detailed description of characterization methods and techniques. The Supporting Information is available free of charge on the ACS Publications website.

AUTHOR INFORMATION

Corresponding Authors

* E-mail rolfmuelhaupt@web.de

* E-mail benjamin.kerscher@fmf.uni-freiburg.de

Notes

The authors declare no competing financial interest.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge financial support by the European Research Area Chemistry (ERA-Chemistry), the National Research, Development and Innovation Office, Hungary (OTKA NN 116252, NN 129366, 112094), and the German Research Foundation (DFG; MU 836/13-1, 269965048). The authors give thanks to Kristin Anne Lehmann and Carolin Daniela Guth for assistance in laboratory work and to Dr. Victor Pacheco Torres and Dr. Manfred Keller for technical assistance in NMR spectroscopy analysis.

REFERENCES

- (1) Kennedy, J. P.; Smith, R. A. New Telechelic Polymers and Sequential Copolymers by Polyfunctional Initiator-Transfer Agents (Inifers). II. Synthesis and Characterization of α,ω -Di(tert-chloro)polyisobutylenes. *J. Polym. Sci., Polym. Chem. Ed.* **1980**, *18*, 1523–1537.
- (2) Faust, R.; Kennedy, J. P. Living Carbocationic Polymerization. IV. Living Polymerization of Isobutylene. *J. Polym. Sci., Part A: Polym. Chem.* **1987**, *25*, 1847–1869.
- (3) Kennedy, J. P.; Iván, B. *Designed Polymers by Carbocationic Macromolecular Engineering: Theory and Practice*; Hanser: Munich, 1992.
- (4) Mach, H.; Rath, P. Highly Reactive Polyisobutene as a Component of a New Generation of Lubricant and Fuel Additives. *Lubr. Sci.* **1999**, *11*, 175–185.
- (5) Kostjuk, S. V. Recent progress in the lewis acid co-initiated cationic polymerization of isobutylene and 1,3-dienes. *RSC Adv.* **2015**, *5*, 13125–13144.
- (6) Kennedy, J. P.; Chang, V. S. C.; Smith, R. A.; Iván, B. New Telechelic Polymers and Sequential Copolymers by Polyfunctional Initiator-Transfer Agents (Inifers) V. Synthesis of

α -tert-Butyl- ω -isopropenylpolyisobutylene and α,ω -Di(isopropenyl)polyisobutylene. *Polym. Bull.* **1979**, *1*, 575–580.

(7) Iván, B.; Kennedy, J. P.; Chang, V. S. C. New Telechelic Polymers and Sequential Copolymers by Polyfunctional Initiator-Transfer Agents (Inifers). VII. Synthesis and Characterization of α,ω -Di(hydroxy)polyisobutylene. *J. Polym. Sci., Polym. Chem. Ed.* **1980**, *18*, 3177–3191.

(8) Iván, B.; Kennedy, J. P. Living Carbocationic Polymerization. XXX. One-Pot Synthesis of Allyl-Terminated Linear and Tri-Arm Star Polyisobutylenes, and Epoxy- and Hydroxy-Telechelics Therefrom. *J. Polym. Sci., Part A: Polym. Chem.* **1990**, *28*, 89–104.

(9) Li, J.; Sung, S.; Tian, J.; Bergbreiter, D. E. Polyisobutylene supports—a non-polar hydrocarbon analog of PEG supports. *Tetrahedron* **2005**, *61*, 12081–12092.

(10) Ummadisetty, S.; Kennedy, J. P. Quantitative syntheses of novel polyisobutylenes fitted with terminal primary –Br, –OH, –NH₂, and methacrylate termini. *J. Polym. Sci., Part A: Polym. Chem.* **2008**, *46*, 4236–4242.

(11) Magenau, A. J. D.; Chan, J. W.; Hoyle, C. E.; Storey, R. F. Facile polyisobutylene functionalization via thiol–ene click chemistry. *Polym. Chem.* **2010**, *1*, 831–833.

(12) Stuart, F. A.; Anderson, R. G.; Drummond, A. Y. California Research Corporation, Alkenyl Succinimides of Tetraethylene Pentamine, US 3202678, 1965.

(13) Puskas, J. E.; Chen, Y. Biomedical Application of Commercial Polymers and Novel Polyisobutylene-Based Thermoplastic Elastomers for Soft Tissue Replacement. *Biomacromolecules* **2004**, *5*, 1141–1154.

(14) Puskas, J. E.; Chen, Y.; Dahman, Y.; Padavan, D. Polyisobutylene-Based Biomaterials. *J. Polym. Sci., Part A: Polym. Chem.* **2004**, *42*, 3091–3109.

- (15) Lim, T. G.; Valente, S. A.; Hart-Spicer, C. R.; Evancho-Chapman, M. M.; Puskas, J. E.; Horne, W. I.; Schmidt, S. P. New biomaterial as a promising alternative to silicone breast implants. *J. Mech. Behav. Biomed. Mater.* **2013**, *21*, 47–56.
- (16) Götz, C.; Lim, G.-T.; Puskas, J. E.; Altstädt, V. The effect of carbon black reinforcement on the dynamic fatigue and creep of polyisobutylene-based biomaterials. *J. Mech. Behav. Biomed. Mater.* **2014**, *39*, 355–365.
- (17) Kang, J.; Kennedy, J. P. Hydrolytically Stable Polyurethanes. *J. Polym. Sci., Part A: Polym. Chem.* **2015**, *53*, 1–4.
- (18) Mishra, A.; Seethamraju, K.; Delaney, J.; Willoughby, P.; Faust, R. Long-term in vitro hydrolytic stability of thermoplastic polyurethanes. *J. Biomed. Mater. Res., Part A* **2015**, *103*, 3798–3806.
- (19) Trant, J. F.; McEachran, M. J.; Sran, I.; Turowec, B. A.; de Bruyn, J. R.; Gillies, E. R. Covalent Polyisobutylene-Paclitaxel Conjugates for Controlled Release from Potential Vascular Stent Coatings. *ACS Appl. Mater. Interfaces* **2015**, *7*, 14506–14517.
- (20) Toth, K.; Nugay, N.; Kennedy, J. P. Polyisobutylene-Based Polyurethanes. IX. Synthesis, Characterization, and Properties of Polyisobutylene-Based Poly(urethane-ureas). *J. Polym. Sci., Part A: Polym. Chem.* **2016**, *54*, 2361–2369.
- (21) Zhou, Y.; Pinchuk, L. Innolene LLC, Crosslinked Polyolefins for Biomedical Applications and Method of Making Same, US 9382357B2, 2016.
- (22) Delaney, J. T., Jr.; Gurung, N.; Willoughby, P.; Wulfman, D. R.; Adenusi, A. O.; Aremu, A. O. Cardiac Pacemakers, Inc., Polyisobutylene-Polyurethanes and Medical Devices Containing the Same, US 2017/0174845A1, 2017.
- (23) Aoi, K.; Okada, M. Polymerization of oxazolines. *Prog. Polym. Sci.* **1996**, *21*, 151–208.
- (24) Kobayashi, S.; Uyama, H. Polymerization of Cyclic Imino Ethers: From Its Discovery to the Present State of the Art. *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40*, 192–209.

- (25) Rossegger, E.; Schenk, V.; Wiesbrock, F. Design Strategies for Functionalized Poly(2-oxazoline)s and Derived Materials. *Polymers* **2013**, *5*, 956–1011.
- (26) Verbraeken, B.; Monnery, B. D.; Lava, K.; Hoogenboom, R. The chemistry of poly(2-oxazoline)s. *Eur. Polym. J.* **2017**, *88*, 451–469.
- (27) Huber, S.; Jordan, R. Modulation of the lower critical solution temperature of 2-Alkyl-2-oxazoline copolymers. *Colloid Polym. Sci.* **2008**, *286*, 395–402.
- (28) Hoogenboom, R.; Thijs, H. M. L.; Jochems, M. J. H. C.; van Lankvelt, B. M.; Fijten, M. W. M.; Schubert, U. S. Tuning the LCST of poly(2-oxazoline)s by varying composition and molecular weight: alternatives to poly(N-isopropylacrylamide)? *Chem. Commun.* **2008**, 5758–5760.
- (29) Diehl, C.; Schlaad, H. Thermo-Responsive Polyoxazolines with Widely Tuneable LCST. *Macromol. Biosci.* **2009**, *9*, 157–161.
- (30) Weber, C.; Hoogenboom, R.; Schubert, U. S. Temperature responsive bio-compatible polymers based on poly(ethylene oxide) and poly(2-oxazoline)s. *Prog. Polym. Sci.* **2012**, *37*, 686–714.
- (31) Guerrero-Sanchez, C.; Gohy, J.-F.; D'Haese, C.; Thijs, H.; Hoogenboom, R.; Schubert, U. S. Controlled thermoreversible transfer of poly(oxazoline) micelles between an ionic liquid and water. *Chem. Commun.* **2008**, 2753–2755.
- (32) de la Rosa, V. R.; Hoogenboom, R. Solution Polymeric Optical Temperature Sensors with Long-Term Memory Function Powered by Supramolecular Chemistry. *Chem. Eur. J.* **2015**, *21*, 1302–1311.
- (33) Kim, J.-H.; Jung, Y.; Lee, D.; Jang, W.-D. Thermoresponsive Polymer and Fluorescent Dye Hybrids for Tunable Multicolor Emission. *Adv.Mater.* **2016**, *28*, 3499–3503.

- (34) de la Rosa, V. R.; Zhang, Z.; De Geest, B. G.; Hoogenboom, R. Colorimetric Logic Gates Based on Poly(2-alkyl-2-oxazoline)-Coated Gold Nanoparticles. *Adv. Funct. Mater.* **2015**, *25*, 2511–2519.
- (35) Kim, J.-H.; Koo, E.; Ju, S.-Y.; Jang, W.-D. Multimodal Stimuli-Responsive Poly(2-isopropyl-2-oxazoline) with Dual Molecular Logic Gate Operations. *Macromolecules* **2015**, *48*, 4951–4956.
- (36) Goddard, P.; Hutchinson, L. E.; Brown, J.; Brookman, L. J. Soluble polymeric carriers for drug delivery. Part 2. Preparation and in vivo behaviour of N-acylethylenimine copolymers. *J. Controlled Release* **1989**, *10*, 5–16.
- (37) Gaertner, F. C.; Luxenhofer, R.; Blechert, B.; Jordan, R.; Essler, M. Synthesis, biodistribution and excretion of radiolabeled poly(2-alkyl-2-oxazoline)s. *J. Controlled Release* **2007**, *119*, 291–300.
- (38) Kronek, J.; Kroneková, Z.; Lustoň, J.; Paulovičová, E.; Paulovičová, L.; Mendrek, B. In vitro bio-immunological and cytotoxicity studies of poly(2-oxazolines). *J. Mater. Sci.: Mater. Med.* **2011**, *22*, 1725–1734.
- (39) Luxenhofer, R.; Sahay, G.; Schulz, A.; Alakhova, D.; Bronich, T. K.; Jordan, R.; Kabanov, A. V. Structure-property relationship in cytotoxicity and cell uptake of poly(2-oxazoline) amphiphiles. *J. Controlled Release* **2011**, *153*, 73–82.
- (40) Woodle, M. C.; Engbers, C. M.; Zalipsky, S. New Amphipatic Polymer–Lipid Conjugates Forming Long-Circulating Reticuloendothelial System-Evading Liposomes. *Bioconjugate Chem.* **1994**, *5*, 493–496.
- (41) Zalipsky, S.; Hansen, C. B.; Oaks, J. M.; Allen, T. M. Evaluation of Blood Clearance Rates and Biodistribution of Poly(2-oxazoline)-Grafted Liposomes. *J. Pharm. Sci.* **1996**, *85*, 133–137.

- (42) Adams, N.; Schubert, U. S. Poly(2-oxazolines) in biological and biomedical application contexts. *Adv. Drug Delivery Rev.* **2007**, *59*, 1504–1520.
- (43) Hoogenboom, R. Poly(2-oxazoline)s: A Polymer Class with Numerous Potential Applications. *Angew. Chem. Int. Ed* **2009**, *48*, 7978–7994.
- (44) Konradi, R.; Acikgoz, C.; Textor, M. Polyoxazolines for Nonfouling Surface Coatings – A Direct Comparison to the Gold Standard PEG. *Macromol. Rapid Commun.* **2012**, *33*, 1663–1676.
- (45) Luxenhofer, R.; Han, Y.; Schulz, A.; Tong, J.; He, Z.; Kabanov, A. V.; Jordan, R. Poly(2-oxazoline)s as Polymer Therapeutics. *Macromol. Rapid Commun.* **2012**, *33*, 1613–1631.
- (46) Najer, A.; Wu, D.; Vasquez, D.; Palivan, C. G.; Meier, W. Polymer nanocompartments in broad-spectrum medical applications. *Nanomedicine* **2013**, *8*, 425–447.
- (47) de la Rosa, V. R. Poly(2-oxazoline)s as materials for biomedical applications. *J. Mater. Sci.: Mater. Med.* **2014**, *25*, 1211–1225.
- (48) Morgese, G.; Benetti, E. M. Polyoxazoline biointerfaces by surface grafting. *Eur. Polym. J.* **2017**, *88*, 470–485.
- (49) Moreadith, R. W.; Viegas, T. X.; Bentley, M. D.; Harris, J. M.; Fang, Z.; Yoon, K.; Dizman, B.; Weimer, R.; Rae, B. P.; Li, X. *et al.* Clinical development of a poly(2-oxazoline) (POZ) polymer therapeutic for the treatment of Parkinson’s disease – Proof of concept of POZ as a versatile polymer platform for drug development in multiple therapeutic indications. *Eur. Polym. J.* **2017**, *88*, 524–552.
- (50) Bludau, H.; Czapar, A. E.; Pitek, A. S.; Shukla, S.; Jordan, R.; Steinmetz, N. F. POxylation as an alternative stealth coating for biomedical applications. *Eur. Polym. J.* **2017**, *88*, 679–688.

- (51) Hoogenboom, R. Poly(2-oxazoline)s: Alive and Kicking. *Macromol. Chem. Phys.* **2007**, *208*, 18–25.
- (52) Schlaad, H.; Diehl, C.; Gress, A.; Meyer, M.; Demirel, A. L.; Nur, Y.; Bertin, A. Poly(2-oxazoline)s as Smart Bioinspired Polymers. *Macromol. Rapid Commun.* **2010**, *31*, 511–525.
- (53) Hoogenboom, R.; Schlaad, H. Bioinspired Poly(2-oxazoline)s. *Polymers* **2011**, *3*, 467–488.
- (54) Kelly, A. M.; Wiesbrock, F. Strategies for the Synthesis of Poly(2-oxazoline)-Based Hydrogels. *Macromol. Rapid Commun.* **2012**, *33*, 1632–1647.
- (55) Hoogenboom, R.; Schlaad, H. Thermoresponsive poly(2-oxazoline)s, polypeptoids, and polypeptides. *Polym. Chem.* **2017**, *8*, 24–40.
- (56) Kempe, K. Chain and Step Growth Polymerizations of Cyclic Imino Ethers: From Poly(2-oxazoline)s to Poly(ester amide)s. *Macromol. Chem. Phys.* **2017**, *218*, 1700021.
- (57) Glassner, M.; Vergaelen, M.; Hoogenboom, R. Poly(2-oxazoline)s: A comprehensive overview of polymer structures and their physical properties. *Polym. Int.* **2018**, *67*, 32–45.
- (58) Smith, W. L.; Kelyman, J. S.; Jones, L. The Dow Chemical Company, Ashless Oil Dispersants, US 4120804, 1978.
- (59) Tomalia, D. A.; Huffines, J. D. The Dow Chemical Company, Surfactants, US 4261925, 1981.
- (60) Vocher, L.; Tessier, M.; Brigodiot, M.; Marechal, E.; Parc, G.; Dawans, F. Institut Francais Du Petrole, Modified butene polymers, GB 2149799A, 1985.
- (61) Campbell, C.; Storey, R. F. Synthesis of polyisobutylene-poly(2-phenyl-2-oxazoline) block copolymers via macroinitiator and click chemistry approaches, Abstracts of Papers, 248th ACS National Meeting & Exposition, San Francisco, CA, United States, POLY-550, August 10-14, 2014.

- (62) Percec, V.; Guhaniyogi, S. C.; Kennedy, J. P.; Iván, B. New Telechelic Polymers and Sequential Copolymers by Polyfunctional Initiator-Transfer Agents (Inifers): 11. Synthesis, Extension and Crosslinking of Oxycarbonyl Isocyanate Telechelic Polyisobutylenes. *Polym. Bull.* **1982**, *8*, 25–32.
- (63) Dean, B. D. Atlantic Richfield Company, Impact Modifier for Imide Containing Copolymers, US 4703085, 1987.
- (64) Dean, B. D. Impact modification of imide containing copolymers. *J. Appl. Polym. Sci.* **1989**, *37*, 1727–1730.
- (65) Nuyken, O.; Sanchez, J. R.; Voit, B. Synthesis of amphiphilic graft copolymers by ring-opening polymerization of 2-methyl-2-oxazoline initiated by poly[isobutene-co-(p,m-chloromethylstyrene)] macroinitiators. *Macromol. Rapid Commun.* **1997**, *18*, 125–131.
- (66) Nuyken, O.; Sanchez, J. R.; Voit, B. Hydrolysis and Subsequent Quaternization of Poly[(Isobutene-co-(m,p)-chloromethylstyrene)-g-2-methyl-2-oxazoline] and Poly((m,p)-Chloromethylstyrene-g-2-methyl-2-oxazoline). *J. Macromol. Sci., Part A: Pure Appl. Chem.* **1997**, *34*, 1261–1267.
- (67) Nuyken, O.; Rueda-Sanchez, J.; Voit, B. Synthesis of graft copolymers by ring-opening polymerization of 2-nonyl- and 2-phenyl-2-oxazoline initiated by macroinitiators containing benzylchloride functions. *Polym. Bull.* **1997**, *38*, 657–664.
- (68) Grasmüller, M.; Rueda-Sanchez, J. C.; Voit, B. I.; Nuyken, O. Polyfunctional polyisobutenes as building blocks for amphiphilic graft polymers. *Macromol. Symp.* **1998**, *127*, 109–114.
- (69) Yuan, J.; Antonietti, M. Poly(ionic liquid)s: Polymers expanding classical property profiles. *Polymer* **2011**, *52*, 1469–1482.
- (70) Mecerreyes, D. Polymeric ionic liquids: Broadening the properties and applications of polyelectrolytes. *Prog. Polym. Sci.* **2011**, *36*, 1629–1648.

- (71) Yuan, J.; Mecerreyes, D.; Antonietti, M. Poly(ionic liquid)s: An update. *Prog. Polym. Sci.* **2013**, *38*, 1009–1036.
- (72) Xu, W.; Ledin, P. A.; Shevchenko, V. V.; Tsukruk, V. V. Architecture, Assembly, and Emerging Applications of Branched Functional Polyelectrolytes and Poly(ionic liquid)s. *ACS Appl. Mater. Interfaces* **2015**, *7*, 12570–12596.
- (73) Kerscher, B.; Schüler, F.; Evers, A.-K.; Mülhaupt, R. in *Bio-inspired Polymers*, ed. Bruns, N.; Kilbinger, A. F. M., The Royal Society of Chemistry, Cambridge 2016, RSC Polymer Chemistry Series No. 22, p. 259-285: Chapter 7: Polymeric Ionic Liquids with Micelle-like Topologies and Functions.
- (74) Kohno, Y.; Saita, S.; Men, Y.; Yuan, J.; Ohno, H. Thermoresponsive polyelectrolytes derived from ionic liquids. *Polym. Chem.* **2015**, *6*, 2163–2178.
- (75) Schulz, R. C.; Schwarzenbach, E. Macromonomers on the basis of 2-phenyl-2-oxazoline. *Macromol. Symp.* **1988**, *13-14*, 495–505.
- (76) Waschinski, C. J.; Tiller, J. C. Poly(oxazoline)s with Telechelic Antimicrobial Functions. *Biomacromolecules* **2005**, *6*, 235–243.
- (77) Einzmann, M.; Binder, W. H. Novel functional initiators for oxazoline polymerization. *J. Polym. Sci., Part A: Polym. Chem.* **2001**, *39*, 2821–2831.
- (78) Bergbreiter, D. E.; Su, H.-L.; Koizumi, H.; Tian, J. Polyisobutylene-supported N-heterocyclic carbene palladium catalysts. *J. Organomet. Chem.* **2011**, *696*, 1272–1279.
- (79) Zare, P.; Stojanovic, A.; Herbst, F.; Akbarzadeh, J.; Peterlik, H.; Binder, W. H. Hierarchically Nanostructured Polyisobutylene-Based Ionic Liquids. *Macromolecules* **2012**, *45*, 2074–2084.
- (80) Stojanovic, A.; Appiah, C.; Döhler, D.; Akbarzadeh, J.; Zare, P.; Peterlik, H.; Binder, W. H. Designing melt flow of poly(isobutylene)-based ionic liquids. *J. Mater. Chem. A* **2013**, *1*, 12159–12169.

- (81) Yahya, R.; Craven, M.; Kozhevnikova, E. F.; Steiner, A.; Samunual, P.; Kozhevnikov, I. V.; Bergbreiter, D. E. Polyisobutylene oligomer-bound polyoxometalates as efficient and recyclable catalysts for biphasic oxidations with hydrogen peroxide. *Catal. Sci. Technol.* **2015**, *5*, 818–821.
- (82) Samunual, P.; Bergbreiter, D. E. Recyclable soluble polyisobutylene-bound oxidizing agents. *Tetrahedron Lett.* **2016**, *57*, 3272–3276.
- (83) Frenzel, F.; Folikumah, M. Y.; Schulz, M.; Anton, A. M.; Binder, W. H.; Kremer, F. Molecular Dynamics and Charge Transport in Polymeric Polyisobutylene-Based Ionic Liquids. *Macromolecules* **2016**, *49*, 2868–2875.
- (84) Appiah, C.; Akbarzadeh, J.; Stojanovic-Marinow, A.; Peterlik, H.; Binder, W. H. Hierarchically Mesostuctured Polyisobutylene-Based Ionic Liquids. *Macromol. Rapid Commun.* **2016**, *37*, 1175–1180.
- (85) Hongfa, C.; Su, H.-L.; Bazzi, H. S.; Bergbreiter, D. E. Polyisobutylene-Anchored N-Heterocyclic Carbene Ligands. *Org. Lett.* **2009**, *11*, 665–667.
- (86) Tian, J. PhD Thesis, Polyisobutylene-Supported Catalysts, Texas A&M University, 2008.
- (87) Däbritz, F. PhD Thesis, Hyperstern-Polymere mit hochverzweigten Kernen und polaren Armen - ihre Synthese, Charakterisierung und Anwendung als Reaktivbinder in Epoxy-basierten Photo- und Thermolacken, Technische Universität Dresden, 2011.
- (88) de la Rosa, V. R.; Tempelaar, S.; Dubois, P.; Hoogenboom, R.; Mespouille, L. Poly(2-ethyl-2-oxazoline)-block-polycarbonate block copolymers: from improved end-group control in poly(2-oxazoline)s to chain extension with aliphatic polycarbonate through a fully metal-free ring-opening polymerisation process. *Polym. Chem.* **2016**, *7*, 1559–1568.
- (89) Hoffmann, H.; Ulbricht, W. Surfactant gels. *Curr. Opin. Colloid Interface Sci.* **1996**, *1*, 726–739.

- (90) Malo de Molina, P.; Gradzielski, M. Gels Obtained by Colloidal Self-Assembly of Amphiphilic Molecules. *Gels* **2017**, *3*, 30.
- (91) Israelachvili, J. N. *Intermolecular and Surface Forces*, Third edition; Elsevier Academic Press: Amsterdam, 2011.
- (92) Volet, G.; Chanthavong, V.; Wintgens, V.; Amiel, C. Synthesis of Monoalkyl End-Capped Poly(2-methyl-2-oxazoline) and Its Micelle Formation in Aqueous Solution. *Macromolecules* **2005**, *38*, 5190–5197.
- (93) Obeid, R.; Maltseva, E.; Thünemann, A. F.; Tanaka, F.; Winnik, F. M. Temperature Response of Self-Assembled Micelles of Telechelic Hydrophobically Modified Poly(2-alkyl-2-oxazoline)s in Water. *Macromolecules* **2009**, *42*, 2204–2214.
- (94) Obeid, R.; Tanaka, F.; Winnik, F. M. Heat-Induced Phase Transition and Crystallization of Hydrophobically End-Capped Poly(2-isopropyl-2-oxazoline)s in Water. *Macromolecules* **2009**, *42*, 5818–5828.
- (95) Osváth, Z.; Iván, B. The Dependence of the Cloud Point, Clearing Point, and Hysteresis of Poly(N-isopropylacrylamide) on Experimental Conditions: The Need for Standardization of Thermoresponsive Transition Determinations. *Macromol. Chem. Phys.* **2017**, *218*, 1600470.
- (96) Tölle, F. J.; Fabritius, M.; Mülhaupt, R. Emulsifier-Free Graphene Dispersions with High Graphene Content for Printed Electronics and Freestanding Graphene Films. *Adv. Funct. Mater.* **2012**, *22*, 1136–1144.
- (97) Davis, R. A.; Madison, N. L. The Dow Chemical Company, Polyoxazoline-Modified, Paper Coating, US 4436789, 1984.
- (98) Ma, S.-H.; Rodriguez-Parada, J. N. E. I. du Pont de Nemours and Company, Block Copolymers of Oxazolines and Oxazines as Pigment Dispersants and their use in Ink Jet Inks, US 5854331, 1998.

