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Compartmentalized Ionic Systems

Hyperbranched Polymeric Ionic Liquids with Onion-like Topology as Transporters and Compartmentalized Systems**

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Among the rapidly expanding families of ionic liquids (ILs),[1] amphiphilic polymer electrolytes, containing IL moieties either in their backbone or side chains, offer attractive opportunities for designing novel nano- and mesophase materials, including unique compartmentalized systems. Polymeric ionic liquids (polyILs) combine attractive IL properties, such as negligible vapor pressure, low flammability, and ionic conductivity, with properties typical for polymers, particularly durability, low toxicity, as well as their potential for facile construction of highly multifunctional systems, combined with easy polymer processing. Dispersions, films, and moldings are fabricated without encountering leakage problems associated with low-molecular-weight ILs.[2] Envisioned applications range from electrolytes to solvents, sorbents, liquid separation media, catalyst scaffolds, dispersing agents, and compartmentalized fluids that can be used as nano- and microreactors for particle preparation and as transporters for shuttling a great variety of functional materials. An important research objective is to establish novel versatile synthetic routes, enabling easy scale-up and tuning of molecular architectures for polarity design and facile tailoring of multifunctional systems without the need for tedious multi-step syntheses and extensive purification. Moreover, to qualify as polymer additives, polyILs must be extremely robust and able to withstand the high shear forces and temperatures well above 200 °C during polymer melt compounding.

The recent focus of polyIL development has shifted towards controlled nanostructure formation. A great variety of nanostructured polyelectrolytes, mesoporous polymers, and nanoparticles have been prepared from IL monomers. Highly ordered polyIL nanoparticles with a tunable multilamellar or unilamellar vesicular inner structure, resembling liposomes, were formed by precipitation polymerization from water.[3] Moreover, the self-assembly of ionic block copolymers[4] and of ionic liquid-crystalline polymers[5] has been exploited to create polyIL nanostructures for applications in electronics. The integration of 3D-ordered macropores in polyILs has led to a new generation of smart materials as tunable photonic crystals, electro-optical switches, and functional surfaces.[6] PolyILs are known as very effective phase-transfer media that enable transport of carbon nanotubes (CNT) from aqueous into non-aqueous phase.[7] New polyIL/CNT nanohybrid materials were reported to be electroactive nanomaterials.[8] There is substantially less information available for highly branched polyILs as cascade macromolecules with micelle-like molecular architectures, which are very attractive on account of their considerably lower viscosity, shear- and pH-independent stable conformation, and multifunctionality compared to linear polyILs. Sophisticated dendritic polyILs were prepared by means of multistep syntheses[9] and assembled to form cylindrical nano-objects.[10] In view of the potential industrial applications, the preparation of hyperbranched polyILs ("hyperILs") is a much more viable synthetic route to highly branched polyILs. A prominent example is the commercially available hyperbranched polyethyleneimine, prepared by cationic aziridine polymerization, which has been functionalized in various ways to produce a great variety of multifunctional nanoparticles targeting different applications, for example, microbiocides.[11] Another facile route to hyperILs exploits ionene chemistry, for example, poly(*N*-alkylation) of lutidine derivatives.[12] Although such hyperbranched ionenes could be used as the core for micelle-like hyperILs, it is more attractive to create the inverse structures with IL moieties as the shell. By attaching IL groups to a flexible non-ionic highly branched polymer core, the functional groups in the shell are rendered more accessible. Softening temperatures and viscosities are markedly lowered, approaching those of ILs. The first example of this type of hyperIL was prepared by esterification of polyglycidol with ω-bromoacyl chlorides and alkylation of tertiary amines. The resulting hyperILs containing pyridinium or imidazolium groups in the shell were used as scaffolds for recyclable catalysts.[13] Similar hyperILs were prepared by tosylation of polyglycidol and substitution of the tosyl groups by 1-methylimidazole.[14]

Although it would be feasible to render such hyperILs amphiphilic by creating a hydrophobic outer shell, most of these hyperILs, including polyethyleneimines, have limited thermal and thermoxidative stability. This prompted us to design a novel hyperIL family with an onion-like topology containing hyperbranched poly(3-ethyl-3-hydroxymethyloxetane) (PEHO) as the core, an inner shell of covalently linked imidazolium cations with variable counteranions, and an outer shell of *n*-alkyl chains with variable chain length. In

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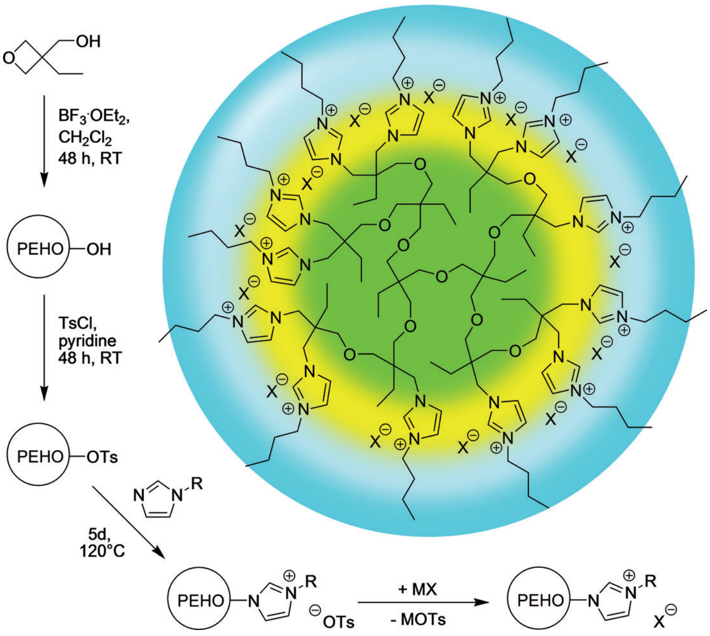
contrast to polyglycidol, which contains a mixture of primary and less-reactive secondary hydroxy groups, PEHO contains only primary hydroxy groups. Moreover, PEHO does not contain any hydrogen atoms in β position and consists exclusively of sterically shielded 1,3-diether groups. This is of particular interest for improving both the thermal and chemical stabilities in harsh environments, for example, for battery electrolytes, reaction media, and polymer melt dispersion processes.

As illustrated in Scheme 1, ring-opening cationic polymerization of 3-ethyl-3-hydroxymethyl oxetane, following procedures reported by Bednarek et al.,[15] produces hyperbranched polyoxetanes with number-average molar masses of 1800–2400 $g\,mol^{-1}$, polydispersities of 1.5–2, and degrees of branching of 50 % (detailed information is given in the Supporting Information). Subsequently, the hydroxy groups are tosylated and used to alkylate 1-(*n*-alkyl)imidazoles to produce hyperImOTs with methyl, butyl, dodecyl, and octadecyl *N*-substituted imidazolium cations and tosylate counteranions. As nearly quantitative conversion is achieved in both polymer analogous reactions, this method produces hyperILs with degrees of modification that generally lie well above 90 %. By means of very effective anion exchange reactions, the tosylate anions can be exchanged for a variety of other anions, which are listed in Table 1.

Table 1: HyperILs with different alkyl chains and anions.

CnhyperImX	Alkyl substituent	Anion[a]	T_g[b] [°C]	T_m[b] [°C]
C1hyperImOTs	methyl	OTs	25	–
C1hyperImOTf	methyl	OTf	14	–
C1hyperImBF$_4$	methyl	BF$_4$	16	–
C1hyperImPF$_6$	methyl	PF$_6$	41	–
C1hyperImNTf$_2$	methyl	NTf$_2$	−2	–
C1hyperImDBS	methyl	DBS	18	–
C4hyperImOTs	*n*-butyl	OTs	18	–
C4hyperImOTf	*n*-butyl	OTf	−3	–
C4hyperImBF$_4$	*n*-butyl	BF$_4$	0	–
C4hyperImPF$_6$	*n*-butyl	PF$_6$	19	–
C4hyperImNTf$_2$	*n*-butyl	NTf$_2$	−12	–
C12hyperImOTs	*n*-dodecyl	OTs	31	–
C18hyperImOTs	*n*-octadecyl	OTs	–	37

[a] OTs = tosylate, OTf = triflate, NTf$_2$ = bis(trifluoromethylsulfonyl)-imide, DBS = 4-dodecylbenzenesulfonate. [b] T_g = glass transition temperature, T_m = melting temperature.



Scheme 1. Routes to nanostructured hyperILs with onion-like topology and facile polarity design. Ts = *p*-toluenesulfonyl (tosyl).

Two strategies have been established for rendering water-soluble *N*-methyl-substituted C1hyperImOTs soluble in organic solvents. First, the *n*-alkyl chain length was increased to enhance the hydrophobicity of hyperImOTs, as reflected by the very low water solubility and excellent toluene solubility for octadecyl substitution (C18hyperImOTs). It should be noted that common polyelectrolytes, low-molecular-weight ionic surfactants,[16] and even the corresponding IL 1-methyl-3-octadecylimidazolium tosylate (C1C18ImOTs) exhibit very poor solubility in toluene. Second, the outer shell was rendered hydrophobic by exchanging the tosylate anion with hydrophobic anions, such as 4-dodecylbenzenesulfonate (DBS) to form C1hyperImDBS, which is the only methyl-substituted C1hyperIm that dissolves in chloroform. Variation of both the *n*-alkyl chain length and the type of counter-anion afford excellent control of polarity, which is readily matched with that of fluids and even polymers. A detailed overview of the influence of *n*-alkyl substitution and the anion of the hyperIL on the solubility in water and various organic solvents is given in the Supporting Information.

As is apparent from Table 1, the majority of the hyperIL tosylates are amorphous, with glass transition temperatures at around room temperature. Only C18hyperImOTs crystallizes at 37 °C, owing to crystallization of the octadecyl groups. This greatly facilitates handling of such solid materials in polymer processing. As a function of the substitution patterns, it is possible to lower the glass transition temperatures well below room temperature. According to the thermogravimetric analysis, no weight loss occurs upon heating to 300 °C. Consequently, all hyperImOTs are remarkably robust under polymer processing conditions and qualify for the envisioned application as a polymer additive.

The novel organophilic hyperIL tosylates (C18hyperImOTs), which contain an outer nonpolar octadecyl shell and an inner imidazolium shell, are highly effective phase-transfer agents and transporters. This is illustrated for the transport of the water-soluble food colorant Brilliant Blue FCF (E133), a blue triphenylmethane dye, into the organic phase of chloroform and polypropylene (PP). As illustrated in Figure 1, E133 is transferred completely from the aqueous phase to the chloroform phase immediately after adding C18hyperImOTs. Moreover, the dye can be solubilized and loaded in C18hyperIL. This dye-loaded C18hyperIL was

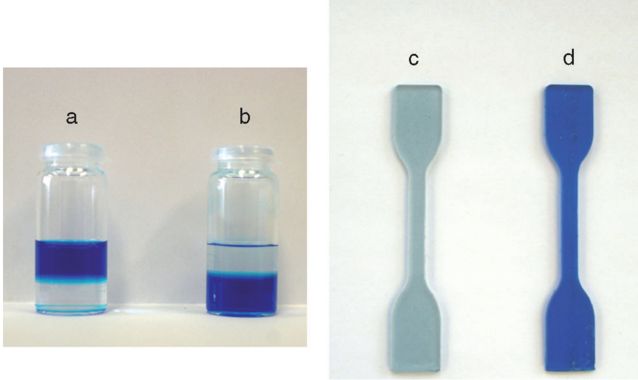


Figure 1. C18hyperImOTs as phase-transfer agent and transporter for the water-soluble dye E133 in chloroform/water (left; b) and PP (right; d). E133 without C18hyperImOTs in water/chloroform (a) and PP (c) is shown for comparison.

added to PP during melt extrusion at 200 °C. As shown in Figure 1, even a low content of 0.11 wt % E133 and 0.50 wt % C18hyperImOTs affords very effective brilliant blue coloration of PP. Without C18hyperImOTs, the hydrophilic dye is poorly dispersed in the nonpolar PP matrix. The dye transport using C18hyperIL does not occur by host–guest "molecular bottle"-type transportation, as proposed for dendritic amphiphiles. Clearly, the dye is too large to fit inside the C18hyperIL. Close inspection of the morphology of C18hyperImOTs/PP blends by means of scanning electron microscopy (SEM) reveals the presence of uniformly distributed C18hyperIL nanodroplets (Figure 2). The average nanodroplet size increases with increasing C18hyperImOTs content from 121 nm at 0.25 wt % to 163 nm at 2.0 wt % without affecting the shape and uniform distribution. In contrast, the less compatible *N*-butyl-substituted C4hyperImOTs affords a significantly larger diameter of 489 nm at 0.25 wt % and increases into the micrometer range with 1453 nm at 2.0 wt%, accompanied by broadening of the particle size distribution. For average particle sizes of C18hyperImOTs phases ranging from 120 to 160 nm, the color is formed exclusively by light absorption, whereas at much larger particle sizes in the micrometer range for C4hyperImOTs, scattering of light impairs light transmission. The C18hyperImOTs-analogous low-molecular-weight IL C1C18ImOTs, which was used for comparison, affords a very inhomogeneous dispersion of E133 in PP. More detailed information is given in the Supporting Information.

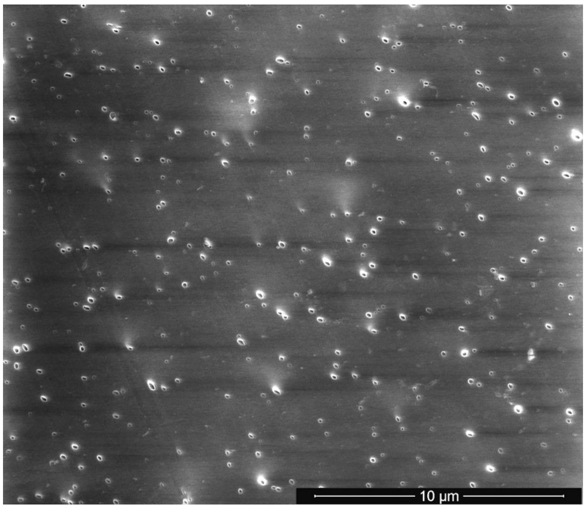


Figure 2. SEM image of PP melt-compounded with 2.0 wt % C18hyperImOTs.

C18hyperImOTs was also found to be a highly effective dispersing agent for many other (nano) materials, including graphenes. Functionalized graphene (FG), prepared by thermal reduction of graphite oxide, is readily dispersed in polar solvents by means of high-pressure homogenization, and forms mainly single FG nanosheets.[17] In the presence of C18hyperImOTs, stable FG dispersions are formed in nonpolar media, such as toluene, whereas dispersions of FG in pure toluene undergo rapid sedimentation. In fact, as can be seen in Figure 3, when C18hyperImOTs (10:1 by mass with respect to FG) is added to toluene, the graphene nanosheets are transferred from water into the organic phase. The ability of C18hyperImOTs to stabilize FG in organic media can be utilized to disperse graphene nanosheets in polystyrene (PS). When PS is dissolved in C18hyperIL-stabilized FG dispersions in toluene, melt-processable PS/graphene nanocomposites are formed. At 2.5 wt % graphene content, the addition of the same amount of C18hyperImOTs results in a 20-fold increase in the electrical conductivity with respect to the composite containing 2.5 wt % graphene and no hyperIL, namely from $3.6\times10^{-5}\,\mathrm{S\,cm^{-1}}$ to $7.7\times10^{-4}\,\mathrm{S\,cm^{-1}}$. As shown in Figure 3, very effective FG nanosheet dispersion and formation of conducting networks is achieved in the presence of C18hyperImOTs. Presumably, C18hyperImOTs assembles at the graphene surface and changes its conformation in an octopus-like fashion to produce ultrathin C18hyperIL coatings on FG nanosheets, thus accounting for very effective steric and electrostatic stabilization without preventing percolation.

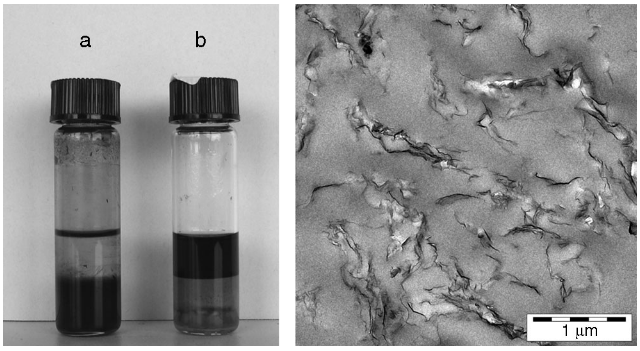


Figure 3. Left: FG in water/toluene after ultrasonification in the a) absence and b) presence of C18hyperImOTs. Right: TEM image of a melt compounded PS nanocomposite containing 2.5 wt % FG and 2.5 wt % C18hyperImOTs.

In conclusion, a novel facile synthetic route has been developed to produce new families of hyperbranched polymeric ionic liquids with an onion-like topology, containing a core of hyperbranched poly(1,3-diether), a polar inner imidazolium cation shell, and an nonpolar outer *n*-alkyl shell. High thermal stability up to 300 °C and extraordinary robustness enable these hyperILs to be used in reaction media, dispersion processes, and even in the harsh environment encountered in polymer melt compounding. It is possible to tailor the polarity as a function of the *n*-alkyl chain length and the type of counteranion, thus enabling highly effective dispersion of hyperILs in fluids and even PP melts. The average size of the dispersed C18hyperImOTs nanophases in PP varies between 120 and 160 nm and is governed by the hyperIL content. Such hyperIL nanophases represent attractive compartments for applications as nanoreactors and hosts for a variety of functional materials. The hyperILs are very effective phase-transfer systems, enabling extraction of nanomaterials from the aqueous phase and dispersion in a great variety of fluids and polymers. This attractive combination of robustness, phase transfer activity, and compartmentalization offers unique opportunities for designing novel functional materials and polymer nanocomposites for highly diversified applications in advanced materials and systems.

All experimental details, including analytical data, are given in the Supporting Information.

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