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Hierarchically Nanostructured Polyisobutylene-Based Ionic Liquids

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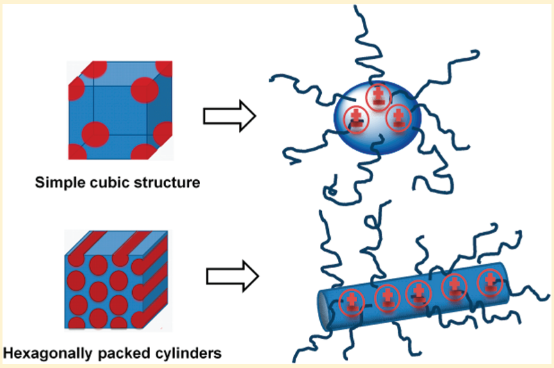
Supporting Information



ABSTRACT: A new type of highly temperature stable ionic liquid (IL) with strongly temperature dependent nanostructures is reported. The molecular design relies on the use of a liquid polymer with an ionic liquid headgroup, introducing liquid properties by both the polymeric and the ionic liquid (IL) headgroup. The IL polymers (poly(isobutylene)s) **3a**−**3c** (PIB-ILs) were prepared by a combination of living carbocationic polymerization (LCCP) and subsequent "click" chemistry for attachment of methylimidazolium (**3a**), pyrrolidinium (**3b**), and triethylammonium cations (**3c**). All three investigated PIB-ILs exhibited pronounced nanostructural organization at room temperature depending strongly on the nature of the anchored cation. Whereas the morphology of the imidazolium-based PIB-IL **3a** shows high thermal stability up to the decomposition temperature, order−order (OOT) and lattice disorder−order transitions (LDOT) characteristic for common ionomers could be observed in the case of pyrrolidinium **3b** and ammonium-based **3c** PIB-ILs. Control of flow behavior as well as adjustable relaxation times from the liquid to the viscoelastic regime can be adjusted by choice of the appropriate IL headgroup.

INTRODUCTION

Recently, polymeric ionic liquids (POILs),[1−6] carrying constrained cationic and anionic components of ionic liquids (ILs)[7−10] within the monomer units, have been developed as a new class of polymeric materials with widespread importance in science and technology. In contrast to (low molecular weight) ionic liquids (ILs), which are salts with arbitrary defined melting points below 100 °C, POILs are usually solids at room temperature, combining the unique properties of ILs with increased mechanical stability,[5] improved processability,[6,11] and more complex self-assembling ability of polymeric materials.[4,12,13] Similar to ILs, POILs generally consist of bulky nonsymmetrical organic cations (such as an imidazolium,[14] pyridinium,[15] ammonium,[16] or phosphonium cation[17]) together with various organic or inorganic anions, displaying unique properties such as extremely low vapor pressure, nonflammability, high polarity, high thermal stability, favorable electrochemical properties, and unorthodox and tunable miscibility behavior.[7,9] Therefore, POILs find widespread use, e.g., as polymer electrolytes for electrochemical devices,[5,18,19] sensors,[2] supports for catalysts,[20] polymeric dispersants,[21] CO_2 absorbing resins,[22] microwave absorbing materials,[23] or self-healing materials.[24] The latter application specifically requires detailed control over molecular relaxation and reorganization within POILs, as both their structure and dynamics can be controlled by the corresponding internal nanostructure.

Because of their self-assembling behavior,[25] both monomeric ILs as well as POILs display a subtle micro- and nanostructural organization resulting from the separate aggregation of apolar and ionic regions.[26,27] Since the pioneering work of Canongia Lopes and Pádua[26] numerous studies have confirmed the nanostructural organization of monomeric ILs.[27−29] Investigated ILs show first sharp diffraction peaks (FSDPs)[30] in X-ray[25,29] or neutron diffraction structure functions,[27a,31] which indicates the presence of intermediate range order (~5−10 Å). On the one hand, such intermediate range order can originate from either charge ordering (similar to the classical molten salts[30]) or, on the other hand, from the interdigitation of "bilayered" alkyl chains. Because of their nanostructural organization and hence their extraordinary miscibility behavior, ILs can be used as entropic drivers (the "IL effect") for the preparation of well-defined nanoscale structures with extended order, either in the bulk phase or at the gas/vacuum interface.[32] Because of their structural similarity to classical ionomers, POILs may form ionic aggregates, so-called "multiplets". Such ionic clustering and self-aggregation of POILs can lead to an increase of ionic conductivity of POILs, making them suitable for applications as valuable polyelectrolytes.[5] Furthermore,

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several investigators have reported that POILs containing monomers with mesogen character tend to self-assemble into various liquid-crystalline phases with different organization.[4−6,33] Thus, a pronounced case of liquid-crystalline order was achieved by Ohno et al.,[34] who synthesized mesogen POIL containing tris(alkoxy)phenyl groups attached to acryloyl groups. Structural changes of IL monomer led to the formation of columnar phases which produced oriented one-dimensional ion conductive channels; thus, subsequent photopolymerization of ionic liquid film resulted in a well-ordered, highly conductive, liquid-crystalline POILs. The same working group further increased the conductivity of POIL materials via design of thermotropic bicontinuous cubic liquid-crystalline POILs based on a polymerizable ammonium moiety complexed with a lithium salt and thus obtained lithium ion-conductive solid polymeric films having 3D interconnected ionic channels.[35] A different approach for increasing the conductivity of POIL electrolytes is the specific design of ionic liquid block copolymers.[12,36,37] Thus, the use of microphase separating block copolymers displays numerous advantages such as a higher level of ionic conductivity by lowering the glass transition temperatures (T_g) or the increase of mechanical properties by selective cross-linking of ionic liquid monomers in one phase of an POIL.[12] Weber et al.[37] have shown that microphase separation of ionic liquid block copolymers strongly influences their conductivity. Well-structured lamellar microphase morphology of styrene−ionic liquid copolymers led to a 10-fold increase in conductivity as compared to copolymers with poorly organized hexagonal morphologies. Thus, control of the nanostructural organization of POILs is the key point in their application in many of the aforementioned uses, particularly when relaxation and flow behavior dominate major structural properties.

In this paper we for the first time report on a nanostructured IL with new features based on the high fluidity of a polymeric backbone in addition to the presence of ionic moiety similar to ionic liquids (ILs). The basic idea is the use of a polymer with an extremely low glass transition temperature (T_g) so as to introduce liquid properties already into the native polymer of the POIL. Additionally, the extremely large difference between the hydrophobic polymer and the attached IL end groups (affixed to one end group of the polymer) can induce significant nanostructural order within the then polymeric ionic liquid. Until now predominantly ionic liquid cations have been incorporated into polymer backbones obtained from vinyl,[1,38] styrenic,[22a] methacrylic,[39] ethylene glycol,[40] vinyl ether,[41] and norbornene monomers.[22c,39,42] As only few polymers display such liquid properties in themselves we have chosen poly(isobutylene) as polymer with such highly liquid properties. The use of poly(isobutylene) as biocompatible polymer with high hydrophobicity and chain mobility (as exemplified by its low glass transition temperature, $T_g = -80$ °C) has found increased use in fields of supramolecular polymer science,[43,44] amphiphilic conetworks,[14,45] and self-healing materials.[46] In contrast to the previously predominantly used radical polymerization, we have applied living carbocationic polymerization (LCCP) for the preparation of POILs, thus allowing for chain-length control and therefore control of the nanostructure's dimension.[47] The projected PIB-ILs were prepared by combining LCCP with a microwave-assisted azide/alkyne "click" reaction between an azido telechelic PIB and the corresponding alkyne containing IL headgroup. As significant phase separation effects were expected, detailed small-angle X-ray scattering (SAXS) investigations as well as rheology studies have been conducted to reveal structure and relaxation behavior of the prepared POILs.

■ EXPERIMENTAL SECTION

Materials. All materials were obtained from Sigma-Aldrich and used without further purification if not mentioned otherwise. 1-Methylimidazole, 1-methylpyrrolidine, and *N,N,N*-triethylamine was distilled over CaH_2 prior to use. Dichloromethane and toluene were predried over $CaCl_2$ and freshly distilled over CaH_2, sodium, and benzophenone.

Instrumentation. *^{1}H NMR and ^{13}C NMR spectra* were recorded on a Varian Gemini 2000 FT-NMR spectrometer (400 MHz) and a Varian Unity Inova 500 (500 MHz). MestRec-C software (version 4.9.9.6) was used for data interpretation. Deuterated chloroform ($CDCl_3$) and dimethyl sulfoxide (DMSO-d_6) were used as solvents. All chemical shifts (δ) are reported in parts per million (ppm) relative to tetramethylsilane (TMS) and referenced to the significant solvent signals. Coupling constants (J) are given in hertz (Hz).

Gel permeation chromatography (GPC) analysis was performed on a Viscotek GPCmax VE2001 system combined with a Viscotek TDA302 (triple detector array) using polyisobutylene standards and THF as solvent. PIB standards with a molecular weight of 340, 1650, 7970, 26 300, 61 800, and 87 600 g/mol were used for calibration. Data were analyzed with the OmniSec (4.5.6) software. The polystyrene−divinylbenzene-based column set consists of a H_{HR}-HGuard-17,369 precolumn followed by a GMH_{HR}-N-Mixed Bed 18055 (1000 to 4×10^5 Da) and a $G2500H_{HR}$-17,354 (100 to 2×10^4 Da) column. Both the detector and the column temperature was set to 35 °C, with flow rate of 1 mL min^{-1}, and injection volume of 100 μL.

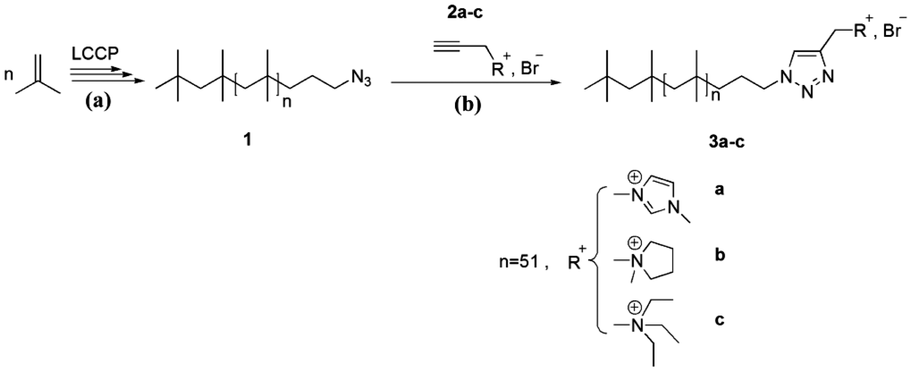
Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF-MS) experiments were performed on a Bruker Autoflex III system operating in reflection and linear modes. The data evaluation was carried out on flexAnalysis software (version 3.0). Ions were formed by laser desorption (smart beam laser at 355, 532, 808, and 1064 ± 6.5 nm; 3 ns pulse width; up to 2500 Hz repetition rate), accelerated by a voltage of 20 kV, and detected as positive ions. The matrix solution was prepared by dissolving 1,8,9-anthracenetriol (dithranol) in THF at a concentration of 20 mg mL^{-1}. Polymers were dissolved in THF at a concentration of 10 mg mL^{-1}; salts sodium trifluoroacetate (NaTFA) and potassium chloride (KCl) were dissolved at a concentration of 10 mg mL^{-1} in THF. Solutions of the matrix, the polymer, and the salt were mixed in a volume ratio of 100:10:1, and 1 mL of each mixture was spotted on the MALDI-target plate. Baseline subtraction and smoothing of the recorded spectra were performed using a three point Savitzky−Golay algorithm. The instrument was externally calibrated with poly(ethylene glycol) standards (M_w = 2000 and 4200 g mol^{-1}) applying a quadratic calibration method with an error of 1−2 ppm.

Thermogravimetric analysis (TGA) was conducted on a Mettler Toledo (DSC-H22) instrument. The sample was heated in a Pt pan, under a nitrogen atmosphere, over a temperature range 25−800 °C, with a heating rate of 10 °C min^{-1}.

Differential scanning calorimetry (DSC) was conducted on Perkin-Elmer Pyris Diamond instrument. The glass transition temperatures were determined by cooling the samples at −90 °C and then heating up to 150 °C, both at rate 10 °C min^{-1}. The glass transition temperature is taken as a midpoint of a small heat capacity change upon heating from amorphous glass state to a liquid state.

Small-angle X-ray scattering (SAXS) experiments were carried out under vacuum with a rotating copper-anode X-ray generator (Nanostar, Bruker AXS), Cu Kα radiation (wavelength 0.1542 nm) monochromatized and collimated from crossed Goebel mirrors, and a 2-D position sensitive detector (Vantec 2000). For the *in situ* SAXS measurement a specially designed X-ray transparent furnace was developed, which allows stepwise heating of the samples from room temperature to 550 °C with an accuracy of ±0.5 °C. The samples were placed either in a quartz glass capillary with a diameter of 1.5 mm and a wall thickness of 10 μm (from Hilgenberg, Germany) or between

Scheme 1. Synthetic Route toward Nonsymmetric Ionic Liquid-Functionalized PIBs 3a–3c[a]



[a](a) Living carbocationic polymerization (LCCP):[47c] (i) synthesis of allyl-functionalized PIB; (ii) synthesis of hydroxyl-functionalized PIB; (iii) synthesis of bromide functionalized PIB; (iv) synthesis of azide functionalized PIB (**1**).[48] (b) Azide/alkyne "click" reaction. Reaction conditions are given in the Experimental Section.

commercial aluminum foils. The samples were heated up to the desired temperature, kept at this temperature for 5 min to ensure thermal equilibrium, and measured for 15–30 min depending on the scattering intensity of the respective samples. With a sample-to-detector distance of 108 cm an accessible q-range from 0.1 to 2.8 nm^{-1} was obtained. The SAXS patterns were radially averaged in order to obtain the scattering intensities $I(q)$, where $q = (4\pi/\lambda)\sin\theta$ is the scattering vector and 2θ the scattering angle. The d_{100} peak (the strongest Bragg reflection) was fitted with a Lorentzian function. This results in numerical values for the peak position (corresponding to the distance of the crystalline units in real space) and the peak breadth (proportional to the domain size).

Rheological measurements were performed on an Anton Paar MCR 101-DSO rheometer using parallel plates (diameter 8 mm). The sample temperature was regulated by thermoelectric cooling/heating in a Peltier chamber under a dry oxygen atmosphere. Frequency sweep measurements were performed within the LVE (if not mentioned otherwise). Temperature sweep measurements were performed with a heating rate of 1 °C/min at ω = 10 rad/s. Before each measurement the sample was annealed for 30 min.

Synthesis. Allyl telechelic PIB was synthesized via living carbocationic polymerization (LCCP) based on procedure known from the literature.[47c] Isobutylene was polymerized via LCCP in the presence of 2-chloro-2,4,4-trimethylpentane (TMPCl) and $TiCl_4$ as initiator and co-initiator (for details see Supporting Information S2). Quenching of the polymerization with allyltrimethylsilane (ATMS) resulted in allyl-functionalized PIB. Azido telechelic PIB (M_n = 2920 g/mol; M_w/M_n= 1.14) was synthesized via further modification of allyl telechelic PIB following procedure described by Binder et al.[48] The allyl moiety was converted into the hydroxyl group by hydroboration of the double bond using 9-borabicyclo[3.3.1]nonane (9-BBN) and subsequent oxidation with *m*-chloroperoxybenzoic acid (*m*-CPBA). Bromination of the obtained PIB was accomplished in the presence of carbon tetrabromide and triphenylphosphine with a yield of 99%. Bromo-functionalized PIB was converted to the azide using tetrabutylammonium fluoride (TBAF) and azidotrimethylsilane (TMSA) with a yield of 89%. The pure product PIB (**1**) was characterized using NMR and GPC (see Supporting Information, S2–S4).

General Procedure for the Synthesis of Compounds 2a–2c. To a solution of propargyl bromide (1 equiv) in dry toluene corresponding amine (1.2 equiv) was added dropwise. The reaction mixture was stirred at 50 °C. Then, the solvent was removed from reaction mixture under reduced pressure, and the obtained crude product was washed with ethyl acetate.

*1-Propargyl-3-methylimidazolium Bromide (**2a**).* 1-Methylimidazole (1.02 g, 12.43 mmol) was added dropwise to a solution of propargyl bromide (1.23 g, 10.36 mmol) in dry toluene (25 mL). After stirring the reaction mixture for 20 h, the obtained product was purified by washing with ethyl acetate. Yield of (**2a**): 84% (1.74 g, 8.70 mmol), as a brownish powder. ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 9.29 (s, 1H), 7.81 (t, J = 1.8, ^{1}H), 7.78 (t, J = 1.8, 1H), 5.24 (d, J = 2.56, 2H), 3.89 (s, 3H), 3.84 (t, J = 2.6, 1H). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ (ppm): 136.2, 123.7, 121.8, 78.8, 75.9, 38.4, 35.8.

*1-Propargyl-1-methylpyrrolidinium Bromide (**2b**).* After addition of 1-methylpyrrolidine (1.06 g, 12.43 mmol) to a solution of propargyl bromide (1.23 g, 10.36 mmol) in dry toluene (25 mL), the reaction mixture was stirred for 24 h. After purification the product was obtained as slightly yellow solid with yield of 88% (1.69 g, 8.28 mmol). ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 4.50 (d, J = 2.5, 1H), 4.01 (dt, J = 2.45, 0.74, 2H), 3.63–3.49 (m, 4H), 3.15 (s, 3H), 2.18–2.05 (m, 4H). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ (ppm): 81.6, 72.9, 63.0, 52.3, 48.7, 21.4.

*N-Propargyl-N,N,N-triethylammonium Bromide (**2c**).* According to the general procedure *N,N,N*-triethylamine (1.25 g, 12.72 mmol) was added to a solution of propargyl bromide (1.23 g, 10.36 mmol) in dry toluene (20 mL), and it was stirred for 16 h. The purification of the product resulted in a white solid with 82% (1.87 g, 8.49 mmol) yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 4.34 (d, J = 2.56, 2H), 4.01 (t, J = 2.53, 1H), 3.30 (q, J = 7.2, 6H), 1.23 (t, J = 7.2, 9H). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ (ppm): 82.1, 71.9, 52.9, 30.5, 7.3.

General Procedure for the Synthesis of PIBs Containing an Ionic Moiety via "Click" Reaction (3a–3c). Azido telechelic PIB (**1**, 1 equiv, M_n = 2920 g/mol; M_w/M_n = 1.14) and the corresponding ionic liquid containing alkyne (2 equiv) were dissolved in a solvent mixture of toluene/water/isopropanol (2:1:1) and placed in a microwave vial. After addition of *N,N*-diisopropylethylamine (DIPEA) (10 equiv), the vial was closed with a septum and the solution was purged with nitrogen for 30 min. Then copper(I) iodide (CuI) (0.2 equiv) was added to the mixture, and the solution was again purged with nitrogen for more than 30 min. Subsequently, the vial was sealed, placed in a microwave reactor, and irradiated under 70–80 W for several hours. After termination of the irradiation, the organic phase was separated and washed with water (3 times). The crude product which was obtained after removal of the solvents was purified by column chromatography (stationary phase: SiO_2; eluent: chloroform) to eliminate the unreacted azido-telechelic PIB. Then the eluent was changed to chloroform/methanol (15:1), and the fraction with R_f = 0.2 was collected. After evaporating of the solvent, the residue was dissolved in a small amount of chloroform and precipitated into methanol. The precipitate was collected and dried under high vacuum.

*3-Methyl-1-imidazolium Telechelic PIB (**3a**).* 3-Propargyl-1-methylimidazolium bromide (**2a**, 12.09 mg, 0.06 mmol), azido-telechelic PIB (100 mg, 0.03 mmol), CuI (10 mg); irradiation conditions: 80 W, 85–90 °C, 17 h. Yield of **3a**: 58% (67 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 10.70 (s, 1H) 8.47 (s, 1H), 7.63 (s, 1H), 7.09 (s, 1H), 5.86 (s, 2H), 4.29 (t, 2H, J = 7.5), 3.98 (s, 3H), 1.94–1.83 (m,

Table 1. Reaction Conditions, Molecular Weight Data, Decomposition ($T_{d,onset}$), and Glass Transition Temperature (T_g) of the PIB Ionic Liquids 3a−3c

entry	POIL	catalyst	reaction condition[a]	conv[b] (%)	yield (%)	$M_{n(NMR)}$ (g/mol)	$M_{n(GPC)}$ (g/mol)	PDI	$T_{d,onset}$ (°C)	T_g (°C)
1	**3a**	CuI (0.03 mmol)	75 W/75 °C/16 h	86	58	3256	3241	1.2	310	−70.6
2	**3b**	CuI (0.03 mmol)	75 W/75 °C/16 h	81	52	3259	3207	1.2	398	−71.4
3	**3c**	CuI (0.03 mmol)	70 W/75 °C/16 h	74	48	3334	4700	1.2	352	−70.9

[a] Reaction condition is reported based on irradiation power (W), reaction temperature (°C), and duration (h). [b] Conversions were determined by ^{1}H NMR, comparing integration ratio of cationic moiety signals to the rest of the polymer chain, especially unreacted $-CH_2-N_3$.

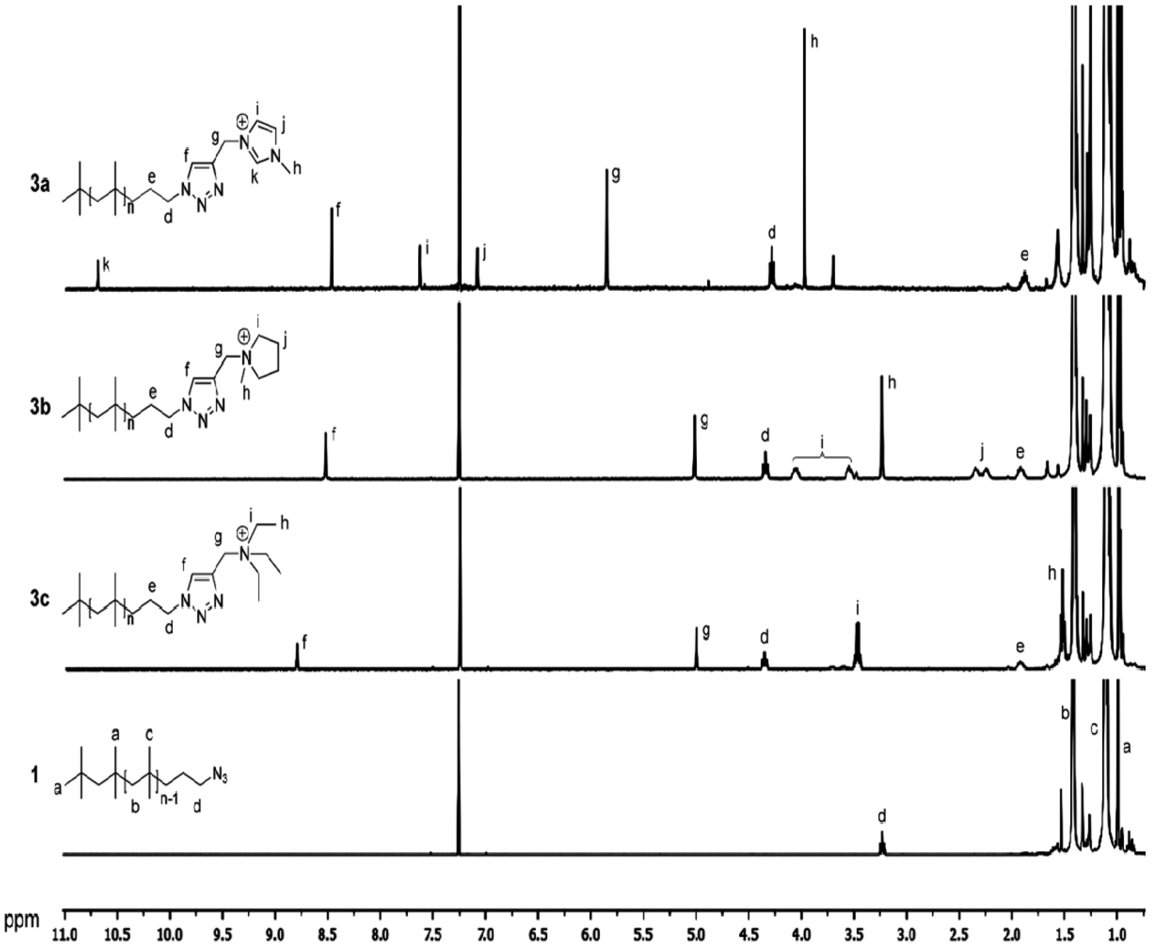


Figure 1. ^{1}H NMR spectra of the PIB-ILs (**3a**−**3c**) and the starting material (azido-telechelic PIB (**1**)).

2H), 1.47−1.36 (m, 104H), 1.16−1.05 (m, 312H), 1.00−0.97 (m, 15H). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ (ppm): 139.8, 137.8, 125.2, 122.7, 122.5, 59.5, 58.8, 58.2, 55.9, 51.5, 44.4, 42.2, 38.1, 36.6, 34.8, 32.6, 32.5, 31.2, 30.8, 29.1, 25.5.

*1-Methylpyrrolidinum Telechelic PIB (**3b**).* 1-Propargyl-1-methylpyrrolidinum bromide (**2b**, 12.24 mg, 0.06), azido-telechelic PIB (100 mg, 0.03 mmol), CuI (8 mg); irradiation conditions: 80 W, 85−90 °C, 17 h. Yield of **3b**: 52% (56 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.52 (s, 1H), 5.02 (s, 2H), 4.34 (t, 2H, J = 7.5), 4.11−4.00 (m, 2H), 3.60- 3.50 (m, 2H), 3.24 (s, 3H), 2.40−2.18 (m, 4H), 1.98−1.81 (m, 2H), 1.47−1.36 (m, 104H), 1.16−1.05 (m, 312H), 1.00−0.97 (m, 15H). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ (ppm): 128.4, 63.9, 59.5, 58.8, 58.2, 57.6, 55.9, 51.6, 49.4, 42.2, 38.2, 37.8, 34.8, 32.6, 32.4, 31.2, 30.8, 29.2, 25.5, 21.9.

*N,N,N-Triethylammonium Telechelic PIB (**3c**).* *N*-Propargyl-*N,N,N*-triethylammonium (**2c**, 13.20, 0.06 mmol), azido-telechelic PIB (100 mg, 0.03 mmol), CuI (10 mg); irradiation conditions: 80 W, 85−90 °C, 17 h. Yield of **3c**: 48% (51 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.81 (s, 1H), 5.01 (s, 2H), 4.36 (t, 2H, J = 7.5), 3.48 (q, 6H, J = 7.3), 1.98−1.88 (m, 2H), 1.52 (t, 9H, J = 7.2), 1.45−1.36 (m, 102H), 1.15−1.05 (m, 306H), 0.99−0.95 (m, 15H). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ (ppm): 135.1, 128.4, 59.5, 58.8, 58.2, 55.9, 53.5, 51.9, 51.5, 42.1, 38.2, 37.9, 37.8, 34.8, 32.6, 32.4, 31.2, 30.8, 29.1, 25.4, 7.8.

■ RESULTS AND DISCUSSION

Synthesis of Polyisobutylene-Based Ionic Liquids (PIB-ILs). In general, POILs can be prepared either via direct polymerization of IL monomers or via chemical modification of existing polymers. Both strategies often involve polymerization techniques such as conventional[6] and living radical polymerization (ATRP[49] and RAFT[41,50]), ring-opening metathesis polymerization,[51] or chemical and electrochemical oxidative polymerization.[52] Our synthetic route for the preparation of polyisobutylene-based ionic liquids (PIB-ILs) follows the use of living carbocationic polymerization (LCCP) as presented in Scheme 1. It should be noted that for end-group modification of polyisobutylene with strongly polar moieties (as the IL groups are), only a few qualitatively useful reactions are

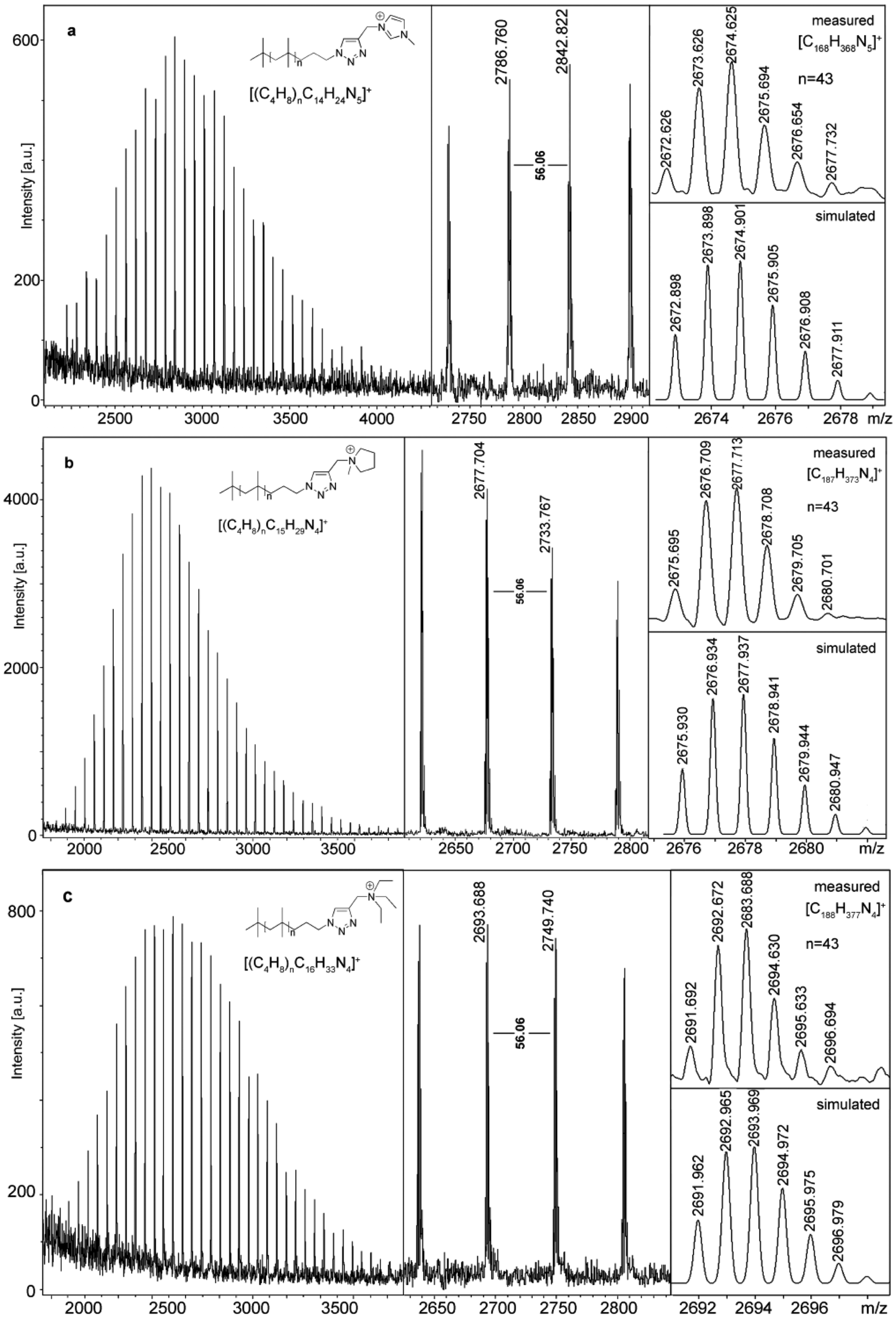


Figure 2. MALDI-TOF mass spectra of the PIB-ILs (**3a**–**3c**): (a) Compound **3a**, inset: simulation for $[C_{186}H_{368}N_5]^+$ with 43 units of isobutylene. (b) Compound **3b**, inset: simulation for $[C_{187}H_{373}N_4]^+$ with 43 units of isobutylene. (c) Compound **3c**, inset: simulation for $[C_{188}H_{377}N_4]^+$ with 43 units of isobutylene.

known.[47c,e,f,53] The azide/alkyne "click" reaction to attach these highly polar moieties therefore represents the best method to achieve this goal.

Allyl-functionalized telechelic PIB was synthesized via living carbocationic polymerization (LCCP) using 2-chloro-2,4,4-trimethylpentane (TMPCl) as described elsewere.[47c] Transformation of the allyl-functionalized PIB to the azido-telechelic PIB (**1**) was conducted according to the method developed earlier by us,[48] yielding PIB$_n$-N$_3$ (M_n = 2920 g/mol; M_w/M_n = 1.14) in 90% overall yield. Subsequent microwave-assisted azide/alkyne "click" reaction between PIB$_n$-N$_3$ (**1**) and the alkyne containing ILs (**2a**–**2c**) with a copper(I) catalyst resulted in the desired ionic-liquid-functionalized PIB. Upon testing different Cu(I) catalysts (Cu(I) iodide, Cu(I) bromide and tris(triphenylphosphine)copper(I) bromide, [Cu(PPh$_3$)$_3$Br]), only [Cu(PPh$_3$)$_3$Br] and CuI proved conversions between 30 and 86% (see Table 1 and Supporting Information, Table S1). Best results were achieved using copper(I) iodide under microwave irradiation conditions, with a strong influence of the microwave-irradiation power on the obtained yields. Although the increase of irradiation power often leads to higher conversions, the formation of side products via Hofmann elimination could be observed. Lowering of the irradiation power also resulted in a decline of conversion. Therefore, optimization of microwave irradiation conditions for all three compounds led to a good conversion of the azide (conversions 74–86%, see Table 1).

Characterization of the PIB-ILs. The structure of the prepared PIB- ionic liquids (**3a**–**3c**) was confirmed via ^{1}H and ^{13}C NMR spectroscopy (see Figure 1 and Supporting Information, S8–S10) as well as MALDI-TOF-MS measurements (see Figure 2). Chromatographic and NMR spectroscopic data are shown in Table 1, revealing a good agreement between the $M_{n(GPC)}$ and $M_{n(NMR)}$ data and hence indicating a complete end-group functionalization. After purification by column chromatography it was possible to obtain pure compounds **3a**–**3c**, thus removing eventually present impurities or incompletely functionalized polymers.

All compounds showed the expected resonances in NMR spectroscopy as well as the expected absolute molecular weights in the respective mass spectra. The successful "click" reaction was confirmed by the proton shift of the terminal CH_2– group of poly(isobutylene) chain (triplet d in Figure 1) from 3.21 ppm for azido telechelic PIB (**1**) to 4.29–4.36 ppm in the case of PIB-ILs **3a**–**3c** and the appearance of a resonance of the triazole ring in the range between 8.47 and 8.81 ppm (signal f in Figure 1). Furthermore, no signals originating from the unreacted azido-telechelic PIB could be observed in ^{1}H NMR spectra of the PIB-ILs **3a**–**3c** (see Figure 1). MALDI-TOF-MS spectra of synthesized polymeric ionic liquids are shown in Figure 2. All three spectra show one main series with 56 Da differences which corresponds to the mass of one repeating unit. The observed signals in all three cases can be simply assigned to PIB containing cationic moiety. According to Figure 2a, the signal appearing at 2672.626 Da can be assigned to PIB containing imidazolium cation with chemical formula of $[C_{186}H_{368}N_5]^+$ with $n = 43$ units of isobutylene. In Figure 2b, the signal at 2675.695 Da can be represented by $[C_{187}H_{373}N_4]^+$, and the PIB-containing ammonium moiety can be identified by its signal at 2691.692 Da, which is assigned for $[C_{188}H_{377}N_4]^+$ (Figure 2c). The simulated isotopic pattern of the synthesized polymeric ionic liquids for repeating unit of $n = 43$ shows an excellent match with the pattern of the observed signals in MALDI spectra which confirms the formation of expected structures.

All three investigated PIB-ILs exhibit glass transition temperatures in the range −70.6 to −71.4 °C (see Table 1), indicating the increase of T_g compared to the PIB (−80 °C) due to the presence of the ionic moieties.

As thermal stability is an important selection criterion for a high-temperature use, thermogravimetric analysis of the PIB-ILs was performed (see Figure 3), indicating only one decomposition step with the onset decomposition temperature in the range between 310 and 398 °C (see Table 1). As expected, the thermal stability of the presented PIB-ILs **3a**–**3c** is higher compared to the classical monomeric ionic liquids[54] and lies in the range of other previously investigated POILs.[5]

SAXS Measurements of PIB Ionic Liquids. As already reported in the literature, the morphology of some POILs exhibits a behavior similar to those described for ionomers.[4,5,12] As the structure of prepared polyisobutylene-based POILs shows distinct resemblance to the structure of classical ionomers, composed of a polymeric tail and ionic groups at the end positions, similar microphase separation may be expected. According to the multiplet-cluster model for the description of morphology of random ionomers postulated by Eisenberg et al.,[55,56] ion pairs aggregate to structures named "multiplets". Electrostatic interactions between "multiplets" favor their agglomeration to form phase-separated regions (clusters), whereas the elastic forces of free polymer chains are opposing cluster formation. Additionally, the mobility of the polymer chain in the immediate vicinity of the "multiplets" is strongly restricted, resulting in a region of restricted mobility surrounding each multiplet. As the ion content increases the average distance between "multiplets" decreases, resulting in overlap of regions with restricted mobility of polymer chains. After a certain critical ion concentration is reached cluster formation becomes more energetically favorable, therefore resulting in the formation of aggregates. As a consequence, the presence of clusters leads to the existence of large regions of material with restricted mobility. Since the stability of microphase separation is strongly temperature dependent, a loss of the internal structure at higher temperature due to the weakening of electrostatic interactions is expected. However, after cooling and distinct relaxation time re-establishment of the internal structure can be observed, indicative of the self-healing properties of such ionomers.[24c,56,57]

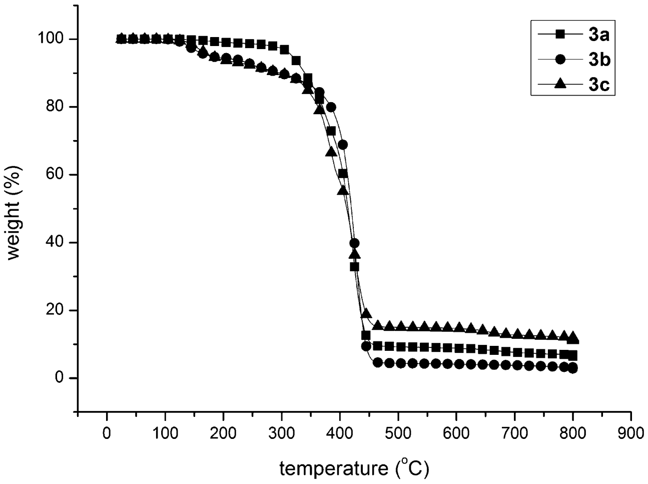


Figure 3. Thermogravimetric analysis (TGA) of the PIB-ILs (**3a**–**3c**) at a heating rate of 10 °C min^{-1} under a nitrogen atmosphere.

In order to investigate the morphologies of prepared PIB-ILs, SAXS measurements were conducted (see Figures 4–6 and Supporting Information, S11–S12).

The observed Bragg reflections in the SAXS patterns can be interpreted as the formation of ordered clusters in POILs, predominantly representing intracluster spacings. Both **3a** and **3b** show five reflections, which could be attributed to a simple cubic lattice with a *d*-spacing (the distance of the units) of 7.6 and 6.9 nm for **3a** and **3b**, respectively. The ammonium-containing compound (**3c**) exhibits four reflections, clearly indicating an arrangement in the form of 2-D hexagonally packed cylinders with a *d*-spacing of 7.95 nm (see also Supporting Information, S11–S12). Thus, it can be assumed that PIB-ILs **3a** and **3b** form "multiplets" clustered in a micellar fashion at room temperature, while **3c** assembles as a cylindrical phase (see Figure 4).

In the next step, PIB-IL samples were also subjected to variable-temperature *in situ* SAXS to identify any disorder–order or order–order transition in the range 25–300 °C and to further understand the relaxation of structural changes. As can be seen in Figure 5b, compound **3b** shows a lattice disorder–

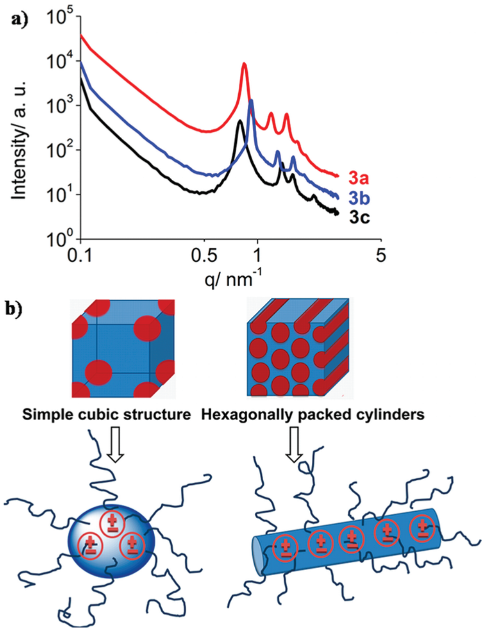


Figure 4. (a) SAXS profiles of PIB-based ILs (**3a**−**3c**) at room temperature. Each curve is shifted in the intensity axis (y-axis) for clarity. (b) Schematic illustration of simple cubic and hexagonally packed cylindrical nanostructure formed by PIB-ILs. The "multiplets" are representing the inner phase of the structures.

order transition (LDOT) at 80 °C, indicated by the broadening of the first and the gradual disappearance of higher order peaks. This resembles the phase disordering process of micelles during heating, which was distinguished by Han et al.[58] from the demicellation/micellation transition (DMT) at still higher temperatures. The increase of temperature leads to a gradual weakening of the electrostatic forces between ionic clusters. After reaching the transition temperature, loss of the internal structure due to the electrostatic interaction can be observed (loss of all four higher order scattering maxima). Breaking of the ionic clusters between "multiplets" subsequently leads to an increase in mobility of polymer chains, resulting in a shift and broadness of the main peak. After cooling to room temperature and waiting for a relaxation time of 132 h a clear re-establishment of the nanostructure can be observed (see Figure 5b). The relaxation time of **3b** is comparable with the results obtained by Varley et al.[24c] for classical ionomers with relaxations times up to 7 days.

Additionally, the obtained data were fitted with Lorentzian function, and the variation of the main peak position as well as its half-width at half-maximum (hwhm) with temperature are plotted. The variation of the main peak position with temperature and after relaxation is presented in Figure 6 (see also Supporting Information, S13−S14), indicating a continuous shift of the main peak to larger q values with increasing temperature, which corresponds to the formation of smaller structures. After a relaxation time of 132 h the original nanostructure is almost completely restored, which is in accordance with the observations of Eisenberg[56,57d] and others[57] regarding the thermal behavior of classical ionomers. Therefore, the investigated ionic liquid **3b** exhibits self-healing characteristic for ionomers.

However, a markedly different behavior was observed in the case of PIB-IL **3a** (see Figure 5a). The internal cubic nanostructure of the imidazolium-based IL **3a** is stable even at higher temperatures. Only a partial loss of the nanostructure can be observed at 275 °C (loss of the smallest two peaks). The strong electrostatic interactions between imidazolium cations, probably combined with pronounced $\pi-\pi$ stacking between adjacent imidazolium rings, lead to the significantly stable internal structure. In the range between 275 and 300 °C the order−disorder transition can be observed, followed by the extreme broadening of the main peak. However, this loss of internal structure is probably due to the thermal decomposition of the compound, rather than due to the thermal transition of nanostructural organization. Furthermore, even after 1 week no structural relaxation could be observed, suggesting the irreversible thermal decomposition of the starting compound at 300 °C, which is in accordance with the thermal stability data obtained with TGA (see Figure 3).

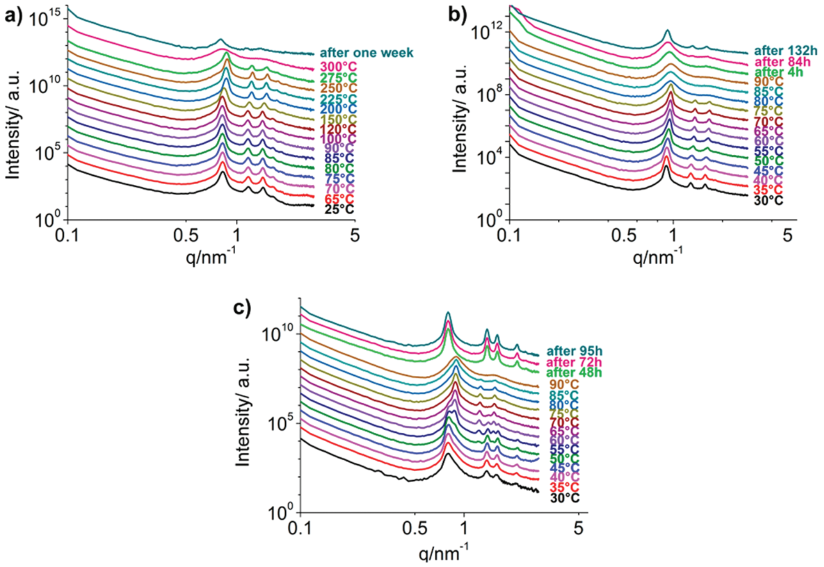


Figure 5. SAXS profiles of the prepared PIB-containing ionic liquids at different temperatures and after relaxation: (a) **3a**; (b) **3b**; (c) **3c**. Each curve is shifted in the intensity axis (y-axis) for clarity.

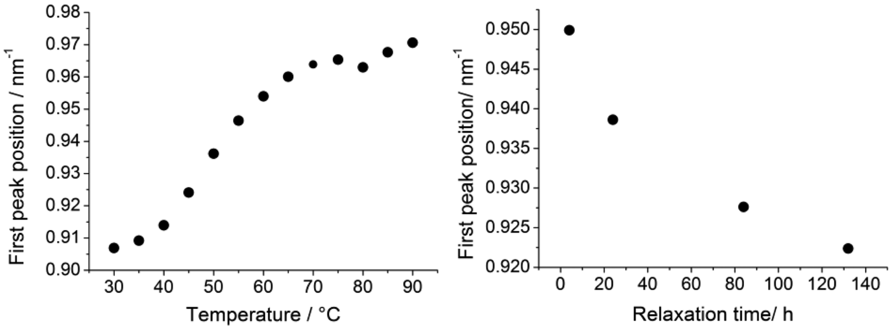


Figure 6. Variation of the main peak position with temperature (left), after heating to 90 °C, and relaxation at room temperature (right) obtained for **3b** via temperature-dependent SAXS measurements.

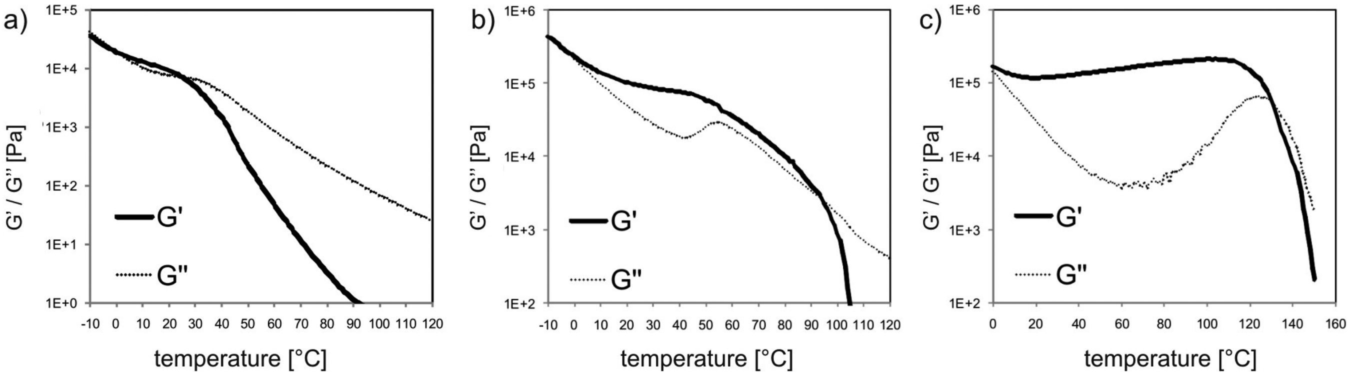


Figure 7. Temperature-sweep measurements for PIB-ILs: (a) for sample **3b**, (b) for sample **3c**, and (c) for sample **3a**. The heating rate was 1 °C/min at ω = 10 rad/s.

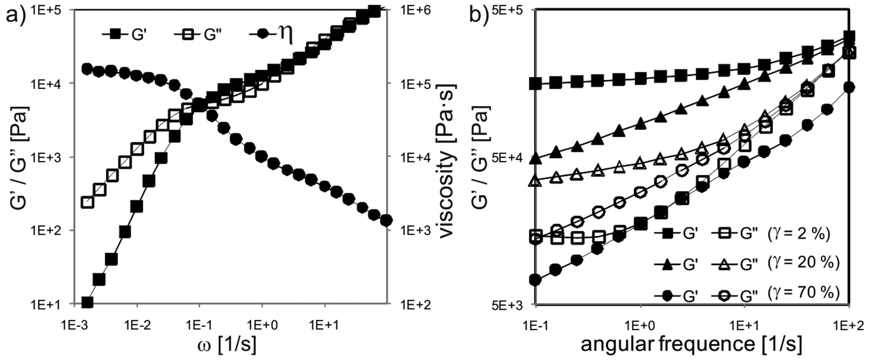


Figure 8. (a) Frequency-sweep measurement of **3b** at 20 °C (γ = 2%). (b) Frequency-sweep measurements of **3c** with different strains at 20 °C.

Whereas in the case of the compounds **3a** and **3b** no order−order transition (OOT) could be observed at any temperature, this is clearly the case for compound **3c** (see Figure 5c). Starting from the hexagonally packed cylindrical morphology at room temperature, the first OOT can be observed at 50 °C where the coexistence of hexagonally packed cylindrical and simple cubic morphology is clearly visible (see also Supporting Information, S11−S12). At 65 °C a second OOT can be observed, indicating the loss of the hexagonally packed cylindrical morphology. Finally, at 90 °C the loss of the cubic morphology and hence the order−disorder transition can be observed. Corresponding to the much more flexible structure of the cation in compound **3c**, significantly shorter relaxation times were observed compared to PIB-IL **3b** (see Figure 5c). After cooling to room temperature and only 48 h relaxation time the hexagonally packed cylindrical morphology of **3c** was almost completely re-established. Our results clearly indicate that the self-assembly and the stability of the microphase morphology of the presented POILs strongly depends on the nature of the cation anchored on the polymeric chain.[36]

Rheology Measurements of PIB Ionic Liquids. A closer look on the order/order and order/disorder transitions was achieved by melt rheology,[59] as in our samples the relaxation behavior expectedly stems from two different contributions. On the one hand, microphase separation should influence the viscous behavior similar to conventionally microphase-separated block copolymers above the T_g, whereas the ionic multiplets should strongly tend to retain the (cubic) structure due to their high stability even at high temperatures.[60] As shown in Figure 7, the samples exhibited strongly different rheological behavior, depending on the nature of the cation anchored onto the polymeric chain. At low temperatures only the PIB-IL **3b** shows terminal flow, as exemplified by the dependency of $G' \sim \omega^2$; $G'' \sim \omega^1$ at $\omega\tau \ll 1$, indicative of a viscoelastic fluid.

This behavior can be explained by the internal cubic structure of the PIB-IL, which consists of (spherical) ionic multiplets. These multiplets slide over each other similar to the model described by Antonietti et al.[61] for spherical microgels. Therefore, a small (rubbery) plateau can be observed, which fits into the model of viscous flow via cooperative movements of the ionic multiplets upon shear. Depending on the size of the multiplets (**3b** (6.9 nm); **3c** (7.24 nm); **3a** (7.6 nm) as determined via SAXS), flow is then achieved at increasing temperatures 40, 105, and 140 °C, respectively (see frequency-sweep measurement at ω = 10 rad/s in Figure 7). As our polymers are below the entanglement limit, the formation of a plateau by entangled chains can be definitely ruled out. However, in accordance with the work of Hadjichristidis,[59] a deaggregation of the ionic clusters at lower frequencies cannot be excluded. In contrast to the other PIB-ILs (**3a**, **3b**), PIB-IL **3c** shows a significant transition around T = 50 °C, which matches with the order/order-transition from cubic to hexagonal as observed in SAXS. Thus, a strongly shear-dependent behavior of G' and G'' at low strain (γ = 2−70%) was observed (see Figure 8b and Supporting Information, S15−19), similar to the behavior of nanotubes, dispersed in a IL matrix.[62] The tubular structures can form a transient network, which can then be broken by the applied forces with increasing strain. However, the obtained results may also indicate the alignment of the aggregates of the ionic groups under the applied strain.[63] As those two possibilites can hardly be discriminated, and the SAXS data point to the former behavior of cluster retainment, we tend to the first hypothesis. In general, the observed data clearly demonstrate an entirely different behavior than expected for conventional block copolymers, which are introduced by the ionic liquid head groups. Clearly fascinating is this strong change by the presence of only one small ionic headgroup within the comparable long polymer chain.

■ CONCLUSIONS

A new IL with a strongly temperature-dependent nanostructure is reported in this paper, relying on the synthesis of a liquid polymer with a IL headgroup, thus introducing liquid properties by both the polymer and via the IL headgroup. Thus, the poly(isobutylene)s containing polymeric ionic liquids **3a**−**3c** were prepared, and their temperature-dependent self-assembly behavior was investigated by SAXS. The synthetic approach combined living cationic polymerization with azide/alkyne "click" chemistry and enabled a full end-group transformation to the final polymeric ionic liquids, modified with either imidazolium, pyrrolidinium, or triethylammonium end groups.

SAXS measurements at different temperatures revealed a similar behavior of prepared PIB-ILs to classical ionomers. All three investigated PIB-ILs exhibited pronounced nanostructural organization at room temperature. However, the thermal stability of the nanophasic separation shows strong dependence on the nature of an anchored cation. Whereas the nanostructural morphology of the imidazolium-based PIB-IL **3a** shows high thermal stability up to the decomposition temperature, order−order and lattice disorder−order transitions characteristic for common ionomers could be observed in the case of pyrrolidinium **3b** and ammonium-based **3c** PIB-ILs. Furthermore, also the relaxation time and thus the re-establishment of the nanostructural organization after cooling at room temperature are strongly dependent on the nature of ionic group, with the relaxation time of compound **3c** being significantly shorter as compared to the **3b** with the rigid, cyclic pyrrolidinium cation. The reported PIB-ILs represent new types of ionic liquids, where both the polymeric part and the IL headgroup can be used to tune both the nanostructure and the rheological properties. Because of their additional high thermal stability, the so-identified ILs therefore are important candidates for strongly shear- and wear-resistant fluids in science and technology, in particular aiming at self-healing polymers, where the relaxation time can now be engineered by the IL end group, together with the strong shear- and temperature-dependent flow behavior.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Optimization of reaction conditions, synthetical procedure for the compound **1**, NMR spectra of the compounds **1**, **2a**−**2c**, and **3a**−**3c**, GPC of the compound **1**, SAXS (including fitted Lorentzian curves), and rheology data of compounds **3a**−**3c**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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