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ARTICLE

Formation of Polyimide Nanoparticles in Heterophase with an Ionic Liquid as Continuous Phase

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ABSTRACT: Polyimide nanoparticles were obtained by the heterophase polycondensation of different aromatic tetracarboxylic acids and diamines in imidazolium-based ionic liquids (IL) as continuous phase. Because of the amphiphilic character of the IL, no additional surfactant is required for the stabilization of the employed dispersions. The low vapor pressure and high thermal stability of the reaction medium allow the use of high temperatures needed for the condensation reaction. The reaction takes place without commonly added extra components like LiCl or pyridine. The obtained polyimide was characterized by IR spectroscopy and gel permeation chromatography (GPC). Electron microscopy (TEM and SEM) shows a homogeneous morphology of the nanoparticles.

Introduction

A heterophase polymerization in water allows the formation of different polymeric nanoparticles as environmentally friendly latex dispersions, for example in a miniemulsion system, where the nanodroplets are formed prior to the polymerization process. In miniemulsion, different polymerization reactions could successfully be performed from radical, anionic, enzymatic, and oxidative polymerization to polycondensation and polyaddition reactions.[1] A special challenge is the synthesis of polyimides which usually requires for the ring closure temperatures which are significantly higher than what can be obtained in a normal polycondensation reaction using water as reaction media. If water is used in such a reaction, special precautions must be taken because of the pressurized system.[2−5] Therefore, a continuous phase is desired which allows the use of high temperature without any special precautions and at the same time is still immiscible with the monomers.

As conceptual solution, ionic liquids can be used as such a continuous phase. Ionic liquids (ILs) are organic salts with melting points below 100 °C. Because of their properties, they are widely used in numerous chemical applications. Especially the very low, nondetectable vapor pressure makes them highly attractive as "green" solvents, and therefore they can substitute common organic solvents with a high volatility.[6] A broad variety of applicable anions and cations allows the adjustment of the physical properties of the ILs like, e.g., their hydrophobicity. Nowadays, there are about 1000 ILs mentioned in the literature and more than 300 ILs are commercially available.

In the past years, there were several reports about the use of ILs as solvents in different kinds of polymerization reactions. First, solution polymerizations of butyl methacrylate (BMA) and methyl methacrylate (MMA) were reported using 1-alkyl-3-methylimidazolium cations and tetrafluoroborate or hexafluorophosphate anions as solvents.[7,8] Block copolymers consisting of styrene and BMA/MMA were obtained by atom transfer radical polymerization[9] and group transfer polymerization, respectively.[10] Direct polycondensation reactions of carboxylic acids and diamines in ILs as solvents are also described.[11] Here, the ionic liquid could be used as solvent without any other additional component.[12] In other cases triphenyl phosphite is reported as activator and condensing agent.[13,14]

To our knowledge, the polymerization in heterophase with ILs as continuous phase in order to obtain stable polymeric nanoparticles is not yet reported. Compared to common heterophase polymerizations in water, the polymerization in an IL has several advantages: (1) the polymerization can be performed easily at temperatures above 100 °C under ambient pressure, (2) the nature (e.g., hydrophilicity, temperature stability) of the ionic liquid can be tuned to immiscibility with the monomer and/or polymer so that a heterophase system can be obtained, and (3) the use of additional surfactants can be avoided since the IL itself possesses amphiphilic character and thus might act as a surfactant. Therefore, it was our hypothesis that ILs should be well suited for the formulation of heterophase systems for polymerization reactions even at high temperatures.

In this paper, we present as proof of concept a heterophase polycondensation in an ionic liquid, 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfon)imide, (EMI)Tf_2N, as continuous phase without the use of any other additional components such as surfactants or activators in order to obtain stable polyimide nanoparticles.

In the literature, the first step of the formation of polyimides is usually performed at relatively low temperatures (up to 100 °C), whereas the ring closure requires often temperatures of more than 300 °C.[15] Because of their special properties like high thermal and chemical resistance and mechanical properties, polyimides are used in many different applications like electric industry, high-temperature materials, and adhesives.[16] An alternative approach toward the synthesis of high-temperature stable polyimides by the use of a green solvent is described by Groth et al.[2−5] Here, the reactions are performed in water in sealed glass vessels at 20 psi and about 130 °C. The main advantage of ionic liquids as reaction media over water is their negligible vapor pressure also at elevated temperatures and, thus, no need of special precautions.

Experimental Section

Chemicals. 1,2,4,5-Benzenetetracarboxylic dianhydride (97%), 4,4′-(hexafluoroisopropylidene)diphthalic anhydride 6FDA (99%), and 2,3,5,6-tetramethyl-1,4-phenylenediamine (97%)

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were purchased from Aldrich. 4,4′-Diaminodiphenyl ether, 1,4-phenylenediamine (1,4-PhDA), *N*-methylimidazole, and bromoethane (>99%) were obtained from Merck. Lithium bis(trifluoromethanesulfonyl)imide was purchased from TCI Europe. All chemicals were used as received. The ionic liquid was dried in vacuo before using it as continuous phase. 1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfon)imide, (EMI)-Tf_2N, was synthesized as described by Bonhôte et al.[17]

The density of the ionic liquid is ρ[(EMI)Tf_2N] = 1.53 g/mL. The surface tension was measured by the Du-Noüy ring method to be σ[(EMI)Tf_2N] = 38.74 ± 0.01 mN/m. The melting points of the different monomers are as follows: 4,4′-(hexafluoroisopropylidene)diphthalic anhydride, mp 241−244 °C; 1,2,4,5-benzenetetracarboxylic anhydride, mp 283−287 °C; 1,4-diaminobenzene, mp 139−141 °C; 2,3,5,6-tetramethyl-*p*-phenylenediamine, mp 150−153 °C; 4,4′-diaminodiphenyl ether, mp 189−193 °C. Both dianhydrides show no solubility in the ionic liquid. The different diamines used for the synthesis of the polyimides show a very poor solubility in the ionic liquid, depending on their molecular structure and the temperature of the continuous phase.

Characterizations. The vacuum-dried polyimides were characterized by IR spectroscopy as KBr pellets on a Bruker IFS-113v FT-IR spectrometer.

For the dynamic light scattering (DLS) measurements, 3 drops of the heterophase were diluted by 5 mL of ethanol (which is miscible with the IL) and analyzed by DLS on a Nicomp instrument at 90°. Because of the negligible amount of IL, the properties of ethanol were used as settings for the refractive index and the dynamic viscosity during the DLS measurement. In the case of the sample redispersed in water, the parameters of water were used.

The transmission electron microscopy images were taken on a Philipps EM 400 microscope. One droplet of the redispersed polyimide nanoparticles in water or ethanol was applied to a carbon-coated copper grid and dried at room temperature. For the preparation of the samples the particles were redispersed in water or ethanol without any additional surfactant by using an ultrasonication bath for 5 min, and then 3.5 μL of the dispersion was dropped on a copper-coated TEM grid. The size of the particles was determined by measuring at least 100 particles on TEM pictures.

For the high-resolution field emission scanning electron microscopy analysis, some grains of the vacuum-dried polyimide **2** were fixed on a metal bench using double-faced carbon tape. The device was a Hitachi S-5200 microscope.

The thermal stability was measured by thermal gravimetrical analysis (TGA). The samples were analyzed using a TGA/SDTA851e Mettler-Toledo apparatus under a nitrogen atmosphere and a heating rate of 10 °C min^{-1}.

The molecular weight of the THF-soluble polyimides was analyzed by gel permeation chromatography (GPC) using a Waters 410 differential refractometer and a UV detector, a Dionex P580 pump, and a PSS linear M (5 μm) column. The molecular weight was calculated on the basis of narrow molecular weight distribution PS standards using PSS (Mainz) software.

The nuclear magnetic resonance spectroscopy (^1H, ^{19}F NMR) analyses were made on a 500 MHz Bruker DRX 500. For the analyses, the dispersion was measured in a coaxial system with D_2O as external standard.

Ultrapure water (>18.6 MΩ cm^{-1}) from a Milli-Q water system was used for the redispersion of the particles.

Polycondensation. As a typical experimental procedure for the synthesis of a polyimide in IL as continuous phase at 90 °C, an equimolar mixture of the tetracarboxylic dianhydride (see Table 1) and the diamine was added to 4 mL of (EMI)Tf_2N and heated to 90 °C with stirring for 5 days in a 15 mL screw-cap glass. After the polymerization, the polyimide was isolated by adding 30 mL of ethanol to the heterophase mixture and centrifuging off the solid. To remove small amounts of remaining ionic liquid, another 30 mL of ethanol was added to the polymer, the mixture was refluxed for 1 day, and the polymer was again separated by centrifugation and dried in vacuo. The polyimides are obtained as white or beige powders. The ionic liquid was recycled by stirring the centrifugate with charcoal for 1 day. Then the charcoal was removed by filtration, and the ethanol was evaporated. About 85% of the primarily used ionic liquid could be successfully recycled.

Table 1. Overview of the Different Reaction Parameters of the Polyimides Synthesized in a Heterophase System with an IL as Continuous Phase

sample	monomer A	monomer B	reaction temperature (°C)	amount of A and B (mmol)
1	1	3	90	0.23
2	1	3	90	1.13
3	1	4	90	1.13
4	1	5	90	1.13
5	2	3	90	1.13
6	1	3	190	1.13
7	2	3	190	1.13

The names and the structures of the different monomers A (1 and 2) and B (3, 4, and 5) are shown in Figure 1.

Two further polycondensation reactions (**6** and **7**, see Table 1) were run at 190 °C in the IL. **6** consists of 6FDA and 1,4-phenylenediamine as monomers. The reaction mixture became clear after 15 min reaction time. The polyimide was precipitated by the addition of methanol and purified as described above. **7** consists of 1,2,4,5-benzenetetracarboxylic dianhydride and 1,4-phenylenediamine as monomers. The obtained reaction mixture does not become clear in the course of the reaction. After 10 h reaction time the polymer was isolated as described above.

Results and Discussion

All the monomers employed for the formation of polyimides are listed in Table 1 and Figure 1. As none of the dianhydrides is soluble in the ionic liquid (EMI)Tf_2N, different monomer combinations could be used to form stable emulsions. It should be noted that no additional surfactant had to be added since the surface activity of IL (see Experimental Section) was sufficient to emulsify the monomers in the IL which act simultaneously as continuous phase.[12] Therefore, the relatively small shear forces of vigorous stirring were already sufficient in order to obtain finely dispersed droplets in the continuous phase. Since two monomers are used which do not show exactly the same solubilities in the continuous phase, we assume that one acts as osmotic pressure agent for the other and therefore as costabilizer for the droplets as known for miniemulsion droplets.[1] At the start of the synthesis, all systems were turbid; during reaction the system consisting of 6FDA and 1,4-PhDA cleared up (see below).

Figures 2 and 3 show the different polycondensation reactions of the monomers in Figure 1. In the first step, a polyamic acid is formed. The next step is the ring-closing reaction in which the final imide ring is formed. Figure 2 shows the formation of a polyimide made of pyromellitic acid dianhydride and a diamine as in **5** and **7** (see Table 1). In Figure 3 the formation of a polyimide of 6FDA and a diamine as in **1**, **2**, **3**, **4**, and **6** is presented. In the literature, the first step is usually performed at relatively low temperatures (up to 100 °C), whereas the ring closure requires often temperatures of more than 300 °C.[15]

During the polycondensation reaction, water is released as byproduct. Although (EMI)Tf_2N is a highly hydrophobic ionic liquid, those small amounts of water are soluble in the continuous phase as experimentally confirmed.

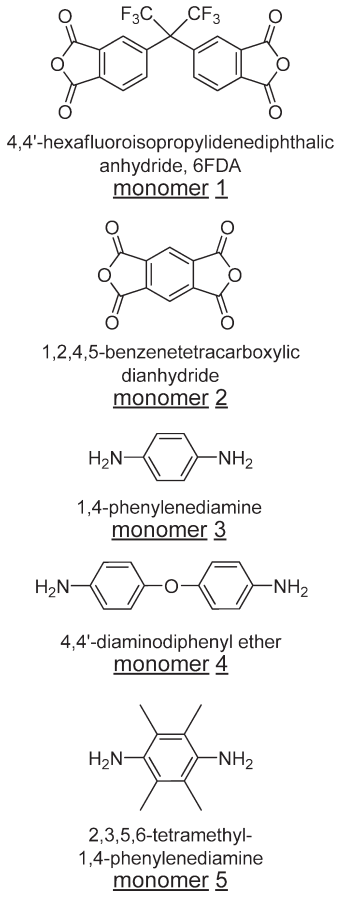

Figure 1. Monomers (A = 1, 2; B = 3, 4, 5) used for the formation of polyimides.

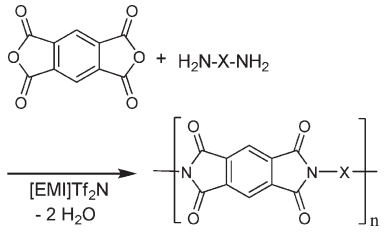

Figure 2. Polyimide made from pyromellitic acid dianhydride and diamine, (see Table 1, entries **5** and **7**).

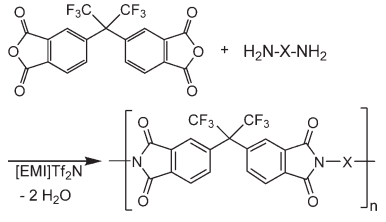

Figure 3. Polyimide made from 6FDA and diamine, (see Table 1, entries **1**, **2**, **3**, **4**, and **6**).

The yield of the polyimides obtained after precipitation with ethanol or methanol and drying in vacuo was in the range of 92−98%. Even after the purification step by refluxing with ethanol some traces of (EMI)Tf_2N might still be attached to the particles and therefore slightly distort the calculation. Ultracentrifugation as an alternative method for the separation of the polymer from the ionic liquid seems to be not appropriate because of the similar densities ((EMI)Tf_2N: ρ = 1.53 g/cm^3; polyimides: ρ = 1.42−1.47 g/cm^3).[18] Additionally, the rather high viscosity of (EMI)Tf_2N may hamper kinetically the separation in a reasonable time.

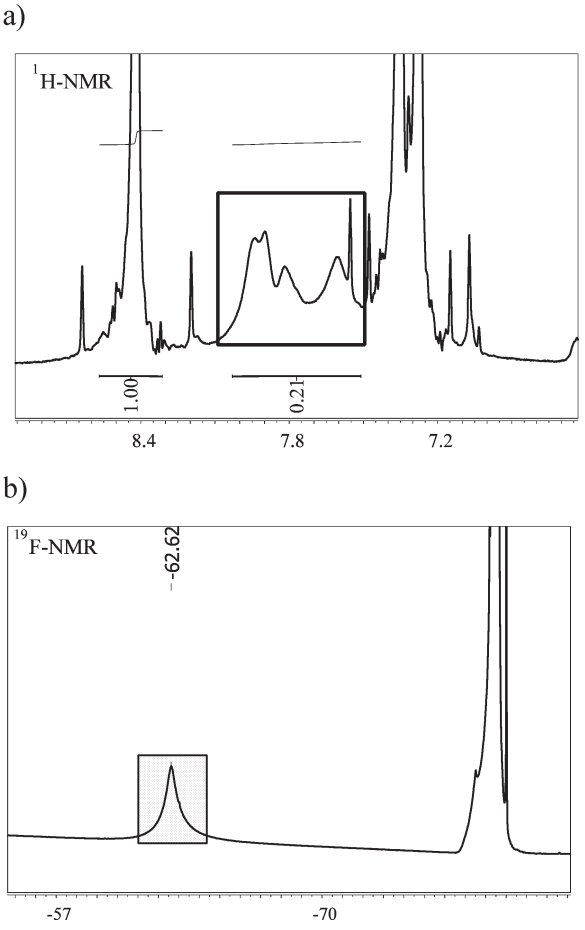

Figure 4. (a) ^{1}H NMR and (b) ^{19}F NMR spectra of polyimide **2** in (EMI)Tf_2N.

Polycondensation Reaction in IL at 90 °C. The different monomer mixtures dispersed by stirring vigorously in the IL were heated to 90 °C for polymerization. In most of the cases, the synthesized polyimides are insoluble in the IL. However, using 6FDA and 1,4-phenylenediamine as monomers, the reaction mixture clears up during the polymerization process. Before the polymerization, the monomers form a milky heterophase with the IL which is still detectable in the early polymerization stages, but during the course of the polycondensation the dispersion becomes clear, indicating an isorefractive system, very small sized particles or (partial) solubility/swellability of the polymer particles in the solvent or combinations of those conditions. In order to analyze the state of the produced polyimide, some NMR investigations were performed for understanding the occurrence of the polyimide in the ionic liquid. If the polymer is molecularly dissolved in the ionic liquid and exists as molecularly mobile polymer chains, the ^{1}H and ^{19}F NMR solution spectroscopy should show—due to the mobility of the chains—sharp signals; in the presence of solid(like) aggregates or particles the signals are too broad to be detected in the displayed ppm range. A ^{1}H and a ^{19}F NMR spectrum of the clear reaction mixture of sample **2** after 5 days were taken (see Figure 4a,b).

Both spectra clearly show the presence of mobile polymer chains (dissolved or swollen) indicated by the relatively sharp signals in the area of the polymer signals. From the ratio of the ^{1}H NMR peak integrals for the solvent and for the

polymer only 30% of the polymer can be detected as mobile chains if we assume a 100% conversion. This points to the fact that around 70% of the polymeric chains are present in an immobilized state (as particles) which suggests that despite the clear appearance of the reaction mixture, it represents a heterophase system. Such a clear appearance of a micellar solution of a block copolymer in an IL was already reported in the literature.[19,20] The apparently increased partial solubility (or swellability) of the polymer compared to its monomers seems to be counterintuitive since usually during polymerization the solubility decreases due to entropic reasons. However, enthalpic effects can have a strong influence due to a change in hydrophilicity from the monomer to the polymer.

In order to give more evidence for the existence of a heterophase system, TEM and dynamic light scattering measurements were performed. For the DLS measurements, the IL-based (clear) heterophase was diluted with ethanol, which is miscible with the IL. A DLS measurement in the pure ionic liquid was not possible because of the very low intensity of the signal, contrary to measurements of a corresponding system reported in the literature.[19,20] We assume that the small difference of the refractive indices is responsible for the low intensity. After the addition of ethanol, the system shows a light turbidity. The system stays stable during dilution, and no coagulation occurs. The analyses revealed particles with a size of 69 nm and a standard deviation of 7.3 nm (10.7%) in the number-weighted distribution analysis. Please note that due to the addition of ethanol, IL-swollen particles (see NMR results above) could have been shrunken and therefore could appear smaller than they were before in the IL. Additionally, TEM pictures (Figure 5) were taken. Here, the dried particles were redispersed in neat ethanol. The heterophase in ethanol itself again is stable. There is no coagulation or other signs of instability like clumping.

Both TEM pictures present nanosized particulate structures with a diameter of about 70 nm. The particles show some coalescence which can be attributed to drying artifacts or to the use of ethanol for the preparation.

In the case of the other polymers, still stable milky dispersions were successfully obtained after a reaction time of 5 days. No partial solubility or swellability of the particles is observed.

The polymers were characterized by IR spectroscopy. The IR spectra show in all cases the characteristic bands of the imide ring at 1785 and 1725 cm^{-1}, respectively, indicating the successful formation of a polyimide even at those relatively low temperatures. There are no bands detected in the characteristic region for free carboxyl groups at around 1680 cm^{-1} and for amide bands at around 1650 cm^{-1}, which is indicative for the complete transformation to the polyimide. Figure 6a,b shows exemplarily the IR spectra of **1** and **4**. The inset exhibits in detail the area with the two characteristic polyimide bands at 1785 and 1725 cm^{-1}. The band of the anhydride at 1810 cm^{-1} has completely disappeared.

The thermal properties of the synthesized polyimides were analyzed by TGA. Figure 7 shows a typical TGA for polyimide **1**. The thermal decomposition starts at about 500 °C, and the inflection point is located at about 570 °C. The other polyimides exhibit similar decomposition temperatures (see Table 2), clearly indicating the high thermal stability of these polymers. The TGA shows a loss of about 45 wt % at 580 °C, fairly corresponding to the mass fraction of the heteroatoms. Thus, we assume that the polyimides graphitize at around 600 °C.

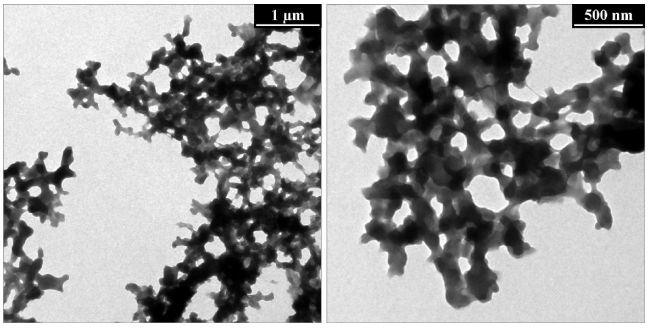

Figure 5. TEM images of sample **2** at different magnifications.

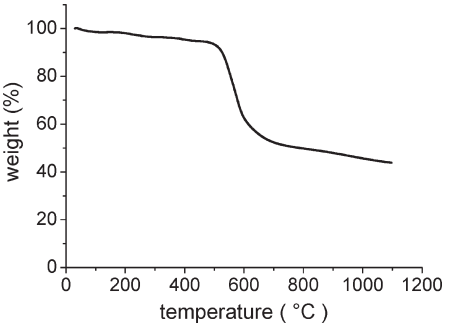

Figure 7. TGA trace of polyimide **1** with an inflection point at about 570 °C.

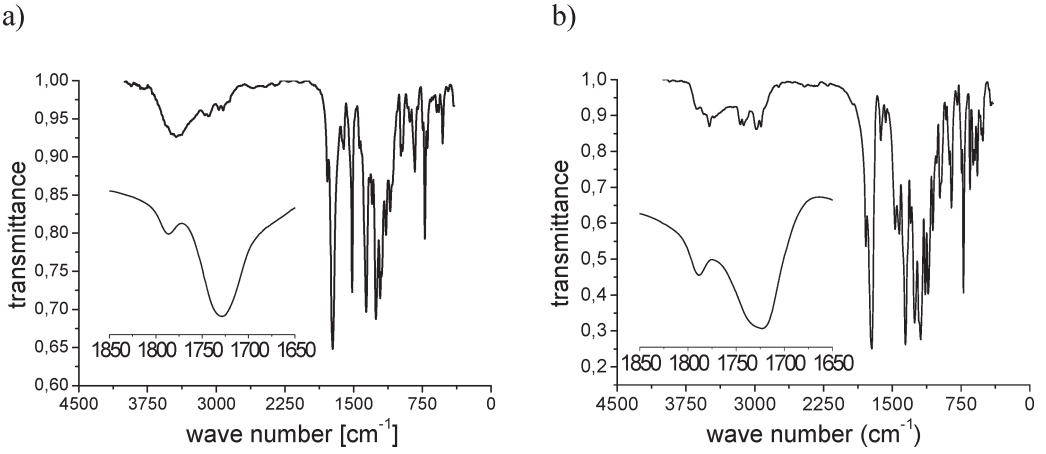

Figure 6. (a) IR spectrum of **1** and (b) IR spectrum of **4**.

Table 2. Characterization of the Polyimide Particles

	size (DLS)[a]			size (TEM)[b]		
sample	diameter (nm)	std deviation (nm)	std deviation (%)	diameter (nm)	PD[c]	T_{Decomp}[d] (°C)
1	69	47.3	68.9	60	0.125	570
2	103	13.9	13.4	97	0.108	536
3	98	6.2	6.3	101	0.136	561
4	72	4.9	6.8	*e*	*e*	557
5	189	26	13.8	*e*	*e*	538
6	134	15.5	11.6	*e*	*e*	562
7	112	15.2	13.6	*e*	*e*	650

[a] Average diameter by DLS after redispersion in water. [b] Average diameter by TEM of at least 100 particles per sample. [c] PD is defined as standard deviation divided by the number-average diameter. [d] Decomposition temperature from TGA (inflection point). [e] Not determined by TEM since deformation of the particles while drying occurred.

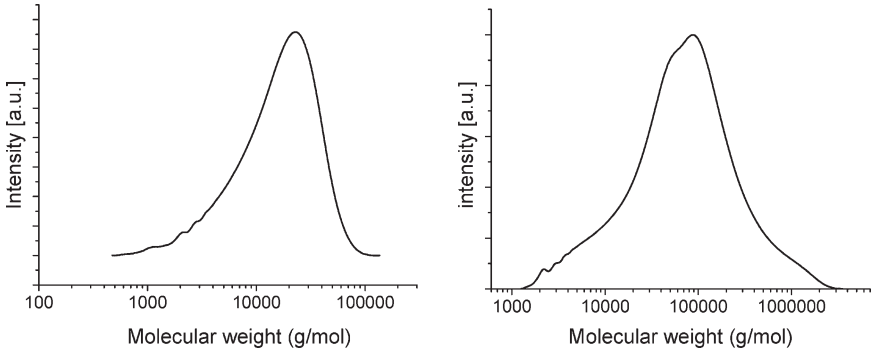

Figure 8. (a) Molecular weight distribution of the THF-soluble polyimide **1** as determined by GPC and (b) molecular weight distribution of the THF-soluble polyimide **4**. The molecular weights were calibrated against PS standards.

DSC measurements of a few exemplary samples showed the presence of a melting transition pointing to a certain degree of crystallinity of the as-synthesized polyimides (see TEM characterization below). For example, the DSC analysis of **1** revealed a melting temperature at ~460 °C during the first heating run.

For the determination of the molecular weight of the soluble polyimides samples **1** and **4** were dissolved in THF and analyzed by GPC calibrated against PS standards (Figure 8). **1** shows a monomodal distribution with $M_w = 2.0 \times 10^4$ g mol^{-1} and $M_n = 1.0 \times 10^4$ g mol^{-1}. Hence, the polydispersity represents the ideal value of 2.0 for a step-growth polymerization. No molecular weights above 1×10^5 g mol^{-1} can be detected. In the case of **4** the molecular weight was determined to be significantly higher with $M_w = 1.3 \times 10^5$ g mol^{-1} and $M_n = 2.9 \times 10^4$ g mol^{-1}. Here, the polydipersity increases to 4.5. Furthermore, a multimodal distribution can be detected with very high molecular weights of more than 1×10^6 g mol^{-1}. The higher molecular weight in sample **4** might be explained by the higher hydrophobicity of the diamine and therefore lower solubility in the continuous phase. Both of the dianhydrides and the tetracarboxylic acid show absolutely no solubility in the ionic liquid. The different diamines used for the synthesis of the polyimides show a very poor solubility in the ionic liquid, depending on their molecular formula and the temperature of the reaction. We believe the little difference in the solubility of the two different amines induces the slight differences in the molecular weight.

In order to follow the kinetics of the polycondensation reaction qualitatively samples of **2** were taken at different times. When the system was still a turbid heterophase, the ionic liquid was removed as described by the addition of acetone and the precipitate centrifuged and dried in vacuo. When the reaction mixture became clear after ca. 3 days, the polymer was precipitated by addition of methanol, centrifuged, and dried in vacuo. All the samples were analyzed by IR spectroscopy. The absorbance spectra were normalized and two ranges with defined limits were chosen. The first range (A_1) from 1625 to 1696 cm^{-1} involves the vibration attributed to the free carboxylic group at 1680 cm^{-1}. The second range (A_2) between 1696 and 1796 cm^{-1} with the peak maximum at 1725 cm^{-1} is assigned to the polyimide group. Then the ratio $R = A_2/A_1$ of the corresponding areas was plotted versus the reaction time. The plot is shown in Figure 9, presenting the general tendency of the reaction. After the fourth day, when the heterophase disappears and the product becomes soluble, one can see that there is a large increase of R. This indicates that the ring-closing step takes place; the polyimide is formed and becomes soluble in (EMI)Tf_2N. The spectrum on the sixth day shows no more carboxylic peak; the value of A_1 is only the background signal.

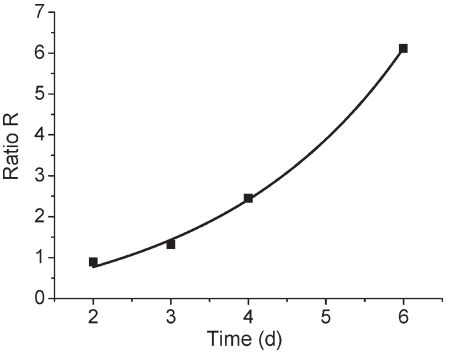

Figure 9. Ratio R of the two peak areas between 1625 and 1696 cm^{-1} and between 1696 and 1796 cm^{-1} vs time of reaction on sample **2** with the fit for the second-order reaction kinetics on the R values.

The plot in Figure 9 combines the four calculated R values with the fitting for the kinetics of a second-order consecutive reaction showing a very good agreement between experimental and theoretical data ($R^2 = 0.998\,26$). A more detailed

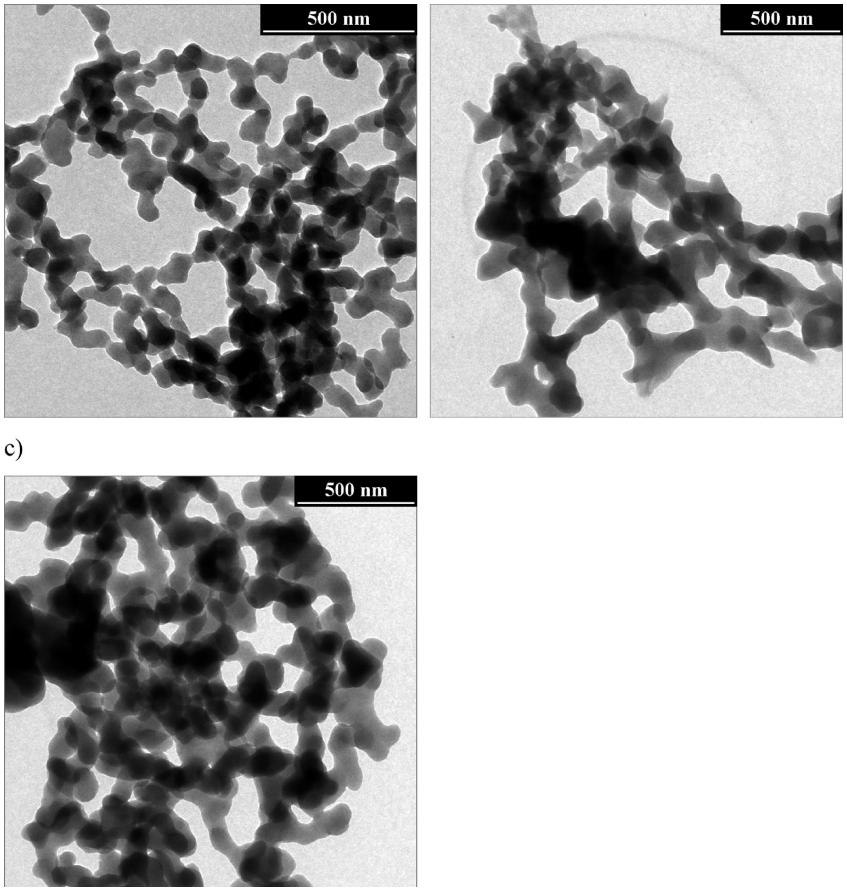

Figure 10. TEM pictures of samples (a) **1**, (b) **3**, and (c) **2**.

analysis of the fitting curve is not performed as the oscillator strengths of the corresponding vibrational transitions are not known. So the polycondensation reaction can be qualitatively described as the consecutive reaction A → B → C. In the first step, the polyamic acid is formed and in the second step the ring closing mechanism takes place and the polyimide is formed.

TEM analysis of different polyimides (Figure 10) shows a particulate morphology. The deviation from spherical shape of the particles might be attributed to the crystallinity of the polymer as already detected by DSC (see above). The particles' size was determined by measuring at least 100 particles. The sizes were found in the range between 50 and 110 nm with a quite narrow particle size distribution depending on the sample; the results by the analyses of the TEM pictures are listed in Table 2.

In order to check whether the coalescence of the particles in Figure 10 is present in dispersion or only occurs during drying for the TEM preparation, the particles were redispersed in water by using ultrasound and analyzed by DLS as summarized in Table 2. The DLS size corresponds nicely to the TEM values; the formation of aggregates is not observed. Therefore, the coalescence of some of the particles must appear during the preparation for the TEM and might be due to small traces of remaining ionic liquid. This remaining liquid works as glue between the single particles. Since polyimides are high-temperature stable polymers with T_g > 250 °C, the particles are not expected to be sensitive to beam damage.

SEM images give information on the surface morphology of the particles. The SEM pictures in Figure 11 show particles of **2** with a structured surface and some small dimples in different magnifications.

High-Temperature Polycondensation at 190 °C. In order to analyze the influence of the temperature for the polycondensation process, the polymerization temperature was increased to 190 °C. The ionic liquid (EMI)Tf_2N is thermally stable up to 500 °C. Because of the negligible vapor pressure, this polycondensation reaction could also be performed in a standard screw-cap glass. Two different polymers (see Table 1, entries **6** and **7**) were synthesized. **6** is composed of 6FDA and 1,4-phenylenediamine as monomers. At 190 °C the reaction mixture becomes homogeneous already after 15 min in contrast to 3 days as observed for the synthesis at 90 °C. The polyimide was precipitated by the addition of methanol and purified as described above.

The dried polymer was characterized by IR spectroscopy. Figure 12 shows the spectrum of the polymer precipitated after 10 h. Already after this time, the IR spectrum exhibits the characteristic bands of the imide ring at 1785 and 1725 cm^{-1} (see inset in Figure 12). No bands in the characteristic areas for free carboxyl groups at 1680 cm^{-1} and amide bands around 1650 cm^{-1} are observed.

7 consists of 1,2,4,5-benzenetetracarboxylic dianhydride and 1,4-phenylenediamine as monomers. The obtained polyimide is completely insoluble in the ionic liquid. A sample was taken after 10 h and the polymer isolated as described above. Figure 13 shows the IR spectrum of the isolated polymer after 10 h with the characteristic bands of the imide ring at 1785 and 1725 cm^{-1}. No bands indicate the presence of free carboxyl groups (1680 cm^{-1}) or amide bands (1650 cm^{-1}).

If the IR spectrum of **7** is compared with the corresponding spectrum of the product **5** obtained at 90 °C reaction temperature (Figure 14), one can easily recognize the coincidence of both spectra. Thus, the chemical structure of the polyimides does not depend on the reaction temperature.

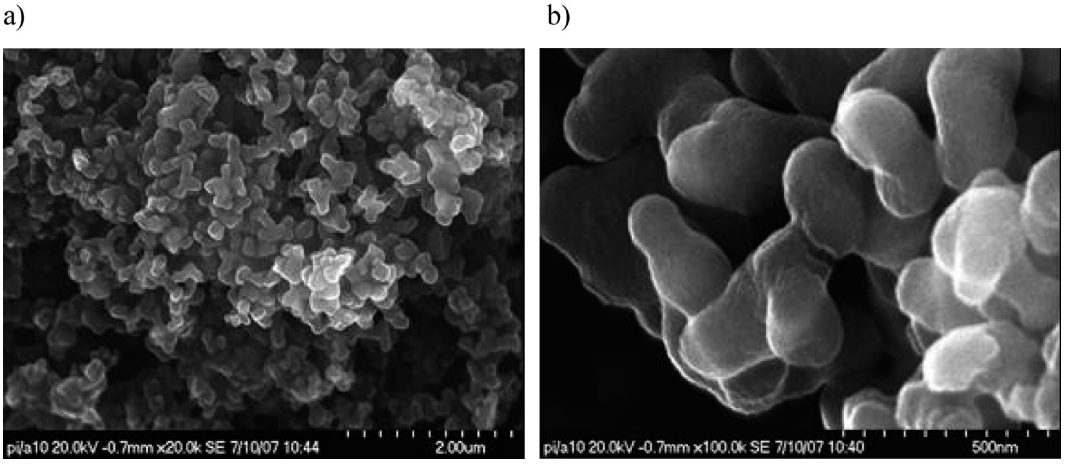

Figure 11. (a) SEM pictures of particles from sample **2** and (b) the same sample at a higher magnification.

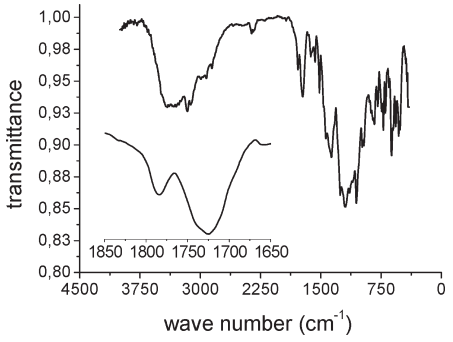

Figure 12. IR spectrum of sample **6** synthesized at 190 °C (inset: magnified area of the C═O stretching vibration region).

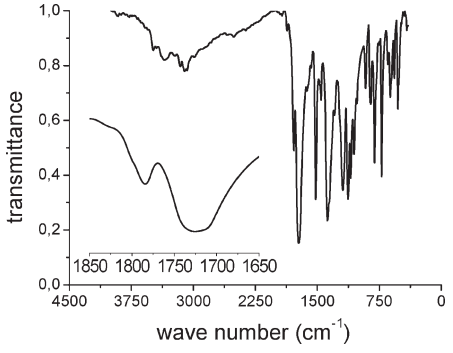

Figure 13. IR spectrum of sample **7** synthesized at 190 °C for 10 h.

The thermogravimetric analysis of **7** is also indicative for the presence of a polyimide showing a decomposition temperature of about 650 °C. It has to be noted that contrary to literature protocols for the synthesis of polyimides in common organic solvents no further additives like triphenyl phosphite or pyridine as activator are required for the reaction in IL.[13] Furthermore, the negligible vapor pressure of the IL even at such high temperatures of 190 °C does not require special technical equipment like high-pressure reactors or cooling devices. The elevated reaction temperature causes a significant increase of the reaction rate so that full conversion is already reached after 1 day.

Conclusion

These results show that polyimide nanoparticles in the range of 100 nm can be prepared by heterophase polycondensation in (EMI)Tf_2N as ionic liquid without the addition of any further activating or stabilizing agents. The polyimides which are insoluble in the ionic liquid could be easily separated by precipitation with a bad solvent and centrifugation. The polyimide made of 6FDA and 1,4-phenylenediamine is soluble in the IL and can also be separated by centrifugation after the precipitation with methanol. Characterization of the polymers by IR spectroscopy reveals full conversion of the anhydride and amine groups to imide groups. SEM images show that the surface of the particles is structured and has some small dimples. All particles show a high thermal stability by TGA and a decomposition temperature at around 520 °C.

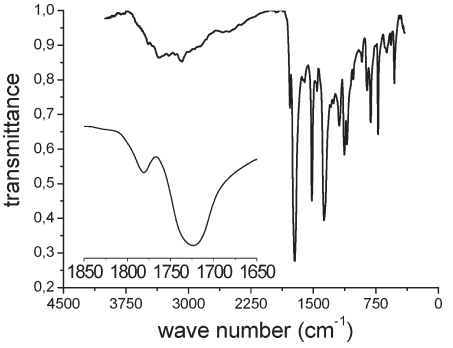

Figure 14. IR spectrum of sample **5** synthesized at 90 °C (inset: magnified area of the C═O stretching vibration region).

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