Research Article

Journal of Labelled Compounds and Radiopharmaceuticals

Received 12 November 2008, Revised 23 December 2008, Accepted 20 January 2009 Published online 26 February 2009 in Wiley Interscience

(www.interscience.wiley.com) DOI: 10.1002/jlcr.1591

Synthesis of the perdeuterated cellulose solvents 1-ethyl-3-methylimidazolium acetate (EMIM-OAc-d_{14}) and 1-butyl-3-methylimidazolium acetate (BMIM-OAc-d_{18}) and of 2-^{13}C-butyl-3-methylimidazolium acetate

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The syntheses of two perdeuterated ionic liquids (ILs), which have found use as solvents for cellulose derivatization and processing in addition, are described: 1-ethyl-3-methylimidazolium acetate (EMIM-OAc-d_{14}) and 1-butyl–3-methylimidazolium acetate (BMIM-OAc-d_{18}). The targets were obtained from imidazole in three-step sequences starting with butylation and ethylation, respectively. The resulting 1-alkyl imidazoles were purified, and subsequently methylated according to a novel protocol using dimethylcarbonate-d_6. To obtain the 1-alkyl-3-methylimidazolium moiety, methylation of 1-alkylimidazoles proved to be superior to the conventional approach of alkylating 1-methylimidazole. Addition of acetic acid-d_4 caused traceless degradation of the methylcarbonate counter anions, which were neatly exchanged for acetate. The IL 2-^{13}C-butyl-3-methylimidazolium acetate, in which the isotopically enriched C-2 is a good NMR-indicator of side reactions and solvent–solute interactions, was synthesized according to the same reaction sequence, starting from 2-^{13}C-1-alkylimidazole which, in turn, was obtained by reaction of glyoxale, alkylamine, ammonia and paraformaldehyde-^{13}C.

Keywords: cellulose solvents; ionic liquids; NMR solvents; BMIM acetate; EMIM acetate

Introduction

Recently, ionic liquids (ILs) have attracted much interest in cellulose chemistry as dissolution[1,2] and derivatization media.[3–5] Studies are going on to use ILs for large-scale production of cellulosic fibers.[6,7] The swelling and dissolution of cellulose in ILs (and in other cellulose solvents as well) are still far from being understood on a molecular level. Direct solution studies by NMR are hampered by the unavailability of perdeuterated cellulose-dissolving ILs. In this study, the two most commonly used IL-type cellulose solvents BMIM-OAc and EMIM-OAc were synthesized in perdeuterated form to allow for such experiments.

Moreover, it has been demonstrated recently that ILs do not behave as inert solvents to cellulose, but react with the reducing end of the polymer under formation of a carbon–carbon bond at C-2.[8] To study such reaction by NMR was impossible because of the signal intensities of the reacting centers being negligibly small as compared with the several hundred non-reacting glucopyranose units of the polymer and the large excess of non-reacting IL. By introducing a ^{13}C label at C-2 this situation is improved in a way that the side reaction between solvent and solute becomes directly observable. The second synthetic target communicated here is 2-^{13}C-butyl-3-methylimidazolium acetate to be used in such solution studies of cellulosics.

Results and discussions

Synthesis of perdeuterated ionic liquids 1-ethyl-3-methylimidazolium acetate and 1-butyl-3-methylimidazolium acetate

The syntheses of the two ILs 1-ethyl–3-methylimidazolium acetate (EMIM-OAc-d_{14}, **8**) and 1-butyl-3-methylimidazolium acetate (BMIM-OAc-d_{14}, **9**) proceeded in an analogous way. In

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principle, two pathways are viable for the synthesis of 1-alkyl-3-methylimidazolium salts. Most commonly, 1-methylimidazole as the starting material is *N*-alkylated. This protocol is simple and suitable for large-scale preparations. In addition, 1-methylimidazole is widely available. Alternatively, imidazole can be alkylated first into 1-alkylimidazole and then be methylated in the following step. We chose this second approach, applying dimethylcarbonate as a methylating agent that so far had not been used in the preparation of imidazole-based ILs. It neatly quaternizes 1-alkylimidazoles into the 1-alkyl-3-methylimidazolium cations without side reactions and discoloration of the reaction mixtures, but the reaction times are longer than in the case of methyl halides or dimethyl sulfate as the alkylating agents, and a pressurized vessel is required for the reaction. However, dimethyl carbonate offers one big advantage, which was decisive in our case: it leaves the methylcarbonate counterion that can afterwards tracelessly be replaced by other anions if needed. In the case of common alkylating agents, such as alkyl halides, traceless exchange of the halide for the desired anion is not trivial. In the case of dimethylcarbonate used for alkylation of the 1-alkylimidazole, the resulting methylcarbonate is simply decomposed into carbon dioxide and methanol by addition of acetic acid, and the desired acetate remained as the counteranion.

In the synthesis of perdeuterated material (Scheme 1), the starting compounds were imidazole-d_4 (**1**) and a perdeuterated alkyl halide (ethyl iodide, butyl iodide) for introduction of the 1-substituent. The perdeuterated intermediates, 1-(pentadeuteroethyl)imidazole-d_3 (**2**) and 1-(nonadeuterobutyl)imidazole-d_3 (**3**), respectively, can be conveniently purified by microdistillation. The quaternization reaction with 1.2 equivalents of dimethylcarbonate-d_6 (**4**) proceeded at 210°C in a teflon-coated autoclave over 2 h, catalyzed by acidic aluminum oxide (Brockmann grade I). The resulting reaction mixture was colorless, which is not at all common for the syntheses of ILs that are mostly accompanied by chromophore generation. From the intermediates 1-ethyl-3-methylimidazolium methylcarbonate-d_{14} (**5**) and 1-butyl-3-methylimidazolium methylcarbonate-d_{18} (**6**), excess dimethylcarbonate-d_6 was removed under vacuum; non-reacted 1-alkylimidazole was not detected. Addition of excess acetic acid-d_4 (**7**) at 80°C afforded directly the desired products 1-ethyl–3-methylimidazolium acetate-d_{14} (**8**) and 1-butyl–3-methylimidazolium acetate-d_{18} (**9**), respectively. Carbon dioxide and methanol, resulting from the methylcarbonate anions, as well as excess acetic acid-d_4 were conveniently removed by once more applying vacuum at 80°C, leaving behind the colorless and pure products as confirmed by microanalysis and UV spectrometry. Applying ethereal DCl instead of acetic acid-d_4 introduced the chloride anion, producing the corresponding 1-alkyl-3-methylimidazolium chlorides in neat form (data not shown). In addition, in this case the decomposition products of the methylcarbonate anions, carbon dioxide and methanol, and excess DCl and solvent are conveniently removed by applying vacuum.

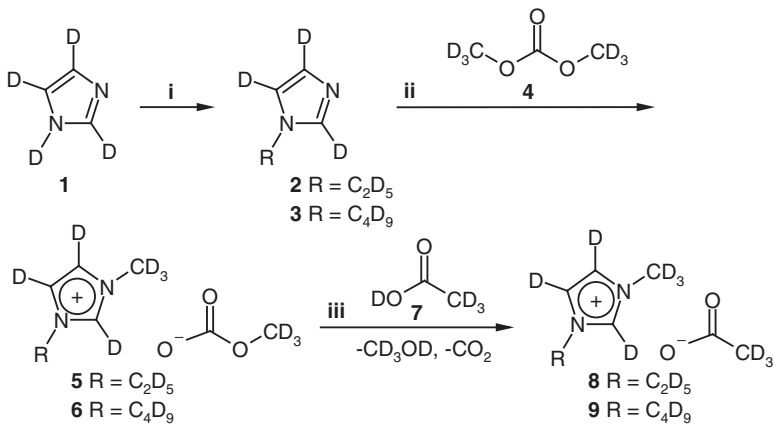
Synthesis of 2-^{13}C-1-butyl-3-methylimidazolium acetate

For a ^{13}C-label to be introduced into 2-position of the BMIM heterocycle, the imidazole core has to be constructed. From the several approaches available,[9,10] the use of ^{13}C-paraformaldehyde was the most appropriate one, allowing the 1-butylimidazole to be built directly without the need to isolate imidazole itself. Although the yields of the corresponding four-component reaction[11–13] (see Scheme 2) were only modest (56%), the good separability of the product, the low prices of the labeled compound and the good upscaling potential were the decisive pros. With the 2-^{13}C-1-butylimidazole (**10**), the subsequent steps were as described above in Scheme 1, providing the target molecule **11** in a 76% overall yield in analytically pure form.

Experimental

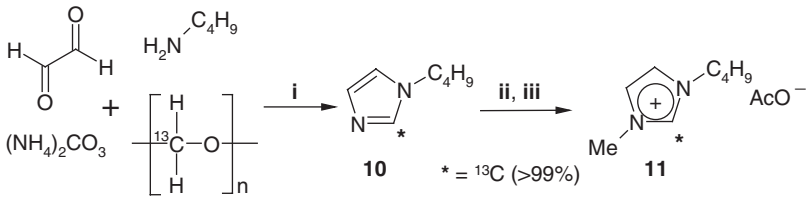
Materials

All chemicals were commercially available. Thin layer chromatography was performed on silica gel 60 plates (5 × 10 cm, 0.25 mm) with fluorescence detection under UV light at 254 nm. Column chromatography was performed on silica gel G60 plates (40–63 mm). Melting points, determined on a Kofler-type micro hot stage with Reichert-Biovar microscope, are uncorrected. ^{1}H NMR spectra were recorded at 400.13 MHz,



i: autoclave, C_2D_5-I / C_4D_9-I (1 eq.), Na_2CO_3 / NaOH, toluene, 150°C, 5h (79% of **5**, 84% of **6**), **ii**: a) autoclave, Al_2O_3 (acidic), 1.2 eq. **4**, r.t. to 210°C, 2h, **iii**: 80°C, 1.5 eq. **7**, 30 min, overall 76% of **8**, overall 81% of **9**.

Scheme 1. Synthesis of perdeuterated 1-ethyl-3-methylimidazolium acetate (**8**) and 1-butyl-3-methylimidazolium acetate (**9**), employing dimethylcarbonate-d_6 as alkylating agent and precursor of a conveniently exchangeable anion.



i: autoclave, components equimolar, 200°C, 4h (56%),
ii: Me_2CO_3 (1.2 eq.), autoclave, Al_2O_3 (acidic), r.t. to 210°C, 2h,
iii: AcOH (1.5 eq.), 80°C, 30 min, overall 76%

Scheme 2. Synthesis of 2-^{13}C-1-butyl-3-methylimidazolium acetate (**11**), employing a four-component reaction to construct the imidazole ring with ^{13}C-paraformaldehyde as the source of the ^{13}C-label.

^{13}C NMR spectra at 100.42 MHz in $CDCl_3$ as the solvent and TMS as the internal standard, if not stated otherwise. NMR data are given for the deuterated compounds, and also for non-deuterated title products and key intermediates for comparison. It should be noted that in standard attached proton test (APT) spectra of BMIM-type ILs the resonance of C-2 can be inverted or even 'missing'. The large C–H coupling constant at this position (>220 Hz) – in combination with the standard APT pulse sequence – is responsible for this effect, so that for spectral assignment the APT technique is less suitable than conventional ^{13}C spectra.[14]

1-Ethylimidazole-d_8 (2)

Into a stainless steel autoclave with teflon coating, imidazole-d_4 (0.72 g, 10 mmol), ethyl iodide-d_5 (1.61 g, 10 mmol), freshly powdered, anhydrous sodium carbonate (1 g), freshly powdered sodium hydroxide (ground from dry NaOH pellets), and dry toluene (100 mL) were added. The vessel was flushed with argon, sealed and heated under efficient stirring at 150°C for 5 h. After cooling to r.t., solids were removed by filtration, and the residue was microdistilled twice to provide 1-ethylimidazole-d_8 (823 mg, 79%) as colorless liquid.

^{1}H NMR ($CDCl_3$, 0.1 M): δ 2.5 (s, br, H_2O). ^{13}C NMR (DMSO-d_6): δ 15.3 (sept., $J_{C,D}$ = 22 Hz, CD_3 in ethyl), 41.0 (pent, $J_{C,D}$ = 20 Hz, CD_2–N), 118.1 (t, $J_{C,D}$ = 18 Hz, CD), 129.1 (t, $J_{C,D}$ = 18 Hz, CD), 136.1 (t, $J_{C,D}$ = 20 Hz, CD). Comparison to the non-deuterated product (1-ethylimidazole): ^{1}H NMR ($CDCl_3$, 0.1 M): δ 1.40 (s, 3H, CH_3 in ethyl), 3.92 (q, 2H, CH_2 in ethyl), 6.92 (s, 1H, CH), 7.04 (s, 1H, CH), 7.48 (s, 1H, CH). ^{13}C NMR (DMSO-d_6): δ 16.3, 41.5, 118.5, 128.9, 136.5. Microanalysis: calcd. for $C_5D_8N_2$ (104.18): C 57.65, H 7.74, N 26.89; found: C 57.85, H 7.37; N 27.01.

1-Ethyl-3-methylimidazolium acetate (EMIM-OAc-d_{14}, 8)

1-Ethylimidazole-d_8 (**2**, 520 mg, 5 mmol), dimethylcarbonate-d_6 (**4**, 580 mg, 6.03 mmol) and acidic aluminum oxide (Brockmann grade I, 0.2 g) was charged into a stainless steel autoclave with teflon coating, and the mixture was heated at a rate of 5°C/min to 210°C, kept at this temperature for 2 h, and cooled to r.t. The vessel was opened, the colorless white remainder triturated with diethyl ether (ca. 50 mL), and the solids removed by filtration. The ether was evaporated and the viscous remaining solid was heated to 80°C under vacuum, which provided a small amount of recovered dimethylcarbonate-d_6 (not quantified). Under ambient pressure and efficient stirring at 80°C, acetic acid-d_4 (**7**, 0.5 g, 7.8 mmol) was added, upon which the clear liquid turned cloudy due to evolved gases. After stirring for additional 30 min, vacuum (10^{-3} Torr) was applied for another 30 min. After cooling to r.t. mixture, 1-ethyl-3-methylimidazolium acetate-d_{14} (**8**) was obtained as colorless liquid (866 mg, 96%). ^{1}H NMR (DMSO-d_6, 0.1 M): δ 3.56 (s, br, H_2O/HDO). ^{13}C NMR (DMSO-d_6): δ 14.3 (sept., $J_{C,D}$ = 22 Hz, CD_3 in ethyl), 24.9 (sept, $J_{C,D}$ = 21 Hz, CD_3 in acetate), 35.8 (sept., $J_{C,D}$ = 20 Hz, CD_3–N), 45.4 (pent, $J_{C,D}$ = 20 Hz, CD_2–N), 121.5 (t, $J_{C,D}$ = 18 Hz, CD), 122.8 (t, $J_{C,D}$ = 18 Hz, CD), 137.5 (t, $J_{C,D}$ = 20 Hz, CD), 174.0 (s, COO in acetate). Comparison to the non-deuterated product (1-ethyl–3-methylimidazolium acetate): ^{1}H NMR ($CDCl_3$, 0.1 M): δ 1.42 (t, 3H, CH_3 in ethyl), 1.58 (s, 3H, CH_3 in acetate), 3.85 (s, 3H, N–CH_3), 4.19 (q, 2H, N–CH_2), 7.92 (t, 1H, CH), 8.00 (t, 1H, CH), 10.32 (s, 1H, CH). ^{13}C NMR (DMSO-d_6): δ 15.2, 26.1, 36.5, 45.5, 122.1, 123.9, 137.5, 173.6. Microanalysis: calcd. for $C_8D_{14}N_2O_2$ (184.30): C 52.14, H 7.60, N 15.20; found: C 52.36, H 7.88; N 14.98.

1-Butylimidazole-d_{12} (3)

The same procedure was used as described above for the preparation of **2**, with the following alterations: imidazole-d_4 (0.72 g, 10 mmol) and butyl iodide-d_9 (1.94 g, 10 mmol) were employed to provide 1-butylimidazole-d_{12} (1.09 g, 84%) as colorless liquid. ^{1}H NMR ($CDCl_3$, 0.1 M): δ 4.5 (s, br, HDO). ^{13}C NMR (DMSO-d_6): δ 12.9 (sept., $J_{C,D}$ = 22 Hz, CD_3 in butyl), 19.3 (pent, $J_{C,D}$ = 20 Hz, CD_2 in butyl), 33.8 (pent, $J_{C,D}$ = 20 Hz, CD_2 in butyl), 46.0 (pent, $J_{C,D}$ = 19 Hz, CD_2–N), 118.0 (t, $J_{C,D}$ = 18 Hz, CD), 127.3 (t, $J_{C,D}$ = 18 Hz, CD), 137.0 (t, $J_{C,D}$ = 20 Hz, CD). Comparison to the non-deuterated product (1-butylimidazole): ^{1}H NMR ($CDCl_3$, 0.1 M): δ 0.92 (t, 3H, CH_3), 1.39 (sext, 2H, CH_3–CH_2), 1.76 (pent, 2H, N–CH_2–CH_2), 3.90 (t, 2H, N–CH_2), 6.85 (s, 1H), 7.04 (s, 1H), 7.49 (s, 1H). ^{13}C NMR (DMSO-d_6): δ 13.6, 19.4, 34.2, 46.8, 118.4, 129.5, 137.2, 173.6. Microanalysis: calcd. for $C_7D_{12}N_2$ (136.26): C 61.70, H 8.88, N 20.56; found: C 61.86, H 9.02; N 20.22.

1-Butyl-3-methylimidazolium acetate (BMIM-OAc-d_{18}, 9)

The same procedure was used as described above for the preparation of **8**, with the following alterations: 1-butylimidazole-d_{12} (**3**, 680 mg, 5 mmol), dimethylcarbonate-d_6 (**4**, 580 mg, 6.03 mmol), and acidic aluminum oxide (Brockmann grade I, 0.2 g) were used for the heterogeneous gas–solid phase reaction. The amount of recovered dimethylcarbonate-d_6 was 82 mg (0.85 mmol). Acetic acid-d_4 (**7**, 0.5 g, 7.8 mmol) was used to introduce the anion, and 1-butyl-3-methylimidazolium acetate-d_{18} (**9**) was obtained as colorless liquid (1.04 g) in 96% yield. ^{1}H NMR (CDC_{l3}, 0.1 M): δ 2.5 (s, br, H_2O). ^{13}C NMR (DMSO-d_6): δ 12.0 (sept., $J_{C,D}$ = 22 Hz, CD_3 in butyl), 18.1 (pent, $J_{C,D}$ = 20 Hz, CD_2 in butyl), 24.9 (sept, $J_{C,D}$ = 21 Hz, CD_3 in acetate),

30.8 (pent, $J_{C,D} = 20$ Hz, CD_2 in butyl), 34.8 (sept., $J_{C,D} = 21$ Hz, CD_3–N), 47.4 (pent, $J_{C,D} = 19$ Hz, CD_2–N), 121.5 (t, $J_{C,D} = 18$ Hz, CD), 122.8 (t, $J_{C,D} = 18$ Hz, CD), 138.0 (t, $J_{C,D} = 20$ Hz, CD), 174.0 (s, COO in acetate). Comparison to the non-deuterated product (BMIM-OAc): ^{1}H NMR (DMSO-d_6, 0.1 M): δ 0.84 (t, 3H, CH_3 in butyl), 1.19 (sext, 2H, CH_3–$C\underline{H}_2$ in butyl), 1.58 (s, 3H, CH_3 in acetate), 1.72 (pent, 2H, N–CH_2–$C\underline{H}_2$ in butyl), 3.88 (s, 3H, N–CH_3), 4.19 (q, 2H, N–CH_2), 7.92 (t, 1H, CH), 8.01 (t, 1H, CH), 10.33 (s, 1H, CH). ^{13}C NMR (DMSO-d_6): δ 13.2, 18.8, 26.1, 31.5, 35.4, 48.2, 122.3, 123.7, 138.2, 173.6. Microanalysis: calcd. for $C_{10}D_{18}N_2O_2$ (216.38): C 55.51, H 8.31, N 12.95; found: C 55.21, H 8.22; N 13.32.

2-^{13}C-1-butylimidazole (10)

Glyoxal (580 mg, 10 mmol), 1-butylamine (731 mg, 10 mmol), ammonium carbonate (961 mg, 10 mmol) and ^{13}C-paraformaldehyde (310 mg, 10 mmol) were charged into a teflon-coated stainless steel autoclave, and heated to 200°C for 4 h. The mixture was cooled to r.t. and distilled under reduced pressure. After a small amount of butylamine distilling off, the main fraction consisted of the target product (706 mg, 56%). The remainder mainly contained imidazole and non-identified condensation products of glyoxal. ^{1}H NMR ($CDCl_3$, 0.1 M): δ 0.94 (t, 3H, CH_3), 1.39 (sext, 2H, CH_3–$C\underline{H}_2$), 1.75 (pent, 2H, N–CH_2–$C\underline{H}_2$), 3.92 (t, 2H, N–CH_2), 6.86 (s, 1H, CH), 7.04 (s, 1H, CH), 7.49 (s, 1H, CH, $J_{C,H} = 144$ Hz). ^{13}C NMR (DMSO-d_6, 4 scans): δ 138.1. ^{13}C NMR (DMSO-d_6, 512 scans): δ 13.7, 19.4, 34.3, 46.6, 118.6, 129.4, 138.1, 173.1. Microanalysis: calcd. for $C_6^{13}CH_{12}N_2$ (125.19): C 67.70, H 9.74, N 22.56; found: C 67.88, H 9.53; N 22.14.

2-^{13}C-1-butyl-3-methylimidazolium acetate (BMIM-OAc, 11)

The same procedure was used as described above for the preparation of **9**, with the following alterations: 2-^{13}C-1-butylimidazole (**10**, 272 mg, 2 mmol), dimethylcarbonate (**4**, 290 mg, 3.02 mmol), and acidic aluminum oxide (Brockmann grade I, 0.2 g) were used for the heterogeneous gas–solid phase reaction. Excess dimethylcarbonate was not recovered. Glacial acetic acid (0.3 g) was used to introduce the anion, and 2-^{13}C-1-butyl-3-methylimidazolium acetate (**11**) was obtained as colorless liquid (303 mg) in 76% yield. ^{1}H NMR (DMSO-d_6, 0.1 M): δ 0.86 (t, 3H, CH_3 in butyl), 1.20 (sext, 2H, CH_3–$C\underline{H}_2$ in butyl), 1.59 (s, 3H, CH_3 in acetate), 1.74 (pent, 2H, N–CH_2-$C\underline{H}_2$ in butyl), 3.86 (s, 3H, N–CH_3), 4.20 (q, 2H, N–CH_2), 7.90 (t, 1H, CH), 8.00 (t, 1H, CH), 10.28 (d, 1H, CH, $J_{C,H} = 225$ Hz[14]). ^{13}C NMR (DMSO-d_6, 4 scans): δ 138.3. ^{13}C NMR (DMSO-d_6, 512 scans): δ 13.2, 18.9, 26.0, 31.8, 35.2, 48.4, 122.5, 123.7, 138.3, 174.6. Microanalysis: calcd. for $C_9^{13}CH_{18}N_2O_2$ (199.27): C 60.58, H 9.15, N 14.13; found: C 60.89, H 8.99; N 13.97.

Conclusion

Syntheses of the perdeuterated ionic liquids (ILs) 1-ethyl-3-methylimidazolium acetate-d_{14} (**8**) and 1-butyl–3-methylimidazolium acetate-d_{18} (**9**) started from imidazole-d_4, which was ethylated-d_5 (butylated-d_9, respectively) to give the corresponding perdeuterated 1-alkylimidazoles. Introduction of the 3-methyl substituent used dimethylcarbonate-d_6 according to a novel protocol, utilizing a clean and quantitative gas–solid reaction under elevated pressure, catalyzed by acidic aluminum oxide. The intermediate perdeuterated 1-alkyl-4-methylimidazolium methylcarbonates were neatly converted into the target acetates by addition of acetic acid-d_4, establishing methylcarbonate as a traceless replaceable counteranion. Construction of the 1-butylimidazole moiety with a ^{13}C-label at position 2 employed a four-component reaction with ^{13}C-paraformaldehyde as the source of the isotopic label. Conversion into the final target, 2-^{13}C-1-butyl-3-methylimidazolium acetate (**11**), proceeded in a way analogous to the perdeuterated ILs **8** and **9**.

Besides having the advantages of high reproducibility and good yields, the syntheses presented in Schemes 1 and 2 have two general benefits: they are cheap – which is a factor that should not be underestimated – and they are able to provide gram amounts of the perdeuterated products. The issue of availability in larger amounts is crucial in the case of NMR solvents: in standard NMR experiments about 0.5 mL of solvent are employed, which cannot be fully purified and recycled in all cases.

Acknowledgement

The financial support by the Austrian Fonds zur Förderung der wissenschaftlichen Forschung, project P-17426 and by the Christian Doppler Research Society (CD lab 'Advanced Cellulose Chemistry and Analytics') is gratefully acknowledged. The authors would like to thank Dr Andreas Hofinger, Department of Chemistry at the University of Agricultural Sciences, Vienna, for recording the NMR spectra.

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