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Fatty acid-based (bis) 6-membered cyclic carbonates as efficient isocyanate free poly(hydroxyurethane)s precursors

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(Bis) 6-membered cyclic carbonates were prepared from methyl 10-undecenoate, which is produced from ricinoleic acid, a main constituent of castor oil. Kinetics on these new fatty acid-based 6-membered cyclic carbonates revealed that they are much more reactive than their homolog 5-membered ones (30 times). Poly(hydroxyurethane)s (PHUs) were then synthesized from these bis 6 membered cyclic carbonates at a temperature as low as room temperature and in solvent or bulk. Unexpectedly, chemical gels were obtained. The latter were the consequence of side reactions of carbonate ring-opening with the hydroxyl groups of the formed poly(hydroxyurethane)s. Quenching with a large excess of hexylamine enabled the breaking-up of the gel with the formation of urea linkages.

The most explored alternative route to isocyanate free polyurethanes apply to vegetable oils is based on the reaction of 5-membered cyclic carbonates and amines.[1-4] This strategy has been investigated to prepare cross-linked as well as linear poly(hydroxyurethane)s (PHUs). Besides, the functionalization of triglycerides or derivatives with cyclic carbonates includes almost exclusively the epoxidation followed by carbonation of the double bonds. Therefore, the so-formed 5-membered cyclic carbonates are linked to one or two electron-releasing alkyl chain(s) (if synthesized from methyl undecenoate or methyl oleate respectively), which deactivate(s) the cyclic carbonate.[3,5-8] In addition, 5-membered cyclic carbonates are known to be stable over ring opening polymerization.[1,2,4] Thus, long reaction time, high polymerization temperatures and bulk conditions are necessary to obtain high conversion and subsequent high molar masses. While regarding the literature, few authors have developed PHUs from more reactive fossil-based cyclic carbonates; either with an electro-withdrawing group nearby the cyclic carbonate[9-20] or by using larger size ring cyclic carbonates.[20-24] For instance, Endo and coll. synthesized petroleum-based 6 and 7-membered cyclic carbonates and their corresponding poly(hydroxyurethane)s.[21-23]

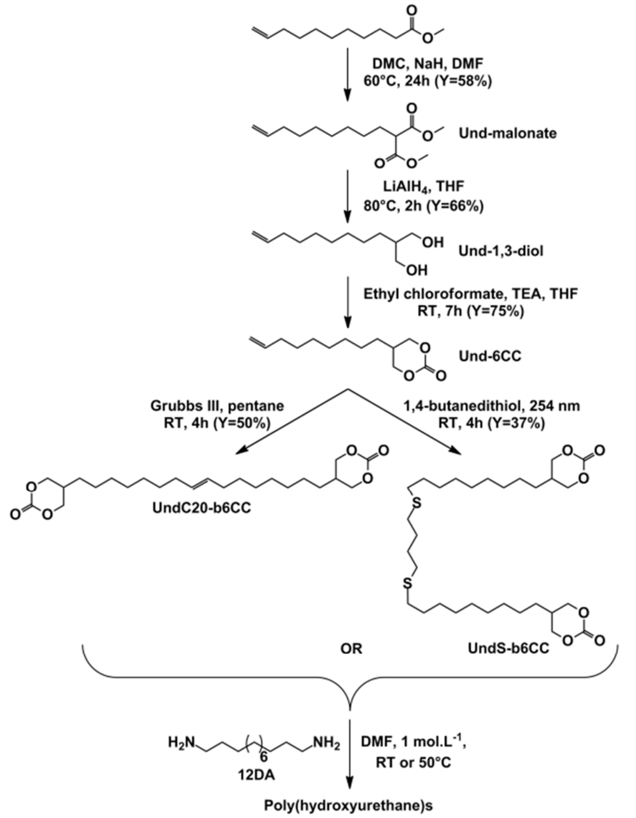
To our knowledge, no literature has been published on the preparation of vegetable oil-based bis 6-membered cyclic carbonates. In the present communication, the synthesis of 6-membered cyclic carbonate from methyl undecenoate (Und-6CC) is reported via malonate and 1,3-diol intermediates. To prepare the fatty acid-based malonate, the approach developed by Meier and coll[25,26] was preferred due to the use of non-toxic DMC. The coupling of Und-6CC was done under mild conditions, by metathesis or thiol-ene reactions allowing the preparation of bis 6-membered cyclic carbonates: UndC20-b6CC and UndS-b6CC respectively. In addition, a kinetic study on ring opening of carbonates by hexylamine has been performed to demonstrate the high reactivity of Und-6CC. The bis 6-membered cyclic carbonates were then examined in polymerization with dodecane-1,12-diamine (12DA) in solution. Unexpectedly, network has been obtained due to a side reaction of carbonate opening via hydroxyl functions. The bridge can be broken by urethanization and the released PHUs were then fully characterized.

Bis 6-membered cyclic carbonate (b6CC) synthesis

As illustrated in Scheme 1, the synthesis of Und-6CC involved three steps which are (i) the malonate synthesis from methyl undecenoate (Und-malonate), (ii) the reduction of the malonate into a 1,3-diol (Und-1,3-diol) and finally (iii) the cyclization into a 6-membered cyclic carbonate (Und-6CC). The chemical structures of the synthesized Und-6CC, UndC20-b6CC and UndS-b6CC compounds as well as the different intermediates were assessed by NMR and FTIR-ATR spectroscopies.

After optimization of reported conditions on dimethyl sebacate (see ESI), Und-malonate was synthesized at 60°C for 24 hours from methyl undecenoate using 40 eq. of DMC, 2.5 eq. of NaH and 1 eq. of DMF. The conversion of methyl undecenoate into Und-malonate was confirmed by ^{1}H NMR spectroscopy. After the work up, the percentage of unreacted methyl undecenoate (26.7%) was determined through ^{1}H NMR. Moreover, the Claisen-condensation side product was detected in proportion between 2.4% and 3% depending on the batch using the optimized conditions. After purification, Und-malonate was isolated with a yield of 58%. Reduction of Und-malonate was carried out under reflux for 2 hours using 4.1 eq. of $LiAlH_4$ in dried THF (Yield 66%). In FTIR-ATR, the disappearance of the band corresponding to the carbonyl and the appearance of a large band around 3280 cm^{-1} clearly indicate the reduction of malonate into diol. The synthesis of Und-1,3-diol was also confirmed by ^{1}H NMR. Cyclization of the Und-1,3-diol into

Und-6CC has been managed using ethyl chloroformate and a stoichiometric amount of TEA at room temperature in THF and diluted conditions. This method was preferred over non-phosgene route due to the compared high conversion obtained. However, non-phosgene routes can be also largely feasible as reported in the literature.[27-35] After the reaction, remaining ethyl chloroformate and Und-1,3-diol (3%) as well as side products formed (16% of dialkyl carbonate obtained by the reaction of Und-1,3-diol and 1 eq. ethyl chloroformate) were removed by flash chromatography. The purity of the final Und-6CC was 99.5% as determined by GC-FID (Yield 75%).



Scheme 1: General synthetic route to Und-6CC, UndC20-b6CC and UndS b6CC, as well as the poly(hydroxyurethane)s syntheses.

The monofunctional Und-6CC was then "dimerized" thanks to the terminal double bond on its long alkyl chain, by metathesis (UndC20-b6CC) or thiol-ene (UndS-b6CC) reactions. These reactions have gained attention in the last decades as green methodologies[36-38] and were chosen due to the mild conditions required. The Figures 1-(1) to 1-(3) present the stacked ^{1}H NMR respectively for the purified Und-6CC, UndC20-b6CC and UndS-b6CC. The metathesis reaction of Und-6CC was performed at room temperature in dried pentane with 3rd generation Grubbs catalyst (1/200). The reaction was driven thanks to the precipitation of the formed product. A conversion of 67% was achieved after 4 hours as estimated by ^{1}H NMR. The product was then purified with flash chromatography using a mixture of cyclohexane and ethyl acetate as eluent (Yield 50%).[39] In the line with the environmentally friendly and high efficiency process, the thiol-ene addition, which has already been valorized with vegetable oil derivatives,[38] was also carried out to couple Und-6CC. The thiol-ene reaction was carried out under UV irradiations at room temperature. The reaction was monitored with ^{1}H NMR spectroscopy with the disappearance of the double bond protons. The poor yield (37%) can be explained by the formation of side products presumably by ring opening of the cyclic carbonate by a nucleophile. Indeed, compounds with higher molar masses were present in the crude mixture as observed in SEC. (see ESI).

Fig. 2: Stacked ^{1}H NMR spectra of (1) Und-6CC, (2) UndC20-b6CC, (3) UndS-b6CC (analyses in $CDCl_3$) and (4) PHU-2 after 6 hours of polymerization (conversion of 76.6%) (analysis in $C_2D_2Cl_4$). (*) Remaining 12DA.

Cyclic carbonates reactivity toward hexylamine

In order to identify precisely the difference in reactivity between 6-membered and 5-membered cyclic carbonates, the monitoring of the kinetic of the reaction was followed *in situ* by NMR spectroscopy. Various cyclic carbonate substrates such as trimethylene carbonate (6CC), Und-6CC, ethylene carbonate (5CC) and Dec-5CC (obtained by carbonatation of 1,2-epoxy-9-decene as a 5-membered ring cyclic carbonate equivalent of Und-6CC) have been investigated on the reaction with hexylamine at 50°C and 1 $mol.L^{-1}$ in DMSO-d6, using TCB as internal reference. Otherwise mentioned, the ratio between cyclic carbonate and amine was 1:1 and confirmed by ^{1}H NMR. In the case of Und-6CC for instance, as the reaction was going, the signals for the protons $C\underline{H}_2$-O of the cyclic carbonate at 4.40 ppm and 4.09 ppm decreased. Moreover, three signals at 3.94 ppm ($C\underline{H}_2$-OCONH), 3.41 ppm ($C\underline{H}_2$-OH) and 2.98 ppm (CH_2-N$\underline{H}$COO), corresponding to the formation of the urethane appeared. Regarding the kinetic reaction order, best fits were obtained considering a second order in all cases (see ESI), as mostly reported in the literature.[23,40-42] Table 1 gives the estimated initial apparent reaction rate constants (k_{app}) obtained for the different cyclic carbonates.

As reported in the literature,[21-23] trimethylene carbonate appeared much more reactive than ethylene carbonate (k_{6CC}/k_{5CC}=2.5). In a similar way, Und-6CC demonstrated a higher reactivity than Dec-5CC, with reaction rate constants of 0.93 $L.mol^{-1}.h^{-1}$ and 0.03 $L.mol^{-1}.h^{-1}$ respectively ($k_{Und\text{-}6CC}/k_{Dec\text{-}5CC}$=31). In the case of 6-membered cyclic carbonate, the effect of an alkyl group with +I inductive effect in β position appears limited since the difference in reactivity between trimethylene carbonate and Und-6CC is quite low. However, the difference between the kinetic curves of ethylene carbonate and Dec-5CC clearly demonstrated the effect of a +I inductive effect substituent in α position on the reactivity of the 5-membered cyclic group. This observation underlined the low reactivity of the usually prepared fatty acid-based 5-membered cyclic carbonates.[1,2,4] An acceleration (deviation from the 2nd order) was observed with the 6-membered cyclic carbonates after a certain time (see ESI). On the opposite, a deceleration was observed for the 5-membered cyclic carbonates. These behaviours may be due to the interaction of the formed hydroxy groups with the reactant.

Table 1: Reaction rate constants obtained for the different model reactions at 50°C in DMSO

Cyclic carbonate (CC)	[CC] (mol.L^{-1})	T (°C)	k_{app} (L.mol^{-1}.h^{-1})[a]
Und-6CC	1	30	0.46
	1	50	0.93
	1	70	1.92
	0.2	50	0.15
	5	50	1.77
trimethylene carbonate 6CC	1	50	1.41
ethylene carbonate 5CC	1	50	0.56
Dec-5CC	1	50	0.03

[a] Calculated from the kinetics performed in NMR using a second order law. (see ESI for the equations)

The kinetic of the reaction between Und-6CC and hexylamine increases with the reactant concentration and temperature (see ESI). The reaction rate constants are 0.15, 0.93 and 1.77 L.mol^{-1}.h^{-1} at 0.2, 1 and 5 mol.L^{-1} respectively. This again testified a complex behavior and additional interactions between amines and/or carbonates with H donors appear to impact the kinetic rate. The reaction rate constants at 30, 50 and 70°C, are 0.46, 0.93 and 1.92 L.mol^{-1}.h^{-1} respectively for an initial concentration of 1 mol.L^{-1}. From the Arrhenius plot, the activation energy (Ea) can be estimated as 21 kJ.mol^{-1} for Und-6CC. Moreover, a slight deviation from the 2nd order can be noticed at 5 mol.L^{-1} and at 70°C. One should note that no urea formation was observed in all these experiments.

Finally the amine ratio has also an influence on the reaction kinetic between Und-6CC and hexylamine. As the starting concentration of amine is higher, the reaction rates increase. (see ESI) This underlines the positive effect of the amine on the kinetic.

Isocyanate free poly(hydroxyurethane)s

PHUs were synthesized from the two bis 6-membered cyclic carbonates: UndC20-b6CC or UndS-b6CC and dodecane-1,12-diamine (12DA) as comonomer. (see Scheme 1) The polymerizations were performed in DMF[43] at 1 mol.L^{-1}, at RT or 50°C. PHU formation was confirmed by FTIR-ATR by the appearance of bands at 1686 cm^{-1} and 1534 cm^{-1}, which correspond to the urethane linkage C=O and CN vibrations respectively. Besides, a large band at 3620 cm^{-1}-3158 cm^{-1} was attributed to the NH and OH vibrations. The chemical structures of the PHUs were also supported by NMR analyses, as illustrated in Figure 1-(4) for PHU-2. The signals for the protons corresponding to the opening of the 6-membered cyclic carbonate appeared in the ranges 4.00-4.15 ppm and 3.42-3.50 ppm. The formation of the urethane linkage was confirmed by the presence of the signal at 3.11 ppm, which corresponds to the protons $C\underline{H_2}$-NHC(O)O of the urethane function.

SEC data in Table 2, indicate the formation of PHUs with molar masses in the range 9 000 to 23 000 g.mol^{-1} after one day in solvent. As expected, higher molar masses were obtained at 50°C compared to room temperature, which is coherent with the different conversion. Besides, the reactivities of UndC20-b6CC and UndS-b6CC are similar as can be seen in the Table 2. The dispersities were in the range 1.4-1.7 while in step-growth polymerization, the dispersity must theoretically reach 2. Thus by improving the reaction conditions, the molar masses could still be improved. In conclusion, we successfully polymerized in mild conditions (solvent and at low temperature: RT-50°C) fatty acid-based bis 6-membered cyclic carbonates.

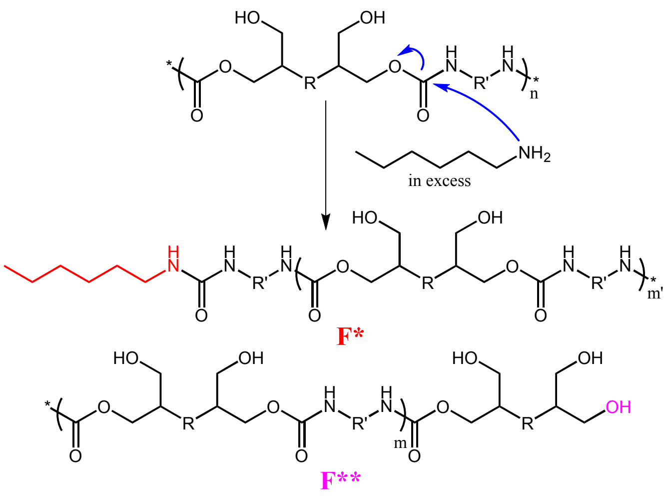
Table 2: Molar masses and dispersity of the PHUs from 6-membered cyclic carbonate polymerized in DMF (1mol.L^{-1}).

PHU	b6CC	T °C	Time	Conv. (%)[a]	$\bar{M}_n$ (g.mol^{-1}) [c]	Đ
1	UndC20 -b6CC	30	30min	0	3 400	1.0
			4h	1.3	6 700	1.0
			6h	3.3	9 600	1.1
			1d	43.4	8 900[d]	1.2
			2d	89.3	14300[d]	1.4
2	UndC20 -b6CC	50	30min	14.0	6 700	1.0
			4h	66.5	9 300[d]	1.2
			6h	76.6	11500[d]	1.2
			8h	83.2	12 800[d]	1.4
			1d	90.3^2	21600	1.5
			2d	-	22300	1.3
3	UndS-b6CC	50	30min	8.2	7 000	1.0
			4h	46.9	8200[d]	1.0
			6h	63.3	6500	1.0
			8h	73.5	11100[d]	1.2
			1d	90.0[b]	22600	1.7
			2d	-	20000	1.4

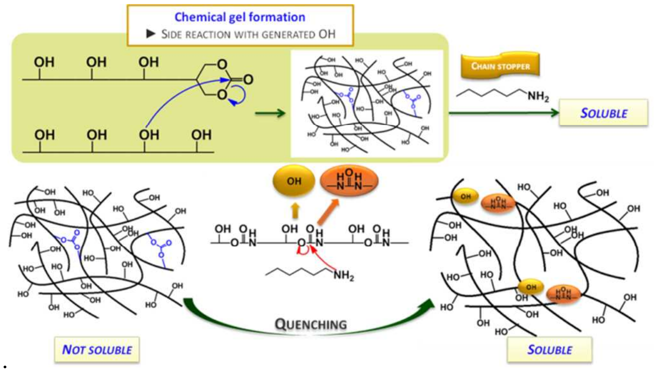
[a] Calculated by ^{1}H NMR. [b] Calculated by FTIR-ATR. [c] SEC in DMF with 1wt% LiBr - calibration PS standards. [d] Multi modal molar masses.

After one day at 50°C, the polymerization mixtures appeared as gels and were not soluble anymore, which can be explained by the formation of side reactions between the hydroxyl groups present in the polymer backbone and the remaining cyclic carbonates. This hypothesis has been confirmed for model compounds trimethylene carbonate and hexylamine, by the detection of side products thanks to ESI-TOF MS, showing the carbonate ring-opening by alcohol (see ESI). Similar side products were detected with the Und-6CC. These carbonate linkages between PHU chains explain the 3D network formation during the bis-carbonate / bisamine polymerization.

After quenching, the polymerization medium with a large excess of hexylamine, the polymers were surprisingly fully soluble again and MALDI-TOF MS analyses were carried out on the PHUs (Figure 2), (see also ESI for MALDI-TOF MS of quenched PHU-2 and detailed explanations). While analyzing the different signals, three PHU families (F1-3) were detected (see ESI): (F1) terminated with two cyclic carbonates quenched, (F2) with one cyclic carbonate quenched and one amine and (F3) with two amines. In the particular case of PHU-2, the isomerizations that have taken place during the metathesis were clearly visible with peaks sets separated by 14. The repeated unit was clearly visible for both PHU-2 (M_{unit}=624 + x*M_{CH2} g.mol^{-1}) and PHU-3 (M_{unit}=775 g.mol^{-1}). Moreover, smaller signals assignable to urea side reactions (see Scheme 2) were also observable, corresponding both to the formation of urea (F*) and the generation of the alcohol (F**) from F1 and F2 families. The fact that F3* was not visible confirmed that the side reactions occur during the quenching of the sample and not during the polymerization. These side reactions of trans-urethanization and/or urea formation explained the breaking-up of the chemical gel formed during the polymerization (see Scheme 3).



Scheme 2: Generation of F* and F** from F2 PHU family during the quenching with an excess of hexylamine.



Scheme 3: Hypothesis of chemical gel formation and reactions occurring during the quenching allow solubility.

Finally, the PHUs from UndC20-b6CC were amorphous and present glass transition temperatures around 0°C determined by DSC (see ESI). The PHU from UndS-b6CC was amorphous as well, with a glass transition temperature of -20°C. This lower Tg can be explained by the presence of the sulfur atom, which is known to impart flexibility to the polymer chains. PHUs exhibited degradation temperature up to 310°C under N_2 (see ESI).

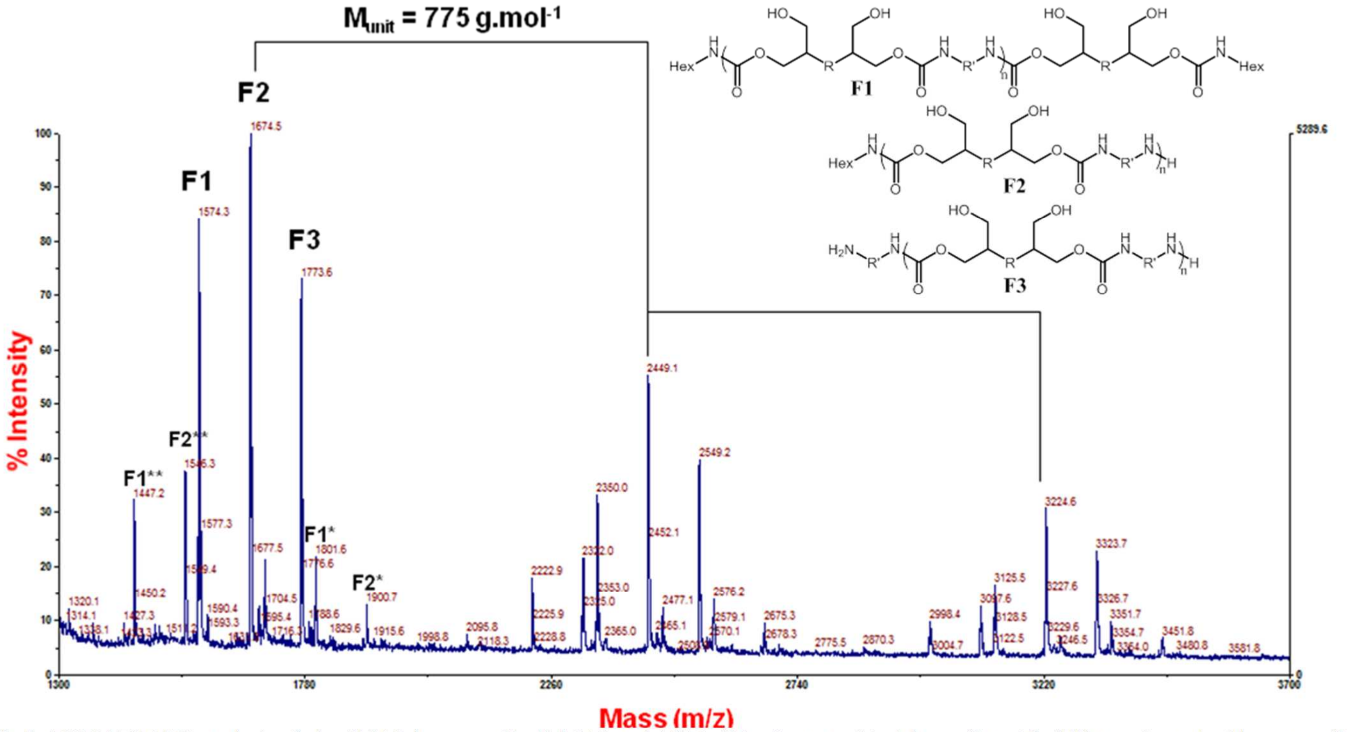


Fig.2: MALDI-TOF MS analysis of the PHU-3 between UndS-b6CC and 12DA. (Matrix trans-3-indoleacrylic acid). (F1) terminated with two cyclic carbonates quenched, (F2) with one cyclic carbonate quenched and one amine and (F3) with two amines

Conclusions

In conclusion, two bis 6-membered cyclic carbonates were synthesized from methyl undecenoate via malonate, 1,3-diol and monofunctional 6-membered cyclic carbonate intermediates. The latter was coupled by metathesis or thiol-ene reactions to produce the two bis 6-membered cyclic carbonates, one with an internal double bond (UndC20-b6CC) or one with sulfur atoms (UndS-b6CC). The model reaction kinetics were performed to validate the higher reactivity ($k_{Und\text{-}6CC}/k_{Dec\text{-}5CC}$=31) of the fatty acid-based 6-membered cyclic carbonate compared to the 5-membered ones.

The synthesized bifunctional 6-membered cyclic carbonates were effectively used as building blocks for thermoplastic isocyanate free PHUs in combination with dodecane-1,12-diamine as comonomer. Molar masses up to 23 000 g.mol^{-1} (dispersity of 1.7) were obtained after only one day in DMF (1 mol.L^{-1}) at 50°C. At higher conversion, a chemical gel is obtained probably due to cyclic carbonate ring opening by the formed hydroxide. Finally, results demonstrated the possibility to break-down this network by adding in second step a mono-amine via urea formation.

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Electronic Supplementary Information (ESI) available: [Experimental methods, NMR, SEC, MALDI-TOF spectra of the different compounds]. See DOI: 10.1039/c000000x/

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