Hyperbranched Thermolabile Polycarbonates Derived from a A_2+B_3 Monomer System

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Summary: Hyperbranched polycarbonates were synthesized successfully via the A_2 + B_3 route by the reaction of a bis(carbonylimidazolide) with triethanolamine. These polymers containing the carbonate group as thermolabile moiety are decomposing into volatile products at around 200°C. The polymers were characterized with $^1H/^{13}C$ NMR spectroscopy, SEC, DSC and TGA techniques.

Keywords: degradation; hyperbranched; NMR; polycarbonate; thermal properties

Introduction

Developing thermolabile polymers is of interest for several applications like imaging[1] or for use as porogen in polymer matrices.[2] Nanoporous polymers have a high potential e.g. as ultra low dielectric constant material for use in microelectronic devices.[3,4] In this application the thermolabile polymer used as porogen has to fulfill several conditions. To achieve voids in nanometer scale the porogen or template has to be miscible with the polymeric matrix material. Furthermore, its decomposition temperature has to be below the glass transition temperature (T_g) and above the crosslinking temperature of the matrix materials. Hyperbranched polymers are of interest as pore template due to their globular structure and molecular dimensions and the high density of functional groups in the structure. They are usually much easier synthesized than dendrimers but exhibit a not perfect, irregular branched structure and a broad molar mass distribution. Due to the possibility of incorporating many thermally labile parts in the hyperbranched structure the polymer should decompose into small volatile products which can diffuse out of the matrix leaving the desired voids. In previous studies, photo- and thermally labile triazene units could be incorporated into hyperbranched polyesters[5] and the material was

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successfully incorporated and decomposed in a tetramethyldivinylsiloxane-bisbenzocyclobutane (DVS-BCB) matrix leading to reduced dielectric constants.[6]

Polycarbonates are known to have sharp decomposition temperatures depending on the structural environment of the carbonate group.[7, 8, 9] Polycarbonates derived from tertiary alcohols have lower decomposition temperatures as those derived from primary alcohols and the decomposition temperature can be further reduced even below 100°C in the presence of acids.[1] Aromatic polycarbonates are thermally quite stable. Until now only hyperbranched polycarbonates derived from phenolic structures have been synthesized[10, 11] which seem not to be suitable for use as porogen.

Experimental

Materials: Dry toluene (Fluka), potassium hydroxide (Fluka, 86%), 2,5-dimethyl-2,5-hexanediol (Fluka, 97%) and carbonyldiimidazole (Merck, 98%) were used as received. Dichloromethane (Acros) and triethanolamine (Fluka, 99%) were dried before use over molecular sieve (4 Å).

Measurements: The NMR measurements were performed with a Bruker DRX 500 NMR spectrometer at 500.13 MHz for ^1H NMR spectra and at 125.75 MHz for ^{13}C NMR spectra. DMSO-d_6 was used as solvent for all NMR experiments. For internal calibration the solvent peaks of DMSO were used: δ (^{13}C) = 39.60 ppm; δ (^1H) = 2.50 ppm. Signal assignment was done by ^1H-^1H-COSY, ^1H-^{13}C-HMQC and ^1H-^{13}C-HMBC 2D NMR experiments using standard pulse sequences provided by Bruker. Thermal analysis were carried out with a Perkin Elmer TGA 7 instrument at a heating rate of 10 K/min for the dynamic measurement and a DSC 7 at a scan rate of 20 K/min. SEC was performed with MERCK LiChrogel PS40-column with a flow rate of 1.0 ml/min with linear polystyrene as standard and a Knauer RI-detector. Melting points were determined with Mettler Toledo FP62.

Synthesis of 2,5-dimethyl-2,5-hexanedicarbonylimidazole (3)

A solution of 8.53 g (58 mmol) 2,5-dimethyl-2,5-hexanediol and 20.11 g (120 mmol) carbonyldiimidazole (CDI) were dissolved in 150 ml dry toluene under argon atmosphere. To the solution 40 mg (1 mmol) KOH were added. The mixture was stirred for 5 hours at 60°C. After cooling to room temperature the reaction mixture was poured onto ice. After separation of the organic layer the aqueous layer was extracted twice with 20 ml toluene. The organic layers were unified and washed until neutralization. The organic layer was dried over anhydrous sodium sulfate. After evaporation of the solvent the crude product was recrystallized from a hexane/ethylacetate mixture to give colorless crystals (yield: 94%). mp: 93.8°C

^{1}H NMR (ppm, DMSO-d_6): δ = 8.17 (s, 2H, H_1); 7.51 (s, 2H, H_3); 7.06 (s, 2H, H_2); 2.00 (s, 4H, H_7); 1.58 (s, 12H, H_8).

^{13}C NMR (ppm, DMSO-d_6): δ = 146.74 (C_4); 137.13 (C_1); 130.11 (C_3); 117.44 (C_2); 87.07(C_5); 33.78(C_7); 25.41(C_6).

Synthesis of the hyperbranched polycarbonate 5 (selected example)

4 g (12 mmol) of **1** and 1.16 g (8 mmol) triethanolamine **(4)** were dissolved in 20 ml dichloromethane under argon atmosphere. 14 mg (0.2 mmol) KOH were added and the mixture was refluxed for 12 h. After cooling to room temperature the mixture was poured onto ice. The organic layer was separated and the aqueous was extracted two times with 20 ml dichloromethane. The organic layers were unified and washed with water till neutralization. The organic layer was dried with sodium sulfate and evaporation of the solvent gave 2 g crude colorless oily product. For purification the product was dissolved in dichloromethane and precipitated in cold ether to give 0.98 g of polymer. (M_w: 10400 g/mol; M_n: 3300 g/mol)

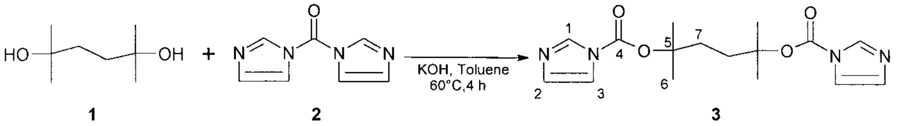
^{1}H NMR (ppm, DMSO-d_6): δ = 8.16 (H_{14}); 7.51 (H_{16}); 7.03 (H_{15}); 4.25 (H_1); 4.07 and 3.99 (H_5, also in cyclic structures); 3.41 (H_2); 2.75 and 2.71 (H_4, also in cyclic structures); 2.58 (H_3); 1.88 (H_9 and H_{10}); 1.85 (H_{17} in $[a_2b_2]_c$); 1.74 (H_{17}); 1.55 (H_{12}); 1.39 – 1.34 (H_8 and H_{18}, also in cyclic structures).

^{13}C NMR (ppm, DMSO-d_6): δ = 152.85, 152.78, 152.71 (all C_6); 146.6 (C_{13}); 137.1 (C_{14}); 130.0 (C_{16}); 117.4 (C_{15}); 86.9 (C_{11}); 82.8 (C_7); 64.8 – 64.3 (several signals, C_5, also in cyclic structures); 59.40 ($b_2\mathbf{B}$), 59.34 ($b\mathbf{B}_2$), 58.70 ($[a_2b_2]_c\mathbf{B}$) (all C_2); 56.96 ($b\mathbf{B}_2$), 56.71 ($b_2\mathbf{B}$), 58.70 ($[a_2b_2]_c\mathbf{B}$) (all C_3); 53.45 ($[a_2\mathbf{b}_2]_cB$), 53.30 ($[a_2\mathbf{b}_2]_cb$), 53.06 ($\mathbf{b}B_2$), 52.90 ($\mathbf{b}_2B$), 52.8 – 52.6 ($\mathbf{b}_3$), 51.52 $[a_2b_2]_c\mathbf{b}$)

(all C_3); 34.20 (C_{10}); 33.7 (C_{17}); 33.2 (C_9); 31.70 and 31.68 (C_{17} in $[a_2b_2]_c$); 26.59 (C_{18} in $[a_2b_2]_c$); 25.55 and 25.50 (C_8); 25.4 (C_{18}); 25.28 (C_{12}).

Results and Discussion

There are two ways to build up hyperbranched structures: first the classical AB_n (with $n \geq 2$) route which can not lead to crosslinked products according to Flory [12] and second the $A_n + B_m$ (with $n = 2$ and $m \geq 3$) approach. The second approach offers an easier accessibility of monomers but during the polymerization crosslinking might take place and the resulting structures are far more complex. The $A_2 + B_3$ approach was followed for the synthesis of the hyperbranched polycarbonates. The A_2 monomer **(3)** was obtained analogue to Rannard et al.[13] from the reaction of 2,5-dimethyl-2,5-hexandiol **(1)** with CDI **(2)** in toluene with a catalytic amount of KOH (Scheme 1).

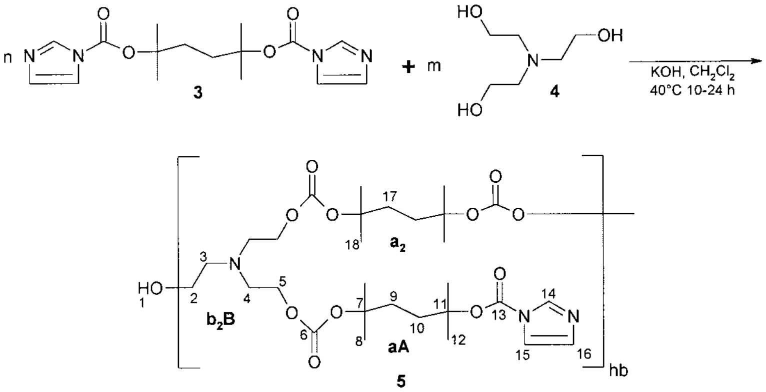


Scheme 1: Synthesis of $\mathbf{A_2}$

The polymerization reaction was carried out using different ratios n : m (with n = 3 to 1 and m = 1 to 2) of A_2 and B_3 and different concentrations (0.01 wt% to 15 wt%) of **3** in dichloromethane under reflux (Scheme 2). Using higher concentrations of **3** leads to insoluble products. Not converted B_3 monomer was removed during work up by washing with water and remaining A_2 monomer was removed by precipitating the crude polymer from dichloromethane into cold diethylether. With the precipitation also a fractionation of the polymer took place resulting in a high molecular weight fraction which was not soluble in diethylether and a low molecular weight fraction which could be recovered from the diethylether (Fig. 5). The resulting polymers are viscous colorless substances.

In the following the results obtained for a hyperbranched polycarbonate prepared in a 15 wt%

solution of **3** in dichloromethane with a ratio A_2 : B_3 of 3:2 are discussed.

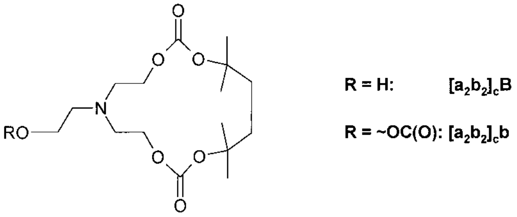


Scheme 2: Polymerization reaction leading to polycarbonate **5**

NMR Analysis

NMR analysis proved to be highly effective for the structural characterization of hyperbranched structures.[5,14] The ^1H NMR spectrum of polymer **5** (Fig. 1) proves the presence of all the expected structural units and allows the quantification both of unreacted A and B units. More structural information can be obtained by ^{13}C NMR spectroscopy looking at specific reaction mixtures. Depending on the different degree of conversion of B units it can be distinguished between the B_3 (monomer), bB_2 and b_2B structures from the ^{13}C signals of the B unit (Fig. 2a). In contrast, the signals of the b units are less sensitive on different substitution patterns. Furthermore, it can be differentiated between unreacted A_2 monomer, half reacted aA where one carbonylimidazole group has reacted with one hydroxy group and a_2 where both carbonylimidazole groups have reacted with hydroxy groups as shown in the spectrum in Figure 2b, obtained from a reaction mixture with a high excess of A_2. In conclusion, the ^{13}C NMR spectra prove the existence of branched structures.

Additional signals were observed besides the ones of the regular structure shown in Scheme 2. These are caused by further structural units within the branched macromolecule. From the observed chemical shift effects, signal intensity ratios and from 2D NMR it can be concluded that these signals are caused by the cyclic structures $[a_2b_2]_cB$ or $[a_2b_2]_cb$ (Scheme 3), which are formed when both A functionalities of an A_2 monomer react with the same B_3 monomer. As expected the content of this structure increases with decreasing concentration of monomers the feed. Whereas this smallest cyclic system can still be identified by NMR spectroscopy, larger ring systems result in the same chemical shifts as non-cyclic structures.



Scheme 3: Ring formation

Ring formation has consequences for the determination of the number of terminal groups and the calculation of the degree of branching. The structure $[a_2b_2]_cb$ (Scheme 3) appears with respect to the B_3 monomer as dendritic unit but is a terminal unit and terminates the polymer growth. Similar considerations are possible for larger cyclic structures. So the calculation of a meaningful degree of branching is not possible for this polymer system.

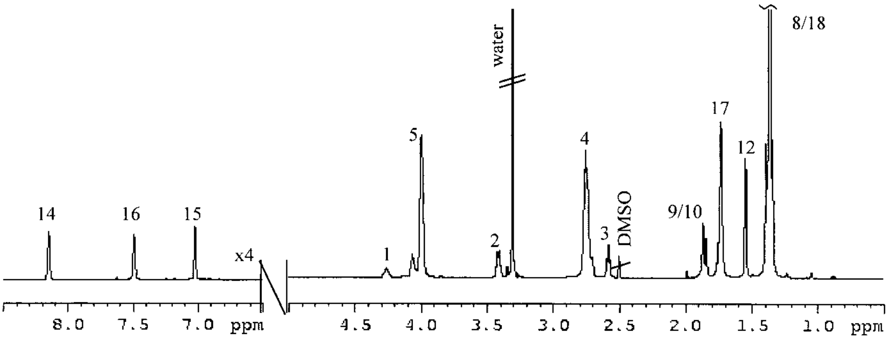


Fig. 1: ^{1}H NMR spectra of hb polycarbonate **5** (A_2:B_3 = 3:2, 15 wt% in CH_2Cl_2) in DMSO-d_6 (for peak assignment see Scheme 2)

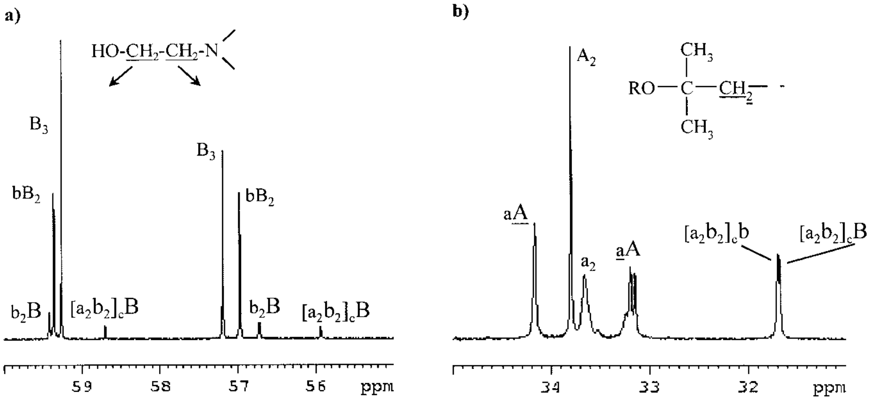


Fig. 2: ^{13}C NMR spectra regions of different reaction mixtures: a) A_2:B_3 = 1:2 and b) A_2:B_3 = 2:1 showing characteristic signals for differently substituted B_3 units a) and A_2 units b) in DMSO-d_6

Thermal behavior

The thermal behavior was studied by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The DSC of the polymer **5** shows a T_g of -14°C. The dynamic TGA measurement indicates that the polymer decomposes in three steps. The main process was found at 221°C and the decomposition is completed at 250°C (Fig. 3). With isothermic TGA measurements it is possible to determine the decomposition velocity at a certain temperature. The isothermal measurement at the beginning of the main decomposition step at 200°C shows that the decomposition goes near to completion in about 15 min (Fig. 4). Therefore the polycarbonate should be suitable to function as porogen in matrices.

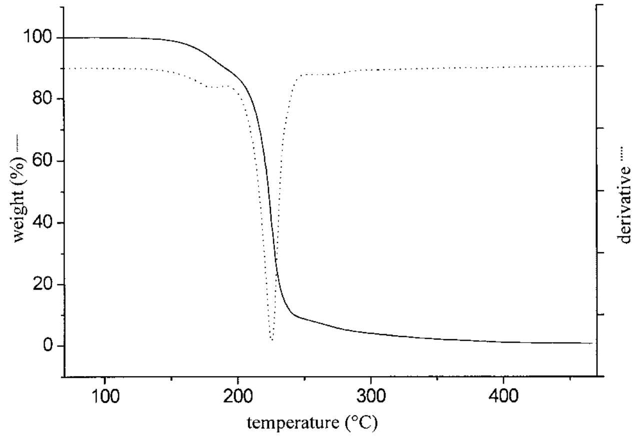


Fig. 3: Dynamic TGA-measurement of A_2+B_3 polycarbonate **5** at a heating rate of 10 K/min

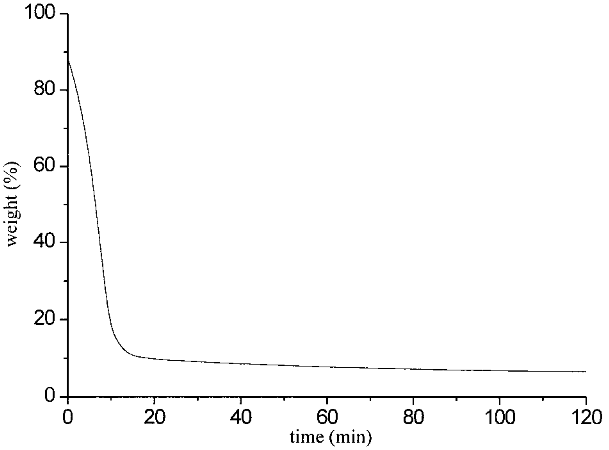


Fig. 4: Isothermic TGA-measurement of A_2+B_3 polycarbonate **5** at 200°C

Size Exclusion Chromatography - Analysis

In general size exclusion chromatography (SEC) is not suitable for molar mass determination of hyperbranched polymers. The SEC is calibrated with linear polystyrene as standard and, due to the more compact structure of hyperbranched polymers in comparison to linear polymers, the molar mass should be higher than the results indicated by SEC. Therefore the measured molar masses of M_n = 3300 g/mol and M_w = 10400 g/mol of the precipitated fraction of hb polycarbonate **5** should be considered as probably too low compared to the real molar mass. The broad polydispersity of 3.2 is usual for hyperbranched polymers obtained by A_2 + B_3 polymerization.

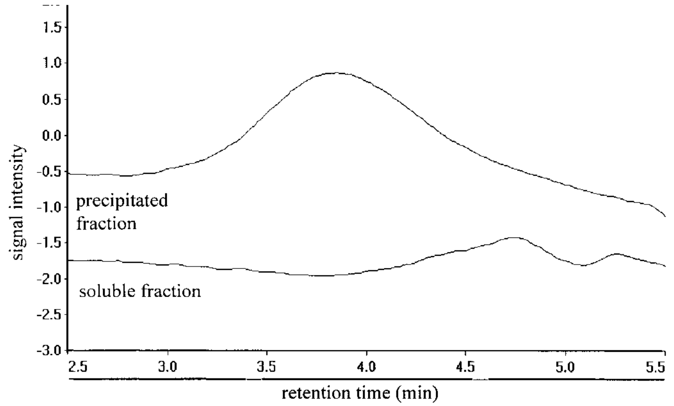


Fig.5: SEC curves of A_2 + B_3 polycarbonate **5** (M_n of the precipated fraction = 3300 g/mol)

Conclusions

Fully soluble hyperbranched polycarbonates were synthesized successfully via the A_2 + B_3 route by the reaction of a bis(carbonylimidazolide) with triethanolamine. SEC molar masses (M_w) of up to 10000 g/mol were achieved. NMR analysis proved the existence of the branched structure but also the presence of internal cyclics. These low T_g polymers (T_g = -14 °C) containing the carbonate group as thermolabile moiety are decomposing completely into volatile products at about 200°C. Therefore the use of these thermolabile highly branched structures as globular polymeric template for the preparation of nanoporous polymeric materials seems possible.

Acknowledgement

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