Reversible Click Chemistry at the Service of Macromolecular Materials. 2. Thermoreversible Polymers Based on the Diels-Alder Reaction of an A-B Furan/Maleimide Monomer

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INTRODUCTION The dwindling of fossil resources, together with their unpredictable price fluctuations, raise serious questions about the medium-term pursuit of their exploitation, whether as a source of energy and/or as purveyors of organic commodities and materials, with the additional concern of the ecological impact related to their exploitation. Hence, the ensuing surge of initiatives devoted not only to the search for alternative sources of energy providers, but also to the context of polymers from renewable resources, namely the vegetable biomass.^{1,2} Among these, polymers from furan monomers constitute a unique class of materials based on vegetable renewable resources, whose structures can simulate virtually all their current fossil-derived counterparts.^{2,3}

One of the peculiar chemical features of the furan heterocycle is its pronounced dienic character, which makes it particularly suited to intervene in the [4 + 2] Diels-Alder (DA) cycloadditon as the dienic reagent. The DA reaction is a splendid example of reversible click chemistry, which has opened new ways to synthesize polymers with unique properties, including self-mendability and network recyclability through reversible cross-linking.^{2–4} Scheme 1 illustrates the essence of the mechanism involved in the DA and retro-DA reactions, between a furan and a maleimide end-group:



SCHEME 1 The DA equilibrium between growing species bearing, respectively, furan and maleimide end groups.

The emphasis here is on the role of the temperatures chosen to shift drastically the equilibrium from predominant adduct formation (polymerization–DA), viz. around 65 °C for a reasonable reaction rate, to the predominant reversion to its precursors (depolymerization—retro-DA), viz. around 110 °C. We have undertaken a systematic study on the application of the DA and retro-DA reactions, first to model monofunctional systems, then to linear polymerizations with difurans (A-A) and bismaleimides (B-B),⁵ as well as to non-linear systems using A₃ and B-B monomers.⁶ It is from our preliminary study on equilibrium position and kinetics related to the model compounds⁵ that the choice of both forward and backward reaction temperatures was made for the subsequent polymerizations^{5,6} and hence also for this investigation.

The use of A-B monomers bearing both the furan and the maleimide moieties in their structure represents an interesting alternative for linear polymerizations, because it ensures the ideal initial stoichiometry. The synthesis of a monomer of this type was first explored by Mikroyannidis,⁷ who investigated a series of such structures comprising different bridging moieties. However, the spectroscopic characterization of the monomers did not provide convincing evidence in favor of the expected structures, and no NMR spectra of the final materials could be taken, because they were not soluble in any tested solvent, despite the fact that they should all have had a linear macromolecular structure, given the difunctional character of their precursors. A few years later, the same issue was briefly investigated by Goussé and Gandini,8 who prepared, characterized, and polymerized monomer I, but the single methylene bridge joining the two complementary DA moieties made the molecule difficult to handle, and the study was not pursued. More viable AB structures (II) have now been synthesized in our laboratory using aminoacids as precursors, providing, on the one hand, stable

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monomers and, on the other hand, the possibility of using both precursors derived from renewable resources.



The present communication deals specifically with monomer II with n = 2.

EXPERIMENTAL

Materials and Instrumentation

3-Aminopropanoic acid (β -alanine, 99+%), *exo*-3,6-epoxy-1,2,3,6-tetrahydrophthalic anhydride (furan-maleic anhydride DA adduct, 90%) and anhydrous sodium carbonate were purchased from Acros Organics. *N*,*N'*-dicyclohexylcarbodii-mide (DCC, 99%), 4-dimethylaminopyridine (DMAP), and 1,1,2,2-tetrachloroethane- d_2 (TCE- d_2) were purchased from Sigma-Aldrich. All reagents and solvents (analytical grade) were employed as received. The IR measurements were performed using a Mattson 7000 spectrophotometer working in the ATR mode. ¹H NMR and ¹³C NMR spectra were acquired with a Brucker advance spectrometer working, respectively, at 300.13 MHz and 75.47 MHz.

Synthesis of 3-(exo-3,6-epoxy-1,2,3,6tetrahydrophthalimido)propanoic Acid (3)

 β -alanine (1) (2.41 g, 27.1 mmol) was slowly added to a solution of furan-maleic anhydride DA adduct (2) (4.5 g, 27.1 mmol) and Na₂CO₃ (2.87 g, 27.1 mmol) in MeOH (200 mL). The solution was stirred at 56 °C for 6 days. Then the solvent was removed under reduced pressure, and the white residue dissolved in 100 mL of CH_2Cl_2 and washed with 3 \times 100 mL of 0.6 M aqueous HCl. The organic layer was dried over anhydrous sodium sulphate and concentrated under reduced pressure. The expected product was obtained as white crystals with a yield of 3.77 g (59.0%).⁹ IR (ATR): 3050 (0-H), 3014 (=CH), 2926 (asCH₂), 2852 (sCH₂), 1779, 1702 and 1689 (C=O), 1258 and 1161 (C-O), 877 (C-H) cm⁻¹. ¹H NMR (acetone- d_6): δ (ppm) = 2.55 (t, J = 7.75 Hz; NCH₂CH₂CO), 2.92 (s; =CHCHCHC(0)N), 3.67 (t, J = 7.76 Hz; NCH₂CH₂CO), 5.13 (s; =CHCHCHC(0)N), 6.58 (s; =CHCHCHC(0)N). 13 C NMR (acetone- d_6): δ (ppm) = 32.0 (NCH₂CH₂CO), 34.8 (NCH₂CH₂CO), 48.2 (=CHCHCHC(0)N), 81.6 (=CHCHCHC(0)N), 137.3 (=*C*HCHCHC(0)N), 171.8 (C=O_{acid}), 176.8 (C=O_{imide}).

Synthesis of (2-furfuryl)-3-(exo-3,6-epoxy-1,2,3,6-tetrahydrophthalimido)propanoate (5)

A solution of **3** (4.74 g, 20 mmol), furfuryl alcohol (**4**) (5.89 g, 60 mmol) and DMAP (1.95 g, 16 mmol) in dry dichloromethane (20 mL) was prepared and after 5 min. of stirring, DCC (4.54 g, 22 mmol) was added to it, and the reaction mixture left overnight at room temperature under N₂. The precipitated dicyclohexylurea (DCU) formed during the reaction was removed by filtration and the filtrate washed with 0.5 M aqueous HCl (2×5 mL) and a saturated sodium hydrogen carbonate aqueous solution (2×5 mL). Additional DCU was precipitated and removed by filtration. The organic phase was dried over anhydrous sodium sulfate and concentrated under reduced pressure. The expected product was obtained as a yellow solid with a yield of 5.66 g (90.0%).¹⁰ Compound **5** was stable and could not undergo DA condensation since the maleimide moiety was protected as its furan adduct.

IR (ATR): 3124 (furan =CH), 3000 (=CH), 2933 (asCH₂), 2857 (sCH₂), 1775, 1736 and 1693 (C=O), 1503 (furan C=C), 1274, 1226, and 1150 (C-O), 1016 (ring breathing), 915, 811, and 734 (furan C-H), 877 (C-H), 593 (ring deformation) cm⁻¹. ¹H NMR (CDCl₃): δ (ppm) = 2.64 (t, *J* = 7.33 Hz; NCH₂CH₂CO), 2.82 (s; =CHCHCHCO), 3.78 (t, *J* = 7.34 Hz; NCH₂CH₂CO), 5.05 (s; OCH₂-2-Furan), 5.26 (s; =CHCHCHCO), 6.35 (d, *J* = 3.29 Hz; furan H3), 6.40 (dd, *J* = 3.24, 1.86 Hz; furan H4), 6.52 (s; =CHCHCHCO), 7.42 (d, *J* = 1.60 Hz; furan H5). ¹³C NMR (CDCl₃): δ (ppm) = 31.8 (NCH₂CH₂CO), 34.5 (NCH₂CH₂CO), 47.3 (=CHCHCHC(O)N), 58.3 (OCH₂-2-Furan), 80.8 (=CHCHCHC(O)N), 110.6 and 110.9 (furan C3 and C4), 136.5 (=CHCHCHC(O)N), 143.3 (furan C5), 149.0 (furan C2), 170.1 (C=O_{ester}), 175.8 (C=O_{imide}).

Polycondensation of the A-B Monomer (Deprotected 5)

A typical procedure follows: 0.6 M solution of **5** (0.19 g, 0.6 mmol) in TCE- d_2 (1.0 mL) was prepared and left at 110 °C for 24 h under N₂ atmosphere. This step promoted the retro-DA elimination of furan from the adduct moiety and the ensuing maleimide function was hence set free to polymerize. The solution was transferred to a NMR tube and the corresponding ¹H NMR spectrum taken immediately at room temperature. The tube was then left in a bath at 65 °C for 96 h, while spectra were taken at regular intervals.

RESULTS AND DISCUSSION

Scheme 2 depicts the steps leading to the protected A-B monomer **5**. Its FTIR spectrum was consistent with its expected structure, through the presence of all the relevant peaks and the absence of the OH and C=O bands of the



SCHEME 2 Synthesis of the protected A-B monomer 5.



SCHEME 3 Deprotection of 5 and A-B polymerization.

carboxylic moiety. This was further corroborated by both its ¹H NMR and ¹³C NMR spectra. In the ¹H NMR spectrum, the most relevant features included the methylene protons of the ester function at 5.05 ppm (OCH₂-2-Furan) and the furan protons at 6.4 (H4), 6.3 (H3), and 7.4 (H5) ppm. The ¹³C NMR spectrum displayed, among others, resonances at 58.3 ppm (OCH₂-2-Furan), 110.6 and 110.9 (furan C3 and C4), 143.3 (furan C5), 149.0 (furan C2) and the *C*=O_{ester} peak at 170 ppm.

After the *in situ* deprotection of the maleimide moiety at high temperature, followed by cooling to 65 °C to promote polymerization of the ensuing A-B monomer, the polycondensation (Scheme 3) was followed by ¹H NMR spectroscopy (Fig. 1).

Figure 1 shows the ¹H NMR spectra of the initial A-B solution taken after the deprotection process as well as the progression of its DA polycondensation. Apart from traces of



FIGURE 1 ¹H NMR spectra taken during the AB-polimerization at 65 °C (*TCE-d₂; **traces of DCU), where t = 0 corresponds to the initial spectrum of the solution containing the deprotected A-B monomer 6 run at room temperature. The top spectrum was taken after 3 days at 65 °C, followed by 11 days at room temperature.



FIGURE 2 ¹H NMR spectra taken during the A-B retro-DA depolymerization (24 h at 110 °C). The spectrum run after 6 h shown here was essentially identical to that taken after 24 h. The top spectrum represents the second DA polycondensation and was taken after 3 days at 65 °C (*TCE-d₂; **traces of DCU).

residual DCU ($\delta = 1.10$ –1.74 ppm) and evidence of the incipient polymerization (see discussion below), the initial spectrum clearly confirmed the presence of the unprotected A-B monomer through the maleimide C*H*=C*H* protons at δ 6.8 ppm. The expected pattern of the A-B polycondensation was corroborated by the observation of the progressive decrease in the peak intensity of the monomer's relevant protons and the corresponding increase in that of the peaks related to the corresponding formation of the adducts. Concurrently, as the reaction proceeded, the viscosity of the medium also increased.

The retro-DA reaction was then followed at 110 °C for 24 h (Fig. 2) and within 6 h the solution already displayed the resonances of the starting monomer. After 24 h, the system was allowed to cool to 65 °C to favor a second polymerization, as shown in Figure 2. The corresponding ¹H NMR was similar to that taken at the end of the first polymerization, thus confirming the reversible nature of the system.

The ensuing polymers, isolated by precipitation in hexane, filtration and drying to constant weight, had a DPn of 30–35, as measured from their ¹H NMR spectra, and a Tg of 45–50 °C, pending the optimization of the system.

CONCLUSIONS

The furan-maleimide A-B monomer described here is the first example of such structures for which clean-cut DA polymerization-depolymerization cycles were shown to apply. Work is in progress to extend the scope of this investigation to other A-B monomers, as well as to AB_2 and A_2B structures capable of generating thermally-reversible hyperbranched macromolecules.

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