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Optimization of the synthesis of poly(hydroxyurethane)s using dynamic rheometry.

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2
3 ABSTRACT
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5 Poly(hydroxyurethane)s produced by the reaction between dicyclocarbonate and diamine groups
6 are often presented as possible candidates to substitute classical poly(urethane)s based on
7 isocyanate precursors. In the literature, the synthesis of this class of polymers is often performed
8 according to arbitrary conditions of time and temperature without any scientific justification.
9 Then, the real potential of poly(hydroxyurethane)s is probably badly known. Numerous
10 contradictions in previous published results seem to support this hypothesis. Our paper proposes
11 two methodologies based on dynamic rheometry to determine the optimized conditions for the
12 synthesis of PHUs. The case of a polyhydroxyurethane formed by the reaction between 1,10-
13 diaminodecane and a dicyclocarbonate bearing a central aromatic group is described more
14 precisely. The first approach consists in conducting different rheological experiments (kinetics,
15 thermomechanical analyses) *in-situ* on the reactive mixture. The second one retains the same
16 technique to qualify the viscoelastic properties of poly(hydroxyurethane)s synthesized according
17 to different conditions. In this latter case, all samples present a thermomechanical behavior of
18 amorphous thermoplastic polymer. But discrepancies are observed with regard to the value of the
19 Tg and the existence or not of a rubbery zone. The confrontation of these data with SEC results
20 shows that these differences are direct consequences of the polymer molecular weight that can be
21 predicted using macromolecules theory. The properties of the poly(hydroxyurethane)s obtained
22 after optimization of the polymerization reaction were compared with literature data in order to
23 complete the evaluation of the efficiency of the rheological methodology.
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51 **Keywords:** poly(hydroxyurethane), rheology, glass transition temperature, renewable resources,
52 molecular weight.
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1 - Introduction

Polyurethanes are very interesting polymeric materials that allow a huge variety of industrial applications from paints, adhesives and binders to materials for aeronautic industry (propellants). They are synthesized from **diol and diisocyanate reactants** that produce a carbamate (urethane) bond. According to the nature and length of diol chains, a large range of polyurethanes can be developed with specific physico-chemical properties. This versatility explains the spreading of polyurethanes over the world. Polyurethanes remain at the 6th position (tons) of most used polymers in the world. The major problem of polyurethanes is **related** to the toxicity of diisocyanate precursors.^[1] A non-hazardous for human and environment-isocyanate-free route to generate carbamate groups is based on a reaction between a cyclocarbonate and an amine.^[2-4] Various methods of preparation of cyclocarbonates have already been described.^[5] A first chemical route is based on the use of carbon dioxide with either epoxy resins or 1,2-diols.^[6-9] A second approach consists in preparing five-membered ring cyclocarbonates from phosgene and 1,2-diols.^[10-12] A third method lies in a *trans*-carbonatation reaction by an exchange between organic carbonate and hydroxyl compound.^[13] An alternative route consisting in the reaction between urea and 1,2- or 1,3-diols is another carbonatation method.^[14-15] Finally, a last methodology uses the direct esterification of glycerin cyclocarbonate with carboxylic acid or acyl chloride to yield corresponding ester bearing cyclocarbonate. Reaction with acyl chloride is rapid and quantitative, whereas carboxylic acid lead to slow and reversible reactions (**transesterification**).^[16]

As mentioned hereabove, cyclocarbonates are valuable for the synthesis of isocyanate-free poly(urethane)s also designed as poly(hydroxyurethane)s or PHUs. This class of polymers arises a great interest in the academic and industrial communities.^[17-19] Endo et al. undertook an

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3 important fundamental work with the synthesis and description of different kinds of linear
4 poly(hydroxyurethane)s.^[10-12, 20-22] The approach based on cyclic dicarbonates and diamines was
5 also retained by Burgel and Fedtke to prepare other thermoplastic PHUs.^[23] In fact, a large range
6 of poly(hydroxyurethane)s could be prepared and their characteristics were interpreted as being
7 influenced by the nature of the diamine and cyclocarbonate comonomers.^[4,16,21,24,25] For instance,
8 Ubaghs prepared PHU series from the reaction of phenoxy-carbonyloxymethyl ethylene carbonate
9 with five linear aliphatic diamines $H_2N-(CH_2)_n-NH_2$, n ranging from 2 (*i.e.* 1,2-diaminoethane) to
10 6 (*i.e.* 1,6-diaminohexane).^[16] Its research showed in particular that the glass transition
11 temperature (T_g) of the PHU decreased with increasing number of methylene groups in the
12 diamine structure, *i.e.* with growing flexibility of the chain between the hydroxyurethane groups
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27 **(Table 1).**

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32 **Insert Table 1.**

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36 Steblyanko conducted an analogous investigation with thermoplastic PHUs produced by the
37 reaction between an aromatic dicyclocarbonate and various diamines.^[4] But, in this latter case,
38 the author did not observe a continuous decrease of the polymer T_g with the size of the diamine
39 chain (**Table 2**). The highest value was obtained with the material based on a sequence of three
40 methylene units. The reported evolution could remind the even-odd effect due to the number of
41 methylene units and that was already described with some polyamides^[26-28] and polyurethane
42 ureas.^[29] But, in these particular cases, the critical temperatures of the polymer (T_g and/or
43 melting point) are always lower when there is an odd number of methylene groups in the
44 diamine. Indeed, for an even number of methylene units the packing of the crystals is operated in
45 planar zig-zag conformation while an odd number of CH_2 groups does not allow the same regular
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3 packing. It is important to note that in ref [4], the evolution of the Tg is purely contrary. So, the
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5 even-odd effect seems not to be relevant for PHUs.
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10 **Insert Table 2.**
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14 A new apparent contradiction as regards PHUs properties could be reported by the comparison of
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16 two researches dealing with the properties of a same poly(hydroxyurethane) formed by the step-
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18 growth polyaddition of another aromatic dicyclocarbonate with hexamethylene diamine. In the
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20 first study^[21], the Tg of the polymer was measured close to 34°C while it was about 47°C in the
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22 second one.^[25]
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26 **These important discrepancies seem to show that the conditions used for the synthesis of these**
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28 **PHUs were not optimal.** In each case, the conditions of time and temperature were fixed without
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30 any form of justification. To our knowledge, no work examined the influence of these synthesis
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32 parameters on the final characteristics of PHUs. In other words, PHUs properties described up to
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34 now do not probably reflect the real potential of this class of polymers. **Given this situation, we**
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36 **wished to report here an efficient methodology, based on the use of rheometry, to synthesize**
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38 **PHUs under optimal conditions. To illustrate our approach, a new poly(hydroxyurethane) was**
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40 **prepared by reaction between an aromatic dicyclocarbonate named terephthaloyl**
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42 **dicyclocarbonate (DCter) and an aliphatic diamine, 1,10-diaminodecane (DA10) (Scheme 1).** As
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44 rheological measurements can usually be carried out on polymers of very different nature ranging
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46 from the solid to the liquid state, we proposed two routes to evaluate the best temperature and
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48 time conditions that lead to a DCter-DA10 PHU with optimal properties. The first method
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50 consisted in conducting thermomechanical experiments directly on the **reactive mixture** to
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52 determine the temperature range where the polymerization occurred. In addition, rheological
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3 kinetics were conducted to define the time to complete the reaction at several fixed temperatures.
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5 The second method was based on the description and understanding of the thermomechanical
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7 behavior of samples made of the same poly(hydroxyurethane) but prepared according to variable
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9 synthesis conditions. The glass transition temperature and the molecular weight between
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11 entanglements were chosen as evaluation criteria. The consecutive confrontation of these results
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13 was undertaken with the information obtained by SEC and DSC techniques to examine the real
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15 merits of the rheological methodology.
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Insert Scheme 1

2 - Experimental Section

2.1 - Materials

The aromatic dicyclocarbonate named terephthaloyl dicyclocarbonate (**DCter**) was prepared by esterification of terephthalic acid using glycerin cyclocarbonate according to a methodology already reported.^[30] 1,10-Diaminodecane (**DA10**) was purchased from Aldrich (Aldrich, France). Dimethylformamide (DMF) from SDS Carlo Erba (Val de Reuil, France) was dried according to current methods, distilled and stored under argon atmosphere before final use. DMSO-*d*₆ was purchased from Eurisotop (Saint-Aubin, France).

2.2 - Physicochemical characterization

2.2.1 – Analytical techniques

¹H and ¹³C spectra were recorded on a Bruker DRX 400 MHz spectrometer operating at a frequency of 400 MHz. IR spectra were obtained with a Nicolet 210 FTIR. Size exclusion chromatography (SEC) was performed on a Varian ProStar Model 210 equipped with an RI

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3 refractive index detector. Two PLgel 5 μm MIXED-C 600 mm were used at 70 $^{\circ}\text{C}$ with a 0.8 mL
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5 min⁻¹ flow rate of DMF, calibrated using PMMA standards.
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10 **2.2.2 – Physical characterization**

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12 Differential scanning calorimetry (DSC) analyses were performed with a calorimeter DSC1 from
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14 Mettler Toledo. The polymer was set in an aluminium pan that was consecutively placed in the
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16 measurement heating cell and an empty pan was used as reference. These calorimetric
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18 experiments were realised under inert atmosphere with a heating rate fixed at 10 $^{\circ}\text{C}$ min⁻¹. The
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20 thermo-oxidative stability of the polymer was examined using a TGA Q50 apparatus from TA
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22 Instruments[®] under air flow (25 mL min⁻¹). The analysis consisted in registering the weight loss
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24 of the sample as a function of temperature from the ambient up to 550 $^{\circ}\text{C}$. The temperature ramp
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26 was set at 10 $^{\circ}\text{C}$ min⁻¹. Rheological experiments were performed using a stress-controlled
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28 dynamic rheometer (AR2000Ex from TA). This apparatus was equipped with an environmental
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30 testing chamber to allow the registering of the complex shear modulus $G^* = G' + j G''$ under
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32 precise control of the temperature. The component G' , called “storage modulus”, represents the
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34 mechanical rigidity of the sample (i.e. its elastic contribution) whereas the loss modulus G''
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36 relates to the dissipated mechanical energy. The behaviour of the reactive mixture was
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38 investigated using a cup-plate geometry that was suitable to characterize an evolutive system
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40 from the liquid to the solid state (Scheme 1). The inner diameter of the cup was 25 mm while the
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42 upper plate was much smaller (10 mm) to prevent undesirable side effects. The
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44 spectromechanical behavior of the polymer was characterized with the same rheometer but
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46 equipped with parallel plates geometry (diameter 25 mm) under fixed temperature and with an
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48 angular frequency ranging from 10⁻² to 100 rad s⁻¹ in decreasing mode. Rectangular torsion
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3 geometry was judged more adapted for characterizing the thermomechanical response of the
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5 polymer from the solid state. In this latter case, typical dimensions of the specimens were 40 mm
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7 x 8 mm x 1 mm. The thermomechanical tests were carried out at a heating rate of 3° °C min⁻¹
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9 from -150 °C up to the molten state and at a constant oscillating angular frequency ($\omega=1$ rad s⁻¹).
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11 The reproducibility of our rheological results was checked repeating twice our analyses. As
12
13 regards the polymer Tg, the uncertainty of measurement was found to be ± 1 °C
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20 2.3 - Synthesis of poly(hydroxyurethane)s from DCter and DA10

21 2 g of DCter (5.46 mmol) and 0.45 mL of DA10 (5.46 mmol) were introduced in a schlenk under
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23 nitrogen flux and solubilized in 4 mL of freshly distilled DMF. The mixture was stirred during 48
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25 h at a fixed temperature but ranging from 70 °C to 120 °C. After completion of the reaction,
26
27 DMF was removed by evaporation and the residue was dissolved in methanol (5 mL) and
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29 precipitated with diethyl ether (5 mL). The product was obtained as a white solid. In the case of a
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31 reaction temperature of 75 °C, the yield was about 95 %.
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38 ¹H NMR (DMSO d₆) δ (ppm): 8.11-8.05 (4H, CH_{aro}), 7.18-7.16 (2H, NH), 5.37-4.00 (5H_x + 5H_y,
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40 CH-O and CH₂-O), 3.57 (OH), 2.92-2.90 (4H, CH₂NH), 1.33-1.18 (16H, CH₂ of diamine).
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43 ¹³C NMR (DMSO d₆) δ (ppm): 164.63 (C=O_{ester}), 155.62 (C=O_{urethane}), 133.31 (C_{aro}), 129.26
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45 (CH_{aro}), 66.10-66.31 (CH₂-O), 64.42 (CH-O), 39.68 (CH₂-N), 28.77 (CH₂ of diamine), 26.02
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47 (CH₂-CH₂-NH).
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50 FTIR (KBr) ν (cm⁻¹): 3338 (OH), 1701 (C=O, urethane), 1542 (NH, urethane).
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3 - Results and Discussion

3.1 - Rheological characterization of the reactive mixture in DMF solution

3.1.1 - Thermomechanical analysis

It is well established by now that the polymerization of a reactive mixture can be studied using a large range of experimental methods including differential scanning calorimetry. We used this technique to investigate the reaction between the dicyclocarbonate **DCter** and diamine **DA10** units in DMF. Unfortunately, no exothermic phenomenon was detected in the thermogram from ambient temperature up to 150 °C. Nevertheless, chemical analyses of the sample at the end of the calorimetric experiment made undeniable the transformation from the monomer to the polymer. Consequently, the enthalpy associated to the polymerization was judged too reduced to permit the detection by DSC of the step-growth polyaddition of the comonomers.

Then, a new approach based on the conduction of rheological measurements was explored. A first experiment carried out in dynamic mode consisted in registering the evolution of the rheological behavior of the comonomers in DMF solution as a function of the temperature.

Figure 1 presents the results of the analysis conducted from 30 °C up to 185 °C. In this temperature range, the thermomechanical behavior of the reactive formulation could be divided into five characteristic zones. In the first one ranging from 30 °C to 75 °C, the viscous character of the solution was predominant ($G'' > G'$) and the values of both moduli decreased with temperature as observed with classical viscoelastic fluids (zone ①). In the following domain that goes from 75 °C to 100 °C, one could observe that the reduction of G' and G'' was much less marked. In a second step, both moduli even increased with temperature. Due to this evolution, the zone ② could be interpreted as being characteristic of the step-growth polyaddition between

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3 **DCter** and **DA10**. Indeed, the formation of macromolecular chains was expected to produce an
4 increase of the viscoelastic moduli. The effect was much more significant with the storage
5 modulus because of the progressive increase of the relaxation time of the material. Nevertheless,
6 the polymer in solution presented a rheological response characteristic of a viscoelastic liquid due
7 to the presence of DMF solvent. **NMR analyses conducted on samples issued from the reactive**
8 **mixture submitted to a regular heating were performed to verify the reaction temperature onset.**
9 **The formation of characteristic bands of the poly(hydroxyurethane) were detected for $T \sim 75\text{ }^{\circ}\text{C}$**
10 **what appeared consistent with the interpretation of zone ②.**

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22 A new reduction of both rheological curves was observed between $100\text{ }^{\circ}\text{C}$ and $115\text{ }^{\circ}\text{C}$ (zone ③).
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24 This evolution was likely provoked by a combination of two effects: i) a reduction of the
25 polymerization rate because of the progressive consumption of the monomers and ii) the resume
26 of the thermo-thinning effect. This latter evolution seemed to show that the polymer formed was
27 a thermoplastic. But, in the zone ④ ranging from $115\text{ }^{\circ}\text{C}$ up to $175\text{ }^{\circ}\text{C}$, both moduli restarted to
28 continuously rise due to the solvent evaporation. The resulting increase of the polymer
29 concentration also induced a predominancy of the elastic character. For temperatures higher than
30 $175\text{ }^{\circ}\text{C}$, a rapid increase of both moduli with temperature could be observed once more. **At the**
31 **same time, the color of the molten polymer passed from yellowish to brown and many bubbles**
32 **appeared. Further TGA analyses performed on poly(hydroxyurethane)s produced at much lower**
33 **temperature showed that above $170\text{ }^{\circ}\text{C}$, these phenomena were likely provoked by the polymer**
34 **degradation.**

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Insert Figure 1.

3.1.2 - Rheological kinetics

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3 To complete the rheological characterization of the polymerization process, the kinetic of the
4 reaction was analyzed by the conduction of measurements operated under constant shearing
5 frequency and at different fixed temperatures. According to the thermomechanical data
6 previously reported, the polymerization seemed to produce itself at a temperature comprised
7 between 75 °C and 115 °C. A first kinetic rheological analysis was logically led in this
8 temperature range at T = 80 °C (**Figure 2**). At the beginning of the analysis, the reactive mixture
9 was a viscoelastic liquid ($G'' > G'$). Afterwards, the values of both moduli quickly increased with
10 time and even tend towards an asymptotic limit. This evolution could be attributed as being a
11 consequence of the polymer formation: the macromolecular chains were much less mobile than
12 the initial monomers what provoked the increase of the complex shear modulus. At this
13 temperature, the viscous character remained predominant because the polymer was still
14 solubilized in DMF.
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34 **Insert Figure 2.**
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38 A new kinetic experiment was performed at higher temperature (T = 100 °C). To make easier the
39 comparison of the corresponding data, we plotted in **Figure 3** the evolution of the magnitude of
40 the complex shear modulus $|G^*| = \sqrt{G'^2 + G''^2}$ as a function of the time. For sake of clarity, the
41 only experimental data that are proposed are those which are representative of the first moments
42 of the rheological analysis (t < 4 h). Compared to the kinetic measurements carried out at 80 °C,
43 the increase of the moduli at T = 100 °C occurred at a higher rate. This was attributed to the
44 temperature activation of the reaction between **DCter** and **DA10**.
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3 Then, a last rheological kinetic was undertaken at $T = 120\text{ }^{\circ}\text{C}$. Even if this temperature was
4 located above the polymerization **range** determined previously in dynamic mode, the step-growth
5 was judged likely to occur. Apparently, the temperature of $120\text{ }^{\circ}\text{C}$ did not provide any
6 acceleration of the polymerization process. Indeed, the evolution of the shear modulus in the first
7 times was almost confounded with that registered at $T = 100\text{ }^{\circ}\text{C}$. This result indicated that a
8 temperature of $120\text{ }^{\circ}\text{C}$ was likely excessive to guaranty a polymerization process of quality. The
9 higher final value of the modulus was attributed to the solvent evaporation. This phenomenon
10 was considered as an undesirable phenomenon responsible of reduction of the monomers
11 dissolution and consequently their lower reactivity. In other words, better polymerization
12 conditions seemed to be encountered **for T close to $100\text{ }^{\circ}\text{C}$** .
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30 **Insert Figure 3.**

31 **3.2 - Study of the poly(hydroxyurethane)**

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33 The influence of the synthesis parameters was also evaluated by the study of the final properties
34 of the polymer. For this purpose, different poly(hydroxyurethane) samples, A to D, were
35 synthesized at specific temperatures T_p comprised between $75\text{ }^{\circ}\text{C}$ and $120\text{ }^{\circ}\text{C}$ but by keeping
36 constant the reaction time (**Table 3**). This latter parameter was fixed at 48 h because this duration
37 was found sufficient to observe the stabilization of the moduli in the different rheological
38 kinetics.
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52 **Insert Table 3.**

53 **3.2.1 - Calorimetric and SEC characterizations**

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3 Calorimetric experiments were undertaken from -50 °C to 150 °C to determine the glass
4 transition temperature of each polymer and investigate the possible presence of a melting zone.
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6 An example of thermogram is proposed in **Figure 4** and concerns the sample B. A discontinuity
7
8 in the calorimetric signal was interpreted as being characteristic of the polymer glass transition.
9
10 Taken down at the midpoint, the T_g was measured at 48 °C. In the temperature domain explored,
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12 no endothermic phenomenon, related to the melting of a crystalline phase, was detected. Then,
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14 the poly(hydroxyurethane) sample was considered as being fully amorphous. This seemed logical
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16 since the material aspect was yellowish and transparent. Similar conclusions were obtained with
17
18 the other samples A, C and D whatever the conditions used for the synthesis. Nevertheless, little
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20 differences could be noted in the values of the glass transition temperature.
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30 **Insert Figure 4.**
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34 The higher values of T_g were obtained for the polymerizations conducted in the range 90-100 °C
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36 (Table 3). A temperature $T_p = 120$ °C seemed excessive since it provoked the formation of a
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38 polymer (sample D) with a reduced value of glass transition temperature. These results were
39
40 consistent with the first conclusions proposed after the rheological kinetic studies. To go further
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42 in the scientific discussion, SEC analyses were conducted on the different samples A, B, C and
43
44 D. The corresponding data, also presented in Table 3, showed that the average number molecular
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46 weight of the poly(hydroxyurethane) was closely dependent on the temperature used during the
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48 synthesis step. The higher value ($M_n = 20000$ g mol⁻¹) was **obtained** with the temperature of 90
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50 °C (sample B). But, this synthesis temperature also produced at the same time a maximal
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52 polydispersity index I_p . At $T_p = 120$ °C, the value of the molecular weight was much lower (8000
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54 g mol⁻¹) bearing out that this temperature was less convenient for the polymer synthesis due to
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3 the parasitic evaporation of the solvent. In fact, all these data agreed with the hierarchy proposed
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5 previously from the rheological and calorimetric experiments.
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10 **3.2.2 - Rheological properties of the poly(hydroxyurethane) samples**

11 Further characterization of the different samples of poly(hydroxyurethane) focused on the
12 evolution of their viscoelastic properties as a function of temperature. **Figure 5** shows as example
13 the thermomechanical profile registered with the polymer synthesized at 90 °C (sample B). This
14 rheological analysis indubitably showed that the poly(hydroxyurethane) was an amorphous
15 thermoplastic polymer. Indeed, different characteristic zones were successively observed. In the
16 low temperature region ($T < 40$ °C), the material was in the glassy state ($G' \sim 10^9$ Pa). Afterward,
17 the curve of the elastic modulus G' showed a deflection while the G'' curve presented a relaxation
18 peak. Both phenomena were attributed to the mechanical relaxation of the amorphous chains
19 during the glass transition of the polymer. The polymer T_g could be evaluated by taking the
20 temperature at the maximum of the peak on the G'' .
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43 **Insert Figure 5.**

44 Above this critical temperature, the decrease of the shear modulus with temperature was
45 important but the elastic response became **again** predominant in the temperature ranging from $T =$
46 58 °C up to $T = 81$ °C. This domain, characteristic of the **rubbery zone** of the polymer, revealed
47 that the polymer chains constituting the sample B presented an average molecular weight that
48 was high enough to permit the formation of entanglements.^[31,32] The molecular weight between
49 entanglements M_e in this temporary network could be evaluated according to the classical theory
50 of rubber elasticity and using the following equation:^[33,34]
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$$M_e = \rho RT / G'_r \quad (1)$$

where ρ is the polymer density (taken close to 1000 kg.m^{-3}), R the gas constant ($8.31 \text{ J mol}^{-1} \text{ K}^{-1}$), G'_r the value of the elasticity taken down at the middle of the **rubbery zone** and T the corresponding temperature. Finally, the flow zone of the polymer, characterized by $G'' > G'$, was observed for $T > 81^\circ\text{C}$. No crystalline plateau was detected during the thermomechanical analysis. Then, considering that this polymer should verify the equivalency time-temperature, spectromechanical analyses were carried out at various fixed temperatures. Taking as a reference that registered at the lowest temperature ($T = 55^\circ\text{C}$), a master curve could be easily built by translation of the other analyses along the ω -axis (**Figure 6**). This analysis made it possible the plain description of the different domains previously detected by the thermomechanical experiment. Actually, the rheological behavior initially detected at high temperature was observed at low frequency and vice-versa.^[31] At $\omega < 3 \cdot 10^{-3} \text{ rad s}^{-1}$, the flow zone of the polymer was clearly shown. The **rubbery zone** was identified for ω ranging from $3 \cdot 10^{-3}$ to $1.5 \cdot 10^{-1} \text{ rad s}^{-1}$. For higher ω values, the increase of both moduli was characteristic of the transition zone. The thermoplastic and amorphous characters of DCter-DA10 PHU were considered as indisputable. In that sense, this PHU was considered as quite different from the poly(hydroxyurethane)s developed by Javni^[35], Diakoumakos^[36], or Webster.^[37] It resembled more to the class of PHUs proposed by Kihara^[21] or Rokicki.^[38]

Insert Figure 6.

The characterization of the thermomechanical response of the other poly(hydroxyurethane) samples (A, C and D) led to the same conclusions about the polymer morphology (**Figure 7**).

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3 However, the glass transition temperature taken down at the maximum of G'' curve differed from
4 one sample to the other. The different values remained close to that obtained previously by
5 calorimetry (Table 3). A direct confrontation of our results with that reported in the literature was
6 considered as really interesting. In particular, we chose to use the data summarized in **Table 2**
7 because they were registered with PHUs made with the same dicyclocarbonate DCter. The only
8 difference was brought by the diamine length. Our material was based on 1-10-diaminodecane
9 that was expected to be logically more flexible than 1-3-diaminopropane and 1-6 diaminohexane
10 used by Steblyanko.^[4] In other words, our polymer would have to present the lowest Tg but the
11 reverse case was observed. This result confirmed the necessity to investigate for each kind of
12 PHU, the best conditions of time and temperature used during the synthesis step. As evidence,
13 **these latter factors should not be considered** as universal parameters.
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32 **Insert Figure 7.**
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36 Going further in the description of the samples A to D, one could note that the **trend** established
37 from the Tg values agreed with the classification that can be built from the SEC data (Table 3).
38 More precisely, the evolution of the PHUs' Tg as a function of the average molecular weight M
39 was satisfactorily described using the equation (2) initially proposed by Fox and Flory but
40 modified by Bicerano:^[39]
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$$48 \quad T_g = T_g(\infty) - 2.715 \times T_g(\infty)^3 / M \quad (2)$$

49 where $T_g(\infty)$, expressed in Kelvin, is the value of Tg for very high molecular weight and M the
50 average molecular weight (kg mol^{-1}).
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3 The best adjustment of the experimental data in **Figure 8** with eq.2 was obtained with $Tg(\infty) =$
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6 325 K = 52 °C. This latter value was evaluated quite close to the Tg of the sample B ($Tg = 48$ °C)
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8 assessing once more that this PHU was synthesized with excellent conditions of temperature and
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10 time.

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15 **Insert Figure 8.**
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19 Besides the glass transition temperature, the value of molecular weight also influenced the
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21 existence and the size of the **rubbery zone**. As defined before, this domain was encountered for
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23 the polymer B from 58 °C to 79 °C and at a lower extent for the sample C from 56 °C up to 70 °C
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25 **(Figure 7)**. In other words, the **rubbery zone** was more extended of 7 °C in the case of sample B
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27 in comparison with polymer C. This seemed logical since the former was characterized by a
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29 higher molecular weight. Anyway, this experimental temperature difference $\Delta T = 7$ °C agreed
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31 with the value calculated using the Equation 3:^[31]
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$$\Delta T = 100 \times \log(M_B / M_C) \quad (3)$$

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36 with M_B and M_C are the respective average weights of the poly(hydroxyurethane)s B and C.
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38 Inversely, the rubbery state was not observed for the polymers of lowest molecular weights
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40 (samples A and D). If it is well-known that entanglements can only be formed if the polymer size
41
42 exceeds a critical size, the exploitation of the specific data of the sample B was considered as
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44 useful to estimate the threshold value. The elastic modulus taken at the middle of the **rubbery**
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46 **zone** presented a value $G'_r = 5.7 \cdot 10^5$ Pa at $T = 63$ °C = 336 K. Considering that the polymer
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48 density was unity, the molecular weight between entanglements M_e calculated **according to**
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50 equation (1) is close to 5000 g mol^{-1} . Then, the critical number-molecular weight M_c above which
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3 entanglements were possible could be evaluated according to Graessley theory: $M_c = 2.5 M_e =$
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5 12500 g mol^{-1} .^[40-42] This result is worthy of note because it seemed to be able to justify why the
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7
8 samples B and C, characterized by an average number molecular weight $M_n > M_c$, were the only
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10 ones to present a rubbery plate. Once more, the synthesis temperature T_p conducting to a polymer
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12 with enhanced mechanical properties was found to be close to $90 \text{ }^\circ\text{C}$ with a synthesis period of
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4 - Conclusion

This paper proposed an original methodology based on dynamic rheometry in order to determine the best synthesis conditions attached to a PHU produced from the reaction between DCter and DA10 polymer. A first way consisted in using the rheometer as an instrumented reactor to investigate with dedicated experiments, the temperature domain and the kinetic characteristic of the step-growth polyaddition. It quickly showed that the polymerization required a minimal temperature close to 80 °C. At the same time, the reaction should not be carried beyond 120°C due to the beginning of the solvent evaporation. The second approach investigated the thermomechanical characterization of different poly(hydroxyurethane)s prepared with the same co-monomers but according to arbitrary conditions. It presented the great advantage to furnish useful information to evaluate the quality of the final PHU. If the glass transition temperature could be used as a reliable criterion, our research showed that the characteristics of the rubbery zone earned to be exploited in terms of molecular weight. These results allowed the accurate definition of the time and temperature conditions that had to be retained during the synthesis step in order to produce a PHU with optimal properties. Both rheological methods agreed to designate the synthesis temperature of 90°C as ideal for the production of polymer chains with high molecular weight. If the viscoelastic data agreed with the results obtained separately by SEC analyses and DSC techniques, it is important to remind that rheometry offered a more complete description of the poly(hydroxyurethane). Ultimately, the good correspondence between experience and several theoretical concepts was considered as another evidence of the effectiveness of the method. The possible application of this rheological methodology to other dicyclocarbonate-diamine couples will be examined in a future work.

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CAPTIONS

Figure 1. Effect of the temperature on the rheological properties of the reactive mixture (G' : ○ and G'' : ▲).

Figure 2. Evolution of the viscoelastic properties of the reactive mixture versus time at $T = 80^\circ\text{C}$ and $\omega = 10 \text{ rad s}^{-1}$ with G' : (•••) and G'' : (—).

Figure 3. Superposition of the evolution of **the magnitude of the complex shear modulus** of the reactive mixture as a function of time at three different temperatures T_p (80°C : □ ; 100°C : ▲ ; 120°C : ●) and $\omega = 10 \text{ rad s}^{-1}$.

Figure 4. Calorimetric analysis of the poly(hydroxyurethane) B as a function of temperature (synthesis conditions: 48 h at 90°C)

Figure 5. Thermomechanical analysis of the poly(hydroxyurethane) B with G' : ● and G'' : △

Figure 6. Master curve of the poly(hydroxyurethane) B built from three spectromechanical analyses: 55°C (reference), 75°C and 115°C .

Figure 7. Influence on the synthesis parameters on the final thermomechanical properties of the poly(hydroxyurethane). (the curves are arbitrarily shifted along a vertical axis for clarity, G' : ● and G'' : △)

Figure 8. Evolution of the T_g of the DCter-DA10 PHU as a function of the average molecular weight. The symbols correspond to the experimental data while the solid line is given by Eq. 2

Scheme 1. Implementation of rheometry at the different stages of poly(hydroxyurethane) synthesis by reaction of DCter with DA10.

Table 1. **Influence of the diamine length on the T_g of PHU based on a same aliphatic cyclocarbonate**

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2
3 **Table 2.** Tg values characteristic of PHUs obtained by the reaction of a same aromatic
4 dicyclocarbonate with different aliphatic diamines
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9 **Table 3.** Synthesis conditions and properties of the different samples of **DCter-DA10**
10 poly(hydroxyurethane)
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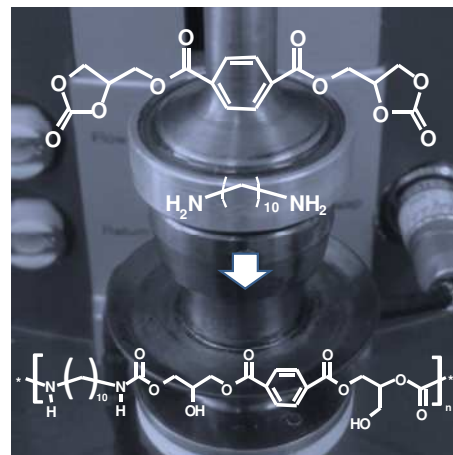
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3 **For Table of Contents Use Only**
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6 **Optimization of the synthesis of poly(hydroxyurethane)s using dynamic rheometry.**
7

8
9 Sofia Benyahya, Bernard Boutevin, Sylvain Caillol, Vincent Lapinte, Jean-Pierre Habas*
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12 The temperature and time of polymerization reactions
13 that lead to poly(hydroxyurethane)s with optimal
14 properties have been determined according to
15 rheological studies.
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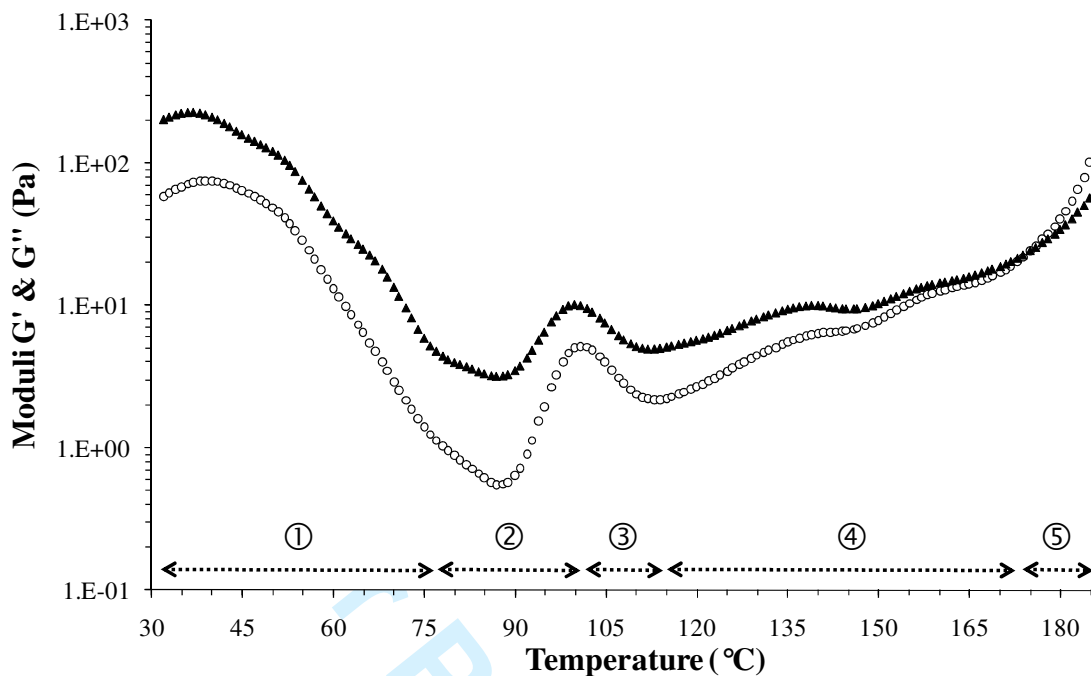


Figure 1. Effect of the temperature on the rheological properties of the reactive mixture (G' : \circ and G'' : \blacktriangle).

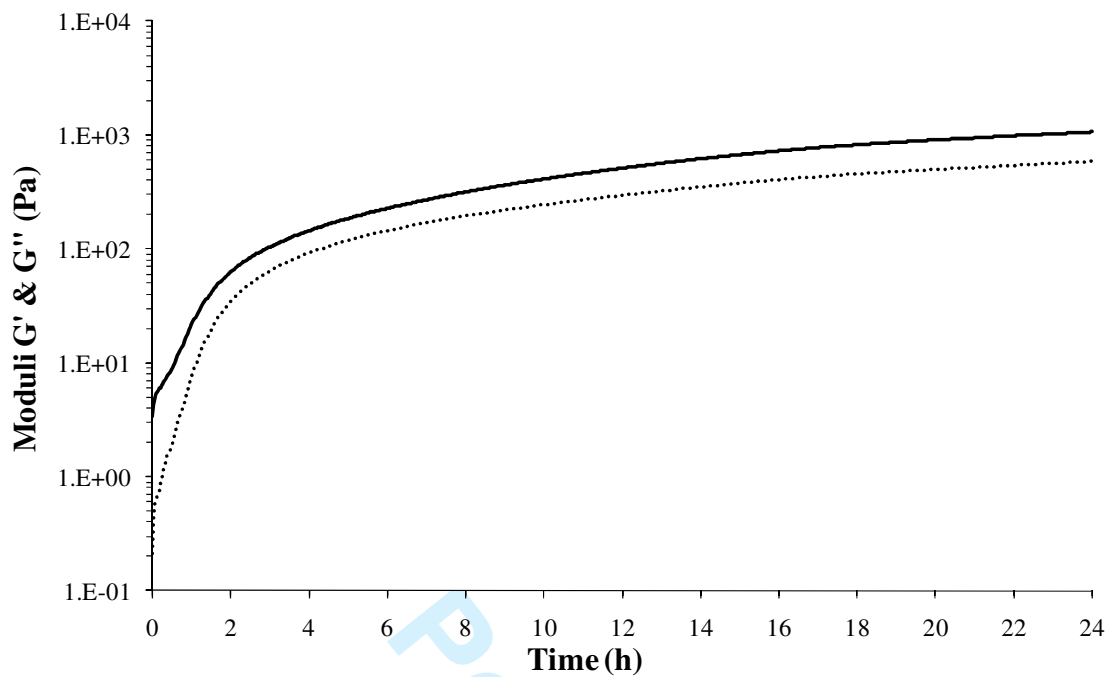


Figure 2. Evolution of the viscoelastic properties of the reactive mixture versus time at $T = 80^\circ\text{C}$ and $\omega = 10 \text{ rad s}^{-1}$ with G' : (•••) and G'' : (—).

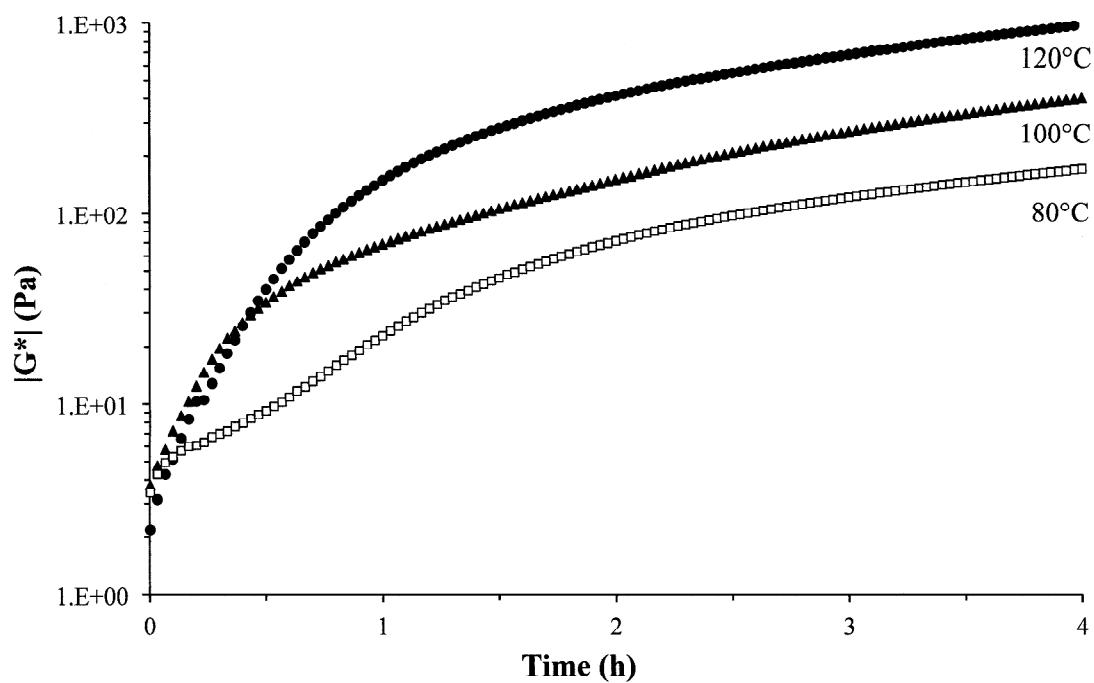


Figure 3. Superposition of the evolution of the magnitude of the complex shear modulus of the reactive mixture as a function of time at three different temperatures T_p (80°C: \square - 100°C: \blacktriangle - 120°C: \bullet) and $\omega = 10 \text{ rad s}^{-1}$.

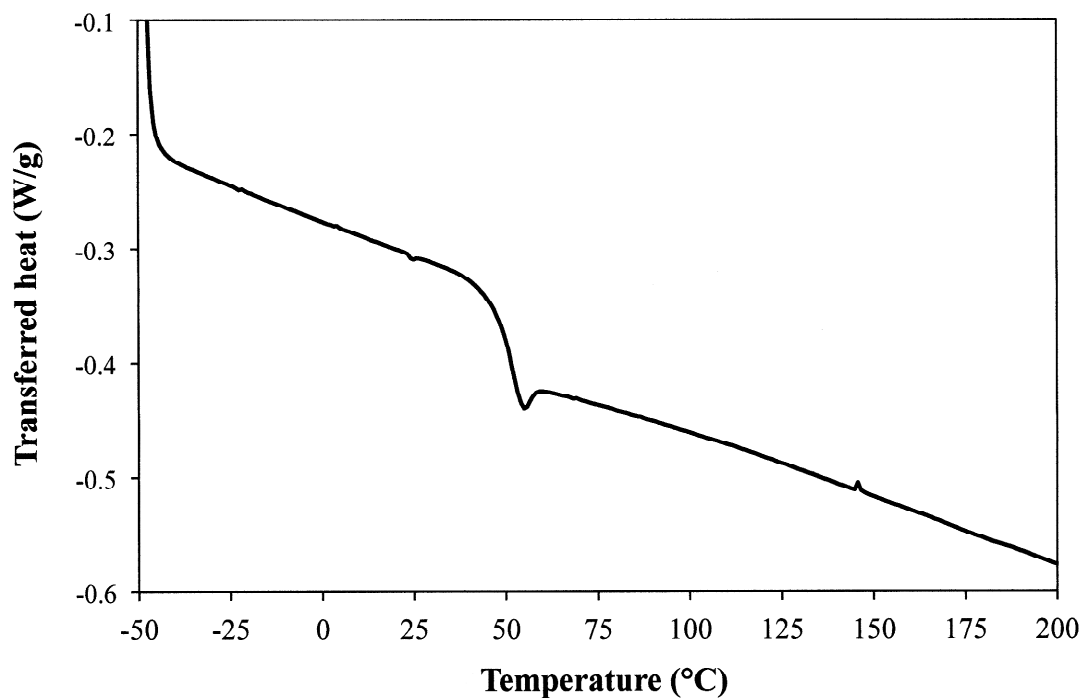


Figure 4. Calorimetric analysis of the poly(hydroxyurethane) B as a function of temperature (synthesis conditions: 48 h at 90°C)

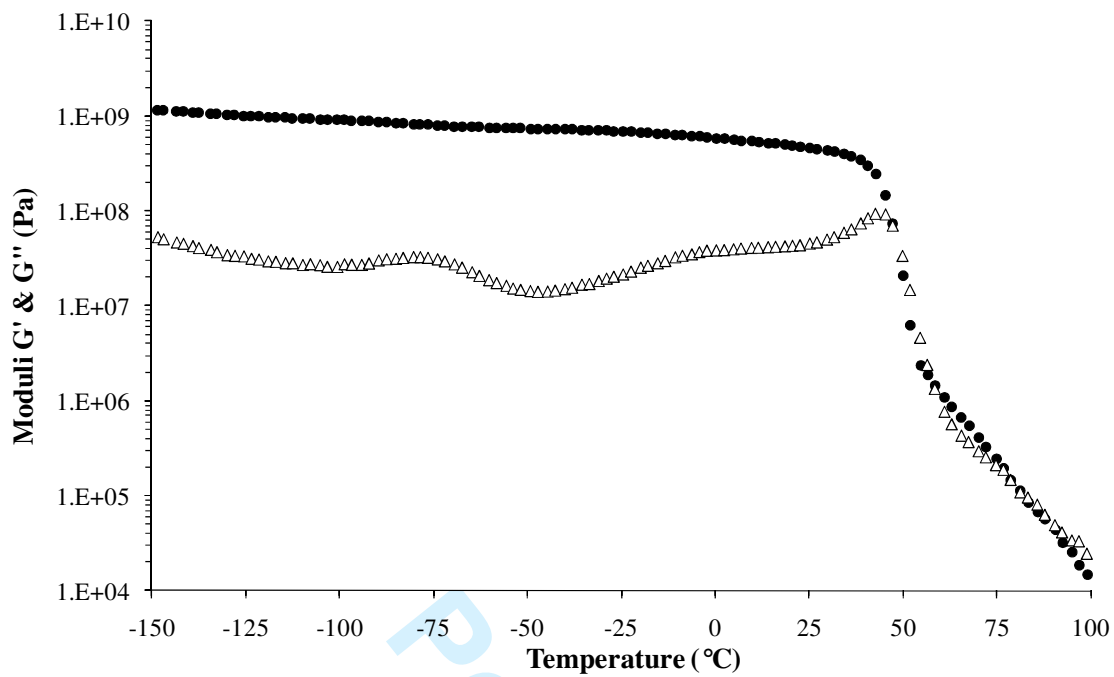


Figure 5. Thermomechanical analysis of the poly(hydroxyurethane) B with G': ● and G'': △

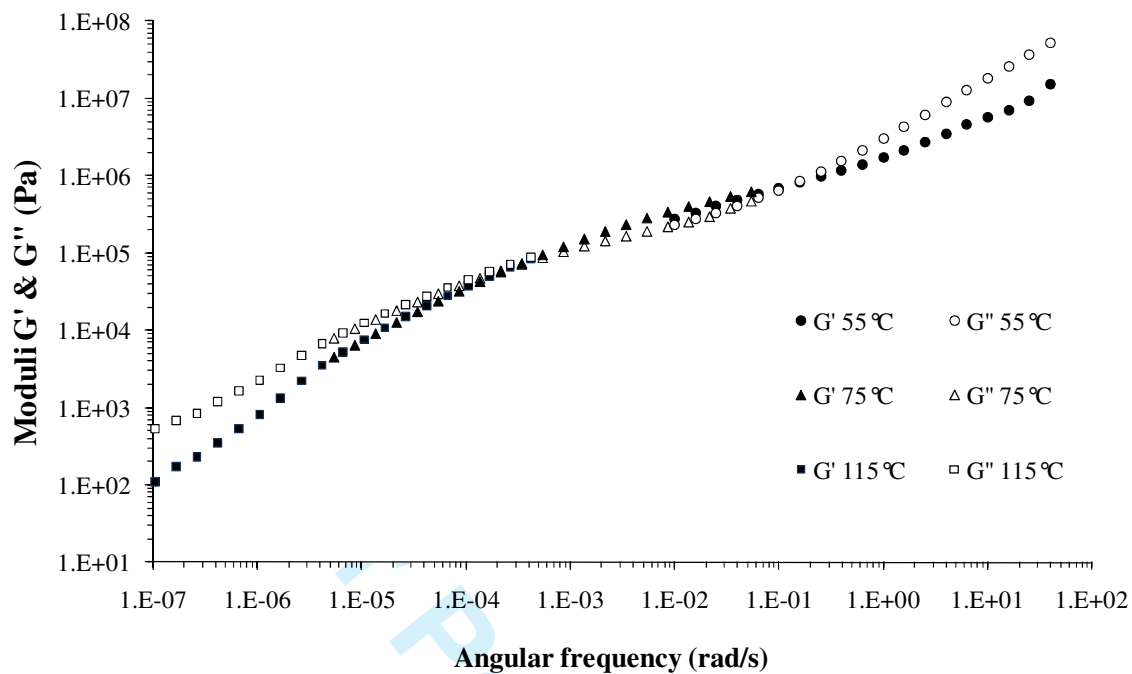


Figure 6. Master curve of the poly(hydroxyurethane) B built from three spectromechanical analyses: 55°C (reference), 75°C and 115°C.

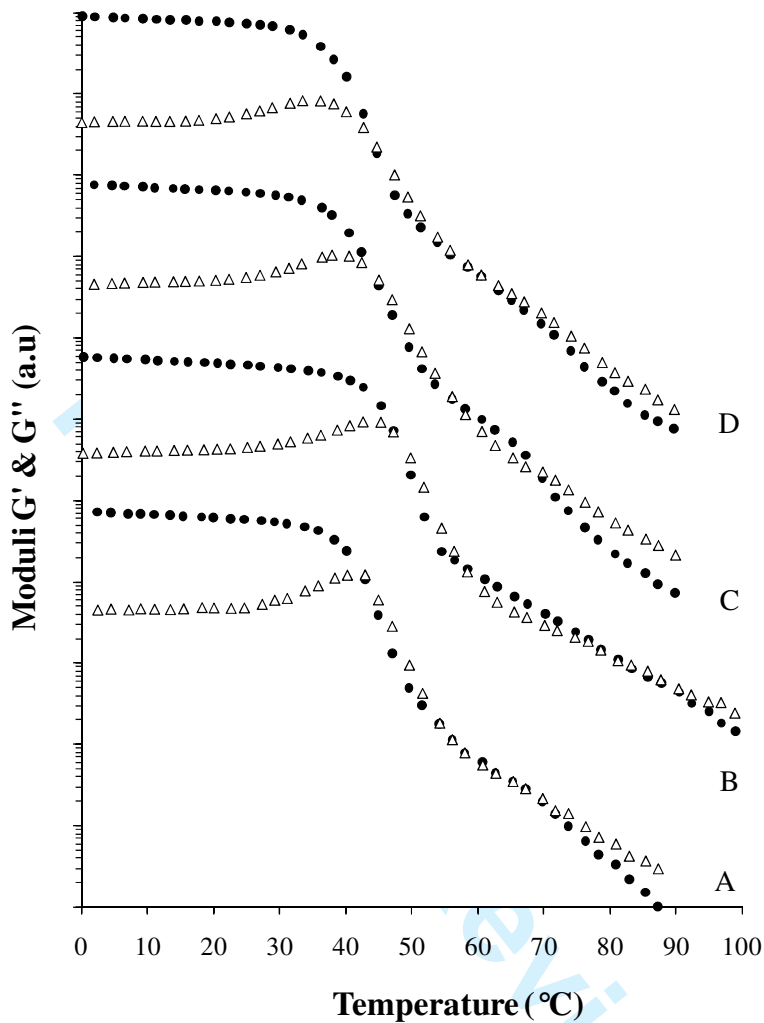


Figure 7. Influence on the synthesis parameters on the final thermomechanical properties of the poly(hydroxyurethane). The curves are arbitrarily shifted along a vertical axis for clarity,

G': ● and G'': △, and the letters refer to samples designated in Table 3.

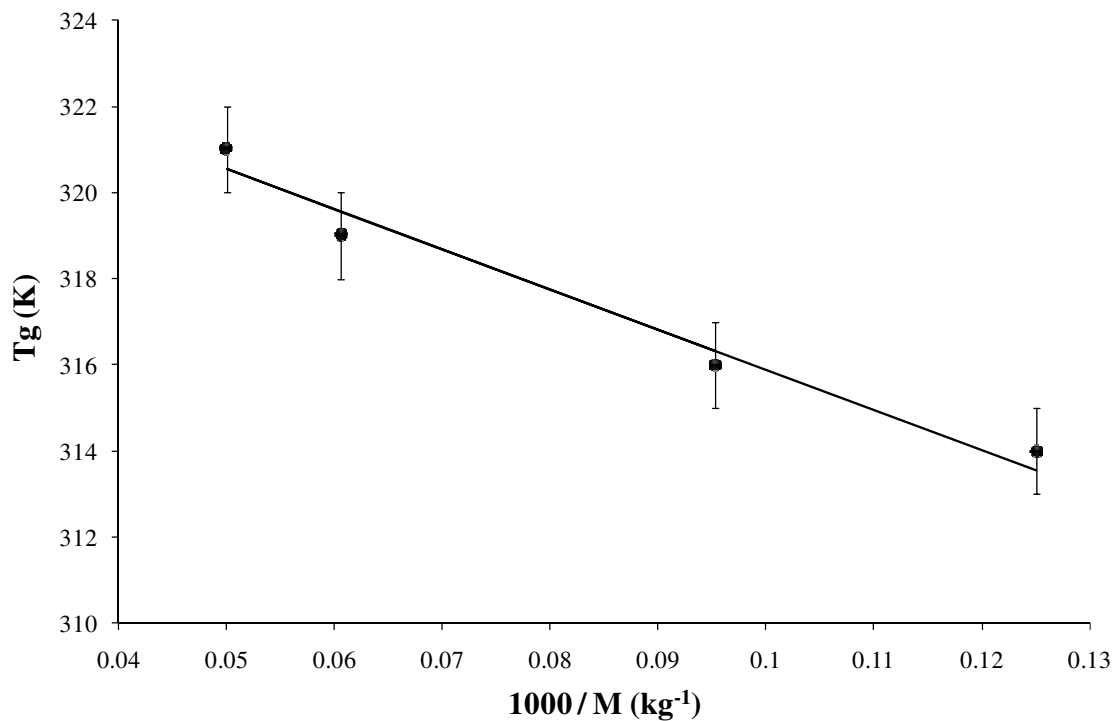
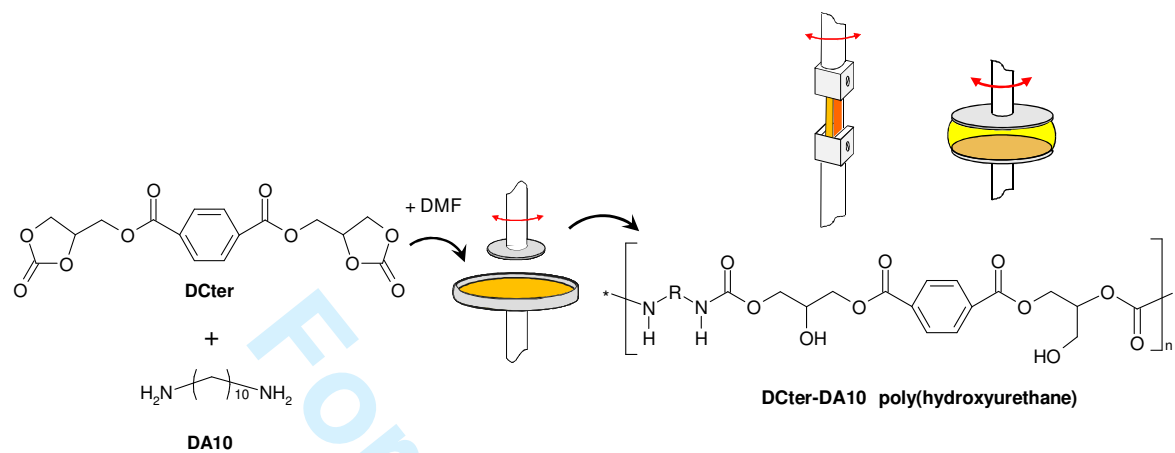


Figure 8. Evolution of the Tg of the DCter-DA10 PHU as a function of the average molecular weight. The symbols correspond to the experimental data while the solid line is given by Eq.

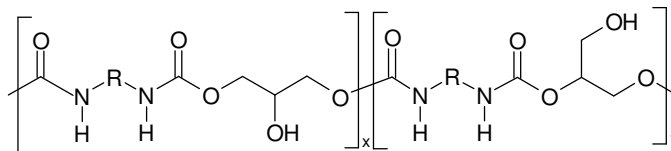
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Scheme 1



Scheme 1. Implementation of rheometry at the different stages of poly(hydroxyurethane) synthesis by reaction of DCter with DA10.

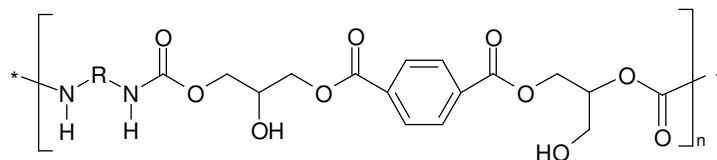
Table 1. Influence of the diamine length on the T_g of PHU based on a same aliphatic cyclocarbonate



R	(CH ₂) ₂	(CH ₂) ₃	(CH ₂) ₄	(CH ₂) ₅	(CH ₂) ₆
T _g (°C) ^{a)}	53	45	42	37	23

^{a)}: Data extracted from [25].

Table 2. Tg values characteristic of PHUs obtained by the reaction of a same aromatic dicyclocarbonate with different aliphatic diamines



R	(CH ₂) ₂	(CH ₂) ₃	(CH ₂) ₆
Tg (°C) ^{a)}	21	29	3

^{a)}: Data extracted from [4].

Table 3. Synthesis conditions and properties of the different samples of **DCter-DA10** poly(hydroxyurethane)

Sample	T _p (°C)	T _g DSC ^{a)} (°C)	T _α ^{b)} (°C)	M _n ^{c)} (g/mol)	I _p ^{c)}
A	75	43	41	10500	2.3
B	90	48	45	20000	2.5
C	100	46	43	16500	1.9
D	120	41	38	8000	2

a): ± 2°C

b): ± 1°C

c): Determined by SEC (RI detector, DMF-eq PMMA).