



Short communication:

Synthesis and characterization of a polyurethane prepared by frontal polymerization

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Abstract: Frontal polymerization (FP) has been successfully applied to the preparation of a polyurethane (PU) having practical interest. By comparing the classical PU synthetic route with FP, the latter allowed for the obtainment of both higher molecular weights and yields. Furthermore, reaction times have been significantly reduced. Eventually, FP materials are characterized by higher glass transition temperature and lower melting point than their batch counterparts.

Introduction

Polyurethanes (PUs) are a well-known class of polymers commonly used for technical applications especially as sealants, lining, foams, paints etc. [1] A wide choice of diols and diisocyanates is available for their preparation; in particular, aliphatic and aromatic diisocyanates (e.g., 1,6-hexamethylene diisocyanate (HDI), 4,4'-methylenebis(phenyl isocyanate), tolylene 2,4-diisocyanate, etc.) are used in combination with short-chain diols (e.g., ethylene glycol (EG), butylene glycol, 1,6-hexanediol (HD), etc.) and long-chain diols which are preformed polymers, such as polyester or polyether diols ($450 \leq M_n \leq 6000$): e.g., poly(ϵ -caprolactone) diol (PCLD), Terathane[®] etc.

These latter form the flexible component of the polyurethane (flexible or soft segment). Conversely, the combination of a diisocyanate with a short-chain diol produces the rigid (or hard) component.

The reaction involving aromatic diisocyanates and diols is generally fast. On the contrary, in the case of aliphatic diisocyanates, a fast reaction occurs only when a catalyst (Sn, Mo, W salts) is used. However, in both cases highly exothermic polymerizations are commonly observed.

In our previous work [2], we have exploited the aforementioned features to perform the frontal polymerization (FP) of the polyurethane derived by the reaction of HDI and EG in the presence of dibutyltin dilaurate as a catalyst. Indeed, in FP the exothermicity of a reaction is used for promoting the occurrence of a hot travelling polymeri-

zation front able to self-sustain by converting the monomer close to the reacting zone into polymer. If heat losses are not excessive, a steady state is reached and FP can continue indefinitely.

After the first studies of Chechilo *et al.* on the high pressure FP of methyl methacrylate [3], an extensive study was performed by Pojman *et al.* on acrylic monomers [4-6] and epoxy resins [7]. Lately, Mariani *et al.* have developed FP chemistry. Namely, frontal ring opening metathesis polymerization (FROMP) of dicyclopentadiene (DCPD) [8], polyurethanes [2,9], interpenetrating polymer networks [10], polyester resins [11] and their related materials have been obtained by FP for the first time.

Currently, an increasing number of papers report on FP as a technique useful for practical applications: the curing of thick composite materials [12], the preparation of thermochromic composites [13], homogeneous polymer blends [14], copolymers [15], hydrogels [16], polymer-dispersed liquid crystals [17,18] and the consolidation of porous materials [19].

In the present work, our previous study on the obtainment of the first PU by FP has been extended to another system having more interest as a commercial product [20], namely that prepared by reaction of HDI with HD and PCLD. Furthermore, a series of control samples has been prepared by the classical batch method with the purpose of comparing their features with those of their FP counterparts.

Experimental part

HDI, HD, PCLD (MW = 530), dibutyltin diacetate (DBTDAc), and pyrocatechol (PC) were purchased from Aldrich. Cab-osil[®] was received from Riedel-de-Haën and *m*-cresol from Carlo Erba. All chemicals were used as received.

Technical equipment: K-type thermocouple connected to a digital thermometer reader Delta Ohm model DO 9416. DSC measurements were obtained with a Mettler DSC 30 in a temperature range between -100 and 200°C and a heating rate of 10°C/min. Viscosity measurements were performed in *m*-cresol at 25°C with an Ubbelohde type viscometer.

FP runs

In a typical run, a glass test tube was loaded with a suitable quantity of PC dissolved in an appropriate amount of HD and PCLD (see later). The tube was gently warmed to 40°C to obtain a homogeneous mixture and rapidly cooled to 20°C. Cab-osil (2.5 wt.-%) and HDI were added to the above mixture, which was then vigorously shaken. The molar composition was HDI : HD : PCLD = 1 : 0.65 : 0.35 [20].

A K-type thermocouple was placed in the mixture and located c. 2 cm from the bottom of the tube (c. 3 cm from the upper liquid layer); the temperature was monitored by a digital thermocouple reader (sampling rate: 1 Hz). FP reactions were triggered by heating the upper side of the liquid with a hot soldering iron tip until the formation of a travelling front started. After the FP run, the tube was allowed to cool to room temperature. Afterwards, the obtained polyurethane was dissolved in *m*-cresol and centrifuged to separate Cab-osil from the end product. The organic phase was poured into diethyl ether and the resulting precipitated polymer was dried at 60°C for 24 h in vacuum.

Batch runs

A series of specimens having the same composition as those prepared by FP were synthesized by the classical method [20] in a batch reactor immersed in a thermostated oil bath set at 80°C. The reactions were carried out for 1 h. After cooling, the obtained polymers were purified as described above.

Results and discussion

In a first step, a number of preliminary experiments were performed to determine the conditions in which pure FP (*i.e.*, with no presence of simultaneous spontaneous polymerization, SP) occurred. As a consequence of the high mutual reactivity of HDI and diols in the presence of DBTDAC, this goal was attained by adding a small amount of inhibitor (PC) to the reaction mixture in order to extend its pot-life [2]. Nevertheless, after FP ignition the occurrence of SP was observed as a consequence of 'fingering'. This phenomenon takes place in descending fronts when a polymer is molten at the front temperature and consists in the formation of polymer drops, which move into the monomer, thus resulting in local SP. Such an event can be prevented by increasing medium viscosity, for instance by using fumed silica (Cab-osil) [21]. This method was used in the present work also taking into account the well-known properties of such a component as a filler in polymeric (nano)-composites [22].

In Fig. 1, a temperature profile recorded during a typical FP experiment is shown. The horizontal part of the curve, related to zones far from the incoming front, indicates the absence of SP. Indeed, if this is not the case, the heat released during the polymerization reaction results in a temperature increase before the thermocouple junction is crossed by the propagating front. These plots, recorded for any FP run, have been used to verify whether pure FP was occurring and to determine the maximum temperature (T_{max}) reached by the travelling front.

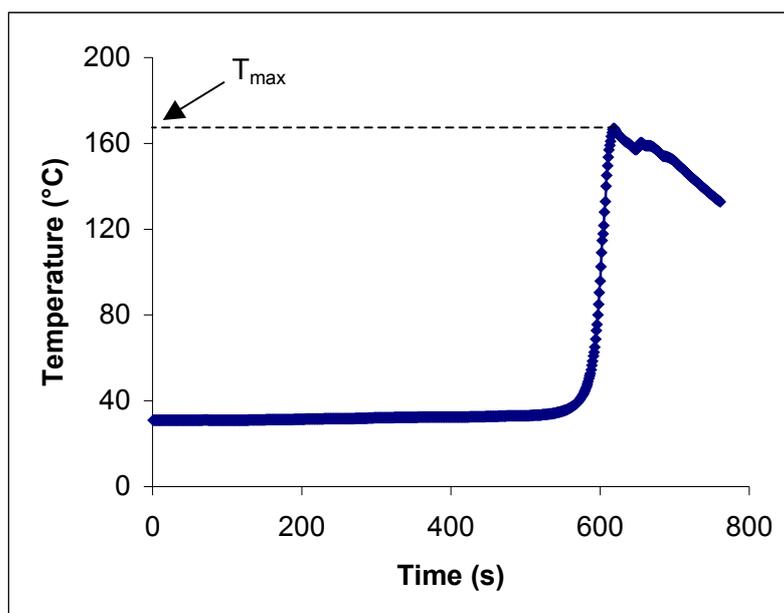


Fig. 1. Temperature profile of a typical FP run (sample F1: [DBTDAC]/[HDI] = 1.0 mol-%; [PC]/[DBTDAC] = 6 mol/mol)

T_{\max} and front velocity (V_f) are considered the two main parameters to be checked during an FP experiment. This latter is easily calculated by plots such as that depicted in Fig. 2 in which the position of the front as a function of time for a typical FP run is reported. As can be seen, experimental data are well fitted by a straight line, thus indicating that FP propagates through the reactor at constant velocity, a feature typical of many FP systems.

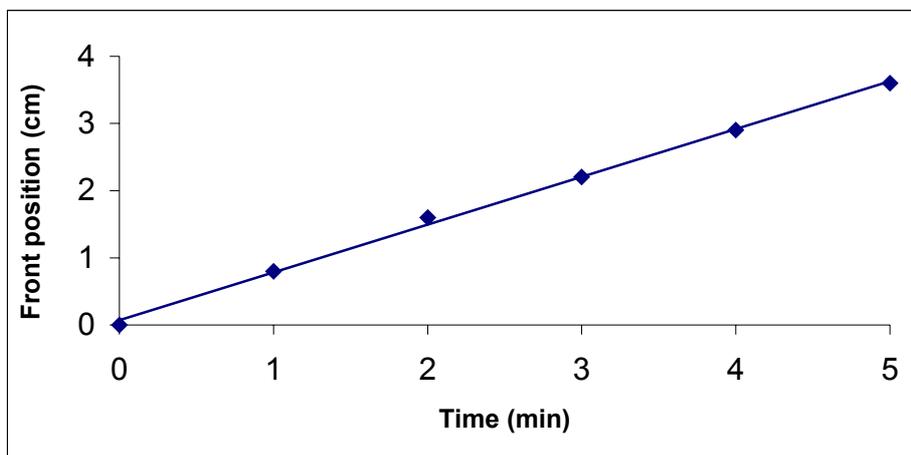


Fig. 2. Front position as a function of time in a typical FP synthesis (sample F1)

Effect of catalyst and inhibitor concentration

Three series of experiments were performed to determine the catalyst concentration range in which pure FP takes place. These series were characterized by a different amount of PC, namely, $[PC]/[DBTDAC] = 6, 8$ and 11 mol/mol. It should be noticed that smaller amounts of PC resulted in shorter pot-lives, and SP. It was found that, independent of the inhibitor content, when an amount of DBTDAC > 2 mol-% (referred to HDI) was used, simultaneous SP was observed. Conversely, for DBTDAC < 0.6 mol-%, FP did not self-sustain. For this reason, the experiments herein discussed refer to such concentration range only.

In Fig. 3 and Fig. 4, the dependence of T_{\max} and V_f on the concentration of catalyst is reported for the aforementioned contents of PC. As can be seen, for the minimum amount of catalyst ($[DBTDAC] = 0.6$ mol-%) no differences among the three series are found. Namely, in such conditions all these are characterized by the same T_{\max} and V_f values (c. 177°C and 0.6 cm/min, respectively).

Fig. 3 shows that the T_{\max} curves related to $[PC]/[DBTDAC] = 8$ and 11 remain almost superimposed in the considered region as a whole, ranging between 177 and 168°C (at $[DBTDAC] = 0.6$ and 2.0 mol-%, respectively). At variance, higher T_{\max} values ($181 - 183^\circ\text{C}$) were found when $[PC]/[DBTDAC] = 6$ mol/mol. It is noteworthy that the decrease of the amount of inhibitor results in an increase of front temperature, behaviour already found in our previous work on the FP of polyurethanes [2].

As previously mentioned, at $[DBTDAC] = 0.6$ mol-% the three systems are characterized by the same V_f (≈ 0.6 cm/min). Conversely, for larger catalyst contents the three curves diverge. Indeed, while for $[PC]/[DBTDAC] = 6$ and 8 mol/mol, V_f tends to become larger as the concentration of catalyst increases (up to 0.83 and 0.72 cm/min, respectively), for $[PC]/[DBTDAC] = 11$ mol/mol fronts propagated progressively slower (down to 0.43 cm/min).

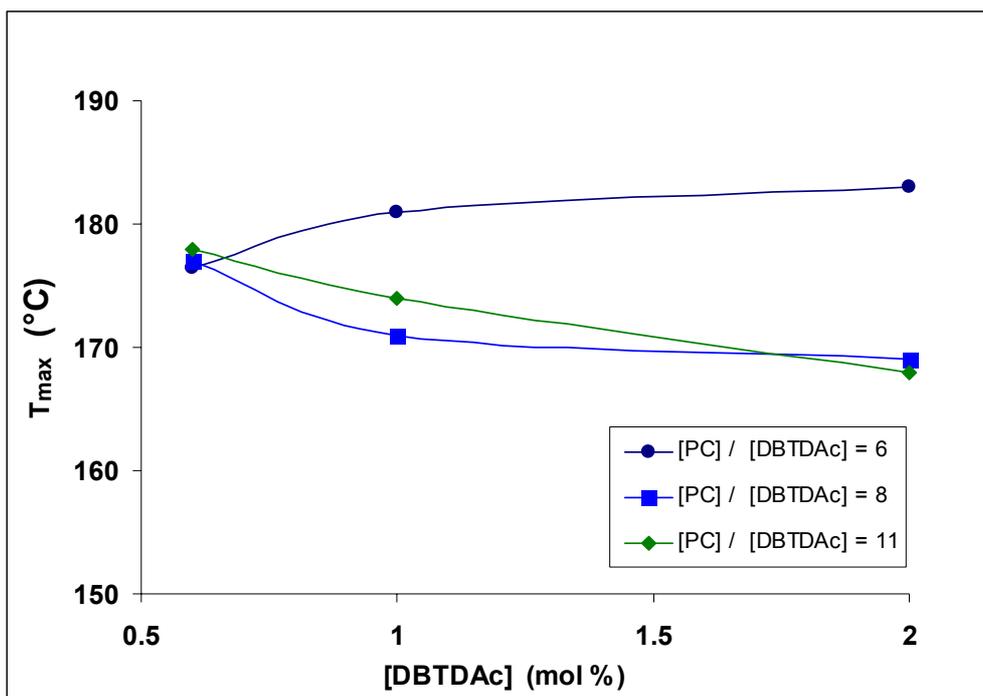


Fig. 3. T_{max} as a function of catalyst concentration

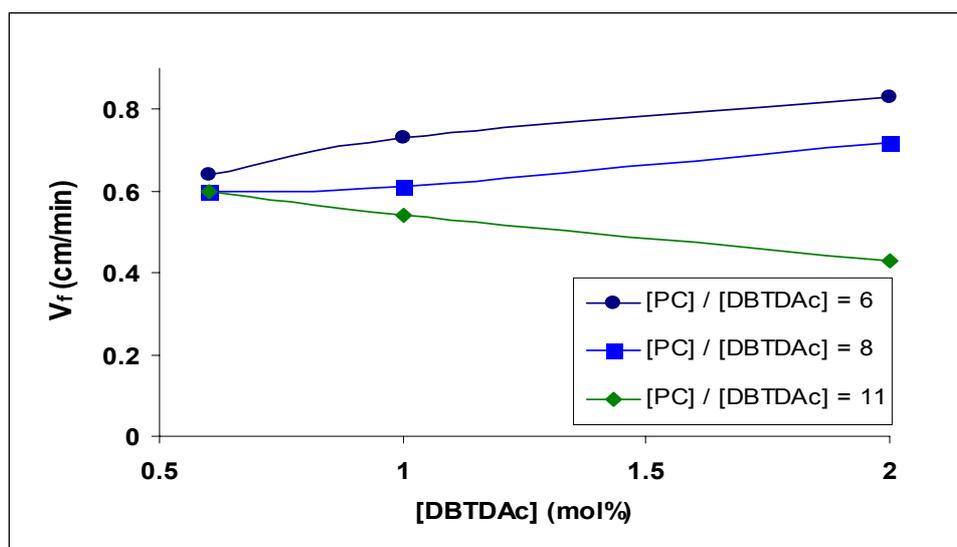


Fig. 4. V_f as a function of catalyst concentration

Furthermore, the effect of the amount of inhibitor on both T_{max} and V_f can be considered. It looks evident that the larger the amount of inhibitor, the lower T_{max} and V_f . This finding is consistent with what has been previously reported by us for the FP of PU obtained by HDI and EG [2] and for the FROMP of dicyclopentadiene [8].

Differential scanning calorimetry (DSC)

FP specimens were analyzed by DSC experiments and their thermal behaviour was compared with that of their batch counterparts. For brevity, we report here two DSC traces concerning a typical FP and a typical batch sample (named F1 and B1,

respectively) having the same initial composition (HDI : HD : PCLD = 1 : 0.65 : 0.35; 2.5 wt.-% Cab-osil; [DBTDAc]/[HDI] = 1.0 mol-%; [PC]/[DBTDAc] = 6 mol/mol). In Fig. 5, the DSC thermogram of F1 (2nd heating scan) is reported; two thermal transitions are evident: the former, located at low temperature (glass transition temperature $T_g \approx -24^\circ\text{C}$) confirms the presence of an amorphous phase; the latter evidences the presence of a crystalline phase which melts at $T_m = 121^\circ\text{C}$ with an enthalpy of fusion equal to 37.1 J/g.

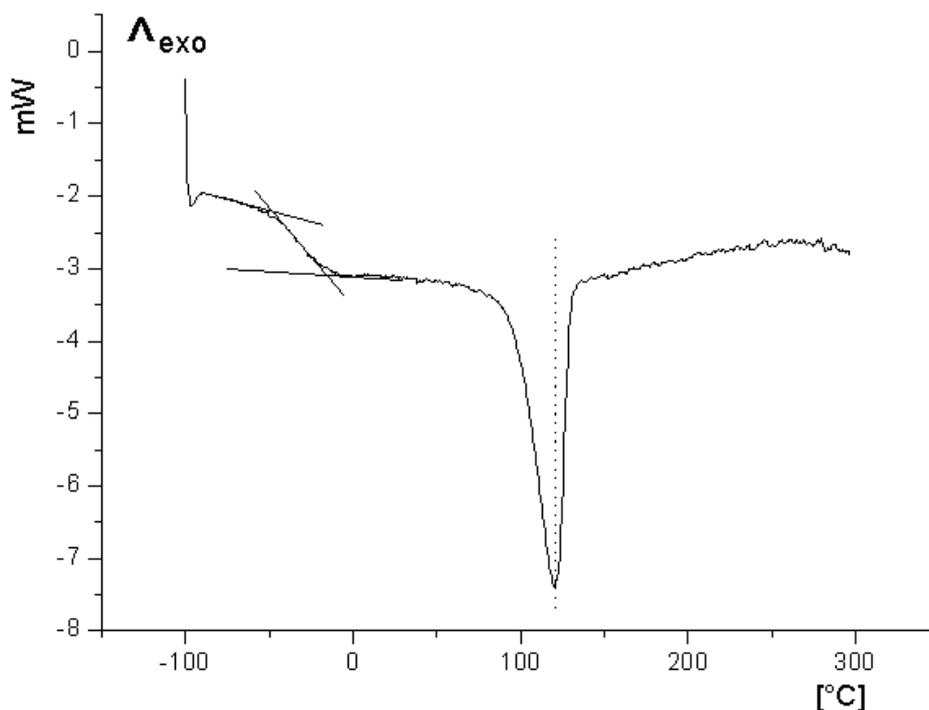


Fig. 5. DSC thermogram of sample F1

By comparing the thermal behaviour of the above samples (Fig. 5 and Fig. 6), some differences can be pointed out: first of all the thermal transitions characterizing F1 are present also in the B1 thermogram. However, these latter are located at different temperatures. In particular, the T_g value of B1 is shifted towards lower temperatures (-50.4°C) with respect to F1. Moreover, the batch product melts at higher temperature ($+139^\circ\text{C}$) and shows a higher enthalpy of fusion ($\Delta H_m = 59.6 \text{ J/g}$). Therefore, the crystallinity of the F1 product is lower than that of B1. The endothermic peak at $+55^\circ\text{C}$ evidenced by B1 can be attributed to PCL segment melting [23].

The dissimilar thermal behaviour of the two polymers can be attributed to the different reaction processes used for their preparation. In particular, the batch reaction allows the product to crystallize in a better way than FP. Indeed, this latter proceeds faster than the batch reaction thus reducing the ability of the polymer to crystallize and inducing the disappearance of endothermic signals due to the presence of pure PCL blocks.

As far as the shift of T_g towards lower temperatures is concerned, it might be firstly attributable either to the different reactivity of the two diols (HD and PCLD) in the reaction with HDI at two different temperatures (*i.e.*, the temperature of the batch reaction is lower than that reached during the FP) or to a plasticizing effect due to the

presence of partially reacted groups in the batch sample, which indeed exhibits lower conversion with respect to F1 (see later).

Moreover, the aforementioned differences of T_g , T_m and ΔH_m values of B1 with respect to F1 could also be attributed to phase separation phenomena occurring between soft and hard segments. Therefore, the shift of F1 T_g toward higher temperatures might indicate that PU soft and hard segments are more miscible in FP samples than in their batch counterparts.

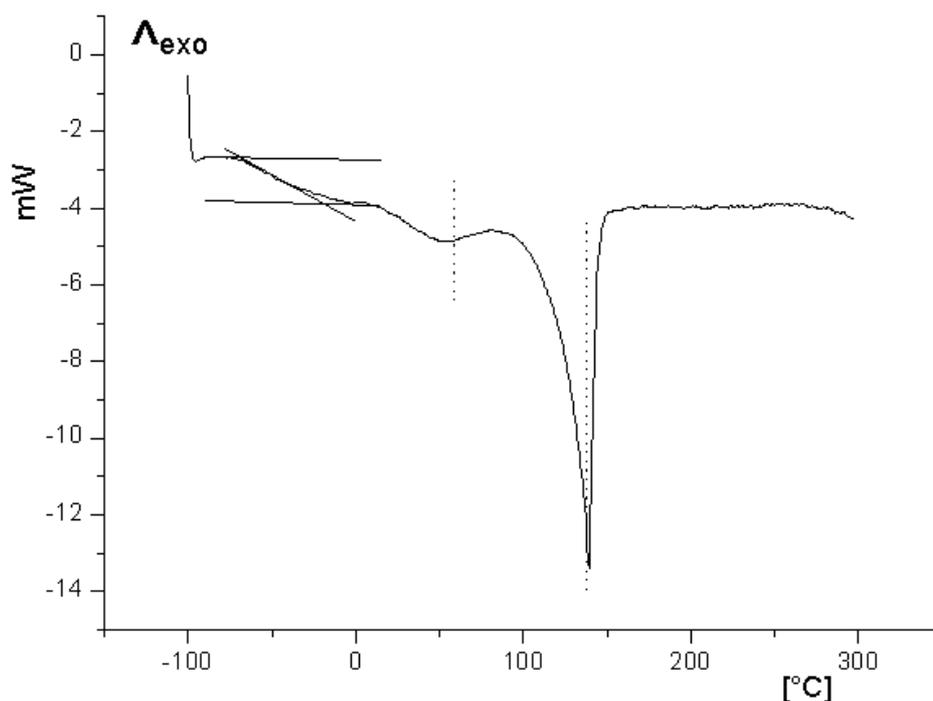


Fig. 6. DSC thermogram of sample B1

Viscosity

F1 and B1 were also compared in terms of solution viscosity (*i.e.*, molecular weight). F1 is characterized by $[\eta] = 0.43$ dl/g, while for B1 $[\eta] = 0.35$ dl/g, thus confirming that higher MW polyurethanes are obtainable by FP, a result similar to that reported by us in ref. [2]

Yield

The FP technique looks advantageous also in terms of yields. Namely, sample F1 was prepared in 75% yield, whereas B1 in 50%, only.

Conclusions

FP has been confirmed to be a promising route for the synthesis of polyurethanes.

Frontal polymerization reactions are significantly faster (just a few minutes) than those classically performed (at least one hour).

The resulting materials are obtained in larger yields and characterized by higher molecular weights than corresponding batch samples.

Furthermore, as far as the thermal behaviour is concerned, both FP and batch samples show a semicrystalline structure, having a T_g below room temperature and T_m above 120°C. However, FP materials are characterized by higher T_g and lower T_m than their batch counterparts.

Eventually, although FP samples have been prepared at higher temperatures than B materials, the short time taken for their synthesis does not seem to allow for the occurring of side reactions, at least to a significant extent. For instance, the well-known formation of crosslinked structures due to the self-reaction of isocyanates does not occur, all materials being soluble. However, further studies aiming to clarify this aspect are in progress.

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