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First Synthesis of a Polyurethane by Frontal Polymerization

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ABSTRACT: The first synthesis of a polyurethane by frontal polymerization has been successfully carried out. Namely, the two reactants (1,6-hexamethylene diisocyanate and ethylene glycol) and the catalyst (dibutyltin dilaurate) were mixed together at room temperature in the presence of an additive (pyrocatechol, necessary for extending pot life), dimethyl sulfoxide (as the solvent), and a filler (fumed silica, added for stabilizing the propagating front). The reactions were thermally ignited at one end of the tubular reactor, and the resultant hot fronts were allowed to self-propagate throughout the reaction vessel. The effects of relative amounts of the above components on the most relevant parameters relating to frontal polymerization (temperature profile, front velocity, and temperature) were thoroughly investigated.

Introduction

Most chemical reactions can be divided into two categories depending on the mutual reactivity of components: those to be performed in heated vessels and those resulting from the simple mixing of reactants at room temperature or below. A third category comprises those reacting systems being almost inert at room temperature but very reactive if ignited. The most common example belonging to this group is represented by combustion reactions.

In the field of polymer synthesis the first two classes are commonly used, whereas the third has not yet been similarly utilized and studied. However, the possibility of triggering off a polymerization reaction and achieving high monomer conversion in a short time often represent desirable features. This is particularly true in some practical applications that need to be carried out in situ (e.g., consolidation and restoration, paving, cementing, etc.). In addition, in these cases heated reactors or molds cannot be used.

Sometimes, an alternative solution is provided by photopolymerization. However, this technique is not applicable to all chemical systems; moreover, the resulting light intensity gradient prevents the curing of thick parts,[1] especially in the case of opaque composite materials. In these situations, frontal polymerization (FP) might represent a valid alternative.

FP is an approach to macromolecular syntheses which exploits the heat released by the reaction itself. This heat, in turn, induces the polymerization of monomer molecules close to the hot zone. If heat loss is not too large, the result is a self-sustaining hot front which propagates step by step through the reacting system.

The first studies on FP were performed in the former Soviet Union in the mid-1970s by Chechilo and Enikolopyan, who applied this technique to methyl methacrylate (MMA) monomer.[2,3] The reaction was carried out in adiabatic conditions under high pressure (>3000 atm).

After this preliminary work, a number of different vinyl monomers were polymerized by FP at ambient pressure.[4−8] Because of the high temperature reached by the travelling fronts, polymerization runs can successfully be performed without removing the inhibitor from the monomers, thus allowing for longer pot lives for the latter. The method was then effectively applied to epoxy resins[9,10] and their interpenetrating polymer networks (IPN).[11]

Morbidelli et al. reported on the advantageous application of FP to the obtainment of polymer blends.[12] Namely, it was found that PMMA/polystyrene blends prepared by FP were characterized by reduced phase separation if compared with those obtained either by mechanical mixing and the classical synthetic route. A similar result was reported by Pojman et al., who found that more homogeneous composites can be obtained by such a technique.[13] In both these studies, phase separation was limited by the high conversion rate which “freezes” the various components of the mixture in a metastable situation.

Furthermore, FP has been found useful also in the preparation of copolymers.[14] Indeed, the temperatures reached by the fronts make both reactivity monomer ratios equal to the unity. As a consequence, all copolymer chains were characterized by the same composition independent of monomer conversion and with no need of feed correction during the reaction.

To extend the number and type of both chemical systems and practical applications, Mariani et al. have first polymerized dicyclopentadiene by frontal ring-opening metathesis polymerization (FROMP)[15] and subsequently prepared its IPNs with acrylates.[16] In particular, in this latter work it was found that it is possible to take advantage of the heat released by DCPD polymerization to sustain the front of a second monomer (MMA), not able to frontally polymerize alone. This finding can open the accessibility of FP to a larger number of polymer systems not yet considered.

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Recently, FP was used by Washington and Steinbock[17] for the obtainment of temperature-sensitive hydrogels, by Fortenberry and Pojman for the solvent-free synthesis of polyacrylamide,[18] and by Mariani et al. for the preparation of polymer-dispersed liquid crystal films of improved homogeneity[19] and for the consolidation of porous materials having an historical–artistic interest.[19,20]

Furthermore, polyester/styrene resins prepared by FP have been found to be characterized by a higher conversion degree than those obtained by the usual batch technique.[19,21]

In addition to the above features of interest, it should be underlined that, FP being a self-sustaining reaction, it should also be considered an energy-saving way of producing polymer materials, with the additional advantage of short reaction times.

On the basis of what is summarized above, it is evident that FP is a very promising technique and one to be widely explored. In particular, significant scientific efforts should be made with the aim of extending the chemistry available to this synthetic approach. For each new suitable system found, a thorough systematic study on the influence of the relative ratios among all components of the reaction mixture has to be carried out. Specifically, front velocity and its maximum temperature are the parameters of main interest. Indeed, as mentioned above, most of the advantages of such an approach are a direct consequence of the high conversion rate due to high front temperatures. On the other hand, if these are excessively high, ceiling and/or degradation temperature can be reached, thus compromising the real usefulness of the method.

In the present paper we report on our recent results devoted to setting up experimental conditions for the first synthesis of a polyurethane by the FP technique.

Because of the high mutual reactivity of 1,6-hexamethylene diisocyanate (HDI) and ethylene glycol (EG) when mixed together with a suitable catalyst (dibutyltin dilaurate, DBTDL), a small amount of an additive (pyrocatechol) was added to the reaction mixture in order to increase its pot life.[22] Indeed, to achieve a *pure* FP, a sufficiently long pot life of the reaction medium must be present.[15,16] If this is not the case, spontaneous polymerization (SP) occurs which competes with, and sometimes prevents, FP.

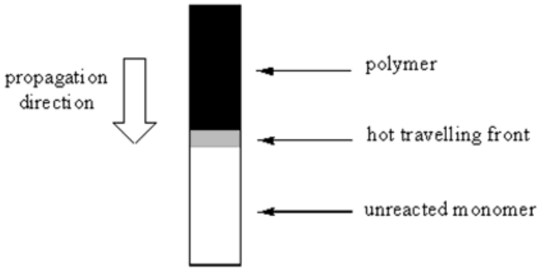
In the following, the influence of catalyst and additive concentrations, as well as those of the other components of the reaction mixture, will be presented. Furthermore, a comparison with some samples obtained in batch will be reported.

Experimental Section

Materials. 1,6-Hexamethylene diisocyanate, pyrocatechol, dibutyltin dilaurate, dimethyl sulfoxide (DMSO), and *m*-cresol were purchased from Aldrich; ethylene glycol and Cabosil were obtained from Fluka. All materials were used as received.

Frontal Polymerizations. In a typical run, a glass test tube (i.d. 16 mm) was filled with the appropriate amounts of HDI and EG (always used in equimolar amounts), DBTDL, dimethyl sulfoxide (as the solvent), and 3 wt % fumed silica (Cabosil). The vessel was shaken in order to obtain a homogeneous mixture, and a K-type thermocouple, connected to a digital thermometer, was utilized to monitor the temperature change (instrument precision ±0.3 °C). The junction was immersed at about 4 cm from the free surface of the liquid. The front position (±0.5 mm) was recorded as a function of time.

Scheme 1. Schematic Representation of FP Occurring along a Tubular Reactor



The upper layer of the mixture was then heated by a soldering iron until the formation of a hot propagating front began (Scheme 1). Front propagation occurred at constant velocity by conversion of monomer to polymer with almost no formation of bubbles. After reaction completion, the samples were allowed to cool to room temperature and kept at that temperature for an hour. Subsequently, they underwent Soxhlet extraction for 24 h using boiling methanol, and the residue was dissolved in *m*-cresol in order to remove silica by centrifugation. Thereafter, the clear solution was poured into 5% aqueous NaOH and the white precipitate filtered, washed with water, acetone, and diethyl ether, and finally dried in a vacuum oven at 40 °C for 24 h. Polymer yields were almost quantitative.

Batch Polymerizations. Several batch runs have been performed in order to compare the resultant samples with the corresponding ones obtained by FP. In typical syntheses, the same amounts of each component as quoted above were mixed in a reaction vessel, immersed in a thermostatic oil bath set either at 80 or 180 °C, and allowed to react for an hour. The samples underwent the same purification procedure described above.

Characterization. NMR characterization was performed on a 300 MHz spectrometer (Varian) in DMSO-d_6: δ 1.3 (m, 8H), δ 2.9 (m, 4H), δ 4.1 (m, 4H), δ 7.2 (s, 2H). Intrinsic viscosities were measured in *m*-cresol at 25 °C.

Glass transition temperature (T_g), melting temperature (T_m), and degree of crystallinity (x_c) of FP and batch samples were measured by a Mettler differential scanning calorimeter (DSC) model TC 10A. All samples underwent the following cycle of three temperature scans in order to eliminate residual solvents and to standardize the thermal history of polyurethane samples: a first heating from 0 to 240 °C (at 20 °C/min), followed by cooling from 240 to 0 °C (at 20 °C/min) and a second heating from 0 to 240 °C (at 20 °C/min). Only T_g, T_m, and x_c values observed during the second heating have been taken into consideration in the following.

Results and Discussion

Preliminary Experiments. Several preliminary runs were performed in order to verify whether FP could be a suitable route for obtaining polyurethanes. Namely, we have found that, by the simple mixing of EG, HDI, and DBTDL at room temperature in the presence of DMSO (necessary to prevent phase separation), an instantaneous SP reaction occurs. Although a longer pot life could be attained by maintaining the above mixture at temperatures ranging between −50 and −100 °C, a pure FP was not achieved by this approach, both SP and FP taking place simultaneously with the formation of "fingering".[5,23,24] This phenomenon occurs when a polymer is denser than the corresponding monomer and melts at the front temperature; it is revealed by descending drops of hot polymer material that contaminate the lower zones of unreacted monomer, resulting both in heat removal from the front (sometimes even quenching it) and in local SP. As suggested in the literature,[23,24] depending on the polymerizing system

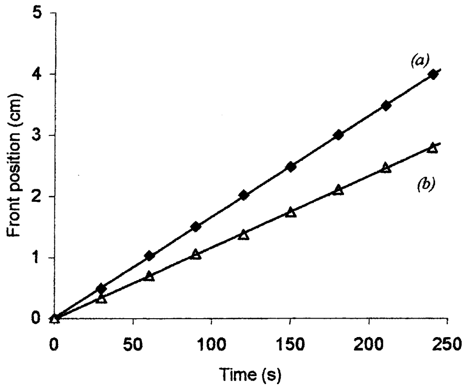


Figure 1. Front position vs time for a typical run of (a) and (b) series. (a) [DBTDL]/[HDI] = 1.9×10^{-3} mol/mol; [pyrocatechol]/[DBTDL] = 11 mol/mol; DMSO = 18 wt %; Cabosil = 3 wt % (FP7). (b) [DBTDL]/[HDI] = 1.9×10^{-3} mol/mol; [pyrocatechol]/[DBTDL] = 28 mol/mol; DMSO = 18 wt %; Cabosil = 3 wt % (FP8).

there are several means of preventing this phenomenon such as tube rotation, high-frequency low-amplitude oscillatory vibrations, and increased viscosity of polymerization medium by viscosifier addition (e.g., small amounts of ultrafine fumed silica). In subsequent experiments we selected the latter approach, also taking into account that in several applications silica could be used as a filler in polyurethane-based formulations.

In addition, Damman and Carlson[22] have shown that an extended pot life in the synthesis of polyurethanes can be achieved by adding suitable amounts of an additive (pyrocatechol) to the above reaction components. The effect of pyrocatechol is that of tin complexation, with the consequence of depressing catalyst activity at room temperature, yet ensuring a high reactivity at the higher temperatures typically reached by propagating fronts. As a matter of fact, by pyrocatechol addition (≥ 0.5 wt %) a pot life 25 min long was achieved in our reacting system, as compared to the almost instantaneous reaction in its absence. This finding allowed us to perform pure FP runs without simultaneous occurrence of SP.

As already indicated, the role of relative amounts of catalyst, reactants, additive, and DMSO will be described in detail and related to the most relevant FP parameters such as front velocity, temperature profile, and its maximum value.

All syntheses have been performed in nonadiabatic reactors in order to test the applicability of this technique to process conditions often found in practice.

For two typical runs, the position of the hot front as a function of time is given in parts a and b of Figure 1 (samples FP7 and FP8, respectively). As can be seen, the experimental data for both sets of experiments are well fitted by straight lines, meaning that the propagation of the polymerization front moves at a constant velocity. This behavior represents the first experimental evidence that pure FP is occurring. In fact, deviations from the linearity are generally observed when a simultaneous SP is present. These deviations are mainly due to heat dispersion caused by the monomer fraction polymerizing by SP and to the related change of medium viscosity.

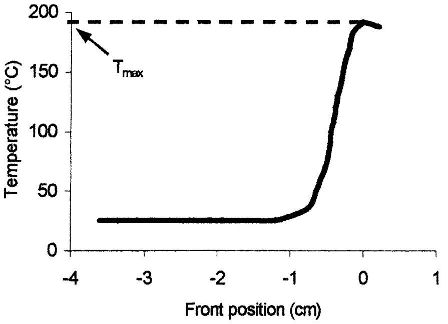


Figure 2. A typical temperature profile. [DBTDL]/[HDI] = 7.1×10^{-4} mol/mol; [pyrocatechol]/[DBTDL] = 28 mol/mol; DMSO = 18 wt %; Cabosil = 3 wt % (FP4).

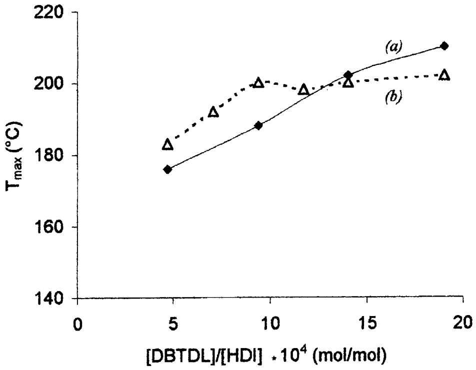


Figure 3. Maximum temperature reached by the front vs [DBTDL]/[HDI] ratio: (a) [pyrocatechol]/[DBTDL] = 11 mol/mol, DMSO = 18 wt %, Cabosil = 3 wt %; (b) [pyrocatechol]/[DBTDL] = 28 mol/mol, DMSO = 18 wt %, Cabosil = 3 wt %.

Further evidence to support the above statement is given by the temperature profile of sample FP4 shown in Figure 2. The horizontal part of the curve, ascribing a constant temperature value to zones far from the incoming hot front, points out that SP is not occurring simultaneously; otherwise, because of the exothermicity of the reaction, a temperature increase should be observed.

On the basis of the above results, it can be inferred that, by choosing suitable amounts of reactants, catalyst, and additive, only FP is occurring in our reacting system.

Effect of Catalyst Concentration. Two series of experiments have been carried out, each of them keeping constant a specific [pyrocatechol]/[DBTDL] ratio. In the runs performed at [pyrocatechol]/[DBTDL] = 11 (mol/mol), the [DBTDL]/[HDI] ratio was allowed to vary between 0 (no catalyst added) and 2.4×10^{-3} (mol/mol), but reproducible FP data were obtained only in the range between 4.7×10^{-4} and 1.9×10^{-3} (mol/mol). For lower ratios, no FP was observed. Conversely, for [DBTDL]/[HDI] > 1.9×10^{-3} a significant amount of SP was always present.

Also in the runs performed at [pyrocatechol]/[DBTDL] = 28 (mol/mol), the range in which a pure FP was observed was $4.7 \times 10^{-4} \leq$ [DBTDL]/[HDI] $\leq 1.9 \times 10^{-3}$. Again, at lower ratios the propagating front was not able to self-sustain, whereas at larger contents of catalyst, FP was in competition with SP.

For the two sets of experiments, the temperature of the propagating front ($T_{\max}$, as defined in Figure 2) is plotted in Figure 3 as a function of the [DBTDL]/[HDI] molar ratio, within the above range of values causing pure FP to occur. It should be emphasized once more that our experiments are performed in nonadiabatic conditions and, for this reason, their $T_{\max}$ values are not constant but dependent on the experimental parameters chosen. Namely, slow fronts allow more time for heat

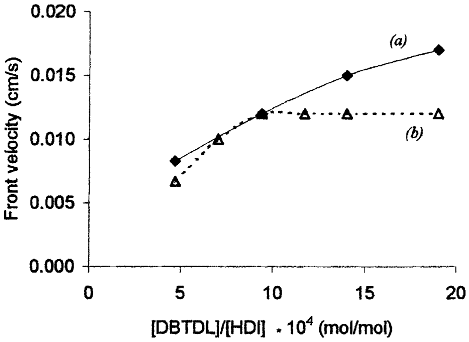


Figure 4. Front velocity vs [DBTDL]/[HDI] ratio: (a) [pyrocatechol]/[DBTDL] = 11 mol/mol, DMSO = 18 wt %, Cabosil = 3 wt %; (b) [pyrocatechol]/[DBTDL] = 28 mol/mol, DMSO = 18 wt %, Cabosil = 3 wt %.

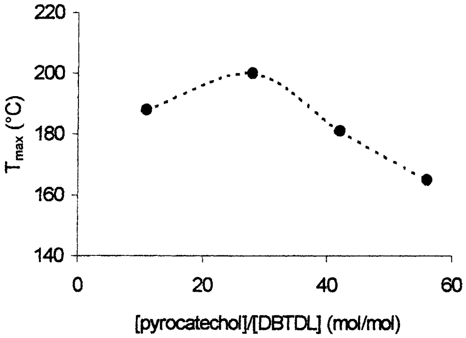


Figure 5. Maximum temperature vs [pyrocatechol]/[DBTDL] ratio. Experimental conditions: [DBTDL]/[HDI] = 9.4 × 10^{-4} mol/mol, DMSO = 18 wt %, Cabosil = 3 wt %.

loss, and consequently, lower T_{max} values are found. Indeed, data in Figure 3 are rather far from the limiting value pertaining to the adiabatic temperature (232 °C).

For the first set of experiments (curve a), an almost linear dependence of T_{max} on [DBTDL]/[HDI] is present in the whole range of molar ratios, whereas for the other set (curve b) a more complex pattern is shown, with a curve approaching a *plateau* value for the [catalyst]/[reactant] ratio ≥ 9 × 10^{-4}. In other words, at variance from what has been found for (a) systems, a linear dependence of T_{max} on the [catalyst]/[reactant] ratio is present only in the lower range of catalyst concentrations (4.7 × 10^{-4} ≤ [DBTDL]/[HDI] ≤ 9.4 × 10^{-4}). For higher values, T_{max} remains almost constant at ca. 200 °C.

For the first set of experiments, a quasi-linear relationship is present also between the front velocity and the [DBTDL]/[HDI] ratio (Figure 4a). Namely, an increase of catalyst concentration from [DBTDL]/[HDI] = 4.7 × 10^{-4} to 1.9 × 10^{-3} mol/mol caused an increase of front velocity from 0.0083 to 0.017 cm/s.

Conversely, for the second set of experiments (Figure 4b), the front velocity dependence on the [catalyst]/[reactant] ratio levels off at values of the above ratio ≥ 9 × 10^{-4} in a way very similar to the corresponding T_{max} trend.

Effect of Additive Concentration. For this set of experiments [DBTDL]/[HDI] was kept constant and equal to 9.4 × 10^{-4} mol/mol, while the [pyrocatechol]/[DBTDL] molar ratio was allowed to vary between 11 and 56 (for [pyrocatechol]/[DBTDL] < 11, SP has always been observed).

Figure 5 shows T_{max} vs [pyrocatechol]/[DBTDL] ratio. As mentioned above (Figure 3), an increase of this ratio from 11 to 28 resulted in a corresponding rise of T_{max} from 188 to 200 °C. The latter value represents the highest temperature reached in this set of experiments. In fact, all runs carried out in the presence of larger amounts of pyrocatechol were characterized by lower values of T_{max}, with an almost linear decrease down to 165 °C for [pyrocatechol]/[DBTDL] = 56 mol/mol. Front velocity as a function of the [pyrocatechol]/[DBTDL] ratio is reported in Figure 6. The plot shows that the larger the concentration of additive, the slower the propagating front is, for molar ratios ≥ 28. This result is also confirmed by comparing the slope of the two straight lines reported in Figure 1 that refers to the largest [DBTDL]/[HDI] ratio which allows for a pure FP to occur (1.9 × 10^{-3} mol/mol).

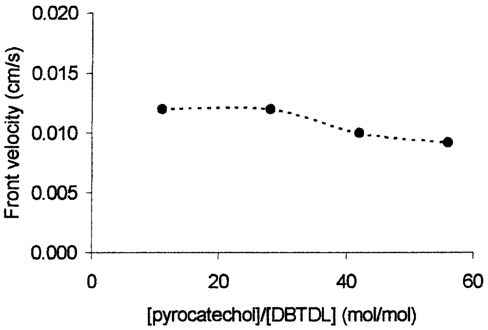


Figure 6. Front velocity vs [pyrocatechol]/[DBTDL] ratio. Experimental conditions: [DBTDL]/[HDI] = 9.4 × 10^{-4} mol/mol, DMSO = 18 wt %, Cabosil = 3 wt %.

If we analyze in detail the curve trends given in Figures 1 and 4, it may be pointed out that the two experiments shown in Figure 1 as typical examples of pure FP pertain to the highest [catalyst]/[reactant] ratio, i.e., 1.9 × 10^{-3}. As a consequence, they are characterized by the highest front velocity of each series. The slope of example (b) being lower, at first it might be suggested that one of the effects linked to the presence of larger amounts of additive (pyrocatechol) be that of diminishing front velocity. However, the above consideration does not in reality have any general validity if the detailed behavior of front velocity is examined in the whole range of additive concentration (Figure 4). Indeed, for 4.7 × 10^{-4} ≤ [DBTDL]/[HDI] ≤ 9.4 × 10^{-4}, front velocity does not seem to be appreciably influenced by the amount of additive, the two curves being almost superimposed. Only for [DBTDL]/[HDI] > 9.4 × 10^{-4}, the behavior of the two systems sharply differs: while for lower amounts of pyrocatechol ((a) series) front velocity remains almost proportional to [DBTDL]/[HDI], for larger amounts of additive ((b) series) a *plateau* value of ca. 0.012 cm/s is reached.

The relationship between front velocity and T_{max} for the two series is shown in Figure 7. As can be seen, all experimental data of the (a) series are characterized by higher velocity when compared to those obtained with larger additive concentrations for the same T_{max}. Moreover, for the (a) series the relationship found is linear, with a doubling of front velocity from 0.0083 to 0.017 cm/s for a T_{max} increase from 176 to 210 °C.

Different behavior characterizes the (b) series for which, again, a tendency to reach a *plateau* value has been found: after an almost linear increase from 0.0067 cm/s at 183 °C to 0.012 cm/s at 198 °C, the latter value of front velocity is kept almost constant up to 202 °C.

Effect of Reactant Dilution. As mentioned above, a small amount of DMSO is necessary in order to obtain a good mixing of all components. The results discussed

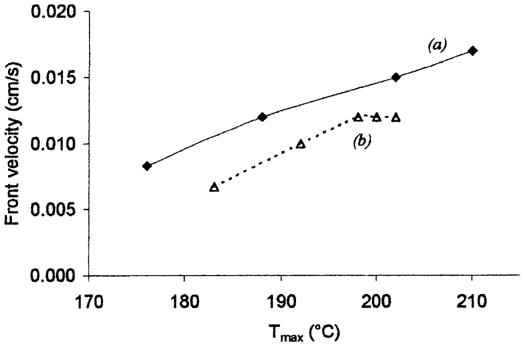


Figure 7. Front velocity as a function of T_{max} for (a) and (b) series. (a) [DBTDL]/[HDI] = 4.7×10^{-4}–1.9×10^{-3} mol/mol; [pyrocatechol]/[DBTDL] = 11 mol/mol; DMSO = 18 wt %; Cabosil = 3 wt %. (b) [DBTDL]/[HDI] = 4.7×10^{-4}–1.9×10^{-3} mol/mol; [pyrocatechol]/[DBTDL] = 28 mol/mol; DMSO = 18 wt %; Cabosil = 3 wt %.

Table 1. Effect of DMSO Content in the Reaction Mixture on T_{max} and Front Velocity[a]

sample	amount of DMSO (wt %)	T_{max} (°C)	front velocity (cm/s)
FP1	18	188	0.012
FP5	24	183	0.0067
FP6	30	180	0.0050

[a] [DBTDL]/[HDI] = 9.4×10^{-4} mol/mol; [pyrocatechol]/[DBTDL] = 11 mol/mol; Cabosil = 3 wt %.

so far refer to compositions containing 18 wt % of DMSO, i.e., the minimum amount of solvent which allows a single phase of the polymerization mixture to occur (with the obvious exception of fumed silica).

We have also tried to investigate the influence of larger quantities of DMSO on both T_{max} and front velocity. The resultant data are listed in Table 1.

As might be expected, a dilution of the reactants resulted in a slight decrease of T_{max} from 188 to 180 °C, for DMSO content ranging from 18 to 30 wt %. The effect of dilution on front velocity is more evident, going from 0.012 down to 0.0050 cm/s.

Characterization Data and Comparison between Samples Obtained by Frontal and Batch Polymerization. *DSC Analysis.* As mentioned in the Experimental Section, DSC traces referring to the second heating of the samples have been considered, and no relevant difference in terms of T_m, T_g, and x_c has been observed. As an example, the DSC trace of a typical FP sample (FP3) is shown in Figure 8, in which T_m and T_g can be observed at 167 and 37 °C, respectively. By comparison, the DSC trace of the corresponding batch polymer (B1) is plotted in the same Figure: T_m and T_g values are 166 and 35 °C, respectively. In addition, FP samples have been characterized in term of crystallinity degree, with values ranging from between 31 and 38%, similar to those of the batch samples, for which x_c = 30–38%.

Viscosity Measurements. Table 2 lists the intrinsic viscosities of some representative samples prepared by FP. As shown in the table, the larger the amount of catalyst and T_{max}, the higher [η] is, ranging from 0.20 to 0.76 dL/g for a [DBTDL]/[HDI] ratio going from 4.7×10^{-4} to 1.4×10^{-3} (mol/mol).

Samples B1 and B2 have been synthesized by the usual batch technique, starting from the same recipe of sample FP3 at two different temperatures: 80 and 180 °C. The first of these two values has been chosen because it is that suggested in the literature (80 °C)[22] whereas the second is in the same range reached by FP travelling fronts. [η] data show that, in this case, increasing temperature sharply decreases the molecular weight of the resultant polymer (0.46 and 0.23 dL/g, respectively). Furthermore, it can be seen that both B1 and B2 are characterized by [η] values lower than FP3 (0.76 dL/g). In other words, the effect of FP on molecular weights (i.e., on monomer conversion) is very peculiar and thus does not lead to the temperature effect found in the batch synthesis of polyurethanes.

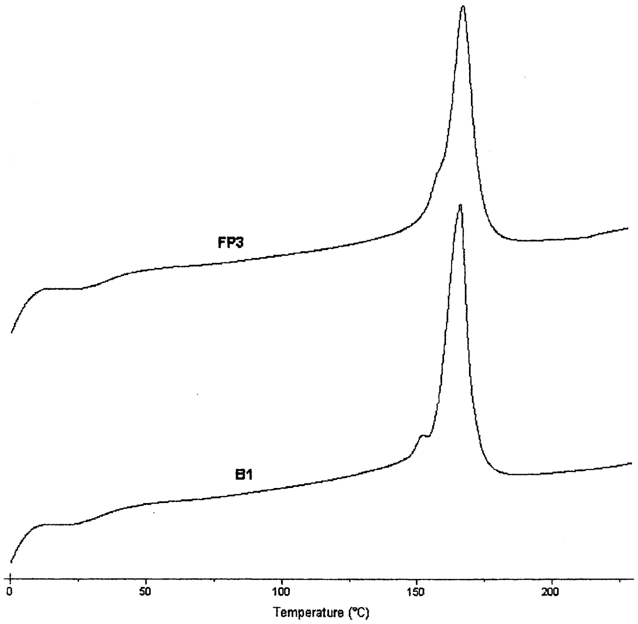


Figure 8. DSC traces of two typical samples obtained by FP (FP3) and batch polymerization (B1).

Table 2. Intrinsic Viscosity Data of Some Polyurethane Samples Obtained by FP and Batch Polymerization[a]

sample	[DBTDL]/[HDI] (mol/mol)	T_{max} (°C)	T_{bath}[b] (°C)	[η][c] (dL/g)
FP2[d]	4.7×10^{-4}	176		0.20
FP1[d]	9.4×10^{-4}	188		0.47
FP3[d]	1.4×10^{-3}	202		0.76
B1[e]	1.4×10^{-3}		180	0.23
B2[e]	1.4×10^{-3}		80	0.46

[a] Other reaction conditions common to all samples: [pyrocatechol]/[DBTDL] = 11; DMSO = 18 wt %; Cabosil = 3 wt %. [b] Reaction temperature. [c] In *m*-cresol at 25 °C. [d] Samples obtained by FP. [e] Samples obtained by batch polymerization.

On the basis of the comparative results shown above, FP can be considered a reliable alternative approach to be used for the synthesis of polyurethanes in short times, at relatively low cost (no energy has to be provided except for that igniting the polymerization reaction) and with properties comparable with those characterizing the corresponding materials synthesized by the classical method.

Conclusions

The first synthesis of a polyurethane by frontal polymerization has been successfully carried out. In this model system, the relative amounts of the reaction components have been allowed to vary in a large composition range in order to find their influence on the polymerization parameters. Namely, SP has been prevented, and only pure FP has occurred with very high yields and in rather short times.

The obtained polymer materials are characterized by features similar to, possibly better than, those obtained by the classical batch route. In particular, higher molecular weight and conversion have been reached. The above results allow us to conclude that FP can be exploited as an alternative means of polyurethane synthesis with the additional advantages of high velocity and low cost.

Further studies with the aim of extending this technique to other polyurethane formulations, including PU networks, are in progress and will be reported elsewhere.[25]

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