

Frontal Polymerization of Diurethane Diacrylates

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ABSTRACT: This work deals with the preparation of poly(urethane acrylates) by using two different polymerization techniques. Namely, the classical batch procedure has been compared with frontal polymerization (FP). A thorough study on the effect of initiator type, concentration, and on the velocity of the front and its maximum temperature has been carried out. Moreover, two different synthetic ways have been studied: the one step poly(urethane acrylate) preparation starting directly from 1,6 diisocyanato hexane and 2-hydroxyethyl acrylate, and the two step procedure consisting of the synthesis of the corresponding diurethane diacrylate and of its subsequent polymerization. The first method has the advantage of being faster but some caution is necessary due to the excessive heat that is generated if the reaction conditions are not properly chosen. The second approach requires a further step but has the advantage of being more controlled. DSC analysis did not show any significant difference by comparing the thermal properties of the materials obtained by the two techniques (batch and FP). However, since FP runs are very easy and fast to be performed, FP should be seriously taken into proper account when these materials have to be prepared. © 2008 Wiley Periodicals, Inc. *J Polym Sci Part A: Polym Chem* 46: 3344–3352, 2008

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INTRODUCTION

Diurethane diacrylates (DDs) are a class of monomers widely used in polymer preparations; namely, their reaction with diols or diamines is often preferred for the obtainment of polyurethane and polyureas, respectively.^{1–4}

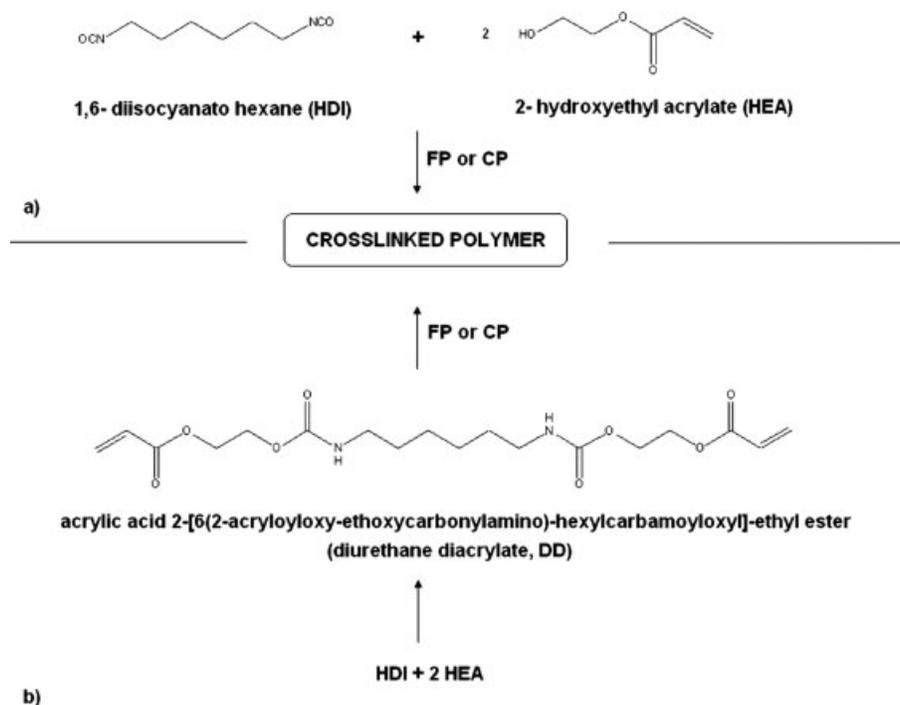
Prompted by the general interest on these products, we have experimented the use of Frontal Polymerization (FP) as alternative approach for the synthesis of poly(urethane acrylates).

FP is a technique exploiting the heat released during the polymerization reaction to promote a self-sustaining front which travels along the reactor by converting monomer into polymer. In principle, once reached a steady state, FP could propagate indefinitely.

FP was initially investigated by Chechilo et al.,⁵ and lately extensively studied by Pojman

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Scheme 1. Materials, polymerization routes and techniques used in the present work.

and coworkers who polymerized acrylic monomers^{6–8} and epoxy resins.⁹ Mariani et al. obtained poly(dicyclopentadiene),¹⁰ polyurethanes,^{11,12} interpenetrating polymer networks,¹³ and unsaturated polyester/styrene resins.¹⁴ White and coworkers investigated the curing of epoxy-based materials.¹⁵ Pojman and coworkers prepared thermochromic composites¹⁶ and polymer-dispersed liquid crystal (PDLC) materials,¹⁷ Morbidelli and coworkers obtained homogenous polymer blends¹⁸ and copolymers,¹⁹ Washington and Steinbock synthesized hydrogels.²⁰ Mariani et al. prepared PDLC films²¹ and applied FP to the consolidation of porous materials.²² Pojman et al. demonstrated FP with thiol-ene chemistry.²³ McFarland et al. used FP with microencapsulated initiators.^{24,25} Crivello studied the design and synthesis of glycidyl ethers that undergo FP,^{26,27} and hybrid free radical/cationic FP.²⁸ Recently, Mariani et al. prepared polymer-based nanocomposites with montmorillonite²⁹ and polyhedral oligomeric silsesquioxanes,³⁰ Hu et al. frontally copolymerized urethane-acrylates in dimethyl sulfoxide.³¹ Chen et al. studied the FP of hydroxyethyl acrylate (HEA),³² *N*-methylolacrylamide,³³ and the preparation of its hybrids with methylacrylamide,³⁴ moreover, they studied the obtainment of

epoxy resins/polyurethane hybrid networks,³⁵ and of polyurethane-nanosilica hybrid nanocomposites.³⁶

Moreover, there are several patents relating to FP.^{37–43} In this article, we report the first application of FP:

- i. To the components of the reaction between 1,6-diisocyanato hexane (HDI) and HEA (molar ratio [HDI]/[HEA] = 0.5 mol/mol [Scheme 1(a)].
- ii. To the DD derived by the preliminary reaction of the above compounds [Scheme 1(b)].

Moreover, the obtained samples were compared with the analogous ones prepared by the conventional batch technique (CP). In Scheme 1, HDI, HEA, and DD molecular structures are depicted.

EXPERIMENTAL

HDI, HEA, dibutyltin dilaurate (DBTDL), pyrocatechol (PC), 2,2'-azobis-isobutyronitrile (AIBN), benzoyl peroxide (BPO), Aliquat[®] 336, *t*-butylperoxy-2-ethylhexylcarbonate (Luperox[®])

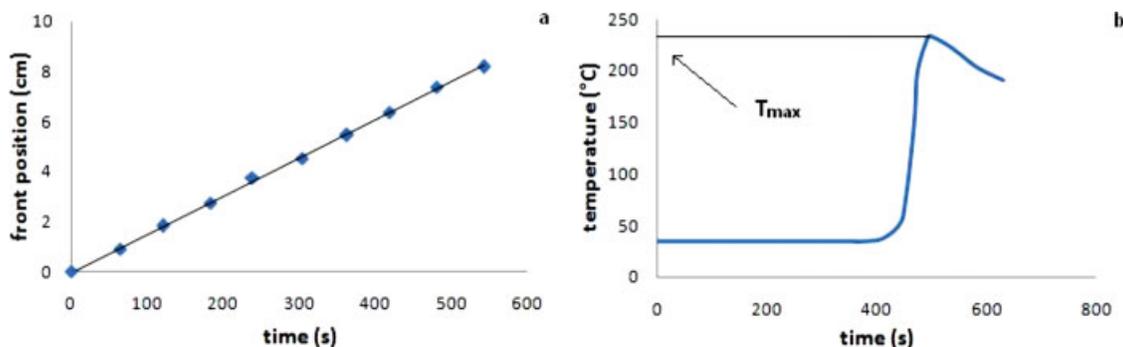


Figure 1. *In situ* formation of DD and its FP: typical front position (a) and temperature profile (b) as a function of time. Conditions: [DBTDL]/[HDI] = 0.1 mol %, [APS]/[HEA] = 0.6 mol %, [PC]/[DBTDL] = 6 mol/mol.

TBCE), *t*-butyl peroxide (tBP), and ammonium persulfate were purchased from Sigma-Aldrich and used without further purification.

Aliquat persulfate (APS) was prepared as described in the literature⁴⁴ starting from Aliquat[®] 336.

Temperature profiles and the maximum temperature reached by the front [T_{\max} , Fig. 1(b)] were measured using a K-type thermocouple placed into the above mixture at 2 cm (± 5 mm) from the bottom of the tube. The thermocouple was connected to a digital thermometer (Delta Ohm 9416) used for temperature reading and recording (sampling rate: 1 Hz). The position of the front (easily visible through the glass wall of test tubes) was also measured as a function of time [Fig. 1(a)].

Reproducibility of T_{\max} data was ± 15 °C and that of front velocity, V_f , was ± 0.2 cm/min. Error bars in the following plots indicate these variation ranges.

DSC measurements were performed using a Mettler DSC 30 Instr. equipped with a low temperature probe. On each sample, two consecutive scans were carried out in nitrogen atmosphere in the temperature range from -80 up to $+200$ °C with a heating rate of 10 °C/min. T_g values were determined by the 2nd thermal scan.

Synthesis of Acrylic acid 2-[6-(2-Acryloyloxyethoxycarbonylamino)-hexylcarbamoyloxy]-ethyl ester (DD)

A round bottom flask was loaded with 30 g (0.18 mol) of HDI and 0.2 g (3.1×10^{-4} mol) of DBTDL dissolved in 200 mL of anhydrous tetrahydrofuran. A little amount of *t*-butylcatechol was added as radical inhibitor. A solution of 41 g

(0.36 mol) of HEA dissolved in 20 mL of anhydrous tetrahydrofuran was added dropwise at 5 °C. After 30 min, temperature was raised to 50 °C and the reaction prolonged for 20 min. When the reaction was accomplished, the solution was poured into petroleum ether. The obtained white precipitate was collected by filtration and dried under vacuum. Yield 90%, Scheme 1(b).

¹H NMR (DMSO-*d*₆; δ_H in ppm): 6.47 (2H); 6.13 (2H); 5.88 (2H); 4.31 (4H); 4.29 (4H); 3.17 (4H); 1.48 (4H).

In situ Formation of DD (from HEA and HDI) and its FP [Scheme 1(a)]

In a typical run, a nonadiabatic glass test tube (inner diameter: 16 mm) was loaded with appropriate quantities of HDI, DBTDL and PC (see Results and Discussion). The mixture was homogeneously mixed with an adequate amount of HEA ([HDI]/[HEA] = 0.5 mol/mol) and a radical initiator (APS, BPO, or AIBN).

A K-type thermocouple was placed into the above mixture at 2 cm (± 5 mm) from the bottom of the tube, and the temperature monitored by a digital thermocouple reader. The FP reaction was triggered by means of a hot soldering iron tip ($T \approx 300$ °C), by heating the external wall of the tube in correspondence of the upper solution layer, until the formation of a traveling front.

After FP was accomplished, the test tube was cooled to room temperature. Afterwards, the crosslinked polymer was extracted in Soxhlet with diethyl ether to remove the unreacted products, and dried under vacuum for 12 h at 50 °C.

Table 1. *In Situ* Formation of DD and Its FP: Blank Runs

Sample	[APS]/[HEA] (mol %)	[DBTDL]/[HDI] (mol %)	[PC]/[DBTDL] (mol/mol)	Polymerization Mode
BR1	–	–	–	No polymerization
BR2	–	0.17	6	FP (self-ignition)
BR3	0.60	–	6	No polymerization
BR4	–	–	6	No polymerization
FP1	0.60	0.17	6	FP

[HDI]/[HEA] = 0.5 mol/mol.

FP of DD [Scheme 1(b)]

In a typical run, a nonadiabatic glass test tube (inner diameter: 16 mm) was loaded with suitable quantities of DD (kept melt at ~ 90 °C) and a radical initiator (Luperox TBCE or tBP). The mixture was rapidly homogenized and cooled to ~ 70 °C (solid state mixture).

A K-type thermocouple was placed into the above mixture at 2 cm (± 5 mm) from the bottom of the tube and the temperature monitored by a digital thermocouple. The FP reaction was ignited as described earlier.

After FP was accomplished, the test tube was cooled to room temperature. Afterwards, the crosslinked polymer was extracted in Soxhlet with diethyl ether to remove the unreacted products, and dried under vacuum for 12 h at 50 °C.

Batch Samples

The same reaction mixtures as described earlier were also allowed to polymerize by the CP in nonstirred batch reactors at 100 °C for 1 h.

RESULTS AND DISCUSSION

As well as it happens in many frontal reactions, all FP runs were characterized by constant V_f [Fig. 1(a)]. In Figure 1(b), a typical FP temperature profile is depicted with the definition of T_{\max} ; this is the maximum temperature experimented by the thermocouple junction and corresponds to the front temperature.

In situ Formation of DD and its Frontal Polymerization [Scheme 1(a)]

As known, free-radical polymerization of acrylates and step-growth synthesis of polyurethanes

are very exothermic. Starting from this consideration, we have investigated a system derived from the *in situ* reaction of HDI and HEA ([HDI]/[HEA] = 0.5 mol/mol).

Some FP blank runs were performed to ascertain the actual polymerization mode (Table 1).

As reported in Table 1, it is evident that only FP1 was obtained by pure FP (NOTE: with the term “pure” FP we mean that no simultaneous “spontaneous polymerization,” SP, occurs. SP is the process related to the spontaneous tendency of the reaction mixture to polymerize at room temperature, even in absence of any ignition). Indeed, BR2 mixture led to the formation of the blocked diisocyanate (as described in the experimental section) followed by self-ignited FP.⁴⁵ This term is used when a reaction mixture, without any external localized stimulus, undergoes local ignition (generally due to a local temperature increase) and subsequent FP. SP differs from self-ignited FP in that, whereas the first phenomenon happens simultaneously in the whole reaction mixture, generally with a gradual increase of temperature, self-ignited FP occurs as a consequence of a sudden increment of temperature in a restricted area.

It should be underlined that a certain amount of PC was necessary to achieve pure FP, its role being that of increasing the pot-life as a consequence of partial DBTDL inhibition.

Starting from this preliminary study, we have first oriented our research work to the obtaining of compositions which undergo pure FP.

Although APS was chosen as the preferred radical initiator, AIBN and BPO were used as well. APS was mainly utilized because it does not give rise to bubbles during the polymerization reaction. DBTDL was used as the catalyst for urethane formation and PC as the inhibitor to increase the pot-life of the mixture,^{11,12} which was stable for several hours (pot life ≥ 8 h depending on the composition).

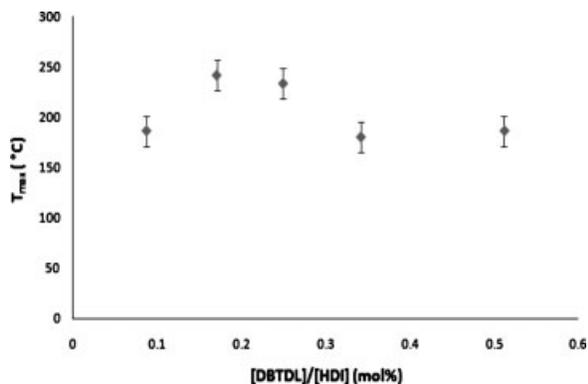


Figure 2. *In situ* formation of DD and its FP: T_{\max} as a function of the [DBTDL]/[HDI] ratio. ([APS]/[HEA] = 0.6 mol %, [PC]/[DBTDL] = 6 mol/mol).

In Figure 1, the position of the front as a function of time, and a temperature profile for a typical FP experiment are depicted ([DBTDL]/[HDI] = 0.1 mol %, [APS]/[HEA] = 0.6 mol %, [PC]/[DBTDL] = 6 mol/mol). These plots are useful for the calculation of V_f and T_{\max} .

In a series of experiments, the catalyst concentration was varied ($0.1 \leq [\text{DBTDL}]/[\text{HDI}] \leq 0.5$ mol %), keeping constant the ratios [PC]/[DBTDL] = 2 mol/mol and [APS]/[HEA] = 5 mol %.

T_{\max} and V_f as functions of the [DBTDL]/[HDI] ratio are reported in Figures 2 and 3, respectively.

Pure FP was observed only in the range $0.1 \leq [\text{DBTDL}]/[\text{HDI}] \leq 0.5$ mol %. For [DBTDL]/[HDI] < 0.1 mol %, FP did not self-sustain while, when [DBTDL]/[HDI] > 0.5 mol %, simultaneous SP occurred. CAUTION: particular attention has to be paid when high concentrations of APS or DBTDL are used (i.e., when [APS]/[HEA] \geq 0.6 mol % or [DBTDL]/[HDI] \geq 0.2 mol %): in

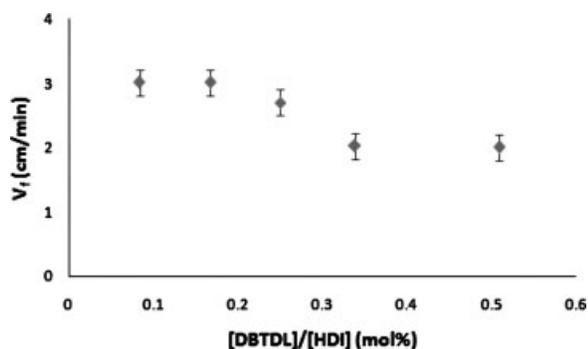


Figure 3. *In situ* formation of DD and its FP: V_f as a function of the [DBTDL]/[HDI] ratio. ([APS]/[HEA] = 0.6 mol %, [PC]/[DBTDL] = 6 mol/mol).

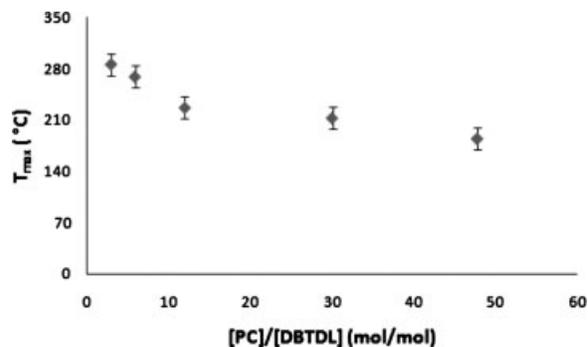


Figure 4. *In situ* formation of DD and its FP: T_{\max} as a function of the [PC]/[DBTDL] ratio. ([APS]/[HEA] = 0.6 mol %, [DBTDL]/[HDI] = 0.17 mol %).

fact, due to the elevated temperature reached, tube explosion may occur.

In the composition range explored, T_{\max} has a maximum at [DBTDL]/[HDI] = 0.17 mol %; beyond this value, a temperature drop is evident, it reaching a plateau for [DBTDL]/[HDI] \geq 0.34 mol % (Fig. 2).

In Figure 3 and 5, V_f shows a decreasing trend. Starting from the maximum value of 3.0 cm/min for [DBTDL]/[HDI] = 0.1 mol %, it decreases down to 2.0 cm/min for [DBTDL]/[HDI] approaching 0.5 mol %.

The effect of the [PC]/[DBTDL] ratio on T_{\max} and V_f is reported in Figures 4 and 5.

Pure FP was found in the range $3 \leq [\text{PC}]/[\text{DBTDL}] \leq 48$ mol/mol ([DBTDL]/[HDI] = 0.2 mol %; [APS]/[HEA] = 0.6 mol %). For relatively low inhibitor concentration (i.e., [PC]/[DBTDL] < 3 mol/mol) simultaneous SP was present while, when [PC]/[DBTDL] > 48 mol/mol, no FP occurrence was observed (the urethane formation was completely inhibited and, consequently, no heat was released by this reaction).

As can be seen in Figure 4, T_{\max} decreases as [PC]/[DBTDL] increases. In particular, as stated earlier, the reason of no FP occurrence for [PC]/[DBTDL] > 48 mol/mol can be attributed to the excessively large inhibiting PC effect on catalyst reactivity.

In Figure 5, V_f is reported as a function of the [PC]/[DBTDL] ratio. As observed for T_{\max} , also V_f decreases as the [PC]/[DBTDL] ratio increases, from 4.0 cm/min for [PC]/[DBTDL] = 3 mol/mol to 1.4 cm/min for [PC]/[DBTDL] = 48 mol/mol ([DBTDL]/[HDI] = 0.17 mol %; [APS]/[HEA] = 0.6 mol %).

Moreover, we varied the [APS]/[HEA] ratio to assess the effect of radical initiator concentration.

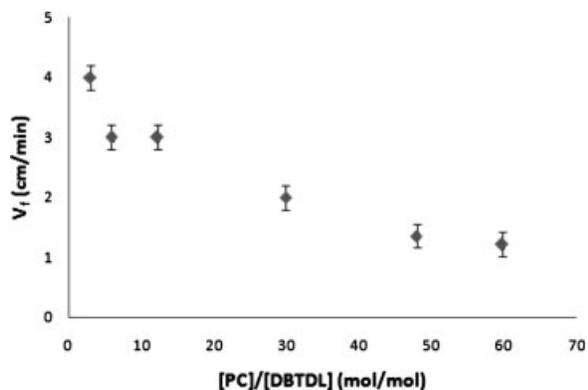


Figure 5. *In situ* formation of DD and its FP: V_f as a function of the [PC]/[DBTDL] ratio. ([APS]/[HEA] = 0.6 mol %, [DBTDL]/[HDI] = 0.17 mol %).

In Figures 6 and 7, T_{\max} and V_f are, respectively, reported as functions of the [APS]/[HEA] ratio by keeping constant [DBTDL]/[HDI] = 0.17 mol % and [PC]/[DBTDL] = 6 mol/mol.

The influence of the [APS]/[HEA] ratio on T_{\max} seems to be negligible (T_{\max} always ~ 190 °C). In any case, the presence of APS was essential for promoting the FP of HEA. As a consequence, when APS was absent, lower temperature values and no self-sustaining fronts were found. In detail, it should be highlighted that an increase of temperature was actually observed ($T_{\max} = 132$ °C) but, since the corresponding front was not self-sustaining, its T_{\max} and V_f (which gradually decreases from 0.5 to 0 cm/min in less than 2 cm from the ignition point and along the reactor) are not respectively, reported in Figures 6 and 7. By contrast, the increase of T_{\max} (above 132 °C) and the occurrence of self-sustaining fronts having $V_f \geq 1.5$ cm/min observed in the presence of APS are the

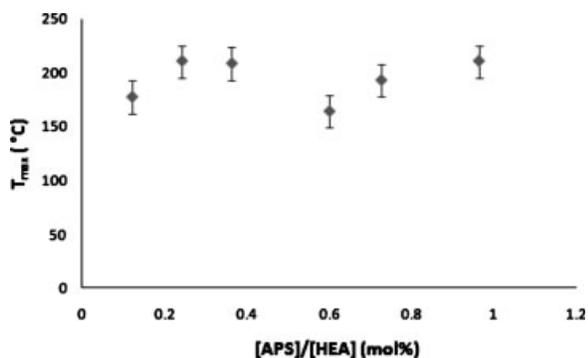


Figure 6. *In situ* formation of DD and its FP: T_{\max} as a function of the [APS]/[HEA] ratio. ([PC]/[DBTDL] = 6 mol/mol, [DBTDL]/[HDI] = 0.17 mol %).

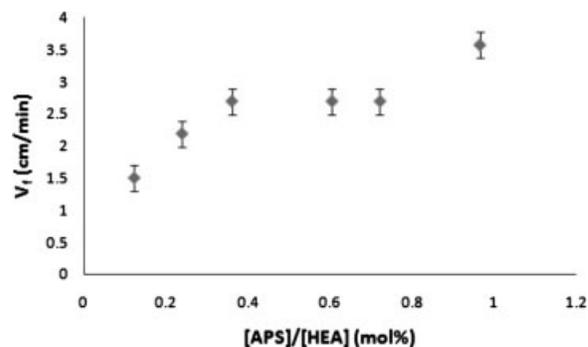


Figure 7. *In situ* formation of DD and its FP: V_f as a function of the [APS]/[HEA] ratio. ([PC]/[DBTDL] = 6 mol/mol, [DBTDL]/[HDI] = 0.17 mol %).

results of the larger amount of heat release due to HEA radical polymerization which happens together with the urethane linkage formation.

V_f significantly increases with APS concentration. In particular, when [APS]/[HEA] < 0.12 mol % no FP occurred but, when this ratio was overcome, a V_f increment was evident up to 3.6 cm/min ([APS]/[HEA] = 0.96 mol %, [DBTDL]/[HDI] = 0.17 mol % and [PC]/[DBTDL] = 6 mol/mol). The pure FP threshold value was individuated at [APS]/[HEA] = 0.96 mol %: when this concentration was got over, simultaneous SP was observed but with a notable V_f value of 30 cm/min, which is one of the highest found so far in any FP system.

Table 2. *In situ* Formation of DD and Its FP: Effect of Type and Concentration of Radical Initiator on T_{\max} and V_f

Sample	Initiator	[Initiator]/[HEA] (mol %)	T_{\max} (°C)	V_f (cm/min)
FP2	APS	0.12	276	1.5
FP3		0.36	290	2.7
FP1		0.60	270	2.7
FP4 ^a		1.20	–	>30
FP5	AIBN	0.12	264	2.4
FP6		0.36	316	3.4
FP7		0.60	336	2.5
FP8		1.20	306	3.6
FP9	BPO	0.12	297	2.5
FP10		0.36	314	2.4
FP11		0.60	300	2.4
FP12		1.20	303	4.0

[DBTDL]/[HDI] = 0.17 mol %, [PC]/[DBTDL] = 6 mol/mol.

^a Simultaneous presence of FP and SP.

Finally, we investigated the effect of the type of radical initiator on T_{\max} and V_f . The obtained results are listed in Table 2.

Namely, APS, AIBN, and BPO were chosen as representatives of different radical initiator families.

As will be shown, their effect on both T_{\max} and V_f is quite different. At present we can not provide an explanation for that and further studies aimed to investigate this aspect are in progress.

Namely, as can be seen from Table 2, the use of AIBN resulted in an increment of T_{\max} as a function of the [AIBN]/[HEA] ratio ([DBTDL]/[HDI] = 0.17 mol %, [PC]/[DBTDL] = 6 mol/mol). In particular, although the maximum temperature was 336 °C for [AIBN]/[HEA] = 0.6 mol %, when this ratio was exceeded, a slight T_{\max} decrease was observed. CAUTION: particular attention during the performing of such reaction is necessary due to the explosive behavior of some of these samples, that is, when [AIBN]/[HEA] \geq 0.6 mol %.

V_f shows a *plateau* pathway. In fact, for [AIBN]/[HEA] > 0.12 mol % just a little increment in V_f was observed and its average value was found to be \sim 3.0 cm/min.

BPO was chosen as a radical initiator belonging to the class of peroxides. As for AIBN, T_{\max} was poorly influenced by the [BPO]/[HEA] ratio with values always close to 300 °C.

V_f remained almost constant (2.4–2.5 cm/min) in the range $0.12 \leq$ [BPO]/[HEA] \leq 0.6 mol % whereas, for [BPO]/[HEA] = 1.2 mol %, it suddenly increased up to 4.0 cm/min.

FP of Preformed DD

Preformed DD (PDD) was prepared as described in the Experimental section. Some preliminary runs were unsuccessfully carried out using APS, BPO or AIBN as radical initiators. However, since PDD is a powder, homogeneous mixtures with the above initiators could be obtained only after heating at $T > 80$ °C (melted mixture), which is a temperature too high to guarantee that no initiator dissociation occurs before ignition. For such a reason, higher dissociation temperature radical initiators were chosen, namely Luperox[®] TBCE and *t*-BP, both belonging to the class of peroxides.

PDD was molten at ~ 90 °C, rapidly mixed with the radical initiator and immediately after cooled down to ~ 70 °C, thus obtaining the

Table 3. FP of PDD: Effect of Type and Concentration of Radical Initiator

Sample	Initiator	[Initiator]/ [PDD] (mol %)	T_{\max} (°C)	V_f (cm/min)
FP13	LUPEROX	1.0	186	2.4
FP14		3.0	185	3.0
FP15		5.0	168	3.9
FP16		10	172	3.8
FP17	tBP	1.0	185	0.6
FP18		3.0	204	0.8
FP19		5.0	210	1.0
FP20		10	190	1.4

required homogeneous solid mixture on which FP was performed.

No FP reaction was obtained for initial temperature lower than 70 °C. Indeed, unsuccessful runs were carried out starting at temperatures of 25, 50 and 60 °C.

As reported in Table 3, T_{\max} is hardly dependent on the [Luperox]/[PDD] ratio, ranging from between 168 to 186 °C (for $1.0 \leq$ [Luperox]/[PDD] \leq 10 mol %). On the contrary, in the same range V_f increases from 2.4 cm/min ([Luperox]/[PDD] = 1.0 mol %) to 3.9 cm/min ([Luperox]/[PDD] = 5.0 mol %). Overcome this value, it remains almost constant (3.8 cm/min for [Luperox]/[PDD] = 10 mol %).

In the same Table, the results obtained by using *t*BP as a radical initiator are also listed.

Similarly to what previously mentioned for the Luperox/PDD system, T_{\max} was slightly affected by the initiator concentration ($185 \leq T_{\max} \leq 210$ °C). On the contrary, V_f showed an almost linear increment as [tBP] increased, ranging from 0.6 cm/min when [tBP]/[PDD] = 1.0 mol % up to 1.4 cm/min when that ratio was equal to 10 mol %.

Thermal Characterization

Since no significant differences were found along each series, only some selected, significant results are collected in Table 4.

As can be evinced by the reported data, the highest T_g values of FP samples were obtained by using APS as radical initiator. In particular, such values result higher than both those of the corresponding batch samples (thus probably indicating a larger conversion of the former ones) and of those obtained by using BPO or AIBN. This result is quite unexpected; indeed,

Table 4. *In situ* Formation of DD and Its FP: T_g Values (2nd Scan) of Some Selected Samples

Sample	Initiator	Initiator Concentration (mol %)	Polymerization Technique	T_g (°C)	T_{max} (°C)
FP3	APS	0.36	FP	50.6	290
CP3			Batch	44.9	–
FP1	BPO	0.60	FP	60.0	270
CP1			Batch	45.5	–
FP11	BPO	0.60	FP	48.0	300
CP11			Batch	44.1	–
FP6	AIBN	0.36	FP	44.2	316
CP6			Batch	48.8	–

since APS has a large molecular weight (930), it may act also as a possible plasticizer. For instance, sample FP1, which is characterized by the highest T_g , contains an amount of APS as high as 5 wt % to be compared with 1.2 wt % of initiator when the same BPO concentration (0.6 mol %) is present.

As already mentioned, T_g data do not differ significantly. However, a possible correspondence between T_{max} and T_g can be proposed. In fact, it looks like the higher T_{max} , the lower T_g , thus probably indicating that the high temperature reached by the front has a negative effect on the conversion. The high temperature reached during FP reactions could promote some thermal degradation phenomena, with a subsequent lowering of the T_g values. However, the possible occurrence of these phenomena should be considered acceptable in that their effect on T_g is quite small when compared with the analogous samples prepared by the classical method.

CONCLUSIONS

In the present work, a thorough study on the possibility of using FP as an alternative technique for the synthesis of poly(urethane acrylates) has been performed. These macromolecular compounds have been obtained: (i) directly starting from HDI and HEA, thus performing urethane formation and vinyl polymerization at the same time, and (ii) in two steps by allowing to react the corresponding preformed diurethane diacrylate. The first method has the advantage of being faster but some caution is necessary due to the excessive heat that is generated if the reaction conditions are not properly chosen. The second approach requires a further step but

has the advantage of being more controlled; however, since the DD monomer is solid, to have a homogenous monomer-initiator mixture, it has to be heated and melted before polymerization occurrence.

After a comparison between FP and the classical method (prolonged external heating at a given temperature), no significant differences have been found in terms of T_g . However, since FP runs are carried out in minutes instead of the hours typically necessary for the batch methods, and required very easy protocols and apparatuses, FP can be once again considered a valid and convenient alternative way for the preparation of polymer materials.

A careful study on thermal and mechanical properties of all the obtained materials is in progress and will be reported soon.

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