



Frontal atom transfer radical polymerization of tri(ethylene glycol) dimethacrylate

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Abstract: The first frontal atom transfer radical polymerization (FATRP) has been successfully carried out using tri(ethylene glycol) dimethacrylate as a monomer. The effect of the catalyst/initiator ratio has been investigated and related to the front velocity and its maximum temperature. By comparing this new approach with classical radical polymerization routes and with conventional frontal polymerization, it was found that the so-obtained polymer is characterized by higher conversion, shorter reaction times, higher degradation temperature, and does not contain entrapped bubbles.

Introduction

Frontal polymerization (FP) is a method that allows the conversion of a monomer to a polymer using the exothermicity of the self-same polymerization reaction. If the heat dissipated is not excessive, the quantity of energy left over may be enough to induce the polymerization of the monomer layer close to the zone heated by the reaction. As a result a hot front can be observed that propagates and sustains itself. FP was introduced in 1972 by Chechilo *et al.* [1] who polymerized methyl methacrylate (MMA) under adiabatic conditions and pressures superior to 3000 atm.

Pojman *et al.* later studied the macrokinetics and dynamics of FP and also considered applications in synthesis [2-4]; in particular, they discovered that with this technique it is possible to obtain more homogenous composites than those obtained in the traditional way [5]. Morbidelli *et al.* have reported on the advantages of the application of FP in obtaining copolymers [6] and blends [7]. It was observed that PMMA/polystyrene blends prepared using FP were characterized by a less evident phase separation than those obtained both by mechanical mixing and via classical synthesis. The separation phase is limited thanks to the high conversion rates that allow the various components in the mixture to be blocked in a metastable phase.

In 1997, Pojman *et al.* published results on the first synthesis of a simultaneous interpenetrating polymer network obtained via binary FP of tri(ethylene glycol) dimethacrylate (by free-radical polymerization) and diglycidyl ether of bisphenol A (using BCl_3 /amine as a curing agent to create an epoxy resin) [8].

FP has also been exploited to prepare materials containing liquid crystals dispersed in polymeric matrices (both as film and other thicker materials) [9,10]. In recent years our group has focused on the extension of the number of monomers that can be polymerized by way of FP and on applying this technique to other mechanisms of both chain and step-growth polymerizations.

In particular, the following have been studied: frontal ring opening metathesis polymerization (FROMP) of dicyclopentadiene [11]; the synthesis of polyurethanes [12,13]; the curing of polyester-styrene resins [14]; the production of interpenetrating polymer networks composed of polydicyclopentadiene and polyacrylates [15]; and the consolidation and protection of porous materials (stone, wood, textiles) with applications in the artistic-historical field [16].

Generally speaking, the successful application of FP implies the stability of a travelling front [17,18]. At ambient pressure, stable fronts are generally descending and are found when: (i) polymers are solid at the temperature reached by the reaction wave, and/or (ii) highly viscous monomer media are polymerized.

Namely, ascending fronts are not stable due to convective motions, which cause an excessive amount of dispersed heat [17,18]. On the other hand, if in descending fronts polymers are soluble in the corresponding monomers or are molten at the temperature reached by the front, the phenomenon of 'fingering' occurs [19]. This is due to pieces of denser polymer materials that drop into the lower monomer, thus dispersing heat and provoking local polymerization and, eventually, interrupting FP. In order to avoid fingering, literature reports that the viscosity of monomer media can be increased by adding fumed silica [20] or another polymer [7]. For the above reasons, multifunctional monomers, which give crosslinked polymers that cannot melt and be solubilized, generally give rise to stable fronts and hence are preferred in FP syntheses.

Among multifunctional monomers, tri(ethylene glycol) dimethacrylate (TGDMA) has been the most used in fundamental studies on FP. For this reason, we have chosen it in order to verify whether frontal polymerization can be joined to, and take advantages of, the atom transfer radical polymerization (ATRP) [21] mechanism.

One of the reasons for such a study is that of solving one of the main problems, which affect classical radical frontal polymerization. Indeed, the latter entails the utilization of radical initiators in such doses as to create several problems connected with their type. If classical initiators are used (e.g., 2,2'-azoisobutyronitrile or benzoyl peroxide, BPO) bubbles are often found within the final product due to the development of gas by initiator decomposition.

To avoid this problem, which limits the potentiality of FP by rendering the mechanical properties of the obtained materials poorer, up to now two methods have been used: working at high pressures [1] or using Aliquat[®] persulfate (APS) as an initiator [22]. However, the former method is not easy to apply, above all if one is working *in situ*; the second leads to materials having relatively low T_g as a result of the plasticizing effect of the very same APS, which, incidentally, has a particularly high molecular weight (561.65) and is hence used in high mass fractions. Therefore, we suppose that the exploitation of the 'chemistry' that characterizes ATRP may lead to more extensive practical use of FP in a growing number of applications.

In the general ATRP mechanism, the radicals, or active species, are generated via a reversible redox process catalyzed by a complex of a transition metal which undergoes one-electron oxidization together with abstraction of an atom of pseudo-halogen

belonging to the dormant species. This process takes place with constant speeds of activation and deactivation. The polymer chains grow as a result of the addition of intermediate radicals to monomers in a similar manner to that in conventional radical polymerization, and with constant speed of propagation.

Usually, ATRP is considered only as one of the methods for achieving controlled/living radical polymerization (CRP). All these methods are based on the generation, in the growth phase, of a rapid dynamic equilibrium between a small quantity of free growing radicals and a large majority of dormant species. In ATRP the dormant chains are alkyl halides, and the radicals are generated by a catalyzed reaction. All CRP methods involve an activation and a deactivation stage. The free radicals that are generated propagate and terminate as in conventional free-radical polymerization. Hence, although termination is brought about, under appropriate conditions this contribution is slight (less than a few percent of the total number of chains) and these radical polymerization processes behave as if they were living or controlled systems.

As already mentioned, in the present work the ATRP mechanism has been extended to new fields of polymer synthesis and applications. In particular, it has not been used as a method of synthesis of 'living' polymers characterized by controlled molecular weight and narrow polydispersities, but rather as a convenient alternative to classical radical polymerization.

Namely, we have synthesized poly[tri(ethylene glycol) dimethacrylate] and have compared the characteristics of the samples obtained with ATRP by the frontal method, by batch polymerization and by spontaneous polymerization. Furthermore, a comparison between classical radical polymerization and ATRP has been carried out on samples obtained by the frontal and batch methods.

Experimental part

TGDMA, CBr_4 , tris(2-aminoethyl)amine (TREN) and CuBr were supplied by Aldrich. Dimethyl sulfoxide (DMSO) and BPO were supplied by Fluka.

In order to verify the easy applicability of FP to practical uses, all materials were used as received, without further purification. In particular, as usual in FP experiments, inhibitor was not removed from the monomer. This is because of the assumption that the high temperatures reached by the front cause rapid inhibitor consumption, thus allowing for FP to occur. Moreover, reaction conditions were not adiabatic.

The temperature profiles of each synthesis were measured using a K-type thermocouple, the junction of which was placed at c. 5 cm from the upper surface of the mixture. The thermocouple was connected to a digital thermometer used for the reading and recording of temperature. The position of the front (easily visible through the glass wall of test tubes) against time was also measured (± 0.5 mm).

Differential scanning calorimetry was conducted with a Mettler DSC 30 in a temperature range of between -100 and $+320^\circ\text{C}$ with a heating rate of $10^\circ\text{C}/\text{min}$ under nitrogen atmosphere. Thermogravimetric analyses were performed in air by means of a LECO TGA-601 Instrument in a temperature range between $+25$ and $+900^\circ\text{C}$ with a heating rate of $3^\circ\text{C}/\text{min}$.

Throughout the discussion section, abbreviations will be used, each is composed of three characters and refers to samples: the first character indicates the technique with which the sample was synthesized (F for frontal polymerization; B for batch

polymerization; S for spontaneous polymerization). The second character refers to the reaction mechanism (A for ATRP; C for classic radical polymerization). The third character is a number used to distinguish the different samples.

The preparation of the samples involved the following methodology: in a typical run (e.g., sample FA1), CuBr ($8.73 \cdot 10^{-5}$ mol) was dissolved in a few drops of DMSO (*i.e.*, the minimum amount that allows for salt to dissolve without affecting T_{\max} and V_f) in an 18 mm inner diameter glass test tube; TGDMA ($3.49 \cdot 10^{-2}$ mol), CBr₄ ($6.98 \cdot 10^{-5}$ mol) and TREN ($8.73 \cdot 10^{-5}$ mol) were added to this mixture. Then, the glass test tube was shaken to a homogeneous solution and immersed in an ice bath. In all the trials carried out, the formation of varying degrees - depending on the concentration of Cu(I) - of a green solid has been noted. This tended to flocculate and dissolved again when the mixture was shaken, resulting in the solution being given an intense green colour. At 0°C, all the prepared samples did not react spontaneously, even after long waiting periods (pot-life > 3 h).

Immediately before polymerization, the above test tubes were immersed in a water bath set at 25°C until the mixture equilibrated at this temperature. FP reactions were ignited by applying heat to part of the mixture close to the upper surface using the tip of a soldering iron until the formation of a hot propagation front was noted.

Batch polymerizations were performed for 1 h on the above mixtures and in the aforementioned vessels placed in a thermostatic oil bath set at 60°C. The series of samples held at room temperature in the above vessels displayed a progressive rise in temperature; this increase continued until bulk spontaneous polymerization of the entire mixture took place (*i.e.*, after a spontaneous increase of temperature and the subsequent cooling to room temperature).

All polymerizations were carried out without stirring. After all polymerization experiments, the obtained transparent green-coloured polymers were grounded and extracted in a Soxhlet with CH₂Cl₂ for 24 h. Finally, they were dried in a vacuum oven at 40°C for 72 h.

In the following sections [CuBr], [TREN] and [CBr₄] are expressed in mol-% with reference to 100 mol of TGDMA. Reproducibility of T_{\max} data (defined in Fig. 1) was $\pm 5^\circ\text{C}$ and that of front velocity was ± 0.05 cm/min. Error bars in the following plots indicate these variation ranges.

Results and discussion

Several preliminary tests were conducted with the aim of discovering a system that allows a widespread and detailed study of the phenomenon. Amongst the various types of radical initiators mentioned in the literature on ATRP, particular attention has been given to the α -haloesters and alkyl halides, the latter both mono- and polyhalogenated.

TREN was chosen for its high reactivity, which confers to the metal catalyst [23]. In fact, it should be noticed that its hexamethyl derivative, which imparts less reactivity to the catalyst, is used in conventional controlled ATRP. In fact, the high tendency of TREN catalysts to react entails a large radical concentration, a condition that is in contrast with the possibility of having 'living' polymers and narrow polydispersities. However, this high reactivity is exploited in frontal polymerization.

Although we have found that other halogenated compounds worked well as initiators (ethyl 2-bromopropionate, hexachloroethane, 1,1,2,2-tetrabromoethane, CH₂Br₂) and

also copper(I) acetate could be used as salt, after several trials it was deemed worthwhile to focus attention on a system composed of CBr_4 as initiator and CuBr/TREN as catalyst.

This choice is justified by the wide interval of concentrations, both of the catalyst and of the radical initiator, reference to which can be made in the gathering of *pure* FP experimental data. With the term *pure* we mean that FP is the only polymerization mode occurring in the reactor at a given time. In particular, it indicates that spontaneous polymerization is not simultaneously occurring.

Amongst the various trials, blank experiments were also conducted, *i.e.*, the effective indispensability of each component of the mixture to the polymerization process was checked. In fact, the absence of one of the components each time, in comparison to a trial in which all were present, was reflected by the fact that polymerization did not take place.

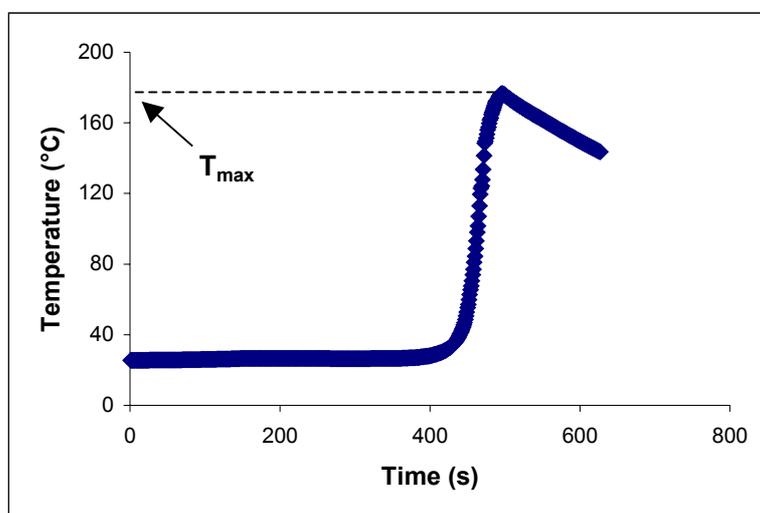


Fig. 1. Temperature profile recorded during an FATRP run ($[\text{CBr}_4] = 0.2$ mol-%; $[\text{CuBr}] = [\text{TREN}] = 0.5$ mol-%)

Pure frontal ATRP (FATRP) experiments

The graph in Fig. 1 illustrates a typical example of a temperature profile recorded at a point that was a few centimeters from the upper surface of the mixture, after this had undergone setoff. The temperature jump displayed by the profile corresponds to the instant in which the front reaches the junction of the thermocouple and is typical of frontal reaction.

The temperature reached by the front, T_{max} , which can be estimated from these graphs, is one of the principal points of interest in FP and will be referred to in later considerations. In fact, this parameter, which depends on monomer medium composition, influences the rate of the process and the characteristics of the final polymer materials such as conversion and crosslinking degrees, thermal and mechanical properties, *etc.*

A second parameter typically taken into consideration in work on FP is the velocity of propagation of the front, V_f . This latter influences T_{max} and is influenced by it. This means that it also depends on the composition of the monomer mixture. V_f can be

calculated from graphs such as that in Fig. 2. Frontal polymerizations generally present constant V_f values.

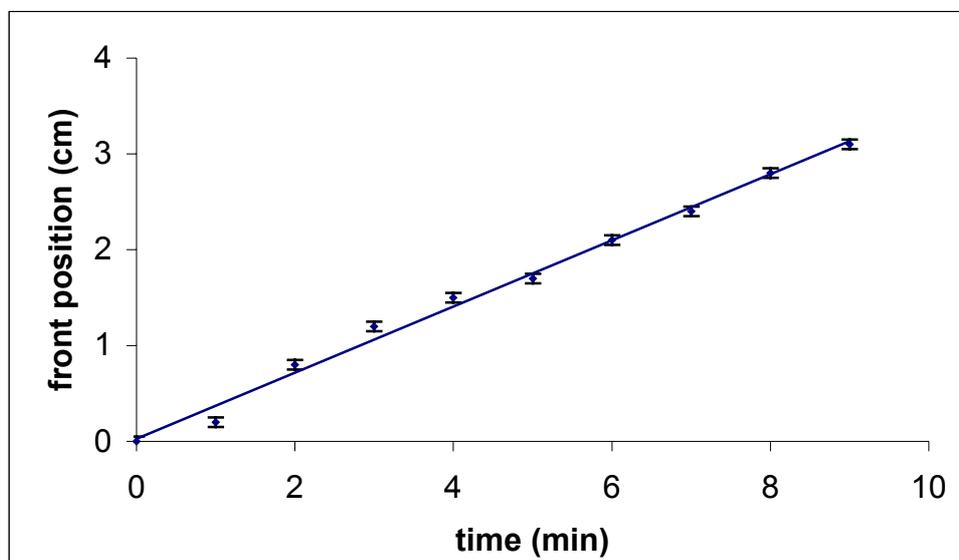


Fig. 2. Front position as a function of time ($[\text{CBr}_4] = 0.2 \text{ mol-}\%$; $[\text{CuBr}] = [\text{TREN}] = 0.5 \text{ mol-}\%$)

In the example that has been given, one may note how the linear correlation between the position of the front and time may be considered as very good. The only point that varies slightly from the interpolated line is that which corresponds to the first minute of propagation: this anomaly is due to the fact that the front is still in a stabilization phase in the seconds immediately following ignition. In fact, during this first lapse of time, front is not flat, and steady state has not been reached yet.

For the reasons stated above, the following studies were aimed at determining the T_{max} and V_f values in relation to variation of the concentrations of the components, while maintaining CuBr and TREN in equimolar quantities. Three types of study were carried out: the first involved variation of the concentrations of CuBr/TREN while keeping the initiator dose constant ($[\text{CBr}_4] = 0.2 \text{ mol-}\%$); the second and the third regarded the effect of CBr_4 concentration when that of the catalyst was constant, in particular with the following amounts: $[\text{CuBr}] = 0.2$ and $0.5 \text{ mol-}\%$.

The effect of catalyst concentration

As already noted, this study dealt with variations in the concentrations of the CuBr/TREN catalyst with constant relative proportions between CuBr and TREN ($[\text{CuBr}] = [\text{TREN}]$). The initiator concentration was also kept constant ($[\text{CBr}_4] = 0.2 \text{ mol-}\%$). The study was carried out varying the catalyst concentration between 0.2 and 1.5 mol-%.

The V_f trend in relation to CuBr/TREN concentrations is displayed in Fig. 3. It may be noted that with very low catalyst concentrations (0.2 mol-%) the front moves very slowly ($V_f = 0.24 \text{ cm/min}$). An increase in CuBr/TREN concentrations from 0.20 to 0.25 mol-% is mirrored by a V_f figure that has almost doubled (0.43 cm/min). For greater concentrations this figure continues to increase until it reaches an upper limit of c. 0.6 cm/min for CuBr/TREN quantities exceeding 1.0 mol-%.

Fig. 4 displays the corresponding data for T_{\max} . In an analogous way to the findings for V_f , low concentrations of catalyst resulted in relatively low values of T_{\max} (149°C; 0.2 mol-%). The increase of concentration led to an escalation of the T_{\max} values, reaching a plateau at c. 170°C for CuBr/TREN amounts above 0.4 mol-%.

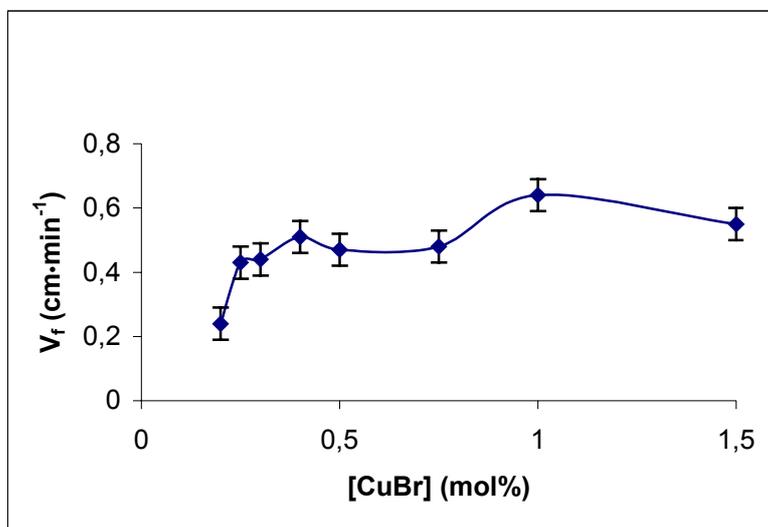


Fig. 3. V_f in relation to the catalyst (CuBr/TREN) concentration ($[CBr_4] = 0.2$ mol-%)

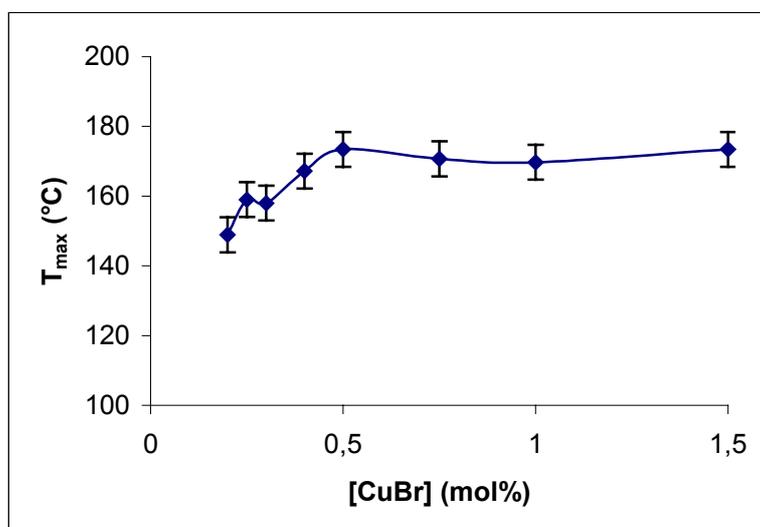


Fig. 4. T_{\max} as a function of CuBr/TREN concentration ($[CBr_4] = 0.2$ mol-%)

The effect of initiator concentration

This second study involved variation of initiator (CBr_4) concentration while that of the CuBr/TREN catalyst was maintained constant ($[CuBr] = [TREN] = 0.2$ mol-%). In this set of experiments the range of values within which pure FP occurs was found to be $0.2 \leq [CBr_4] \leq 0.5$ mol-%. Indeed, while for $[CBr_4]$ above 0.5 mol-% spontaneous polymerization took place simultaneously, for $[CBr_4] < 0.2$ mol-% FP did not self-sustain. However, as can be seen in Tab. 1, in the interval of the concentrations concerned, V_f and T_{\max} remain practically constant with variations comprised within the reproducibility ranges indicated in the Exptl. part ($145^\circ\text{C} \leq T_{\max} \leq 153^\circ\text{C}$; $0.24 \leq V_f \leq 0.28$ cm/min).

Tab. 1. V_f and T_{max} for $[CuBr] = [TREN] = 0.2 \text{ mol-}\%$

$[CBr_4]$ in mol-%	V_f in cm/min	T_{max} in °C
0.2	0.24	149
0.3	0.27	147
0.4	0.26	153
0.5	0.28	145

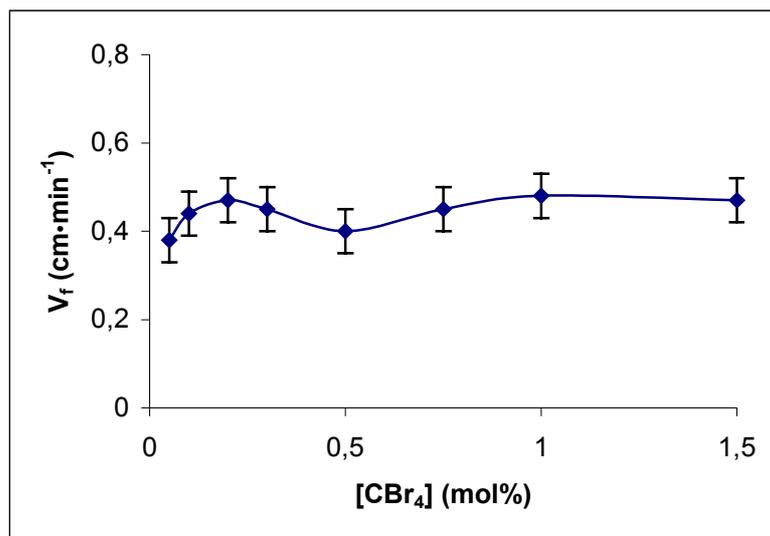


Fig. 5. V_f as a function of initiator concentration ($[CuBr] = 0.5 \text{ mol-}\%$)

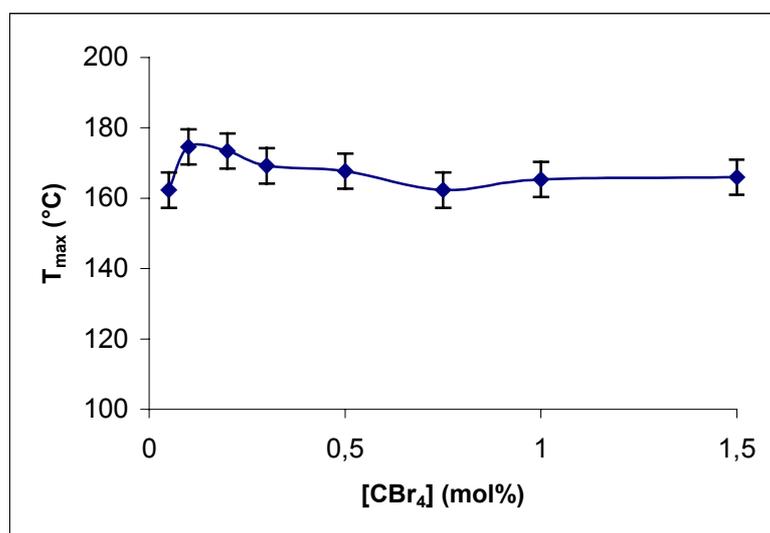


Fig. 6. T_{max} as a function of initiator concentration ($[CuBr] = 0.5 \text{ mol-}\%$)

Analogous to the study described above, another one was conducted keeping the catalyst concentration constant at 0.5 mol-% rather than at 0.2 mol-%. Under these conditions, pure FP was observed at $0.05 \leq [CBr_4] \leq 1.5 \text{ mol-}\%$. V_f and T_{max} as functions of initiator concentration within the above interval are reported in Fig. 5 and Fig. 6. Also on these levels of catalyst concentration, it may be noted that this

parameter has no particular influence on V_f and T_{max} , which remain almost constant at 0.4 - 0.5 cm/min and 160 - 170°C, respectively.

Comparison with 'classical' radical FP

It is important to note that in none of the frontal atom transfer radical polymerizations the development of bubbles was observed. With reference to this, FP tests were carried out using the classic reaction initiated by BPO. These experiments showed extensive production of bubbles even when the quantities of initiator were low.

From comparison between the two mechanisms used (ATRP and classical radical polymerization), it can be noted that with equal concentrations of initiator, both V_f and T_{max} are slightly higher in the case of the BPO-initiated polymerization. However, these differences are not particularly significant (Tab. 2).

Tab. 2. Comparison between samples obtained by classical radical FP and by FATRP

Sample	[BPO] in mol-%	[CBr ₄] in mol-%	[CuBr] in mol-%	Bubble formation	V_f in cm/min	T_{max} in °C
FC1	0.2	0	0	yes	0.50	183
FC2	1.0	0	0	yes	0.90	183
FA3	0	0.2	0.2	no	0.24	149
FA4	0	1.0	0.2	FP did not occur		
FA5	0	0.2	0.5	no	0.47	173
FA2	0	1.0	0.5	no	0.48	165

DSC and TGA characterization of the cured materials

All the samples investigated showed evidence of an amorphous structure with T_g values exceeding room temperature (from +34°C up to +40°C) as reported in Tab. 3.

Tab. 3. T_g (in °C) of the samples investigated

FA1	BA1	SA1	FA2	BA2	SA2	FC1	BC1	FC2	BC2
+39.3	+36.9	+37.1	+33.8	+37.8	+36.0	+36.9	+37.0	+34.0	+34.0

In Fig. 7, DSC thermograms relating to the first scan carried out on samples FA1, SA1 and BA1 are reported. This first series of analyses were carried out up to temperatures higher than that of degradation onset. As it was also confirmed by TGA analysis, DSC traces revealed that all the cured materials were found to have started to decompose at temperatures above 200°C. DSC first scans evidenced the different curing degree of the above samples. A weak and broad exothermal signal relating to the occurrence of residual thermal polymerization was evident only in the case of samples SA1 (at about +185°C) and BA1 (at +140°C). At variance, the FP polymer did not display any exothermic phenomenon.

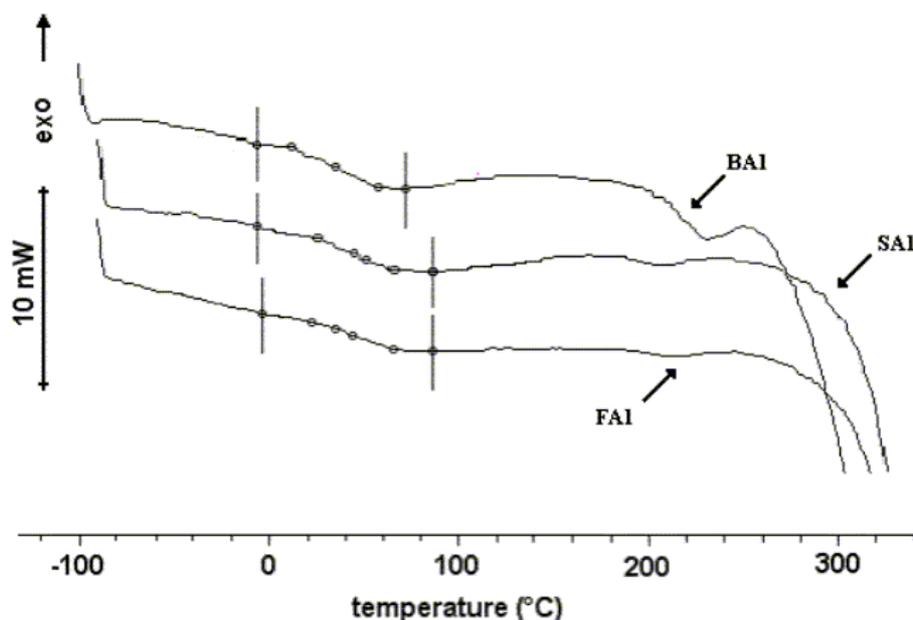


Fig. 7. DSC thermograms relating to samples FA1, SA1 and BA1

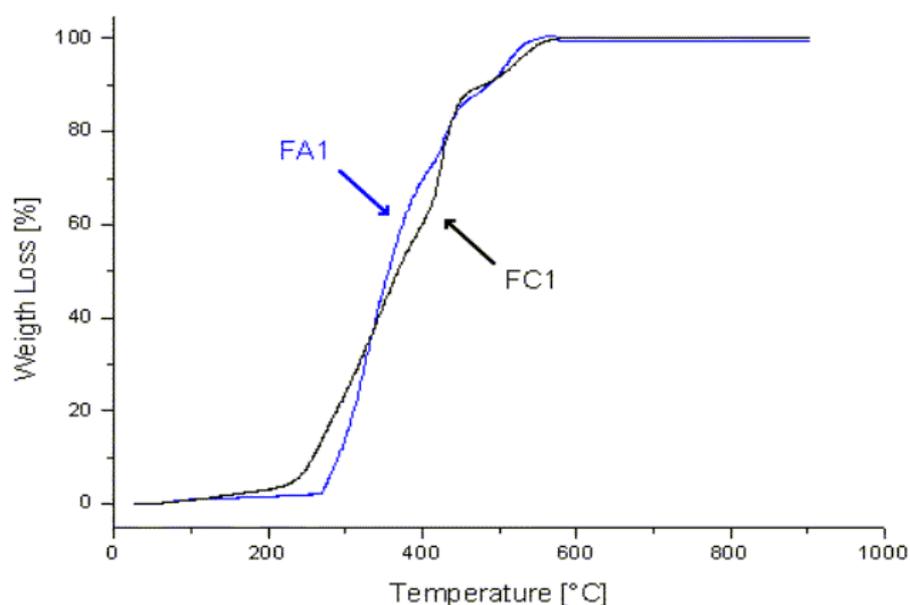


Fig. 8. TGA thermograms of samples FA1 and FC1

On a second set of the above pristine materials (FA1, SA1, and BA1), two DSC scans were performed, the first without crossing the decomposition temperature. It was found that the aforementioned exothermic peak, present in samples SA1 and BA1, completely disappeared when a second thermal scan was performed. Therefore, we can conclude that, with respect to spontaneous or batch polymerization, FP permits the preparation of polymer materials having higher (full) conversion.

If we compare the thermal behaviour of samples FC1 and FA1, we can note that their T_g values and DSC traces are similar and no exothermic peak can be found on these latter, thus indicating that both FP mechanisms allow for full monomer conversion. However, the difference that can be stated is the temperature at which the degradation starts. TGA thermograms reported in Fig. 8 clearly indicate that T_{onset} of FA1 is

significantly higher than that of FC1 (280 vs. 235°C). Therefore, the materials obtained through FATRP seem to have better thermal resistance with respect to those prepared by classical radical FP. No explanation of such behaviour can be given now and further studies aiming to clarify this point are in progress.

Conclusions

In previous works on FP of vinyl monomers, bubble-containing polymers were generally obtained. On the other hand, so far ATRP has been mostly used as a method for obtaining 'living' soluble polymers characterized by narrow polydispersities.

The present work overcomes the above drawback of FP and extends the use of ATRP by taking advantage of their joined exploitation. In particular, ATRP was used in the FP of a difunctional monomer, TGDMA, for obtaining a crosslinked material. At variance to what is generally found when classical radical frontal polymerization is used, the so-obtained polymers did not contain entrapped bubbles. This latter feature represents a significant improvement in FP of vinyl monomers although green-coloured polymer materials were synthesized.

Furthermore, it was found that FATRP samples have better thermal resistance with respect to those prepared by classical radical frontal polymerization. Moreover, FP materials are characterized by higher conversion than those obtained by conventional methods. Eventually, it has been confirmed that FP allows for faster syntheses (a few minutes, depending on V_f and reactor length, instead of 1 h) than conventional ATRP and radical polymerization routes.

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- [1] Chechilo, N. M.; Khvilivitskii, R. J.; Enikolopyan, N. S.; *Dokl. Akad. Nauk SSSR* **1972**, *204*, 1180.
- [2] Pojman, J. A.; *J. Am. Chem. Soc.* **1991**, *113*, 6284.
- [3] Khan, A. M.; Pojman, J. A.; *Trends Polym. Sci.* **1996**, *4*, 253.
- [4] Chekanov, Y.; Arrington, D.; Brust, G.; Pojman, J. A.; *J. Appl. Polym. Sci.* **1997**, *66*, 1209.
- [5] Nagy, I. P.; Sike, L.; Pojman, J. A.; *J. Am. Chem. Soc.* **1995**, *117*, 3611.
- [6] Tredici, A.; Pecchini, R.; Morbidelli, M.; *J. Polym. Sci., Part A: Polym. Chem.* **1998**, *36*, 1117.
- [7] Tredici, A.; Pecchini, R.; Sliepcevich, A.; Morbidelli M.; *J. Appl. Polym. Sci.* **1998**, *70*, 2695.
- [8] Pojman, J. A.; Elcan, W.; Khan, A. M.; Mathias, L.; *J. Polym. Sci., Part A: Polym. Chem.* **1997**, *35*, 1047.
- [9] Mariani, A.; Fiori, S.; Pedemonte, E.; Pincin, S.; Ricco, L.; Russo, S.; *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **2002**, *43(2)*, 814.

- [10] Perry, M. F.; Volpert, V. A.; Lewis, L. L.; Nichols, H. A.; Pojman, J. A.; *Macromol. Theory Simul.* **2003**, *12*, 276.
- [11] Mariani, A.; Fiori, S.; Chekanov, Y.; Pojman, J. A.; *Macromolecules* **2001**, *34*, 6539.
- [12] Fiori, S.; Mariani, A.; Ricco, L.; Russo, S.; *Macromolecules* **2003**, *36*, 2674.
- [13] Mariani, A.; Bidali, S.; Fiori, S.; Malucelli, G.; Sanna, E.; *e-Polymers* **2003**, no. 044.
- [14] Fiori, S.; Malucelli, G.; Mariani, M.; Ricco, L.; Casazza, E.; *e-Polymers* **2002**, no. 057.
- [15] Fiori, S.; Mariani, A.; Ricco, L.; Russo, S.; *e-Polymers* **2002**, no. 029.
- [16] Mariani, A.; Fiori, S.; Pedemonte, E.; Pincin, S.; Ricco, L.; Russo, S.; *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **2002**, *43(2)*, 869.
- [17] Pojman, J. A.; Willis, J.; Fortenberry, D.; Ilyashenko, V.; Khan, A.; *J. Polym. Sci., Part A: Polym. Chem.* **1995**, *33*, 643.
- [18] Pojman, J. A.; Ilyashenko, V. M.; Khan, A. M.; *J. Chem. Soc., Faraday Trans.* **1996**, *92*, 2825.
- [19] Pojman, J. A.; Craven, R.; Khan, A.; West, W.; *J. Phys. Chem.* **1992**, *96*, 7466.
- [20] Bowden, G.; Garbey, M.; Ilyashenko, V. M.; Pojman, J. A.; Solovyov, S.; Taik, A.; Volpert, V.; *J. Phys. Chem. B* **1997**, *101*, 678.
- [21] Matyjaszewski, K.; Xia, J.; *Chem. Rev.* **2001**, *101*, 2921.
- [22] Masere, J.; Chekanov, Y.; Warren, J. R.; Stewart, F. D.; Al-Kaisi, R.; Rasmussen, J. K.; Pojman, J. A.; *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 3984.
- [23] Xia, J.; Gaynor, S. G.; Matyjaszewski, K.; *Macromolecules* **1998**, *31*, 5958.