Phosphonium-Based Ionic Liquids as a New Class of Radical Initiators and Their Use in Gas-Free Frontal Polymerization

Alberto Mariani,*,† Daniele Nuvoli,† Valeria Alzari,‡ and Marco Pini†

Dipartimento di Chimica, Università di Sassari, INSTM, Via Vienna 2, 07100 Sassari, Italy,
Materials Engineering Centre, Università di Perugia, INSTM, NIPLAB, 05100 Terni, Italy

Received March 19, 2008; Revised Manuscript Received May 12, 2008

ABSTRACT: Two new radical initiators have been synthesized (tetrabutylphosphonium persulfate, TBPPS, and trihexyltetradecylphosphonium persulfate, TETDPPS) and their kinetic parameters of thermal dissociation have been calculated by DSC. It was found that they give rise to radical species without gas evolution in thermal conditions that are analogous to those of Aliquat persulfate (APS), and the well-known benzoyl peroxide (BPO) and 2,2′-azobisisobutyronitrile (AIBN). However, it has been established by TGA that the new initiators are much more thermally stable than the other mentioned above toward thermal degradation resulting in undesired evolution of volatile products. This finding is particularly important when radical polymerizations have to be performed in batch and nonstirred reactors in which the difficulty of gas removal may result in bubble-containing materials thus not directly useful in practical applications. Moreover, all the above initiators have been tested in frontal polymerization experiments. All samples obtained in the presence of TBPPS or TETDPPS contained no bubbles. The maximum temperatures reached in the presence of TBPPS or TETDPPS were lower than those recorded with AIBN or BPO but front velocities were in the same range, thus indicating that the same reaction times can be used but the possibility of polymer degradation is now limited. Also, the minimum molar concentration of radical initiator for a front to self-sustain is extremely low, it being a fifth of that of both AIBN and BPO and a half of those of APS; this finding may result in important positive consequences on the molecular mass when an uncrosslinked polymer has to be prepared.

Introduction

Free-radical chain polymerization is probably the most used route for macromolecular synthesis. As is well-known, in the initiation step, primary (in macromolecular sense) radicals are formed. They can be obtained in several ways; in most cases the use of initiators is preferred, and among them azo and peroxy compounds are the most often used.[1] They act as a thermal source of radicals and have a convenient decomposition rate over a relatively narrow temperature range. On this basis, initiators are often classified according to their half-life and their dissociation constant k_d at a given temperature.[2] Furthermore, one of the main drawbacks of these compounds, especially when used in nonstirred media, is their tendency to give rise to gaseous coproducts. Namely, azo-compounds decompose into a pair of radical species and nitrogen, while peroxides generate peroxy radicals which can undergo further decomposition with formation of CO_2.[3] The result is an undesirable bubble-containing material that, because of this feature, often cannot be directly used in practical applications.

Among the polymerization techniques that can be used in unstirred media, frontal polymerization (FP) is certainly one of the latest and most promising approaches. FP allows the conversion of monomer into polymer by exploiting the heat released by the self-same polymerization reaction to create a self-sustaining front. By locally igniting the polymerization reaction, for instance by heating a reactor in a restricted zone, it is possible to induce the polymerization of the monomer. If the heat released by the reaction is large enough, it can be sufficient to induce the polymerization of the monomer layer close to it. The result is a polymerization front able to self-sustain and propagate along the whole reactor.

By this technique, which was first used by Chechilo and Enikolopyan,[4] an even increasing number of monomers have been polymerized. Namely, Pojman et al. polymerized acrylic monomers[5–7] and epoxy resins;[8] the same author prepared and frontally polymerized ionic liquid monomers,[9] while Washington and Steinbock synthesized hydrogels;[10] Crivello studied the design and synthesis of glycidyl ethers that undergo frontal polymerization,[11,12] Texter and Ziemer synthesized polyurethanes via microemulsion polymerization,[13] Chen et al. studied FP of hydroxyethyl acrylate,[14] and *N*-methylolacrylamide,[15] and the preparation of its ’hybrids’ with methylacrylamide;[16] moreover, they studied the obtainment of epoxy resins/polyurethane “hybrid” networks[17] (note: the term “hybrid” is that used by the original authors and this is the reason why we report it here even if it is probably not correct) and of polyurethane–nanosilica hybrid nanocomposites.[18] Our group obtained poly(dicyclopentadiene),[19] polyurethanes,[20,21] interpenetrating polymer networks,[22] unsaturated polyester/styrene resins,[23] and frontally polymerized diurethane diacrylates.[24] We also prepared polymer-dispersed liquid crystal films[25] and applied FP to the consolidation of porous materials;[26] recently, we prepared polymer-based nanocomposites with montmorillonite[27] and polyhedral oligomeric silsesquioxanes.[28]

However, as mentioned above, one of the main problems that strongly limit the development of FP as a common alternative polymerization technique is the formation of bubbles inside the polymer material due to the radical initiator decomposition. This issue was addressed by Masere et al.[29] who were the first to propose a new gas-free initiator to be mainly used in FP: tricaprylmethylammonium (Aliquat) persulfate, APS. As it happens for ammonium persulfate, it is said that the decomposition products are not gaseous but, if compared with this latter, APS has the advantage of being soluble in many organic media, including a large number of monomers. By contrast, due to its kinetic parameters of thermal dissociation and high molecular weight (930), relatively large amounts of it are necessary in order to have a front able to self-sustain.

Furthermore, its extensive use in radical polymerization is also hampered by the fact that quaternary ammonium salts are

---

* Corresponding author. E-mail: mariani@uniss.it.
[†] Dipartimento di Chimica, Università di Sassari, INSTM.
[‡] Materials Engineering Centre, Università di Perugia, INSTM.

10.1021/ma800610g CCC: $40.75

known for their adverse impact on the final properties of polymer materials. For instance, in the field of polymer nanocomposites in which clays are organo-modified by these compounds, the currently employed alkyl ammonium surfactants have rather low thermal stability and are known to degrade at the high temperatures required for the melt processing of most polymers. This could possibly affect the level of platelet exfoliation and perhaps interfacial bonding, which strongly influence the physical and mechanical properties of the final nanocomposite. In addition, surfactant decomposition often results in unwanted side reactions between the decomposition products and the polymer matrix, which could lead to matrix degradation and color formation in nanocomposites.[30–34]

On the other hand, it has been found that by replacing the interlayer inorganic cations, initially present in pristine montmorillonite, with quaternary phosphonium and ammonium surfactant cations, the polymer−clay samples containing tetrabutylphosphonium (TBP), and butyltriphenylphosphonium ions had an appreciably higher thermal stability than those modified with octadecyltrimethylammonium.[35]

On this basis, starting from the idea of Aliquat persulfate, we have hypothesized that analogous compounds in which ammonium is replaced by phosphonium might be successfully used as gas-free radical initiators with increased thermal stability. In particular, we focused our attention on the class of ionic liquids.

Ionic liquids are organic or organic−inorganic salts that, differently from common inorganic salts, are liquid at relatively low temperature.[36] The interest toward this class of compounds has recently progressively increased with the awareness and demand of the green chemistry approach that uses environmentally friendly chemical technologies. In this respect, some simple physical properties of the ionic liquids that make them interesting are as follows: (i) they are largely compatible toward a wide range of both inorganic and organic materials; (ii) they are often composed of poorly coordinating ions; (iii) they are nonvolatile and therefore much safer than other common solvents; furthermore, they may be used in high-vacuum systems, eliminating many containment problems; (iv) they are not flammable or explosive. Among the most common ionic liquids, we remind here those of imidazolium, pyridinium, ammonium, and phosphonium, the latter being those used in the present work.

General aim of this research has been to increase the number of gas-free radical initiators to be used, not only in FP applications, but also in classical radical polymerization experiments, in which the relatively high process temperature may result in the degradation of the initiator which in turn may lead to the partial degradation of the polymer itself. In particular, as a first example, the present work deals with the synthesis of two new phosphonium-based persulfates and their use as novel radical initiators in the FP of triethyleneglycol dimethacrylate (TGDMA), a monomer chosen on the basis that it is one of the most widely used in FP runs.[22,37,38]

Experimental Section

Tetrabutylphosphonium chloride, trihexyltetradecylphosphonium chloride, ammonium persulfate (AMPS), Aliquat 336, benzoyl peroxide (BPO), 2,2′-azobisisobutyronitrile (AIBN), and TGDMA were purchased from Aldrich and used as received without further purification.

APS was synthesized from Aliquat 336 and $(NH_4)_2S_2O_8$ according to the procedure described in the literature.[22]

DSC measurements on polymer materials were obtained with a DSC Q100 Waters TA Instruments in a temperature range between −90 and +250 °C, with a heating rate of 20 °C/min, under argon atmosphere.

DSC measurements on the radical initiators aimed to calculate their kinetic parameters of thermal dissociation were performed by using the above instrument (heating rate of 1.25 °C/min, from 20 to 150 °C, under argon atmosphere) following the method reported in the literature[39,40] by using *n*-butyl phthalate as the solvent.

TGA measurements were performed using a Seiko TGA Exstar 6000 under either nitrogen or air flow, at a heating rate of 10 °C/min, from room temperature to 500 °C.

Synthesis of Trihexyltetradecylphosphonium Persulfate (TETDPPS). In a separatory funnel, 1.8 g of trihexyltetradecylphosphonium chloride dissolved in 20 mL of ethyl ether was introduced and shaken with 30 mL of an aqueous solution containing 5 g of AMPS. The organic phase was separated and washed three times with water. Anhydrous $MgSO_4$ was added to the organic portion to remove residual water and ethyl ether was removed under vacuum. The final product, TETDPPS (MW = 1159), is a viscous colorless liquid.

IR: 2925 cm^{-1}, CH_2 asymmetric stretching; 2854 cm^{-1}, CH_2 symmetric stretching; 1466 cm^{-1}, CH_3 scissoring; 1378 cm^{-1}, CH_3 symmetric bending; 1278 cm^{-1}, S═O symmetric stretching.

Anal. Calcd: C, 66.28; H, 11.82; O, 11.04; S, 5.53; P, 5.34. Found: C, 66.96; H, 11.89; S, 5.04; P, 5.67.

Synthesis of TBPPS. In a separatory funnel, 1.8 g of tetrabutylphosphonium chloride dissolved in 20 mL of CH_2Cl_2 was introduced and shaken with 30 mL of an aqueous solution containing 5 g of AMPS. The organic phase was separated and washed three times with water. Anhydrous $MgSO_4$ was added to the organic portion to remove residual water, and CH_2Cl_2 was removed under vacuum.

The final product, TBPPS (MW = 710), is a white crystalline solid, $T_m = 82$ °C.

IR: 2959 cm^{-1}, CH_2 asymmetric stretching; 2871 cm^{-1}, CH_2 symmetric stretching; 1465 cm^{-1}, CH_3 methyl group; 710 cm^{-1}, CH_2 rocking; 1277 cm^{-1}, S═O symmetric stretching; 1417 cm^{-1}, P−C stretching.

Anal. Calcd: C, 54.06; H, 10.21; O, 18.00; S, 9.02; P, 8.71. Found: C, 54.56; H, 10.09; S, 8.86; P, 8.76.

FP runs were performed as follows: a nonadiabatic glass test tube (inner diameter 16 mm) was loaded with the appropriate amounts of TGDMA and radical initiator (APS or BPO or AIBN or TBPPS or TETDPPS). The mixture was shaken in an ultrasound bath to obtain a homogeneous solution, and a K-type thermocouple connected to a digital thermometer was utilized to monitor the temperature variations (instrument precision ±0.3 °C). The junction was immersed at about 1 cm from the bottom of the reactor. The upper layer of the mixture was then heated by a hot soldering iron tip ($T \approx 300$ °C) until the formation of a hot propagating front started. The front position (±0.5 mm) was recorded as a function of time. Reproducibility of both temperature and front velocity measurements taken on different samples having the same composition were ca. ±5 °C and ca. ±0.1 cm/min, respectively.

Conversions were always ≥96% independently of the initiator used.

Pot lives were >24 h.

Results and Discussion

TETDPPS and TBPPS have been characterized in terms of their kinetic parameters of thermal dissociation following the method described in the literature[39,40] which can be briefly outlined as follows. The heat released by the dissociation reaction was measured by DSC and plotted as d*H*/d*t* (i.e., heat evolution rate) vs temperature. The total reaction heat *Q* is represented by the area under the curve. If *q* is the amount of heat evolved at a given temperature, the ratio *q*/*Q*, easily measurable by the thermogram, is equal to the fraction of reacted moles. By these simple considerations, for a first-order reaction the dissociation constant is given by

$$k_d = \frac{\frac{dH}{dt}}{Q - q} \qquad (1)$$

The pre-exponential Arrenhius constant (*A*) is simply calculated from the intercept of plots of ln k_d *vs* 1/*T*.

Table 1. Kinetic Data of the Radical Initiators Studied in This Work[a]

initiator	A (s^{-1})	E_a (kJ/mol)	k_d (s^{-1})
BPO	1.27×10^{13}	116.93	6.05×10^{-6}
AIBN	5.11×10^{15}	131.78	1.15×10^{-5}
APS	1.31×10^{13}	101.36	1.71×10^{-3}
TBPPS	2.95×10^{15}	119.06	6.55×10^{-4}
TETDPPS	6.21×10^{13}	108.14	7.11×10^{-4}

[a] Reference temperature is 60 °C.

In Table 1, the calculated values of A, as well as activation energy (E_a), and k_d for these new compounds, together with those pertaining to BPO, AIBN, and APS, are listed.

As can be seen, there are not big differences among the E_a values of the three persulfates and BPO ($E_a \approx 110 \pm 9$ kJ/mol), while that of AIBN is somewhat higher ($E_a \approx 131.78$ kJ/mol). By comparing the k_d values, BPO and AIBN result to be the most stable, while APS is the most reactive. The two phosphonium persulfates are characterized by intermediate reactivity without significant differences between them.

However, these data show that all above initiators may work under analogous temperature conditions. Moreover, probably because of their surfactant-like nature, the three persulfates are soluble in a much larger number of media having very different polarity (e.g., TETDPPS is soluble both in water and CCl_4, etc.).

In Table 2, TGA data concerning all five aforementioned radical initiators are reported together with the definition of specific temperature parameters that will be used hereinafter. As can be noticed, no significant differences were found by performing the analyses under air or nitrogen atmosphere; however, the following discussion will refer to the data obtained in air in that they are those most frequently met in practice, and are those applicable to the FP experiments that will be discussed below. As expected, BPO and AIBN start degradation at temperatures that are much lower than those reached by the three persulfates, thus accounting for the large production of bubbles within the polymer material as a result of the additional formation of undesirable gaseous degradation products. Actually, the three persulfates undergo complete degradation at temperatures that are higher than 280−300 °C (note: obviously, we are not referring here to radical formation but, more generally, to any reaction resulting in weight loss). By comparing T_0 values of APS, TBPPS, and TETDPPS, it can be noticed that the first one completely degrades at about 304 °C, while TBPPS and TETDPPS turn out to be more stable (T_0 equal to 345 and 365 °C, respectively). This trend is confirmed also by the corresponding T_{onset} values, which are equal to 281 °C for APS, while they are 311 and 341 °C for TBPPS and TETDPPS, respectively.

Moreover, these two latter compounds have higher thermal stability, as compared to APS, also at lower temperatures; indeed, in the region before that of maximum degradation, all three persulfates exhibit gradual weight loss due to volatile product release (responsible for bubble formation), but TGA traces have different slope. This behavior accounts for the different $T_{2\%}$ (i.e., temperature at which the sample has lost an amount equal to 2.0% of its original weight, Table 2) values found. Namely, at $T_{2\%} = 154$ °C, APS produces volatile products as much 2.0% of its weight whereas, at the same temperature, the amount of gaseous products derived from TETDPPS decomposition is reduced to 1.6 wt % and, for TBPPS, is as low as only about a third than that of APS (i.e., 0.62 wt %). On the other hand, these two latter initiators undergo the 2 wt % reduction at $T_{2\%} = 173$ (TETDPPS) and 221 (TBPPS) °C.

In this form these values might appear as negligible, but they should not be considered as such. Indeed, if for instance we consider a monomer having molecular weight (MW) equal to ca. 100 and density around 1 g/mL (such as methylmethacrylate, styrene, vinylpyridine, etc.) containing 0.5 mol % of radical initiator, at the above temperature of 154 °C, the increase of volume at ambient pressure (or, conversely, the increase of pressure at constant volume) due to gaseous products having average MW=25 corresponds to 130% for APS and only to 30% for TBPPS. (Note: the value of MW=25 is purely arbitrary; however, it is close to that of NH_3, CH_4, ethylene, etc., which are the most probable gases evolved by the above decomposition.)

These data clearly underline the advantage of using the above phosphonium salts as novel radical initiators with improved thermal stability toward undesired reactions different from the dissociation into radicals.

Experiments of FP

On the basis of what was reported above, we decided to assess the feasibility of FP by using these new radical initiators, also making a comparison with APS and the classical BPO and AIBN. FP represents an interesting benchmark in that, together with many advantages due to its easy protocols, high reaction rates and low cost, it is characterized by several aspects and some drawbacks that sometimes may let one to consider the traditional synthetic routes more convenient. Let us analyze these aspects in detail: namely, FP is carried out in nonstirred reactors, at relatively high temperatures (although kept just for seconds). Indeed, in order for a front to self-sustain a relatively high radical concentration is required, this resulting in a large amount of heat released in short times during the polymerization reaction. This means that high polymerization rates and, consequently, high velocities of the front, V_fs, are generally desirable; however, this goal is generally attained together with the increasing of the maximum temperature reached by the moving front, T_{max}, which, however, may result in partial material degradation or in negative effects on conversion due to ceiling temperature achievement. As a consequence, if a radical initiator can be considered suitable for an FP experiment, it will probably also be so for the classical polymerization techniques, as it does not show the above inconveniences, and this will be especially true for nonstirred and batch reactors.

Before any consideration, it is important to highlight that no bubbles were visible in any synthesis performed by using the above three persulfates. It should be underlined also that they were performed in open reactors thus permitting free volume expansion and gas to separate. By contrast, in the same conditions, any synthesis carried out by using AIBN and BPO resulted in bubble-containing polymer materials, thus probably not useful for most of the practical applications (Figure 1).

In Figure 2, the position of the fronts as a function of time for the concentration of 0.5 wt.-% of each radical initiator studied in the present work is reported. As can be noticed, fronts move at constant V_f, a feature often found in frontal reactions.

Figure 3 shows a typical temperature profile recorded in the present work with the indication of T_{max}. It should be reminded here that these graphs represent the variation of temperature registered by the thermocouple junction as time goes and not the temperature map of the whole mixture at a given time. It can be seen that no temperature increase has been recorded before the front approached the junction, thus indicating that no evolution of heat, presumably linked to possible undesirable and simultaneous reactions different from the frontal polymerization, were occurring.

In Figures 4 and 5, T_{max} and V_f, respectively, as functions of the radical initiator concentration, are reported for all compounds studied in this work. Each curve starts from the minimum concentration of initiator that allows a front to self-sustain while the maximum concentration corresponds, for all initiators, to the weight content of 3–5%. Initiator concentrations are

Table 2. Thermal and Weight Data Concerning the Weight Loss of the Radical Initiators Studied in This Work[a]

initiator	gas used in TGA or in FP runs	T_0 (°C)	T_{onset} (°C)	$T_{2\%}$ (°C)	T_{MIC} (°C)
BPO	air	116 (92.1)	106 (0.47)	107 (2.0)	172 (95.4)
AIBN		126.7 (91.2)	110 (0.34)	92 (2.0)	168 (98.0)
APS		304 (78.5)	281 (6.32)	154 (2.0)	137 (1.43)
TBPPS		345 (78.1)	311 (2.33)	221 (2.0)	137 (0.54)
TETDPPS		365 (83.3)	341 (4.32)	173 (2.0)	141 (1.38)
BPO	nitrogen	121 (56.47)	115 (0.37)	108 (2.0)	
AIBN		142 (53.93)	146 (0.37)	102 (2.0)	
APS		300 (43.06)	281 (6.91)	150 (2.0)	
TBPPS		349 (49.34)	316 (1.82)	228 (2.0)	
TETDPPS		352 (65.47)	343 (4.73)	198 (2.0)	

[a] $T_{>0}$ = temperature of maximum degradation rate (estimated by derivative TGA). T_{onset} = temperature at which degradation begins. $T_{2\%}$ = temperature at which the sample has lost an amount equal to 2.0% of its original weight. T_{MIC} = maximum temperature ($T_{\max}$) reached by the front for the TGDMA FP experiment performed in air by using the minimum concentration of radical initiator still able to allow for a front to self-sustain. In parentheses, the percentages of weight loss at the given temperature are indicated.

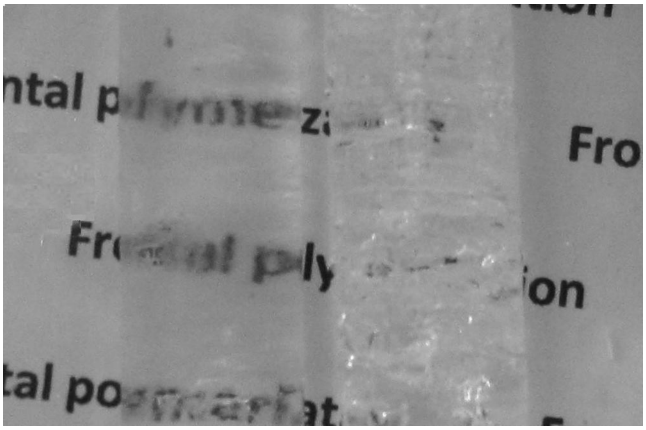

Figure 1. Typical aspect of two FP experiments performed by using TETDPPS (on the left) and AIBN (on the right) as radical initiators. In the second one, bubbles are clearly evident.

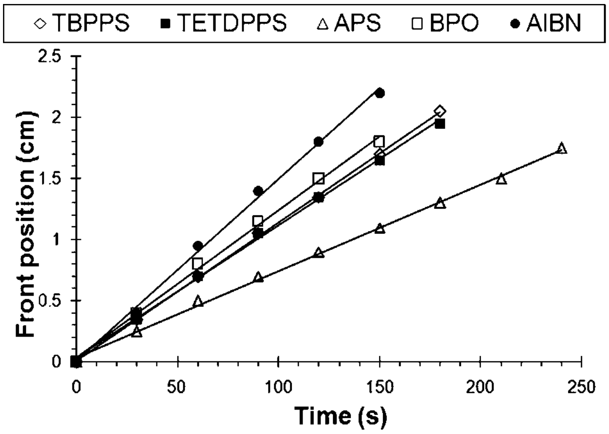

Figure 2. Position of the fronts as a function of time for samples containing 0.5 wt % of radical initiator.

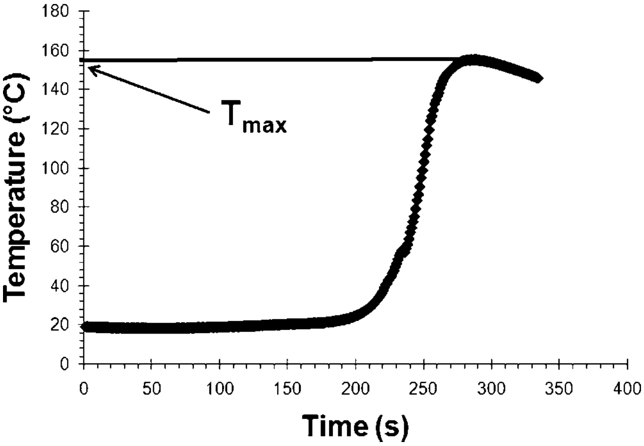

Figure 3. Typical temperature profile recorded during an FP experiment (0.5 wt % of TBPPS).

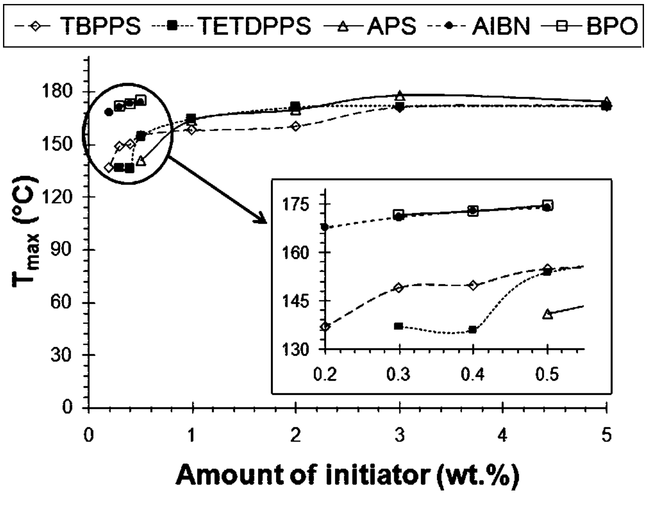

Figure 4. $T_{\max}$ as function of the radical initiator concentration.

expressed as weight percent, because we consider this parameter more meaningful than the corresponding molar value. Indeed, due to the high molecular mass of the three persulfates, even low molar contents may result in large weight/volume amounts with negative consequences on the material properties. This is also why we will compare the effect of all five initiators especially in the region ranging between 0.2 and 0.5 wt %.

As expected, the larger the concentration of initiator is, the higher $T_{\max}$ and V_f are, but the values differ significantly. Namely, at the concentration of 0.5 wt.-%, the use of BPO and AIBN results in the same $T_{\max} \approx 175$ °C and in V_f values of 0.59 and 0.87 cm/min, respectively. By contrast, when the three persulfates are used, $T_{\max}$ values are quite lower (i.e., 141 °C for APS; ca. 155 °C for both phosphonium persulfates), while V_f values are 0.42 cm/min for APS, and ca. 0.7 cm/min for both TBPPS and TETDPPS. This fact underlines that, by using the above phosphonium initiators, it is possible to perform an FP experiment in times that are in the same range of those requested when the classical AIBN and BPO initiators are used, but with the advantage of reaching lower temperatures, thus decreasing the risk of possible polymer degradation.

A further and very important finding is related to the minimum concentration of radical initiators allowing a front to self-sustain. In detail, that is as high as 0.5 wt % for APS (=0.15 mol %), 0.3 wt % for TETDPPS (=0.07 mol %) and only 0.2 wt % for TBPPS (=0.08 mol %), the latter being a minimum

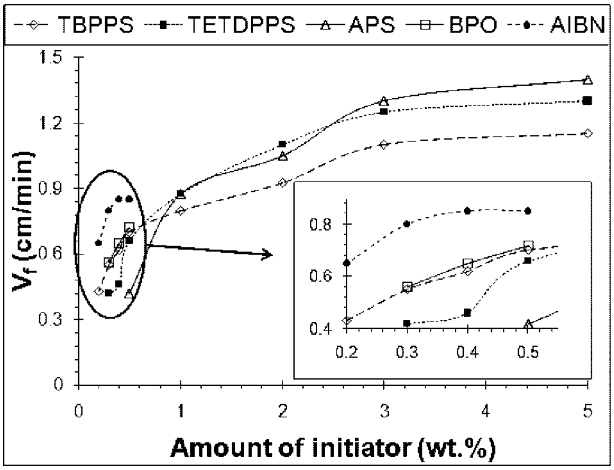

Figure 5. V_f as function of the radical initiator concentration.

concentration reached only also by AIBN. However, in the presence of such amount of this azo compound, the corresponding reaction mixture reached $T_{max} = 168$ °C whereas, by using TBPPS, this value did not exceed 137 °C.

By reasoning in terms of moles, the advantage of using phosphonium persulfates looks even more evident; in fact, the minimum molar concentration is equal to 0.35% for both AIBN and BPO and 0.15% for APS while for TBPPS and TETDPPS it is as a low as 0.08% and 0.07%, respectively. This fact may have important consequences on the possibility of reaching higher molecular masses when monomers that do not give rise to cross-linked polymers are used.

Moreover, in order to have an (even rough) approximation on the amount of gaseous products derived by the decomposition of the various initiators at the minimum temperature at which they allow a TGDMA polymerization front to self-sustain, we have used the data shown in Figures 4 and 5 and those listed in Table 2. For this calculation, we assume the following points: (i) AIBN gives rise to nitrogen; (ii) BPO gives rise to CO_2; (iii) the three persulfates give rise to a gaseous mixture having average MW = 25 in amounts as calculated by the TGA data reported in parentheses in Table 2.

The result is that the increase of volume at ambient pressure (or the increase of pressure at constant volume) due to gaseous products corresponds to 88% for BPO, 43% for AIBN, 9.5% for APS, and only 5.4% for TETDPPS, and it is as low as 1.4% for TBPPS. Although the value from BPO is certainly overestimated in that, actually, only a fraction of BPO degrades to CO_2 before taking part to the initiation reaction, the great improvement resulting by the use of these new initiators looks very clear. Indeed, even by limiting our considerations to the three persulfates only, the amount of gaseous products formed by TETDPPS is roughly only a half of that derived by APS; in the case of TBBPS, such an amount drops down to just a seventh of the APS value.

Conclusions

In the field of polymer synthesis, radical initiators represent a very important class of molecules. However, although a large number of the above chemicals have been studied and used, only a few of them are commonly employed in practical applications and belong in general to the families of azo and peroxy compounds. During polymerization, they undergo thermal degradation forming also gaseous products that, in the case of open and stirred reactors, does not generally cause any drawback for the final polymer material, such as presence of bubbles, worsening of mechanical and optical properties, etc. On the contrary, one of the polymerization methods that are mostly affected by this inconvenience is that of frontal polymerization, in which the reactive monomer mixture cannot be stirred and, in addition, relatively high transient temperatures are reached. The result is that a large amount of gas is produced and the final solid polymer material contains many bubbles.

So far, APS has represented the only attempt of solving this problem. However, its high molecular mass, linked to the need of using it in relatively high molar amounts in order to have a front able to self-sustain, strongly limited its extensive use. In addition, it has been reported that the use of quaternary ammonium salts in polymer systems may result in partial polymer degradation and consequent color formation. The approach proposed by the present work is inspired by the idea of APS but is based on other chemical compounds. Indeed, the cationic moiety of APS has been replaced by those of two phosphonium-based ionic liquids, a class of materials which is known for its much increased thermal stability. Two new radical initiators have been easily synthesized (TBPPS and TETDPPS) and their decomposition kinetic parameters have been calculated by DSC. It was found that they can be used in polymerization temperature conditions that are similar to those of APS, BPO and AIBN, but with the additional advantage of being soluble in a much larger number of reaction media, thus allowing their use with an increased number of monomers.

It has been established by TGA that these two new initiators are much more thermally stable than the others (BPO, AIBN, APS) evaluated in this work. Actually, not only do they start degradation at higher temperatures, but also the amount of their volatile products evolving before T_{onset} is significantly lower, thus resulting in a further advancement toward the solution of the aforementioned drawbacks. The initiators have been tested by performing some FP experiments that evidenced further advantages. Namely, the FP maximum temperatures reached in the presence of TBPPS and TETDPPS were lower than those recorded with AIBN and BPO, while front velocities were in the same range. This means that the same reaction times can be used, but the possibility of polymer degradation are now very limited. Furthermore, despite the large molecular mass of these new ionic liquid initiators, it was found that TBPPS is able to sustain a FP front also in little weight amount, the same amount reached only by AIBN (not by BPO), thus overcoming also the possible drawbacks linked to the worsening of mechanical properties. In addition, in terms of the minimum molar concentration of radical initiator for a front to self-sustain, its value results extremely low, being only a fifth of those of AIBN and BPO, and a half of that of APS. This finding may result in a very relevant increase of its molecular mass when an uncrosslinked polymer has to be prepared.

Of course, it is fair to underline that the present work should be considered as a preliminary set of results related to novel FP approaches aimed to minimize the present drawbacks of the method. A great deal of in-depth work has still to be done on these new compounds and on similar ones. We will fully report on future findings in forthcomings papers.

Acknowledgment. We would like to thank Dr Debora Puglia from the University of Perugia for her kind help in TGA analysis.

References and Notes

(1) Eastmond, G. C., Ledwith, A., Russo, S., Sigwalt, P. Eds.; *Comprehensive Polymer Science*; Pergamon Press: Oxford, U.K., 1989; Vol. *3*, p 97.
(2) Brandrup, J.; Immergut, E. H.; Grulke, E. A. *Polymer Handbook*, 4th ed.; Wiley Interscience: New York, 1999, p. II/1.
(3) Billmeyer, F. *Textbook of Polymer Science*, 2nd ed.; Wiley: New York, 1971; Chapter 9, p 280.
(4) Chechilo, N. M.; Khvilivitskii, R. J.; Enikolopyan, N. S. *Dokl Akad Nauk SSSR* **1972**, *204*, 1180–1181.
(5) Pojman, J. A. *J. Am. Chem. Soc.* **1991**, *113*, 6284–6286.

(6) Khan, A. M.; Pojman, J. A. *Trends Polym. Sci.* **1996**, *4*, 253–257.

(7) Fortenberry, D. I.; Pojman, J. A. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 1129–1135.

(8) Chekanov, Y.; Arrington, D.; Brust, G.; Pojman, J. A. *J. Appl. Polym. Sci.* **1997**, *66*, 1209–1216.

(9) Jiménez, Z.; Pojman, J. A. *J. Polym. Sci., Part A: Polym. Chem.* **2007**, *45*, 2745–2754.

(10) Washington, R. P.; Steinbock, O. *J. Am. Chem. Soc.* **2001**, *123*, 7933–7934.

(11) Crivello, J. V. *J. Polym. Sci., Part A: Polym. Chem.* **2006**, *44*, 3036–3052.

(12) Crivello, J. V. *J. Polym. Sci., Part A: Polym. Chem.* **2006**, *44*, 6435–6448.

(13) Texter, J.; Ziemer, P. *Macromolecules* **2004**, *37*, 5841–5843.

(14) Hu, T.; Chen, S.; Tian, Y.; Chen, L.; Pojman, J. A. *J. Polym. Sci., Part A: Polym. Chem.* **2007**, *45*, 873–881.

(15) Chen, L.; Hu, T.; Yu, H.; Chen, S.; Pojman, J. A. *J. Polym. Sci., Part A: Polym. Chem.* **2007**, *45*, 4322–4330.

(16) Hu, T.; Fang, Y.; Chen, S.; Chen, L.; Pojman, J. A. *Colloid Polym. Sci.* **2007**, *285*, 891–898.

(17) Chen, S.; Tian, Y.; Chen, L.; Hu, T. *Chem. Mater.* **2006**, *18*, 2159–2163.

(18) Chen, S.; Sui, J.; Chen, L.; Pojman, J. A. *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43*, 1670–1680.

(19) Mariani, A.; Fiori, S.; Chekanov, Y.; Pojman, J. A. *Macromolecules* **2001**, *34*, 6539–6541.

(20) Fiori, S.; Mariani, A.; Ricco, L.; Russo, S. *Macromolecules* **2003**, *36*, 2674–2679.

(21) Mariani, A.; Bidali, S.; Fiori, S.; Malucelli, G.; Sanna, E. *e-Polym.* **2003**, *044*, 1–9.

(22) Fiori, S.; Mariani, A.; Ricco, L.; Russo, S. *e-Polym.* **2002**, *029*, 1–10.

(23) Fiori, S.; Malucelli, G.; Mariani, M.; Ricco, L.; Casazza, E. *e-Polym.* **2002**, *057*, 1–10.

(24) Mariani, A.; Fiori, S.; Bidali, S.; Alzari, V.; Malucelli, G. *J. Polym. Sci., Part A: Polym. Chem.* **2008**, *46*, 3344–3352.

(25) Mariani, A.; Fiori, S.; Pedemonte, E.; Pincin, S.; Ricco, L.; Russo, S. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **2002**, *43* (2), 814–815.

(26) Mariani, A.; Fiori, S.; Pedemonte, E.; Pincin, S.; Princi, E.; Vicini, S. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **2002**, *43* (2), 869–870.

(27) Mariani, A.; Bidali, S.; Caria, G.; Monticelli, O.; Russo, S.; Kenny, J. M. *J. Polym. Sci., Part A: Polym. Chem.* **2007**, *45*, 2204–2212.

(28) Mariani, A.; Alzari, V.; Monticelli, O.; Pojman, J. A.; Caria, G. *J. Polym. Sci., Part A: Polym. Chem.* **2007**, *45*, 4514–4521.

(29) Masere, J.; Chekanov, Y.; Warren, J. R.; Stewart, F. D.; Al-Kaysi, R.; Rasmussen, J. K.; Pojman, J. A. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 3984–3990.

(30) Xie, W.; Gao, Z.; Pan, W.-P.; Hunter, D.; Singh, A.; Vaia, R. *Chem. Mater.* **2001**, *13*, 2979–2990.

(31) Xie, W.; Gao, Z.; Liu, K.; Pan, W. P.; Vaia, R.; Hunter, D. *Thermochim. Acta* **2001**, *367−368*, 339–350.

(32) Delozier, D. M.; Orwoll, R. A.; Cahoon, J. F.; Johnston, N. J.; Smith, J. G.; Connell, J. W. *Polymer* **2002**, *43*, 813–822, 3?

(33) Fornes, T. D.; Yoon, P. J.; Paul, D. R. *Polymer* **2003**, *44*, 7545–7556.

(34) Yoon, P. J.; Hunter, D. L.; Paul, D. R. *Polymer* **2003**, *44*, 5341–5354.

(35) Hedley, C. B.; Yuan, G.; Theng, B. K. G. *Appl. Clay Sci.* **2007**, *35* (3−4), 180–188.

(36) Rogers, R. D., Seddon, K. R., Eds. *Ionic Liquids; Industrial Applications to Green Chemistry*; ACS Symposium Series 818; American Chemical Society: Washington, DC, 2002.

(37) Pojman, A. J.; Elcan, W.; Khan, A. M.; Mathias, L. *J. Polym. Sci., Part A: Polym. Chem.* **1997**, *35*, 227–230.

(38) Bidali, S.; Fiori, S.; Malucelli, G.; Mariani, A. *e-Polym.* **2003**, *060*, 1–12.

(39) Barrett, K. E. J. *J. Appl. Polym. Sci.* **1967**, *11*, 1617–1626.

(40) Moze, A.; Malavasic, T.; Vizovisek, I.; Lapanje, S. *Angew. Makromol. Chem.* **1975**, *46*, 89–94.

MA800610G