

Frontal Polymerization with Monofunctional and Difunctional Ionic Liquid Monomers

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ABSTRACT: For the first time, we studied frontal polymerization with ionic liquid monomers. We synthesized a series of compounds from the neutralization reaction between trialkylamines (tributylamine, trihexylamine, trioctylamine, and (2-dimethylamino)ethyl methacrylate) and acrylic or methacrylic acid. For the ionic liquids prepared from the unreactive amines, frontal polymerization could not be achieved without the addition of a diacrylate. With the addition of a diacrylate, the front velocities were slower than for dodecyl acrylate (with the diacrylate), a compound of comparable molecular weight. Monomers prepared from the (2-dimethylamino)ethyl methacrylate could support frontal polymerization alone but the front velocities were lower than dodecyl (meth)acrylate. These results are contrasted with recent results of Jiménez et al. for room temperature kinetics. Finally, the polymers prepared were comparable to those prepared by batch curing at 75 °C except for the monomethacrylate ionic liquid, which lost some tertiary amine by dissociation and evaporation. © 2007 Wiley Periodicals, Inc. *J Polym Sci Part A: Polym Chem* 45: 2745–2754, 2007

Keywords: frontal polymerization; ionic liquid monomers; poly(acrylates); thermogravimetric analysis (TGA); radical polymerization; kinetics (polym.)

INTRODUCTION

Ionic liquids are salts with melting temperatures below the boiling point of water. They possess valuable properties such as nonvolatility, nonflammability, high ion density, and high ionic conductivity.¹ The most commonly studied systems contain ammonium, phosphonium, pyridinium, or imidazolium cations. Common anions that yield useful ionic liquids include hexafluorophosphate, [PF₆]⁻, tetrafluoroborate, [BF₄]⁻, bis(triflyl) imide, [NTF₂]⁻, and chloride, Cl⁻.²

Ionic liquids have been used in free-radical, acid-catalyzed cationic, transition-metal catalyzed,

Ziegler–Natta, metathesis, living radical and other type of polymerizations as solvents, catalysts, and plasticizers.^{1,3–9} But until now they have not been used in frontal polymerization.

Frontal polymerization is a mode of converting a monomer into polymer, via a localized exothermic reaction zone produced by the coupling of thermal diffusion and the Arrhenius kinetics of the exothermic polymerization.¹⁰ The application of heat to one section of the medium will increase the rate of reaction at that point, producing heat that can diffuse and increase the rate of reaction in a neighboring region, and so on.

The most commonly used chemistry is free-radical polymerization, especially with acrylates. Dependence of the front velocity on the initiator concentration has been widely studied for many systems such as methacrylic acid with benzoyl peroxide,¹¹ tri(ethylene glycol) dimethacrylate with

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benzoyl peroxide,¹² acrylamide in DMSO with potassium persulfate,¹³ butyl acrylate with AIBN,¹⁴ 1,6-hexanediol diacrylate (HDDA) in DMSO with different persulfates,¹⁵ HDDA with dissolved and microencapsulated cumene hydroperoxide.¹⁶ The effect of initiator concentration on frontal copolymerizations have also been studied, such as methyl methacrylate–methacrylic acid, acrylic acid–methacrylic acid and methacrylic acid–styrene with benzoyl peroxide,¹⁷ trithiol–triallyl ether with Luperox 231.¹⁸ In all cases, the front velocity increased monotonically as the initiator concentration was increased and usually followed power law dependence. A complete bibliographic review can be found in http://www.pojman.com/FP_Bibliography.html.

Jiménez et al. recently studied the photopolymerization kinetics of ionic liquid monomers prepared by the neutralization reaction between (meth)acrylic acid and tertiary amines.¹⁹ They found that the monoacrylates and monomethacrylates polymerized with comparable rates to typical monoacrylate or monomethacrylate esters. However, if one of the alkyl chains on the ammonium group contained an acrylate or methacrylate, the compounds polymerized with rates comparable to difunctional acrylates or methacrylates. Thus, these complexes acted in the room temperature polymerization as if they were covalent difunctional acrylates or methacrylates.

In this work, we present our study of frontal polymerization with these same monomers. We determined the minimum conditions to obtain frontal polymerization with monofunctional and difunctional (meth)acrylate ionic liquid monomers. Monofunctional monomers would not support a front without the addition of a diacrylate. The critical amounts of the crosslinking agent and thermal initiator were determined, and the effect of the initiator concentration on the front velocities for both types of monomers was determined. The trends previously reported for room temperature curing did not hold for frontal polymerization, viz., the monoacrylates and monomethacrylates produced fronts with slower velocities than (meth)acrylate esters. Also the thermal stability of (meth)acrylate ionic liquid polymers obtained via bulk or frontal polymerization, was analyzed.

EXPERIMENTAL

Materials

Acrylic acid (>99%), methacrylic acid (>99%), 2-(dimethylamino)ethyl acrylate (98.0%), 2-(dime-

thylamino)ethyl methacrylate (98.0%), tri(ethylene glycol) dimethacrylate (TEGDMA, 95%), di(ethylene glycol) diacrylate (DEGDA, 75%), 1,6-hexanediol diacrylate (HDDA, 80%), dodecyl acrylate (90%), dodecyl methacrylate (96%) were used as received from Aldrich Chemical Company; isobutyric acid (>99.5%), butyl acrylate (>99.0%), butyl methacrylate (>99.0%), tributylamine (>99.0%), trihexylamine (>99.0%) and trioctylamine (>99.0%) were purchased from Fluka and used as received; Cabosil (ultrafine silica gel) was used as received from Composites S.A.; and 1,1-bis(*tert*-butylperoxy)-3,3,5-trimethylcyclohexane (Luperox 231, 92%) was used as received from Arkema.

Monomer Synthesis

Tributylammonium acrylate, trihexylammonium acrylate, trioctylammonium acrylate, (2-acrylate)ethyl dimethylammonium 2-propionate, tributylammonium methacrylate, trihexylammonium methacrylate, trioctylammonium methacrylate, (2-methacrylate)ethyl dimethylammonium 2-propionate, (2-methacrylate)ethyl dimethylammonium methacrylate, (2-acrylate)ethyl dimethylammonium methacrylate, and (2-methacrylate)ethyl dimethylammonium acrylate were synthesized and characterized following Jiménez et al.¹⁹ ¹H and ¹³C NMR data were presented in our previous work.¹⁹

An example of the synthesis: 6.55 mL of tributylamine and 1.86 mL of acrylic acid were mixed with constant stirring for 5 h. The reaction was carried out in a room temperature water bath to remove the large heat of neutralization. The same methodology was used with other amines and acids. A 1:1*M* relation for acid:base was used in all cases.

Frontal Polymerization

The ionic liquid mono(meth)acrylate monomer or (meth)acrylate ester was mixed with the appropriate amount of crosslinking agent, thermal initiator and filler, in this respective order. This mixture was allowed to rest until the bubbles disappeared, and then used to fill a 1 cm × 6 cm vial (glass, screw thread, and rubber-lined cap manufactured by Gerresheimer), which was then sealed with its plastic cap. Frontal polymerization was initiated by putting a hot soldering iron on the top of the inverted and sealed

vial. All experiments were performed at ambient temperature.

The concentration of thermal initiator was varied between 0.5 and 4% w/w. In the case of ionic liquid difunctional monomers or di(meth)acrylate esters, the same procedure to run frontal polymerization was used but crosslinking agent was not added. The amount of silica gel added to the monomeric mixture was 3% for all systems.

Because the polymerization reaction is exothermic and produces gases (from the initiator decomposition and from the amine evaporation), the vial can explode; therefore, it is necessary to do the reaction inside a hood and to close the shield after the soldering iron has been taken off to prevent injuries.

Bulk Polymerization

One milliliter of the mixture used to run frontal polymerization was put into a vial and closed but not hermetically sealed to prevent an explosion. The vial was placed in an oven for 48 h at 75 °C and then cooled to ambient temperature.

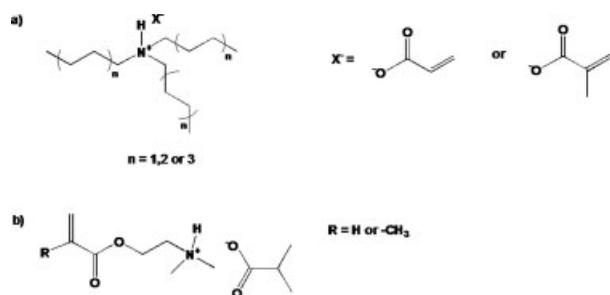
Thermogravimetric Analysis

A Thermogravimetric Analyzer TA Q500 was used to measure the thermal stability of frontally and bulk polymerized ionic liquids over a temperature range of 25–800 °C with a heating rate of 5 °C/min.

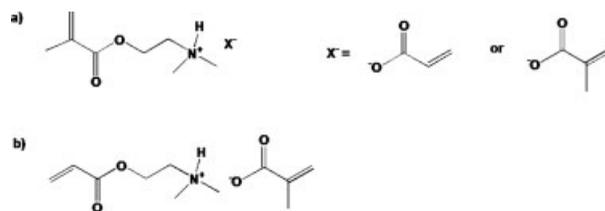
RESULTS AND DISCUSSION

Frontal Polymerization with Monofunctional Ionic Liquid (Meth)acrylates

Monofunctional ionic liquid acrylates and methacrylates (Scheme 1) do not support a front when



Scheme 1. Structures of monofunctional ionic liquid (meth)acrylate monomers. a) trialkylammonium acrylates and methacrylates, and b) [2-(meth)acrylate]ethyl dimethylammonium 2-propionate.



Scheme 2. Structures of difunctional ionic liquid (meth)acrylate monomers. a) (2-methacrylate)ethyl dimethylammonium acrylate or methacrylate, and b) (2-acrylate)ethyl dimethylammonium methacrylate.

combined with a thermal initiator. This can be explained by the high molecular weight of those ionic liquid monomers. According to Nason et al.,²⁰ the existence of a frontal polymerization and the velocity of the front for acrylate systems, depend on the molecular weight/double bond ratio since the value of this ratio affects the amount of heat released per unit volume and thus the front temperature.

Frontal polymerization was also performed with difunctional ionic liquid monomers (Scheme 2). They supported frontal polymerization because of the lower molecular weight per double bond ratio and because of their higher rate of polymerization.

It was necessary to add a certain amount of a crosslinking agent to the ionic liquid monomer—initiator—filler mixture to produce a self-sustaining front. The minimum amount of crosslinking agent needed was determined (Table 1) and different percentages between 10 and 50% of HDDA were tested along with 3% of filler and 2.5% of initiator (Luperox 231) in all cases. Silica gel was used to increase viscosity and prevent convection. The critical amount of HDDA necessary to sustain frontal polymerization is specific to the amount of initiator used, the initial temperature, size of the tube, and ambient temperature.

The ratios (molecular weight/double bond) of the acrylate ionic liquid monomers are 426 > 342 > 257 g/double bond for trioctylammonium, trihexylammonium and a tributylammonium acrylate, respectively. As can be seen in Table 1, trioctylammonium acrylate required the highest amount of HDDA in the acrylate series because its front temperature is the lowest (least amount of heat released per unit volume).

In the case of methacrylate ionic liquid monomers the tendency is different and the amount of crosslinking agent is relatively the same for all of them and independent of the molecular weight.

Table 1. Concentration of Cross-Linking Agent Added to (Meth)acrylate Ionic Liquid Monomers

Ionic Liquid Monofunctional Monomer ^a	Percentage of HDDA (% w/w)	Moles Ionic Liquid Monomer/Moles HDDA
Tributylammonium acrylate	20	4.1
Trihexylammonium acrylate	36	1.1
Trioctylammonium acrylate	40	0.9
(2-acrylate)ethyl dimethylammonium 2-propionate	23	3.8
Tributylammonium methacrylate	40	1.4
Trihexylammonium methacrylate	40	0.9
Trioctylammonium methacrylate	44	0.7
(2-methacrylate)ethyl dimethylammonium 2-propionate	30	2.5

^a The samples contained 2.5% w/w Luperox 231 with 3% w/w silica gel.

In general, methacrylates need more crosslinking agent, as a consequence of the stability of the methacrylate radical that is involved in the polymerization process.²⁰ The stability of the radical results in a reduction of the rate of the propagation; slower fronts allow more time for heat loss.²¹

After finding the minimum concentration of HDDA needed to sustain frontal polymerization with (meth)acrylate ionic liquid monomers, the effect of the initiator concentration on the front velocity was investigated (Figs. 1 and 2). The molar ratio monomer/HDDA was maintained constant, and the Luperox 231 concentration was varied from 0.5 to 4.0 wt %.

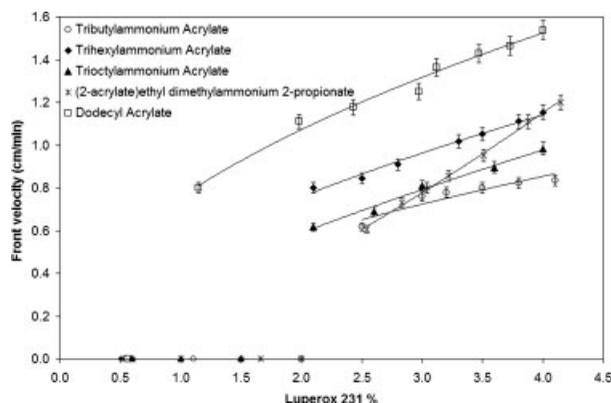


Figure 1. Effect of the thermal initiator concentration on the front velocity for acrylate systems with HDDA (cross-linking agent), Luperox 231 (thermal initiator) and 3 % of Cabosil (filler). The molar ratio of ionic liquid monomer/HDDA was maintained constant as shown in Table 1. For dodecyl acrylate, the amount of HDDA was the same as for tributylammonium acrylate.

By increasing the initiator concentration the front velocity increased too, as expected.^{11–18,22,23} Figures 1 and 2 show the results obtained for the acrylate and methacrylate series; in general, the dependence of the front velocity on the initiator concentration fitted a power function, with the power varying between 0.3 and 1.3.

Also, a minimum amount of initiator is required (because of heat loss) to sustain frontal polymerization, and the amount is specific to each system and the conditions. Accordingly, tributylammonium acrylate, trihexylammonium acrylate, trioctylammonium acrylate, and (2-acrylate)ethyl dimethylammonium 2-propionate required 2.5, 2.0, 2.0, and 2.5 weight percent of

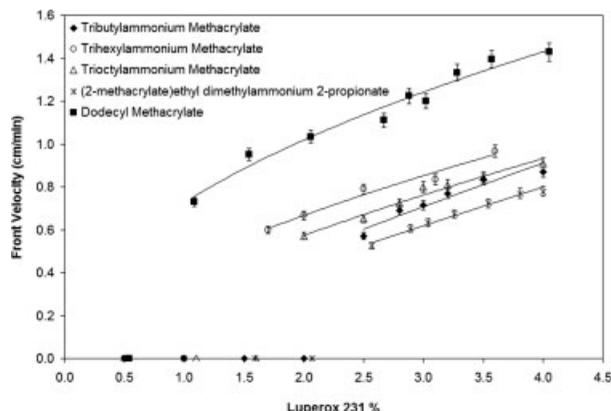


Figure 2. Effect of the thermal initiator concentration on the front velocity for methacrylate systems with HDDA (cross-linking agent), Luperox 231 (thermal initiator) and 3 % of Cabosil (filler). The molar ratio of ionic liquid monomer/HDDA was maintained constant as shown in Table 1. For dodecyl methacrylate, the amount of HDDA was the same as for tributylammonium methacrylate.

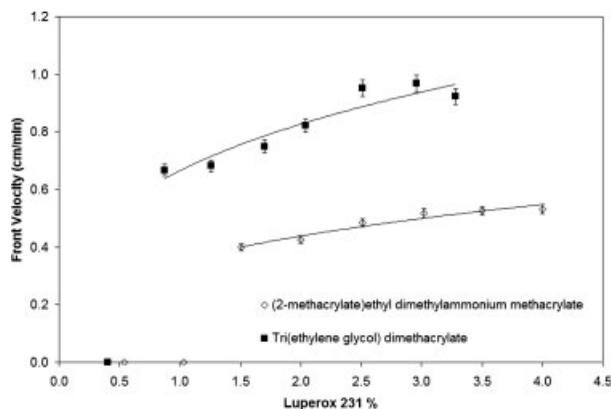


Figure 3. Effect of the thermal initiator concentration on the front velocity for dimethacrylate systems with Luperox 231 (thermal initiator) and 3 % of Cabosil (filler).

Luperox 231 (Fig. 1) for frontal polymerization to occur.

In the case of the methacrylates, tributylammonium methacrylate, trihexylammonium methacrylate, trioctylammonium methacrylate and (2-methacrylate)ethyl dimethylammonium 2-propionate needed 2.5, 1.5, 2.0, and 2.5% in weight of Luperox 231 (Fig. 2), respectively. In all cases, the concentration of crosslinking agent used was the minimum needed for frontal polymerization to occur.

To compare the (meth)acrylate ionic liquid monomers with typical (meth)acrylate esters, do-

decyl acrylate, and dodecyl methacrylate were tested in frontal polymerization, using the same amount of HDDA as for tributyl ammonium (meth)acrylate (Figs. 1 and 2). The molecular weights of dodecyl acrylate ($M_w = 240$ g/mol) and methacrylate ($M_w = 254$ g/mol) are not exactly the same as those for tributylammonium acrylate ($M_w = 257$ g/mol) and methacrylate ($M_w = 271$ g/mol), respectively, as they differ by ~ 17 g/mol. All comparisons made are thus approximate. As can be seen in Figure 1, dodecyl acrylate showed higher front velocities, doubling the value of the velocities obtained for tributylammonium acrylate.

Jiménez et al. found that the maximum photopolymerization rates at room temperature for the ionic liquid monomers were the same.¹⁹ Using the same technique and conditions as in Jiménez et al.,¹⁹ we found that an acrylate ester (butyl acrylate) showed almost the same polymerization rate (2.5 conversion% s^{-1}) as the three ionic liquids (3 conversion% s^{-1}). However, for frontal polymerization, each ionic liquid monomer required a different amount of HDDA to sustain a front. This difference and the large difference in front velocities indicate that not only the amount of heat released per unit volume for an acrylate or methacrylate affects the front velocity.

Results from frontal polymerization with two dimethacrylate monomers are shown in Figure 3. The ionic liquid did not polymerize frontally with concentrations of Luperox 231 below 1.0% wt,

Table 2. Maximum Photopolymerization Rates for (Meth)acrylate Monomers Using Real Time-FTIR Spectroscopy

Compound ^a	Rate of Polymerization ^b (% conversion/s)
Tributylammonium acrylate ^c	3.0
Trihexylammonium acrylate ^c	3.0
Trioctylammonium acrylate ^c	3.0
(2-Acrylate)ethyl dimethylammonium 2-propionate ^c	3.6
Tributylammonium methacrylate ^c	0.35
Trihexylammonium methacrylate ^c	0.61
Trioctylammonium methacrylate ^c	0.58
(2-Methacrylate)ethyl dimethylammonium 2-propionate ^c	0.37
Butyl acrylate	2.4
Butyl Methacrylate	0.10
(2-Methacrylate)ethyl dimethylammonium methacrylate ^c	3.8
Tri(ethylene glycol) dimethacrylate ^c	3.1

^a The samples contained 2.0 wt % Darocure 1173 (photo-initiator).

^b The light intensity used was 18.7 mW/cm² of UV light.

^c Data from Jiménez et al.¹⁷

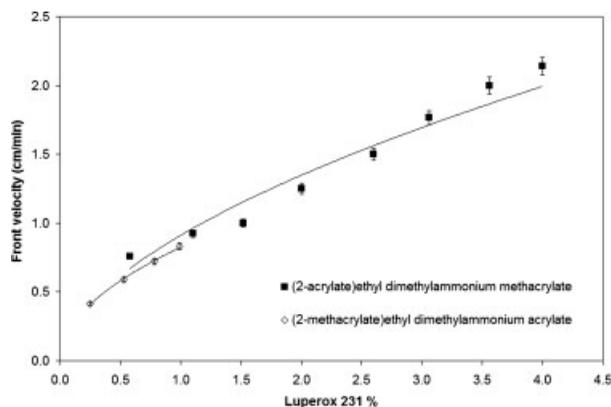


Figure 4. Effect of the thermal initiator concentration on the front velocity for acrylate-methacrylate systems with Luperox 231 (thermal initiator) and 3 % of Cabosil (filler).

and the ester did not polymerize frontally with concentrations below 0.5% wt. Although the ester, triethylene glycol dimethacrylate has a higher molecular weight per double bond, 143 g/double bond, than the ionic liquid (2-methacrylate)ethyl dimethylammonium methacrylate, 122 g/double bond, the former polymerizes faster; showing again the existence of other factors than just the room temperature reactivity affect the front velocity.

Figure 3 shows that fronts with the covalent dimethacrylate are faster than the ionic liquid dimethacrylate. Jiménez et al.¹⁹ had shown that difunctional ionic liquid monomers were as reactive at room temperature as covalent difunctional monomers (Table 2). However, the neutralization reaction is exothermic and so will reverse with elevated temperature. The high temperature in the front will dissociate some of the monomer,

making it polymerize as a mixture of two monofunctional monomers instead of a difunctional one.

Two difunctional ionic liquid monomers containing one methacrylate and one acrylate group in their structures were used to run frontal polymerization, and the results are shown in Figure 4. A change of one methacrylate group by an acrylate group, in the dimethacrylate ionic liquid structure, increased the front velocity. Also the concentration of thermal initiator needed to support the front was lower (below 1% wt). This is consistent with the fact that acrylates are more reactive than methacrylates and show higher polymerization rates.²⁴

In general, monofunctional and difunctional ionic liquid (meth)acrylate monomers showed the same tendency in frontal polymerization, regarding the initiator concentration, that do traditional (meth)acrylate esters; however, the front velocity for the ionic liquid monomers, is one half of the front velocity achieved for (meth)acrylate esters.

Thermal Stability of Polymers Obtained with Monofunctional Ionic Liquid (Meth)acrylates

The thermal stabilities of the polymers obtained by frontal and bulk polymerization with the ionic liquid monomers, tributylammonium acrylate, tributylammonium methacrylate, and (2-methacrylate)ethyl dimethylammonium methacrylate, were evaluated and compared with those obtained for traditional esters dodecyl acrylate, dodecyl methacrylate, and triethylene glycol dimethacrylate.

It was expected the polymers prepared by frontal and bulk polymerization to show the same

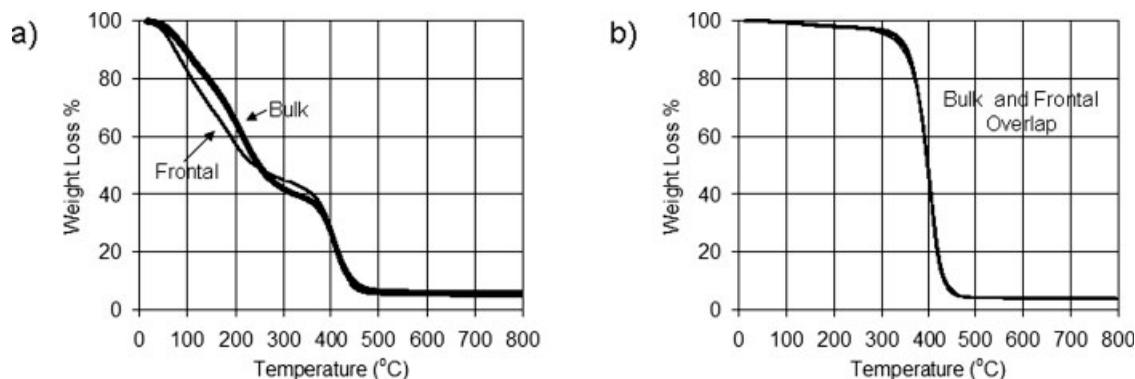
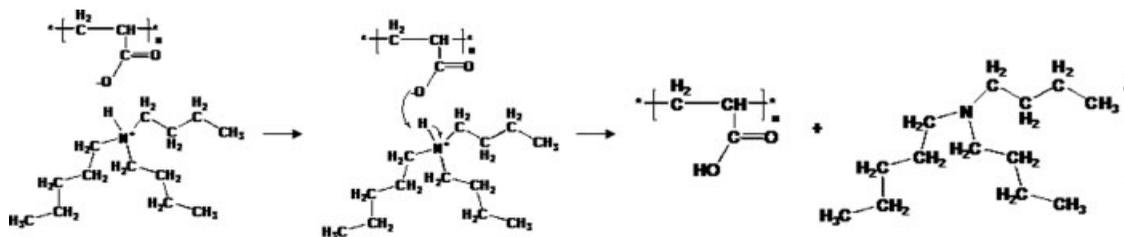


Figure 5. TGA curves for acrylate polymers prepared by bulk and frontal polymerization. a) tributylammonium acrylate and b) dodecyl acrylate. At a heating rate of 5 °C/min.



Scheme 3. Deprotonation of the ammonium moiety in poly(tributylammonium acrylate).

decomposition temperatures, as was reported by Chekanov et al.²⁵ who polymerized an epoxy resin by frontal and bulk polymerization. Additionally, poly(acrylamide) prepared by frontal polymerization had the same decomposition temperature as a commercial sample.²⁶

Figure 5 shows TGA curves for monofunctional poly(acrylate)s prepared by frontal and bulk polymerization. Poly(tributylammonium acrylate–HDDA) lost 57 and 60% in mass, from 20 to 325 °C, for the frontal and bulk polymerized samples [Fig. 5(a)], respectively. This mass corresponds to the ammonium moiety that is around 57% of the total. The poly(acrylate) component decomposed from 325 to 480 °C. According with those percentages, the conversion of acrylate monomer into the polymer is ~91 and 85% for frontal and bulk polymerized samples, respectively. In the case of poly(dodecyl acrylate–HDDA), it reached 100% of conversion, and there is only one decomposition temperature at 325 °C.

Thus, the ionic liquid acrylate polymer is less stable than the traditional acrylate polymer, because the ammonium group dissociated from the

carboxyl group and evaporated (Scheme 3) at lower temperature than the poly(acrylate) decomposed. Because the dodecyl side chain in the acrylate ester is covalently bonded, it does not decompose by itself at a different temperature.

Figure 6 shows TGA curves for monofunctional poly(methacrylate)s, prepared by frontal and bulk polymerization. Poly(tributylammonium methacrylate–HDDA) lost 46 and 34% in mass, from 20 to 325 °C, for the frontal and bulk polymerized samples [Fig. 6(a)], respectively. This mass corresponds to the ammonium moiety that is around 40% of the total. The poly(methacrylate) component decomposed from 325 to 480 °C. The percentage of mass loss for the frontal polymerized sample is higher than the expected (40%) because the methacrylate polymer started decomposing at around 220 °C. For bulk polymerization the mass loss is smaller than expected, probably because some amine left the system during the polymerization because the vial was not hermetically sealed and that methacrylate polymerizations are slower than acrylate polymerizations.

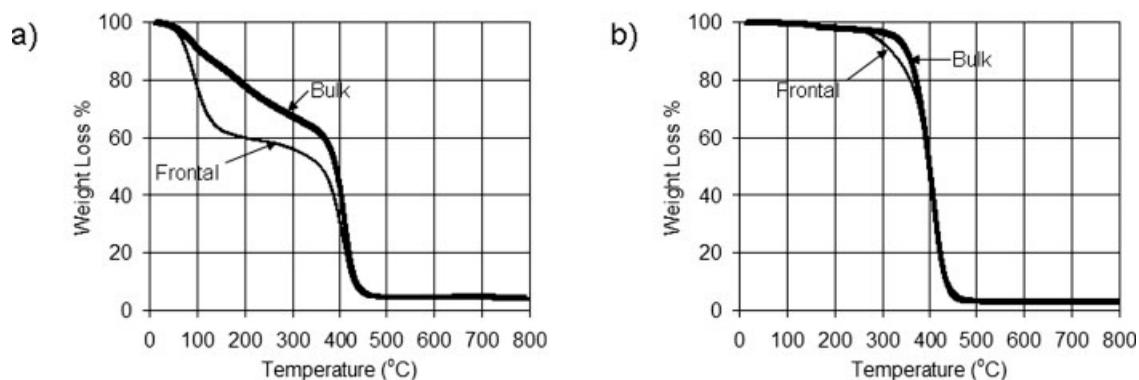


Figure 6. TGA curves for methacrylate polymers prepared by bulk and frontal polymerization. a) tributylammonium methacrylate and b) dodecyl methacrylate. At a heating rate of 5 °C/min.

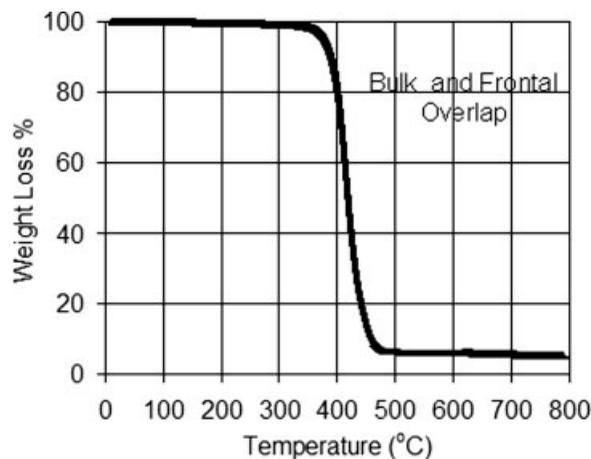


Figure 7. TGA curves for the polymer from 1,6-hexanediol diacrylate (HDDA), prepared by bulk and frontal polymerization. At a heating rate of 5 °C/min.

According to the percentages of weight loss, the conversion of methacrylate monomer into the polymer is ~90% for the frontally polymerized sample. The calculated conversion for the sample polymerized in bulk, is “110%” which is not accurate. This anomalous percentage is due to the release of the amine during the polymerization process, as explained above.

Poly (dodecyl methacrylate–HDDA) decomposed at 325 °C. Thus, the ionic liquid methacrylate polymer is less stable than the traditional methacrylate polymer, for the same reason explained above in the case of acrylate polymers.

As can be seen in Figure 7, HDDA started decomposing at 325 °C, in agreement with the results obtained for the mixtures of (meth)acrylate ionic liquid monomers and HDDA.

Thermal Stability of Polymers Obtained with Difunctional Ionic Liquid Methacrylates

Thermal stability was also checked for (2-methacrylate)ethyl dimethylammonium methacrylate and tri(ethylene glycol) dimethacrylate as the analog. As can be seen in Figure 8(a), the ionic liquid dimethacrylate showed two decomposition temperatures for both bulk and frontally-polymerized samples. The first temperature is ~160 °C, which corresponds to the decomposition of the poly(methacrylate ammonium) moiety, and the second one is around 325 °C, which corresponds to the poly(methacrylate) formed. Because the ammonium group contains a methacrylate group in one of the alkyl chains, no mass loss occurred at 20 °C as in the case of mono(meth)acrylate ionic liquid polymers (see Scheme 4). This fact demonstrated that both methacrylates groups present in the ionic liquid polymerized.

The polymer prepared with the traditional methacrylate ester, tri(ethylene glycol) dimethacrylate, is more thermally stable than the dimethacrylate ionic liquid polymer. The ionic liquid polymer started decomposing at 160 °C [Fig. 8(a)] but the dimethacrylate ester polymers started decomposing at around 220 °C.

The conversions for the methacrylate in the cation are 78 and 84%, and the conversions for the anion methacrylate are 86 and 98% for the frontally and in bulk polymerized samples, respectively.

In general, polymers from (meth)acrylate ionic liquid either monofunctional or difunctional monomers, exhibited thermal lower stability because of the trialkylammonium moiety; however, this

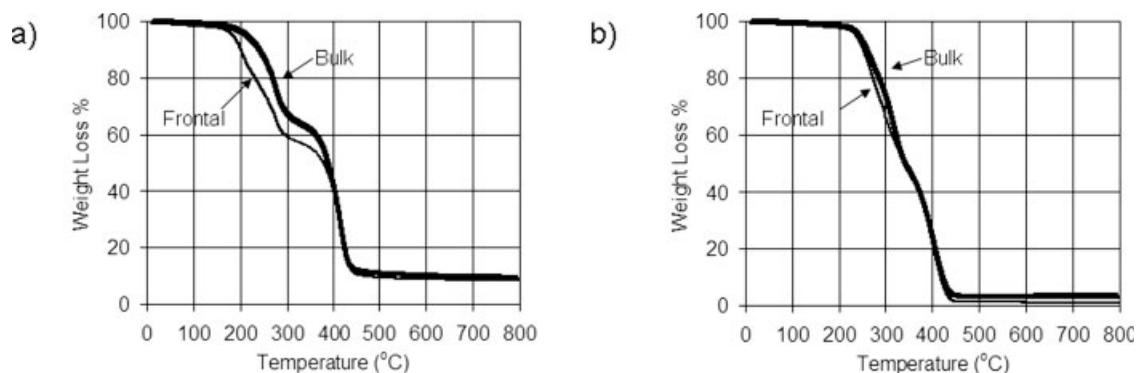
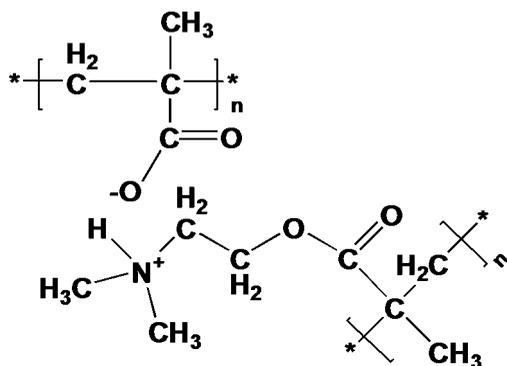


Figure 8. TGA curves for dimethacrylate polymers prepared by bulk and frontal polymerization. a) (2-methacrylate)ethyl dimethylammonium methacrylate and b) tri(ethylene glycol) dimethacrylate.



Scheme 4. Structure of poly[(2-methacrylate)ethyl dimethylammonium methacrylate].

stability was improved by having a polymerizable group in the cation. The short time that frontal polymerization needs to achieve the conversion of the monomer into polymer, is an advantage when using this type of ionic liquids because the amine does not have enough time to evaporate as in the case of bulk polymerization.

CONCLUSIONS

For the first time we studied the free-radical frontal polymerization of ionic liquid monomers. We prepared the monomers from the neutralization reaction between trialkyl amines and acrylic or methacrylic acid. In some cases, an acrylate was present on one of the alkyl chains in the amine to produce a difunctional monomer. Because of the high molecular weight, the monofunctional (meth)acrylate monomers could not support frontal polymerization alone. However, if another reactive and lower molecular weight monomer was added, frontal polymerization could be achieved. On the other hand, difunctional ionic liquid (meth)acrylate monomers represent a great prospect for frontal polymerizable systems thanks to their ability to support the front without extra additives.

Poly[ionic liquid (meth)acrylates] showed less thermal stability than traditional (meth)acrylate esters; however, the difunctional ionic liquid monomers were more stable due to the covalent bond of the ammonium moiety to the polymer chain. Significant differences in conversion, depending on the polymerization method used. The methacrylate ionic liquid lost some of the trialkyl ammonia during bulk polymerization

through dissociation and evaporation, which did not occur with frontal polymerization because of its greater rapidity.

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