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Frédéric Boschet, Georges Kostov, B. Ameduri, Yoshida Toru, Kosuke Kawada. Kinetics of the Radical Copolymerization of 2,2,2-Trifluoroethylmethacrylate with tert-Butyl-a-trifluoromethacrylate. *Journal of Polymer Science Part A: Polymer Chemistry*, 2010, 48, pp.1029-1037. 10.1002/pola.23857 . hal-00447595

**HAL Id: hal-00447595**

**<https://hal.science/hal-00447595>**

Submitted on 18 Jan 2010

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**Kinetics of the Radical Copolymerization of 2,2,2-Trifluoroethyl methacrylate with *tert*-Butyl  $\alpha$ -trifluoromethacrylate.**

Frédéric Boschet<sup>1</sup>, Georgi Kostov<sup>1,2</sup>, Bruno Ameduri<sup>1</sup>, Toru Yoshida<sup>3</sup>, Kosuke Kawada<sup>3</sup>

<sup>1</sup> *Institut Charles Gerhardt, Ingénierie et Architectures Macromoléculaires,  
UMR CNRS 5253, Ecole Nationale Supérieure de Chimie de Montpellier,  
8 Rue de l'Ecole Normale, 34296 Montpellier, France*

<sup>2</sup> *University Prof. Dr. Assen Zlatarov,  
Department of Organic Chemical Technologies,  
1, Prof. Yakimov blvd,  
8010 Bourgas, Bulgaria*

<sup>3</sup> *TOSOH F-Tech, Inc.  
4988, Kaisei, Yamuguchi Shunan, 746-0006 Japan*

*Presented at the 19<sup>th</sup> International Symposium on Fluorine Chemistry, Jackson Hole,  
Wyoming, USA, August 23-28<sup>th</sup> 2009*

# Kinetics of the Radical Copolymerization of 2,2,2-Trifluoroethyl methacrylate with *tert*-Butyl $\alpha$ -trifluoromethacrylate.

Frédéric Boschet<sup>1</sup>, Georgi Kostov<sup>1,2</sup>, Bruno Ameduri<sup>1</sup>, Toru Yoshida<sup>2</sup>, Kosuke Kawada<sup>2</sup>

<sup>1</sup> *Institut Charles Gerhardt, Ingénierie et Architectures Macromoléculaires,  
UMR CNRS 5253, Ecole Nationale Supérieure de Chimie de Montpellier,  
8 Rue de l'Ecole Normale, 34296 Montpellier, France*

<sup>2</sup> *University Prof. Dr. Assen Zlatarov,  
Department of Organic Chemical Technologies,  
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8010 Bourgas, Bulgaria*

<sup>3</sup> *TOSOH F-Tech, Inc.  
4988, Kaisei, Yamuguchi Shunan, 746-0006 Japan*

## ABSTRACT

The radical copolymerization of two different methacrylate monomers, 2,2,2-trifluoroethyl methacrylate (TFEMA) and *tert*-butyl  $\alpha$ -trifluoromethacrylate (TBTFMA) in solution was investigated. The resulting statistic poly(TFEMA-*co*-TBTFMA) copolymers were characterized by NMR spectroscopy to assess their compositions. The kinetics of copolymerization enabled one to determine the reactivity ratios of both

comonomers according to the methods of Fineman-Ross, Kelen-Tüdös, Extended Kelen-Tüdös. Excellent correlations were found between these methods leading to the following reactivity ratios:  $r_{\text{TFEMA}} = 4.87 \pm 1.50$  and  $r_{\text{TBTFMA}} = 0.10 \pm 0.02$  at 74 °C. These values indicated that the structure of the copolymers were composed of poly(TFEMA) micro-blocks separated by one TBTFMA unit. Both yields and molecular weights (ranging between 1,000 and 12,000 g.mol<sup>-1</sup>) increased with the TFEMA content. The thermal stability of these (co)polymers showed that the decomposition temperature at 10 % weight loss increased both with TFEMA content and increasing molecular weights of the poly(TFEMA-*co*-TBTFMA) copolymers.

## KEYWORDS

Radical copolymerization, kinetics, 2,2,2-trifluoroethyl methacrylate, *tert*-butyl  $\alpha$ -trifluoromethacrylate, reactivity ratio, thermal properties

## 1 INTRODUCTION

Fluorine-containing vinyl polymers generally possess a unique combination of thermal and chemical stability, lack of solubility and high hydrophobicity and oleophobicity, which led to special applications.<sup>1,2</sup> They are synthesized by radical (co)polymerization of fluorinated monomers. Among them,  $\alpha$ -trifluoro(meth)acrylates can be prepared from various strategies,<sup>3-5</sup> and are not as often used as conventional fluoroolefins such as tetrafluoroethylene (TFE), vinylidene fluoride (VDF), or chlorotrifluoroethylene (CTFE). However, these functional monomers are very important comonomers for the development of a new family of fluorine-containing polymers for Hi-Tech applications.

$\alpha$ -Trifluoromethacrylic acid (TFMAA) and *tert*-butyl  $\alpha$ -trifluoromethacrylate (TBTFMA), for example, are monomers that drew a lot of interest in the area of lithographic resist materials where partially fluorinated materials are considered to be among the best materials due to the high transparency of the C-F bond in the 157 nm range and higher wavelengths.<sup>6-12</sup> Their other applications include molecularly imprinted polymers (MIPs)<sup>13-16</sup>, adsorbants for solid phase extraction<sup>14,17</sup>, materials for optics<sup>18-21</sup>, dielectric materials<sup>22</sup>, the preparation of polymer electrolyte membranes for fuel cells (PEMFC)<sup>23</sup>, or photocrosslinkable material (mainly polyacrylate containing TFEMA units) with good surface properties for coatings.<sup>24,25</sup> More surprising is their use in stone protecting coatings for the preservation of monuments, especially in Italy due to the photochemical stability of poly(TFEMA-*co*-BVE) copolymers (where BVE stands for butyl vinyl ether)<sup>26-30</sup>. The photochemical stability is improved by the presence of the trifluoromethyl group preventing from cyclization reactions (leading to  $\gamma$ -lactone).

2,2,2-Trifluoroethyl methacrylate (TFEMA) is usually synthesized from 2,2,2-trifluoroethanol as described in a Chinese patent.<sup>5</sup>  $\alpha$ -Trifluoromethylacrylic acid derivatives  $\text{H}_2\text{C}=\text{C}(\text{CF}_3)\text{COR}$  ( $\text{R}=\text{OH}, \text{NEt}_2, \text{OEt}$ ) are prepared by reaction of  $\text{H}_2\text{C}=\text{CXCF}_3$  ( $\text{X}=\text{halogen}$ ) with ROH and CO in the presence of catalysts<sup>3</sup> such as  $\text{PdCl}_2(\text{PPh}_3)_2$ .<sup>31</sup> *Tert*-butyl  $\alpha$ -trifluoromethacrylate (TBTFMA also called MATRIFE) can be used for the preparation of norbornene derivatives by reaction with 1,4-pentadiene as described by Hanzawa et al.<sup>32</sup>, leading to thermally stable copolymers.

The synthesis and characteristics of *tert*-butyl  $\alpha$ -trifluoromethacrylate (TBTFMA), their uses as functional materials was briefly reviewed in 2004 by Tokuhisa.<sup>4</sup>

TBTFMA is known not to homopolymerize under conventional radical conditions initiation (in the presence of 2,2'-azobisisobutyronitrile (AIBN) or dibenzoylperoxide).<sup>33,34</sup> Researchers at IBM have also found that methyl-trifluoromethylacrylate does not homopolymerize<sup>13</sup> with radical initiators. However, Ito et al.<sup>12</sup> indicated that  $\alpha$ -trifluoromethacrylic acid (TFMAA) and *tert*-butyl- $\alpha$ -trifluoromethylacrylate (TBTFMA) monomers, both electron-deficient monomers, can undergo radical copolymerization with electron rich monomers such as norbornenes<sup>9</sup>, vinyl ethers<sup>8,28,33,35</sup>, styrene derivatives, or  $\alpha$ -olefins<sup>33</sup>, and can lead to alternating structures. TBTFMA was also copolymerized with various monomers including 4-(1,1,1,3,3,3-hexafluoro-2-hydroxypropyl)styrene<sup>10</sup>, methacrylonitrile<sup>7</sup>, monomers containing polyhedral oligomeric silsesquioxane (POSS)<sup>11</sup>.

Recently, the radical copolymerization of TBTFMA with 2,2,2-trifluoroethyl- $\alpha$ -fluoroacrylate (FATRIFE) initiated by *tert*-butyl-2,2-dimethylperoxypropanoate was investigated in acetonitrile for optical applications.<sup>36</sup> The reactivity ratios were determined by Kelen-Tudos method ( $r_{\text{FATRIFE}} = 1.71 \pm 0.01$  and  $r_{\text{TBTFMA}} = 0$  at 74 °C) leading to random copolymers.

The radical copolymerizations of  $\alpha$ -trifluoromethacrylic acid (TFMAA) with VDF, initiated by *tert*-butyl-2,2-dimethylperoxypropanoate were investigated in solution<sup>37</sup> or in emulsion<sup>38,39</sup> as well as using iodine transfer polymerization.<sup>38-40</sup> The reactivity ratios were assessed  $r_{\text{VDF}} = 0.33 \pm 0.09$  and  $r_{\text{TFMAA}} = 0$  in solution<sup>37</sup> and  $r_{\text{VDF}} = 1.6$  and  $r_{\text{TFMAA}} = 0$  in emulsion<sup>39</sup> at 55 °C. Then, the radical terpolymerization of TFMAA with VDF and HFP was reported and the thermal properties of the produced materials were discussed.<sup>37</sup>

In contrast to those above investigations concerning the radical copolymerization of  $\alpha$ -trifluoromethacrylates, only a few reports on ionic polymerization are available.<sup>41,42</sup> For example, TBTFMA and TFMAA have been successfully homopolymerized by anionic polymerization.<sup>43,44</sup> Typical anionic initiators for methyl methacrylate (MMA) polymerizations gave rise to complications such as attack on the trifluoromethyl moiety. The  $e$ -value obtained for  $\alpha$ -trifluoromethylacrylates suggested that its radical polymerization was difficult, though anionic polymerization might be preferable. Successful research results have been reported as the anionic polymerization of these monomers takes place by the initiators of relatively low basicity such as alkali metal *tert*-butoxides, organozincic compounds, organoaluminums, potassium salts with 18-crown-6 and pyridine derivatives.<sup>44</sup>

Fluoro- and fluoroalkyl-substituents induce a very high electron-withdrawing inductive effect, hence decreasing the electron density of the vinyl group, and thus increasing its reactivity towards carbanions. To clarify the effect of the trifluoromethyl group on the reactivity of vinyl group, the polymerization of  $\alpha$ -trifluoromethacrylates has been intensively examined during the last fifteen years. So far, it was claimed that the polymerization of  $\alpha$ -trifluoromethyl-substituted vinyl monomers was impossible under moderate radical and was successfully achieved under anionic polymerization conditions.<sup>41,42,44</sup>

2,2,2-Trifluoroethyl methacrylate (TFEMA) is a more reactive monomer, and can be copolymerized with a wide range of comonomers such as vinyl ethers<sup>28</sup>, *N*-vinylpyrrolidone<sup>45</sup>, methyl methacrylate<sup>21,45,46</sup>, methyl acrylate<sup>29</sup>, *n*-butyl methacrylate<sup>47</sup>, methacrylonitrile<sup>22</sup>, acrylonitrile<sup>22</sup>, methyl vinylidene cyanide<sup>22</sup>, styrene<sup>48</sup>. In contrast to

TBTFMA, TFEMA can be easily homopolymerized by radical processes.<sup>24,48,49</sup> It was also used in grafting polymerization onto poly(methyl methacrylate).<sup>46</sup>

However, to the best of our knowledge, the radical copolymerization of TFEMA with TBTFMA has never been reported. Hence, the objective of the present paper concerns the radical copolymerization in solution of both fluorinated methacrylate monomers, where the CF<sub>3</sub> group is located either on the vinylic carbon atom or in the ester group (TBTFMA and TFEMA, respectively). In addition, the kinetics of this radical copolymerization, the characterization by NMR spectroscopy of the resulting poly(TBTFMA-*co*-TFEMA) copolymers, and their thermostability were also evaluated and related to the composition.

## 2 EXPERIMENTAL SECTION

### 2.1 Materials

All reagents were used as received unless stated otherwise.

*tert*-Butyl  $\alpha$ -trifluoromethacrylate (TBTFMA), and 2,2,2-trifluoroethyl methacrylate (TFEMA) were kindly supplied by Tosoh F-Tech, Inc. (Japan). *tert*-Butylperoxyvalate (or *tert*-butyl-2,2-dimethylperoxypropanoate) in solution of isododecane (Trigonox® 25-C75, tBuOOC(O)tBu, TBPPI) (purity 75%) and di-*tert*-butyl peroxide (Trigonox® B, DTBP) (purity 99%) were gifts from Akzo Nobel (Chalons sur Marne, France). Acetonitrile (Chromasolv Grade) and calcium hydride were purchased from Sigma-Aldrich (Saint Quentin-Fallavier, France). Acetonitrile was distilled over calcium hydride prior to use. Deuterated acetone was purchased from Euroiso-top (Grenoble, France) (purity >99.8%).



## **2.2 Synthesis**

The radical copolymerizations were performed in Carrius tubes. In a typical copolymerization, the different reagents were inserted into the tube. They were then degassed by at least 4 thaw-freeze cycles, and sealed under dynamic vacuum. The tubes were then inserted in a custom design apparatus that heats and shakes the tubes at the same time at the desired temperature. The reaction was carried out for 14 hrs at constant temperature (74 °C). After cooling, the tubes were opened, and the mixture removed and rotavaped to isolate the polymer. The polymer was further dried under high vacuum until constant weight. The product was then weighed to assess the yield and characterized by the usual techniques as explained below.

## **2.3 Characterizations.**

**Nuclear Magnetic Resonance** (NMR) spectra were recorded on Bruker AC 400 instruments, using deuterated acetone, as solvent and tetramethylsilane (TMS) (or  $\text{CFCl}_3$ ) as the references for  $^1\text{H}$  (or  $^{19}\text{F}$ ) nuclei. Coupling constants and chemical shifts are given in hertz (Hz) and part per million (ppm), respectively. The experimental conditions for recording  $^1\text{H}$  (or  $^{19}\text{F}$ ) NMR spectra were as follows: flip angle  $90^\circ$  (or  $30^\circ$ ), acquisition time 4.5 s (or 0.7 s), pulse delay 2 s (or 2 s), number of scans 128 (or 1024), and a pulse width of  $5\mu\text{s}$  for  $^{19}\text{F}$  NMR.

**Size Exclusion Chromatography** (SEC) measurements were conducted using a GPC 50 from Polymer Labs (Now Varian) with its corresponding software (Cirrus). The system

used 2 columns PL Gel Mixed C ( $200 < M_w < 20,000,000$  g/mol) with THF as the eluent with a flow rate of 1.0 mL/min at room temperature. Both RI and UV detectors can be used. Polystyrene standards were used for the calibration.

**Thermogravimetric analyses** (TGA) were performed with a TGA/SDTA 851 thermobalance from Mettler DAL 75965 and Lauda RC6 CS cryostat apparatus, under air, at the heating rate of  $5\text{ }^\circ\text{C}\cdot\text{min}^{-1}$  from room temperature up to  $580\text{ }^\circ\text{C}$ .

**Differential scanning calorimetry** (DSC) measurements were conducted using a TA 2920 analyzer from TA Instruments DA 73085, a RCS DA cooler, and Sartorius MC5 weighing machine. Scans were recorded at a heating rate of  $20\text{ }^\circ\text{C}\cdot\text{min}^{-1}$  from  $-100$  to  $+100\text{ }^\circ\text{C}$ , and the cooling rate was  $20\text{ }^\circ\text{C}\cdot\text{min}^{-1}$ . A second scan was required for the assessment of the glass transition temperature ( $T_g$ ), defined as the inflection point in the heat capacity jump.

### **3 RESULTS AND DISCUSSION**

Several (co)polymers were synthesized according to the procedure described in the experimental section (Scheme 1). The radical copolymerizations were carried out in acetonitrile, and initiated by *tert*-butylperoxypivalate (TBPPi) at  $74\text{ }^\circ\text{C}$ . That temperature corresponds to a half-life of 1.0 hr for that initiator. The reaction time of 14 hrs enabled us to ensure the complete decomposition of the initiator. The copolymerizations were designed to cover the whole range of composition including also the synthesis of both

homopolymers. After reaction and purification, the copolymers were dried and characterized by NMR, SEC, DSC, and TGA. The results are displayed in Table 1.

### **Insert Scheme 1**

### **Insert Table 1**

$^{19}\text{F}$  and  $^1\text{H}$  NMR spectra enabled us to determine the composition of these resulting poly(TFEMA-*co*-TBTFMA) copolymers but it was not possible to determine absolute molecular weights this way due to the lack of standards. Indeed, only molar ratios between both comonomers could be assessed.

All  $^1\text{H}$  NMR spectra (**Figure 1**) show some signals specific to both comonomers. Methylene of ester group ( $-\text{O}-\text{CH}_2-\text{CF}_3$ ) of the TFEMA led to a signal centered at 4.6 ppm. The methyl group of TFEMA ( $-\text{CH}_3$ ) showed two singlets at 1.0 and 1.15 ppm while the *tert*-butyl group of TBTFMA signal is centered at 1.5 ppm. Two peaks can be seen for the methyl group of TFEMA where only one could be expected. It was attributed to reverse addition of the TFEMA (head to head or tail to tail) rather than TBTFMA-TFEMA dyads due to the fact that both peaks are visible also on the TFEMA homopolymer. In fact, if it was a peak assigned to the end chain or TBTFMA-TFEMA dyad, it could be argued that only one type of methyl group should be present in the spectrum of TFEMA homopolymer (or at least the second one would be negligible). The methylene groups from the backbone (from both TFEMA and TBTFMA units) were overlapping in a multiplet ranging between 2.0 and 2.2 ppm. It was not possible to use

this latter signal due to the presence of the signal assigned to the solvent (deuterated acetone) centered at 2.05 ppm, overlapping with the signals from the methylenes of the backbone. It was then chosen to use the signal of the ester methylene protons (-O-CH<sub>2</sub>-CF<sub>3</sub>, 4.6 ppm) and that of *tert*-butyl (-C-(CH<sub>3</sub>)<sub>3</sub>, 1.5 ppm), from TFEMA and TBTFMA, respectively, for the assessment of the copolymer composition (equation 1). Residual peaks from impurities (including unreacted TFEMA monomer) can also be observed between 2.7 and 3.0 ppm in several spectra.

$$F_{TFEMA} (^1\text{H NMR}) = \frac{\int_{4.6 \text{ ppm}} (-O-CH_2-CF_3)}{2} \bigg/ \left( \frac{\int_{4.6 \text{ ppm}} (-O-CH_2-CF_3)}{2} + \frac{\int_{1.5 \text{ ppm}} (-C(CH_3)_3)}{9} \right) \quad (1)$$

### **Insert Figure 1**

Acetonitrile is commonly used as the solvent for radical (co)polymerization and our experience in the lab demonstrates that there is no transfer for the polymerization of methacrylates.<sup>50</sup> In case of transfer to acetonitrile, several byproducts can be expected as indicated in Scheme 2.

### **Insert Scheme 2**

Hence, <sup>1</sup>H NMR spectrum should display either a triplet of quartets for the methyne (normal addition) (with a different coupling constants if X=H (<sup>3</sup>J<sub>HF</sub> = ca 7Hz) or X=F

( $^3J_{HF} = \text{ca } 15\text{Hz}$ ) or a singlet at about 0.5-1.5 ppm for the methyl group in the case of reverse addition. When the generated radical  $\bullet\text{CH}_2\text{CN}$  reacts onto TFEMA or TBTFMA leading to  $\text{NCCH}_2\text{CH}_2\text{C}(\text{CX}_3, \text{CO}_2\text{R})\bullet$ , the  $^1\text{H}$  NMR spectrum should exhibit two triplets assigned to methylenes at about 1.5 ppm.

Figure 1 shows all spectra which do not display any of these signals assigned to transfer reactions to acetonitrile (except for 100% TFEMA where a small signal is noted at 0.9 ppm). These statements confirm that no transfer to acetonitrile occurred.

$\text{CO}_2\text{CH}_2\text{CF}_3$  may induce a transfer but we still note whatever the feed content of TFEMA in the copolymerization reaction (Figure 1), the same multiplet centered at 4.6 ppm assigned to  $\text{CO}_2\text{CH}_2\text{CF}_3$  which seems stable. Methyl groups in the tBu are regarded as stable in the conditions used in the present manuscript.

All  $^{19}\text{F}$  NMR spectra (**Figure 2**) only show signals assigned to both perfluoromethyl groups of TFEMA and TBTFMA, centered in -73 to -75 ppm and -63 to -70 ppm zones, respectively. The integrals of both signals enabled us to assess the composition of the copolymers via equation (2).

$$F_{TFEMA} (^{19}\text{F NMR}) = \frac{\int_{-74 \text{ ppm}} (-O-CH_2-CF_3)}{3} \bigg/ \left( \frac{\int_{-74 \text{ ppm}} (-O-CH_2-CF_3)}{3} + \frac{\int_{-68 \text{ ppm}} (-CF_3)}{3} \right) \quad (2)$$

The results on the assessment of the molar ratio of both comonomers in the copolymer are listed in Table 1. These values are in good agreement with the copolymer compositions assessed by  $^1\text{H}$  NMR (**Table 1**). The singlet at -66 ppm is characteristic of

unreacted TBTFMA monomer. A small peak centered at -74.5 ppm was also noted, attributed to a different arrangement of the TFEMA units (dyad, triad) since this peak is prominent only when TBTFMA is present.

### **Insert Figure 2**

The molecular weights and polydispersity indices of the poly(TBTFMA-*co*-TFEMA) copolymers were assessed by size exclusion chromatography. The results (Table 1) showed that the molecular weight increased with the TFEMA content (from 1,000 to 11,700 g.mol<sup>-1</sup>). Regarding the polydispersity, only the homopolymer of TBTFMA showed a lower value (1.20), that could be related to the low molecular weight of this oligomer (1,000 g.mol<sup>-1</sup>). In a similar manner, and as expected, the yield increased with the TFEMA content since TBTFMA does not homopolymerize by conventional radical conditions.<sup>33,34,51</sup> As TFEMA is regarded as more reactive than TBTFMA, it is expected that the yield and molecular weight should increase with TFEMA content as commonly observed for the radical copolymerization of VDF and HFP, TFE and PMVE, VDF and PMVE.<sup>1,2</sup> In addition, the incorporation of TFEMA in the copolymer is anticipated to be higher than that of the feed composition. Results in Table 1 confirmed that assumption.

### **Insert Table 1**

The homopolymerizaion of TBTFMA was unexpected. As indicated in the introduction, several attempts have been made without any success, either with AIBN, dibenzoyl

peroxide or other initiator. The synthesis of an oligomer of poly(TBTFMA) can arise from the peculiarity that TBPPi generates various radicals such as:  $t\text{BuO}^\bullet$ ,  $t\text{BuCO}_2^\bullet$ , that further decomposes into  $t\text{Bu}^\bullet$  and  $\text{CO}_2$ . It is then suggested that at least one of these radicals is very efficient for initiating the polymerization of the  $\alpha$ -trifluoromethacrylate though the propagation remains to be explained.

The compositions of the poly(TBTFMA-co-TFEMA) copolymers were assessed from both  $^1\text{H}$  and  $^{19}\text{F}$  NMR spectra as indicated above. Figure 3 shows the composition diagram, i.e. the copolymer composition of these copolymers vs. the feed composition. The diagram clearly shows that TFEMA is more reactive than TBTFMA. This is expected as the  $\text{CF}_3$  substituent of TBTFMA has a more electron-withdrawing behavior than the  $\text{CH}_3$  of TFEMA which makes the double bond of TBTFMA less reactive towards radical polymerization. In addition, it is known that fluoromethacrylates are less reactive than methacrylates.<sup>51</sup>

### **Insert Figure 3**

From these data presented in **Figure 3**, the models of Fineman-Ross,<sup>52</sup> Kelen-Tüdös,<sup>53</sup> and Extended Kelen- Tüdös.<sup>54-56</sup> were applied to assess the reactivity ratios of TFEMA and TBTFMA. Explanations are given in the supporting information, and the results are displayed in Table 2. The reactivity ratio of TBTFMA being close to zero shows that this monomer does not propagate, and confirms previous works.<sup>33,34,51</sup>

### **Insert Table 2**

Several values of reactivity ratios of alkyl  $\alpha$ -trifluoromethacrylates from the literature<sup>57,58</sup> are gathered in Table 3. It can be noted that TFEMA has a similar reactivity than methacrylonitrile (MAN) but a much higher reactivity than 2,2,2-trifluoroethyl  $\alpha$ -fluoroacrylate (FATRIFE) towards TBTFMA.<sup>36</sup> It can also be noted that most alkyl  $\alpha$ -trifluoromethacrylates have a reactivity ratio of 0, which evidence that most of them do not homopolymerize under radical conditions. Narita<sup>59</sup> showed that TFEMA, involved in the radical copolymerization with styrene, has a similar reactivity as that of styrene, an improvement compared to methyl  $\alpha$ -trifluoromethacrylate. Very low values of  $r_M$  and  $r_{AFMA}$  (when M is styrene, chloromethylstyrene, vinyl ether (FAVE), or vinylidene fluoride in solution) indicate that alkyl  $\alpha$ -trifluoromethacrylates have a tendency to yield alternating copolymers though it is not observed in the present case.

### **Insert Table 3**

$Q$  and  $e$  are intrinsic parameters of a monomer linked to the resonance and to the polarity, respectively.<sup>60</sup> From the reactivity ratios values, it is possible to assess the  $Q$  and  $e$  values for the comonomers, according to the following equations developed by Alfrey and Price:<sup>61</sup>

$$r_{TFEMA} = \frac{Q_{TFEMA}}{Q_{TBTFMA}} \exp \left[ -e_{TFEMA} (e_{TFEMA} - e_{TBTFMA}) \right] \quad (3)$$

$$r_{TBTFMA} = \frac{Q_{TBTFMA}}{Q_{TFEMA}} \exp \left[ -e_{TBTFMA} (e_{TBTFMA} - e_{TFEMA}) \right] \quad (4)$$



Knowing the  $Q$  and  $e$  values for TFEMA (1.13 and 0.98, respectively)<sup>59</sup>, it is possible to solve these equations, and their values for TBTFMA were calculated:  $Q = 0.53$  and  $e = 1.81$ . Some values are given in Table 4 for reference.<sup>35,59,62-66</sup> The high  $e$  value indicates a very electron-attractive monomer, i.e. an electron poor double bond due to the strong electron-withdrawing inductive effect from the trifluoromethyl group. This suggests that TBTFMA is a potentially interesting monomer for anionic polymerization as reported by Narita et al.<sup>59</sup> This clearly demonstrates that the trifluoromethyl group in alpha-position to the double bond stabilizes the radical by captodative effect, and thus prevents its polymerization which is evidenced by a lower reactivity ratio compared to TFEMA (0.10 and 4.87, respectively). In contrast, the macroradical bearing a TFEMA endgroup is not stabilized by captodative effect, and thus can polymerize.

#### **Insert Table 4**

The thermal stability of these poly(TBTFMA-*co*-TFEMA) copolymers was investigated by thermogravimetric analyses (TGA) under air. The thermogram presented in **Figure 4** shows the evolution of the thermostability of the poly(TBTFMA-*co*-TFEMA) copolymers with the composition (from 0 to 100 %). For copolymers rich in TFEMA, the corresponding thermograms present one plateau that is observed above 270 °C, while copolymers rich in TBTFMA, two plateaus are usually observed (at 150 and 240 °C). It is well-known, as indicated in several studies,<sup>7,9,10,35,67</sup> that in copolymers containing TBTFMA heated above 160 °C, the *tert*-butyl ester group decomposes into a carboxylic acid group and releases isobutene, which can explain the first plateau. It could be argued

that the second plateau results from the decomposition of the other ester group (trifluoroethyl from TFEMA). In addition, a progressive weight loss between 50 and 160 °C can be observed, and was more pronounced as the TBTFMA content increases. This was attributed not to a degradation process but to the vaporization of low molecular weights copolymers. As TBTFMA fraction increases, the molecular weights of the copolymers decrease, and this phenomenon has been enhanced. However, further analyses by coupling the TGA with another detector for the analysis of decomposition gases should be performed to confirm the nature of the degradation products.

#### **Insert Figure 4**

From the TGA thermograms (**Figure 4**), the decomposition temperature corresponding to 10 % weight loss was assessed. **Figure 5** shows the evolution of that  $T_{d,10\%}$  value versus the copolymer composition. It can be noted that the decomposition temperature evolves almost proportionally with the TFEMA composition. This was correlated with the observation that the molecular weight (see Table 1) increased with the amount of TFEMA. As expected, for low molecular weights, fluorinated compounds have a high volatility, and lead to weight loss by evaporation rather than thermal decomposition.

#### **Insert Figure 5**

## 4 CONCLUSION

The radical copolymerization of two different fluorinated methacrylates bearing a trifluoromethyl group either on the ethylenic carbon atom or in  $\beta$ -position of the ester group is challenging due to their comparative reactivities, and deserved to be investigated. Hence, the kinetics of radical copolymerization of TFEMA with TBTFMA enabled us to assess the reactivity ratios:  $r_{\text{TFEMA}}=4.87 \pm 1.50$  and  $r_{\text{TBTFMA}}=0.10 \pm 0.02$  at 74 °C. The reactivity ratios were determined from three different methods and the values were in good agreement. These results showed that the hydrogenated methacrylate was more reactive than the  $\alpha$ -trifluoromethacrylate monomer. However, statistic copolymers could be produced. It was also found that both molecular weights and decomposition temperatures (at 10 % weight loss) increased with increasing TFEMA contents as this monomer has a higher reactivity than that of TBTFMA. In addition, the introduction of TBTFMA units allows also to decrease the refractive index for applications such as optical fiber core. Aqueous processes of polymerization (suspension and emulsion) are under investigation to increase the molecular weights and the thermostability of these copolymers. Chemical changes can be anticipated from the  $\text{CO}_2\text{tBu}$  into  $\text{COOH}$  to open a way to functionalized poly(TFEMA) or to poly(TFEMA)-*g*-poly(M) graft copolymers, under investigation.

## 5 SUPPORTING INFORMATION AVAILABLE

Calculations and figures for the determination of reactivity ratios are given. This material is available free of charge via the Internet at [www.interscience.wiley.com](http://www.interscience.wiley.com).

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## SCHEME CAPTIONS

Scheme 1: Radical copolymerization of 2,2,2-trifluoroethyl methacrylate (TFEMA) and *tert*-butyl  $\alpha$ -trifluoromethacrylate (TBTFMA) initiated by *tert*-butylperoxypivalate (TBPPi) in acetonitrile at 74 °C.

Scheme 2: Possible chain transfer reaction with acetonitrile and generated byproducts.

## TABLE CAPTIONS

Table 1. Results of the radical (co)polymerizations between 2,2,2-trifluoroethyl methacrylate (TFEMA) and tert-butyl  $\alpha$ -trifluoromethacrylate (TBTFMA) initiated by tert-butylperoxypivalate at 74 °C for 14 hrs.

Table 2. Reactivity ratios of 2,2,2-trifluoroethyl methacrylate (TFEMA) and tert-butyl  $\alpha$ -trifluoromethacrylate (TBTFMA) computed by the different models.

Table 3. Reactivity ratios of alkyl  $\alpha$ -trifluoromethacrylates (ATFMA) or  $\alpha$ -trifluoromethacrylic acid and comonomer M from the kinetics of the radical copolymerization of ATFMA with M (VDF, TFE, MMA, CMS, FAVE8, MAN, FATRIFE, TFEMA stand for vinylidene fluoride, tetrafluoroethylene, methyl methacrylate, chloromethylstyrene, 1H,1H,2H,2H-perfluorodecyl vinyl ether, methacrylonitrile, 2,2,2-trifluoroethyl  $\alpha$ -fluoroacrylate, 2,2,2-trifluoroethyl methacrylate, respectively)

Table 4. Selected  $Q$  and  $e$  values for different fluoroacrylates.

## FIGURE CAPTIONS

Figure 1.  $^1\text{H}$  NMR spectra of the different poly(TBTFMA-co-TFEMA) copolymers as function of the fraction of TFEMA in the copolymers ( $F_1$ ) recorded in acetone  $d_6$  at room temperature from the crude product.

Figure 2.  $^{19}\text{F}$  NMR spectra of the different poly(TBTFMA-co-TFEMA) copolymers as function of the fraction of TFEMA in the copolymers ( $F_1$ ) recorded in acetone  $d_6$  at room temperature from the crude product.

Figure 3. Copolymer-monomer copolymerization curve for the radical copolymerization of TFEMA with TBTFMA (initiated by TBPPi at 74 °C. The diagram includes the experimental data (diamonds) and the different calculation fits from the Fineman-Ross (full line), Kelen-Tüdös (dashed line), and extended Kelen-Tüdös (dotted line) models.

Figure 4. TGA thermograms of poly(TFEMA-co-TBTFMA) copolymers under air at 10 °C.min<sup>-1</sup>, and where (x %) represents the percentage of TFEMA in the copolymer.

Figure 5. Evolution of the decomposition temperature at 10 wt.% loss versus the copolymer composition ( $F_1$ ) in TFEMA.

## Graphical Abstract

The radical copolymerization and homopolymerization of 2,2,2-trifluoroethyl methacrylate (TFEMA) and tert-butyl  $\alpha$ -trifluoromethacrylate (TBTFMA) in solution was investigated. The resulting statistic poly(TFEMA-*co*-TBTFMA) copolymers were characterized by NMR spectroscopy to assess their compositions. Reactivity ratios were assessed ( $r_{\text{TFEMA}} = 4.87 \pm 1.50$  and  $r_{\text{TBTFMA}} = 0.10 \pm 0.02$  at 74 °C) indicating the higher reactivity of methacrylate compared to  $\alpha$ -trifluoromethacrylate. Both yields, molecular weights and thermostability increased with the TFEMA content.

