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# Control of free-radical polymerization of 2,2,2-trifluoroethyl methacrylate (TEMA) by a substituted fluorinated tetraphenylethane-type INITER

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**Abstract**

This paper deals with the free radical polymerization of 2,2,2-trifluoroethyl methacrylate (TEMA) initiated by a substituted fluorinated tetraphenylethane-type INITER.

The synthesis of a new fluorinated substituted tetraphenylethane is described. This initiator, prepared from benzophenone and 3,3,3-(trifluoropropyl)chlorodimethylsilane behaves as an INITER when used to polymerize TEMA. In the first period of polymerization, telechelic oligomers are formed. They were isolated from the mixture and their structure was characterized by $^1$H-NMR spectroscopy. By thermal cleavage at the bonds between the last monomer unit and the end groups from the initiator, these telechelic oligomers are effective initiators of further free-radical polymerization of ethylenic monomers, yielding block copolymers besides the respective homopolymer. Thus, in a second step, styrene was introduced into poly(TEMA) to produce block copolymers with a macroinitiator efficiency close to 85%. © 2001 Elsevier Science B.V. All rights reserved.

*Keywords:* Polymerization; Fluorinated tetraphenylethanes; INITER; 2,2,2-Trifluoroethyl methacrylate; Telechelic oligomers; Copolymerization

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## 1. Introduction

The most common form for initiator of radical polymerization is a compound which acts as a thermal source of radicals. Such initiators are able to form free-radicals either by thermal decomposition or by activation via a redox mechanism. Both organic peroxides (oxygen–oxygen bond cleavage) and azo compounds (carbon–nitrogen bond cleavage) are potentially useful. However, there are also less common compounds containing a carbon–carbon bond capable of cleavage under heat action.

In contrast to hexaphenylethane, diaryl methyl radicals formed from tetraphenylethanes can initiate a radical polymerization. As they are strongly stabilized, they are also able, under certain conditions, to take part in a reversible coupling reaction on certain propagating radicals and to induce, thus, a certain control over the polymerization. Using tetraphenylethanes as "INITER" gives access first to the synthesis of telechelic oligomers, then, to block copolymers through insertion of a second monomer.

The use of such molecules as initiators has been mainly described by Bledzki and Braun [1–15]. Thus, and contrary to benzopinacol [16,17], when compounds of the type 1,1,2,2-tetraphenyl-1,2-dicyanoethane ($NC–CPh_2–CPh_2–CN$, TPCE) or 1,1,2,2-tetraphenyl-1,2-diphenoxyethane ($Ph–O–CPh_2–CPh_2–O–Ph$, TPPE) are used in the polymerization of α-substituted monomers (methyl methacrylate, butyl methacrylate, methacrylic acid, etc.), telechelic oligomers are obtained. Under certain polymerization conditions (temperature, etc.), the chain ends, constituted by the last monomer unit and the primary radical formed from the initiator, may split up into new radicals able to re-initiate a further polymerization. But it should be mentioned that the degree of polymerization of these oligomers is rather small and therefore, blocks from these oligomers are relatively short compared to the second block which is produced by normal polymerization of the second monomer. The same authors [1] have also demonstrated that, in the case of MMA polymerization in the presence of TPPE, the oligomers which are formed may be used as macroinitiators in the radical MMA polymerization or also as initiators in unsaturated polyester resins [18]. Numerous systems have been

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studied. Let us mention the copolymer prepared from benzyl methacrylate oligomers and styrene [6] or also the copolymer obtained from *tert*-butyl methacrylate oligomers and styrene [19]. A possible application for these oligomers consists in their chemical modification into methacrylic acid oligomers [19,20].

This system may then be used for the preparation of block copolymers where one block is amphiphilic (methacrylic polyacid-b-PS copolymer). Moreover, for special purposes it may be interesting to use polymers with thermosensitive C–C bonds, e.g. for the investigation of the fragmentation processes of polymer chains in solution or even in bulk [21].

More recently, De Léon-Sàenz et al. [22] have briefly described the MMA polymerization initiated by 1,1,2,2-tetraphenyl-1,2-bis(trimethylsiloxy)ethane (TPSE). In agreement with the previous works performed, they observed that the oligomers obtained at the beginning of the polymerization were able to initiate a further polymerization. Also, from such oligomers with $\overline{\text{Mn}} = 7000\,\text{g/mole}$ they prepared a PMMA–PS block copolymer with $\overline{\text{Mn}} = 44000\,\text{g/mole}$.

In 2000, the mechanism of chain growth in TPSE-induced free radical polymerization of MMA and styrene was again investigated by the same authors [23]. In the case of MMA, the diphenylmethyl radicals generated by TPSE are found to reversibly combine with the growing PMMA radicals. In the case of styrene, the mechanism appears to be more complex: chain growth seems to involve a degenerative transfer.

But, although several substituted tetraphenylethanes were synthesized, no fluorinated homologue has been prepared previously. Furthermore, the polymerization of a fluorinated monomer with a tetraphenylethane-type-compound has never been studied. Hence, our purpose is to study the polymerization of the 2,2,2-trifluoroethyl methacrylate (TEMA) initiated by a fluorinated tetraphenylethane-type INITER ($CF_3BP$).

First, the synthesis of this new initiator is detailed and the polymerization mechanism is described. Then a block polymerization system $CF_3BP$–TEMA precursor/styrene is studied.

## 2. Experimental

### 2.1. General comments

Benzophenone (99%), magnesium (turnings, 98%), tetramethylurea (TMU, 99%) were purchased from Aldrich and were used without further purification. Tetrahydrofuran (THF) was distilled over sodium and stored under an inert atmosphere.

3,3,3-(Trifluoropropyl)chlorodimethylsilane (99%, FLUOROCHEM) was distilled and stored under an inert atmosphere prior to use. TEMA (99%, ELF ATOCHEM) was freshly distilled and stored at low temperature before use.

### 2.2. $CF_3BP$ synthesis

An amount of 1.2 g (0.05 ml) of magnesium turnings were placed in a 100 ml three-necked flask, equipped with a condenser with a nitrogen inlet, a dropping funnel and a septum, 50 ml of freshly distilled THF were added. Then, 18.2 g (0.1 mol.) of benzophenone dissolved in 20 ml of THF were added through the dropping funnel followed by 19.15 g (0.1 mol) of 3,3,3-(trifluoropropyl)chlorodimethylsilane and finally 5 ml of TMU were added by a syringe through the septum. The reaction mixture rapidly changed from colorless to yellow, then to purple and finally to green.

The green solution obtained was cooled and stirred at room temperature for 14 h. The solvent was evaporated under reduced pressure and 50 ml of chloroform were added. The solution was filtered to eliminate magnesium salts and then chloroform was evaporated. A yellow colored wax was obtained. The final product can be crystallized easily after adding a small amount of absolute ethanol or hexane.

15.4 g of a fine white powder were obtained ($M = 676$ g/mole; yield 46%).

- $^1$H-NMR (DMSO-d$^6$): $\delta = -0.1$ ppm [s, 6H, $-Si(CH_3)_2$]; 0.6 ppm [m, 2H, $-CH_2-Si$]; 1.9 ppm [m, 2H, $-CH_2-CF_3$]; 7 ppm [m, 10H, aromatic protons].
- $^{19}$F-NMR ($CDCl_3$): $\delta = -74$ ppm [s, 3F, $-CF_3$].

| | C | H |
|---|---|---|
| Theoretical (%) | 63.90 | 5.92 |
| Expected (%) | 63.65 | 5.95 |

### 2.3. Polymerization of the TEMA (general example)

A degassed solution of 1 g of $CF_3BP$, 10 g of TEMA and 20 g of toluene introduced in a 50 ml two-necked flask equipped with a magnetic stirrer, a condenser related to a nitrogen inlet, and a septum, was stirred at 100°C for 2 h. After cooling, the solution was precipitated in a large volume of methanol. The filtrate was evaporated under reduced pressure then dried under high vacuum until the mass remained constant.

### 2.4. Copolymerization

The same procedure was used for the synthesis of block copolymer but in this case, the reaction mixture was composed of $CF_3BP$–TEMA macroinitiator described above and styrene. The copolymerization was carried out at 100°C for 6 h. Cyclohexane was used to extract polystyrene from the block copolymer.

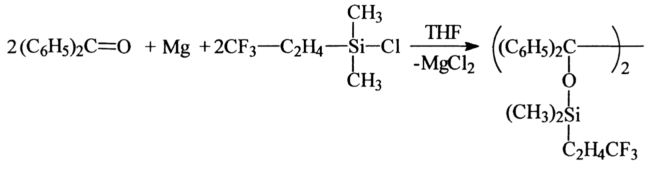
### 2.5. Characterizations

The initiators were characterized by $^1$H- and $^{19}$F-NMR spectroscopy. The letters s and m designate singlet and multiplet, respectively. The conversion of monomer into polymer was determined by $^1$H-NMR. The different spectra were registered at room temperature on a AC 200 BRUKER apparatus, using $CDCl_3$ and DMSO-d$^6$ as solvents. The number average molecular weights for the oligomers and the polymers were measured by size exclusion chromatography (SEC). Chromatograms were recorded on a spectra-physics apparatus equipped with a SP 8850 pump, a shodex RE-61R1 differential refractometer, a SpectroMonitor 3100 (UV detector) and "phenogel" columns ($10^5$, $10^4$, $10^3$, 500 Å) thermostated at 30°C. THF was used as the eluent and the flow rate was 0.8 ml/min. The calibration was performed with PMMA standard samples except for the copolymer TEMA–styrene (styrene standard samples used).

## 3. Results and discussion

### 3.1. Synthesis of the initiator *1*

1,1,2,2-Tetraphenyl-1,2-(dimethyl-3,3,3-trifluoropropylsiloxy)ethane ($CF_3BP$) 1 was prepared from benzophenone, magnesium and 3,3,3-(trifluoropropyl)chlorodimethylsilane according to the method briefly described in 1968 by Calas et al. [24] and detailed more recently by Crivello et al. [25].



$$2(C_6H_5)_2C{=}O + Mg + 2CF_3{-}C_2H_4{-}Si(CH_3)_2{-}Cl \xrightarrow[-MgCl_2]{THF} \left((C_6H_5)_2C(O{-}Si(CH_3)_2{-}C_2H_4CF_3){-}\right)_2$$

1

The $^1$H-spectrum of the initiator is given in Fig. 1.

The kinetics of dissociation of $CF_3BP$ have not been studied. Nevertheless, in 1986, Crivello et al. [25] showed that decomposition of these initiators is highly activated by the nature of the hindering substituent. Those bis(silyl pinacolates) derived from benzophenone show appreciable dissociation to their respective ketyl radicals even at 30yC. For example, TPSE has a rate constant for dissociation of $104x10^{-6}\ s^{-1}$ at 40°C. Thus, we considered that $CF_3BP$ is totally and immediately decomposed at 100°C.

### 3.2. Polymerization of the TEMA

An example of TEMA polymerization in the presence of $CF_3BP$ at 100°C is given in Fig. 2. The conversion of monomer into polymer was followed by $^1$H-NMR.

As could be expected, the curve of conversion versus time is quite similar to that of the classical system MMA–TPSE [6] where two successive steps occur.

1. During the first, named "oligomerization" step, telechelic oligomers were formed. This formation is due to the relatively high concentration of primary radicals which were present in the medium, formed from the initiator.

   In this step, only a very small fraction of the monomer — the monomer conversion did not exceed 1% — was involved in this reaction. So, the conversion rate remained low and only short oligomers were produced (Scheme 1).

   Indeed, the initiation being slow and the primary radicals being strongly stabilized by mesomerism, numerous free radicals play the role of counter-radicals, leaving very few opportunities to the chain to grow.

   The duration of this step, which always occurs, is directly proportional to the initial concentration in initiator $[CF_3BP]_0$ as shown in Fig. 2.
2. During the second step, after most of the radicals have been consumed, the conversion rate increases rapidly. This increase is mainly due to the decomposition of the chain ends. Due to the low concentration of radicals in the medium, the probability for a reversible coupling between them and the growing chain becomes lower and the trend to recombine two propagating species appears.

   All the radicals ($^\bullet CF_2OSi(Me)_2(C_2H_4CF_3)$) formed from the chain ends cleavage may recombine with a propagating species and at the same time generate a new "dormant" species but they are also able to initiate new polymer chains.

   Moreover, this last reaction is responsible of the falling off of the polymerization controlled character as De Léon-Sàenz et al. have explained [22]. Actually if the radicals are irreversibly consumed, they progressively lose their role of counter-radicals propagating species.

   Thus, the probability for the two growing species to recombine increases significantly. This recombination reaction is expressed by a curve $\log([M_0]/[M])$ versus time which is no longer linear as previously observed for the first step.

### 3.3. Telechelic oligomers synthesis

In order to isolate the oligomers at low conversion rate, a fractionated precipitation was performed in absolute ethanol from the crude reaction mixture at $[CF_3BP]_0 = 0.0586$ M. The $^1$H-NMR spectrum of the filtrate is given in Fig. 3.

In this spectrum, we can observe a good correlation between the integrals of $Si(CH_3)_2$ groups (0.65 for 6H) and these of the aromatic protons (1 for 10H).

Indeed, from the $^1$H-NMR spectrum of the filtrate, if one considers that all these oligomers are telechelic, by comparison of the integral of the multiplet at −0.20 ppm corresponding to the methyl groups in the α position to the silicon atoms ($I$ proportional to 12H) and the multiplet at 4.5 ppm corresponding to the methyl groups in the α position to the ester function ($P$ proportional to 2H), we can calculate the molecular weight by NMR according to relations (1)

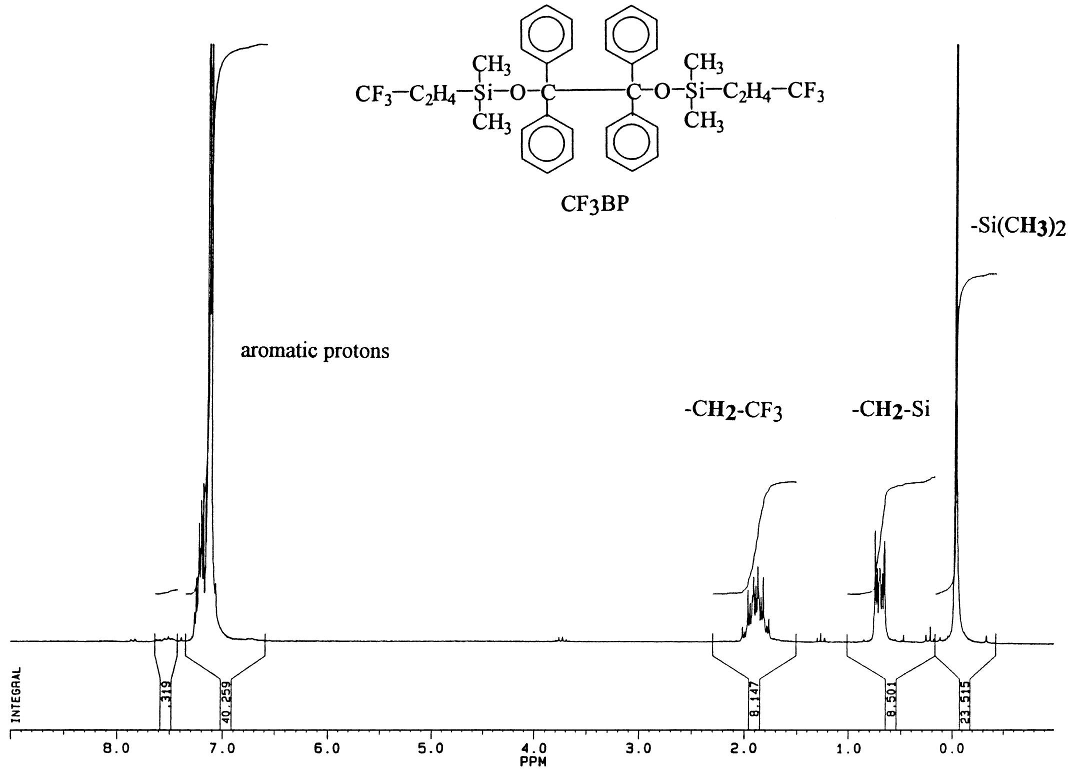


Fig. 1. $^1$H-NMR (DMSO-d$^6$) spectrum of CF$_3$BP initiator.

and (2):

$$\overline{\mathrm{Mn}}(^1\mathrm{H}-\mathrm{NMR}) = [168 \times (\overline{\mathrm{DPn}})_{\mathrm{cum.}}] + \text{weight of the extremities} \qquad (1)$$

$$\overline{\mathrm{DPn}} = \frac{P/2}{I/12} \qquad (2)$$

that is, $\overline{\mathrm{Mn}}\,(^1\mathrm{H}-\mathrm{NMR}) = [168 \times 104] + 676 = 18148$ g/mole.

### 3.4. Block polymerization system

In order to confirm in a chemical way that the oligomers are telechelic and are able to re-initiate a further polymerization to yield block copolymers, a block polymerization of the CF$_3$BP–TEMA precursor previously described ($\overline{\mathrm{Mn}} = 18\,000$ g/mole) was performed with styrene at 100°C for 6 h.

Generally, the oligomers obtained with substituted tetraphenylethanes are effective macroinitiators of free-radical polymerization [6,19,20].

Block copolymers can be easily prepared by adding a monomer and optionally a solvent to the macroinitiator and heating the mixture at a temperature sufficient to achieve a thermal cleavage of the chain ends constituted by the last monomer unit and the primary radical coming from CF$_3$BP.

However, the major drawback of these systems is the presence, in addition to the copolymer, of the homopolymer

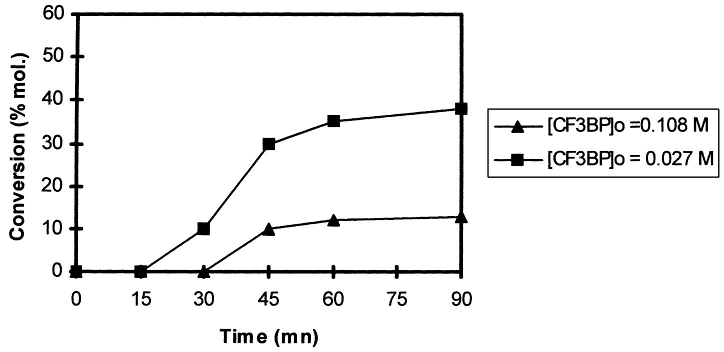
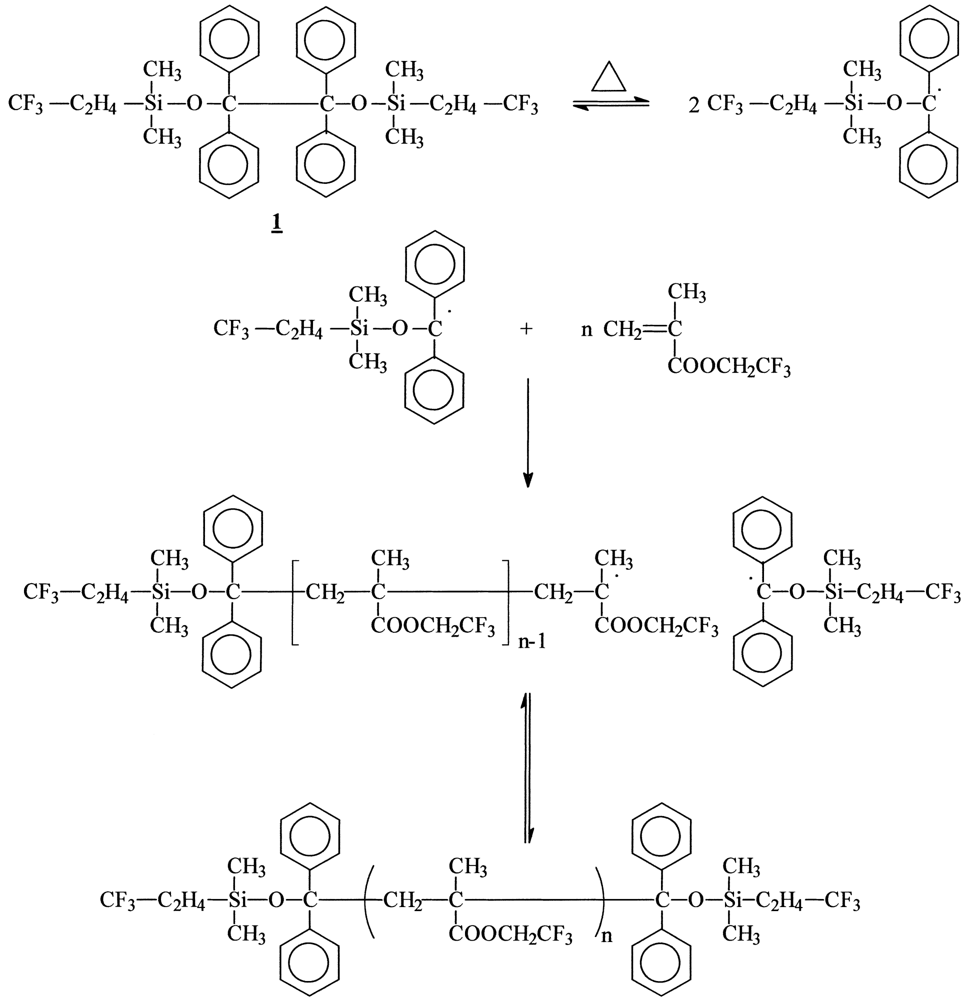


Fig. 2. Kinetic behavior plot for the polymerization in solution of TEMA initiated by CF$_3$BP at 100°C and at different initial concentrations ([TEMA]$_0$ = 1.9 M).



Scheme 1. Polymerization mechanism of 2,2,2-trifluoroethyl methacrylate with $CF_3BP$.

from the second monomer. The formation of this homopolymer corresponding to the second block is expected because the primary radicals released by homolytic cleavage from poly(TEMA) chain extremities are able to initiate polymerization, beside their ability to combine with the growing macroradicals.

In this paper, we chose to limit our investigation to a monomer that undergoes primary termination only by radical coupling, such as styrene. Scheme 2 supplies a representation of the block copolymerization with $CF_3BP$–TEMA macroinitiator and shows the different species which can exist with the block copolymer.

During the thermolysis, the macroinitiator is fragmented to give essentially macroradical species which either can undergo termination by disproportionation (II, III) or combination (IV) to lead to inert homopoly(TEMA) or which can react with styrene to initiate block copolymerization.

Depending on the mode of termination of the growing radical chains and the ability of the primary radicals to play the role of counter-radicals, A–B block copolymers and A–B–A triblock copolymers may be produced.

Indeed, the possibility of generating chain ends that are not functionalized by $CF_3BP$ fragments cannot be ruled out because bimolecular termination does occur to a non-negligible extent.

Moreover, it is worthwhile to consider the energetic states of the reactions described in Scheme 2. First, after thermal decomposition of the macroinitiator, a high energy is required to cause the addition of the stabilized primary radicals to the monomer M. On the other hand, reaction of these persistent radicals with the growing chains $M^\bullet$ is very fast, requiring little activation energy. Considerably more energy is thus, required to cause fragmentation of the M–I bonds to regenerate the original fragments.

In the case of styrene, this bond between the last monomer unit and the primary radical from the initiator is stable at classical temperatures. These species do not undergo further fragmentation.

Consideration of these energies led to the suggestion that the species $I\text{-}(M)_{2n}\text{-}I$ and $I\text{-}(M)_n\text{-}I$ exist in the mixture.

So, according to Scheme 2, three different species can coexist in the crude mixture: the inert homopoly(TEMA),

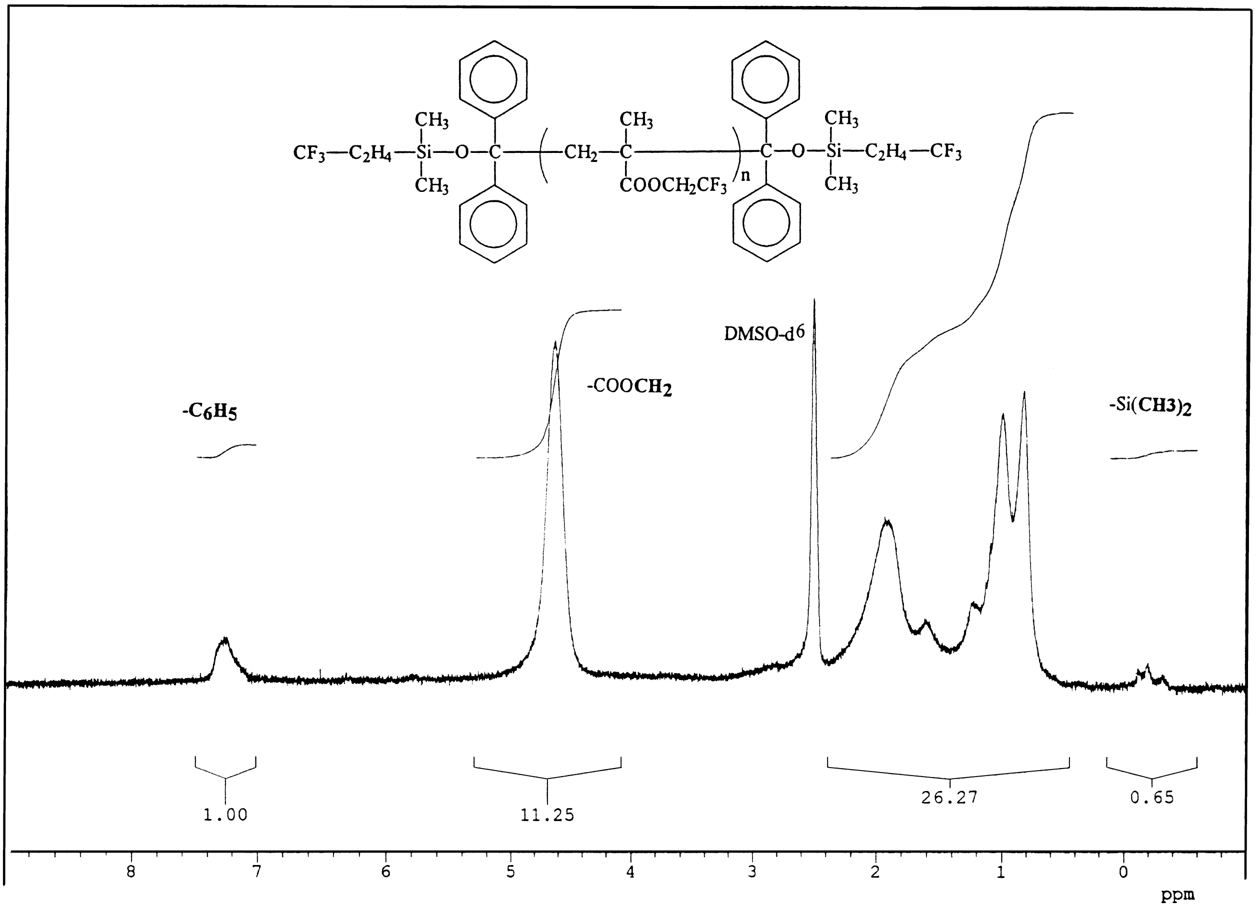
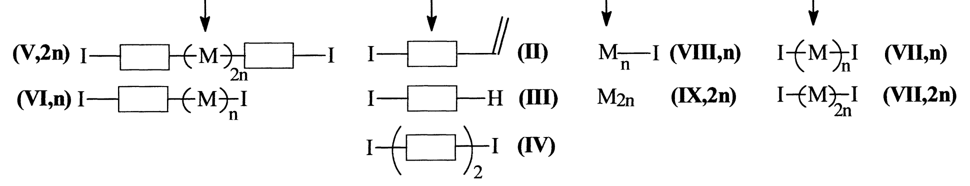


Fig. 3. $^1$H-NMR (DMSO-d$^6$) spectrum of trifluoroethyl methacrylate oligomers ($[CF_3BP]_0 = 0.0586$ M; $T = 100$°C).

the homopolystyrene (thermal and initiated by the primary radicals issued from the chain extremities) and the copolymer (block and triblock copolymers).

In order to separate the homopolystyrene from the methacrylic polymers (dead homopoly(TEMA) and the copolymer), we have attempted to fractionate the mixture using cyclohexane at 40°C.

Polystyrene is soluble in cyclohexane (at temperature above 35°C), a good solvent for styrenic polymers but not for methacrylic polymers. In this case, we have supposed



Scheme 2. Schematic representation of the copolymerization of $CF_3BP$–TEMA macroinitiator with styrene. (I) $CF_3BP$–TEMA macroinitiator; (II, III) $CF_3BP$–TEMA macroinitiator which undergoes termination by disproportionation; (IV) $CF_3BP$–TEMA macroinitiator which undergoes termination by radical coupling (for methacrylic monomers, these species can be neglected); (V, 2n): A–B–A triblock copolymers; (VI, n) A–B block copolymers; (VII, n) PS telechelic oligomers; (VII, 2n): PS initiated by $CF_3BP$ radicals which undergoes bimolecular termination; (VIII, n): polymerization of thermal PS controlled by $CF_3BP$ radicals; (IX, 2n): thermal PS which undergoes termination by radical coupling.

Table 1
Synthesis of block copolymer from the radical polymerization of $CF_3BP$–TEMAprecursor in the presence of styrene ($T$ = 100°C, 6 h)

| Amount of styrene (g) | Amount of macroinitiator (g) | Macroinitiator $\overline{Mn}$ (g/mole) | Raw product composition (%) |  | Block copolymer $\overline{Mn}$ (g/mole) (SEC) |
|---|---|---|---|---|---|
|  |  |  | Home PS (filtrate) | Block copolymer (precipitated) |  |
| 10 | 1 | 18148 | 25 | 75 | 56400 |
| 5 | 1 | 18148 | 32 | 68 | 30500 |

that both the copolymers were not soluble in cyclohexane. Under these same conditions, the macroinitiator was insoluble. Also, in the $^1$H-NMR spectrum of the filtrate, we can only observe homopolystyrene with traces of $Si(CH_3)_3$ groups. The results are given in Table 1.

The SEC chromatograms of the $CF_3BP$–TEMA precursor and the purified block copolymer (18 000/56 000) are given in Fig. 4. The signal assigned to the precursor is shifted to lower elution volumes, evidencing the formation of a block copolymer. A copolymer of $\overline{Mn} = 56\,400\,g/mole$ was formed and no residual amount of precursor was detected.

However, as it is difficult to detect, by SEC, fluorinated polymers which have a refractive index similar to the eluent (THF), it may be possible that a low quantity of residual macroinitiator has not been detected. As a result, this quantity of dead homopoly(TEMA) has been neglected.

The same analytical technique was used with two different detectors. Beside the usual refractive index detector, a UV detector, set at 254 nm, was used to detect aromatic groups in the polystyrene blocks. The response of the block copolymer to these two detectors is identical, indicating that the copolymer has an homogeneous composition. We can conclude that the polymer is composed of covalently linked blocks of PS and poly(TEMA).

The percentage of the styrene in the block copolymer can be easily determined from $^1$H-NMR (Fig. 5) using the integrals of the multiplet situated at 4.3 ppm corresponding to the ester protons from the TEMA block and the multiplet at 6.2–7.2 ppm corresponding to the aromatic protons from the styrene block. This value is close to 87%.

By SEC, this percentage of styrene is about 70% (if we consider that the molecular weight of the styrene block is 40 000 g/mole). This value can be explained by the approximations made on the determination of the molecular weight by SEC (PMMA and PS standard samples were used for the calibration).

These experiments show that $CF_3BP$ is an efficient initiator to synthesize block copolymers, demonstrating that the first poly(TEMA) block was obtained in the conditions corresponding to a controlled process.

### 3.5. Determination of the macroinitiator efficiency

In all cases, we can calculate the macroinitiator efficiency ($f$) according to the relation (3):

$$f = \frac{\%\,\text{block copolymers}}{\%\,\text{block copolymers} + \Delta} \tag{3}$$

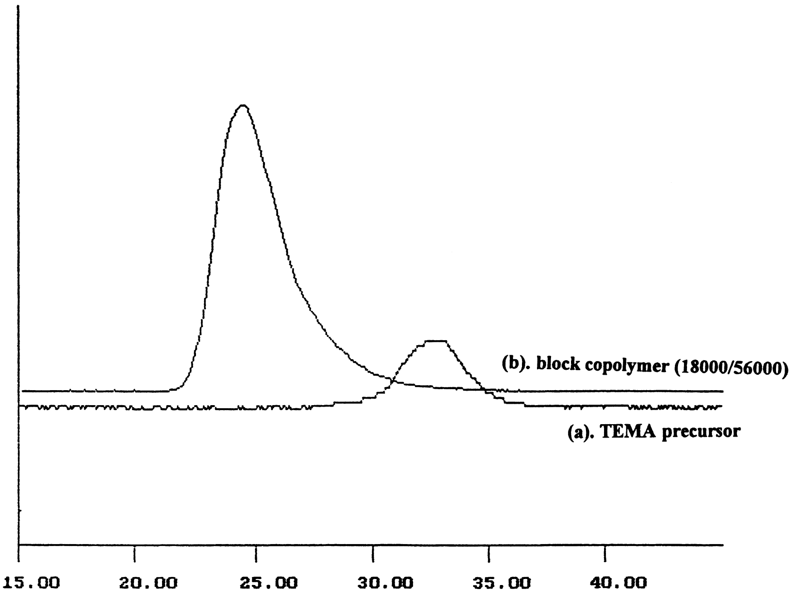


Fig. 4. Evolution of SEC curves during the block copolymerization: (a) TEMA precursor; (b) purified poly(TEMA)/polystyrene copolymers.

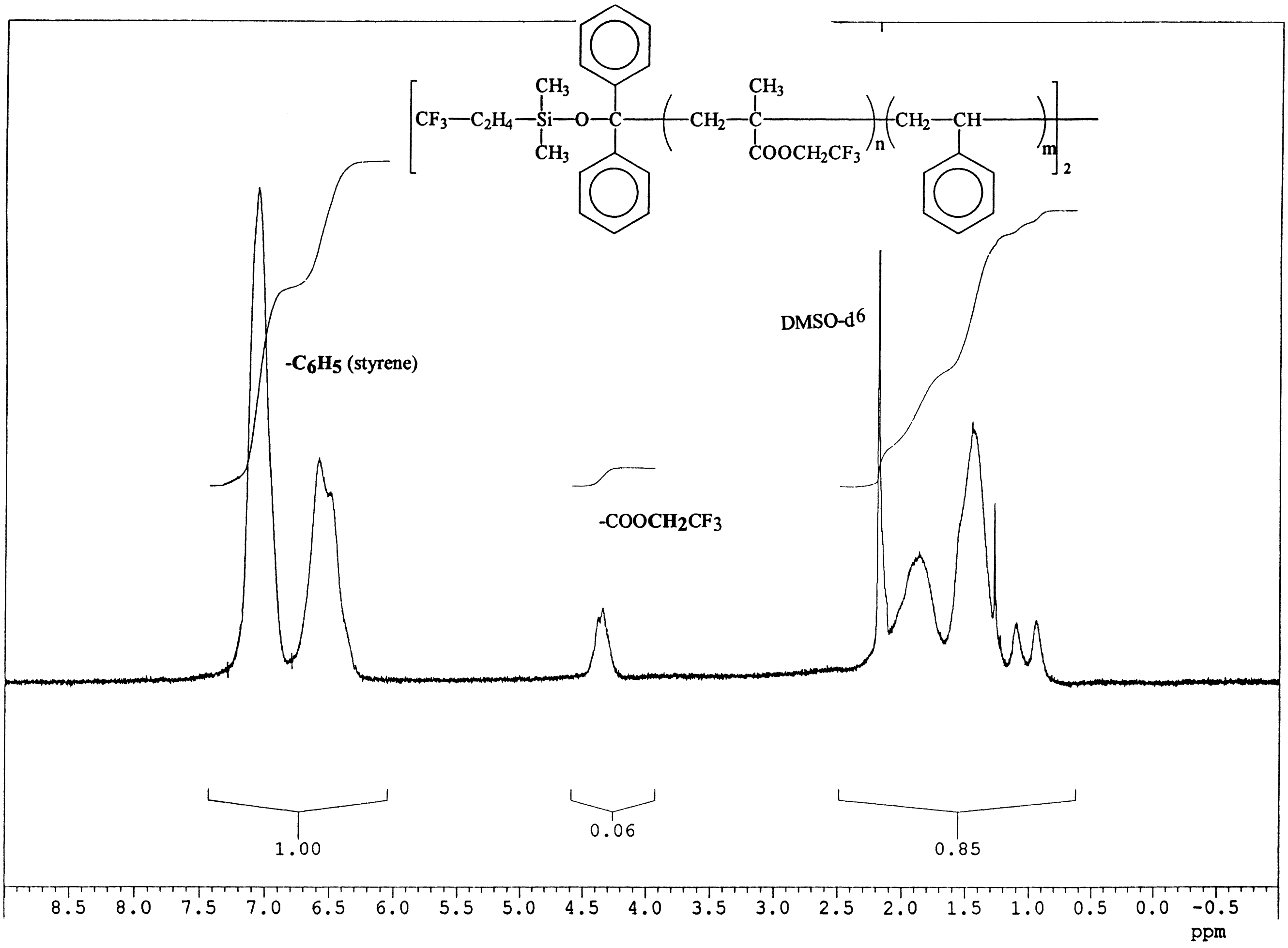
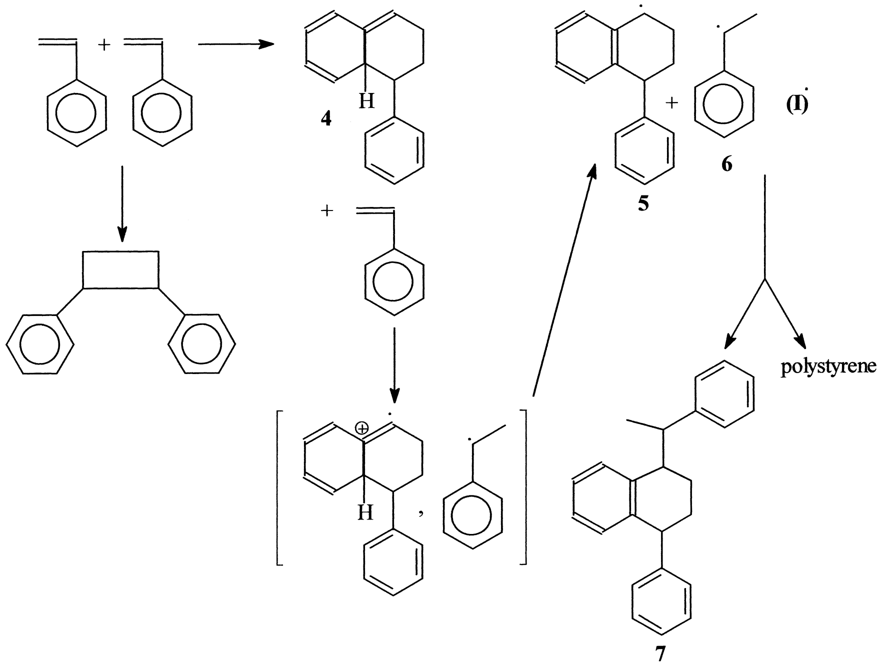


Fig. 5. $^1$H-NMR (DMSO-d$^6$) spectrum of the purified block copolymer.



Scheme 3. Mechanism of thermal autopolymerization of styrene in bulk.

where $\Delta$ = [% homopolystyrene obtained] − [% homopolystyrene thermally initiated (species (VIII, n) and (IX, 2n) on Scheme III-2)].

In fact, $\Delta$ represents the quantity of PS initiated by the primary radicals formed from the macroinitiator chain extremities (species (VII, n); (VII, 2n)).

However, in order to estimate the real quantity of thermal PS, it is necessary first to examine the autopolymerization mechanism of styrene previously described by Mayo [26] and Hamielec [27] (Scheme 3).

The reaction begins with a DIELS–ALDER cycloaddition between two styrene molecules to produce **4** which then undergoes a one electron transfer reaction with another styrene molecule to form after proton transfer the two benzylic radicals **5** and **6** noted ($I^{\bullet}$). Products **5** and **6** can combine to form **7** or add monomer to initiate polymerization.

This mechanism can be summarized as:

$$\text{monomer} + \text{monomer} \rightarrow Z^{+} \xrightarrow{\text{monomer}} \text{radicals (I)}$$

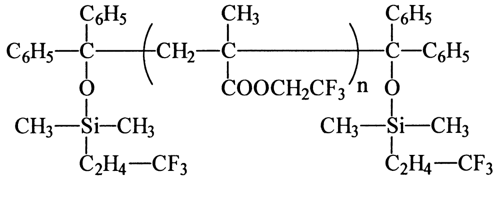
According to Hamielec [27], the rate of thermal autopolymerization of styrene at 100°C is close to 2%/h. Thus, for a reaction time of 6 h, we can write (copolymer 18 000/56 000):

$$f = \frac{75}{75 + \{25 - (6 \times 2)\}} = \frac{75}{88} = 0.85$$

This allows to conclude that at least 85% of the macroinitiator has initiated the polymerization of styrene.

## 4. Conclusion

1,1,2,2-Tetraphenyl-1,2-(dimethyl-3,3,3-trifluoropropylsiloxy)ethane was prepared from benzophenone and 3,3,3-(trifluoropropyl)chlorodimethylsilane in 46% yield. This new substituted fluorinated tetraphenylethane behaves as a thermal “INITER” when used to polymerize 2,2,2-trifluoromethacrylate. The polymerization with this initiator is characterized by two different stages; in the first period, telechelic oligomers from TEMA and primary radicals are formed by radical termination:



In the second step, these telechelic oligomers are effective initiators for a further free radical polymerization. After consumption of the primary radicals with increasing conversion, normal propagation occurs. Telechelic oligomers, isolated at low conversion, characterized by $^{1}$H-NMR, were used to re-initiate the polymerization of styrene, yielding block copolymers beside the homopolystyrene.

Fractionation of the crude copolymerization products in cyclohexane at 40°C allowed us to estimate the effective quantity of copolymers and homopolystyrene, thermal and initiated by the primary radicals. Thus, the efficiency of the 2,2,2-trifluoromethacrylate macroinitiator is close to 85%.

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