# Triorganosilyl methacrylates: kinetic studies of radical homopolymerization and radical copolymerization with methyl methacrylate

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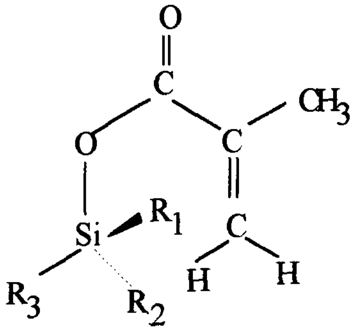
Various R silyl methacrylates (with R = t-butyl dimethyl (**1**), t-butyl diphenyl (**2**), and diphenyl methyl (**3**)) were copolymerized with methyl methacrylate (MMA) in bulk at 60°C, and the reactivity ratios were determined. In all cases, the electronegativity of silicon leads to $r_2$ having values which were less than one. The superimposition of this effect on the steric effect produces $r_1$ values which are also less than one. **1** was copolymerized with methyl acrylate (MA) under the same conditions. Despite the effect of the vinyl methyl group of **1**, $r_1$ is found to be equal to one in this case. This is confirmation of a steric effect in which both macroradical and monomer are sterically hindered. Homopolymerization reactions were carried out using methacrylates **1**, **2**, and **3** and triphenylsilyl methacrylate (**4**) in order to determine their kinetic constants, and also to examine the influence provided by the R substituents on the silicon. The following order of reactivity was revealed: **1**>**2**>**3**>**4**. This showed that the phenyl substituent de-activated the macroradical, an observation which correlated with the relative reduction in electronic density of the monomer double bond in this series of compounds.

**(Keywords: organosilyl methacrylates; copolymerization; kinetics)**

## INTRODUCTION

Up to the present time, the polymerization of triorganosilyl methacrylates has not been widely studied. Aylward[1] studied the radical polymerization of trimethylsilyl methacrylate, and in particular the stereoregularity of the chain of the macromolecule. Other studies have been conducted on the copolymerization of diorganosilyl bismethacrylate with various vinyl monomers. After specific hydrolysis of the silyl esters, the resulting copolymers consist of contiguous sequences of free acids[2].

In more recent years, these products have been patented in the development of new binders for anti-fouling paints[3,4]. Indeed, numerous studies in this field have been conducted within the last few years following the prohibition of organotin-polymer-based paints, which are now known to be a danger to the environment. In addition to their biocidal effect, a particularly valuable property of these tin-based binders is the slow erosion of successive layers of the coatings[5,6]. The type of binder which can be obtained from various triorganosilyl methacrylate monomers could have a wider spectrum of applications in addition to its use as an anti-fouling agent. If the kinetic characteristics obtained for the erosion of tin derivatives could be reproduced with silyl derivatives, then the non-toxicity of the group which is produced after hydrolysis of the latter suggests that they may be considered as a matrix for testing the leaching of active compounds[7]. This requires a homogenous series of compounds with similar behaviour profiles, from which a compound best suited for a particular use could subsequently be selected. In this work, a series of compounds with the following general structure were chosen:



where the various substituent groups are as shown in *Table 1*.

In a previous study[8], we have studied the copolymerization of t-butyl dimethylsilyl methacrylate (**1**) with methylmethacrylate (**0**) under various conditions. In this present study we have investigated the homopolymerization of these four monomers, which have been synthesized in our laboratory. The kinetic constants for these polymerization reactions were determined, and the comparative reactivities of the compounds were assessed. The influence of the silicon atom substituents on these parameters is also discussed.

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**Table 1** Triorganosilyl methacrylates studied in this work

| | **1** | **2** | **3** | **4** |
|---|---|---|---|---|
| $R_1$ | t-Bu | t-Bu | Me | $C_6H_5$ |
| $R_2$ | Me | $C_6H_5$ | $C_6H_5$ | $C_6H_5$ |
| $R_3$ | Me | $C_6H_5$ | $C_6H_5$ | $C_6H_5$ |

**Table 2** Initial compositions of the reaction medium

| Methacrylate system | $[\text{Monomer}]_0$ (M) | $[\text{AIBN}]_0$ (M) |
|---|---|---|
| **1** | 2.0 | 0.01 |
| **2** | 1.0 | 0.005 |
| **3** | 1.0 | 0.005 |
| **4** | 0.4 | 0.002 |

Following this, the copolymerization of monomers **1**, **2** and **3** with methyl methacrylate and of monomer **1** with methyl acrylate (**5**) was investigated. The values of the reactivity ratios were estimated and discussed in relationship to the structural changes that have taken place.

## KINETIC STUDY OF THE HOMOPOLYMERIZATIONS

### *Syntheses*

The syntheses of the four monomers described above were carried out by using a procedure that was developed in our laboratory. The physical constants and the i.r. and n.m.r. spectra of the products that were obtained correspond well with those previously reported[8].

### *Polymerizations*

The polymerization reactions were carried out in sealed tubes; these were degassed by three vacuum cycles after cooling in liquid nitrogen, and were then sealed under vacuum. The reactions were conducted in toluene at 60°C, and were initiated by azobisisobutyronitrile which had been recrystallized from ethanol.

As the molar masses of the monomers that were being studied were relatively high, the kinetic profiles were monitored by following the change with time in the residual concentration of the monomers by using size exclusion chromatography: the signal of the monomer was separated from that of the solvent at all times. A Waters 501 chromatogram was used for these experiments, with the instrument being equipped with a U410 differential refractometer and a set of different columns (100, 500 and 1000 Å). THF, at a flow rate of $1\,\text{ml min}^{-1}$, was used as the eluant. Retention times (in min) for the various monomers were as follows: **1** (28.2), **2** (27.5), **3** (28.0) and **4** (27.8).

### *Processing of the data*

A time limit was fixed for the duration of the homopolymerization reactions (i.e. a maximum of 5 h) with the initial concentrations (*Table 2*) being chosen such that the maximum level of conversion was obtained within this time. As the duration of the experiment was much shorter than the half-life of the initiator, its concentration did not vary by more than 10% and can thus be considered as being constant, therefore giving the classical expression for the relationship between the degree of conversion $X$ and the time $t$[9,10]:

$$-\ln(1-X)=\ln([\mathrm{M}]_0/[\mathrm{M}])=P_\mathrm{p}[\mathrm{I}]^{1/2}t \qquad (1)$$

where

$$X=([\mathrm{M}]_0-[\mathrm{M}])/[\mathrm{M}]_0$$

and

$$P_\mathrm{p}=k_\mathrm{p}(2fk_\mathrm{d}/k_\mathrm{t})^{1/2}$$

and in which $P_\mathrm{p}$ is the global polymerization rate constant, $k_\mathrm{d}$, $k_\mathrm{p}$, and $k_\mathrm{t}$ are the initiation, propagation and termination rate constants, respectively, and $f$ is the efficiency factor of the initiator.

## COPOLYMERIZATION STUDY

### *Experimental*

Copolymerizations were carried out in bulk in sealed tubes in accordance with the procedure described above for the homopolymerization reactions. Methyl methacrylate (MMA) or methyl acrylate (MA), were used as comonomers, with AIBN (at a concentration of 0.001 mol per mol of monomer) being used as the initiator.

The analysis of the composition of the copolymers was carried out as follows: the copolymers were dissolved in THF and then acidified to hydrolyse the silyl ester only. In the case of the copolymer containing monomer **2**, cold hydrolysis could only be achieved in an alkaline medium. The products were then precipitated in three times the volume of petroleum ether, and purified by a reprecipitation process. The conversion rate was determined gravimetrically. The compositions of the copolymers were determined by potentiometric titration of the free acid groups by using a Mettler memotitrator DL 21.

### *Processing of the data*

The conversion rates for all of the copolymerization reactions studied were restricted to 10%. Under these conditions, the experimentally determined composition can be considered unchanged since the initial time and can be related to the initial composition by means of the classical Mayo–Lewis equation[11], as modified by Fineman and Ross[12]:

$$G=Hr_1-r_2 \qquad (2)$$

with

$$G=\frac{F_1}{F_2}\left(\frac{f_1-f_2}{f_1}\right)$$

and

$$H=\frac{f_2}{f_1}\left(\frac{F_1}{F_2}\right)^2$$

and where $F_1$ and $F_2$ are the molar fractions of the monomers in the initial mixture, $f_1$ and $f_2$ are the molar fractions in the copolymer, and $r_1$ and $r_2$ are the reactivity ratios of the respective monomers.

If one plots $G$ *versus* $H$, $r_1$ is the slope and $r_2$ is the intercept. However, this method is not invariant for the permutation of indices. For example, permutation of the indices can lead to different results:

$$I=Jr_2-r_1 \qquad (3)$$

with

$$I=\frac{F_2}{F_1}\left(\frac{f_2-f_1}{f_2}\right)$$

and

$$J=\frac{f_1}{f_2}\left(\frac{F_2}{F_1}\right)^2$$

If one plots $I$ *versus* $J$, a new pair of reactivity ratios is found. This difference gives an idea of the experimental errors that may be encountered. However, when the compositions are within a restricted range, it is preferable to use the method of Kelen–Tüdos[13].

$$\eta=(r_1+r_2/\alpha)\xi-r_2/\alpha \qquad (4)$$

where $\eta$ and $\xi$ are functions of $f_1$ and $F_1$, as defined above. The parameter $\alpha$ is selected so that it gives a maximum amplitude to $\xi$. The equation of the composition in relationship to $r_1$ and $r_2$ is expressed as follows:

$$f_i=\frac{F_i^2(r_1-1)+F_i}{F_i^2(r_1+r_2-2)+2F_i(1-r_2)+r_2} \qquad (5)$$

with $i=1$ or 2.

## RESULTS AND DISCUSSION

### *Homopolymerizations*

As the solubility of **4** in toluene is much lower than that of the other monomers, it had to be maintained at a lower concentration than the other compounds: this causes greater doubt regarding the accuracy of the value of the global rate constant that was obtained.

*Figure 1* displays plots of $\ln([M]/[M]_0/([I]^{1/2})$ *versus* time for the four monomers. The relationship is linear for each of the reactions: this shows that monomer consumption is therefore a first-order reaction. The global polymerization rate constant, $P_p$, is determined from the slope of each of the straight lines (equation (1)). These values of $P_p$ are displayed in *Table 3*, which also shows the number of aromatic rings possessed by each monomer, in order to illustrate the relationship with this rate constant.

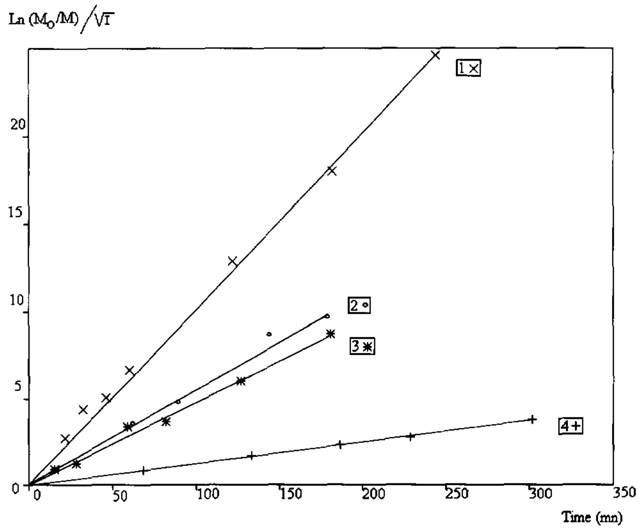

**Figure 1** Homopolymerization kinetics of the triorganosilyl methacrylates. Logarithm of the ratio of the mass (M) at a given time to the initial mass ($M_0$) of the monomer, divided by the square root of the initial concentration of the initiator (I) as a function of time: (×) **1**; (○) **2**; (✱) **3**; (+) **4**

**Table 3** Global homopolymerization rate constants of the monomers, showing the relationship with the number of aromatic rings of the silyl group

| Monomer | 4 | 3 | 2 | 1 |
|---|---|---|---|---|
| $P_p$ (x$10^4$ mol$^{-1/2}$ l$^{1/2}$ s$^{-1}$) | 2.0 | 8.0 | 9.3 | 17.0 |
| Number of $C_6H_5$ rings | 3 | 2 | 2 | 0 |

The decreasing order in the rate constants (i.e. 1, 2, 3, 4) can be correlated to the number of aromatic rings attached to the silicon atom. The presence of phenyl substituents tends, by an inductive effect, to cause two non-opposing effects: (a) de-activation of the growing macroradical and (b) a reduction in electronic density of the double bond, site of addition and consequently, reduction of the reactivity of the monomer. We assume that the termination rate constants are equal in this homogeneous series. In all cases, the conversion is low, hence the segmental diffusion is more likely to be the step which controls the termination process[14].

### *Copolymerization*

Only monomers **1**, **2** and **3** were used in the copolymerization reactions. A reaction involving monomer **4** could not be carried out on account of its marginal solubility in MMA (15%), which was too low for a kinetic study.

The polymers which are obtained are resinous and transparent. They are soluble in common solvents and are film forming. Following the specific hydrolysis of the silyl ester, the solubility changes rapidly with the relative composition. Intermediate compositions of ~50% give polymers which are soluble in only a very few solvents; this has already been observed for MMA–methacrylic acid copolymers in which the simultaneous presence of polar and non-polar groups renders them insoluble in most solvents[15]. For this reason, we have studied the two extremes of the composition range. In this case, the compounds are either markedly hydrophilic or hydrophobic in nature, which makes them soluble in solvents of one type or the other: the free acid functions can thus be assayed. The principal results obtained with the four series of compounds are displayed in *Table 4*.

The method of calculation has little effect on the reactivity ratios (*Table 5*). The values of $r_1$ and $r_2$ calculated by the method of Kelen–Tüdos are barely affected by changes in $\alpha$ in the region of its optimal value. Subsequently, given the small $F$ variation for certain series, we have used only these values. These given the composition curves (*Figure 2*) by using the composition relationship of equation (5).

To compare the reactivity ratios of **1** with respect to methyl methacrylate (**0**) and with respect to methyl acrylate (**5**), let us define these as follows:

$$r_{10}=\frac{k_{11}}{k_{10}} \quad \text{and} \quad r_{15}=\frac{k_{11}}{k_{15}}$$

which gives:

$$\frac{r_{10}}{r_{15}}=\frac{k_{15}}{k_{10}}$$

The experimental value of this ratio (0.66) illustrates the comparatively greater reactivity of macroradical **1** with respect to MMA than with respect to MA. This greater

**Table 4** Results obtained for the copolymerization of monomers **1**, **2** and **3** with methyl methacrylate (MMA) and for monomer **1** with methyl acrylate (MA), all in the bulk at 60°C

| Copolymerization system | Initial molar fraction, $F_1$ | Conversion rate (%) | Molar fraction in the polymer, $f_1$ | $\bar{M}_w$ ($\times 10^{-3}$)$^a$ | $\bar{M}_n$ ($\times 10^{-3}$)$^a$ | $I_{pd}$ |
|---|---|---|---|---|---|---|
| **1** and MMA | 0.05 | 2 | 0.055 | 79.9 | 48 | 1.66 |
| | 0.15 | 2 | 0.151 | – | – | – |
| | 0.30 | – | 0.297 | – | – | – |
| | 0.30 | 1.5 | 0.305 | 116.6 | 61.6 | 1.89 |
| | 0.35 | 2 | 0.343 | – | – | – |
| **1** and MA | 0.191 | 9.1 | 0.357 | 151.7 | 36.9 | 4.3 |
| | 0.269 | 10.4 | 0.435 | 71.4 | 14.4 | 4.8 |
| | 0.563 | 9 | 0.646 | 52.8 | 21.8 | 2.4 |
| | 0.6 | 7 | 0.669 | 41.3 | 18.2 | 3 |
| | 0.8 | 9.5 | 0.841 | – | – | – |
| **2** and MMA | 0.0492 | 7 | 0.071 | 174.5 | 52.4 | 3 |
| | 0.0983 | 6.4 | 0.128 | 295.5 | 205.9 | 1.5 |
| | 0.1548 | 7 | 0.191 | 177.9 | 79.9 | 2.2 |
| | 0.199 | 6 | 0.240 | 172.4 | 75.9 | 2.2 |
| | 0.261 | 8 | 0.287 | 170.2 | 70.1 | 2 |
| **3** and MMA | 0.0922 | 3.5 | 0.159 | 162.8 | 53.3 | 3 |
| | 0.2371 | 3 | 0.315 | 111.5 | 22.5 | 3 |
| | 0.583 | 3.5 | 0.556 | 52 | 15.9 | 3.2 |
| | 0.839 | 2 | 0.720 | 34.2 | 12 | 2.8 |

$^a$ Measured by g.p.c. using polystyrene equivalents

**Table 5** Reactivity ratios of the various monomers **1**, **2** and **3** ($r_1$) for radical copolymerization with methyl methacrylate ($r_2$) and for monomer **1** with methyl acrylate (MA)

| | Fineman–Ross | | | | Kelen–Tüdos | | | |
|---|---|---|---|---|---|---|---|---|
| | $G=Hr_1-r_2$ | | $I=Jr_2-r_1$ | | | | | |
| Copolymer system | $r_1$ | $r_2$ | $r_1$ | $r_2$ | $r_1$ | $r_2$ | $\alpha$ | Azeotropic compositions |
| **1** and MMA | $r_{10}=0.76$ | $r_{01}=0.91$ | $r_{10}=0.62$ | $r_{01}=0.88$ | $r_{10}=0.71$ | $r_{01}=0.89$ | 0.16 | 0.234 |
| **1** and MA | $r_{15}=1.18$ | $r_{51}=0.40$ | $r_{15}=1.03$ | $r_{51}=0.29$ | $r_{15}=1.07$ | $r_{51}=0.31$ | 0.55 | None |
| **2** and MMA | $r_{20}=0.43$ | $r_{02}=0.65$ | $r_{20}=0.35$ | $r_{02}\approx 0.64$ | $r_{20}=0.42$ | $r_{02}=0.65$ | 0.10 | 0.376 |
| **3** and MMA | $r_{30}=0.34$ | $r_{03}=0.39$ | $r_{30}=0.42$ | $r_{03}=0.46$ | $r_{30}=0.38$ | $r_{03}=0.44$ | 0.76 | 0.464 |

reactivity is due to the electron donating effect of the vinylic methyl group. Similarly, the definition of $r_{52}$ is:

$$r_{52}=\frac{k_{55}}{k_{51}}=0.31$$

where activation of the double bond of **1** by the vinyl methyl group gives a value of $k_{51}$ which is three times greater than $k_{55}$.

To compare the reactivity ratios of **1**, **2** and **3** with respect to methyl methacrylate (**0**), let us define these relationships as follows:

$$r_{01}=\frac{k_{00}}{k_{01}}=0.89;\quad r_{02}=\frac{k_{00}}{k_{02}}=0.65;\quad r_{03}=\frac{k_{00}}{k_{03}}=0.44$$

These ratios provide an estimation of the reactivities of the various silicon monomers with respect to the macroradical of MMA, in relation to that of the non-silicon monomer, with respect to the same macroradical. All three $k_{0i}$ are greater than $k_{00}$, a result which can be explained by the relative difference in electro-

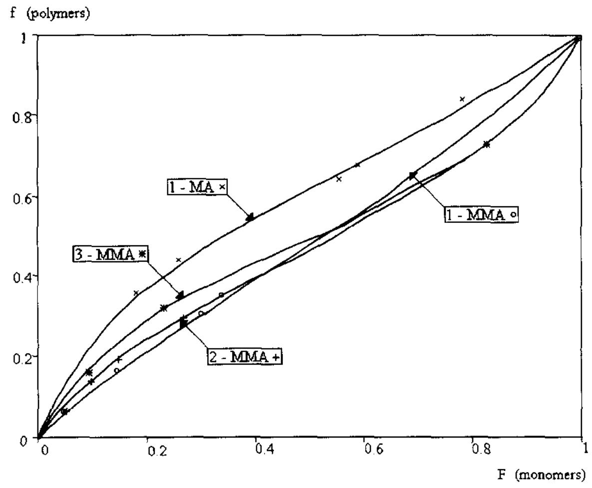

**Figure 2** Composition curves of $F$ (molar fraction of the silicon monomer in the reaction mixture) as a function of $f$ (molar fraction of the silicon monomer in the polymer) for the various triorganosilyl methacrylate copolymer systems: (○) **1** and MMA; (+) **2** and MMA; (*) **3** and MMA; (×) **1** and MA

negativities of the silicon and carbon atom (1.9 and 2.5, respectively). In contrast, the relative order of reactivity is **3**>**2**, which is directly related to the steric hindrance of the t-butyl group, compared to the methyl group.

The relevant relationships for these kinetics are as follows:

$$r_{10}=\frac{k_{11}}{k_{10}}=0.71;\quad r_{20}=\frac{k_{22}}{k_{20}}=0.42;\quad r_{30}=\frac{k_{33}}{k_{30}}=0.38$$

These three values are less than 1, which illustrates a greater affinity of the three growing radicals for MMA than for their own monomers. The electrostatic effects alone would lead us to expect values which are greater than 1. A steric effect is thus superimposed on this effect, due to the very large volume of the substituents carried by both the growing radical and by the monomer; this effect diminishes the rate constants $k_{11}$, $k_{12}$ and $k_{13}$ and therefore $r_{10}$, $r_{20}$ and $r_{30}$, which is observed.

In the same manner, $r_{15}$ is equal to one (*Table 5*), and shows no preference for the macroradical **1** to react with **1** on which a vinyl methyl group is present, when compared to MA. In this case, the electrostatic and steric effects seem to be of the same order. Such steric effects were also displayed in the series of methyl (MA), ethyl (EA) and butyl (BA) acrylates when compared to the same macroradical, for which the following order of reactivity, i.e. MA<BA<EA, was explained in terms of steric effects[16]. Moreover, $r_1$ has been found to be lower than unity for the tributyltin methacrylate/MMA couple[17].

On the one hand, we have shown that when both the macroradical and the monomer are sterically hindered, this parameter is predominant. On the other hand, when the monomer is the only hindered species, then the electrostatic effect is predominant.

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