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Living Radical Polymerization of Styrene Derivatives Containing Trialkylmetal Groups

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Fourteenth group oganometallic styrene derivatives were synthesised by nitroxide-mediated controlled radical polymerization using di-*tert* butyl nitroxide (A-T) as initiator. This is the first time that nitroxide-controlled radical polymerization has been successfully adapted for the synthesis of new polystyrenes bearing organometallic species with controlled molecular weights and narrow polydispersities. Monomer reactivity ratios were determined in controlled nitroxide-mediated radical copolymerization between styrene and substituted styrene. All experiments permitted the synthesis of new organometallic polymers that will be used for the development of a polymer capsule for Inertial Confinement Fusion Experiments.

Keywords: Living radical polymerization, substituted styrene

1 Introduction

Recent progress in controlled radical polymerization methods has provided new synthetic routes to well-defined polymers (1). One of the most extensively studied systems is the polymerization of styrene mediated by stable nitroxides such as TEMPO (2,2,6,6-tetramethyl-l-piperdinyloxy) or its derivatives. However, the bond formed between the polymer radical and these nitroxides becomes labile around 120°C. This high temperature facilitates both thermal polymerization and side reactions such as transfer or termination by dismutation between the growing chain and the stable radical. Catala (2) developed an alkoxyamine to minimize these reactions, i.e. the di-*tert*-butylnitroxide (A-T), which permits polymerization of styrene and *p*-*tert*-butylstyrene at 90°C.

The aim of this study was to check that the process can be extended to substituted *p*-styrene monomers.

Noltes (3) reported the polymerization of *p*-trimethylmetalstyrene (atoms such as Si, Ge, Sn and Pb). He found that all the derivatives of styrene monomers polymerized at 70–90°C in the presence of AIBN, and that under comparable conditions the 14th group organometallic styrene derivatives displayed appreciable differences in rates of polymerization in the order Pb > Si > C > Ge > Sn.

Herz (4) and Yamazaki (5) demonstrated independently the anionic living polymerization of 4-(trimethylsilyl)styrene in THF at –78°C with typical anionic initiators such as *n*-butyllithium, sodium naphthalenide and oligo (α-methylstyryl)potassium. The resulting polymers were found to possess predictable molecular weights in the range 5000–250000 and narrow molecular weight distributions.

We report here the development of organic materials doped with a 14th group organometallic element such as silicium, germanium or tin (Fig. 1). These polymers must have a average molecular weight (M_n) close to 100000 g/mol, a low polydispersity index ($M_w/M_n < 1.3$) and metallic species between 0.3 and 1% of atomic content.

Such polymers can be used as parts of targets for various experiments in plasma physics with energy driver beams from High Power Laser (Laser Mégajoule) (6). The use of different styrenic monomers doped with the above specific metals permits study of the influences of the metallic species, the group fixed on the metal, and the length of the alkyl chain on the reactivity of the opposite styrene. The kinetics, evolution of M_n over time and reactivity ratios were determined.

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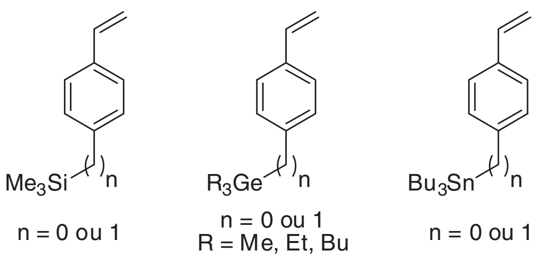


Fig. 1. Molecular structures of trialkylmetal styrenic monomers used in homopolymerization and copolymerization with styrene.

We first obtained several styrenic trialkylmetal derivatives containing silicium, germanium or tin (Fig. 1). In the second step, the homopolymerization and the copolymerization of these compounds with styrene by nitroxide-mediated free radical polymerization were evaluated.

2 Experimental

2.1 Semi-Empirical Calculations

Semi-empirical molecular orbital calculations were carried out using the AM1 method.

2.2 Materials

Tetrahydrofuran was refluxed from sodium and benzophenone under nitrogen atmosphere and distilled. Styrene was purified by distillation under vacuum just before polymerization. The di-*tert*-butylnitroxide was prepared using the procedure described by Catala: 1-(bromoethyl)benzene reacts with di-*tert*-butylnitroxyl sodium salt under argon. *p*-Chlorostyrene, chlorotrimethylsilane, chlorotributyltin and bromotrialkylgermanes were used as received.

2.3 Typical Procedure for the Synthesis of 4-Trialkyl (silyl, germyl, stannyl)styrene (7)

We recently reported a new method using the Barbier procedure to access *p*-substituted styrene derivatives by reaction between organometal halides, magnesium turnings and *p*-bromostyrene or *p*-chloromethylstyrene under ultrasound conditions.

2.4 Polymerization

Polymerization procedures were carried out under argon in sealed glass reactors. Polymer solutions were degassed under argon. The controlled radical polymerization of styrene and derivatives was performed with A-T and submitted to heat at 90°C for given times. Before polymer precipitation, the conversion yield was determined by ^{1}H NMR, then the polymer was precipitated in methanol and purified by repeated re-precipitation from THF to methanol. Molecular weights and polydispersity index were determined by gel permeation chromatography, polystyrene standards being used for the calibration.

3 Results and Discussion

3.1 Synthesis of Monomers

In the first step, our study focused on synthesis of monomers bearing the metallic species MR_3 (M: Si, Ge, Sn and R: Me, Et, n−Bu). All styrenic monomers (Figure 2) were synthesised from magnesium turnings, 4-bromostyrene or 4-chloromethylstyrene and an appropriate electrophile under ultrasound conditions in a Barbier procedure and provided good yields (7).

The kinetics of homopolymerization of 4-trimethylsilylstyrene and styrenic monomers bearing organometallic species were studied in *para* position, (Fig. 1, $n = 0$), followed by the same groups in the benzyl position (Figure 1, $n = 1$).

3.2 p-Trimethylsilylstyrene: Polymerization of 4-TMSiS as a Model

Experiments were performed at 90°C in order to study the influence of the di-*tert*-butylnitroxide (A-T) concentration on the propagation rate. We chose three concentrations in A-T in order to determine the best concentration to obtain polymers of high molecular weight and low polydispersity index. The results obtained are presented in Figure 3. All data points were located on a straight line and the polymerization rate of the A-T-containing system was exactly equal to that of the thermal polymerization, which means that the polymerization rate was independent of the A-T concentration.

This can be explained by the presence of all or the majority of propagating radicals that are produced by thermal self initiation. This result is in agreement with the results of Catala (8) on polymerization of *p*-*tert*-butylstyrene. Fukuda (9) has proposed a kinetics scheme corresponding to this situation and showed that the polymerization rate was independent of the A-T concentration:

$$R_p = k_p[P^*][M] = (k_p/k_t^{1/2})R_i^{1/2}[M]$$

Figure 4 shows the variations in molecular weight. For each di-*tert*-butylnitroxide concentration, the molecular

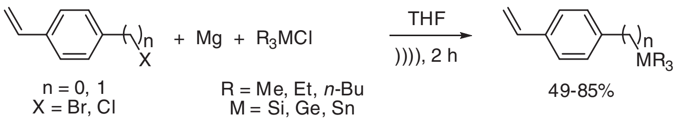


Fig. 2. General synthesis of styrenic monomers under ultrasound conditions in a Barbier procedure.

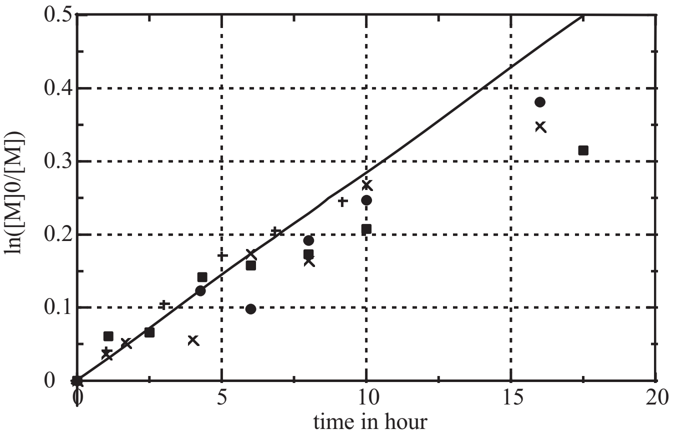


Fig. 3. Conversion-time graph of the polymerization of *p*-trimethylsilylstyrene, in bulk, at 90°C with different di-*tert*-butylnitroxide concentration: (+) thermal, (•) $0.57*10^{-3}$ molL^{-1}, (**x**) $1.16*10^{-3}$ molL^{-1}, (■) $4.97*10^{-3}\text{molL}^{-1}$.

weight increased linearly with yield. This characteristic indicates that the number of macromolecules formed remained constant during the polymerization process.

However, a deviation was observed for the lowest initiator concentration, after 15% of conversion. This can be explained by thermal polymerization which led to the formation of radicals which terminated some of the growing radicals. The nitroxide released may then have capped a growing chain participating in the consumption of monomers. Thus, the number of active sites remained constant during the polymerization process.

It is possible to calculate the theoretical slopes ($\alpha_{th.}$) of these straight lines using the following equation:

$$\overline{Mn} = \frac{PM^*[M]_0}{100^*[A-T]} * R = \alpha * R$$

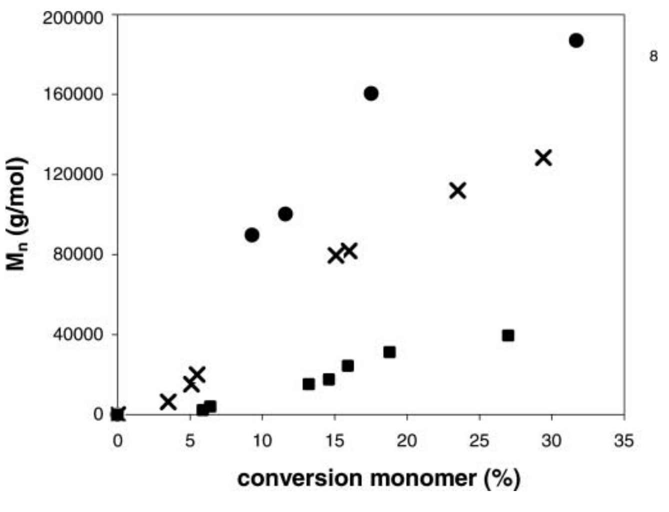


Fig. 4. Mn in relation to *p*-trimethylsilylstyrene conversion polymerized in bulk at 90°C with different initiator concentrations: (•) 0.57×10^{-3} molL^{-1}, (x) 1.16×10^{-3} molL^{-1}, (■) 4.97×10^{-3} molL^{-1}.

Table 1. Polymerization of *p*-trimethylsilylstyrene in bulk at 90°C with different initiator concentrations. Comparison between theoretical and experimental slopes.

[A-T] *mol L^{-1}*	*Theoretical slope: $\alpha_{th.}$*	*Experimental slope: $\alpha_{exp.}$*
$0.57*10^{-3}$	15600	9085
$1.16*10^{-3}$	7664	6200
$4.97*10^{-3}$	1778	1702

PM = molar mass of trimethylsilylstyrene and R = % yield

Comparison between the theoretical and experimental slopes in Table 1 shows the good agreement for higher A-T concentrations. This suggests that each initiator molecule leads to the formation of one macromolecule. At the same time, the polydispersity index remained below 1.25 (Fig. 5), but there is a difference for low A-T concentrations and the polydispersity index increase to 1.6. The deviations at lower A-T concentrations were due to increased numbers of macromolecules during polymerization, indicating the presence of irreversible termination reactions. Thus, if the A-T concentration is too low, control of the average molecular weight would not be satisfactory.

3.3 Polymerization of p-Trialkylmetalstyrene

3.3.1. *Kinetics study*

Styrenic monomers bearing the organometallic species in the *para* position were polymerized in the presence of A-T at 90°C over increasing periods of time.

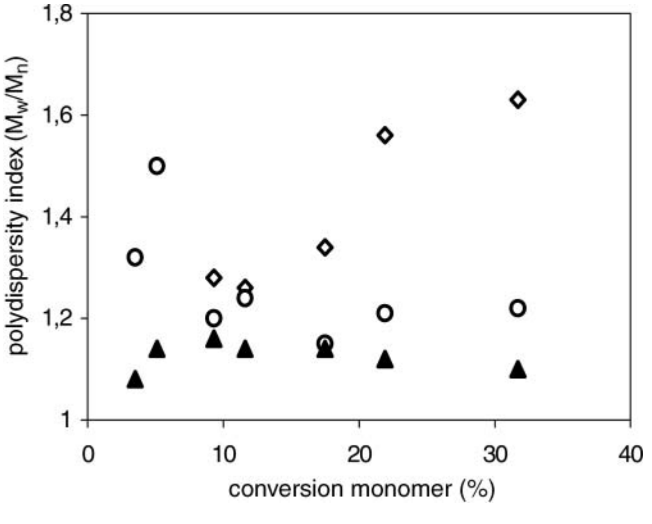


Fig. 5. Polydispersity index in relation to *p*-trimethylsilylstyrene conversion polymerized in bulk at 90°C with different initiator concentrations: (◇) 0.57×10^{-3} molL^{-1}, (○) 1.16×10^{-3} molL^{-1},(▲) $4.97\times 10^{-3}\text{molL}^{-1}$.

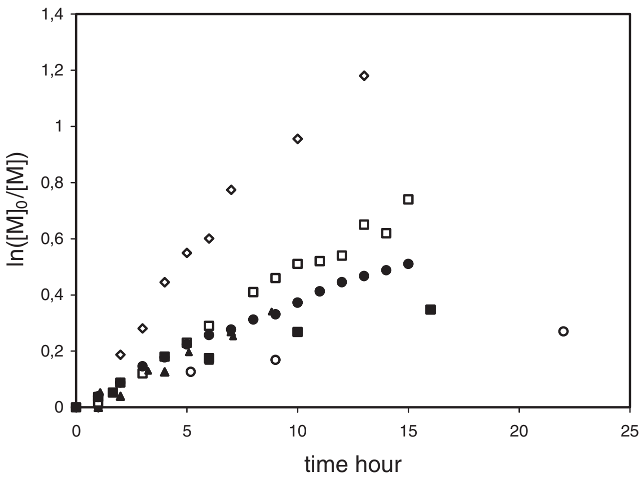
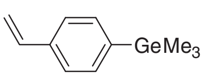
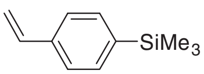
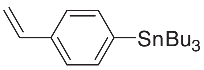
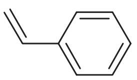


Fig. 6. Conversion time graph of the polymerization of $R_3M^{14}C_6H_4\text{-}CH{=}CH_2$ in bulk at 90°C with A-T. (◇) 4-tributylgermylstyrene, (●) 4-triethylgermylstyrene, (▲) 4-trimethylgermylstyrene, (*blbox*) 4-trimethylsilylstyrene, (○) 4-tributylstannylstyrene, (■) 4-tributylsilylstyrene.

Table 2. Addition rate constants of lithium diethylamide on monomers. Solvent,18.5 mL THF; temperature, 0°C; 5 mmol lithium diethylamid; 50 mmol diethylamine; 5 mmol monomer. ^{13}C-NMR chemical shift of vinyl β-carbon and net charges related to styrene

Monomer	*10^4k mol^{-1}l. s^{-1}*	*^{13}C NMR δ of vinyl β-carbon*	*10% Net charge*
	26.7	113.9	+34
	32.0	114.2	+44
	—	113.7	—
	5.9	113.1	0

The conversion data thus obtained is shown in Figure 6 where monomer consumption is plotted against time. It can be seen that under comparable conditions the substituted styrene polymerised more rapidly than styrene itself (10), thus, the trialkylmetal group had little effect on monomer reactivity or on the charge distribution on the vinyl group.

As the slope of these straight lines is equal to $k_p[P^\bullet]$, this indicates that k_p and/or the concentrations of active species is/are greater than for substituted styrenes. It is known that the reactivity of organosilicon compounds is greatly influenced by their substituents. For example, R-Si groups in phenyl-substituted silicon compounds show an electron withdrawing effect(11) and this can be seen in Table 2. More generally Imoto (12) demonstrated that styrenic monomers with electron-withdrawing groups polymerize more rapidly than styrenic monomers with electron releasing groups.

Thus, the k_p for substituted styrenic monomers must be greater than that of styrene. The radical concentration in the stationary state can be interpreted as either a faster rate of initiation or a slower rate of termination. For the first explanation it is possible to calculate the constant formation rate of thermal radicals by equalising the thermal initiation rate with the termination rate. In considering the initiation with a third order:

$$k_a[M]^3 = k_t[M^\bullet]^2 \qquad (1)$$

and

$$DPn = k_pX[M][M^\bullet]/k_t[M^\bullet]^2 \qquad (2)$$

with X = 1 if it is a dismutation termination and X = 2 if it is a recombination termination.

Therefore, with (1) and (2), $k_a = k_pX[M^\bullet]/DPn[M]^2$

Substituted styrenes are monomers which lead to the formation of higher concentrations of thermal radicals in the mixture, whatever the termination step (either combination or dismutation) (Table 3).

One plausible explanation for the increase in monomer consumption over time with the substituted styrene compared to styrene may be radical stability.

As above, the trialkylmetal group in our monomers showed an electron-withdrawing effect. Thus, when we polymerized a substituted monomer, the polymer radical was less stable than the polystyryl radical, because it is less well-stabilized. Consequently, the polymer radical reactivity towards substituted monomers was greater.

3.3.2. *Evolution of Molecular Weight and Polydispersity Index*

Variations in molecular weight compared to yield are represented in Fig. 7. The molecular weight of each monomer increased linearly with yield. This indicates that the number of macromolecule chains formed throughout the polymerization process remained unchanged. However comparison between the theoretical slopes and the experimental slopes of these straight lines showed a slight difference: the experimental slope was lower than the theoretical slope, thus proving the presence of termination reactions.

At the same time, the polydispersity index remained below 1.30 for lower rate conversion (<20%) as reported in

Table 3. Comparison of constant rates of thermal radical formation. With X = 1 in the case of dismutation termination and X = 2 in the case of recombination termination

styrene (X=2)	*0.011*	*4610*	*8.74*	*$1.7*10^{-11}$*
4-trimethylsilystyrene	0.027	1989	5.05	$1.5*10^{-10}*$ X
4-trimethylgermylstyrene	0.034	1631	4.94	$2.3*10^{-10}*$ X
4-tributylstannylstyrene	0.021	1272	2.86	$5.6*10^{-10}$ * X

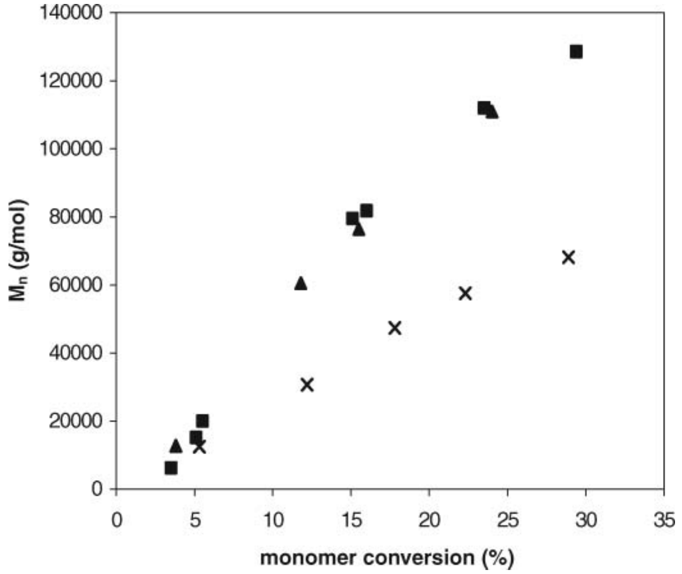


Fig. 7. M_n in relation to monomer conversion polymerized in bulk at 90°C. (x) 4-trimethylgermylstyrene, [A-T] = $2.49*10^{-3}$ $molL^{-1}$; (▲) 4-tributylstannylstyrene [A-T] = $1.4*10^{-3}$ $molL^{-1}$; (■) 4-trimethylsilylstyrene.

3.4 Polymerization of p-(Trialkylmetalmethyl)styrene

3.4.1. *Kinetics study*

Styrene monomers bearing an organometallic species in the benzyl position were polymerized in bulk at 90°C in the presence of di-*tert*-butylnitroxide (Fig. 9). A similar rate of monomer consumption was seen for thermal polymerization and for the solution containing A-T in accordance with a previous study. The same mechanism is therefore involved in aryl substituted styrene monomers and with benzyl monomers. The system reached the stationary state in radicals resulting from competition between formation of thermal radicals and termination reactions.

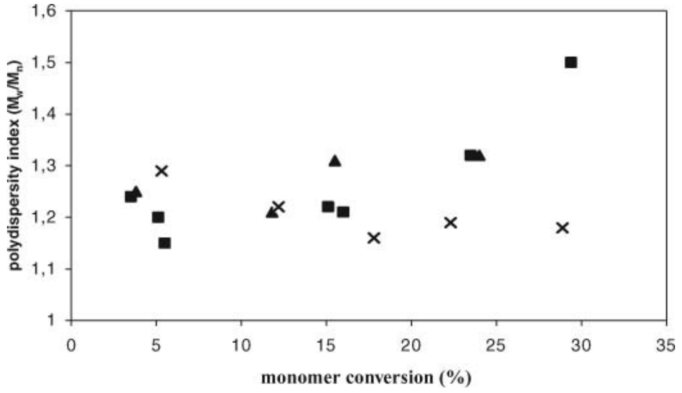


Fig. 8. Polydispersity index in relation to monomer conversion polymerized in bulk at 90°C. (x) 4-trimethylgermylstyrene, [A-T]= $2.49*10^{-3}$ $molL^{-1}$;(▲) 4-tributylstannylstyrene [A-T]= $1.4*10^{-3}$ $molL^{-1}$; (■) 4-trimethylsilylstyrene.

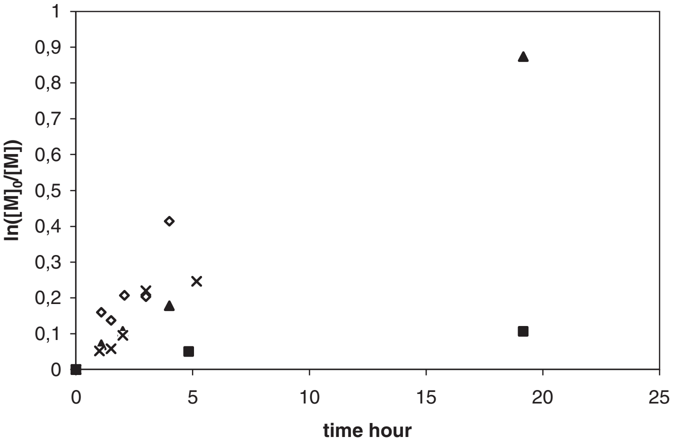


Fig. 9. Conversion time plot for polymerization of styrene derivatives in bulk at 90°C; (▲) 4-(tributylgermylmethyl) styrene, (x) 4-(tributylstannylmethyl)styrene, (◇) 4-(trimethylgermylmethyl)styrene, (■) 4-(trimethylsilylmethyl)styrene.

Monomer consumption was faster in the case of 4-(tributylstannylmethyl)styrene (4-TBSnMS) than in the case of styrene. As for substituted styrene in the aryl position, and bearing in mind that an electron-releasing effect was observed for the substituted benzyl position, the propagation rate constant, $k_{p,}$ for 4-TBSnMS must be lower than that of styrene. The slope was greater for 4-TBSnMS suggesting that the concentration of active species in the stationary state is higher than in the case of styrene.

Variations in molecular weight compared to yield are represented in Figure 10. The molecular weight of each monomer increased linearly with yield. This indicates that the number of macromolecule chains formed throughout the polymerization process remained unchanged.

In parallel, the polydispersity index remained controlled between 1.30 and 1.50 (Figure 11). The higher values than in the case of trialkylmetalstyrene were due to higher

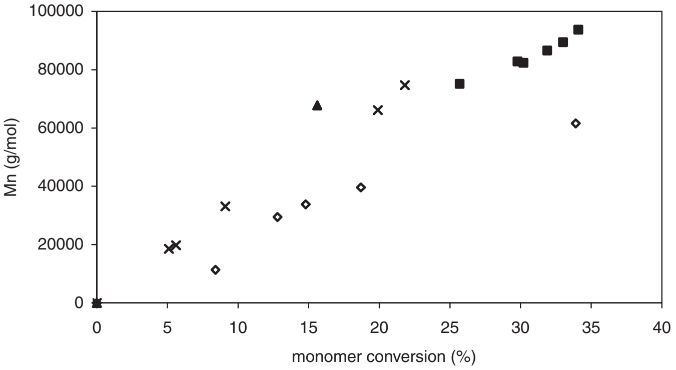


Fig. 10. Mn as a function of monomer conversion polymerized in bulk at 90°C. (▲) 4-(tributylgermylmethyl)styrene, (x) 4-(tributylstannylmethyl)styrene, (◇) 4-trimethylgermylmethyl) styrene, (■) 4-(trimethylsilylmethyl)styrene.

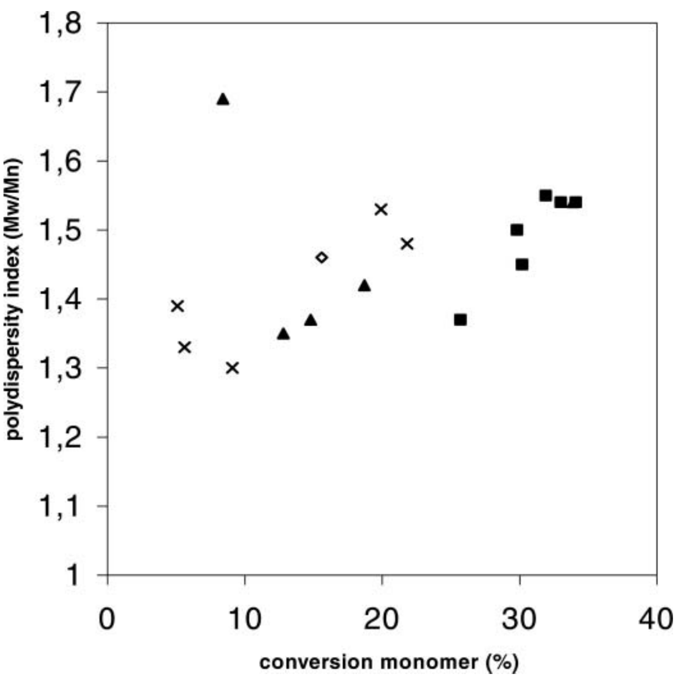
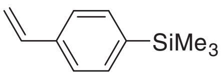
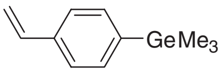
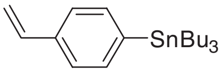
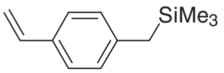
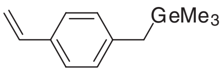


Fig. 11. Polydispersity index as a function of monomer conversion polymerized at 90°C in bulk. (▲) 4-(tributylgermylmethyl)styrene, (x) 4-(tributylstannylmethyl)styrene, (◇) 4-(trimethylgermylmethyl)styrene, (■) 4-(trimethylsilylmethyl)styrene.

concentrations of radicals. Another phenomenon implies transfert reactions on the benzylic position. Similar results have already been reported by Boutevin (13). The trialkylmetalstyrene benzylic site is capable of transfert reactions because of the possible conjugation with the aromatic cycle (14).

Table 4. Copolymerization parameters (r) of substituted styrene monomers (M_1) compared to styrene (M_2)

M_1	M_2	r_1	r_2
	styrene	1.03	1.20
	styrene	1.11	0.87
	styrene	1.30	0.78
	styrene	0.75	0.88
	styrene	0.82	0.72

3.5 Reactivity Ratio and Controlled Doping Level

To obtain polymers with a controlled doping level, it was necessary to determine the reactivity ratio between all styrene derivatives containing functional groups and styrene. Several poly (styrene-*co*-substituted styrene) copolymers were synthesized and the yield of each copolymer was low (between 5 and 10%). The copolymer compositions F_1 (in moL fractions of substituted styrene units) were calculated from the ^{1}H-NMR data. The relationship between the co-monomer feed composition f_1 and the copolymer composition F_1 can be seen in Figure 12.

The curve in Figure 12 was used to evaluate the reactivity ratios r_1 and r_2 for system styrene substituted/styrene each using the Mayo-Lewis equation. This curve translates the equation of Mayo which connects the composition of a copolymer consisted of two monomers Ma and Mb, in the

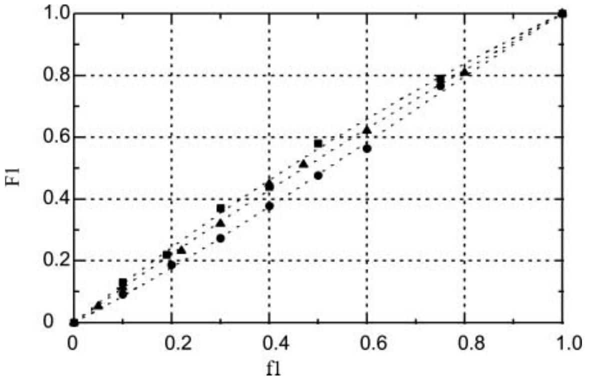
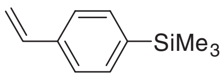
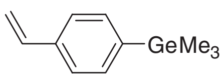
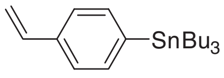
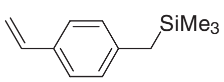
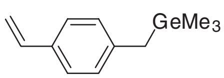


Fig. 12. Evolution of copolymer composition F_1 (moL fractions of substituted styrene units in the copolymer) with comonomer feed composition f_1 (moL fractions of substituted styrene in the feed). (●) 4-trimethylsilylstyrene, (■) 4-tributylstannylstyrene, (▲) 4-trimethylgermylstyrene.

Table 5. Molecular weights and polydispersdity obtained for different polymers. Atomic metal composition evaluated by NMR spectroscopy

M_1	M_2	*Mn Mw/Mn*	*metal (%)*
	styrene	16340 1.15	0.51
	styrene	84200 1.24	0.31
	styrene	70700 1.17	0.58
	styrene	50950 1.18	0.67
	styrene	68320 1.19	0.62

concentration of both monomers and reactivity ratio r_1 and r_2.

$$F_A = \frac{r_1 f_A^2 + f_A(1 - f_A)}{r_1 f_A^2 + 2 f_A(1 - f_A) + r_2(1 - f_A)^2}$$

The results are listed in Table 4. The product $r_1 * r_2$ is almost equal to unity, indicating that the copolymerization was ideal, and thus that the radicals had the same preference for both monomers.

3.6 Evaluation of Incorporation of Metal Doping Level

All previous studies have demonstrated that it is possible to obtain copolymers with predefined molecular weights, a low polydispersity index and a controlled doping level. The molecular weights, polydispersity index and atomic composition of some polymers are represented in Table 5.

4 Conclusions

In summary, this is the first time that nitroxide radical polymerization has been successfully adapted to the synthesis of new polystyrenes bearing an organometallic specie with controlled molecular weights and narrow polydispersity ranges. Calculation of the reactivity ratio provided verification of the atomic composition of copolymers in terms of silicium, germanium and tin, thus demonstrating that the new organometallic polymers can be used for the development of new materials for Inertial Confinement Fusion experiments with High Power Laser (Laser Mégajoule).

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