

# Synthesis of carboxy-terminated telechelic oligostyrenes by Dead End Polymerization

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**Abstract:** Styrene was polymerized with 4,4'-azobiscyanovaleric acid (ACVA) in order to obtain carboxy-telechelic polystyrene (CTPS) using the Dead-End Polymerization (DEP) conditions. First, we focused on experimental conditions leading to oligomers with molecular weights about 2000 g mol<sup>-1</sup>. Second, we demonstrated by-products of ACVA radicals are also synthesized in the DEP conditions by combination or by disproportionation. The purification of CTPS was investigated in order to extract the by-products of ACVA. An extraction of these by-products in H<sub>2</sub>O pH 7 is suggested. Finally, the acid functionality of oligostyrene is evaluated by <sup>1</sup>H NMR and conductimetric titrations. A functionality about 2 is obtained that confirmed the synthesis of CTPS.

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**Keywords:** carboxy-telechelic polystyrene; Dead-End Polymerization; MALDI-TOF

## INTRODUCTION

The synthesis of block copolymers appears as an important economic topic because these copolymers may find applications in technical materials. Block copolymers of well-defined structure and composition can be used as high-performance polymers or as compatibilizers for mechanical blend systems of two immiscible polymers.<sup>1–4</sup> Block copolymers are produced by polycondensation of telechelic prepolymers, which have two condensable functions at the extremities. Generally, block copolymers associate rigid and soft blocks in a properly chosen composition range. They are also called thermoplastic elastomers.<sup>5,6</sup> For instance, the polyaddition in the molten state of carboxy-telechelic oligoamide ( $T_m = 120^\circ\text{C}$ ) with hydroxy-telechelic polyether ( $T_g = -60^\circ\text{C}$ ) leads to PEBA (polyether-block-amide synthesized by Atofina.<sup>7,8</sup>) The combination of a polyether sequence and a polyamide sequence does not change the thermal property ( $T_g$ ) of the soft phase over a wide range of temperature. HYTREL (synthesized by Dupont de Nemours) is another such block copolymer where the hard sequences are poly(butanediol-terephthalate) and soft sequences are polyoxytetramethylene.<sup>9–14</sup>

To obtain block copolymers, it is necessary to synthesize telechelic polymers. Many studies concerning the synthesis of telechelic oligomers have already

been published.<sup>15–18</sup> In this paper, the synthesis of carboxy-telechelic oligostyrene is studied with  $M_n$  about 2000 g mol<sup>-1</sup>. Several methods can lead to carboxy-telechelic polystyrene (CTPS).<sup>19–23</sup> Carboxy-terminated polystyrene can be prepared by end-capping the polystyrene living anion with carbon dioxide. Mansson<sup>19</sup> developed this method and mentions the appearance of by-products such as dipolystyrylketone or tripolystyrylmethanol. He used chromatography on silica gel medium for the separation of functionalized polystyrenes, which are eluted in a methylcyclohexane/THF mixture. Rimmer and Ebdon<sup>23</sup> synthesized telechelic oligostyrene with  $M_n$  of 2000 g mol<sup>-1</sup> by ozonolysis of poly(styrene-*stat*-butadiene). However, styrene must be protected against ozone attack by the use of di-*N*-alkylamides as sacrificial ozone scavengers.

Dead-End Polymerization (DEP) seems to be a good method for the synthesis of telechelic oligomers.<sup>24,25</sup> Heitz *et al*<sup>26,27</sup> were the first to obtain CTPS by dead-end polymerization with AIBN as initiator. Telechelic  $\alpha,\omega$ -bis(1-carboxy-1-methylethyl)oligostyrene was obtained by hydrolysis of the nitrile end-groups at 240°C. So the use of carboxy-telechelic diazoic initiators appears to be more judicious. Several authors<sup>28–30</sup> have prepared CTPS with 4,4'-azobis(cyanovaleric acid) (ACVA). However these authors synthesized carboxy-telechelic oligostyrene

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with  $M_n$  close to  $10\,000\text{ g mol}^{-1}$ . They did not work in DEP conditions where initiator concentrations and initiator  $t_{1/2\text{ life}}$  are higher and so  $M_n$  values obtained would be lower. In our experience, when DEP conditions are used, this method leads to by-products of the initiator.

This paper aims reports the radical synthesis, purification and characterization of carboxy-telechelic oligostyrene.

## EXPERIMENTAL

Styrene (99%), supplied by Aldrich, was distilled and stored under inert atmosphere at  $5^\circ\text{C}$ . 4,4'-Azobis(cyano valeric Acid) (ACVA) (97%) was also supplied by Aldrich and used without further purification. Propionitrile, toluene and THF were used as delivered by suppliers.

### Synthesis

*Synthesis of carboxy-telechelic oligostyrene ( $[M]_0=2\text{ mol l}^{-1}$ ,  $C_0=0.1$ )*

Into a 100-ml round-bottom flask were introduced 10 g of styrene (0.096 mol), 2.7 g of ACVA ( $9.6 \times 10^{-3}$  mol), and solution completed with 30 g of propionitrile. The solution was bubbled with  $\text{N}_2$  for 10 min. The polymerization was carried out at  $90^\circ\text{C}$  under inert atmosphere.

*Synthesis of carboxy-telechelic oligostyrene ( $[M]_0=2\text{ mol l}^{-1}$ ,  $C_0=0.05$ )*

Reaction was as above using 10 g of styrene (0.096 mol), 1.35 g of ACVA ( $4.8 \times 10^{-3}$  mol) and 30 g of propionitrile.

*Synthesis of carboxy-telechelic oligostyrene ( $[M]_0=2\text{ mol l}^{-1}$ ,  $C_0=0.01$ )*

Reaction was as above using 10 g (0.096 mol) of monomer and 0.27 g ( $9.6 \times 10^{-4}$  mol) of initiator.

*Synthesis of carboxy-telechelic oligostyrene ( $[M]_0=2\text{ mol l}^{-1}$ ,  $C_0=0.001$ )*

Reaction was as above using 10 g (0.096 mol) of monomer and 0.027 g ( $9.6 \times 10^{-5}$  mol) of initiator.

### Purification of carboxy-telechelic oligostyrene

After cooling, the solvent and residual monomer were evaporated under vacuum. The obtained product was dissolved in 50 ml of THF and then precipitated. The different solvents used for the precipitation were methanol, ethanol, n-butanol, propan-2-ol, which solubilize ACVA by-products. The ratio of solvent to non-solvent was 1/20.

Pentane was also used for the precipitation of CTPS. However, before precipitation, ACVA by-products were extracted from the organic medium (toluene) by washing three times with water pH 7. The water/toluene ratio was 1/1. The toluene was then evaporated, the product obtained dissolved in 50 ml of THF and precipitated with pentane.

## Characterizations

Molecular weights ( $M_n$ , number average molecular weight) were measured by size exclusion chromatography (SEC; Spectra-Physics SP 8430 RI Detector; SP 8800/8810 LC Pump) in THF, with a polystyrene calibration.

The chemical structure of products was determined by the  $^1\text{H}$  NMR (Brüker AC 200 MHz) at room temperature in  $\text{CDCl}_3$  and DMSO solutions.

Acid functionality of CTPS was determined by titration of CTPS in THF using a 0.05 N methanolic potassium hydroxide solution. Titrations were made with phenolphthalein by conductimetry with acetonitrile as solvent of CTPS.

MALDI-TOF MS experiments were conducted at the Service Central d'Analyse du CNRS (Solaize-France) using a VOYAGER DE STR from Perkin-Elmer equipped with a  $\text{N}_2$  laser ( $\lambda=337\text{ nm}$ ). The matrix was made of 1,8,9-anthracenetriol containing NaI ( $\text{MNa}^+$ ). The weight concentration of polymer was 0.1%. The spectra were recorded in linear mode over the range  $m/z$  750–7000 Da.

Conversion degree in monomer was calculated by the ratio of the mass of oligomers on the mass of starting monomer.

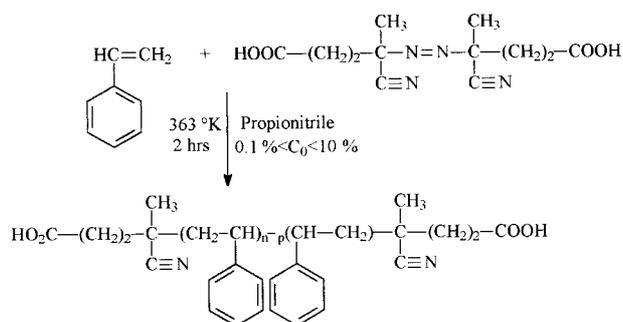
## RESULTS AND DISCUSSION

There is an important difference between radical polymerization and DEP. In radical polymerization, the monomer conversion degree and the molecular weights of polymers are very high, which is the consequence of a low initiator  $t_{1/2\text{ life}}$ . In DEP, the conditions of polymerization are very different. First, the initial initiator concentration and the reaction temperature are very high. Second, the concentration in radicals is very important, which favours the primary radical termination and then decreases the reaction of propagation. Tobolsky<sup>31,32</sup> explained that the phenomenon of DEP is observed when there is a complete consumption of the initiator before maximum conversion of monomer to polymer is reached. The consequence of these conditions is the synthesis of oligomers. Moreover, Heitz<sup>33</sup> showed that oligomers could be telechelic if initiators are telechelic and if monomers present a termination reaction only by recombination.

### Synthesis of carboxy-telechelic oligostyrene

Previously, we have noted that the synthesis of telechelic oligomers by DEP is possible if the reaction termination of macroradicals is mainly a combination process. Styrene constitutes a good candidate because the termination is mainly done by combination. Several authors<sup>34–37</sup> found 80% of combination but, more recently, Bessière *et al*<sup>38</sup> polymerized styrene with fluorinated azoic initiator and found 100% of combination using fluorine elemental analysis.

Transfer reactions in the solvent usually lead to a decrease of functionality and stop radical growth.



**Scheme 1.** Synthesis of carboxy-telechelic polystyrene by Dead-End Polymerization.

However, propionitrile (boiling point = 93 °C) can be used because of its low transfer reaction. Moreover, propionitrile is a good solvent of polystyrene.

With these assumptions, the polymerization of styrene with ACVA was carried out in acetonitrile at 90 °C (Scheme 1).

First, the theoretical consumption of monomer and initiator was determined with initial Styrene and ACVA concentrations of 2 and 0.2 mol l<sup>-1</sup>, respectively, that is an initial molar ratio  $C_0$  of 10% ( $C_0 = [\text{ACVA}]_0 / [\text{styrene}]_0$ ).

Equations (1) and (2) respectively represent the monomer (M) and initiator (I) consumption:

$$\ln \frac{[M]_0}{[M]} = 2 \frac{k_p}{\sqrt{k_t}} \times \sqrt{\frac{f}{k_d}} \times \sqrt{[I_2]_0} \times \left(1 - e^{-\frac{k_d t}{2}}\right) \quad (1)$$

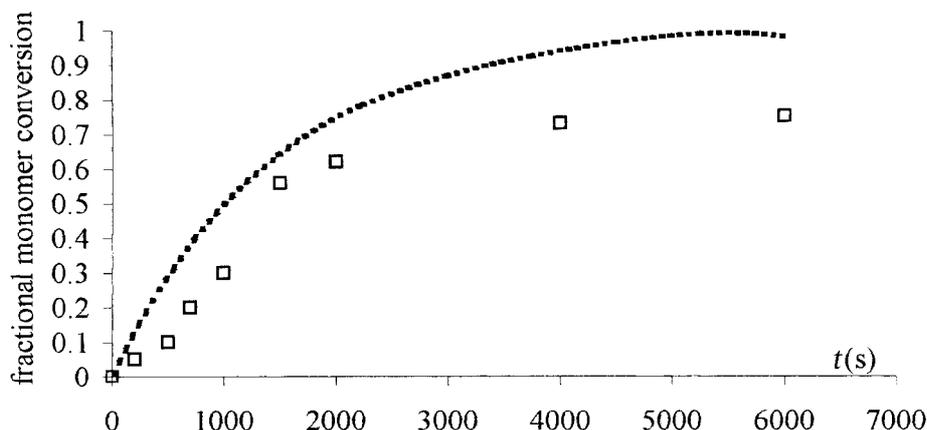
$$[I_2] = [I_2]_0 \cdot e^{-k_d t} \quad (2)$$

With constant values of styrene and ACVA at 90 °C (Table 1) eqns (1) and (2) become:

$$\ln \frac{[M]_0}{[M]} = 1.49 \cdot (1 - e^{-3.45 \cdot 10^{-4} \cdot t})$$

$$[I_2] = 0.2 \cdot e^{(-6.9 \cdot 10^{-4} \cdot t)}$$

The consumption profiles of styrene and ACVA are represented in Fig 1 and very well characterize DEP behaviour. The consumption of styrene reached about



**Figure 1.** Plots on conversion rate versus time for the polymerization of styrene with ACVA at 90 °C with  $C_0 = 10\%$ .

**Table 1.** Kinetic constant values for styrene and ACVA

Notation	Value
$k_d$ (s <sup>-1</sup> ) <sup>39</sup>	$6.9 \times 10^{-4}$
$k_p$ (1 mol <sup>-1</sup> s <sup>-1</sup> ) <sup>40</sup>	$6.7 \times 10^2$
$k_t$ (1 mol <sup>-1</sup> s <sup>-1</sup> ) <sup>40</sup>	$1.45 \times 10^8$
$f_{\text{ACVA}}$ <sup>29</sup>	0.62

75% for complete consumption of ACVA. Consequently the monomer conversion was limited by the initiator conversion, as expected.

Parameters that lead to carboxy-telechelic oligo-styrene were then determined with  $M_n$  about 2000 g mol<sup>-1</sup> and with conversion degree higher than 50%. For this, a kinetic study was investigated where the initial molar ratio  $C_0$  ( $C_0 = [I_2]_0 / [M]_0$ ) was monitored from 0.1% to 10% at 90 °C. The experimental monomer conversion degree and experimental molecular weights were determined after 2 h when initiator is totally consumed. The results are gathered in Table 2. The theoretical maximal conversion degrees  $\alpha_m$  are also represented for different  $C_0$  values. Knowing the rate constants of monomer and initiator (Table 1),  $\alpha_m$  can be calculated from eqn (3), obtained from eqn (1) considering infinite time:

$$-\ln(1 - \alpha_m) = 2 \sqrt{\frac{k_p^2 \cdot f}{k_t \cdot k_d}} \times \sqrt{[I_2]_0} \quad (3)$$

Table 2 shows that the theoretical maximal conversion degrees are in good agreement with the experimental data. Moreover, the synthesis of  $M_n \leq 2000$  g mol<sup>-1</sup> requires an initial molar ratio  $C_0 \geq 5\%$ . In addition, for  $C_0 \geq 5\%$  a monomer conversion rate higher than 50% was obtained.

### Purification

Many authors have worked on decomposition of diazoic compounds. For instance, Bickel and Waters<sup>41</sup> studied by-products of the AIBN decomposition in toluene. They observed various products and tetra-

**Table 2.** Influence of  $C_0$  molar ratio on molecular weight and monomer conversion (experimental and theoretical) degree in DEP of styrene with ACVA at 90 °C

$C_0$ (%)	$M_n$ ( $g\ mol^{-1}$ )	Experimental monomer conversion degree (%)	Theoretical monomer conversion degree (%)
0.1	25000	13	14
1	4900	35	38
5	1900	62	65
10	1500	80	78

methylsuccinonitrile was the major product formed (90%), coming from coupling of AIBN radicals. In our case, by-products of ACVA were also observed in steric exclusion chromatography (SEC) of carboxy-telechelic oligostyrene after 15 min and 240 min of reaction between ACVA and styrene at 90 °C (Fig 2).

A large peak was observed on the two chromatograms, which was attributed to oligomers of CTPS (retention time about 33 min). A second peak was also found corresponding to ACVA and by-products of ACVA (retention time about 43 min) after 15 min of reaction. After 240 min of reaction, ACVA was totally consumed. Thus the peak at 43 min of retention characterized only by-products of ACVA. We could also assume that these by-products were formed at the beginning of the reaction and remained unchanged until the end of the reaction. Consequently, a purification procedure was necessary in order to extract the by-products of ACVA.

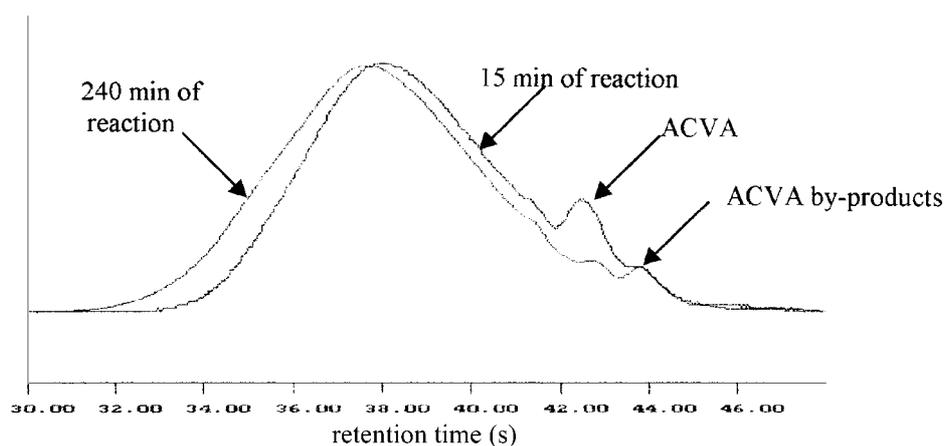
Initially, the procedure of Ohishi *et al*<sup>29</sup> was studied.

They had synthesized CTPS using ACVA at 90 °C and obtained  $M_n$  about 20000  $g\ mol^{-1}$ . The purification of CTPS initiated by Ohishi *et al* was investigated in order to extract ACVA by-products. They suggested a treatment using methanol as a non-solvent of carboxy-telechelic oligostyrene and as a solvent of ACVA by-products. These authors developed this experimental protocol for CTPS with values of  $C_0$  less than 1% and with molecular weight up to 20000  $g\ mol^{-1}$ .

In our case, oligostyrene was synthesized with molecular weights of about 2000  $g\ mol^{-1}$ . Table 2 shows that  $M_n \leq 2000\ g\ mol^{-1}$  required  $C_0 \geq 5\%$ , which led to more significant quantity of by-products. So the treatment proposed by Ohishi *et al* was used and, in a second run molecular weights of carboxy-telechelic oligostyrene were determined (Table 3).

We can note that, with  $C_0 < 1\%$ , the precipitation does not induce noticeable differences in the molecular weights of oligomers. For  $C_0 \geq 1\%$ , a large difference in the molecular weight was observed before and after precipitation. Purification induced an increase in molecular weights above 2000  $g\ mol^{-1}$ . For instance, with  $C_0 = 10\%$   $M_n$  is 1500  $g\ mol^{-1}$  but after precipitation with methanol  $M_n$  was greater than 4000  $g\ mol^{-1}$ . So, after precipitation in methanol, oligomers of lower molecular weight, which are preponderant in our case, were solubilized. We also tried to quantify the weight loss of oligomers after precipitation with high initiator concentration, and to evaluate the final monomer conversion degree (Table 3).

Table 3 shows that, with  $C_0 = 5\%$ , the experimental monomer conversion degree was about 62% at the end

**Figure 2.** Chromatograms of CTPS ( $C_0 = 5\%$ ) after 15 min and 240 min of reaction.**Table 3.** Molecular weights and final yields for DEP of styrene with ACVA at 90 °C after precipitation with methanol

$C_0$ (%)	$M_n$ after 2 h of reaction ( $g\ mol^{-1}$ )	$M_n$ after precipitation with methanol ( $g\ mol^{-1}$ )	Experimental monomer conversion degree after 2 h of reaction and without purification (%)	Final yield after precipitation with methanol (%)	Oligomer weight loss after precipitation with methanol (%)
0.1	25000	28000	13	11	15
1	4900	5100	35	26	25
5	1900	4600	62	45	27
10	1500	4400	80	40	50

**Table 4.** Influence of different solvents on the weight loss and molecular weight of oligomers after precipitation (molecular weight before precipitation = 1500 g mol for  $C_0=10\%$ )

Solvents	Weight loss of oligomers after precipitation (%)	Final yield after precipitation (%)	Molecular weight after precipitation ( $\text{g mol}^{-1}$ )
n-Butanol	93	5	6071
Propan-2-ol	59	33	4600
Ethanol	86	11	5759
Methanol	50	40	4400
Pentane	0	80	1500

of reaction, measured by weighing the mixture after evaporation. After precipitation with methanol, 27% of oligomers were lost giving a final yield of 45%. With  $C_0=10\%$ , the final yield was 40% since 50% of oligomers are soluble. So with  $C_0=10\%$  the weight loss in oligomer was much more important than with  $C_0=5\%$ . Moreover, with  $C_0=10\%$  the molecular weight of oligostyrene was lower than with  $C_0=5\%$ . Thus, methanol extracted selectively oligomers with lower molecular weight. Working with very high initiator concentration induces great quantities of by-products, which were extracted simultaneously with low  $M_n$  oligomers. We can conclude that the precipitation with methanol is not suitable for the synthesis of carboxy-telechelic oligostyrene with molecular weight  $\leq 2000 \text{ g mol}^{-1}$ .

The purification of CTPS was studied with other alcohols to keep all oligostyrenes insoluble and the by-products of ACVA soluble. Carboxy-telechelic oligostyrenes were synthesized with  $C_0=10\%$  and several solvents are used for the precipitation of oligomers. Molecular weights and final yields were determined (Table 4).

Table 4 shows that alcohols keep ACVA by-products soluble because the peak of ACVA by-products were not observed after precipitation. However too much of a weight loss of oligomers was found after precipitation in alcohols.

Pentane was also used for the precipitation of oligostyrene. Pentane seems to be a better solvent for precipitation (Table 4) because no weight loss of oligomers was observed after precipitation. However the chromatogram of carboxy-telechelic oligostyrene obtained after precipitation with pentane presents the peak corresponding to ACVA by-products. An extraction of ACVA by-products was also investigated before precipitation with pentane.

Since ACVA by-products have acid functions, we try to extract them by washing the organic medium (CTPS, ACVA by-products, and toluene) with water at pH 7 and then CTPS are precipitated with pentane. ACVA by-products are effectively soluble in water at pH 7 since we do not observe corresponding peak on the chromatogram after washing.

In the same manner as previously, we controlled the weight loss of oligomers after extraction in water at pH 7 and precipitation with pentane. The molecular weight of oligostyrene and the monomer conversion degree are compared at the end of reaction and after washing with water at pH 7 (Table 5).

Table 5 shows that the oligomers with the lower molecular weights are solubilized by washing with water at pH 7. For example, with  $C_0=10\%$ , carboxy-telechelic oligostyrenes are obtained with molecular weights of 1500 g mol; after washing, oligomers have molecular weights of  $1800 \text{ g mol}^{-1}$ , constituting a weight loss of 25%. With  $C_0=5\%$ , the weight loss in oligomers after extraction was lower (11%) and is explained by the fact that oligomers synthesized with  $C_0=5\%$  have  $M_n$  higher than for  $C_0=10\%$ . So water at pH 7 keeps soluble oligomers with very low  $M_n$  in solution much better than those from the reaction with  $C_0=10\%$ . In our case we needed to work with  $C_0$  less than 10% and the reaction with  $C_0$  of 5% is a good alternative for synthesis of oligostyrene with  $M_n$  of  $2000 \text{ g mol}^{-1}$ .

Moreover, the final yields obtained after precipitation with methanol (Table 3) were lower than those obtained after washing and precipitation with pentane (Table 5). For example, for  $C_0=10\%$  the final yield is about 60% after precipitation with methanol whereas we obtain about 60% after washing and precipitation with pentane. Therefore, a purification by washing with water at pH 7 followed by a precipitation in pentane was adapted to the synthesis of CTPS with low  $M_n$  (about  $2000 \text{ g mol}^{-1}$ ). In contrast, the precipitation with methanol could be used for polymers with higher  $M_n$ .

#### Characterization of the acid functionality

The acid functionality of oligostyrene synthesized with  $C_0=5\%$  and 10% was evaluated after extraction in water at pH 7 and precipitation in pentane. Two techniques were used:  $^1\text{H NMR}$  and conductimetric titration.

#### $^1\text{H NMR}$

With  $^1\text{H NMR}$ , in  $\text{DMSO-d}_6$ , we observe the proton

**Table 5.** Results of purification of carboxy-telechelic oligostyrene after extraction by washing with water at pH 7 and precipitation with pentane for  $C_0=5$  and 10%

$C_0$ (%)	Monomer conversion degree at the end of reaction (%)	Weight loss in oligomer after extraction by washing (%)	Final yield (%)	Molecular weight of oligomer at the end of reaction ( $\text{g mol}^{-1}$ )	Molecular weight of oligomers after washing ( $\text{g mol}^{-1}$ )
5	62	11	55	2000	2100
10	80	25	60	1500	1800

**Table 6.** Acid functionality of oligostyrene obtained by two techniques for reactions with  $C_0=10\%$  and  $5\%$ 

	$C_0$ (%)	$^1\text{H NMR}$	Conductimetric titration*
Functionality	10	1.96	1.85
$F_{\text{COOH}}$	5	1.90	1.90

\*  $F_{\text{COOH}} = \frac{V_{\text{OH}} \times C_{\text{OH}} \times M_n}{m}$  with  $M_n$  ( $\text{g mol}^{-1}$ ) determined by SEC,  $V_{\text{OH}}$  (l) the volume of titrant obtained by conductimetric and volumetric titrations,  $C_{\text{OH}}$  the concentration of titrant ( $0.05 \text{ mol l}^{-1}$ ),  $m$  (g) mass CTSP used for titration.

of the acid function. The comparison of the aromatic protons integration at 7 ppm ( $5 \times \overline{DP_n}$ ) with the acid protons integration at 12 ppm gave the acid functionality of oligostyrene. However, the results obtained by NMR have an accuracy of only  $\pm 5\%$  so that the acid content of different oligomers must be confirmed by conductimetric titration.

#### Conductimetric titration

The titration of acid functions was conducted using

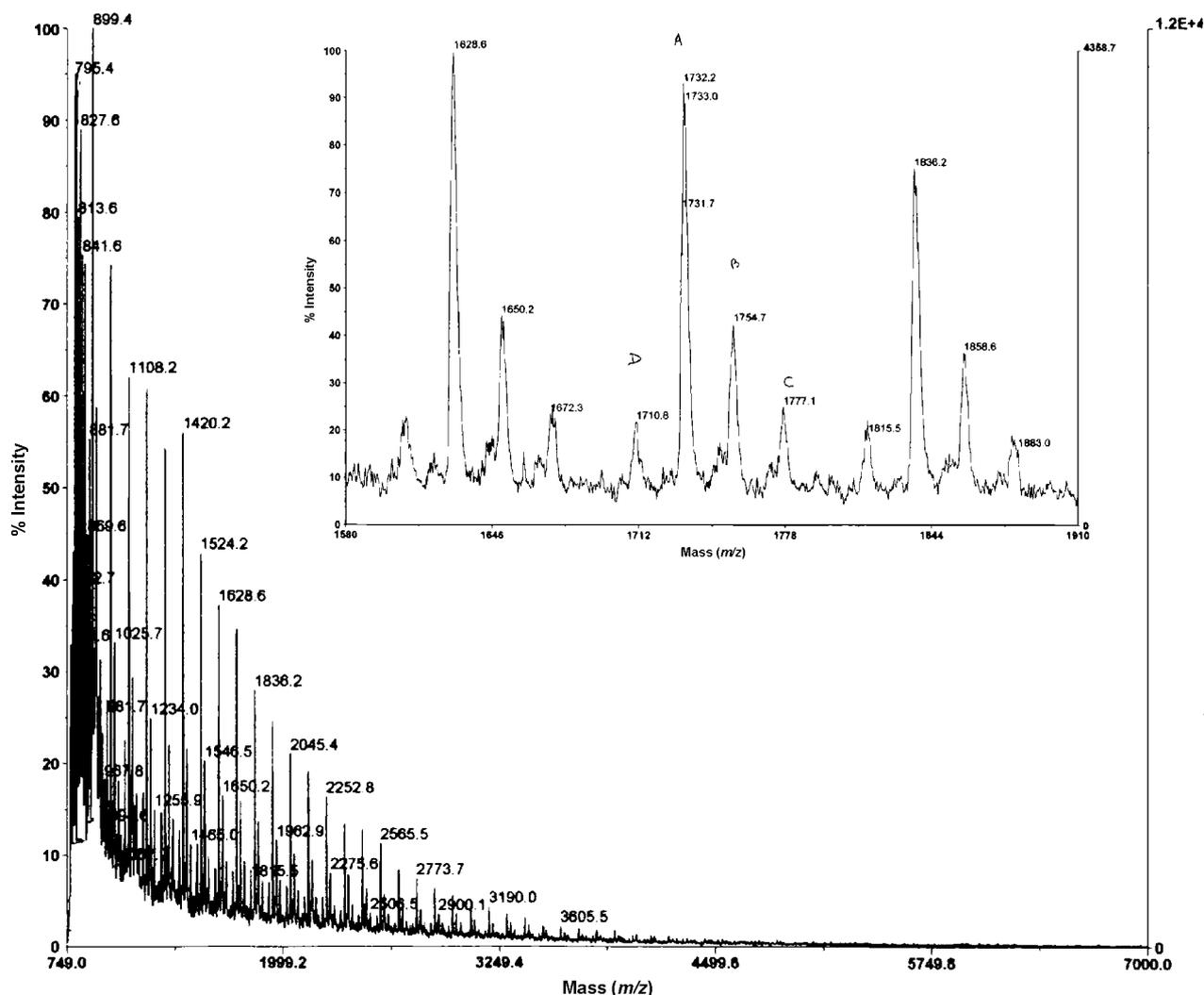
potassium hydroxide in methanol. Acetonitrile is preferred to THF as solvent because acetonitrile is a more dissociating solvent than THF. The acid functionality of oligostyrene can be calculated by using  $M_n$  determined by SEC and by volume of titrant.

The results are summarized in Table 6 and show that the two techniques give equivalent results for the synthesis of oligostyrene with  $C_0=5\%$  and  $10\%$ . We can therefore conclude that the products synthesized had two acid functions because the values of functionality are close to 2.

Lastly, a MALDI-TOF study was used in order to show that the major product obtained after purification is a carboxy-telechelic oligostyrene.

#### MALDI-TOF study

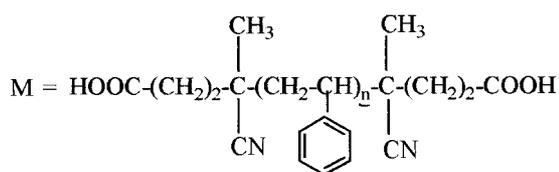
MALDI-TOF study of oligostyrene was investigated in linear mode. The chromatogram is showed in Fig 3. The reflectron mode was not used because, surprisingly, the signal-to-noise ratio was very bad. Thus the resolution was not good enough to reach the mono-isotopic mass but only more generally the average mass of each peak. However, the assignment of each peak



**Figure 3.** Analysis of oligostyrene via MALDI. Inset is an expansion of the mass spectrum showing several oligomer series.

**Table 7.** Four products of oligo-styrene obtained in the range from 1580–1910 Da

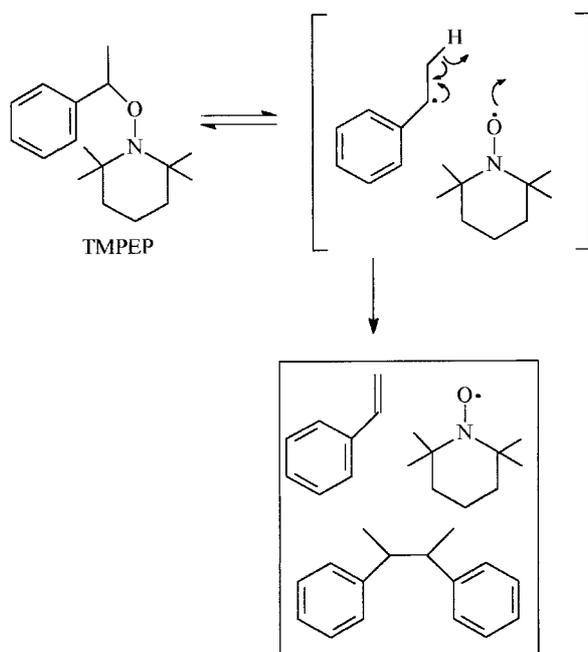
Series	Experimental mass (Da)	Calculated monoisotopic mass (Da)	Calculated average mass (Da)	Species	Structure
A	1731.7 1732.2 1733.0	1731.9771	1733.3899	1	$[M-Na]^+$ $n = 14$
B	1754.7	1753.9591	1755.3717	1	$\text{HOOC}-(\text{CH}_2)_2-\overset{\text{CH}_3}{\underset{\text{CN}}{\text{C}}}-\underset{\text{Ph}}{\text{(CH}_2-\text{CH})}_n-\overset{\text{CH}_3}{\underset{\text{CN}}{\text{C}}}-\text{(CH}_2)_2-\text{COONa}, \text{Na}^+$ $n = 14$
C	1777.1	1775.9410	1777.3535	1	$\text{NaOOC}-(\text{CH}_2)_2-\overset{\text{CH}_3}{\underset{\text{CN}}{\text{C}}}-\underset{\text{Ph}}{\text{(CH}_2-\text{CH})}_n-\overset{\text{CH}_3}{\underset{\text{CN}}{\text{C}}}-\text{(CH}_2)_2-\text{COONa}, \text{Na}^+$ $n = 14$
D	1710.8	1708.9764	1710.3987	2	$\text{HOOC}-(\text{CH}_2)_2-\overset{\text{CH}_3}{\underset{\text{CN}}{\text{C}}}-\underset{\text{Ph}}{\text{(CH}_2-\text{CH})}_n-\text{CH}=\underset{\text{Ph}}{\text{CH}}, \text{Na}^+$ $n = 14$
	not observed	1710.9921	1712.4147	3	$\text{HOOC}-(\text{CH}_2)_2-\overset{\text{CH}_3}{\underset{\text{CN}}{\text{C}}}-\underset{\text{Ph}}{\text{(CH}_2-\text{CH})}_n-\text{CH}_2-\underset{\text{Ph}}{\text{CH}_2}, \text{Na}^+$ $n = 14$



could be made. Four series were assigned for peaks ranging from 750 to 3900 Da corresponding to a maximum number average degree of polymerization of 34 as seen in the expansion of Fig 3. The inset in Fig 3 is labelled to show the four series A, B, C and D in the range of 1580–1910 Da. The major series A (Table 7) corresponds to the polystyrene diacid  $[MNa]^+$  and the series B and C to  $(M+2Na)^+$  and  $[M+3Na]^+$ , respectively. This peculiar behaviour has already been observed with matrices which are acid products and are very often cationized in the form  $(\text{COONa} + \text{Na})^+$  or  $(\text{COONa} + \text{K})^+$  or  $(\text{COOK} + \text{K})^+$ . Series D corresponds to the species 2 obtained by disproportionation

as already described in the literature.<sup>42</sup> Unfortunately the MALDI TOF spectrum cannot prove the presence of the species 3. Either species 3 with average mass of 1712.41 Da was very near species 2 with 1710.39 Da and so could be differentiated from it, or another kind of termination could operate as it has been shown by Li and Howell<sup>43</sup> with nitroxide-terminated polystyrene (Scheme 2).

The molecular weight of oligoStyrene, synthesized with  $C_0 = 10\%$  and after purification by washing, was calculated as  $c 1789 \text{ g mol}^{-1}$ . This result is an agreement with the molecular weight obtained by SEC of  $c 1800 \text{ g mol}^{-1}$  (Table 5).



**Scheme 2.** Mechanism of 2,2,6,6-tetramethyl-1(1-phenylethoxy)piperidine (TMPEP) decomposition.

## CONCLUSION

Styrene was polymerized with ACVA in DEP conditions to obtain carboxy-telechelic oligostyrene.

First, a kinetic study demonstrated that it was necessary to work with  $C_0$  about 5% in order to synthesize oligomer with molecular weight about  $2000 \text{ g mol}^{-1}$ . Thus a monomer conversion degree about 60% was obtained.

Second, SEC analysis characterizes the formation of many by-products of ACVA in DEP conditions. The extraction of these by-products was investigated and Ohishi's treatment was not suitable for the synthesis of carboxy-telechelic oligostyrene with molecular weight about  $2000 \text{ g mol}^{-1}$ . With this treatment, oligomers with lower molecular weight were extracted selectively in methanol.

Third, the purification of oligostyrene is optimized in order to extract ACVA by-products. Since ACVA by-products have acid functions these by-products are extracted in water at pH 7. With this technique, the loss in oligomer weight was lower: after extraction molecular weights of about  $2100 \text{ g mol}^{-1}$  with a final yield about 60% were obtained.

Finally, the acid functionality of oligostyrene was evaluated by  $^1\text{H}$  NMR and conductimetric titration. The two techniques led to a functionality of oligostyrene close to 2 with  $C_0$  of 5 and 10% which confirmed the synthesis of carboxy-telechelic oligostyrene.

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