Free-Radical Polymerization of Dimethyl Vinylbenzylphosphonate Controlled by Tempo

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ABSTRACT: The free radical polymerization of a phosphonated styrene, dimethyl vinylbenzylphosphonate (VBP), in the presence of stable nitroxide 2,2,6,6-tetramethyl-1-piperidinyloxyl radical (TEMPO), initiated by dicumyl peroxide (DCP) at 125 °C, has been studied. The apparent rate of polymerization $K_p[M^\bullet]$ is eight times higher than that of styrene, but the "living" character of the polymerization could not be verified by SEC. So, a macromolecular initiator PS−TEMPO was used in order to follow the evolution of average number molecular weights $\overline{M_n}$ by ^{1}H NMR. Under these conditions, the "living" character of the polymerization could be checked and various block copolymers (11000/7500; 11000/11000) were prepared. As for vinylbenzyl chloride and other monomers bearing electroattractive groups, the polymerization was shown to be much faster than that of styrene.

Introduction

Block copolymers with controlled architectures can find various industrial applications, for example, as dispersants, comptabilizers, and viscosity modifiers. The block copolymer synthesis can be carried out by ionic or radical polymerization. Ionic polymerization[1,2] is really the best method for the synthesis of such copolymers according to a living process with an excellent control of the polydispersity index (lower than 1.1). However, this method requires highly pure reagents, and the variety of monomers thus polymerizable is rather limited.

On the other hand, radical polymerization which is easier to perform, can be applied to a wide range of monomers. In the literature, different methods have been reported for the synthesis of block copolymers by radical polymerization[3] and they involve the use of multifunctional initiators[4−7] or macroinitiators,[8,9] bis telomerization,[10] or the telomerization with chemical modifications.[11,12] However, copolymers produced by these different ways cannot be compared to those synthesized by ionic polymerization, as far as molecular weights are concerned.

Recently, new methods of "living" nitroxide mediated radical polymerization have been proposed for the preparation of well-defined polymers with low polydispersities,[13−17] and the synthesis of block copolymers has been extensively studied[18−21] when using styrene as monomer. The radical polymerization controlled by TEMPO can be carried out in bulk, in solution, in suspension, or in emulsion. Up to now, no polystyrene/poly(dimethyl vinylbenzylphosphonate) (PS/PVBP) block copolymer has been synthesized. Only random copolymers were produced by chloromethylation of polystyrene[22] or from the copolymerization of polystyrene/poly(chloromethylstyrene)[23,24] followed by the phosphonation of these polymers by a Michaelis−Arbuzov reaction. It is the reason we have been interested in synthesizing these kinds of functional block copolymers (PS/PVBP). These block copolymers may be hydrolyzed in order to obtain an amphiphilic character.

The purpose of this work concerns the preparation and the characterization of this kind of block copolymers by TEMPO-mediated free-radical polymerization.

Experimental Section

Materials. Styrene (99%; Aldrich) was distilled over calcium hydride under reduced pressure before use. Dimethyl vinylbenzylphosphonate (VBP) (meta/para isomers mixture) was synthesized according to an Arbuzov[25,26] or a Michaelis−Becker[27] reaction. TEMPO (99%; Aldrich), Dicumyl peroxide (DCP) (98%; Aldrich) and the solvents were used as received.

Characterizations. Molar masses and polydispersities (in the case of PS−TEMPO) were determined by size exclusion chromatography (SEC) calibrated with polystyrene standards, using samples taken directly from the reaction mixture.

Size exclusion chromatography (SEC) was performed with a Spectra Physics Instruments SP 8810 pump and a Shodex Rise-61 refractometer detector (with tetrahydrofuran as the eluent at 30 °C and 0.8 mL/mn; two columns of PL gel mixed D).

^{1}H NMR spectra were obtained with a 200 MHz Bruker spectrometer (reference TMS). Monomer conversions were assessed by ^{1}H NMR using samples taken directly from the reaction. Molar masses of PS-*b*-PVBP-TEMPO block copolymers were also determined by ^{1}H NMR.

Purified phosphonated homopolymer (PVBP-TEMPO) and block copolymers (PS-*b*-PVBP-TEMPO) were also analyzed by ^{31}P NMR spectroscopy. Spectra were obtained on a 250 MHz Bruker spectrometer.

Polymerization of Styrene. In a Schlenk vessel, a solution of DCP (0.214 g, 7.95×10^{-4} mol) and TEMPO (0.248 g,15.9×10^{-4} mol) in styrene (25 g, 0.24 mol) was flushed thoroughly with argon for 30 mn. The reaction mixture was then immersed in an oil bath, which was preheated to 125 °C. The polymerization was conducted under argon atmosphere with magnetic stirring. For kinetic analyses, samples were withdrawn from the reactor. The monomer conversions were determined by ^{1}H NMR analysis on crude samples dissolved in $CDCl_3$. Molecular weights were determined by size exclusion

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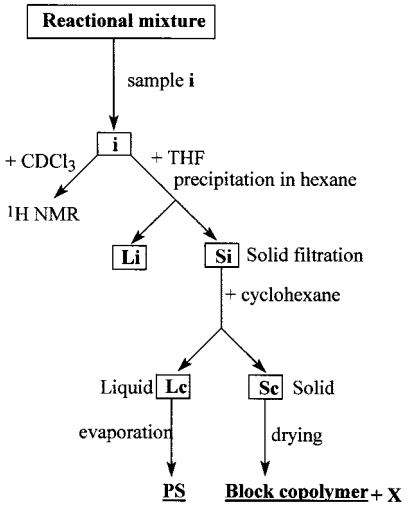
Scheme 1. General Scheme of Reactional Mixture Treatment



chromatography (SEC). When the desired molar mass was obtained, the reaction mixture was cooled, diluted with THF, and precipitated into an excess of methanol. TEMPO-terminated polystyrene was isolated by filtration and dried under vacuum (10^{-2} mmHg) at 25 °C for 2 h to yield a white powder.

Polymerization of Phosphonated Styrene (VBP). The same procedure was used as that for styrene but with a solution of DCP (40.55 mg, 150 μmol) and TEMPO (46.87 mg, 300 μmol) in phosphonated styrene (6.00 g, 26.5 mmol). The phosphonated styrene conversion was determined by ^{1}H NMR analysis on crude samples dissolved in acetone-d_6. The final PVBP−TEMPO was isolated by precipitation in an excess of hexane and dried under vacuum (10^{-2} mmHg) at 25 °C for 2 h to yield a white powder.

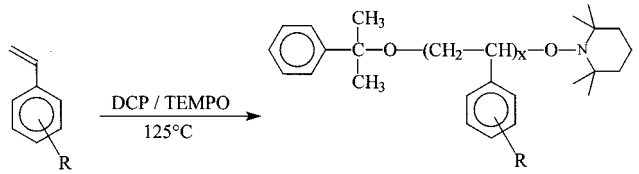
The thermal homopolymerization of VBP was succeeded by heating 6.0 g of VBP in *tert*-butylbenzene (3.0 mL) at 125 °C under argon atmosphere with magnetic stirring. For kinetic analyses, samples were withdrawn from the reactor. Conversion was determined by ^{1}H NMR analysis on crude samples dissolved in acetone-d_6. The final homopolymer (PVBP) was isolated by precipitation in an excess of hexane and dried under vacuum (10^{-2} mmHg) at 25 °C for 2 h to yield a white powder.

Polymerization of Phosphonated Styrene with PS—TEMPO as the Macroinitiator: Synthesis of Block Copolymers. In a typical run, 3.00 g (272.7 μmol) of PS−TEMPO ($\overline{M}_n$ = 11 000 g mol^{-1}, I_p = 1.18) and 6.00 g of VBP (13.3 mmol) were dissolved in *tert*-butylbenzene ([VBP] = 8.85 mol L^{-1}) in a Schlenk reactor. The mixture was flushed thoroughly with argon for 30 min and then immersed in an oil bath preheated to 125 °C. In the course of the polymerization, samples were taken directly from the mixture and treated as shown in Scheme 1. One part of each sample was dissolved in $CDCl_3$ and analyzed by ^{1}H NMR to assess the conversion. The remaining sample was first diluted in THF, and then the mixture was dropped into hexane to precipitate all the polymers and copolymers. These solid products (Si), after extractions in cyclohexane, gave copolymers (Sc) which were dried under vacuum at 40 °C and analyzed. Molar masses were determined by ^{1}H NMR as shown previously. The liquid phase (Lc), after evaporation, may contain the homopolymer PS−TEMPO (soluble in cyclohexane) which was analyzed by ^{1}H NMR.

Results and Discussion

I. Synthesis of Polystyrene and Phosphonated Polystyrene Terminated by TEMPO. The controlled radical polymerization of various monomers by nitroxide radicals initiated with different initiators has been extensively studied by many authors.[14] After a review of the literature,[28,29] we chose dicumyl peroxide (DCP) as the initiator for the study presented herein. In contrary to benzoyl peroxide, no reaction should occur between TEMPO and DCP.[28,29] The decomposition temperature of the initiator must be below 130 °C in order to avoid a major contribution of the thermal polymerization. This initiator has been reported to have an efficiency close to one and a half-life of 1 h at 125 °C.[28,29]

Scheme 2. Homopolymerization of Styrene or Dimethyl Vinylbenzylphosphonate



The general scheme is given in Scheme 2.

For the first time, the polymerization of styrene in bulk controlled by TEMPO was carried out with DCP at 125 °C (Scheme 1, R = H). The reagents were used in the following ratios:

$$[T]_0/[I_2]_0 = 2; \quad [M]_0/[T]_0 = 150; \quad \text{and } [I_2]_0/[M]_0 = 1/300$$

where T, I_2, and M represent TEMPO, initiator (DCP), and monomer, respectively.

In the course of the polymerization, samples were taken directly from the mixture and were characterized by ^{1}H NMR to evaluate the conversion of styrene, and they were analyzed by SEC to determine the average number molecular weights and the polydispersity index. The final alkoxyamine (PS−TEMPO) was recovered by precipitation in methanol, dried under vacuum (10^{-2} mmHg), and characterized by ^{1}H NMR (Figure 1).

In Figure 1, besides the characteristic signals for polystyrene, a signal corresponding to the protons of TEMPO was noted at about 1 ppm.

Figure 2 shows the evolution of the experimental molar masses $(\overline{M}_n)_{exp}$ vs the styrene conversion. The linear character of the plots and the good agreement with the theoretical curve of molecular weights confirm the "living" character of the polymerization.

As shown in Figure 3, the plot of $\ln([M]_0/[M])$ vs time is linear. The slope of this line that corresponds to $K_p[M^\bullet]$ is equal to 4.2×10^{-5} s^{-1} (polymerization of styrene).

Bertin et al.[28,29] obtained the value 2.5×10^{-4} s^{-1} when they worked in conditions close to ours. Puts[30] and Veregin,[31] who performed the polymerization with the BPO/TEMPO system, found a value close to 3×10^{-5} s^{-1}. These surveys show that our results are suitable.

This method has been used to prepare a large quantity of PS−TEMPO ($\overline{M}_n$ = 11 000 g mol^{-1}).

To show that PS−TEMPO is able to reinitiate the polymerization of styrene, we have carried it out with this macroinitiator at 125 °C. The results show that molar masses, determined by SEC, increase linearly according to the reaction time.

I.2. Synthesis of Poly(dimethyl vinylbenzylphosphonate)—TEMPO (PVBP—T). The polymerization of phosphonated styrene controlled by TEMPO was

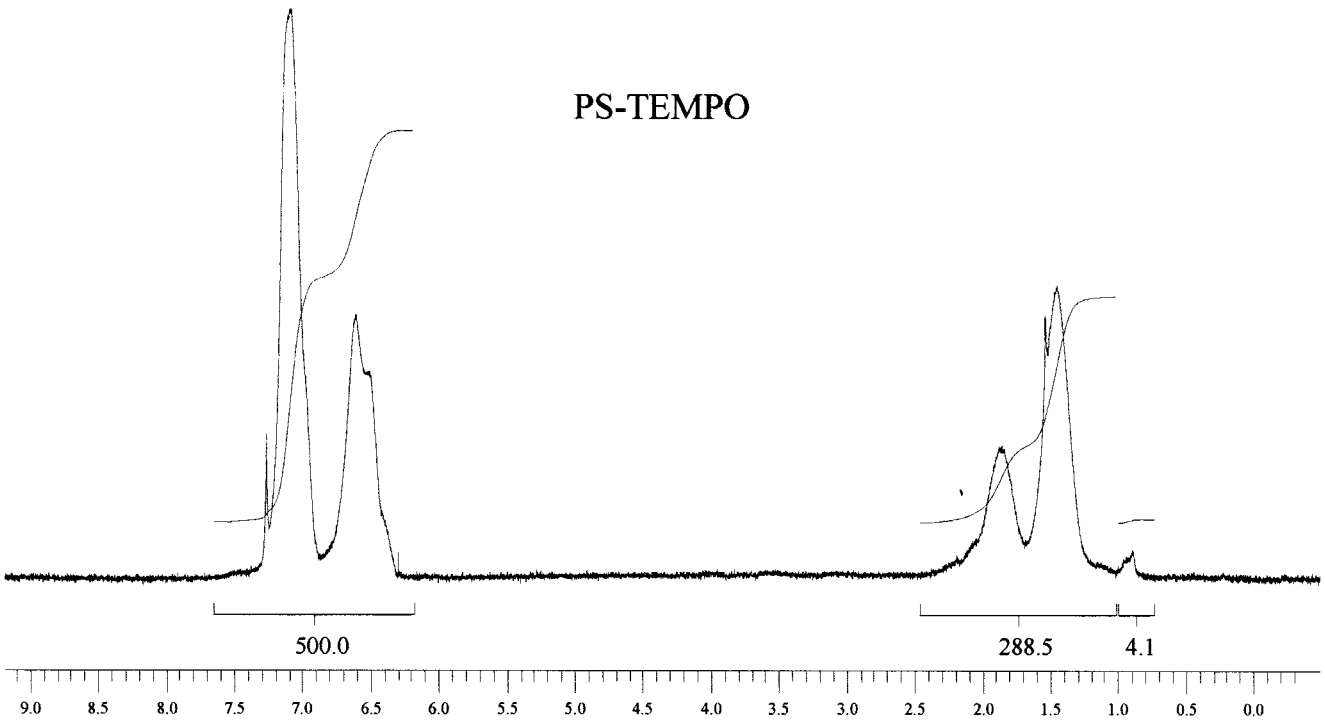


Figure 1. ^{1}H NMR spectrum ($CDCl_3$) of PS−TEMPO.

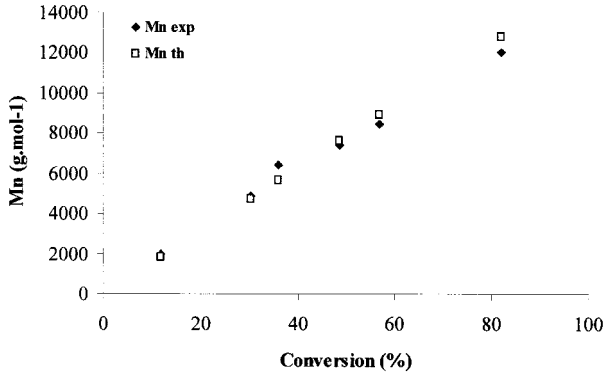


Figure 2. $\overline{M_n}$ dependence vs conversion for bulk polymerization of styrene at 125 °C.

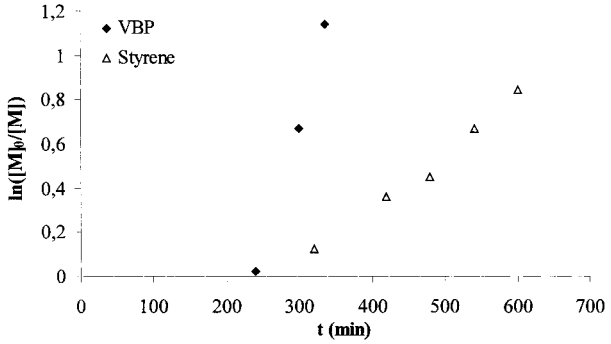


Figure 3. Variation of $\ln([M]_0/[M])$ vs time for bulk polymerizations of styrene and dimethylvinylbenzylphosphonate (VBP) at 125 °C in the presence of DCP/TEMPO system.

studied, and as it is not possible to control the average number molecular weights by SEC taking into account the special adhesive properties of phosphonates, we have only studied the variation of the phosphonated monomer concentration vs time.

The polymerization of the phosphonated styrene (VBP) in the presence of DCP/TEMPO system was carried out in bulk at 125 °C according to Scheme 1 (R = $CH_2-P(O)(OCH_3)_2$) involving the reagents in the following proportions:

$$[T]_0/[I_2]_0 = 2; \quad [M]_0/[T]_0 = 88;$$
$$\text{and } [I_2]_0/[M]_0 = 1/176$$

In the course of the polymerization, aliquots were sampled directly from the mixture and characterized by ^{1}H NMR to evaluate the conversion of the phosphonated monomer.

According to Figure 3 it is noted that the polymerization of VBP in the presence of DCP/TEMPO system at 125 °C is very fast. The slope $K_p[M^\bullet] = 1.93 \times 10^{-4}$ s^{-1} is about five times higher than that assessed in the case of styrene.

Lacroix-Desmazes et al.[32] have reported that the polymerization of vinylbenzyl chloride (VBC) in the presence of AIBN/TEMPO system at 130 °C was much faster than that of styrene. The value of $K_p[M^\bullet]$ for VBC is 1.2×10^{-4} s^{-1}.

Similarly, Quillot[33] reported that the introduction of electrowithdrawing groups such as SiR_3, located in the para-position, resulted in a 3-fold increase of the slope. That could be due to a decrease of the electron density in the double bond.

In the ^{1}H NMR spectrum (Figure 4), besides the signals of the polystyrene, two other signals at 3.1 and 3.6 ppm are observed, corresponding respectively to the methylene group between the aromatic ring and the phosphorus atom, while both methoxy groups of the phosphonate integrations confirm the structure (II, *x*).

II. Synthesis of PS-*b*-PVBP—TEMPO Block Copolymers. It was worth synthesizing polystyrene-*b*-poly(phosphonated styrene) block copolymers with controlled architecture and average number molecular weights of about 11000/4000 (amphiphilic character). As the PS−TEMPO must be in excess compared to phosphonated styrene, which is slightly viscous, it was

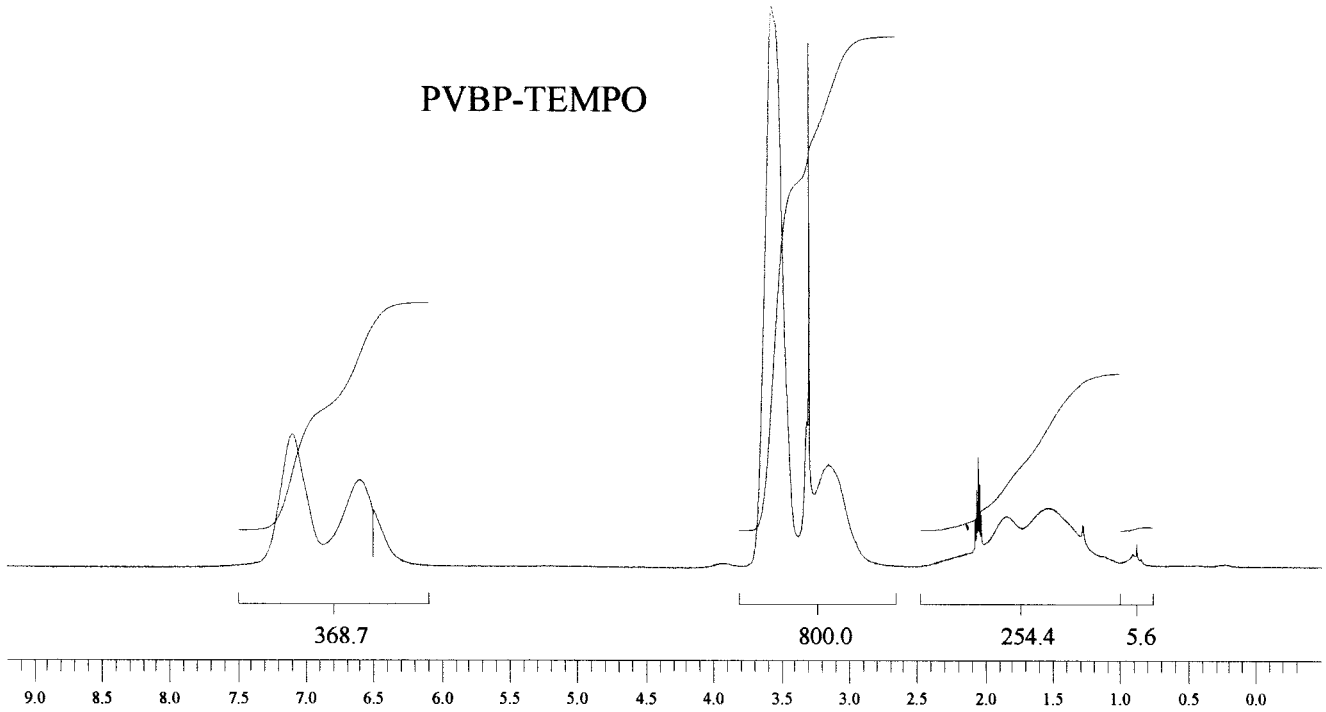
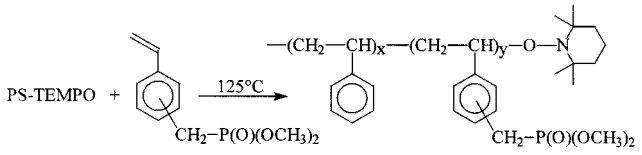


Figure 4. ^{1}H NMR spectrum (acetone-d_6) of PVBP−TEMPO.

Scheme 3. Synthesis of PS-*b*-PVBP Block Copolymer



difficult to dissolve PS−TEMPO into the phosphonated monomer. Interestingly, the literature mentions that several solvents were used for the synthesis of block copolymers such as ethyl acetate,[34] DMSO,[34] DMF,[35] xylene,[36,37] or benzene.[38,39] To avoid the transfer reactions to solvent with TEMPO,[40] *tert*-butylbenzene was selected as solvent. Although its boiling point is high (169 °C), this solvent does not transfer.

The polymerization of VBP initiated by PS−TEMPO (I, x) ($\overline{M}_n$ = 11 000 g mol^{-1}) was carried out in *tert*-butylbenzene at 125 °C (Scheme 3).

We first proved the existence of block copolymers and then we improved the reaction conditions in finding a dilution value and a method to control the molecular weights since the SEC does not give access to these fundamental data.

II.1.1. Proof of the Existence of Block Copolymers. Several experiments were required to prove that the products resulting from copolymerization were mainly block copolymers. First, a research of specific solvents to solubilize or precipitate the three potential components of crude product of the reaction. So, we prepared PS and PVBP homopolymers with molar masses corresponding to those aimed in copolymerization. Those homopolymers precipitated from methanol and from hexane but not in acetone or in tetrahydrofuran that are regarded as good solvents of both homopolymers. Only cyclohexane is a peculiar solvent because it solubilizes PS but not PVBP. From 2.50 g of the crude product of the reaction and after the solubility test in cyclohexane we obtained 0.10 g (12%) of a polymer whose ^{1}H NMR analysis shows the characteristic NMR chemical shifts of polystyrene without any ambiguity. As a matter of fact, polystyrene can be either PS−T, which did not react, or inactive PS produced by bimolecular recombination in the course of the synthesis of the PS−T (Priddy et al.[41] estimated its quantity to 10%) or finally the result of various transfers.

There remained 88% of a mixture which could be the block copolymer and or the homopolymer PVBP obtained by thermal initiation taking in account the peculiar behavior of styrenic derivatives. We have studied this reaction at 125 °C in *tert*-butylbenzene under the same conditions of the copolymerization (6.00 g of VBP in 3.0 mL of solvent). Figure 7 represents ln([M]$_0$/[M]) vs time from the copolymerization and the thermal homopolymerization. That shows clearly that the latter is very slow and that more than 90% of the mixture was composed of the block copolymer.

II.1.2. Determination of Molar Masses by ^{1}H NMR. Since it was not possible to determine the average number molecular weights of these phosphonated block copolymers by SEC, the ^{1}H NMR was used to assess these $\overline{M}_n$, according to the ratio of the integral of the eight protons from the phosphonic groups −C**H**$_2$−P(O)(OC**H**$_3$)$_2$ and the aromatic protons.

Considering a block copolymer of general developed formula (III, x, y) (Scheme 3) and the ^{1}H NMR spectrum (Figure 5), the ratio x/y can be calculated according to the following method:

If h_e represents the integral of all protons of −C**H**$_2$−P(O)(OC**H**$_3$)$_2$ and h_a that of the aromatic protons, it can be written as

$$\begin{bmatrix} 8y \sim h_e \\ 5x + 4y \sim h_a \end{bmatrix} \Rightarrow \frac{x}{y} = \frac{8}{5h_e}\left(h_a - \frac{h_e}{2}\right)$$

with $x = [\overline{M}_n(\text{PS−T}) - M(\text{TEMPO}) - M(\text{DCP}/2]/104$

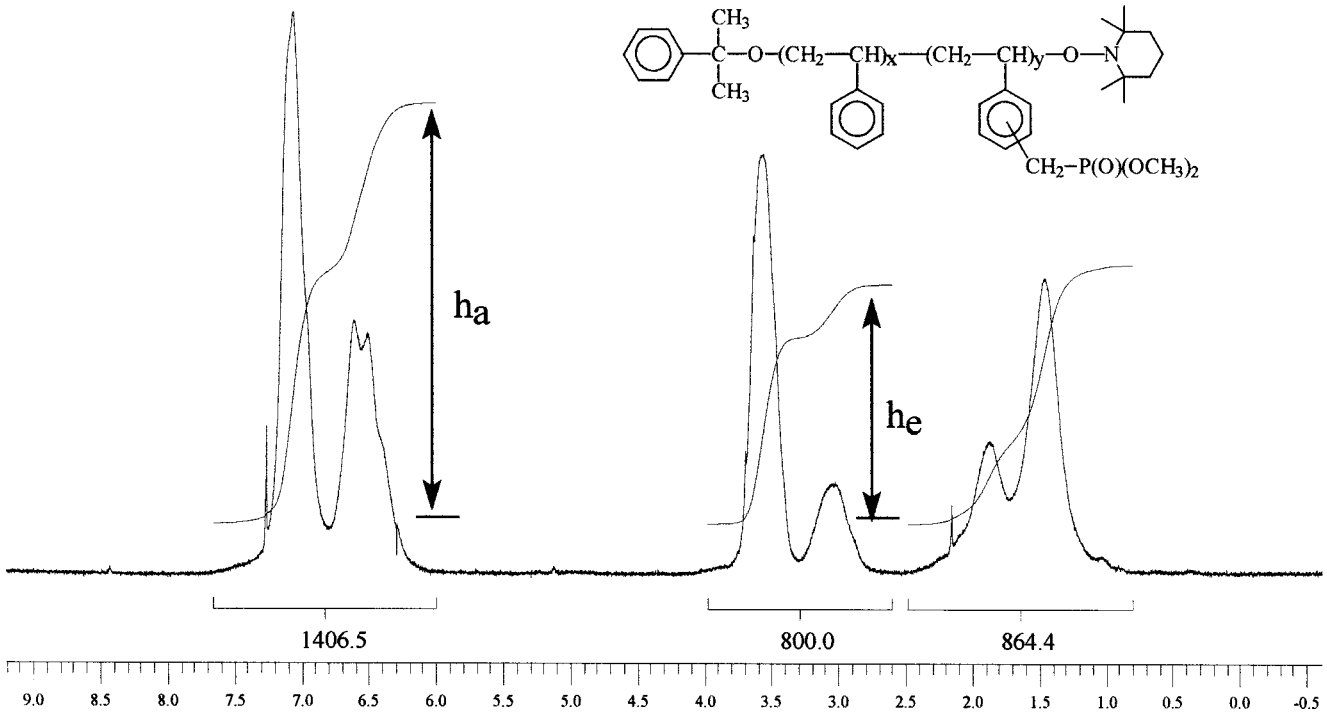


Figure 5. ^{1}H NMR spectrum ($CDCl_3$) of PS−PVBP−TEMPO.

Table 1. Operating Conditions, $\overline{M_n}$ and I_p of Block Copolymers Prepared at 125 °C in Solution (*tert*-Butylbenzene) Using PS−TEMPO ($\overline{M_n}$ = 11000 g·mol^{-1}, I_p = 1.18) as Macroinitiator

m_{VBP}/m_{PS-T}	[VBP] (mol·L^{-1})	duration (h)	convn (%)	*y*/*x*	$\overline{M_n}$exp (^{1}H NMR) (g mol^{-1})	$\overline{M_n}$th (g mol^{-1})	$\overline{M_n}$exp (SEC) (g mol^{-1})	I_p
0.69	0.90	76	70	0.32	18 500	16 500	12 100	1.18
2.00	3.23	03	53	0.47	22 000	22 700	10 250	1.17

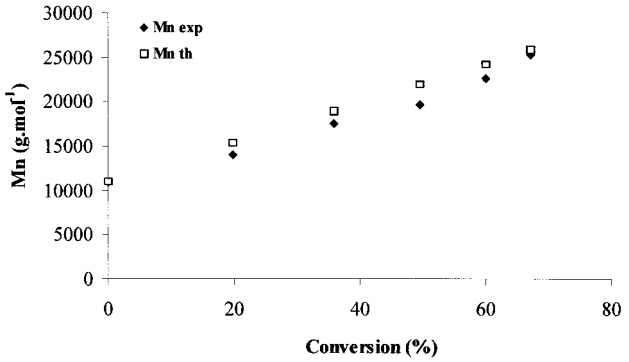


Figure 6. Evolution of $\overline{M_n}$ vs the VBP conversion for polymerization of dimethyl vinylbenzylphosphonate (VBP) initiated by PS−TEMPO macroinitiator at 125 °C.

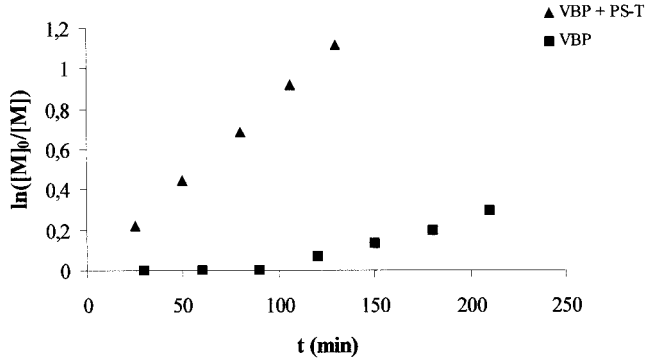


Figure 7. Evolution of ln([M]$_0$/[M]) vs time for the thermal homopolymerization of dimethyl vinylbenzylphosphonate (VBP) and for its copolymerization with PS−TEMPO at 125 °C.

and $\overline{M_n}$(PS-T), *M*(TEMPO), and *M*(DCP)/2 being 11000, 156.5, and 135, respectively.

II.1.3. Influence of the Dilution. Two experiments were performed, and the results are summarized in Table 1. After purification, the resulting block copolymers were analyzed by ^{1}H NMR. The results show that the reaction slows down when the dilution increases. This phenomenon is in agreement with the results reported in the literature regarding the influence of the solvent on the living free radical polymerization of styrene.[36,42] On the other hand, in both cases, $(\overline{M_n})_{th}$ and $\overline{M_n}$ (assessed by ^{1}H NMR) were in good agreement.

Moreover, the evolution of ln([M]$_0$/[M]) vs time gave both following values of K_p[M$^\bullet$]: 5 × 10^{-6} and 4 × 10^{-5} for a weight ratio ($m_{(VBP)}/m_{(PS-TEMPO)}$) of 0.69 and 2, respectively (where $m_{(VBP)}$ and $m_{(PS-TEMPO)}$ represent the corresponding weights used in the copolymerization). We observe that the last value (4 × 10^{-5}) is comparable to the one obtained for polymerization in bulk (1.93 × 10^{-4} s^{-1}). Hence, a $m_{(VBP)}/m_{(PS-TEMPO)}$ weight ratio value of 2 was chosen for the study below.

II. 1.4. Confirmation of the "Living" Character of VBP Free Radical Polymerization. To confirm the living character of polymerization of phosphonated styrene in the presence of PS−TEMPO and in solution (*tert*-butylbenzene), the reaction was carried out according to the following conditions:

$$m_{(VBP)}/m_{(PS-T)} = 2 \quad \text{and} \quad [VBP] = 3.23 \text{ mol L}^{-1}$$

The molar mass was 33000 g mol^{-1} with 100% monomer conversion.

In the course of the polymerization, samples were taken directly from the mixture and analyzed as described in the Experimental Section. We adopted the same treatment as first described (Scheme 1) for the purification of block copolymers. Thus, only pure phosphonated block copolymers remain in the resulting samples.

The evolution of $\overline{M}_n$ (assessed by ^1H NMR) vs monomer conversion is linear (Figure 6), which shows the "living" character of polymerization of VBP initiated by TEMPO. However, $\overline{M}_n$ determined by SEC do not confirm this living character although the proportion of PVBP block increases with the reaction time in the block copolymer.

Figure 7 represents the $\ln([M]_0/[M]) = f(t)$ relationship, which is linear, and $K_p[M^\bullet] = 1.43 \times 10^{-4}\ s^{-1}$. This value confirms the one of homopolymerization of phosphonated styrene ($1.93 \times 10^{-4}\ s^{-1}$). VBP polymerization is faster than that of styrene in the presence of DCP/TEMPO system ($4.2 \times 10^{-5}\ s^{-1}$) at 125 °C.

Conclusion

The radical polymerization of styrenic monomer bearing phosphonic groups of formula $CH_2{=}CH{-}C_6H_4{-}CH_2{-}P(O)(OCH_3)_2$, in the presence of stable nitroxide radicals (TEMPO) and initiated by dicumyl peroxide at 125 °C was studied. Considering the difficulty of direct analyses by SEC to evaluate the molar masses, a macromolecular initiator (PS−TEMPO) with a molar mass of 11000 g mol^{-1} was prepared and ^1H NMR spectroscopy was used for a kinetic study of the polymerization. This polymerization was perfectly controlled and original copolymers, potentially amphiphiles after hydrolysis of phosphonic esters were prepared (11000/7500 and 11000/11000). Moreover, it was shown from the values of $\ln([M]_0/[M])$ vs time, that polymerization of VBP was 5−8 times faster than that of styrene depending on the dilution and that confirms the effect of electrowithdrawing groups linked to an aromatic ring.

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