

Controlled radical polymerization

Synthesis of chloromethyl styrene/styrene block copolymers

Denis Bertin, Bernard Boutevin

Laboratoire de Chimie Appliquée, UPRES A 50760, Ecole Nationale Supérieure de Chimie de Montpellier, 8, Rue de l'Ecole Normale, F-34053 Montpellier Cedex 1, France

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Summary

The free radical polymerization of chloromethylstyrene (CMS) with benzoyl peroxide (BPO) as initiator and 2,2,6,6-tetramethyl-1-piperidinyl-1-oxyl (Tempo) as counter radical was studied. The living character was demonstrated by the linear dependence of \overline{M}_n versus conversion like that the control with polydispersity lower than 1.5. In a second step, styrene was introduced in polychloromethylstyrene capped with Tempo to produce PCMS-b-PS block copolymers (12,000 / 60,000) with and PCMS-Tempo macroinitiator efficiency closed to 85%.

Introduction

Block copolymers have several applications in industry and several researchers have studied different kinds of polymerization to prepare block copolymers.

Ionic polymerization is really the best method since the "living character" of such a polymerization is now proved (generally the control of the polydispersity of polymers is excellent with polydispersity (PD) lower than 1.1). Nevertheless, this kind of polymers is difficult to prepare (no oxygen, no moisture, high purity of monomers) and quite a few monomers (Styrene, Butadiene, MMA) are consequently involved in industrial processes.

On the other hand, radical polymerization, which is easier to perform, offers a lot of solutions to synthesize block copolymers. The first one concerns the use of initiators which have two thermolabile groups with different decomposition temperatures to realize polymerization in two steps⁽¹⁻³⁾. Other workers⁽⁴⁾ have studied similar initiators but with one thermolabile group whereas the second one is photolabile. But the main problem deals with homopolymers that are produced from one of the fragments of the initiator. In order to

avoid such a drawback, one solution was to introduce a thermolabile group in the polymeric chain^(5,6).

An other way of research is telomerization (bistelomerization⁽⁷⁾ and telomerization with chemical modification^(8,9)) which allows to synthesize block copolymers.

However, copolymers produced by the different ways described above are not really comparable to those synthesized by ionic polymerization, particularly as far as molecular weights are concerned.

In 1980, a new concept was introduced in free radical polymerization : the "Living Character". One of the well known researchers was Otsu et al.⁽¹⁰⁾ who used iniferters (such as tetraalkylthiuram disulfides) by photochemical way in order to obtain the second sequences⁽¹¹⁾. But Iniferters are not a real way to synthesize block copolymers because some researchers^(12,13) have studied more precisely this system and have demonstrated the presence of homopolymers and the lack of functionality in the second step. Other molecules are tetraphenyl ethanes⁽¹⁴⁾ which were used to produced block copolymers but it is necessary that second monomers are disubstituted such as MMA or α -Me-Styrene.

The best way to achieve the "Living Character" was the use of stable free radicals such as nitroxide radicals⁽¹⁵⁻²¹⁾. Actually, nitroxide radicals seem to be the best solution to get rid off transfer reactions, bimolecular termination reactions, and thus free radical polymerization has a similar tendency to behave like ionic polymerization.

In order to synthesize Polychloromethylstyrene/Polystyrene block copolymers, we have searched the different ways of synthesis. Ionic polymerization was eliminated because lateral chlorine atoms deactivate the growing species. Thus, a protection of the functional groups would be necessary. On the other hand, only statistic copolymers are produced by chloromethylation^(22,23) of polystyrene ; however such copolymers can be directly synthesized by the radical polymerization^(24,25). So presently no Polystyrene/Polychloromethylstyrene block copolymers were synthesized. Taking into account our first results on the polymerization of styrene with Tempo⁽¹⁷⁾, where we have shown that autopolymerization of styrene was not a disadvantage, due to a control of all radicals by stable free radicals such as Tempo, we have found interesting to study in this present article the homopolymerization of chloromethylstyrene (CMS) and then use it as macroinitiator with styrene in order to obtain CMS-Styrene block copolymers.

Experimental Section

(a) \square Polymerizations : Bulk polymerizations of styrene or chloromethylstyrene were performed using benzoyl peroxyde (BPO) as initiator in the presence of 2,2,6,6-tetramethyl-1-piperidinyloxy (Tempo) stable free radical.

Polymerizations were carried out with distilled monomers, under a nitrogen flow and vigourous stirring.

Molecular weights and polydispersities were determined by Gel Permeation Chromatography (GPC) calibrated with polystyrene standards, using samples taken directly from the reaction mixture.

Gel permeation chromatography (GPC) was performed with a Spectra Physics instrument SP8810 pump and a Shodex RE 61 RI detector (eluent THF, 30°C, colums PL gel 5 μ , 50 A, 100 A and Styragel HR2).

(b) \square $^1\text{H NMR}$: Spectra were obtained on a Bruker 250 MHz spectrometer. Monomer conversions were determined by $^1\text{H NMR}$ using samples taken directly from the reaction.

Results and Discussion

According to the literature and to our previous works⁽¹⁷⁾, nitroxide radicals allow to achieve the living character of free radical polymerization of styrene in particular by the relationship \overline{M}_n vs monomer conversion correlation and low polydispersity. On the contrary, no study was realized on the polymerization of chloromethylstyrene (CMS). Consequently, we have studied the polymerization of chloromethylstyrene initiated by benzoyl peroxide (BPO) in the presence of Tempo. According to literature⁽¹⁶⁾, benzoyl peroxide is the most used initiator for the polymerization of styrene in the presence of Tempo in a initial molar ratio $\frac{(\text{Tempo})_0}{(\text{BPO})_0} = 1.3$.

This value is due to the low efficiency of BPO (ca 0,6) because there is an induced decomposition of BPO by Tempo (homosolvolytic reaction)^(26,27).

So for the polymerization of CMS, same experimental conditions were used i.e. at 130°C, 4,4.10⁻² mol.l⁻¹ of benzoyl peroxide, 5,6.10⁻² mol.l⁻¹ of Tempo were mixed in 10 g of chloromethylstyrene. Before heating, the mixture was purged and placed under nitrogen atmosphere.

During the polymerization, samples were taken directly from the mixture and were characterized by ^1H NMR for the conversion and analyzed by GPC for the average molecular weight in number and polydispersity.

The experimental molecular weight $(\overline{M}_n)_{\text{exp}}$ was compared to the theoretical one $(\overline{M}_n)_{\text{th}}$. The last one is calculated with the equation giving the degree of polymerization (\overline{DP}_n) as follows : $(\overline{DP}_n)_{\text{cum}} = \frac{\Delta M}{2\Delta I_2}$ where ΔM , ΔI_2 , represent the monomer consumption and the initiator consumption, respectively.

Figure 1 shows average molecular weight in number (\overline{M}_n) versus conversion for the bulk polymerization of chloromethylstyrene.

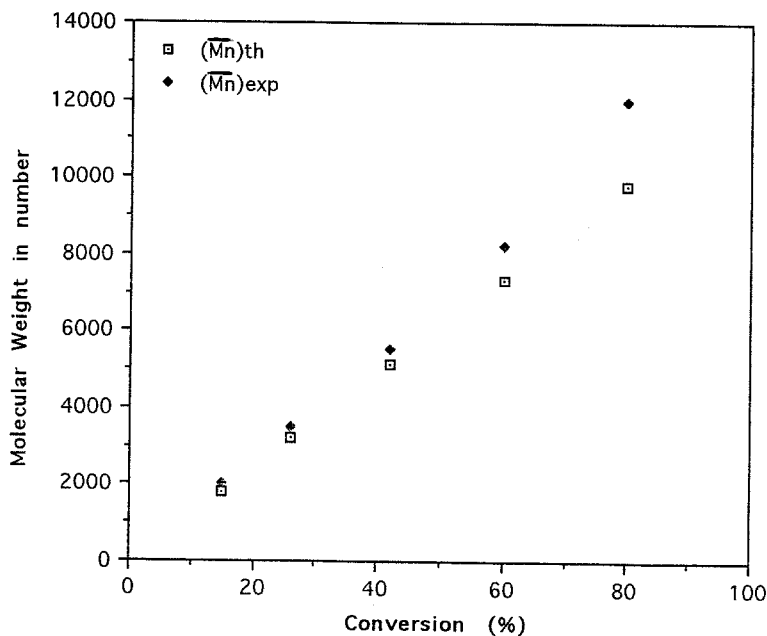


Fig. 1 : \overline{M}_n dependence versus conversion for bulk polymerization of chloromethylstyrene initiated by BPO ($4,4 \cdot 10^{-2} \text{ mol.l}^{-1}$) in the presence of Tempo ($5,6 \cdot 10^{-2} \text{ mol.l}^{-1}$) at 130°C .

Compared to the polymerization of styrene with BPO/Tempo system, the polymerization of chloromethyl styrene is similar with respect to molecular weight, polydispersity and kinetic of polymerization. The living character is evidenced by the linear dependence of \overline{M}_n versus conversion as for styrene.

Furthermore, it can be noted that the theoretical molecular weights are always lower than the experimental ones. This can be explained by the low efficiency of BPO. The presence of benzylchloride groups is confirmed by ^1H NMR spectrum, (Figure 2), by the peak at 4.5 ppm which demonstrates that no transfer exists between chloride atom and Tempo.

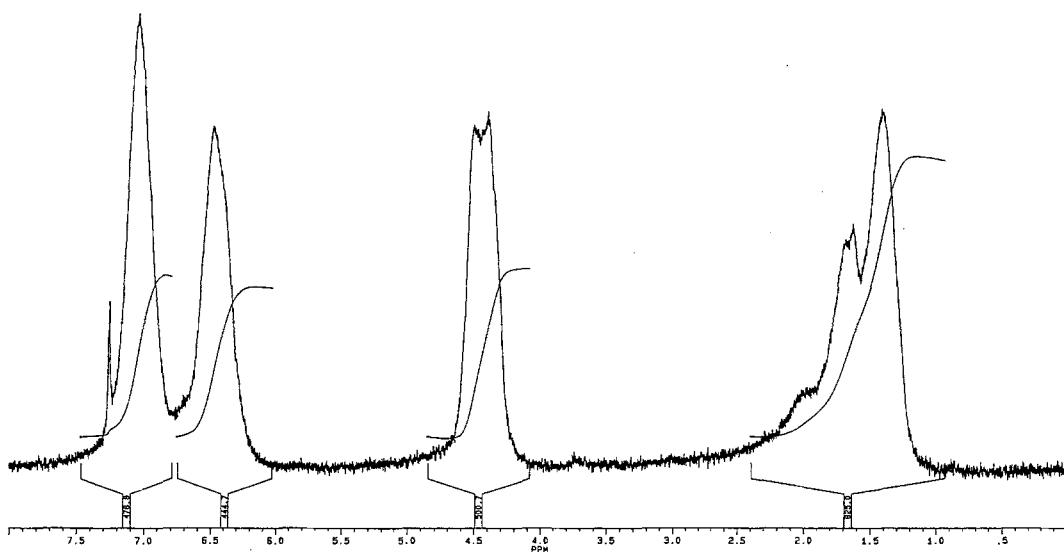
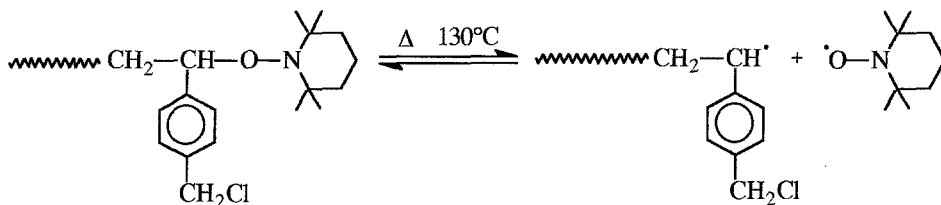


Fig. 2 : ^1H NMR spectrum of the polychloromethyl styrene with $\overline{M}_n = 12,000$ and PD = 1,5

The polychloromethyl styrene purified by precipitation in methanol was used as a macroinitiator, in order to use the reversible termination of such molecules. This concept is represented by Scheme 1 :



Scheme 1 : Reversible termination of alkoxyamines.

As nitroxide radicals can not initiate the polymerization, only macroradicals produced by heating the polychloromethylstyrene higher than 120°C, are able to reinitiate a new polymerization.

The second monomer used was styrene. In order to produce PCMS-b-PS block copolymers, 1 g of polychloromethyl styrene was solubilized in 5 g of styrene and the mixture was heated at 130°C under a nitrogen atmosphere. After only 5 hours, 80% monomer conversion and a polymer with $\overline{M}_n = 72,000$ and PD = 1.8 were observed. The macroinitiator efficiency could be determined by the ratio $(\overline{M}_n)_{th} / (\overline{M}_n)_{exp}$ where $(\overline{M}_n)_{th}$ is the average theoretical molecular weight in number and $(\overline{M}_n)_{exp}$ is the experimental one

$(\overline{M}_n)_{th} = \frac{\Delta[M]}{[P-T]} \times 104 + \overline{M}_{n,P-T}$ where $\Delta[M]$ is the monomer consumption, in mol.l⁻¹, [P-T] the macroinitiator concentration in mol.l⁻¹, 104 the value of the monomer molecular weight in g.mol⁻¹. In this case $\Delta[M] = 6.96$ mol.l⁻¹, $[P-T] = 1.51 \cdot 10^{-2}$ mol.l⁻¹ and $\overline{M}_{n,P-T} = 12000$ g.mol⁻¹, so $(\overline{M}_n)_{th} = 59800$ g.mol⁻¹.

Thus, the efficiency of the macroinitiator is closed to 0.83.

This allows to conclude that at least 83% of the polychloromethylstyrene which is used as macroinitiator is terminated by Tempo. Figure 3 shows the evolution of GPC curves during the second step i.e. the synthesis of PCMS-b-PS copolymers.

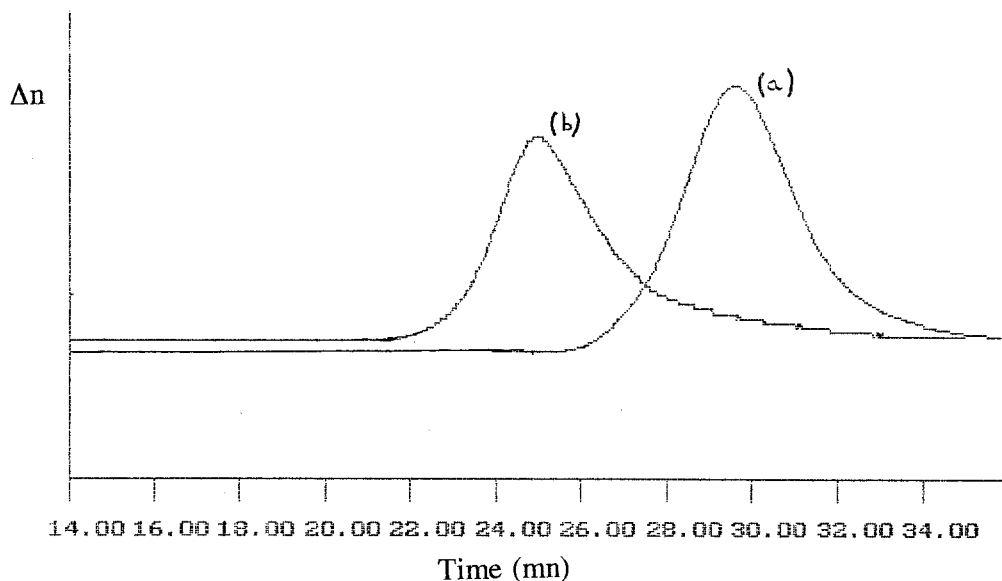


Fig. 3 : Evolution of GPC curves during the block copolymerization ((a) polychloromethylstyrene macroinitiator (b) polychloromethylstyrene/polystyrene block copolymer).

At the end of the reaction, a GPC chromatogram (Figure 3) shows the absence of the peak assigned to the homo CMS. This is in good agreement with the calculation of the efficiency of the macroinitiator towards styrene. Furthermore, the polydispersity of the block copolymers is lower than 2.0 and thus it can be considered that there is still a real control of the polymerization.

In order to confirm the value of the molecular weight in number of the block copolymer, ^1H NMR characterization of the copolymer was performed in CDCl_3 . The ratio between integration of the protons of CH_2Cl at 4.5 ppm group and aromatic protons at 7.8 ppm which is about 1/5 gives the molecular average of polychloromethylstyrene as found by GPC.

Conclusion

The synthesis of block polychloromethylstyrene/polystyrene by free radical polymerization is possible by using nitroxide radicals. The living character of free radical polymerization of chloromethyl styrene is achieved : molecular weight in number increases linearly with conversion. In a second step, in order to demonstrate the reactivity of the CMS homopolymer capped with Tempo, styrene was introduced and block copolymer was

obtained. Furthermore, it is possible to choose the ratio of each block and the molecular weight of the block copolymer. Even if the block copolymer is not really monodispersed as these obtained in ionic polymerization, the advantage is that a protection of functional groups is not required.

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