

Triblock Copolymers Based on Styrene and *n*-Butyl Acrylate by Nitroxide-Mediated Radical Polymerization: Problems and Solutions

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SUMMARY : Controlled radical polymerization (CRP) has been experiencing tremendous developments of late, with spectacular achievements in macromolecular engineering. Well-defined star polymers as well as block copolymers can be obtained using miscellaneous CRP methods. This paper is the second of a series devoted to the synthesis of triblock copolymers by nitroxide-mediated polymerization, using a β -hydrogen containing phosphonylated nitroxide (SG1) as stable radical. It focuses on the problems associated with the sequential polymerization of styrene and *n*-butyl acrylate while synthesizing poly(styrene-*b*-*n*-butyl acrylate-*b*-styrene) copolymers from SG1-based macromolecular alkoxyamines. In particular, it discloses how the blocking efficiency can be improved when growing the second poly(*n*-butyl acrylate) (PBuA) block from the first polystyrene (PS) block. The proportion of dead chains that contaminate such triblock samples is also evaluated.

Introduction

Of the recent methods used to synthesize well-defined polymers through controlled radical polymerization, it is the nitroxide-mediated processes that, because of their simplicity, attract interest. However, not all nitroxides can be used to control the free radical propagation of vinyl monomers; they have to be carefully chosen¹. For instance, (N-*tert*-butyl-N-(1-diethylphosphono-2,2-dimethyl)propyl)nitroxyl (SG1) is a β -hydrogen bearing nitroxide that was found to bring about the controlled polymerization of both styrene and alkyl acrylates when used together with AIBN as initiator². Other β -hydrogen containing nitroxides were recently shown to be suitable for the controlled radical polymerization of various vinylic monomers, including styrene, alkyl acrylates, and 1,3 dienes³.

In a recent paper⁴ we reported that the synthesis of well-defined PS-*b*-PBuA-*b*-PS triblock copolymers by sequential polymerization of the two monomers, using AIBN as initiator, required carefully selected conditions. High blocking efficiency could be achieved while growing the third PS block from PS-*b*-PBuA, but the same could not be obtained for the growth of the second PBuA block from PS, unless tapering it through a statistical poly(S-co-

BuA) block. Both the unfavorable kinetics of cross-addition and the incompatibility between the growing PBuA block and the PS precursor were found to affect the blocking process. One way of preventing the effect caused by these two factors, and thus improving the blocking efficiency, was to grow an intermediate poly(S-co-BuA). However, no reasonable explanation could be given to the improvement observed. The objective of the current paper is to examine in detail the reason for this improvement. Firstly, the effect of the presence of a small amount of styrene on the rate of growth of the second PBuA block, and vice-versa, will be investigated and secondly, the proportion of chains that are deactivated by irreversible termination will be evaluated.

Copolymerization of n-butyl acrylate with a small amount of styrene using molecular alkoxyamines

A small amount of styrene (S) was thus copolymerized with n-butyl acrylate (BuA), with the aim of slowing down the rate of propagation of the latter monomer. It was anticipated that upon slowing down the growth of the PBuA block, the first PS block would have more time to decompose and initiate the polymerization of BuA. In order to obtain PBuA chains that were as pure as possible, only a 5-7% volume of styrene was used,. The alkoxyamine $\text{CH}_3\text{CH}(\text{C}_6\text{H}_5)\text{-SG1}$ (S-SG1) which is a replica of the polystyrene-SG1 precursor, was used instead of the latter initiator for practical purpose, just because the characterization of the composition of the copolymer is easier with a molecular initiator.

Table 1 : *Synthesis of copolymers P(S-co-BuA) at 120°C.*

Exp.	Styrene (%vol) ¹	Time (h)	Conversion ² (%)	$M_{n,th}$ ³ (g/mol)	$M_{n,mes}$ ⁴ (g/mol)	I ⁵
0	0	0.6	94	140,000	61,800	1.40
1	5	1.5	67	67,000	46,100	1.60
2	6.2	2	72	58,500	55,300	1.34
3	6.2	2	81	40,500	39,800	1.39
4	7.5	2	75	90,000	76,700	1.54

¹ Volume percents of styrene with respect to butyl acrylate. ² Measured by gravimetry. ³ Calculated from conversion. ⁴ Measured by SEC using RI detection and PS standards. ⁵ Polydispersity index.

Use of only a few percent of styrene was enough to slow down the rate of polymerization of n-butyl acrylate. As seen in Figure 1, the copolymers obtained exhibited a rather low polydispersity index. For a same amount of styrene used, the rate of polymerization was

found to depend on the concentration of alkoxyamine used (experiments 2 and 3, Table I). The larger the amount of styrene, the slower the polymerization.

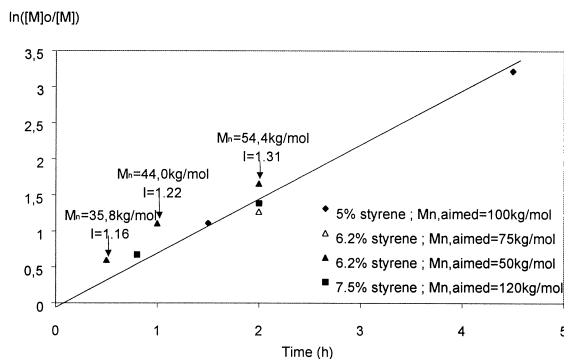


Figure 1 : Evolution of $\ln([M]_0/[M])$ over time during the synthesis of $P(S\text{-}co\text{-}BuA)$ copolymers. Molar masses indicated have been measured by SEC using light scattering detection.

The incorporation of the PS units within the propagating chain was difficult to determine precisely. 1H -NMR spectroscopy was used to analyze the composition of our samples. Table 2 shows the evolution of the chain composition as a function of the conversion in BuA.

Table 2 : Copolymerization of S/BuA (6/94) at $120^\circ C$. Evolution of the conversion of each monomer as a function of time.

Initiator	S ¹ (%)	Time (min)	ρ (S) ² (%)	ρ (BuA) ³ (%)	S ⁴ (%)
S-SG1	6.2	5	0	12	7.8
		10	32	16	6.0
		15	52	20	4.8
		120	84	52	3.1

¹ Volume percent of styrene with respect to butyl acrylate. ² Conversion in styrene measured by 1H -NMR. ³ Conversion in *n*-butyl acrylate measured by 1H -NMR. ⁴ Amount of residual styrene measured by 1H -NMR.

It is further desirable to know how the conversion of the monomers varies and also the rate of conversion of polystyryl radicals into polyacryloyl ones. Assuming the reactivity ratios⁵

$$r_S = \frac{k_{p,S}}{k_{S \rightarrow BuA}} = 0.8 \text{ and } r_{BuA} = \frac{k_{p,BuA}}{k_{BuA \rightarrow S}} = 0.2$$

given in the literature are the same as at 120°C, and knowing the rate constants of propagation of the two monomers at 120°C, we could determine the rate constants of cross propagation at this temperature :

$$k_{S \rightarrow BuA(120^\circ C)} = 2.5 \cdot 10^3 \text{ l.mol}^{-1} \cdot \text{s}^{-1} \text{ and } k_{BuA \rightarrow S(120^\circ C)} = 4.2 \cdot 10^5 \text{ l.mol}^{-1} \cdot \text{s}^{-1}$$

Using the Predici package and the values of rate constants of the different reactions (see Annex), we could simulate the two monomer conversions as a function of time.

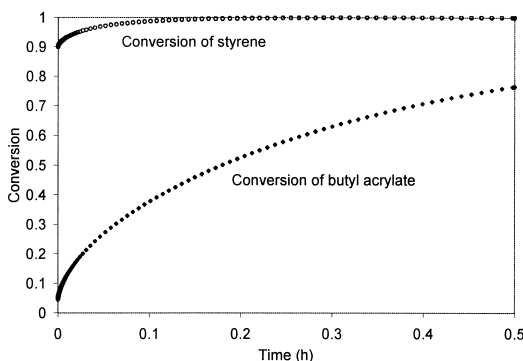


Figure 2 : Simulation of the copolymerization of *n*-butyl acrylate and 5% vol styrene at 120°C. Evolution of the conversion of each monomer.

As seen in Figure 2, it is styrene that is consumed preferably and quite rapidly. However, there is still some styrene that is incorporated in *n*-butyl acrylate even above 40% conversion, meaning that the first part of PBuA chains will contain some styrene units.

Using the same simulation package, one can also determine the concentration profiles of the chains that carry a styryl radical which can give an idea of the rate of conversion of styryl radicals into acrylate ones. By the same methodology, one can also evaluate the concentration of those dormant alkoxyamines –including chains and residual initiators- that are terminated by a last styrene unit covalently attached to SG1. In this way one can determine the exact conversion of BuA above which pure PBuA is formed.

As seen in Figure 3, the proportion of chains that carry a styryl radical remains quite high for a long time, because styrene is preferably incorporated (reactivity ratios) and above all because the equilibrium between active and dormant species is shifted further towards active species in the case of styrene than for *n*-butyl acrylate⁶ :

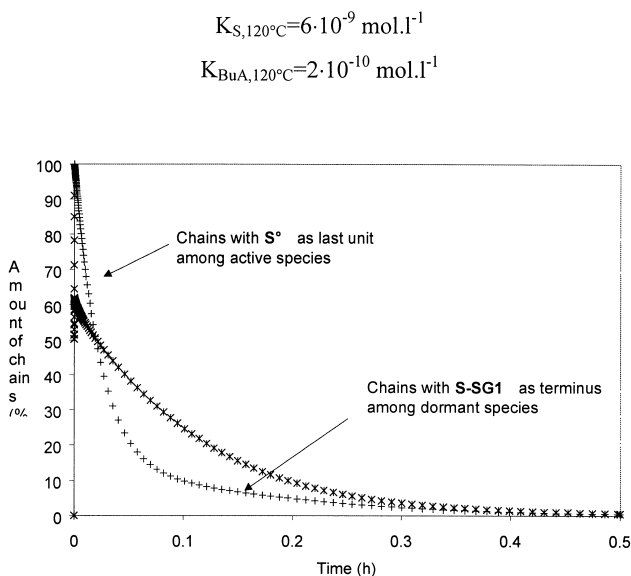


Figure 3 : Evolution of the concentration of PS terminated active species and dormant chains over time, during the copolymerization of styrene and butyl acrylate (5/95, v/v).

The evolution of the number of dormant species that carry a styrene unit as the last unit conforms to our expectation. Notwithstanding the rapid consumption of styrene, it is only above 60% conversion in BuA that the level of chains carrying a styryl radical or a styryl bonded alkoxyamine decreases to negligible values.

This investigation demonstrates why the addition of 5% styrene is an excellent method of improving the blocking efficiency while synthesizing a PS-b-PBuA diblock copolymer from a PS-SG1 macroinitiator. Because the growth of the second PBuA block is slowed down, the time required for all styrene-based precursors –in the latter case S-SG1 alkoxyamine- to disappear by initiation is compatible and actually shorter than that corresponding to the thorough conversion of BuA. Moreover, the preferential and faster consumption of styrene results in the formation of a true tapered block copolymer whose statistical poly(S-co-BuA) sequence can be varied upon adjusting the amount of styrene added.

Copolymerization of styrene with a small amount of n-butyl acrylate using $\text{CH}_3\text{CO}_2\text{CH}_3$ -SG1 (AMe-SG1) as initiator

After demonstrating that styrene is preferentially incorporated in n-butyl acrylate during copolymerization of the latter monomer with a small amount of styrene, we decided to study the symmetrical case, namely, the copolymerization of styrene with a small amount of BuA. It is important to know whether residual BuA affects the polymerization of styrene and to what extent when the last PS block is grown to make PS-b-PBuA-b-PS copolymers. This section describes the copolymerization of styrene with a small amount of BuA, using various initiators.

In view of our objective, i.e. a definition of the conditions best suited to the growth of the last PS block from a PBuA-SG1 precursor, it is logical to use a molecular model of the latter macroinitiator. Other initiating systems including S-SG1 and AIBN/SG1, were also used for the purpose of comparison.

Table 3: Conditions used for the synthesis of P(S-co-BuA) copolymers from various initiators.

Initiator	SG1 ¹ (eq)	Time (h)	Conversion ² (%)	Styrene ³ (%)	M _{n,th} ⁴ (g/mol)	PS ⁵ (%)	M _{n,mes} ⁵ (g/mol)	I ⁶
AIBN	2.5	0	0	87	0	0		
		0.75	6	88	6,000	79		
		5	61	83	61,000	90		
		10	70	83	76,000	91		
S-SG1	0.25	0	0	88	0	0		
		0.75	6	88	6,000	79		
		5	60	88	60,000	88		
		10	79	85	79,000	91	57,800	1.17
AMe-SG1	0.25	0	0	88	0	0		
		0.75	11	88	11,000	93		
		5	68	88	68,000	89	51,100	1.21
		10	70	88	70,000	90	53,900	1.17

¹Ratio of [SG1]/[Initiator]. ²Global conversion measured by gravimetry. ³Molar proportion in styrene measured by ¹H NMR. ⁴Calculated from conversion. ⁵Polystyrene proportion measured by ¹H NMR. ⁵Measured by SEC using RI detection and PS standards. ⁶Polydispersity index measured by SEC using RI detection and PS standards.

One striking feature that can be noticed in Table 3 is that the composition of the copolymer formed remains unchanged throughout polymerization (88% styrene) corresponding almost ideally to the feed composition. As the monomer composition that was chosen was close to the azeotropic composition, there was no compositional drift; styrene and n-butyl acrylate

were consumed at the same rate. Under these conditions, the copolymer formed is a truly statistical copolymer.

As expected, whatever initiation system was used, the same observation could be made, namely the invariance of the copolymer composition with conversion.

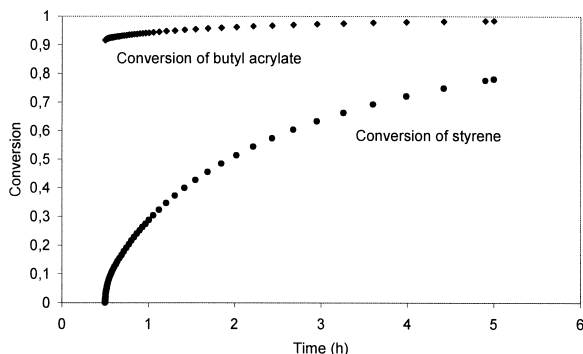


Figure 4 : "One pot" styrene/n-butyl acrylate (87/13) copolymerization from $P(S\text{-}co\text{-}BuA)$ (5/95) macroinitiator.

Using the simulation tool, the conversion curves for styrene and n-butyl acrylate could be established ; it can be seen that BuA is still present until the end of the polymerization.

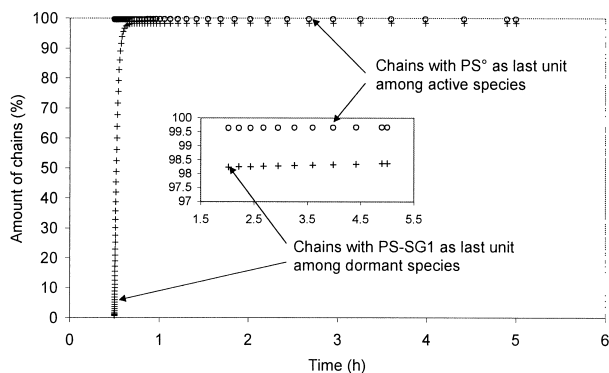


Figure 5 : Chain composition during the synthesis of "one pot" styrene/butyl acrylate (87/13) copolymer from a $P(S\text{-}co\text{-}PBuA)$ (5/95) macroinitiator.

Figure 5 shows the evolution of the proportion of those active chains that carry a styryl radical and the proportion of dormant chains fitted with styrene as the last unit. Soon after the commencement of the polymerization, 98% of dormant and active chains bear a styrene unit or a styryl radical at their end and this remains the same throughout the polymerization. This

means that one BuA unit is incorporated every fifty S units. Styrene is consumed preferably, but n-butyl acrylate is steadily and regularly added to the chain.

Results of this investigation emphasise the necessity to thoroughly remove residual BuA before growing the last PS in the PS-b-PBuA-b-PS triblock copolymer. Unless BuA is eliminated, the block that is eventually formed tends to be a statistical copolymer with a lower T_g than that of pure PS; this is not our aim.

Evolution of dead chains during the synthesis of PS-b-PBuA-b-PS triblock copolymers

Further essential information relevant to the synthesis of block copolymers by CRP is the extent and type of dead chains that are formed throughout polymerization. It has been demonstrated in a previous publication⁶ that the growth of the first PS block results in the loss of about 10% PS chains by irreversible termination in the absence of any excess of SG1. In contrast, the determination of the proportion of PS-b-PBuA chains that are irreversibly neutralized by termination during the second step of the synthesis of PS-b-PBuA-b-PS copolymers is not straightforward.

Using molecular alkoxyamines as initiators, we first synthesized the PBuA block before growing the second PS block. PBuA chains were separated from PS-b-PBuA dormant chains by selective precipitation. As shown in Table 4, the proportion of dead PBuA chains tends to increase with the conversion in BuA and therefore depends on the moment the blocking process is triggered.

Table 4 : Amount of PBuA dead chains produced during the polymerization of PBuA-b-PS block copolymers at 120°C.

Conversion (PBuA block) (%)	$M_{n,mes}^1$ (PBuA block) (g/mol)	$M_{n,mes}^2$ (PBuA-PS) (g/mol)	I^3	PBuA ⁴ (%mass)
30	17,000	85,300	1.16	1.1
71	34,800	87,000	1.16	2.6
89	43,900	113,300	1.38	6.6

¹Measured by SEC using RI detection and PS standards. ²Measured by SEC with light scattering diffusion detection using dn/dc calculated from the copolymer composition (determined by ¹H NMR).

³Polydispersity index. ⁴Amount of PBuA weighed after having precipitated the copolymer in methanol; PBuA dead chains were soluble in methanol whereas PBuA-b-PS chains were not.

One has to acknowledge, however, that this method of determination of the proportion of dead chains by selective precipitation is not a precise one.

Under these circumstances, the best tool to evaluate as precisely as possible the extent of dead chains is certainly the simulation carried out with the help of the Predici package. Figure 6 shows the evolution of dead PBuA chains as a function of the maximal conversion in PBuA prior to the growth of the PS block. The simulation shows that the extent of dead PBuA chains is in the range of 1 to 2%, even for high conversions (90%). These simulated values are in the same range as those determined by selective precipitation, except for one case. Nevertheless, one can conclude that both methods of determination of dead chains yield much lower values than those evaluated for the PS first block, that were found to be around 10%. As theorized by Fischer⁷, each polymer/stable radical system generates its own excess of stable radicals and implies a different extent of dead chains⁶.

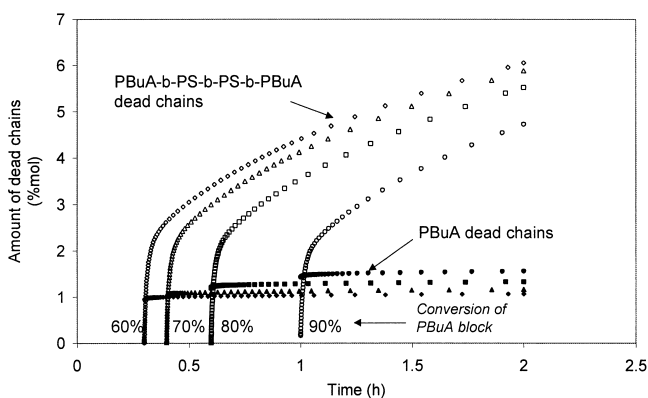


Figure 6 : Evolution of dead chains predicted by simulation during the synthesis of PBuA-b-PS block copolymers.

Conclusions

The aim of this paper was to investigate the conditions that allow the preparation of well-defined PS-b-PBuA-b-PS triblock copolymers using either molecular alkoxyamines or the combination of AIBN and SG1 as initiators. As previously shown, the kinetics of the cross-addition of PS radicals to BuA is not favorable; it results in a blocking efficiency of between 0.7 and 0.8. It was also found that the addition of BuA while about 10% of styrene was still present helped to improve the blocking efficiency.

This paper investigates the reasons of the improvement observed ; the presence of residual styrene helped to curb the rate of growth of the second block, giving in turn enough time for the first PS block to initiate the growth of the second block. Essential information was also obtained about the kind of block copolymers that are grown under these conditions. Because of the presence of about 10% of styrene, the chains formed exhibit a tapered structure/composition that was progressively enriched in BuA as its conversion augments. This tapered block that is located in-between the two pure PS and PBuA blocks is likely to result in the formation of a large interphase between the PS- and PBuA-rich phases, but the characteristics of the latter should not be affected. In contrast, the presence of residual BuA while growing the terminal PS block from PS-b-PBuA precursors may result in the formation of a phase with a lower T_g. In the latter case, it is essential to eliminate residual BuA before growing the third PS block. The kind and proportion of dead chains that are formed were also determined. As the morphology that eventually develops in such copolymers is dependent on the presence of residual homopolymers, it is important to get this information at the time when these materials are studied and characterized.

Acknowledgements

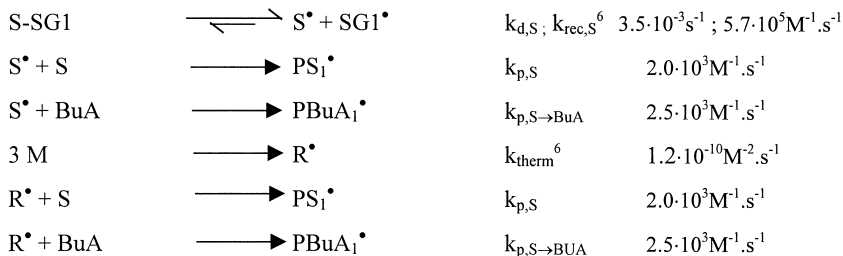
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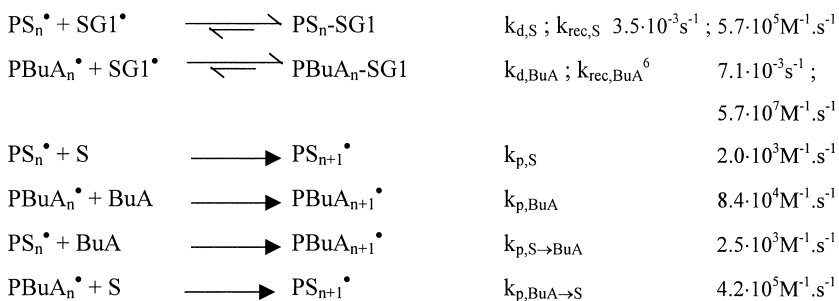
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Annex : Reactions and rate constants considered for the simulation of the SG1-mediated free radical copolymerization of styrene (S) and n-butyl acrylate (BuA), using the Predici package.

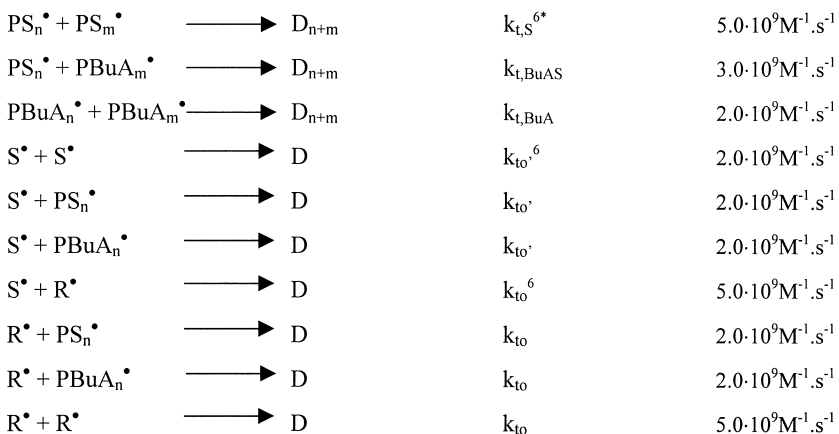
Initiation :



Propagation :



Termination :



*This termination rate constant depends on the polymerization degree (conversion) :

$k_t(DP) = k_t(0) \cdot DP^{\wedge} - (0.664 + 2.02 DP / DP_{amed})$; the value indicated is $k_t(0)$.

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