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Controlled radical polymerization in the presence of β-phosphonylated nitroxide — kinetics, mechanism and macromolecular architecture

Summary — Using a newly designed N-tert-butyl-l-diethylphosphono-2,2--dimethylpropyl nitroxide (DEPN), controlled radical polymerization of styrene and n-butyl acrylate, could be achieved. The rate constant of reversible deactivation of growing radicals by DEPN and the rate of dissociation of the alkoxyamine formed were determined. Miscellaneous macromolecular architectures, including block copolymers, stars and star block copolymers, were derived by this chemistry.

Key words: controlled radical polymerization, N-tert-butyl-1-diethylphosphono-2,2-dimethylpropyl nitroxide, styrene, n-butyl acrylate, block copolymers, star polymers.

Controlled/"living" radical polymerization has recently became a powerful synthetic tool for the preparation of polymers with predetermined molecular weight low polydispersity, controlled composition and functionality [1—3]. Since the works of Rizzardo [4] and Georges et al. [5] on the application of 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) to control free radical polymerizations, nitroxide-mediated polymerization (NMP) has been extensively studied. In this process, control is achieved via capture of growing radicals by the nitroxide and its release upon decomposition of the alkoxyamine formed [6] [equation (1)]. Because the equi-

$$K = k_d/k_{rec}$$
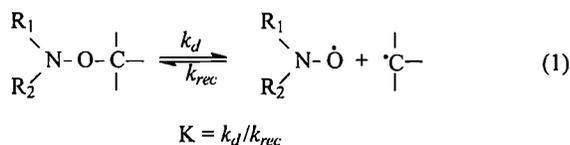
librium of this reaction is shifted to the left-hand side, the concentration of active species is lowered as compared with a regular free radical polymerization and the probability for bimolecular termination is reduced. However, the use of TEMPO was accompanied with restrictions — it could be successfully applied only with styrene derivatives and the polymerization was slow even at high temperature (130°C). As a matter of fact, chain growth occurs in this system because of the con-

stant supply of radicals produced by the thermal autopolymerization of styrene. Eventually, only styrene-based polymers and statistical copolymers could be obtained under controlled conditions in the presence of TEMPO [7]. Recently, other new nitroxides [8, 9] and in particular, N-tert-butyl-1-diethylphosphono-2,2-dimethylpropyl nitroxide (DEPN — I), now available under the trade name SG1, were designed and synthesized to afford the dormant alkoxyamines with a lower carbon-oxygen bond energy. As a result, a wider range of monomers, in particular alkyl acrylates, can be now polymerized under controlled conditions.
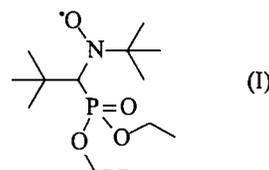
In this paper, we present an information about the controlled free radical polymerization of styrene and n-butyl acrylate (n-BuA) in the presence of SG1. We will focus on the kinetics and on its implications in macromolecular engineering. The conditions that are the most suitable for the preparation of well-defined poly(styrene) (PS) and poly(n-butyl acrylate) (PBuA) homopolymers, the corresponding block copolymers and also star polymers will be thoroughly discussed.

CONTROLLED POLYMERIZATIONS OF STYRENE AND n-BuA

Synthesis of well-defined homopolymers [10]

With 2,2-azobis(isobutyro-nitrile) (AIBN) as initiator, styrene polymerizes much faster in the presence of SG1

than of TEMPO, what results in a higher concentration of propagating active species in the mixture. This indicates that alkoxyamine bond -C-O-N- formed upon recombination of SG1 with the growing polystyryl radicals is much weaker than of TEMPO-based analogues. In spite of higher concentration of propagating species, a linear dependence of $\ln([M_0]/[M])$ on time (Fig. 1) was observed [criterion a)] and molecular weights were found to increase linearly with conversion (Fig. 2), showing low polydispersity ($M_w/M_n \approx 1.2$) [criterion b)]. At temp. 120°C, the best suited experimental conditions to

Fig. 1. $\ln([M_0]/[M])$ versus time for styrene free radical polymerization at temp. 120°C: ♦ — $[AIBN]_0 = 2.2 \cdot 10^{-2}$ M and $[SG1]/[AIBN] = 2.5$, □ — $[AIBN]_0 = 3.6 \cdot 10^{-3}$ M and $[SG1]/[AIBN] = 2.5$, △ — thermal polymerization, × — $[DTBN]/[AIBN] = 2.5$

Fig. 2. M_n versus conversion for SG1 mediated styrene polymerization at temp. 120°C: ♦ — $[AIBN]_0 = 2.2 \cdot 10^{-2}$ M and $[SG1]/[AIBN] = 2.5$, ◊ — planned M_n's with $[AIBN]_0 = 2.2 \cdot 10^{-2}$ M; ▲ — $[AIBN]_0 = 3.6 \cdot 10^{-3}$ M and $[SG1]/[AIBN] = 2$, × — planned M_n's with $[AIBN]_0 = 3.6 \cdot 10^{-3}$ M

obtain a perfect agreement between experimental and theoretical molecular weights were at a ratio of $[SG1]/[AIBN] = 2.5$.

n-BuA could also be successfully polymerized using the same procedure, with AIBN as initiator and SG1 as controlling agent. A perfect agreement of experimental and planned molecular weight could again be observed but the ratio $[SG1]/[AIBN]$ had to be increased to more than 3 to achieve an efficient initiation step. As for styrene, the same two criteria [a) and b)] of "livingness" could be fulfilled in this case as well. SG1 is thus one of the first nitroxides that could be used to control free radical polymerization of acrylic monomers. After demonstrating the ability of SG1 to endow free radical polymerization with a "living"/controlled character, the experiments aiming to determine the rate constants of formation and dissociation of the alkoxyamine were carried out.

Kinetic investigations [11]

SG1-terminated oligomers of polystyrene (PS-SG1) and n-butyl acrylate (PBuA-SG1) of $DP_n = 35$ were first prepared and used for the determination of the rate constants of dissociation k_d and formation k_{rec} of the alkoxyamine by reversible deactivation [equation (2)]. Two oligomers were used to initiate the polymerization of two

$A = -C_6H_5, -CO_2Bu$

respective monomers at temp. 120°C. The evolution of [SG1] with time could be monitored by electron spin resonance spectrometry (ESR), upon carrying out the polymerization of styrene in the spectrometer. As the evolution of [PS$^\bullet$] with time, it could be calculated from the slope of the linear variation of $\ln([M_0]/[M])$ with time. Knowing these two concentrations, and that of [PS-SG1] assumed to be constant, it was easy to estimate the equilibrium constant K between dormant and active species: $K_{styrene} = 6.0 \cdot 10^{-9}$ mol $\cdot$ L^{-1} at temp. 120°C. The latter value was subsequently confirmed by Boutevin et al. [12, 13] who used another kinetic method to determine the same equilibrium constant.

The rate constant of dissociation/activation (k_d) of dormant PS-SG1 could be easily determined using size exclusion chromatography (SEC) [14, 15]. The disappearance of PS-SG1 precursor could be monitored by comparing the areas of the macroinitiator with that of the polymerized part in the SEC chromatogram (Fig. 3). A value of $3.4 \cdot 10^{-3}$ s^{-1} was found for k_d, which is three times higher than the rate constant of dissociation for PS-TEMPO [16].
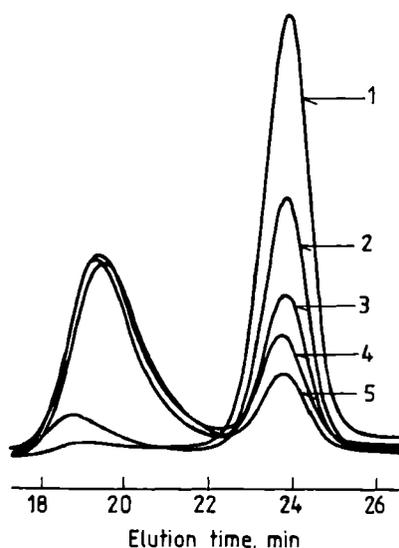
Fig. 3. Disappearance of PS-SG1 at temp. 120°C as followed by SEC; time of reaction (min): 1 — 0, 2 — 1, 3 — 2, 4 — 2.5, 5 — 3

The knowledge of K and k_d allowed us to calculate from relationship $K = k_d/k_{rec}$, the rate constant of formation of PS-SG1 — $k_{rec} = 5.7 \cdot 10^5$ L · mol^{-1} · s^{-1}.

The values of k_d and k_{rec} give the reasons why the polymerization of styrene in the presence of SG1 is much faster than TEMPO-mediated ones: once formed active polystyryl radical PS$^\bullet$ can propagate longer before being trapped by SG1.

The rate constant k_d was then determined at different temperatures and the following Arrhenius expression was found for the rate constant of activation/dissociation:

$$k_d(s^{-1}) = 10^{14} \exp\left(\frac{121 \text{ kJ / mol}}{RT}\right) \qquad (3)$$

At about the same time Goto and Fukuda [17] independently, published a close value of k_d determined by an analogous method based on gel permeation chromatography (GPC). Subsequently to this work, Bertin et al. [18] observed a negligible dependence of k_d on the chain length for SG1-mediated polymerization of styrene and concluded that k_d remains unchanged throughout polymerization.

Computer simulations were used afterwards as a tool to check the usefulness of experimentally determined values of k_d and k_{rec}. All chemical events occurring in such polymerizations, including the degradation of SG1 and the dependence of the rate constant on the chain size [19], were taken into consideration in these simulations. The simulated kinetic plots and those experimentally established were found to come in close agreement, adding credit to the measured values of k_d and k_{rec}.

An identical study was carried out for the SG1-mediated polymerization of n-BuA using the same methodology and the same range of temperature. Similarly to the case of styrene, the rate constants of dissociation/formation of PBuA-SG1 could be measured with the help of ESR and SEC: $K_{BuA} = 1.7 \cdot 10^{-10}$ mol · L^{-1} at 120°C, $k_d = 7.1 \cdot 10^{-3}$ s^{-1} at 120°C, $k_{rec} = 4.2 \cdot 10^7$ L · mol^{-1} · s^{-1} and

$$k_d(s^{-1}) = 1.7 \cdot 10^{15} \exp\left(\frac{-130 \text{ kJ / mol}}{RT}\right) \qquad (4)$$

The lower value of K measured for SG1/n-BuA system — as compared to the SG1/styrene system — indicates that the equilibrium is shifted in the latter case more towards dormant species. Although the concentration of growing radicals [PBuA$^\bullet$] is lower than in the case of styrene, the polymerization proceeds faster because the rate of propagation of n-BuA is 40 times higher. Lacroix-Desmazes et al. [20] also investigated the kinetics of polymerization of n-BuA in the presence of SG1. The value of K_{BuA} they obtained is actually close to ours.

The next step of our investigation was to elucidate dilution effect and its impact on the rate constant of self-termination of radicals and thus on the overall course of polymerization.

Effect of the dilution [21]

For this study, styrene was polymerized in an inert solvent at temp. 120°C and in the presence of SG1. Reacting mixtures of different dilutions were prepared and the kinetics of polymerization was followed as usual. Self-termination is a diffusion-controlled reaction and the pertinent rate constant ($<k_t>$) is known to depend on the chain length and on the viscosity of the medium. The variation of $\ln([M_0]/[M])$ as a function of reaction time, 2/3 power ($t^{2/3}$) (Fig. 4) — according to descriptions [22, 23] — exhibits a linear dependence. Thus, $<k_t>$ could be easily extracted from the slope which corresponds to $\frac{3}{2} k_d \left(\frac{k_d[I_0]}{3k_{rec}k_t}\right)^{1/3}$. $<k_t>$ values determined experimentally and those calculated with the help of computer simulations (Predici Program) were compared for different dilutions (Table 1). On the other hand, the viscosity of the polymerization medium was measured and found to increase with conversion as expected. To our surprise, $<k_t>$ did not vary with the viscosity increase, certainly because low molecular weights (10 000 g/mol) were planned and also because the viscosity observed did not reach values measured at glass transition.
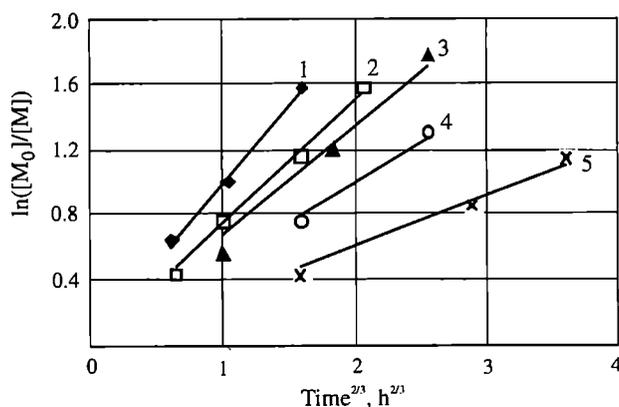
Fig. 4. Plot of $\ln([M_0]/[M])$ versus $t^{2/3}$ at different dilutions in styrene ($T = 120°C$); dilutions: 1 — bulk ($y = 0.9891\,x$, $R^2 = 0.9974$), 2 — 0.80 ($y = 0.7502$, $R^2 = 0.9946$), 3 — 0.55 ($y = 0.6694\,x$, $R^2 = 0.9771$), 4 — 0.30 ($y = 0.4956\,x$, $R^2 = 0.9862$), 5 — 0.12 ($y = 0.3031\,x$, $R^2 = 0.9768$)

T a b l e 1. Experimental and simulated $<k_t>$ values

f_{st}*)	$<k_t>$, $L \cdot mol^{-1} \cdot s^{-1}$	
	calculated	experimental
1 (bulk)	$1.75 \cdot 10^8$	$1.80 \cdot 10^8$
0.80	$3.22 \cdot 10^8$	$3.09 \cdot 10^8$
0.55	$2.96 \cdot 10^8$	$2.90 \cdot 10^8$
0.30	$3.41 \cdot 10^8$	$3.57 \cdot 10^8$
0.12	$4.56 \cdot 10^8$	$6.25 \cdot 10^8$

*) f_{st} — Initial styrene mole fraction.

A good agreement between simulations and experiments was observed confirming our analysis. However, we were surprised to observe that $<k_t>$ does depend on the initial dilution of the polymerization: the lower the initial concentration of styrene, the higher the value of $<k_t>$ measured and simulated. This phenomenon was already observed by Beuermann et al. [24] for other systems: these authors accounted for such phenomenon by the influence of the intra-coil viscosity [25] on the segmental diffusion. One significant result produced by this investigation was the fact that dilution had favoured a non negligible extent self-termination, which in turn had resulted in a higher proportion of dead chains. It is obviously a critical issue to be taken into account when attempting to synthesize block copolymers.

MACROMOLECULAR ARCHITECTURE USING SG1-MEDIATED POLYMERIZATION

Synthesis of poly(styrene-b-n-butyl acrylate) diblock copolymers [26, 27]

PS-b-PBuA diblock copolymers could be obtained in bulk, by sequential polymerization of the corresponding monomers in the presence of SG1. To succeed in such syntheses, it is essential to know the rate constants of cross-addition ($k_{a,b}$ and $k_{b,a}$) and the respective rate constants of propagation of both monomers. When the rate constant of propagation of the second monomer is too high, as compared with the rate constant of cross-addition, the diblocks formed are likely to contain some homopolymers of the first polymerized monomer. Thus, the order of monomer introduction matters and the monomer to polymerize first is the one with the least favourable ratio of $k_{pa}/k_{a,b}$. Knowing the rate constants of cross-addition and those of propagation of styrene/ n-BuA pair of monomers, one can see that n-BuA was polymerized first. Under these conditions, well-defined polymers can be synthesized, whereas the reverse procedure — applying the polymerization of styrene first — afforded ill-defined samples containing an important proportion of PS precursor chains. These experimental features can be simulated and computed using "PRE-DICI®" program. In addition to an unfavourable ratio of the rate of initiation to the rate of growth of the second block, the synthesis of PS-PBuA diblocks was also affected by the occurrence of phase separation in the reaction medium, which contributed to hinder the access to PS block and impaired its incorporation. This phenomenon of phase separation and its consequence on the quality of the diblock formed can be alleviated by using PS precursors of short size (<4300 g/mol) — no phase separation was detected during polymerization and better defined diblock samples were isolated.

Another approach to improve the blocking efficiency in diblocks grown from PS-SG1 precursor was to prepare an intermediate statistical poly(S-co-BuA) block. As a matter a fact, a small amount of styrene (5—7%) was copolymerized with n-BuA. The presence of styrene units was found to slow down the polymerization. With the knowledge of the rate constants of cross addition and propagation, it was easy to demonstrate using simulations that styrene was consumed faster than n-BuA and that above 60% of conversion of the latter monomer a pure PBuA block was formed. Thus, this methodology, which involves the addition of 5% of styrene, helps to slow down the growth of PBuA block and provides enough time for the first block to initiate the second one efficiently. At the same time, it is an elegant method to produce gradient copolymers based on PS and PBuA. The symmetrical case, which is the copolymerization of styrene with a small amount of n-BuA, gave entirely different results. As styrene and n-BuA are consumed at the same rate in this case BuA is still present until the end of the polymerization: what is formed here is a statistical block with a random distribution of styrene and n-BuA.

Synthesis of triblock copolymers poly(styrene-b-n-butyl acrylate-b-styrene) [28]

On the basis of the results on diblock copolymers, we have also explored the possibility to synthesize triblock copolymers from SG1-based dialkoxyamine named

DiF-SG1 (II). The efficiency of DiF-SG1 as a difunctional initiator was checked in the case of both PS and PBuA homopolymers using a slight excess of nitroxide. The first method consisted in subjecting the PS samples ob-

(II)
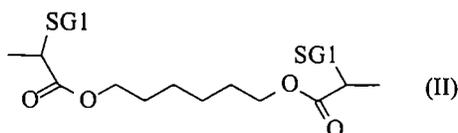
tained to a basic treatment in order to hydrolyse the central ester groups of DiF-SG1. In the latter case an efficiency higher than 0.9 was measured for the dialkoxyamine. However, this method could not be applied to PBuA samples because of the lack of selectivity of hydrolysis. A second method was thus designed to determine the efficiency of the initiation step for PBuA samples: n-BuA polymerization was actually carried out in the presence of a mixture of mono- and dialkoxyamines at 2:1 ratio. Upon characterizing the samples by GPC, a factor of 2 was found between the weight fraction and the molecular weight of the two populations, showing an efficiency of the initiation step close to 1. Well defined triblock copolymers were also synthesized using the same difunctional initiator (DiF-SG1) at temp. 120°C and in the presence of slight excess of SG1 (Fig. 5). Above 40% of styrene conversion the coupling between grow-

Synthesis of well-defined star polymers and star-like copolymers [29]

Trialkoxyamine (III) based on SG1 was also used to initiate the polymerization of styrene and of n-BuA. For the synthesis of three-arm PS star polymers, the temperature was decreased to 100°C to prevent star-star

(III)
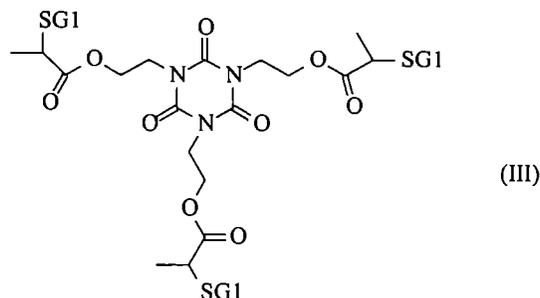
coupling, and the formation of linear homopolymers by autopolymerization. In the presence of an excess of SG1 narrowly distributed PS star polymers with controlled molecular weights could be obtained under these conditions but the time required to obtain such samples was longer. For the synthesis of PBuA star polymers additional excess of SG1 was necessary to control the polymerization, but no pollution by linear polymers nor star-star coupling were detected even at relatively high conversion (Fig. 6). The efficiency of this trialkoxyamine as trifunctional initiator was checked, as previously de-

Fig. 5. SEC images of PBuA macroinitiator and PS-b-PBuA--b-PS block copolymers
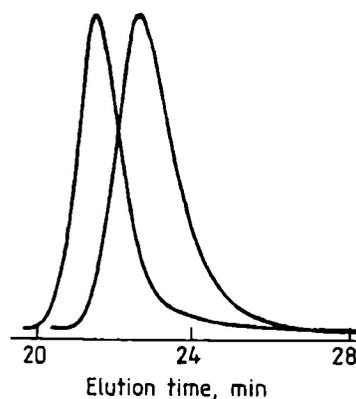
Fig. 6. SEC image of PS star polymer synthesized at temp. 100°C

ing chains could be detected and the triblocks formed were contaminated with multiblock copolymers. Characterization of the triblock copolymers by liquid adsorption chromatography (LAC) confirmed that initiation of PBuA inner block and that of PS outer blocks occurred efficiently. Such triblocks were found to contain some PS chains generated by thermal autopolymerization of styrene.

scribed for dialkoxyamines, by polymerization of a mixture of mono- and trialkoxyamines (ratio 1:3). The same weight fraction was obtained for the two populations and their respective molecular weights values appeared to differ by a factor 3. From such T(BuA-SG1) star polymers, T(PBuA-b-PS-SG1)3 star block copolymers showing a narrow molecular weight distribution can be prepared when outer PS blocks grow.

CONCLUSIONS

SG1 is a radical designed recently that has been successfully used to control free radical polymerization of styrene and *n*-BuA. In contrast to TEMPO-mediated processes, both fast and simultaneously controlled propagation occurred, which opens the way for an industrial implementation. This study actually encompasses all aspects from the kinetics to macromolecular engineering. Some of the structures synthesized are currently characterized as developing materials with specific properties.

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