Lack of Chain Length Effect on the Rate of Homolysis of Polystyryl-SG1 Alkoxyamines

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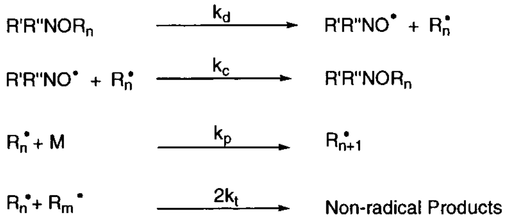
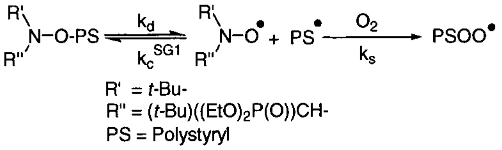
Introduction. Since Rizzardo[1] and Georges[2] controlled the radical polymerization of styrene in the presence of 2,2,6,6-tetramethylpiperidinoxyl radical (TEMPO), the mechanisms and kinetics of the so-called nitroxide-mediated controlled radical polymerizations (NMP) have been extensively studied. In these processes, thanks to their reversible combination with the nitroxide leading to dormant alkoxyamines[3,4] (Scheme 1), the concentration of active species is very low ($\approx 10^{-8}$ M). Activation−deactivation cycles reduce significantly the proportion of bimolecular terminations and allow for preparation of low polydispersity polymers with living alkoxyamine ends. The possibility of using NMP to manufacture materials with well-defined weights, architectures, and compositions[5] revived the scientific interest in radical polymerizations.[6] Considering the rate constants k_d, k_c, k_p, and $2k_t$ (Scheme 1), Fischer[7] and Fukuda[8] have established the kinetic equations that govern NMP. These authors pointed out the key role of the equilibrium constant, $K = k_d/k_c$, and their work stimulated several studies[9,10] on the influence of the alkoxyamine structure on both k_d and k_c. We studied the homolysis of large series of low molecular weight alkoxyamines derived either from *N*-(2-methylpropyl)-*N*-(1-diethylphosphono-2,2-dimethylpropyl)-*N*-oxyl (so-called SG1) or from TEMPO.[9d−g] We observed higher k_d and lower k_c values for the SG1 alkoxyamines,[9d,f] and this observation explains the still unmatched efficiency of SG1 in the NMP of various styrenic and acrylic monomers.[9f,g]

Only few studies have been devoted to the influence of the polymer chain length on the rate constant k_d.[11,12] For a PS−TEMPO macroalkoxyamine ($M_n = 7.6 \times 10^3$ g mol^{-1}, 5% of dead polymer), German[11] using an approach based on the electron paramagnetic resonance (EPR) monitoring of [TEMPO], observed at 120 °C an important 9-fold increase of k_d. Using an approach based on size exclusion chromatography (SEC), Fukuda[12] found a 2-fold increase of k_d for both a PS−TEMPO (M_n = 1700 g mol^{-1}) and a PS−SG1 (M_n = 1960 g mol^{-1}). However, with the same experimental approach than Fukuda, Gnanou[13] established that for the homolysis of a PS−SG1 with $M_n = 3.3 \times 10^3$ g mol^{-1}, k_d (3.4×10^{-3} s^{-1}), A (10^{14} s^{-1}), and E_a (121 kJ mol^{-1}) were very close to those found[9d] ($k_d = 5.5 \times 10^{-3}$ s^{-1}, $A = 1.9 \times 10^{14}$ s^{-1}, and $E_a = 124.5$ kJ mol^{-1}) for the low molecular weight model alkoxyamine (SG1−styryl). These scattered and conflicting results, prompted us to undertake a study of the effect of the polystyryl chain length (10−500 units) on k_d for PS−SG1 macroalkoxyamines. Preliminary results of our study are described herein.

Scheme 1



Scheme 2



Results. The experiments were carried out in the presence of an excess of scavengers (O$_2$ or TEMPO) in *tert*-butylbenzene as solvent.[9d,e] The buildup[9d,e] of SG1 or the decay of TEMPO was monitored by EPR, both nitroxides remaining stable during the experiments.

When O$_2$ is used as a scavenger (Scheme 2),[14] according to the rate constant values ($k_s \approx 10^9$ L mol^{-1} s^{-1} $\gg$ k_c(SG1) $\approx 10^6$ L mol^{-1} s^{-1} for SG1[9f,10] and $[O_2] \approx 2 \times 10^{-3}$ M[15] $>$ [SG1−PS]$_0$), we can assume that the scavenging of released polymer radicals PS• is complete and irreversible. When an excess of TEMPO ([TEMPO] = 2[PS−SG1]$_0$) is used as scavenger, the reaction scheme is different (Scheme 3). However, considering[9f,10] that k_c(TEMPO) $>$ 10k_c(SG1) and k_d(TEMPO) $\leq k_d/10$, the conditions are again combined to assume that all the released polymer radicals PS• are irreversibly trapped by TEMPO.

For both scavengers, rate constants k_d can be estimated from the SG1 buildup curve, using either the plateau method (eq 1) ([SG1]$_\infty$ is the plateau concentration), or the initial slope method ($k_d t$ = [SG1]$_t$/[SG1]$_\infty$ ([SG1]$_\infty$ is the theoretical concentration at infinite time). However, as different experimental factors (concentration of dead polymer, temperature) can easily affect the initial slope of the curve, all the constants k_d (Table 1) were derived from the plateau method and eq 1. When TEMPO is used as a scavenger, the constants k_d can also be deduced from the decay curve of TEMPO using eq 2.

$$\ln\left(\frac{[\mathrm{SG1}]_\infty - [\mathrm{SG1}]_t}{[\mathrm{SG1}]_\infty}\right) = -\,k_d t \tag{1}$$

$$\ln\left(\frac{[\mathrm{TEMPO}]_t - [\mathrm{TEMPO}]_\infty}{[\mathrm{TEMPO}]_0 - [\mathrm{TEMPO}]_\infty}\right) = -\,k_d t \tag{2}$$

To check that a [TEMPO]/[PS−SG1]$_0$ ratio of 2 was appropriate to derive reliable k_d values from eq 2, some experiments were performed using a ratio of 10 and eq 1. As shown in Table 1, both approaches gave very close k_d values. It is worth noticing that, using the plateau

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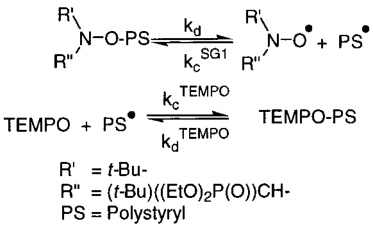
Table 1. Rate Constants[a] at 120 °C[b] for the C−ON Bond Homolysis of Polystyryl−SG1 Alkoxyamines[c]

macroalkoxyamine				scavenger				
				O_2	TEMPO[d]		styrene	
M_n,[e] g mol^{-1}	n[e]	I_p[e]	dead polymer (%)[f]	k_d[g] (10^{-3} s^{-1})	k_d[g] (10^{-3} s^{-1})	k_d[h] (10^{-3} s^{-1})	k_d[i] (10^{-3} s^{-1})	refs
398	0		0	5.6	4.2	5.3		this work
398	0		0	5.5[j]				9d
1400	13	2.5	20	4.8	7.3	5.2		this work
1960	19	1.1	5				11	12
3300	32		33				3.4	13
19 100	184	1.3	10		4.0	4.0		this work
37 200	358	1.1	17	6.4				this work
51 300	495	1.2	40	7.8[k]	5.4[l,m]			this work

[a] Error on the rate constants is less than 10%. [b] $T = 120° \pm 2$ °C. [c] [SG1−polystyryl] = 10^{-4} M. Experiments using either O_2 or TEMPO were carried out with the same solution of SG1−polystyryl. [d] $[\text{TEMPO}]_0 = 2 \times 10^{-4}$ M unless noticed. The samples were degassed by several thaw−freeze−thaw cycles. [e] Measured by GPC. n: number of monomer units. [f] Deduced from the nitroxide concentrations at the plateau. [g] Estimated with eq 1. [h] Estimated with eq 2. [i] SEC technique as described by Fukuda,[12a,b] with styrene as solvent and scavenger and PS−SG1 as macroinitiator. [j] N^{15} TMIO D_{12} and Galvinoxyl as scavengers. [k] At $T = 100$ °C, in the presence of O_2, $k_d = 7.1 \times 10^{-4}$ s^{-1}. [l] [TEMPO] = 10^{-3} M. [m] At $T = 100$ °C, with [TEMPO] = 10^{-3} M; $k_d = 6.7 \times 10^{-4}$ s^{-1}.

Scheme 3



method, we can also estimate the proportion of dead chains in the polymers (see Table 1).

The results listed in Table 1 show unambiguously that k_d for PS−SG1 polymers does not vary significantly with the length of the polymer chain. Considering all the measurements, the average k_d value (5.6×10^{-3} s^{-1}) for PS−SG1 is the same than the value we found[9d] for the low molecular weight model alkoxyamine (SG1−styryl). The small differences observed with the different M_n, could result from small temperature changes within the EPR cavity. The discrepancy between our measurements and the measurement performed by Fukuda et al.[12c] could only result from the use of different experimental approaches.

Presently it is difficult to rationalize the influence of the chain-length on k_d. More work conducted in various media is needed on PS−TEMPO, PS−SG1, and polyacrylates−SG1. This work is in progress in our laboratory.

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