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Mechanism and Kinetics of the Induction Period in Nitroxide Mediated Thermal Autopolymerizations. Application to the Spontaneous Copolymerization of Styrene and Maleic Anhydride

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Summary: Recently we reported an experimental and theoretical (simulation) investigation on the mechanism of the induction period and the initial polymerization stages in the nitroxide mediated autopolymerization of styrene. In this paper we extend some of the results presented there and perform preliminary induction period experiments for the study of the mechanism and kinetics of the spontaneous copolymerization of styrene (S) and maleic anhydride (MA) in the presence of TEMPO and 4-OH-TEMPO. With even small amounts of MA (2% wt) the induction period is dramatically reduced by a factor of about 20 in comparison with the nitroxide-mediated styrene autopolymerization at 120 °C. Our results suggest that the initiation mechanism involves a first step of reaction between S and MA. We speculate that this reaction is a Diels-Alder cycloaddition followed by hydrogen abstraction through a monomer or TEMPO assisted homolysis to form a radical pair (monomer case) or a single radical (TEMPO case), which either initiates polymerization or is trapped by TEMPO depending on the conditions. Hall and Padias have studied similar electron donor-acceptor co-monomer pairs and favor the formation of a tetramethylene diradical as the initiating species for spontaneous copolymerization. In any case, the rate-limiting step would be the initial reaction of S and MA. These induction experiments allow us to obtain an initial estimate of the order of magnitude for the kinetic constant of the rate-limiting step, as 10^{-6} $\mathrm{Lmol^{-1}s^{-1}}$.

Keywords: autopolymerization; kinetics; styrene – maleic anhydride copolymerization

Introduction

Various mechanisms have been proposed to explain the initiation mechanism of self initiated copolymerizations of styrene (S) with electron acceptor monomers such as maleic anhydride (MA), acrylonitrile, vinyliden cyanide or dimethyl 1,1-dicianoethane-2-2-dicarboxylate. They have been proposed to be analogous to the self-initiated styrene homopolymerization.

The oldest mechanism for the self-polymerization of styrene was postulated by Flory[1] and involves the formation of a diradical intermediate which leads to the formation of a 2 + 2 styrene dimer. The diradical can abstract a hydrogen atom from a hydrogen donor forming a monoradical which reacts with styrene to yield polystyrene.

Another mechanism for polystyrene polymerization (Mayo[2]) involves a regioselective (4 + 2) Diels Alder adduct which rapidly undergoes hydrogen abstraction (molecular assisted homolysis) by another

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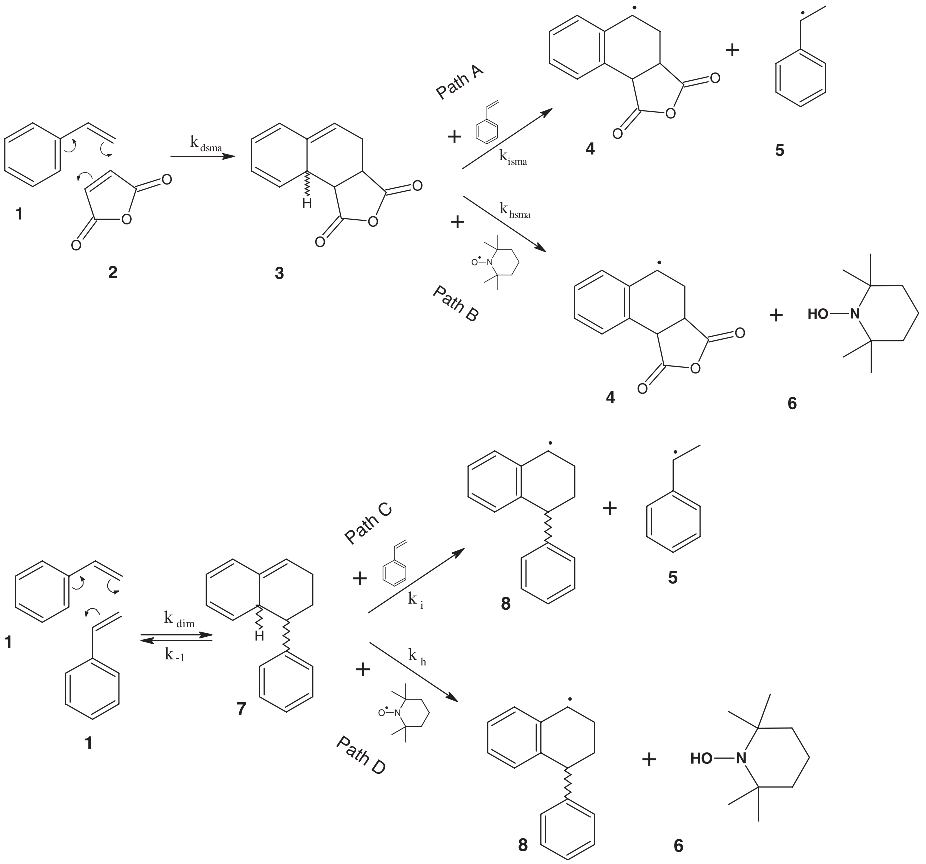
monomer unit to form a radical pair. This radical pair can initiate polymerization or can form a trimer. Evidence supporting the Mayo mechanism includes the isolation of the dimer and the trimer from styrene polymerization and the identification of the dimer as an end group in polystyrene using H NMR and UV spectroscopy.[2,3] Buzanowsky[4] studied the polymerization of styrene in the presence of various acid catalysts and the reactive Diels-Alder dimer was quickly aromatized to the inactive dimer, which decreased the rate of initiation and the formation of the trimer. These results were considered as a further support to the Mayo mechanism. This mechanism has been extended to the spontaneous copolymerizations of styrene with maleic anhydride and other electron-acceptor monomers (see Scheme 1, A).[5] Several authors have studied [6–8] the spontaneous polymerization of styrene with acrylonitrile focusing on isolated trimers that are produced presumably as a result of the initiation step; however, the trimer structures do not suffice to differentiate between the Mayo mechanism and the Flory diradical mechanism.

We provide here experimental evidence about the faster rate of spontaneous radical generation of styrene with maleic anhydride than that present in the spontaneous



Scheme 1.

Paths: A) Mechanism of spontaneous radical formation in styrene-maleic anhydride thermal copolymerization; B) Postulated acceleration of radical generation in styrene-maleic anhydride thermal copolymerization in the presence of TEMPO; C) Accepted mechanism of spontaneous radical formation in styrene thermal polymerization; D) Mechanism of acceleration of radical generation in styrene thermal autopolymerization in the presence of TEMPO.

styrene homopolymerization at the same temperature. From this, it is plausible to postulate that there are two parallel and competing mechanisms for radical generation in the copolymerization case: i) the one operating in styrene homopolymerization, ii) an additional mechanism due to the combined presence of styrene and maleic anhydride.

In this communication we give preliminary results aimed at the elucidation of the mechanism and the estimation of the rate of radical generation in the spontaneous copolymerization of styrene and maleic anhydride. First, we show experiments that give order-of-magnitude estimates of the rate of radical generation in the copolymerization system, as compared with the homopolymerization of styrene. Second, we show additional results that give a preliminary estimation of the corresponding kinetic rate constant under some mechanistic assumptions. Notice that this has not been reported in the past due to the difficulty of separating the initiation and propagation steps. Here, by using carefully planned induction-period experiments of copolymerizations in the presence of stable free radicals, it is possible to make a first separation of the initiation and propagation phenomena.

Radical-Trapping Experiments

Experiments of disappearance of DPPH (2,2′diphenyl-1-picrylhydrazyl radical), which is widely used to test the ability of compounds to act as free radical scavengers or as hydrogen donors at different temperatures, are shown in Figure 1. Fresh distilled styrene or styrene and recently sublimated MA and a solution 10^{-4} M of DPPH were put in a vial in the presence OH-TEMPO or without it, and heated at 80 °, 100 ° or 120 °C after oxygen had been

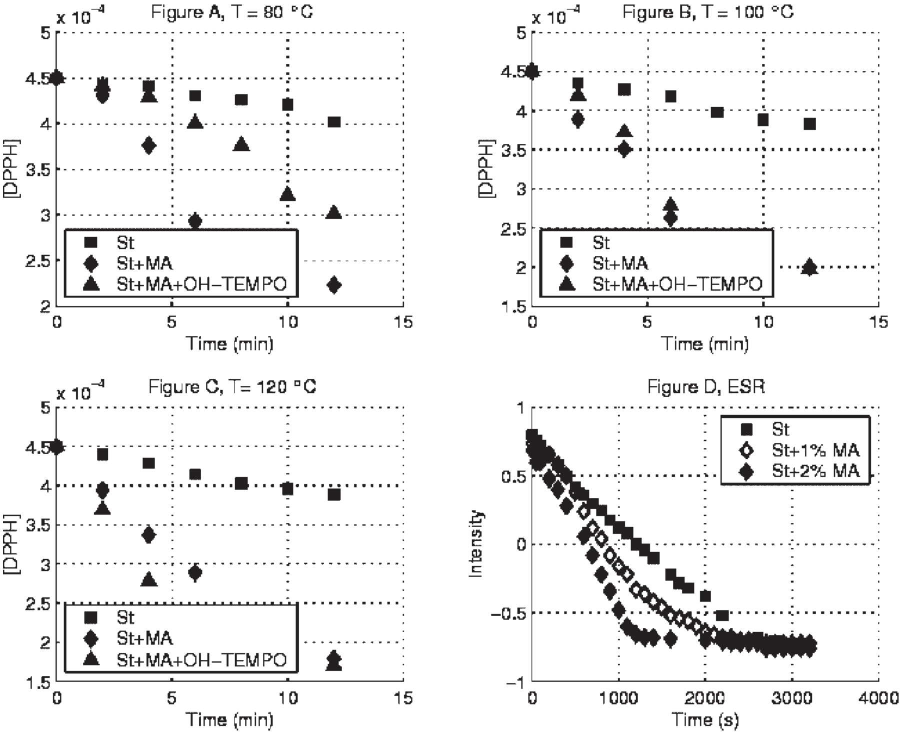


Figure 1.
Concentration decay of DPPH in pure styrene, styrene-MA and styrene-MA in presence of OH-TEMPO at 80, 100 and 120 °C (Figures 1A–1C, respectively). Figure 1D shows the concentration decay of OH-TEMPO detected by ESR in thermal autopolymerization of styrene and of styrene-MA at 80 °C.

evacuated from the vials. Aliquots of the reactions were taken at different times. The decrement of DPPH was measured by UV spectroscopy to detect the appearance of free radicals. At all the temperatures, it is clear that DPPH disappears faster when MA is added to the reaction, therefore, either radicals or hydrogen donors as the cycloadducts are produced faster. The effect of OH-TEMPO in the reaction was assessed to investigate whether this nitroxide competes with DPPH for the benzylic hydrogen in the Mayo adduct. It can be observed that at 80 °C the disappearance of DPPH is slower in the presence of OH-TEMPO. These results might indicate that radicals react either with DPPH or OH-TEMPO, therefore the rate of DPPH is slower than in the absence of OH-TEMPO. At 100 °C rates of S-MA and S-MA- OH-TEMPO are similar, but at 120 °C, when the self-initiation of styrene participates in the production of radicals through the Mayo adduct, the fastest reaction is the reaction with added OH-TEMPO. We attribute this to the increasing importance with temperature of the thermal autoinitiation due only to styrene. This is not evident in absence of OH-TEMPO because, as discussed in several other references [9,10] and extensively in a recent publication of our group,[11] TEMPO (or its derivatives) considerably enhances the rate of radical generation in the thermal autoinitiation of styrene as long as the TEMPO concentration is far from equilibrium, which occurs during the induction period (see Scheme 1D and discussion below).

ESR (electron spin resonance) experiments of disappearance of OH-TEMPO in reactions of polymerization in which pure styrene or styrene with small amounts of MA (1–2% wt.) are heated at 80 °C in the presence of a small amount of OH-TEMPO (4.5×10^{-6} M), are shown in Figure 1D. These indicate that the nitroxide disappears faster when the concentration of MA increases. The disappearance of the nitroxide would be probably due to the formation of the corresponding alkoxyamine. The possibility of reaction with a free radical might be excluded, since this reversible reaction would produce a constant amount of nitroxide.

Mechanism and Kinetics

As relevant background for the mechanism that we propose here, we first review the most accepted mechanism (Scheme 1 path C) for spontaneous radical generation in the thermal styrene autopolymerization. In this path, the Mayo dimer is first formed with two styrene molecules, and then radicals are generated at a relatively slow rate via hydrogen abstraction by another styrene molecule from the Mayo dimer. [2,4] This mechanism is modified in inhibition experiments in which styrene is heated in presence of TEMPO. In this case, the most viable mechanism (Scheme 1, path D)[9,10] implies the formation of the Mayo dimer followed by a fast hydrogen abstraction by TEMPO from the Mayo dimer, generating the dimeric radical **8** and the hydroxylamine **6**. In these cases an induction period whose length is proportional to the initial TEMPO concentration is first experimentally observed, followed by polymerization at the rate of styrene autopolymerization. During the induction period the radicals generated are trapped by TEMPO until this reaches its equilibrium concentration with the dormant species; at this point the induction period is over and the polymerization proceeds in a controlled fashion. Also, during induction, hydrogen abstraction from the Mayo dimer assisted by TEMPO is faster than that assisted by monomer as in the traditional Mayo mechanism (path C), and this leads to two consequences: i) the rate of radical generation is much faster in presence of TEMPO than without it during the induction period (when free TEMPO concentration is relatively high and far from equilibrium) and, ii) apparently, during the induction period in presence of TEMPO, the dimer concentration reaches a quasi-stationary state (QSS) that does not occur in the thermal styrene polymerization in absence of TEMPO.[11,12] This last fact allowed Kothe and Fischer[12] to measure the rate of dimer formation by following the TEMPO consumption with ESR. We recently reviewed in detail the path D by simulation and estimated the kinetic coefficient for the hydrogen abstraction from the Mayo dimer by TEMPO (k_h) as 0.5–1 L mol^{-1} s^{-1}.[11]

By analogy with the mechanisms of spontaneous thermal radical generation for styrene in absence and in presence of TEMPO, and given the stronger donor-acceptor character of the pair S-MA as compared to a pair of styrene molecules, we believe that the radical generation in this spontaneous copolymerization proceeds by the mechanism in Scheme 1 path A (without TEMPO) and path B (in presence of TEMPO). We postulate that an adduct styrene-maleic anhydride (analogous to the Mayo dimer) can be formed in a first step either in a concerted way or via radicals, and this can further react with more monomer to form initiating radicals in the absence of TEMPO (Scheme 1 path A, analogous to the Mayo mechanism), or it can undergo faster hydrogen abstraction by a TEMPO molecule (Scheme 1 path B). Simultaneously, the analogous mechanisms for the spontaneous autopolymerization of styrene would be present generating additional radicals (Schemes 1 paths C and D). Inhibition experiments heating the pair S-MA in presence of TEMPO will likely lead to a QSS concentration of the S-MA adduct, allowing one in principle to measure its rate of formation by monitoring the disappearance of free TEMPO (or the length of the induction period), in a way similar to that used by Kothe and Fischer in the styrene case. A key point here is to select experimental conditions in which the contribution of styrene-styrene radical generation can be minimized and/or substracted from the S-MA contribution. Shorter periods of induction in the copolymerization case as shown in Figure 1D are consistent with a faster dimerization reaction.

Before discussing the kinetics of these mechanisms we provide evidence and theoretical justification for the proposed mechanism. It has been a long controversy on the styrene copolymerization with electron acceptor monomers. In a survey of many experimental data, Hall and Padias[13] have suggested that a tetramethylene biradical initiates the copolymerization of electron rich and electron poor olefins, although there are also evidences that in certain cases, [4 + 2] cycloadditions compete with the tetramethylene type reactions.

Hakko-Hukki[14] and Wagner-Jauregg[15] were able to synthesize styrene-maleic anhydride adducts whose structure was demonstrated by chemical methods and Sato et al.[16] studied the initiation mechanism of the alternating copolymerization of styrene with some electro-accepting monomers in the presence of zinc chloride by the spin trapping technique and showed that the nitroxide obtained in the system styrene-acrylonitrile derived from 1-cyanotetraline-4 radical, produced by the hydrogen abstraction from the Diels Alder adduct. The adduct of styrene-maleic anhydride was also detected by Sato et al.[17] by spin trapping, although they also detected radicals from a charge transfer mechanism in this reaction.

There is no doubt that a cycloadduct can be obtained in the self-initiation of styrene-maleic anhydride, although this is not necessarily a concerted reaction. A semi empirical calculus comparing the energy difference between reactants (styrene and maleic anhydride) and their cycloaduct and between two styrene molecules and their cycloadduct was carried out with the PM3 semi- empirical method provided by the Hyperchem program.[18] Molecular geometries were calculated initially by molecular mechanics and afterwards by the PM3 calculation, at 0.01 convergence limits. The results were $\Delta E = 31.7$ Kcal/mol for the S-MA cycloadduct and $\Delta E = 122.8$ Kcal/mol for the Mayo styrene cycloadduct. However, the formation of the biradical of styrene requires 11.7 Kcal/mol and that of S-MA requires only 5.5 kcal/mol. The resonance stabilization of the biradical would easily produce the cycloadduct.

These data seem to indicate that the cycloadduct can be formed, although a biradical intermediate is possible. The isolation of a Styrene-MA oligomer, obtained by heating a solution of 2.5% MA in styrene during 30 minutes at 80 °C allowed the identification in the ^{1}H NMR spectra (Figure 2) of a signal as a doublet at 4.1 ppm which may be assigned to the benzylic hydrogen which is also alpha to a carbonyl group and beta to other carbonyl group of the maleic anhydride (2.85 ppm for the alpha hydrogen of 1,2,3,4-tetahydronaphtalene + 1.35 ppm from the influence of two carbonyl groups in the alpha and beta positions).[19] The isolation and purification of this oligomer is difficult since at this temperature there is a certain amount of styrene oligomer as a result of the thermal styrene autoinitiation, besides maleic anhydride and styrene in the reaction mixture. Due to the oligomer solubility in dichloromethane, its precipitation is not easy, and the detection of the hydrogen at 4.1 ppm is not always possible. Kothe and Fischer measured the dimer formation rate in the case of styrene autopolymerization in presence of TEMPO. They showed that at *[TEMPO]* >0.05 M it is safe to assume that the dimer concentration is at quasi-steady state (QSS), which implies that the rate controlling step for radical generation is the dimer formation. They measured the rate of consumption of TEMPO, and correlated it with the rate of radical generation. Presumably, the rate limiting step for radical generation in the reaction of S and MA in presence of TEMPO-like nitroxide (*N*) is the formation of the Diels Alder adduct **3**. This adduct rapidly reacts with *N* reaching quasi-steady state. The length of the induction period can be correlated with the initial *N* concentration and the rate constants of the dimerization reactions.

Considering the presence of an *N* radical in the thermal auto-copolymerization of S-MA, and assuming that: i) path A is negligible with respect to path B, ii) path C

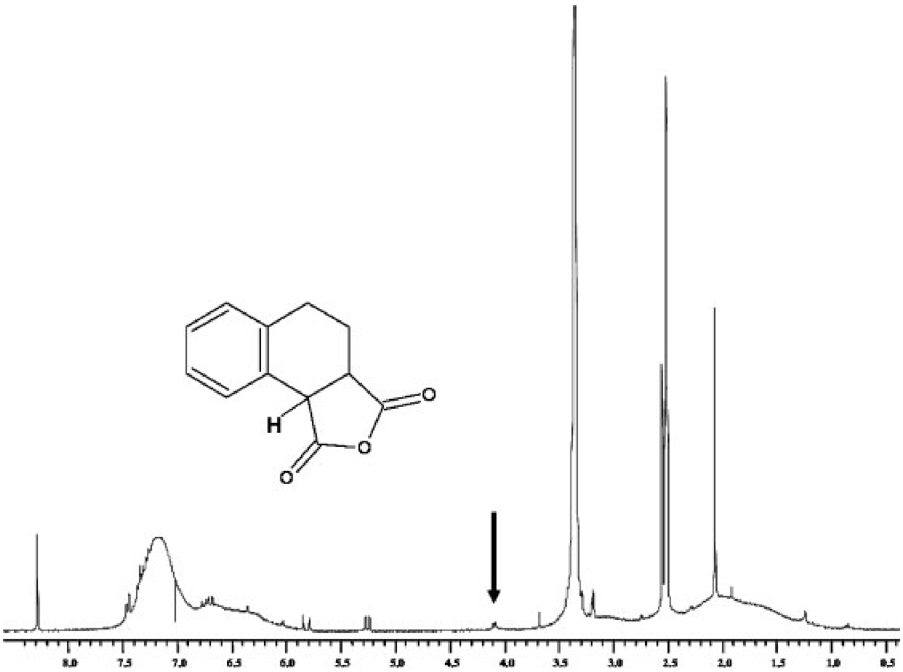


Figure 2.
NMR spectra of S-MA oligomer, evidence of dimer presence.

is negligible with respect to path D, and iii) **3** and **7** are at quasi steady state, then the rate of consumption of *N* radicals is given by the following equation:

$$\frac{d[N]}{dt} = -2k_{dsma}[S][MA] - 2k_{\mathrm{dim}}[S]^2 \tag{1}$$

Where [S] and [MA] are the concentrations of styrene and maleic anhydride respectively, which can be considered constant during the induction period. Assuming also that at the end of the induction period [*N*] is negligible and integrating eq (1), results in:

$$[N]_0 = (2k_{dsma}[S]_0[MA]_0 + 2k_{\mathrm{dim}}[S]_0^2)T \tag{2}$$

Where the sub-index *0* indicates initial conditions and *T* is the induction period. k_{dim} in equation 1 has been measured with precision by Kothe and Fischer as $k_{\mathrm{dim}} = 2.51 \times 10^4 \exp(-93{,}500/(RT))\ \mathrm{L \cdot mol^{-1} \cdot s^{-1}}$ with R in $\mathrm{J \cdot mol^{-1} \cdot {}^{\circ}K^{-1}}$ and T, the temperature, in °K. In order to obtain initial estimates of the value of k_{dsma} we performed reactions for the system S-MA in presence of OH-TEMPO (*[N]*) in a capillary dilatometer in order to measure the induction period and the conversion – time curve after induction. Different compositions of the pair S-MA and of the nitroxide mixture increased its volume by thermal expansion until thermal equilibrium was established. At that point zero time was marked and the volume contraction of the reaction mixture with time was correlated with conversion via standard calculations that use the density of the monomer mixture and the polymer.[20] Table 1 contains a summary of the results and Figure 3 shows conversion – time curves for some of the experiments performed.

The fifth column in Table 1 shows an estimation of the percentage of MA consumed at the end of the induction period in the initiation reaction; this quantity is relevant since the calculation of k_{dsma} assumes constant MA concentration. This estimation is based on the assumption of 1 molecule of MA consumed for each two molecules of nitroxide, since the radical **4** is trapped by a second nitroxide molecule during the induction period. Experiments **4** and **5** are not analyzed in this table because their consumption of MA does not justify to approximate constant concentration of this monomer during the induction period. A second source of deviation for the assumption of constant MA concentration is the fact that some of the reactions show an induction period which is not ''clean''; that is, they exhibit some limited conversion before the polymerization starts at full rate. Such a behavior is rather a retardation period in which inhibition presumably competes with limited propagation. This phenomenon especially affects experiment 6 and, to a lesser extent, experiment 1. Since the conversion at the end of the retardation period is known from the experimental data, it is possible to estimate the total amount of MA that was copolymerized during the retardation period if the composition of the copolymer formed is also known. From measurements of the polymer composition by ^{1}H NMR under different reaction conditions and monomer composition, we consistently obtained copolymer of 50% molar composition of MA, as long as the MA was not completely consumed. This

Table 1.

Experimental conditions and kinetic coefficient estimated for the rate limiting step in S-MA autoinitiation. All the reactions were run in bulk in a capillary dilatometer at 125 °C.

Experiment	[% 4-oxo-TEMPO], M	% MA wt.	Induction time, min	% MA consumed	k_{dsma} L mol^{-1} s^{-1}
1	5.2×10^{-4}	0.1	27	2.8	2.6×10^{-6}
2	5.2×10^{-4}	1	7	0.3	0.9×10^{-6}
3	5.2×10^{-4}	5	2.5	0.06	0.6×10^{-6}
6	5.2×10^{-2}	5	41	11.2	$2.9–5.3 \times 10^{-6}$

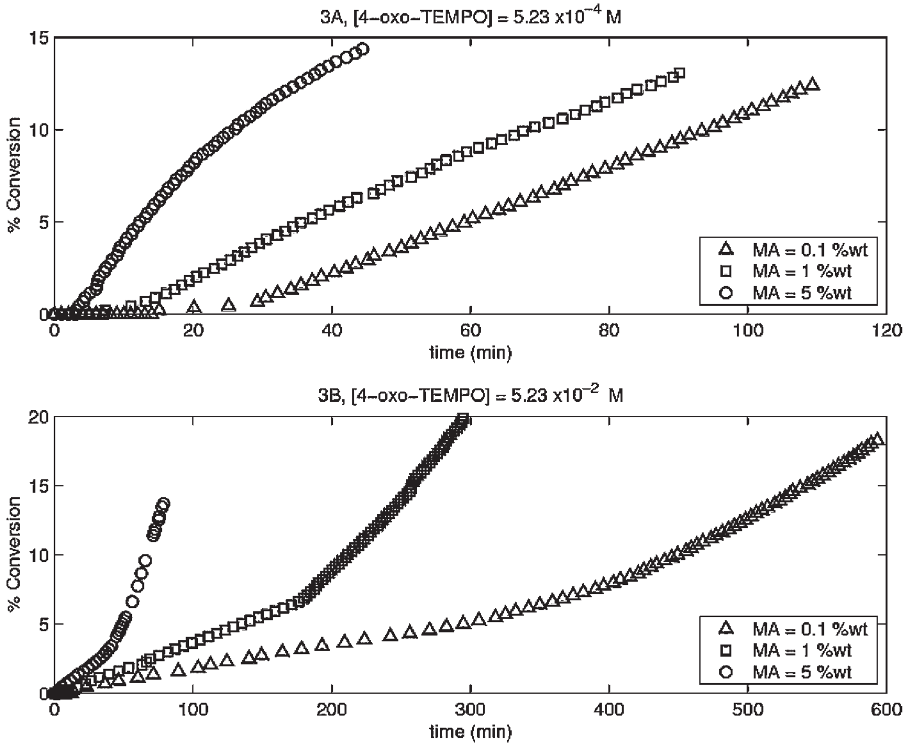


Figure 3.
Conversion vs time data by capillary dilatometry for the system S-MA in bulk at 125 °C.

is consistent with the formation of alternate copolymer of S-MA, that has been widely reported in the literature for copolymerizations performed at lower temperatures. Taking into consideration these two sources of consumption of MA for experiment 6, it is possible to estimate a lower and upper bound for the value of k_{dsma} assuming constant concentration of MA at its initial or final value, respectively (the final value is about 55% of the initial value for experiment 6). In experiments with low oxo-TEMPO concentration (1 to 3) we neglect the second term in the parenthesis of the right hand side of eq (2) for the estimation of the kinetic constant in Table 1. Its contribution must be negligible since it has been reported that path D requires a nitroxide concentration of the order of 0.01 M or above in order to be significant;[13] however, we assume that, due to the presumed higher reactivity of MA with styrene, path B is significant even at this low nitroxide concentration.

Although the variation of the estimated k_{dsma} in Table 1 is relatively large (average value of 2.1×10^{-6} L mol^{-1} s^{-1}) it gives a first order of magnitude estimation of this constant of 10^{-6} L mol^{-1} s^{-1}. This value is considerably larger than that of styrene dimerization at 125 °C, 1.3×10^{-8} L mol^{-1} s^{-1}. Even if the mechanism that we propose here is not the only one operating in this copolymerization, and the initiation via a diradical species, as that suggested by Flory and supported by Hall and Padias, is also contributing initiating radicals, it is still reasonable to assume that the rate limiting step is the reaction between one molecule of each of the two monomers. If both mechanisms have significant contributions, the kinetic constant estimated here is an effective one. In a future publication we will explore a much broader set of experimental conditions in order to have a better estimation of the initiation rate and a stricter test of the validity of the assumptions and kinetic laws proposed.

Conclusions

In this paper we give evidence showing that the rate radical generation in the spontaneous copolymerization of styrene with MA is faster than the corresponding to the spontaneous polymerization of styrene at comparable conditions. We propose that the mechanism of radical generation in the copolymerization case is in good part due to the formation of a Diels-Alder adduct of S and MA, either in a concerted way or via a biradical. Semiempirical calculations and spectroscopic evidence of the adduct support the proposed mechanism. Finally, by inhibition experiments, we make a first order-of-magnitude estimate of the rate constant for the dimerization of S and MA, which results about 2 orders of magnitude larger than that of styrene dimerization at 125 °C.

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[1] P. J. Flory, *J. Am. Chem. Soc.* **1937**, *59*, 241.
[2] F. R. Mayo, *J. Am. Chem. Soc.* **1953**. *75*, 6133.
[3] R. R. Hiatt, P. D. Bartlett, *J. Am. Chem. Soc.* **1959**, *81*, 1149.
[4] W. C. Buzanowsky, J. D., Graham, D. B., Priddy, E. Shero, *Polymer* **1992**, *33*, 3055.
[5] G. Moad, D. H. Solomon, "*The Chemistry of Free Radical Polymerization*", Elsevier Science, New York 1995, p. 95.
[6] K. Kichner, H. Schlapkohol, *Makromol Chem.* **1976**, *177*, 2031.
[7] D. L. Hasha, D. B. Priddy, P. R. Rudolf, E. J. Stark, M. De Pooter, F. Van Damme, *Macromolecules* **1992**, *25*, 3046.
[8] D. Liu, A. B. Padias, H. K. Hall, *Macromolecules* **1995**, *28*, 622.
[9] G. Moad, E. Rizzardo, D. H. Solomon, *Polym. Bull.* **1982**, *6*, 589.
[10] B. Boutevin, D. Bertin, *Eur. Polym. J.* **1999**, *35*, 815.
[11] E. Saldívar-Guerra, J. Bonilla, G. Zacahua, M. Albores-Velasco, *J. Polym. Sci., A. Polym. Chem.* **2006**, *44*, 6962.
[12] T. Kothe, H. Fischer, *J. Polym. Sci. A: Polym. Chem.* **2001**, *39*, 4009.
[13] H. K. Hall, A. B. Padias, *J. Polym. Sci., A. Polym. Chem.* **2001**, *39*, 2069.
[14] Jakko-Hukki, *Acta Chimica Scandinavica* **1951**, *5*, 31.
[15] Th. Wagner-Jauregg, *Ann.* **1931**, *491*, 1.
[16] T. Sato, K. Hibino, T. Otsu, *J., Macromol Sci. Chem.* **1975**, *A9*(7), 1165.
[17] T. Sato, M. Abe, T. Otsu, *Makromol. Chem.* **1977**, *178*, 1061.
[18] Hyperchem 5.01 for Windows. Molecular Model System. Hypercube, Inc.Gainesville, Florida.
[19] E. Pretsch, T. Clerc, J. Seibl, W. Simon, "*Tablas para la elucidación estructural de compuestos orgánicos por métodos espectroscópicos*". 1st Spanish Edition, 1980. Editorial Alambra, S.A.
[20] M. J. Percino, V. M. Chapela, A. Jiménez, *J. Appl. Polym. Sci.* **2004**, *94*, 1662.