

MECHANISM OF INITIATION AND MEASUREMENT OF THE INITIATION RATE IN THE SPONTANEOUS COPOLYMERIZATION OF STYRENE AND MALEIC ANHYDRIDE

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Abstract

Several mechanisms have been proposed to explain the spontaneous initiation in the copolymerization of styrene (St) with electron-acceptor monomers such as maleic anhydride (MA) and acrylonitrile. Styrene self-initiation has been amply studied: Flory postulated the formation of an initiating diradical and Mayo proposed a concerted Diels-Alder reaction between two styrene monomers to form a dimer, which in presence of another styrene molecule generates two initiating radicals. The evidence favours the Mayo mechanism, which has also been extended to explain the spontaneous copolymerization of styrene and maleic anhydride; however no clear evidence has been provided. In this work we show preliminary results elucidating the mechanism of spontaneous initiation in the St-MA copolymerization and provide initial estimates for the rate of radical generation. Spectroscopic (NMR) evidence showing the existence of the Diels-Alder dimer of St-MA is given. Initial estimates of the coefficient rate for the controlling-rate step of radical generation (reaction between St and MA) are also provided. Notice that this has not been measured before in part due to the difficulty of separating the initiation and the propagation steps.

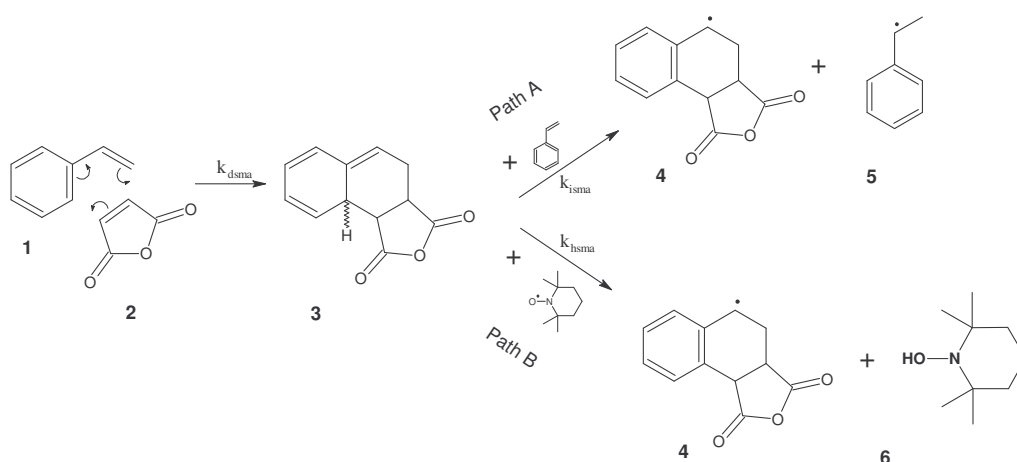
Introduction

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 Flory¹ 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 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}. This mechanism has been speculatively extended⁴ to the spontaneous copolymerizations of styrene with maleic anhydride and other electron-acceptor monomers (see Scheme 1a).

There is experimental evidence and new evidences are presented in this paper about the faster rate of spontaneous copolymerization of styrene with maleic anhydride than that of the spontaneous 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 paper we give preliminary results aimed at the further elucidation of the mechanism and the estimation of the rate of radical generation in the spontaneous copolymerization of styrene and maleic anhydride.



Scheme 1. Postulated mechanism for the spontaneous initiation in St-MA copolymerization in absence (A) and in presence (B) of TEMPO.

Experimental

The 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 solution 10^{-4} M of DPPH were put in a vial in the presence of OH-TEMPO or without it, and heated at 80°, 100° or 120°C after oxygen had been 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.

ESR 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.

Dilatometric conversion – time and induction time measurements. Different compositions of the pair S-MA in addition to nitroxide (4-Oxo-TEMPO, Aldrich) were used. Reactants were premixed and charged to a dilatometer bulb and the dilatometer was then submerged in a controlled temperature circulating bath at 125° C. The reaction 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.

Results and discussion

From the results shown in Fig 1 A-C, 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 TEMPO, therefore the rate of DPPH is slower than in the absence of OH TEMPO. At 100°C rates of St-MA and St-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^[5-7] and extensively in a recent publication of our group,^[8] TEMPO (or its derivatives) considerably enhances the rate of

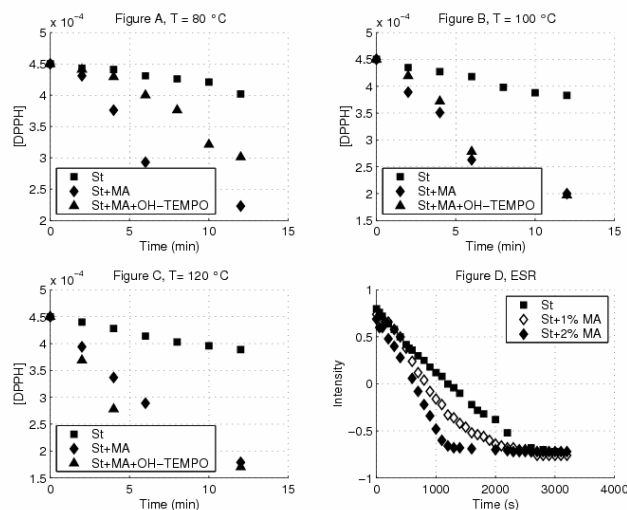


Figure 1 Concentration decay of DPPH in pure styrene (i), styrene-MA (ii) and styrene-MA in presence of OH-TEMPO (iii) at 80, 100 and 120 ° C (Figures 1a, 1b and 1c, respectively). Figure 1D shows the concentration decay of OH-TEMPO detected by ESR in thermal autopolymerization of styrene and of styrene-MA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

radical generation in the thermal autoinitiation of styrene (see discussion below).

Results in Fig 1D 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.

As relevant background for the mechanism that we propose here, we first review the most accepted mechanism for spontaneous radical generation in the thermal styrene autopolymerization. In this case, 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] This mechanism is modified in inhibition experiments in which styrene is heated in presence of TEMPO. In this case, the most viable mechanism^[5-7] implies the formation of the Mayo dimer followed by a fast hydrogen abstraction by TEMPO from the Mayo dimer, generating a dimeric radical and hydroxylamine. 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, and this leads to two consequences: i) the rate of radical generation is much faster in presence of TEMPO than without it and, ii) apparently, in presence of TEMPO the dimer concentration reaches a quasi-stationary state that does not occur in absence of TEMPO.^[6,8] This last fact allowed Kothe and Fischer to measure the rate of dimer formation by following the TEMPO consumption with ESR.

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 1B). Simultaneously, the analogous mechanisms for the spontaneous autopolymerization of styrene would be present generating additional radicals. 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, 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 subtracted from the S-MA contribution. Shorter periods of induction in the copolymerization case as shown in Fig. 1D are consistent with a faster dimerization reaction.

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 ¹HNMR spectra of a signal as a doublet at 4.2 ppm which may be assigned to the benzylic hydrogen which is also α to the anhydride carbonyl in the rearranged Mayo adduct (**4**, Scheme 1), which probably initiates the polymerization (the spectra is not shown here for space reasons, but it will be shown at the meeting). Further confirmation of the plausibility of the mechanism is given by semiempirical calculations to be commented at the meeting. Kothe and Fischer⁶ 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, assuming that the path A is negligible with respect to the path B, and that the adducts are at quasi steady state, then the rate of consumption of N radicals is given by the following equation:

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

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:

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

Where the subindex 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_{dim}* = 2.51 × 10⁴ exp (-93,500/(*RT*)) L · mol⁻¹ · s⁻¹ with *R* in J · mol⁻¹ · °K⁻¹. 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.. Table 1 contains a summary of the results.

Table 1. Estimates of k_{dsma} at different reaction conditions

Experiment	[% 4-oxo-TEMPO], M	% MA wt.	Induction time, min	% MA consumed	k_{dsma} $\text{L mol}^{-1} \text{s}^{-1}$
1	5.2×10^{-4}	0.1	25	2.8	2.9×10^{-6}
2	5.2×10^{-4}	1	7	0.3	0.9×10^{-6}
3	5.2×10^{-4}	5	21	0.06	0.8×10^{-6}
6	5.2×10^{-2}	5	38.5	11.2	$2.9 - 5.3 \times 10^{-6}$

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. 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). Although the variation of the estimated k_{dsma} in Table 1 is relatively large, it gives a first order of magnitude estimation of this constant (average value $2.2 \times 10^{-6} \text{ L mol}^{-1} \text{s}^{-1}$). This value is considerably larger than that of styrene dimerization at 125 C, $1.3 \times 10^{-8} \text{ L mol}^{-1} \text{s}^{-1}$. 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.

Conclusions

In this paper we give evidence showing that the rate of spontaneous copolymerization of styrene with MA is faster than the corresponding spontaneous polymerization of styrene at comparable conditions. We propose that this is in principle due to a faster rate of generation of radicals and 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. Spectroscopic evidence of the adduct supports the proposed mechanism.

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