Macromolecules

Volume 31, Number 16 August 11, 1998

Inhibition of Styrene Polymerization by β-Nitrostyrene. A Novel Inhibition Mechanism

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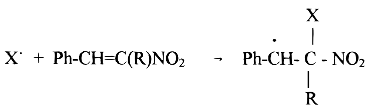
Received August 28, 1997; Revised Manuscript Received May 11, 1998

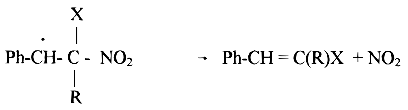
ABSTRACT: The AIBN-initiated polymerization of β-nitrostyrene, as well as its copolymerization with styrene, is negligible. Millimolar concentrations of nitro compound lead to a notable decrease of the polymerization rate of styrene and the molecular weight of the produced polymers. These results, together with the NMR analysis of the polymers, show that β-nitrostyrene acts as a strong inhibitor of styrene polymerization. A mechanism that involves the release of NO_2 is proposed to explain the behavior of β-nitrostyrene as inhibitor.

Introduction

β-Nitrostyrenes are a family of compounds that have been studied mainly from a synthetic and pharmacological point of view, due to the multiple roles that they play in biological systems.[1,2] However, very little is known about their chemistry and photochemistry. Photolysis of the trans compound gives the less stable cis compound, which reverts thermally to the stable isomer in a process that is catalyzed by amines[3] and that seems to involve rather stable free radical-like intermediates.[4] An interesting aspect of the chemistry of these compounds that has been very little considered is their reactivity toward free radicals. The addition of free radicals to the double bonds of these compounds would produce β-nitro radicals that could lose nitrogen dioxide, according to the sequence



$$X^{\cdot} + Ph\text{-}CH{=}C(R)NO_2 \rightarrow Ph\text{-}\dot{C}H\text{-}\underset{R}{\overset{X}{C}}\text{-}NO_2 \qquad (1)$$



$$Ph\text{-}\dot{C}H\text{-}\underset{R}{\overset{X}{C}}\text{-}NO_2 \rightarrow Ph\text{-}CH{=}C(R)X + NO_2 \qquad (2)$$

where step 2 is the back reaction of the reversible addition of nitrogen dioxide to double bonds.[5] The occurrence of this type of process would give to β-nitrostyrenes a very peculiar and unique behavior as monomer, providing a reaction channel not available to other styrene derivatives. To test this hypothesis, we have evaluated the behavior of β-nitrostyrene as monomer and as styrene comonomer in free radical-initiated polymerization processes.

Experimental Section

Polymerization rates (R_P) were determined gravimetrically or by dilatometry. 2,2′-Azobis(isobutyronitrile) (AIBN) was employed as the radical source. Most of the polymerizations were carried out in the dark at 60 °C in monomer/benzene (4:1). Some experiments were also carried out by increasing the rate of free radical production by irradiation of AIBN with light of 366 nm.

The polymers were isolated from the reaction mixture by precipitation with methanol. After washing several times with this solvent, they were dried under vacuum. Polymerization rates were evaluated from the mass of produced polymer or by dilatometry. Molecular weights of the produced polymers were determined by viscosimetry. Measurements were carried out in toluene at 25 °C.

NMR spectra of the polymers were obtained in a Bruker AC 200P (200 MHz) spectrometer in deuterated chloroform.

Styrene (Aldrich) was freshly distilled prior to use. β-Nitrostyrene (Aldrich) was recrystallized from ethanol.

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S0024-9297(97)01296-5 CCC: $15.00

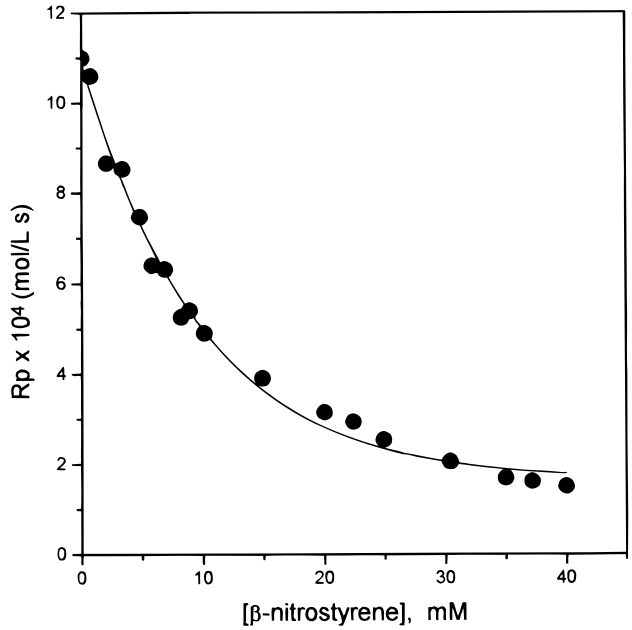


Figure 1. Styrene polymerization rates vs β-nitrostyrene concentration. [AIBN] = 0.028 M, 60 °C.

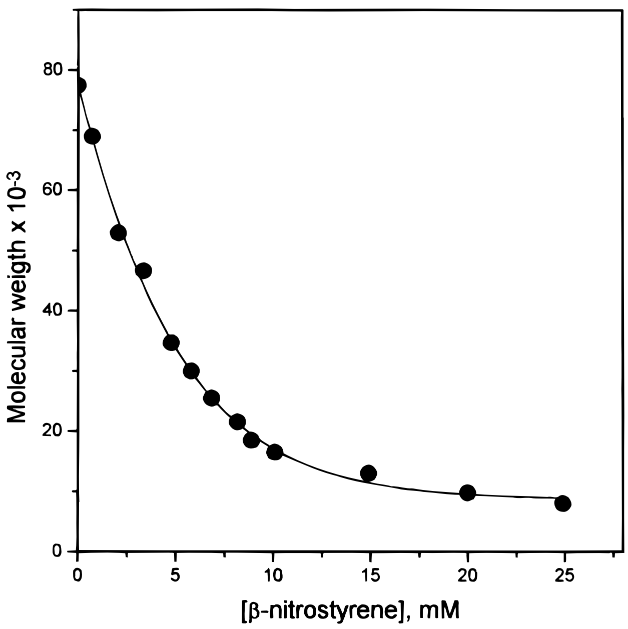


Figure 2. Polystyrene molecular weight as a function of β-nitrostyrene concentration.

Results and Discussion

Attempts to polymerize β-nitrostyrene by employing the pyrolysis of AIBN at 60 °C as free radical source were unsuccessful. Polymer was not produced even when the initiation rate was increased by irradiation of the azo compound. Direct irradiation of β-nitrostyrene in the presence of triethylamine was also unable to produce detectable amounts of polymer. Triethylamine was tested in these assays since it is commonly employed as co-initiator in photopolymerizations.[6] Furthermore, free radicals have been detected (by EPR) when nitrostyrenes are irradiated in the presence of triethylamine.[7]

The copolymerization of styrene and β-nitrostyrene in equivalent amounts was also completely unsuccessful. The presence of the nitro-compound totally prevented the polymerization of styrene. Then, a study was carried out regarding the effect of millimolar concentrations of the nitro compound upon the polymerization rate of styrene and the molecular weight of the produced polymer. The data obtained are collected in Figures 1 and 2. These data show that the presence of nitrostyrene reduces both the polymerization rate and the molecular weight of the polymer. This behavior would indicate that, in the polymerization of styrene, β-nitrostyrene acts as an efficient inhibitor of the chain reaction. A mechanism comprising as termination the reaction of styrene radicals ($P^\bullet$) with the nitro compound

$$P^\bullet + \beta\text{-nitrostyrene} \rightarrow \text{polymer} \qquad (3)$$

predicts that, at high inhibitor concentrations, the polymerization rate must be inversely related to the additive concentration by

$$(R_P)^{-1} = (\alpha k_3[\beta\text{-nitrostyrene}])/(R_i k_P[M]) \qquad (4)$$

where M stands for the monomer, k_3 is the termination rate of styrene radicals, k_P is the propagation rate constant, R_i is the rate of production active free radicals, and α is a parameter that measures the fraction of the primary products of reaction 3 that leads to chain termination. The data obtained conform to this treatment (Figure 3). From the slope of the plot at high β-nitrostyrene concentrations and the known rate of free radical production in the thermolysis of AIBN under our experimental conditions,[8] it can be obtained that

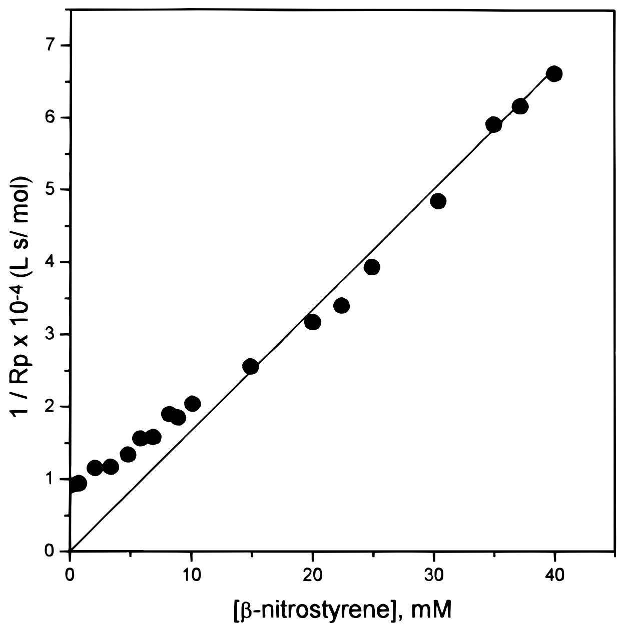


Figure 3. Styrene polymerization rates as a function of β-nitrostyrene concentration, plotted according to eq 4.

$$\alpha k_3/k_P = 4.2 \pm 0.2$$

Evaluation of k_3/k_P by this procedure requires knowledge of the value of α. In the present system it can be assumed that $\alpha = 1$, i.e., that all radicals produced in step 3 quantitatively lead to termination, being unable to reinitiate the polymerization process in a chain transfer-like process. This assumption can be tested by a comparison of the effect of the additive on the polymerization rate and on the average molecular weight of the produced polymer. Figure 4 shows a plot

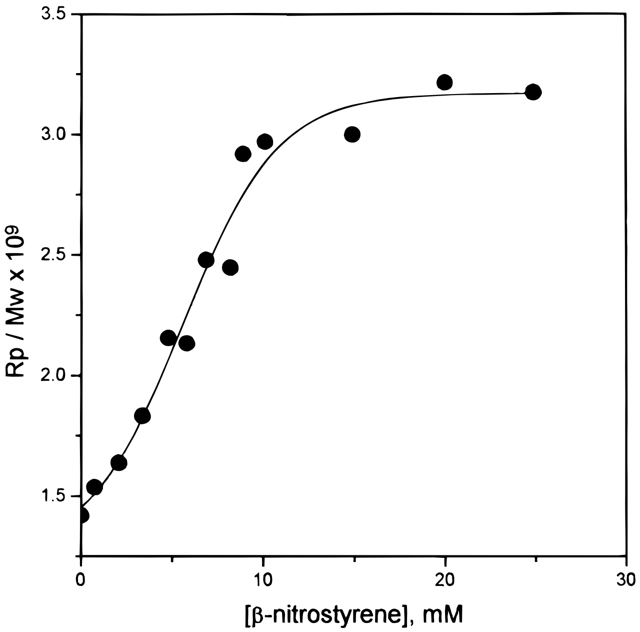
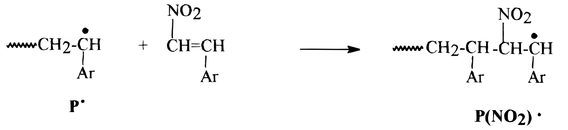


Figure 4. Relation between styrene polymerization rates and the molecular weights of produced polymers as a function of β-nitrostyrene concentration.

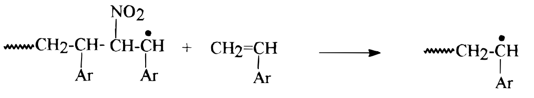
of (R_P/M_w) against the concentration of β-nitrostyrene. Only a moderate increase of a factor 2 is observed, which can be explained in terms of the predominance of the combination process in the self-termination of polystyryl radicals. This would support the assumption that the radicals produced in the initial step of process (3) are completely inactive in reinitiating a new polymeric chain.

To further asses the occurrence of a chain transfer process, we have evaluated the incorporation of nitro groups to the produced polymer. The occurrence of a sequence of reactions such as



$$\sim\!\sim CH_2\text{-}\underset{Ar}{\overset{\bullet}{C}H} + \overset{NO_2}{CH}{=}\underset{Ar}{CH} \longrightarrow \sim\!\sim CH_2\text{-}\underset{Ar}{CH}\text{-}\overset{NO_2}{CH}\text{-}\underset{Ar}{\overset{\bullet}{C}H} \quad (5)$$

$$P^{\bullet} \qquad\qquad P(NO_2)^{\bullet}$$



$$\sim\!\sim CH_2\text{-}\underset{Ar}{CH}\text{-}\overset{NO_2}{CH}\text{-}\underset{Ar}{\overset{\bullet}{C}H} + CH_2{=}\underset{Ar}{CH} \longrightarrow \sim\!\sim CH_2\text{-}\underset{Ar}{\overset{\bullet}{C}H} \quad (6)$$

where $P^{\bullet}$ stands for a macroradical bearing a styryl moiety as the terminal group and $P(NO_2)^{\bullet}$ is a macroradical with a terminal β-nitrostyrene group, would lead to the incorporation of nitro groups into the produced polymer. This was evaluated from the NMR of the polymers. The NMR of the polymer produced in the presence of a large amount of β-nitrostyrene shows the presence of a signal at 4.0 ppm that does not appear in the polymer produced in the absence of the inhibitor (Figure 5). Irradiation at 1.57 ppm produces a decoupling of the signal, rendering a singlet (insert) that can be assigned to a C(H) vicinal to a nitro group, as expected from the incorporation of nitrostyrene to the polymer. To estimate the proportion of nitro groups present in the polymer, this signal was related to the size of the signal corresponding to the styryl groups (between 1.0 and 2.0 ppm). The ratio between these signals is determined by the relative values of k_3 and k_p. This type of treatment implies that the number of nitro groups incorporated per tertiary hydrogen (vicinal to the phenyl group) in the polymer can be expressed as

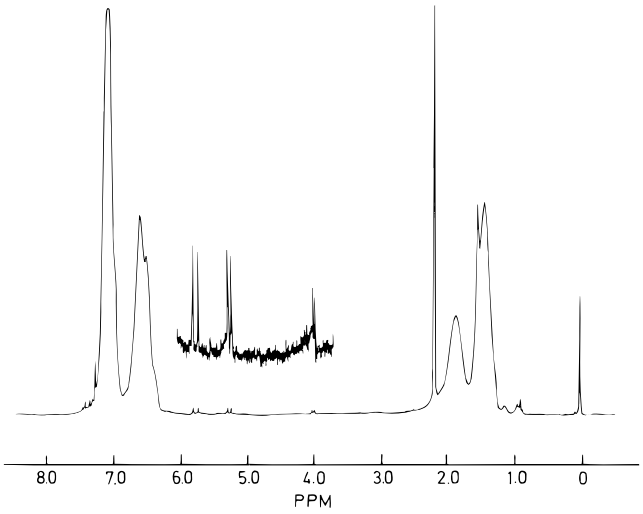


Figure 5. ^{1}H NMR spectrum of polystyrene obtained in the presence of 1 mM β-nitrostyrene. Spectra were measured in $CDCl_3$ at 20 °C.

$$\frac{\text{tertiary H vicinal to nitro group}}{\text{tertiary H vicinal to phenyl group}} = k_3[\beta\text{-nitrostyrene}]/(k_p[M]) \quad (7)$$

The NMR data allow then an independent estimation of k_3/k_P. The signal at 4.0 ppm integrates to 1.1 ± 0.9, and the signals in the region 1.0−2.0 integrate to 439 ± 5. The substitution of these values in eq 7 gives $k_3/k_p \sim 5$. This value, although approximated due to the large error involved in the integration of the small signal associated with the hydrogen atoms vicinal to nitro groups, is of the same order of magnitude as that obtained from polymerization rate data. This indicates that chain transfer is not a significant process.

An estimation of k_3/k_P can also be obtained from the molecular weight of the polymer at high additive concentration. Under this condition, all termination is mediated by reaction 3 and hence

$$M_w = (MW)_{\text{monomer}} k_P[M]/(\gamma k_3[\beta\text{-nitrostyrene}]) \quad (8)$$

where γ is a parameter that gives the number of polymer molecules generated as a consequence of the occurrence of reaction 3. The data obtained at high β-nitrostyrene concentrations give

$$\gamma k_3/k_P \geq 4.1$$

where the inequality is due to the employment of viscosity molecular weights in the calculation of the average size of the polymer.

The results obtained in the present work are compatible with the predominance of the sequence of reactions 9−11 when β-nitrostyrene interacts with the polystyryl radicals:

$$P^{\bullet} + \beta\text{-nitrostyrene} \rightarrow P(NO_2)^{\bullet} \quad (9)$$

$$P(NO_2)^{\bullet} \rightarrow P + NO_2 \quad (10)$$

$$P^\bullet + NO_2 \rightarrow P{-}NO_2 \qquad (11)$$

with minimal contribution of chain transfer steps due to the addition of the $P(NO_2)^\bullet$ radicals and/or NO_2 to the monomer. Step 10 is supported by previous results that have shown that the addition of NO_2 to the double bond is reversible.[9,10] If

$$\alpha = 1$$

and

$$\gamma = 2$$

all data obtained are compatible with

$$k_9/k_P = 4.2$$

where k_9 stands for the rate of addition of chain-carrying radicals to the β-nitrostyrene. Thus, k_9/k_p evaluated in the present work implies a high reactivity of the β-nitrostyrene toward the polystyryl radicals. In fact, the reported values of k_P lead to a value of 7.6×10^2 M^{-1} s^{-1} for k_9. This high value can be explained in terms of the electron donor character of the polystyryl radicals and the electron deficiency of the double bond as a consequence of the nitro substituent. The sequence of processes 9−11 constitutes then a novel and efficient mechanism of inhibition in free radical-mediated polymerization processes.

Acknowledgment. This work was supported by FONDECYT (Grant 1970414), ECOS-CONICYT and DICYT (Universidad de Santiago de Chile).

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MA9712965