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A Product Study of the Nitroxide Inhibited Thermal Polymerization of Styrene

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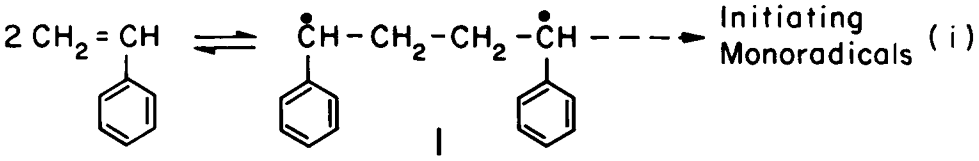
Summary

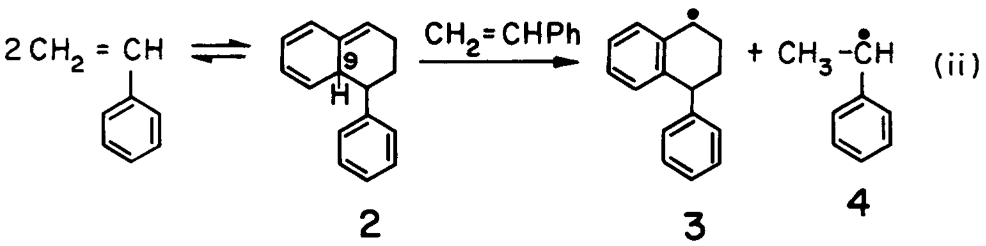
The efficient free radical scavengers 1,1,3,3-tetramethylisoindolinyl-2-oxy and 2,2,6,6-tetramethylpiperidinyl-1-oxy (nitroxides) disappear in styrene at 100°C with near zero order kinetics but at rates which are some 20 times higher than the known rate of initiation of thermal polymerization in the absence of scavenger. A quantitative product analysis has shown that these inhibitors react by hydrogen abstraction from a thermally generated styrene dimer (1-phenyl-1,2,3,9-tetrahydronaphthalene) and to a minor extent by addition to the double bond of styrene monomer.

Introduction

It is well known that certain radical scavengers (diphenylpicrylhydrazyl, benzoquinone, sulfur, oxygen, iodine, galvinoxyl) used to inhibit the thermal polymerization of styrene are consumed at far greater rates than the rate of radical production calculated from the observed kinetics of polymerization in the absence of scavenger (PRYOR and LASSWELL 1975)*. Although explanations for this discrepancy have been offered, none has been supported by a product study which demonstrates, quantitatively, the fate of the inhibitor.



(i)



(ii)

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* The radical scavenger 1,3-bis(diphenylene)-2-phenylallyl has been reported to disappear in styrene at 100°C at a rate approximately equal to the rate of formation of initiating radicals (PRYOR et al. 1977).

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While the precise mechanism for the spontaneous generation of initiating radicals from styrene is yet to be established, two proposals have received the support of considerable circumstantial evidence (PRYOR and LASSWELL 1975). In the first (equation i), the 1,4-diradical **1**, formed by combination of two styrene molecules partitions between intramolecular cyclization to cyclobutanes and unspecified transfer reactions to give initiating monoradicals. In the second (equation ii), the Diels-Alder dimer **2** reacts with styrene to give inactive trimers together with a low yield of the initiating radicals **3** and **4**.

Since the high rate of consumption of inhibitors cannot be explained by the trapping of initiating radicals alone, it has been suggested that they could disappear by reaction with the diradical **1** (RUSSELL and TOBOLSKY 1953; BARR et al. 1978), the Diels-Alder dimer **2** or styrene itself (PRYOR and LASSWELL 1975; ZHULIN and STASHINA 1977).

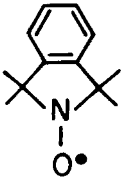
Recently we have taken advantage of the exceptional radical scavenging properties of certain nitroxides to define the reaction pathways of a number of monomers with initiator-derived radicals (RIZZARDO and SOLOMON 1979; MOAD et al. 1982; GRIFFITHS et al. 1982). With the view of obtaining information regarding the mechanism of the spontaneous initiation of styrene polymerization and establishing the fate of inhibitors during this reaction, we have undertaken a quantitative study of the products formed when 1,1,3,3-tetramethylisoindolinyl-2-oxy **5** and 2,2,6,6-tetramethylpiperidinyl-1-oxy **6** are used as inhibitors for the thermal polymerization of styrene. The results are reported in this communication.

Results and Discussion

The nitroxides **5** and **6** disappear in styrene at 100°C with near zero-order kinetics at rates of 2.2×10^{-7} M sec^{-1} and 2.5×10^{-7} M sec^{-1} respectively. These rates, however, are almost 20 times higher than the calculated rate of initiation of the thermal polymerization of styrene at 100°C ($R_{i,th} = 1.3\times10^{-8}$ M sec^{-1} (RUSSELL and TOBOLSKY 1953) and in this respect the behaviour of the nitroxides resembles that of benzoquinone and diphenylpicrylhydrazyl. If we accept the published value for $R_{i,th}$ then the discrepancy in these rates must be due to reactions of the nitroxides with species other than the initiating radicals.

In the present experiments essentially all of the nitroxide **5** consumed can be accounted for by the products **7** (43%), **9** (47%), **11** (2%) and **12** (7%). Although product **9** is formally the trapped radical **3**, and therefore potential evidence for mechanism (ii), its high rate of formation coupled with the concomitant production of approximately equal amounts of the hydroxylamine **7** indicates that other mechanisms contribute to its formation. The suggestion that radical scavengers can react directly with the Diels-Alder dimer **2** (PRYOR and LASSWELL 1975; ZHULIN et al. 1977) appears to be most plausible. Thus, donation of the C-9 hydrogen atom of dimer **2** to nitroxide **5** would yield hydroxylamine **7** and radical **3** which on combination with nitroxide **5** would give the two isomers of the tetrahydronaphthalene derivative **9**. The high yield of **9** is additional evidence (PRYOR and LASSWELL 1975) that dimerization of styrene to the elusive Diels-Alder adduct **2** is a major process that occurs during thermal polymerization.

The isolation of alkoxyamine **11** (formally the product of the phenylethyl radical **4** coupling with the nitroxide **5**) is of considerable interest although, again, it does not constitute rigorous proof for the operation of mechanism (ii) since we also showed that **11** arises by reaction of styrene with the hydroxylamine **7**. Formation of **11** from **7** and styrene is probably an example of reactions that occur via a molecule-assisted homolysis (MAH) mechanism. In this, the styrene-assisted transfer of the O-H hydrogen from **7** to styrene yields the radicals **4** and **5** which can combine to give the observed product **11**. Hydrogen atom transfer to styrene from thiols and certain model compounds for the Diels-Alder dimer **2** is also believed to involve the MAH mechanism. Evidence such as this supports the feasibility of mechanism (ii) for the self-initiated polymerization of styrene (PRYOR 1978).



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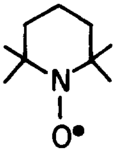

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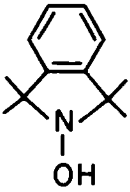

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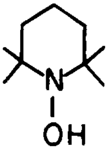

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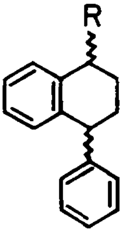
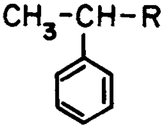
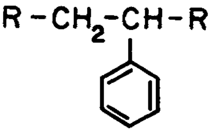


9: R=5
10: R=6



CH_3-CH-R

11: R=5



$R-CH_2-CH-R$

12: R=5
13: R=6

In contrast, transfer of a hydrogen from the hydroxylamine **8** to styrene was not observed and the reaction of nitroxide **6** in styrene at 100°C resulted in the formation of **8** (44%), **10** (45%), and **13** (10%) (based on **6** consumed) with the total exclusion of the product analogous to **11**. This finding is consistent with our observation that hydroxylamine **8** is oxidised (loss of hydrogen) to the nitroxide **6** by molecular oxygen at a lower rate than that of the oxidation of **7** to **5**.

Formation of the *bis*-adducts **12** and **13** is explained most readily by the addition of nitroxide (**5** or **6**) to the olefinic bond of styrene followed by combination of the resulting radical with a second molecule of nitroxide. The nitroxide **6** has a somewhat greater propensity for addition to styrene than nitroxide **5**, as evidenced by its slightly higher rate of disappearance and by the relative yields of the *bis*-adducts **12** and **13**.

Products that would result from the trapping of the 1,4-diradical **1** by nitroxide were not observed although *cis-* and *trans-* 1,2-diphenylcyclobutane accounted for approximately 7% of the total mixture of products. Nitroxides react with carbon-centered radicals at extremely fast rates ($k=10^7-10^9$ M^{-1} sec^{-1}) (SCHMID and INGOLD 1978; ASMUS et al. 1976) and yet the trapping of diradical **1** is not competitive with its intramolecular cyclization to diphenylcyclobutane or to the Diels-Alder dimer **2**, if the latter is formed by a stepwise diradical mechanism (BARR et al. 1978). Clearly then, the proposal (RUSSELL and TOBOLSKY 1953; BARR et al. 1978) that radical scavengers disappear largely by reaction with diradicals during the inhibited thermal polymerization of styrene must be rejected.

Conclusion

The work described in this publication offers, for the first time, a quantitative outline of the processes involved in the consumption of a radical scavenger in styrene. The nitroxides **5** and **6** disappear by reaction with the Diels-Alder dimer of styrene **2** and to a lesser extent by direct addition to monomer. For these reasons, loss of the radical scavengers proceeds at far greater rates than the observed rate of initiation of polymerization in the absence of inhibitor.

Experimental

"High purity" commercial styrene was purified by passage through chromatographic alumina (activity I) and used immediately after fractionation at reduced pressure. The preparation of nitroxides **5** (GRIFFITHS et al. 1982) and **6** (BRIERE et al. 1965) has been outlined previously.

Solutions of the nitroxides (0.05 M) in purified styrene were placed in a vessel equipped with a UV cell as a side-arm, degassed by the freeze-thaw technique, sealed *in vacuo* and then heated at 100±0.5°C for 16 hrs. The disappearance of nitroxides **5** and **6** was found to be linear with time by UV absorbance measurements at 440 nm and 468 nm respectively. The reaction mixtures were analysed by HPLC (Dupont model 850 chromatograph, Ultrasphere ODS or Zorbax ODS columns, methanol/water as the eluent) following removal of most of the styrene (ca. 95%) under reduced pressure. Peak areas obtained by integration of the HPLC trace were corrected using response ratios determined by quantitative analysis of standard solutions of the individual compounds isolated by preparative HPLC.

The products **9**, **11** and **12** exhibited the following spectral characteristics:

trans-**9**: CI/MS *m/e* 398 (M+1). ^{1}H NMR (250 MHz) δ ($CDCl_3$) 1.35 (s, 3H), 1.40 (s, 3H), 1.45 (s, 3H), 1.60 (s, 3H), 1.90 (m, 1H), 2.05 (m, 1H), 2.30 (m, 1H), 2.55 (m, 1H), 4.0 (dd, J=5, 11Hz, 1H), 4.95 (t, J=3Hz, 1H), 6.8-7.7 (complex, 13H).

cis-**9**: CI/MS *m/e* 398 (M+1). ^{1}H NMR (250 MHz) δ ($CDCl_3$) 1.36 (s, 3H), 1.45 (s, 3H), 1.51 (s, 3H), 1.60 (s, 3H), 1.8 (m, 1H), 2.14 (m, 2H), 2.52 (m, 1H), 4.30 (t, J=6Hz), 5.02 (brt, 1H), 6.9-7.7 (complex, 13H).

Product **11**: CI/MS *m/e* 296 (M+1). ^{1}H NMR (100 MHz) δ ($CDCl_3$) 0.90 (s, 3H), 1.21 (s, 3H), 1.39 (s, 3H), 1.55 (d, J=7Hz, 3H), 1.59 (s, 3H), 4.84 (q, J=7Hz, 1H), 6.8-7.3 (complex, 9H).

Product **12:** CI/MS *m/e* 485 (M+1). ^{1}H NMR (100 MHz) δ ($CDCl_3$) 0.84 (s, 3H), 1.29 (s, 3H), 1.39 (s, 12H), 1.52 (s, 3H), 1.70 (s, 3H), 4.09 (dd, J=5, 10Hz, 1H), 4.50 (dd, J=7,10Hz, 1H), 5.00 (dd, J=5,7Hz, 1H), 6.9-7.5 (complex, 13H).

The identities and yields of the hydroxylamines **7** and **8** were determined by UV spectroscopy following their oxidation to nitroxides **5** and **6** respectively by molecular oxygen (ZHULIN and STASHINA 1977). The yield and structure of **8** were confirmed by a GC comparison (3.6% OV17 on chromosorb W.AW at 120°C) with an authentic specimen of **8** prepared by hydrogenation of nitroxide **6** over platinum oxide catalyst. Products **10** and **13** showed similar spectral characteristics to those of **9** and **12** respectively. The spectral properties of *cis*- and *trans*-1,2-diphenylcyclobutanes were in accord with published data (KOPECKY and EVANI 1969).

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