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Thermal decomposition of 2,2,6,6-tetramethyl-1-(1-phenethyloxy) piperidine

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Abstract

The thermal decomposition characteristics of 2,2,6,6-tetramethyl-1-(1-phenethyloxy) piperidine, a stable covalent adduct of a benzylic radical derived from ethylbenzene and a nitroxyl radical, 2,2,6,6-tetramethyl-1-piperidinyloxy have been studied using a variety of techniques. This adduct has been used to initiate the polymerization of styrene. The adduct decomposes thermally to generate a benzylic radical capable of initiating polymerization and a passive nitroxyl radical which reversibly forms a covalent bond with the propagating chain end. Thus the polymerization proceeds under living conditions. The thermal decomposition of the adduct has been examined in detail in an attempt to better understand the reversibility of chain capture during polymerization. The adduct decomposes to form predominately styrene and a hydroxylamine corresponding to the nitroxyl fragment. Small amounts of 2,3-diphenylbutane and ethylbenzene are also formed. The activation energy for the decomposition, which reflects the cleavage of the nitrogen–oxygen bond, is 30.6 kcal/mol. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Polymerization; Thermal decomposition; Nuclear magnetic resonance

1. Introduction

Conventional free radical polymerization is responsible for billions of pounds of production annually. The polydispersity of polymers produced in this way is typically rather large, about two. This is the result of uncontrolled termination processes: radical combination, disproportionation, and chain transfer. If means to control these termination reactions, i.e., to preserve the growing polymer radical could be found, control of free radical polymerization similar to that characteristic of living polymerization might be possible [1]. The utilization of a passive radical, or other, species to reversibly trap the propagating chain end can markedly improve the control of polymerization using free radical initiation [2]. Alkoxyamines which decompose reversibly at moderate temperatures are particularly suitable as initiators which may both initiate and control the propagation of polymerization. For example, 2,2,6,6-tetramethyl-1-(1-phenethyloxy) piperidine (TMEP) smoothly undergoes thermal fragmentation at temperatures approaching 140°C to afford a benzylic ethylbenzene radical capable of initiating polymerization and a passive mediating nitroxyl radical to reversibly cap and preserve the propagating chain end [3,4]. Polymerization of styrene using this initiator affords polymer of much lower polydispersity (1.1–1.4) than that normally observed

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from free-radical polymerization. Further, polymer molecular weight increases linearly with time and conversion and may be calculated from the initial ratio of styrene to 2,2,6,6-tetramethyl-1-(1-phenethyloxy)piperidine (TMPEP). Both because of the potential offered by TMPEP as an initiator and because it serves as a model for the propagating chain end during polymerization, the thermal decomposition of TMPEP has been examined in detail.

2. Experimental

2.1. Materials

The alkoxyamine, TMPEP was prepared and characterized as previously described [5]. Common solvents and reagents were obtained from the Fisher. Spectroscopy solvents were purchased from the Aldrich Chemical or Isotec.

2.2. Instrumentation

Differential scanning calorimetry (DSC) was accomplished using a TA instruments model 2910 cell purged with nitrogen at a rate of 50 ml/min and aluminum sample pans. A TA instruments model 2950 TGA unit was used for thermogravimetry. The TGA cell was swept with nitrogen at 50 ml/min during runs and the sample, approximately 10 mg, was contained in a platinum sample pan. Both the DSC and TGA units were interfaced with the TA instruments Thermal Analyst 2100 control unit. Electron spin resonance (ESR) analyses were performed at 9.5 GHz using a Bruker ESP 300E instrument. The thermal decomposition of TMPEP was monitored as a function of time using both nuclear magnetic resonance (NMR) spectroscopy and high performance liquid chromatography (HPLC). HPLC was performed using a Hewlett-Packard 1090 instrument equipped with a UV-VIS diode array detector and a 4.6 mm id × 150 mm octadecylsilane reversed-phase column. The mobile phase was a gradient of acetonitrile/water (50–100% acetonitrile). Both proton (^{1}H) and carbon (^{13}C) NMR spectra were obtained using a Bruker AC-300 spectrometer. Carbon-13 spectra were recorded at 75.5 MHz. Data acquisition was accomplished at a pulse width for 90°, a delay time of 10 s, an acquisition size of 16 K, an accumulation time of 0.41 s, a sweep width of 20 KHz, exponential apodisation, 5 Hz line broadening, and gated decoupling without NOE. Structures of decomposition products were established by chromatographic and spectroscopic comparison with authentic materials.

3. Results and discussion

The alkoxyamine, TMPEP is readily available by synthesis as a white crystalline solid, melting point 49°C. This is reflected in the DSC plot shown in Fig. 1.

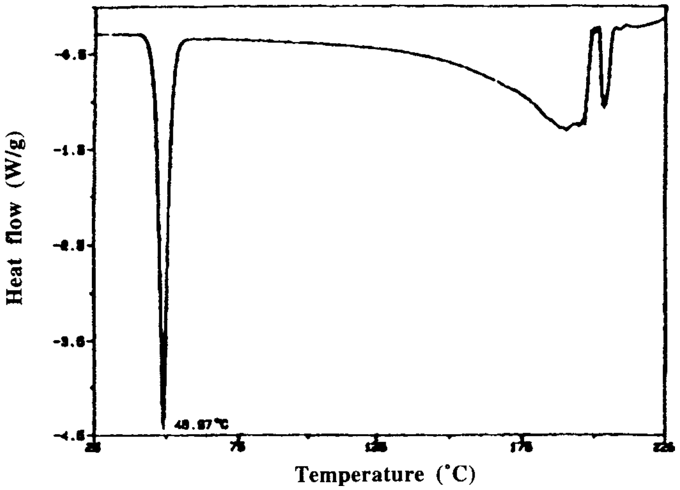


Fig. 1. DSC plot for TMPEP.

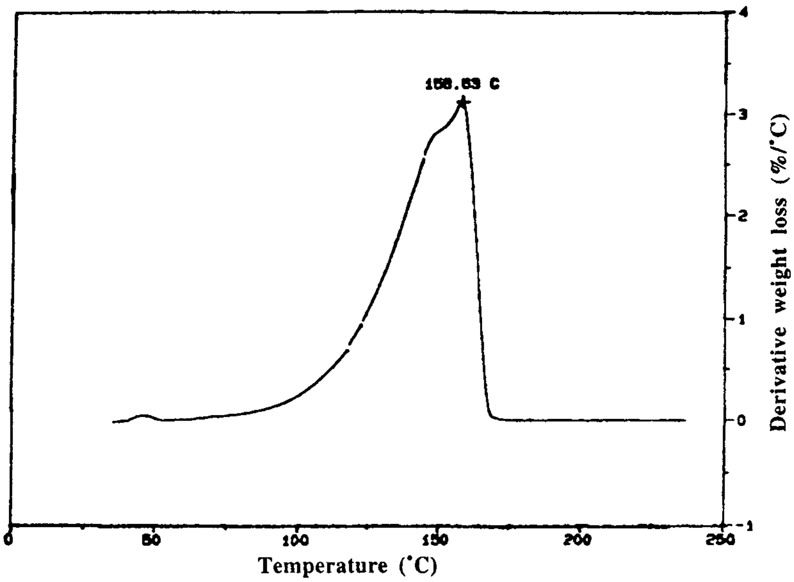


Fig. 2. TGA thermogram for the decomposition of TMPEP.

It is also apparent from this plot that the compound undergoes decomposition well above its melting point. The thermogram presented in Fig. 2 indicates that smooth decomposition occurs at 160°C. That the primary process responsible for decomposition is homolytic cleavage for the carbon–oxygen bond may be established by monitoring the thermal degradation by ESR. As shown in Fig. 3, at ambient temperature TMPEP displays no ESR signal. However, upon being heated to 60°C, a signal corresponding to the 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) radical begins to appear. As shown in Fig. 4, the intensity of this signal continues to increase as a

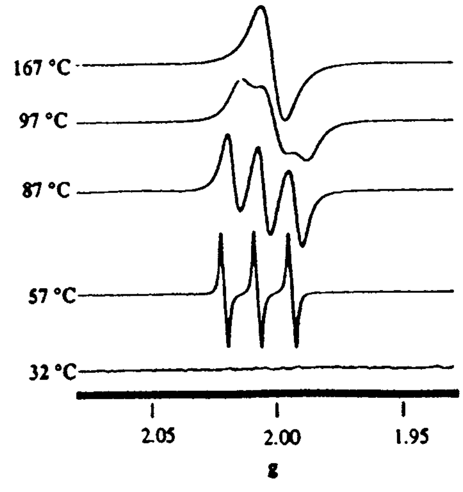


Fig. 3. ESR signal change as a function of temperature for the decomposition of TMPEP.

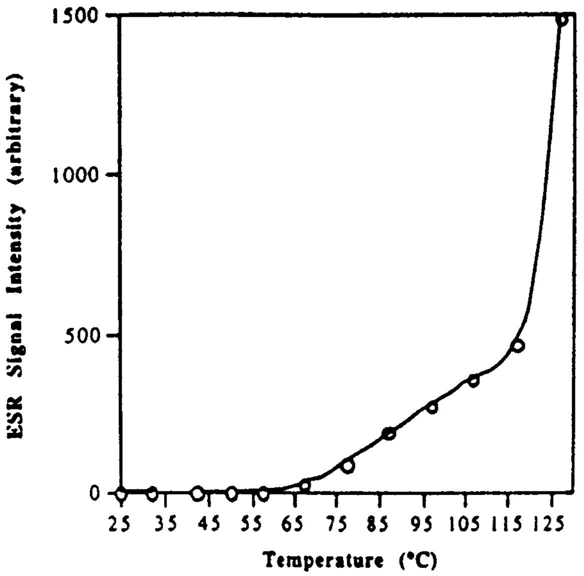


Fig. 4. ESR signal intensity as a function of temperature for the decomposition of TMPEP.

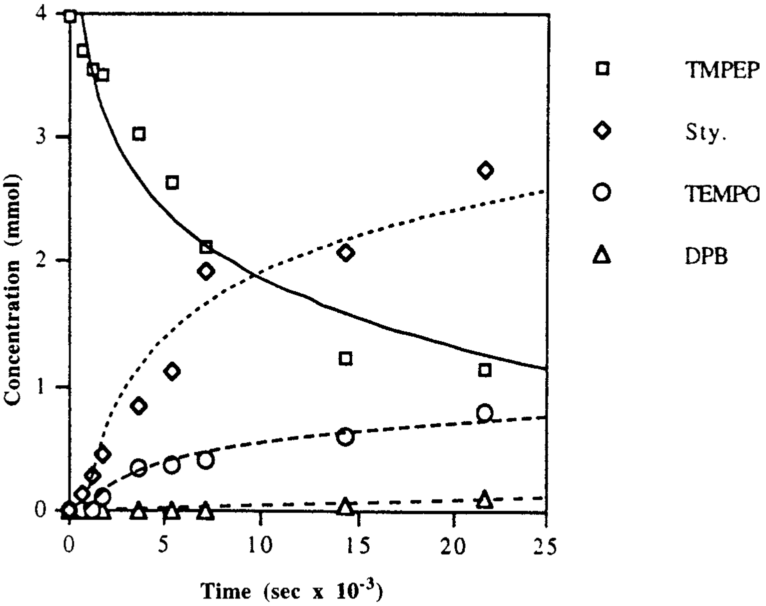
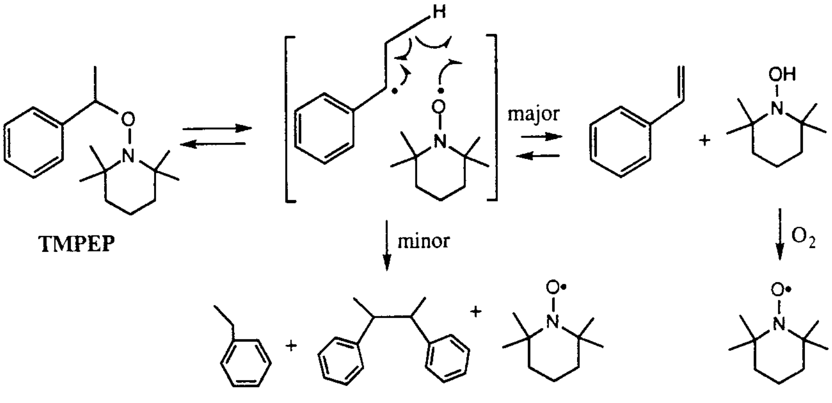


Fig. 5. Loss of TMPEP and formation of products during thermolysis at 140°C.

function of temperature until decomposition is complete. Analysis of the sample from the ESR probe by GC/MS indicated that it contained mainly styrene and TEMPO along with traces of ethylbenzene and 2,3-diphenylbutane. The identity of the products formed was confirmed by spectroscopic NMR and chromatographic HPLC comparison with authentic material. The decomposition in 1,2,4-tichlorobenzene solution at 140°C was monitored as a function of time by HPLC using an acetonitrile/water gradient (50–100% acetonitrile) as mobile phase and biphenyl as an internal standard. The results are displayed in Fig. 5. At this temperature TMPEP undergoes smooth first order decomposition to afford, as major products, styrene and TEMPO. Small amounts of ethylbenzene and 2,3-diphenylbutane also accumulate as a function of time. The decomposition is outlined in Scheme 1. The formation of styrene, i.e., elimination of the hydroxylamine, is due to in-cage decomposition while the formation of 2,3-diphenylbutane and ethylbenzene arise from out-of-cage bimolecular reactions. The rate of decomposition at temperatures between 120°C and



Scheme 1. Mode of decomposition of TMPEP.

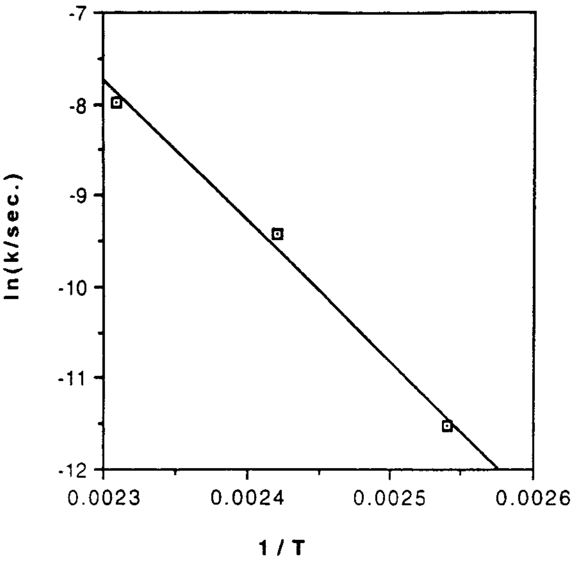


Fig. 6. Arrhenius plot for the thermal decomposition of TMPEP in 1,2,4-trichlorobenzene solution.

160°C could conveniently be followed by monitoring either TMPEP decay or styrene formation. Essentially identical results were obtained by either method. The rate constants determined at 120°C, 140°C and 160°C are 9.98×10^{-6}, 8.16×10^{-5}, and 3.42×10^{-4} s^{-1}, respectively. An Arrhenius plot for these data are shown in Fig. 6. The slope of this plot yields an activation energy for decomposition of 30.6 kcal/mol. Similar rate constants and a comparable value for the activation energy was obtained by monitoring styrene formation as a function of temperature using NMR spectroscopy.

The thermal decomposition of TMPEP in the presence of styrene leads to the formation of low polydispersity polystyrene of high molecular weight ($M_w = 170{,}000$) [4]. The polymerization is characterized by a linear increase of polymer molecular weight as a function of monomer conversion with the ultimate molecular weight reflecting the ratio of monomer to TMPEP initially present. Thus, TMPEP is an efficient initiator of styrene polymerization and its use permits the generation of polystyrene with accurately controlled molecular weight and low polydispersity. Upon completion of the styrene polymerization, addition of a second monomer leads to the formation of a well-defined block copolymer [6].

4. Conclusions

The thermal decomposition of TMPEP, a stable alkoxyamine capable of initiating mediated styrene polymerization, occurs smoothly at temperatures between 120°C and 160°C to afford, predominately, the corresponding hydroxylamine and styrene along with small amounts of ethylbenzene and 2,3-diphenylbutane. The rate-limiting step in the decomposition is the homolysis of the oxygen–carbon bond of the alkoxyamine which occurs with an activation energy of 30.6 kcal/mol.

Acknowledgements

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