Polymer Bulletin 37, 451–456 (1996)

Polymer Bulletin

Synthesis and properties of 2,2,6,6-tetramethyl-1-(1-phenethyloxy)piperidine, an initiator for living free radical styrene polymerization

B. A. Howell*, D. B. Priddy, I. Q. Li, P. B. Smith, P. E. Kastl

Center for Applications in Polymer Science, Central Michigan University,
Mt. Pleasant, MI 48859 and Designed Thermoplastics Research, Dow Chemical Company,
Midland, MI 48667, USA

Received: 30 June 1996/Accepted: 1 July 1996

Summary

An initiator for living free radical polymerization may be prepared by trapping the benzylic ethylbenzene radical with the stable 2,2,6,6-tetramethylpiperidinyl-1-oxy (TEMPO) radical. The adduct, 2,2,6,6-tetramethyl-1-(1-phenethyloxy)piperidine (TMPEP), smoothly undergoes thermal fragmentation at temperatures approaching 140° C to afford an active carbon radical capable of initiating polymerization and a passive mediating nitroxyl radical to reversibly cap and preserve the propagating polymer chain.

Introduction

Conventional free radical polymerization of styrene is widely practiced and is of immense commercial importance. As with other radical polymerizations, the control achieved with anionic and other "living" techniques is not possible. 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 of reversibly trap the propagating chain end can markedly improve the control of polymerization using free radical initiation. Among the systems described for styrene polymerization, those employing nitroxyl radicals as mediating agents are the most attractive (2-9).These radicals are stable to above 100° C, do not initiate polymerization, and react rapidly with carbon-based radicals such as the growing species in the radical polymerization of vinyl monomers. Alkoxyamines, which are products of these reactions, decompose reversibly at elevated temperatures.

An early attempt to control styrene polymerization employed excess 2,2,6,6-tetramethylpiperidinyl-1-oxy (TEMPO), a stable free radical, as a thermally labile capping agent for the propagating chain end (2,3). Reactions were conducted at temperatures at which the half-life of initiator, in this case benzoyl peroxide (BPO), was less than three minutes. Alkoxyamines were generated *in situ* from BPO and TEMPO. It was anticipated that the high temperature (110-140° C), coupled with the promoted dissociation of BPO by the stable nitroxide free radical would ensure that all the active chains would be initiated at the same time. The molecular weight of the polymer produced was proportional to the reciprocal of the concentration of alkoxyamines, and the rate of polymerization could be determined from the stationary concentration of

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* Corresponding author

growing radicals. Molecular weights were observed to increase linearly with time and conversion, and resins were obtained with polydispersities between 1.15 and 1.3. However, long reaction times and the production of low-molecular-weight material limited the usefulness of this process. The bulk polymerization, performed at 125° C, required about 70 h to go to high conversion (> 85%) and provided resins with molecular weights of about 10,000 or smaller. Subsequently means to increase the rate of similar polymerizations and to carry-out the reaction in the absence of excess nitroxide have been developed (7-9). The presence of excess nitroxide in the system can be avoided by using, as initiator, an alkoxyamine which decomposes thermally to generate a carbon radical capable of initiating styrene polymerization and a passive mediating nitroxyl radical which reversibly forms a covalent bond with the propagating chain end. One such species is 2,2,6,6-tetramethyl-1-(1-phenethyloxy)piperidine (TMPEP).

Experimental

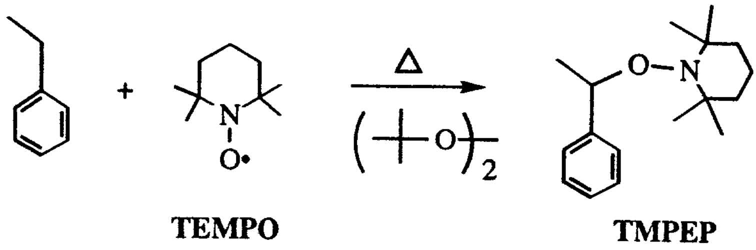
Styrene and ethylbenzene were obtained from the Dow Chemical Company. All reagents were commercial materials from the Aldrich Chemical Company and were used as received. In general, reactions were carried-out in dry glassware under a static atmosphere of dry nitrogen. Progress of reaction was routinely monitored by high performance liquid chromatography (HPLC) using a Hewlett-Packard 1090 instrument equipped with a UV-VIS diode array detector and a 4.6 mm id x 150 mm octadecylsilane reversed-phase column. The mobile phase was a gradient of acetonitrile/water (50-100% acetonitrile). Mass spectra were recorded using a Finnigan SSQ 700 quadruple spectrometer operating in the electron impact and chemical ionization modes. Both proton (^{1}H) and carbon (^{13}C) nuclear magnetic resonance (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 of 90°, a delay time of 10 sec., and acquisition size of 16 K, an accumulation time of 0.41 sec., a sweep width of 20 KHz, exponential apodisation, 5 Hz line broadening, and gated decoupling without NOE.

2,2,6,6-Tetramethyl-1-(1-phenethyloxy)piperidine (TMPEP)

To a solution of 1.46 g (10.0 mmole) of di-*t*-butylperoxide in 30 ml of ethylbenzene was added 3.12 g (20.0 mmole) of 2,2,6,6-tetramethylpiperidinyloxy (TEMPO). The resulting solution was stirred under nitrogen at solvent reflux for 24 h. Excess ethylbenzene was removed by rotary evaporation at reduced pressure to afford a dark brown residual oil. The oil was dissolved in ethanol to provide a solution from which crystals grew at ice bath temperature. The crystals were collected and repeatedly recrystallized from ethanol to afford 2,2,6,6-tetramethyl-1-(1-phenethyloxy)piperidine (TMPEP) as white crystals having a melting point of 44.5-45.0° C.

Results and discussion

Control of free radical polymerization similar to that achieved during anionic polymerization may be realized by utilizing an initiator molecule susceptible to thermal fragmentation to generate an active carbon radical capable of monomer addition and a passive mediating radical to reversibly cap and preserve the propagating chain end. A suitable initiator may be prepared by generating the benzylic ethylbenzene radical in the presence of TEMPO to produce 2,2,6,6-tetramethyl-1-(1-phenethyloxy)piperidine (TMPEP). The proton nmr spectrum of this material is shown in Figure 1. As may be seen the



Scheme 1. Synthesis of 2,2,6,6-Tetramethyl-1-(1-phenethyloxy)piperidine (TMPEP).

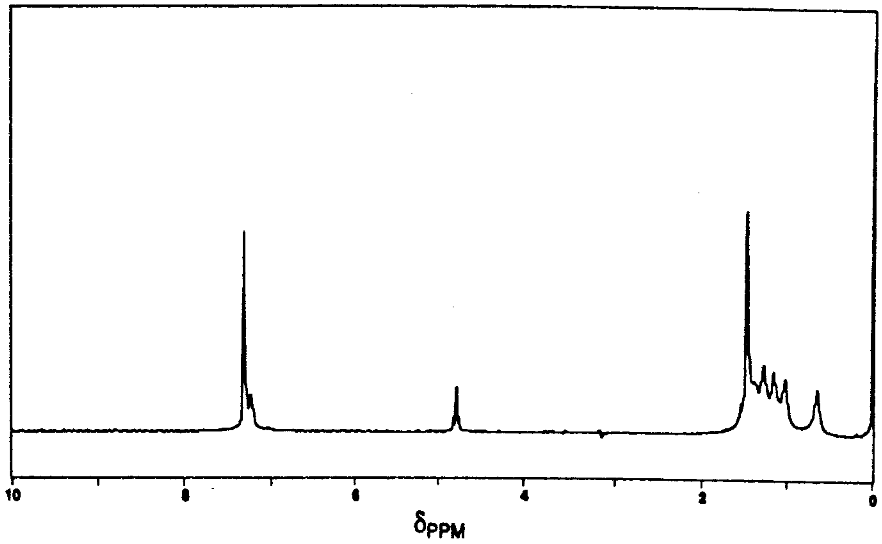


Figure 1. Proton NMR Spectrum of TMPEP.

spectrum contains multiple absorptions near δ 1.0 corresponding to the methylene protons of the piperidine system, a singlet at δ 1.47 for the piperidino methyl protons, a quartet at δ 4.77 due to the benzylic methine proton, and aromatic absorption at δ 7.31. The carbon-13 nmr spectrum of TMPEP is contained in Figure 2. Assignments are as shown in the figure. It can be noted that all elements of the expected structure are apparent in the spectrum. The molecular weight of the TMPEP adduct determined by chemical ionization mass spectrometry was 261.2 g/mole. The corresponding electron impact mass spectrum is displayed in Figure 3. The spectrum contains prominent fragments from both the piperidinyl ($^{m}/_{e}$ 157) and phenyethyl ($^{m}/_{e}$ 105) portions of the molecule.

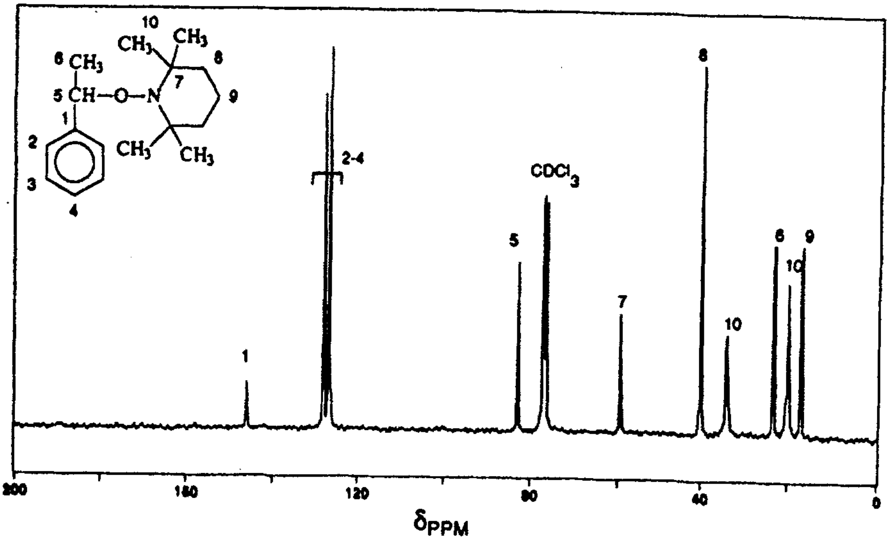


Figure 2. Carbon-13 NMR Spectrum of TMPEP

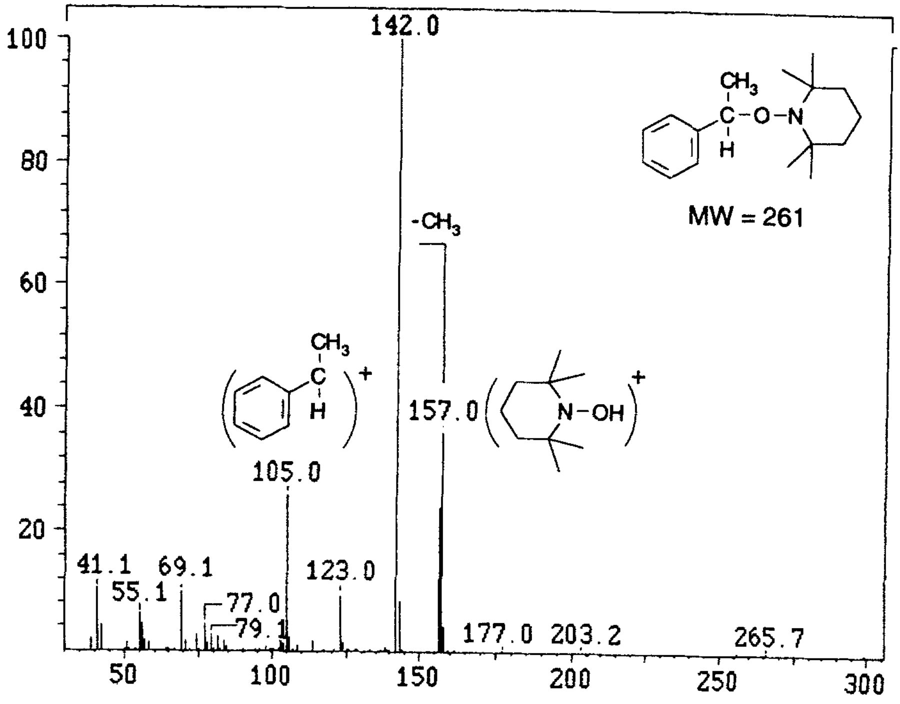
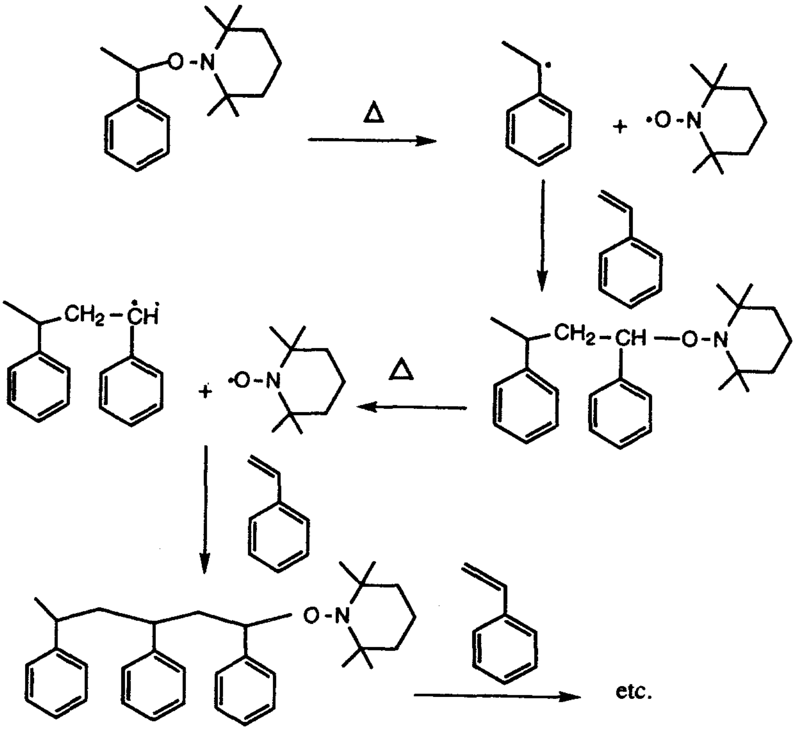


Figure 3. Mass Spectrum of TMPEP.



Scheme 2. Styrene Polymerization Initiated by 2,2,6,6-Tetramethyl-1-(1-phenethyloxy)piperidine (TMPEP).

Table 1. Comparison of the Observed Number-Average Molecular Weight of Polystyrene Prepared at 140° C in the Presence of Camphoroulfonic Acid (2000 ppm) Using TMPEP Initiation with that Expected from the Initial Monomer/Initiator Ratio.

TMPEP(mmol)	M_n(exptl)	M_n(calcd)	PD
6	49605	66833	1.382
12	33095	41417	1.286
16	32775	36369	1.221
22	27438	28814	1.236

Narrow polydispersity polystyrene may be prepared using TMPEP as initiator. As a consequence of this initiating system, one polymer chain end is derived from the active ethylbenzene radical and the other from the TEMPO "counter" radical. The polymerization is illustrated below. The results of ampoule polymerization of styrene in the presence of TMPEP and 2000 ppm camphoroulfonic acid (CSA) at 140° C for 4 h are seen in Table 1. It was necessary to conduct the polymerization in an acidic environment to suppress the spontaneous thermal polymerization of styrene. The experimental molecular weights of the derived polymers are close to the theoretical values calculated from the feed ratio of styrene to TMPEP. At molecular weights below 30,000, the agreement between experimental and calculated M_n values is excellent.

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