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Influence of 2,2,6,6-tetramethylpiperidine and of 2,2,6,6-tetramethylpiperidine-N-oxide on radically induced styrene polymerization

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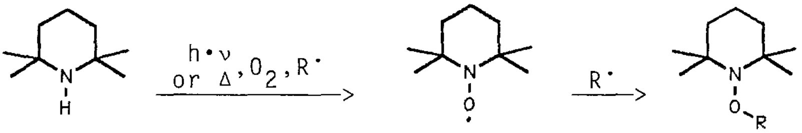
Summary

The influence of 2,2,6,6-tetramethylpiperidine TMP and the corresponding N-oxide TEMPO on the kinetics of the radical polymerization of styrene in bulk is described. Results reveal that the piperidine TMP acts as a chain transfer agent with $c_{tr} = 0.014$ whereas TEMPO is a strong polymerization inhibitor. TEMPO is formed from TMP during polymerization in air saturated styrene.

Introduction

For applicational purposes thermoplastic materials have to be protected against ultraviolet light by stabilizers which reduce or even eliminate photochemical processes as a result of which the polymer is degraded and destroyed. U.v. absorbers in most cases derive from 2-hydroxybenzophenone and during the last decade hindered amine light stabilizers (HALS) have been developed as low molecular weight compounds as well as polymers, among which the simplest model compound of HALS is 2,2,-6,6-tetramethylpiperidine **1** (TMP). Research on the protection mechanisms have revealed that **1** during u.v. irradiation in the presence of oxygen (air) and free radicals (R˙) produces hindered a piperidinoxy radical **2** (TEMPO) according to (1) /1/:



1 **2** **3** (1)

It is generally accepted that in a further reaction sequence the piperidinoxy radical **2** TEMPO is the active site for the u.v. generated alkyl radicals from the polymer source to react with to give a substituted hydroxylpiperidine **3**. From the viewpoint of fundamental radical reaction kinetics in vinyl polymerization, it was of some interest to study the behaviour of TMP **1** and of TEMPO **2** towards a radically induced styrene polymerization.

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Experimental

Styrene (BASF) was purified as usual for kinetic studies. AiBN (Aldrich Chemicals) was recrystallized twice from diethyl ether. 2,2,6,6-tetramethylpiperidine **1** and the N-oxide **2** (Aldrich Chemicals) were used as supplied. For the determination of the rate of bulk polymerization a simple dilatometer (10•70 ccm) was used, all polymerizations for chain transfer constant and conversion determination were carried out in sealed glass tubes under an argon atmosphere or were saturated with air, respectively. GPC was applied to obtain the molecular weight data.

Results and Discussion

TMP **1** exhibits a nitrogen bonded hydrogen which on any air oxidation is readily attacked and substituted (1). In radical styrene polymerization in bulk initiated by AiBN, in an oxygen free system a slight influence of TMP on the rate of polymerization is observed. The kinetics strictly follow the usual law. Nevertheless, **1** takes influence on the molecular weight of the poly(styrene) produced, see data compiled in Tab. 1.

Table 1: Data for determination of chain transfer constant of **1** in radical styrene bulk polymerization

Exp.-nr.		[TMP]/[St] x 10^2	Convers. (%)	M_n (GPC)	Polydispersity
under Ar	1	-	7	95.500	1.84
	2	.69	6.6	91.500	1.85
	3	1.74	6.2	84.700	1.89
	4	3.57	5.2	69.500	2.04
	5	7.54	2.8	48.400	2.26
under air	6	-	6.8	68.700	2.45
	7	.69	6.7	89.000	1.88
	8	1.74	4.4	83.000	1.92
	9	3.57	< .5	-	-
	10	7.54	< .5	-	-

T = 60°C, t = 180 min, [AiBN] = $6.09 \cdot 10^{-3}$ mol/l

The molecular weight data for the experiments under argon extrapolate quite nicely according to the Mayo equation to give a chain transfer constant c_{tr} = 0.014 for TMP **1**, see Fig. 1. As the molecular weight of the polymer decreases, the polydispersity of the probes is increased.

In experiments nr.6-10 styrene had been saturated with dry air prior to polymerization. In the TMP free polymerization nr.6 the molecular weight of the poly(styrene) is considerably lower and polydispersity higher compared to the oxygen free polymerization nr.1 under the same conditions. In exper. nr.7 and 8, respectively, molecular weight and polydispersity of the polymers obtained are almost identical compared with the corresponding experiments nr.2 and 3, respectively. At higher concentrations of **1** in the air saturated systems, conversion drops to almost zero and no polymer is obtained at identical polymerization times.

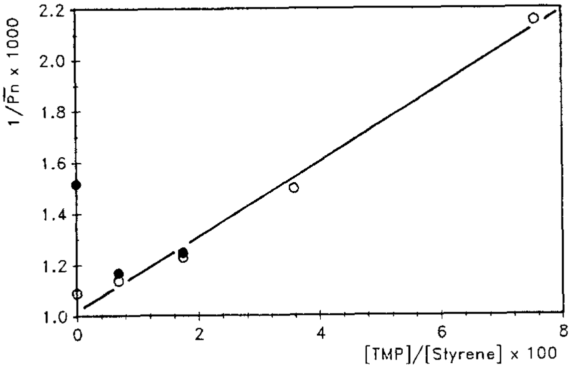

Fig.1: Extrapolation of molecular weight data from Tab. 1 according to Mayo equation for chain transfer constant of **1**

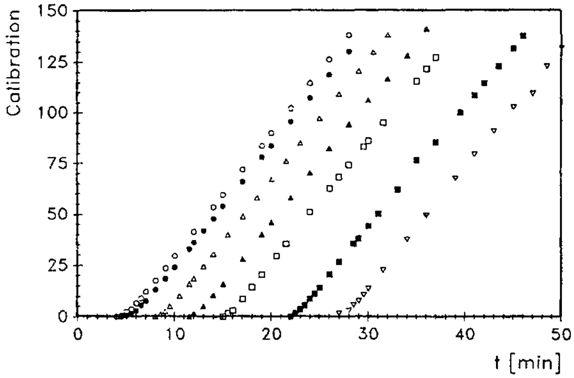

Fig.2: Bulk polymerization of styrene at different concentrations of TEMPO **2**. $[2] \times 10^4$: o = 0, ● = 1.40, Δ = 3.54, ▲ = 5.44, □ = 6.59, ■ = 10.12, ∇ = 12.83 mol/l; [AiBN] = 6.09×10^{-2} mol/l; T = 60°C, air free, calibration: 10 parts ≙ 0,22% conversion

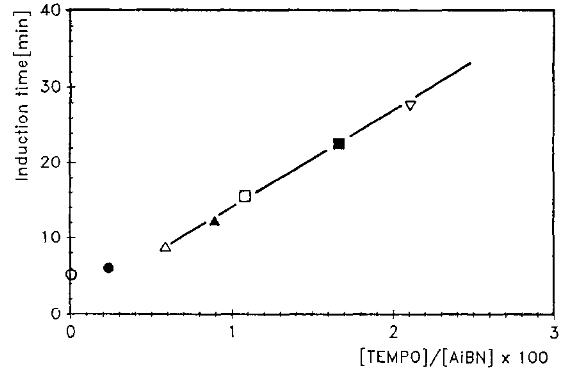

Fig.3: Plot induction time vs. [TEMPO]/[AiBN]; [**2**] see Fig. 2

This observation can be interpreted according to (1). At moderate concentrations of **1**, the piperidine is converted to the N-oxide **2** by the aid of alkyl radicals either from the decomposition of AiBN or the growing polymer chains. As the concentration of **1** is increased in exper.nr.9 and 10, an increase of the stable N-oxide radical **2** is generated which acts as an inhibitor to consume all growing polymer chains and therefore leads to an almost complete suppression of polymerization.

The perfect action of the stable 2,2,6,6-tetramethylpiperidine-N-oxide **2** as inhibitor molecule for radical polymerization is demonstrated in Fig.2. Induction periods related to the concentration of TEMPO **2** (see Fig.3) without retardation (no different slope in Fig.2) were observed.
It should be noted that there is the same inhibition effect of TEMPO irrespective of the oxygen content in styrene.

A forthcoming paper will deal with more detailed discussions of reaction of **1** and **2** with radicals.

Acknowledgements

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Reference

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