Block Copolymer Synthesis and Chain Extension from TEMPO-Terminated Chains Formed by Ultrasonic Chain Scission

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ABSTRACT: Long poly(ethyl methacrylate) (M_n = 2,300,000) and polystyrene (M_n = 1,200,000) chains were subjected to ultrasonic scission in the presence of a radical scavenger, 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO). This procedure yielded polymers with lower molecular weights and TEMPO terminal units. Application of these polymers in stable radical mediated polymerization of styrene resulted in chain extension and block copolymers, depending on the precursor polymer. Block copolymer formation was evidenced by NMR measurement, and chain extension was shown by GPC analysis. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 77: 1950–1953, 2000

Key words: tempo; ultrasound; chain scission

INTRODUCTION

When ultrasound (US) is applied to a long chain polymer, this process preferentially breaks the polymer from the middle, and long chain radicals result.[1–4] Tabata and Sohma[5,6] have shown the formation of macroradicals during ultrasonic chain scission of poly(methyl methacrylate) (PMMA), polystyrene (PS), and poly(vinyl acetate) (PVA), using e.s.r. techniques.[5,6] If there are radical scavengers in the medium, they react with chain radicals, and end-functional polymers are obtained. Chain scission in the presence of the radical scavenger, diphenylpicrylhydrazil (DPPH), results in 2 DPPH molecule per bond.[1–4]

US application in the presence and absence of chloro ethylbenzene (radical scavenger), and deducing the termination mechanism therefrom in the case of polyethyl methacrylate (PEMA),[7] PS, and PMMA,[8] have been reported previously.

Experiments show that during ultrasonic chain scission the mean molecular weight decreases rapidly at first but levels off and does not fall below a limiting value. This is interpreted as long polymer chains easily break but sufficiently short ones are immune to the effect of ultrasound.[1–8]

2,2,6,6-Tetramethyl-1-piperidinyloxy (TEMPO) is a stable free radical and is a well-known radical scavenger that is used in controlled radical polymerization to decrease the heterogeneity index by decreasing the number of uncontrolled chains terminated at the early stages of polymerization.

In the literature, TEMPO has been used together with a radical initiator in the stable radical polymerization of styrene,[9–11] vinyl acetate,[12] and tetrahydrofuran[13] to obtain a narrow molecular weight distribution. Styrene–butyl acrylate[9] and styrene–butadiene[10] copolymers have also been obtained by controlled radical polymerization of styrene with TEMPO.

The aim of this work is to use macroradicals with TEMPO terminal units and apply them to the controlled radical polymerization of styrene. Ultrasonic scission of PS and PEMA chains in the presence of the stable free radical TEMPO results in shorter chains with active TEMPO terminal units. These TEMPO-terminated chains are then used in stable radical-mediated polymerization of styrene. The result is the chain extension when

Table I   Molecular Weights of Polymers before and after Chain Scission

	M_n of the Initial Chain	Sonicating Time	M_n of the Broken Chain	Number of Scissions per Chain
PS	1,200,000 HI = 3	2 h	220,000 HI = 1.75	4
		3 h	182,000 HI = 1.72	6
PEMA	2,300,000	30 min	800,000 HI = 1.36	3
		60 min	500,000 HI = 1.21	5
		90 min	320,000 HI = 1.13	7

the initial chain is PS and block copolymer when the initial chain is PEMA.

The activity of the TEMPO in PEMA/PS and PS/PS systems and the amount of block copolymerization and the chain extension are investigated, respectively.

EXPERIMENTAL

Ultrasonic Chain Scission and Chain Extension

High molecular weight PEMA, (M_n = 2,300,000) and PS (M_n = 1,200,000) were synthesized in our laboratories and were used in ultrasonic chain scission studies in a low-frequency (35 kHz) high-intensity (80 W) US bath at 25°C.

A concentrated polymer solution (PS and PEMA) (12 g/L polymer in toluene) was prepared and saturated with N_2 bubbling for 30 min. TEMPO was added to the polymer solutions, which were then exposed to US for varying times. The molecular weights of PEMA and PS chains before and after chain scission were determined by GPC measurements.

TEMPO terminated chains were used the stable radical polymerization of styrene using three different procedures.

In the first one, a styrene monomer added to the TEMPO-terminated chains and the mixture was heated for 45 h in a thermostat at 130°C in N_2 atmosphere. The extended chains were then precipitated, filtered, and dried *in vacuo.*

In the other two procedures, the styrene monomer and TEMPO-terminated polymers were reacted with and without extra TEMPO in degassed and sealed Pyrex ampoules under vacuum at 125°C for 72 h. The extended chains and copolymers were precipitated, filtered, and dried *in vacuo.* The GPC measurements were performed after chain extension and copolymerization.

If the initial chain was PEMA, the homo PS was extracted by cyclohexane, and the extended amount of styrene in PEMA/PS block was determined from the amount of styrene groups appearing in the aromatic region of the NMR spectrum of the copolymer. Measurement was made in chloroform and acetone mixture using a Bruker HG1513 instrument. GPC measurements were performed using Knauer M-64.

RESULTS AND DISCUSSION

TEMPO terminated polymers are obtained according to the reaction (1) shown below.

The applications of these macro radicals in controlled radical polymerization of styrene is given by reaction (2). The molecular weights of TEMPO-terminated chains measured by GPC before and after chain scission are given in Table I, with the calculated number of scissions per chain being given in the last column.
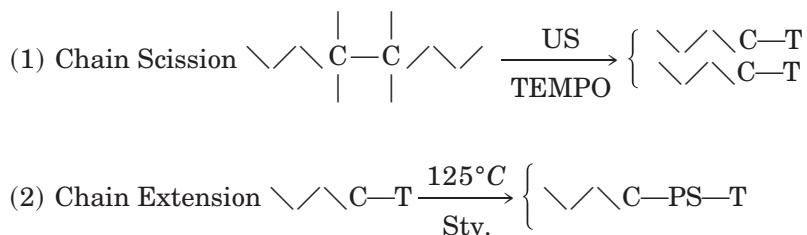
$$(1)\ \text{Chain Scission}\ \diagdown\diagup\diagdown\overset{|}{\underset{|}{\text{C}}}-\overset{|}{\underset{|}{\text{C}}}\diagup\diagdown\diagup\ \xrightarrow[\text{TEMPO}]{\text{US}} \begin{cases} \diagdown\diagup\diagdown\text{C}-\text{T} \\ \diagdown\diagup\diagdown\text{C}-\text{T} \end{cases}$$

$$(2)\ \text{Chain Extension}\ \diagdown\diagup\diagdown\text{C}-\text{T}\ \xrightarrow[\text{Sty.}]{125°C} \begin{cases} \diagdown\diagup\diagdown\text{C}-\text{PS}-\text{T} \end{cases}$$

Table II   Molecular Weights of Sonicated and Extended Polymers before and after Chain Extension

	Before Extension	After Extension Procedure 1	After Extension Procedure 2	After Extension Procedure 3
PS	220,000 HI = 1.75	236,000 HI = 1.99	267,000 HI = 2.02 4,300 HI = 1.34	
	182,000 HI = 1.72	222,000 HI = 1.91		254,000 HI = 2.01
PEMA	800,000 HI = 1.36	840,000 HI = 1.36		
	320,000 HI = 1.13		387,000 HI = 1.6 5,000 HI = 1.33	

As shown in Table I, the molecular weights of PS have decreased five- to sixfold, and the molecular weights of PEMA have also decreased three to sevenfold, depending on the length of irradiation. Because TEMPO is a very effective radical scavenger, from the number of scissions per chain it is possible to deduce that most of the chains have TEMPO units at one or both ends.

When the macroradicals PS (M_n = 220,000) and PEMA (M_n = 800,000) are applied to the stable radical-mediated polymerization of styrene at atmospheric pressure, the resulting molecular weights of extended chains and copolymers are PS (M_n = 236,000) and PMMA (M_n = 840,000), respectively (Table II). Due to the long chain nature of TEMPO-terminated chains, the viscosity of the medium is very high, and the resulting percent of chain extension is low. After extracting the homo PS by cyclohexane, the extended amount of styrene in the polyethyl methacrylate chains is calculated from the NMR spectrum (Fig. 1) as 5%. The amount of styrene extension in the case of polystyrene is also low (approximately 10%).

In the second procedure, TEMPO-terminated chains of PS (M_n = 220,000) and PEMA (M_n = 320,000) are extended by styrene in vacuum with the addition of extra TEMPO. The extra TEMPO is added to compensate for the possible loss of TEMPO groups during chain scission. However, in the GPC measurements of PS, two peaks appear—one peak at PS (M_n = 267,000), and the other at PS (M_n = 4300) (see Table II). In the block copolymerization, a PEMA/PS block copolymer of (M_n = 387,000) and homo PS (M_n = 5000) are obtained (see Table II). The low molecular weight second peaks are caused by the extra amount of TEMPO, which also acts as an initiator. The heterogeneity indexes of these second low molecular weight polymers are also low. The chain extension is considerably higher than the previous case (25%), but the extra amount of scavenger (TEMPO) in the medium causes slow initiation and termination, and the heterogeneity index increases, as shown in Table II.

For this reason, for the third procedure, the controlled radical polymerization of styrene was undertaken in vacuum without addition of the TEMPO. The chain extension is almost 25%, as seen from GPC results in Table II (i.e., 182,000 to 254,000), and the HI increased from 1.72 to 2.01. The GPC curves showing the result of the third procedure for the case of PS chain extension are given in Figure 2.

As a result, TEMPO-ended chains are generated during ultrasonic chain scission and used in
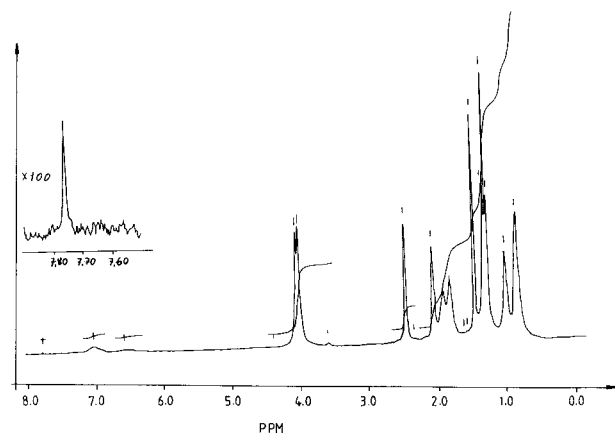
Figure 1   NMR spectrum of the PEMA/PS block copolymer.
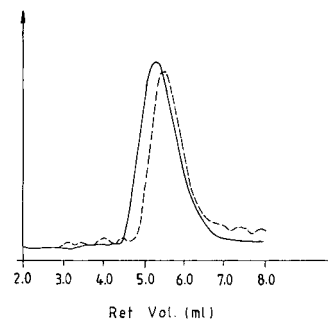
Figure 2   GPC results for extended PS samples. The one on the right is M_n = 182,000, HI = 1.72, and the one on the left is M_n = 254,000, HI = 2.01.

the controlled radical chain extension reactions. The 25% chain extension is obtained during the chain extension step. In the case of PS extension, the heterogeneity index increases from 1.75 and 1.72 to 2.02 and 2.01, and in the case of block copolymerization, it increases from 1.36 and 1.13 to 1.36 and 1.6, respectively.

Similar results, namely high HI indexes, are also reported in the case of styrene–butyl acrylate block copolymerization by Matyjaszewski et al.[9] where an HI 2.20 has been obtained.

Ultrasonic scission breaks nearly 80% of the initial chains. The chains that are shorter than a minimum length are not broken. This minimum length is approximately 300,000 for PEMA and 150,000 for the PS.[7,8] During the application of ultrasonically broken chains in the controlled radical polymerization of styrene, TEMPO-terminated chains extend. However, the short chains are immune to cleavage and keep their original length and the molecular weight distribution is broader. This is a possible cause of the increase in the heterogeneity index. Using more intense ultrasound, the efficiency of TEMPO addition will increase and the length of the blocks can be arranged by monitoring the US power. This enables us to prepare tailor-made polymers.

Twenty-five percent chain extension was obtained in our experiments. However, to change the polymer properties, this low percentage might have a considerable effect. The simplicity of the procedure is another encouraging reason to incorporate US and TEMPO activities.

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