

# Synthesis of Block Copolymers by Radical Polymerization of End-Functional Polystyrene

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**ABSTRACT:** End-functional polystyrenes with an *N,N*-diethyldithiocarbamyl group were prepared by the photopolymerization of styrene with novel diethyldithiocarbamate derivatives as photoiniferters. Under ultraviolet light, the end-functional polymers could initiate a second monomer to polymerize and form block copolymers, such as polystyrene-*b*-poly(methyl methacrylate), polystyrene-*b*-poly(vinyl acetate), and polystyrene-*b*-poly(*n*-butyl acrylate). According to end group analysis and electron spin resonance (ESR) spectroscopy, AB-type block copolymers were produced. The glass transition temperature and thermal stability of the block copolymers were investigated by means of thermal analysis. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **64**: 1169–1174, 1997

**Key words:** *N,N*-diethyldithiocarbamyl end-functional polystyrene, block copolymerization, radical polymerization with photoiniferter

## INTRODUCTION

Because radical polymerization is a very useful method for the preparation of vinyl polymers, the control of architecture by free radical techniques becomes important in order to get polymers with suitable molecular weights and end groups and then to form block copolymers. In the past decades, many articles had reported that block copolymers can be synthesized either by sequential polymerization of vinyl monomers with a living radical polymerization system<sup>1–4</sup> and polyfunctional initiator system<sup>5–8</sup> or by the radical polymerization of vinyl monomers initiated by macroiniferter.<sup>9</sup> In addition, the block copolymer can also be prepared by the radical polymerization of an end-functional polymer obtained from the photopolymerization of vinyl monomer by the photoiniferter technique.<sup>10–12</sup> The end-functional polymer with an *N,N*-diethyldithio-

carbamyl(Et<sub>2</sub>NCSS) end group can form a macrochain radical to initiate block copolymerization under ultraviolet (UV) light due to the homolytic cleavage of a C–S bond.

In our recent work, it was found that the novel diethyldithiocarbamate derivative *N*-(*p*-tolyl)-*N',N'*-diethyldithiocarbamylacetamide was successfully used as a photoiniferter in the polymerization of styrene (St), in which the increase of molecular weight depended on time and the conversion and chain extension of the resulting polystyrene (PS) were observed, respectively.<sup>13</sup> This article describes the synthesis of *N,N*-diethyldithiocarbamyl end-functional PS with suitable molecular weight and the PS-*b*-[poly(methyl methacrylate)] (PMMA), PS-*b*-[poly(vinyl acetate)] (PVAc), PS-*b*-[poly(*n*-butyl acrylate)] (PBA) diblock copolymers thereof.

## EXPERIMENTAL

### Materials

The monomers St, methyl methacrylate (MMA), vinyl acetate (VAc), and *n*-butyl acrylate (BA)

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were distilled under vacuum. Benzene was washed by sulfuric acid and then by water, dried with anhydrous  $\text{CaCl}_2$ , and distilled. 2-Methyl-2-nitrosopropane (MNP) from Aldrich Chem. Co. was used as received. All other reagents were used after ordinary purification.

*N*-(*p*-Tolyl)-*N'*,*N'*-diethyldithiocarbamylacetamide (TDCA) was prepared according to the reference method<sup>14,15</sup> and purified. It was characterized by infrared (IR), <sup>1</sup>H nuclear magnetic resonance (NMR) spectra, and elemental analysis.<sup>13</sup>

### Synthesis of End-Functional PS

The photopolymerization of St was carried out in the presence of TDCA (0.1 mol/L) in bulk under irradiation of UV light with an 80 W UV lamp at 10 cm from sealed glass tubes at room temperature for 12 h. The product was precipitated into methanol, thrice reprecipitated from benzene with methanol, and dried under vacuum. The molecular weight of the resulting polymer was determined by gel permeation chromatography (GPC). End groups of polymers were determined by UV spectroscopy.<sup>13</sup> Photolysis of end-functional PS was investigated by electron spin resonance (ESR) and the spin trapping technique.

### Synthesis of Block Copolymers

End-functional PS (0.2 g), monomers (MMA, 0.2 mL; BA, 0.2 mL; or VAc, 0.4 mL), and benzene (1.0 mL) were polymerized. The procedure is described above. The content was precipitated in an appropriate precipitant, methanol for MMA and petroleum ether for VAc and BA polymer solutions, respectively, and dried under vacuum. The separation of polymers into homopolymers and

block polymers was carried out by extraction with suitable solvents, PS with cyclohexane, PMMA with 95% ethanol, PBA with acetone, and PVAc with methanol. Then, the fractions were examined by IR and <sup>1</sup>H NMR spectra and GPC analysis. It was found that the homopolymer PS (about 25.0 wt %) was obtained in the block copolymerization of MMA with TDCA-PS. However, no homopolymers, i.e., PS, PMMA, PVAc, or PBA, were separated in the block copolymerizations. Therefore, the reaction products obtained were block copolymers, i.e., PS-*b*-PMMA, PS-*b*-PVAc, and PS-*b*-PBA, as determined by IR spectra of extracted products and GPC analysis.

The conversion of block polymerization (Conv. %) was calculated according to the following equation

$$\text{Conv. \%} = \frac{W_1 - W_0}{W_m} \times 100\% \quad (1)$$

where  $W_1$  is the weight of the block polymer,  $W_0$  is the weight of the substrate, and  $W_m$  is the weight of the monomer, respectively. The weight percentages of each block in the total block copolymer molecule were calculated from the molecular weights of block copolymers and TDCA-PS. The data are compiled in Table I.

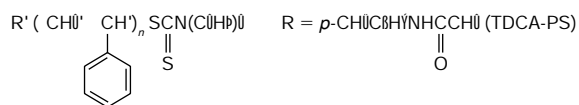
### Measurements

IR and <sup>1</sup>H NMR spectra were recorded on a Nicolet IR 750 spectrometer and a Bruker ARX 400 spectrometer, respectively. GPC was carried out with a Waters 208 instrument equipped with a differential refractometer and Styragel 500 Å columns with tetrahydrofuran as the eluent, and calibration with PS standards. UV spectroscopy was

**Table I** Block Copolymerizations of Second Monomers with End-Functional Polymer<sup>a</sup>

End-Functional Polymer	Second Monomer		Time (h)	Conv. (%)	Block Copolymer		Second Block (wt %)			
	(g)	$M_n$ ( $10^{-4}$ )			(mL)	(g)		$M_n$ ( $10^{-4}$ )	PS Block (wt %)	
TDCA-PS	0.200	0.629	MMA	0.21	21	33.4	0.266	0.965	65.2	34.8
	0.200	0.629	VAc	0.44	40	11.4	0.247	0.839	75.0	25.0
	0.200	0.629	BA	0.22	21	95.4	0.388	1.12	56.2	43.8

<sup>a</sup> Polymerization under irradiation of an 80 W UV light from a distance of 10 cm at room temperature.



Scheme 1

recorded on a Shimadzu UV-250 and UV-2100 instrument (the number of  $\text{Et}_2\text{NCSS}$  end groups was examined by UV spectrum with benzyl  $N,N$ -diethyldithiocarbamate [272 nm] as the standard). The ESR spectrum was obtained on a Bruker ER 200D-SRC ESR spectrometer with the TM cavity at the X-band in a quartz ESR tube with 100 KHz modulation and 1.00 mW microwave power; MNP was used as a spin trapping agent. The glass transition temperature ( $T_g$ ) was determined with a Shimadzu DSC-50 Differential Scanning Calorimeter at a heating rate of  $20^\circ\text{C}/\text{min}$ . Thermogravimetric analysis was carried out with a Shimadzu DT-30 thermal analyzer in nitrogen atmosphere at a rate of  $20^\circ\text{C}/\text{min}$ .

## RESULTS AND DISCUSSION

### Synthesis of End-Functional PS and Its Photolysis Reaction

Earlier studies on the mechanism of the free radical polymerization of St and MMA initiated by monofunctional iniferters, such as 1-( $N,N$ -diethyldithiocarbamyl)ethylbenzene,<sup>12</sup> ethyl 2-( $N,N$ -diethyldithiocarbamyl)isobutyrate,<sup>12</sup> benzyl  $N,N$ -diethyl-dithiocarbamate,<sup>16</sup> benzyl  $N$ -ethyldithiocarbamate,<sup>17</sup> etc., indicate that the resulting polymers have one dithiocarbamate group

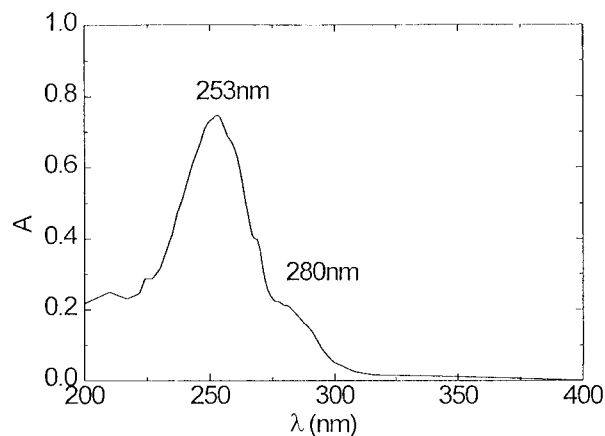


Figure 1 UV spectra of TDCA-PS in tetrahydrofuran.

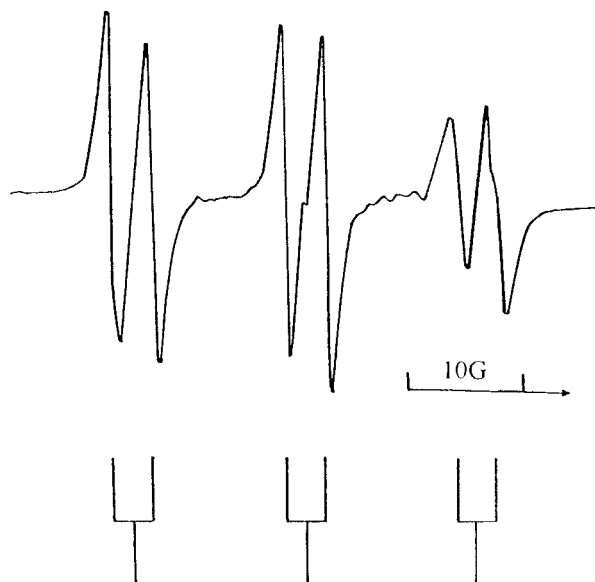
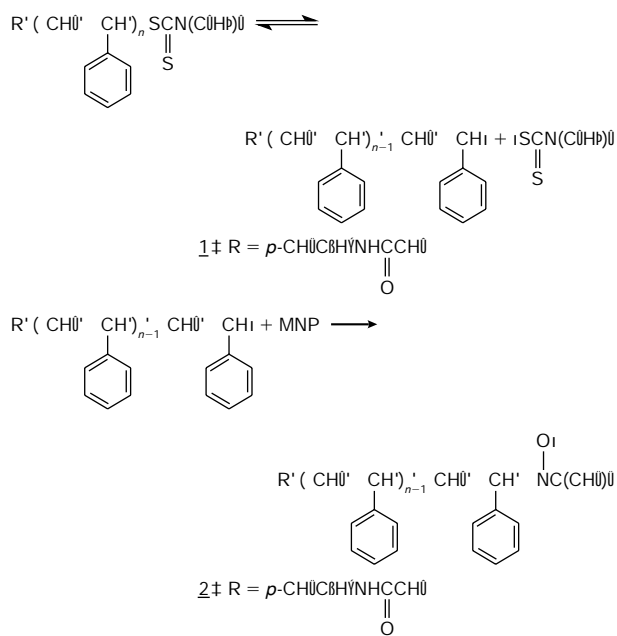
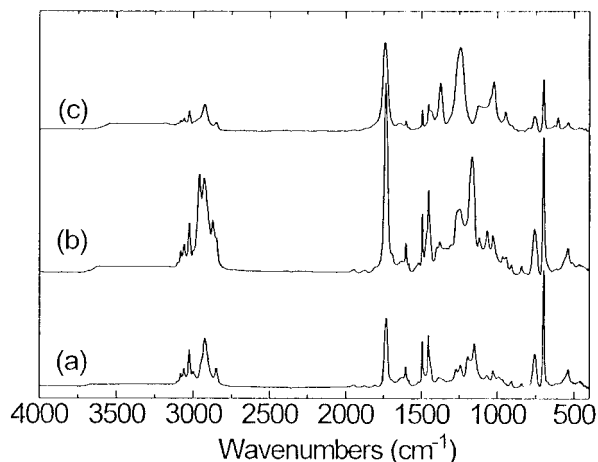


Figure 2 ESR spectra of TDCA-PS/MNP systems obtained after irradiation at room temperature, 1 milli tesla (mT) = 10 gauss (G). TDCA-PS = 0.15 g/mL, MNP =  $7.7 \times 10^{-3}$  mol/L.

in each polymer chain and that the end group is capable of further initiating chain extension and block copolymerization. Similarly, we found that TDCA can initiate the polymerization of St in bulk, in which the molecular weight of the poly-

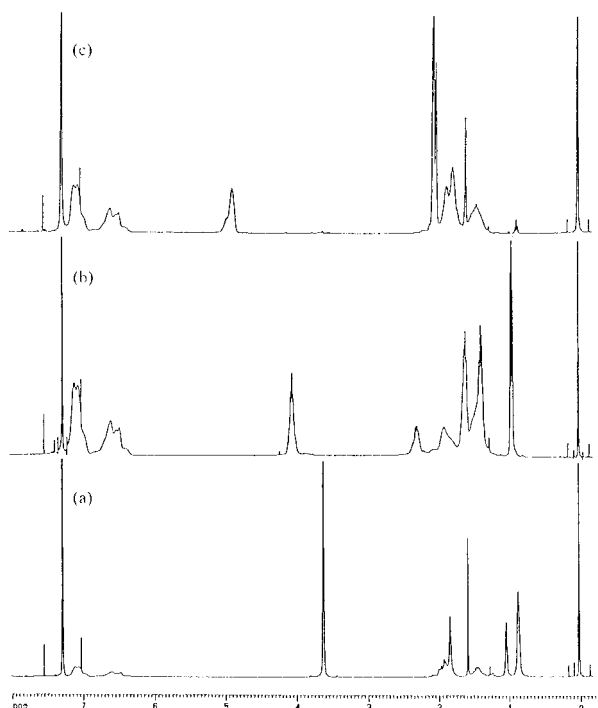


Scheme 2

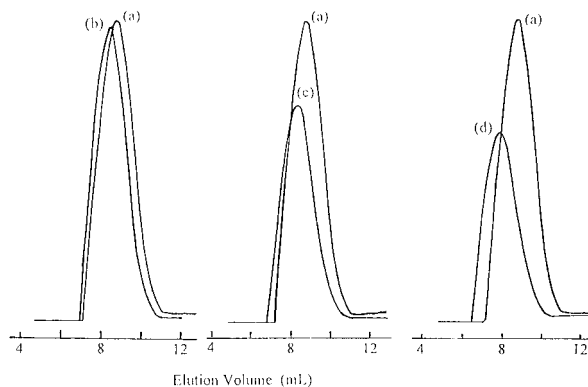


**Figure 3** IR spectra of block copolymers. (a) T-PS-*b*-PMMA, (b) T-PS-*b*-PBA, (c) T-PS-*b*-PVAc.

mer increases with time and conversion and the resulting polymers contain one  $\text{Et}_2\text{NCSS}$  end group on a polymer chain.<sup>13</sup> Therefore, it is easy to obtain the polymer with a suitable molecular weight of about 6,000 and one dithiocarbamyl group, as shown in Scheme 1.



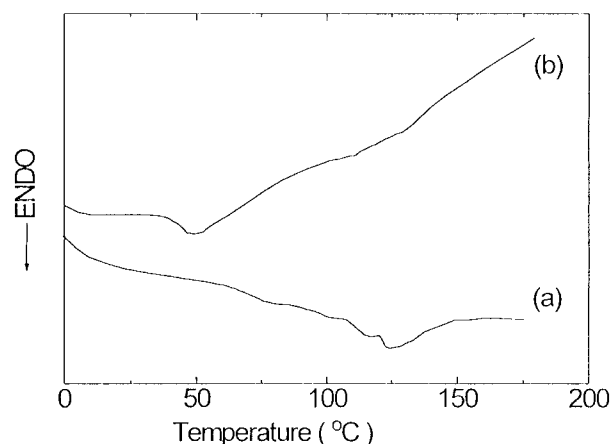
**Figure 4**  $^1\text{H}$  NMR spectra of block copolymers. (a) T-PS-*b*-PMMA, (b) T-PS-*b*-PBA, (c) T-PS-*b*-PVAc.



**Figure 5** GPC traces of polymers. (a) T-PS, (b) PS-*b*-PMMA, (c) PS-*b*-PBA, (d) PS-*b*-PVAc.

UV spectra for TDCA-PS (Figure 1) were in agreement with the formation of the polymer containing two initiator fragments. In Figure 1, 253 nm and 280 nm were corresponding to the  $p\text{-CH}_3\text{C}_6\text{H}_4\text{NHCOCH}_2$  group and the  $\text{Et}_2\text{NCSS}$  group, respectively. The number of  $\text{Et}_2\text{NCSS}$  end groups in TDCA-PS was about a unit (1.05). The number- and weight-average molecular weights of TDCA-PS were 6,290 and 17,500, respectively.

The activity of end-functional polymer was confirmed by ESR study with MNP as a spin trapping agent. The ESR spectrum of the TDCA-PS/MNP system under UV light is shown in Figure 2; it can be seen that the spectrum was assigned to radical  $\underline{2}$  ( $a_\alpha^N = 14.5$  G,  $a_\beta^H = 3.3$  G). The ESR result indicated that in the polymerization, the



**Figure 6** DSC traces. (a) PS-*b*-PMMA, (b) PS-*b*-PVAc.

**Table II**  $T_g$  Data of Block Copolymers

Sample	$T_g$ (°C)		
	PS	PMMA	PVAc
PS- <i>b</i> -PMMA	80.5	107	
PS- <i>b</i> -PVAc	109		42.9

*N,N*-diethyldithiocarbamyl radical  $\text{Et}_2\text{NCSS}$  can reversibly react with the growing radical. As a result, the  $\text{Et}_2\text{NCSS-C}$  in TDCA-PS cleaved to radical  $(\text{C}_2\text{H}_5)_2\text{NCSS}$  and radical 1 and the radical 1 adducted with MNP to produce radical 2, as shown in Scheme 2. However, another end group (amide group in TDCA-PS) was stable at the same condition and did not cleave to produce radicals.

### Synthesis and Characterization of Block Copolymers

According to the description above, the photodissociation of the  $\text{Et}_2\text{NCSS}$  end group on end-functional polymers could initiate the monomer to polymerize. Because the polymer contained a unit of the  $\text{Et}_2\text{NCSS}$  group, and coupling and disproportionation terminations were neglected because of the reaction of radical  $\text{Et}_2\text{NCSS}$  with the growing radical, the result block copolymers were AB-type diblock copolymers. The photocopolymerizations of MMA, BA, and VAc with TDCA-PS were carried out in benzene solutions. The purified block copolymers were confirmed by IR,  $^1\text{H}$  NMR spectra, and GPC. In IR spectra (Fig. 3), the characteristic frequencies of the ester group (PMMA, C O:  $1,730\text{ cm}^{-1}$ , C O:  $1,150\text{ cm}^{-1}$ , PBA: C O:  $1,735\text{ cm}^{-1}$ , C O:  $1,164\text{ cm}^{-1}$ ; PVAc, C O:  $1,740\text{ cm}^{-1}$ , C O:  $1,240\text{ cm}^{-1}$ ) and the phenyl group (PS, H C C:  $3,082\text{ cm}^{-1}$ , C C:  $1,600\text{ cm}^{-1}$ ; monosubstituted benzene,  $700\text{ cm}^{-1}$ )

were observed, respectively. In  $^1\text{H}$  NMR spectra, the phenyl group ( $\text{C}_6\text{H}_5$ ,  $\delta = 6.57\text{--}7.05\text{ ppm}$  in Fig. 4),  $\text{COOCH}_3$  [ $\delta = 3.60\text{ ppm}$  in Fig. 4(a)],  $\text{CH}_3$  of butyl [ $\delta = 0.93\text{ ppm}$  in Fig. 4(b)], and  $\text{CH}_2\text{CH}(\text{OCOCH}_3)$  [ $\delta = 4.87\text{ ppm}$  in Fig. 4(c)] were observed, respectively. Figure 5 was GPC traces of block copolymers and original polymers. The molecular weights of block copolymers were larger than those of original polymers; the weight percentages of each block in the total block copolymer molecule were calculated from GPC analysis, and the data are listed in Table I.

The glass transition temperatures ( $T_g$ ) of the end-functional polymer and block copolymers were determined by differential scanning calorimetry (DSC), and their DSC traces are shown in Figure 6. The values of  $T_g$  are summarized in Table II; two  $T_g$  values indicated that two different chains were immiscible in the block copolymers. Table III shows the comparative weight loss of block copolymers and homopolymers of St and MMA. The block copolymers were shown to be a stable intermediate of PS and PMMA.

### CONCLUSION

The end-functional polymers, which can be used as macroiniferters, were synthesized successfully by the radical polymerization of St with novel photoiniferters, such as *N*-(*p*-tolyl)-*N',N'*-diethyldithiocarbamylacetamide. The AB-type block copolymers were obtained from the photocopolymerization of vinyl monomers in the presence of *N,N*-diethyldithiocarbamyl end-functional PS. ESR studies also confirmed that chain radical and  $\text{Et}_2\text{NCSS}$  radical were formed from the homolytic cleavage of the C S bond in end-functional PS under UV light and that the other end group was stable under the same conditions. Block copolymers, such as PS-*b*-PMMA, PS-*b*-PVAc, and

**Table III** Comparative Thermal Decomposition Characteristics of Block Copolymers

Sample	Weight Loss at Temperature °C					
	10%	25%	50%	75%	90%	Complete
PS	356	390	410	425	445	460
PMMA	297	320	357	390	410	470
Block <sup>a</sup>	334	360	382	415	430	450

<sup>a</sup> Block is PS-*b*-PMMA.

PS-*b*-PBA, were synthesized via this technique and characterized by IR spectroscopy, DSC analysis, and so on.

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