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### Block Copolymerization of Vinyl Monomers with Macroiniferer

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## BLOCK COPOLYMERIZATION OF VINYL MONOMERS WITH MACROINIFERTER

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### ABSTRACT

Block copolymers composed of a polyether, such as poly(oxytetramethylene), and vinyl polymers, such as polystyrene, poly(methyl methacrylate), poly(butyl acrylate), and poly(vinyl acetate), were prepared by photopolymerizations of vinyl monomers initiated with a polyether macroiniferter,  $\alpha$  - ( diethyldithiocarbamylacetyl ) -  $\omega$  - ( diethyldithiocarbamylacetoxo)-poly(oxytetramethylene). ESR spectroscopy and end-group analysis of diethyldithiocarbamyl indicated that block copolymers should be predominantly ABA-type copolymers. The block copolymers were characterized in detail by NMR, GPC, and DSC analysis.

### INTRODUCTION

Generally, polymerization reactions except condensation polymerization are essentially arranged under three mechanistic approaches, i.e., radical, ion (cation and anion), and coordination polymerization, according to monomer structure and initiation system used. Block copolymers can be conveniently prepared by a sequential polymerization of a living polymerization system. Amphiphilic block copolymers, however, with chains of different properties, such as hydrophilic and hydro-

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phobic, are very difficult to prepare by a single polymerization mechanism. Using combinations of living anion–living cation polymerization [1], cation–radical polymerization [2], and anion–radical polymerization [3], these block copolymers could be designed and synthesized. In this strategy, a polymer prepared by a radical or ion mechanism is terminally functionalized, separated, and then subsequently used to initiate a second monomer to polymerize by a different mechanism. Recently, some papers reported that macroiniferters and a polymeric iniferter with the thiuram disulfide group can initiate radical polymerization of vinyl monomer for the synthesis of block copolymers [4–6]. In our recent work we reported that *n*-butyl diethyldithiocarbamylacetate was successfully used as a photoiniferter [7]. As it is a model of end functional diethyldithiocarbamylacetyl-poly(oxytetramethylene), a polyether containing this kind of end group should therefore be used as a macroiniferter. This paper describes the synthesis and the characterization of this macroiniferter,  $\alpha$ -(diethyldithiocarbamylacetyl)- $\omega$ -(diethyldithiocarbamylacetoxo)-poly(oxytetramethylene) (PTHF-I). Its block copolymers with styrene, methyl methacrylate, butyl acrylate, and vinyl acetate were synthesized and investigated by NMR, GPC, and DSC.

## EXPERIMENTAL

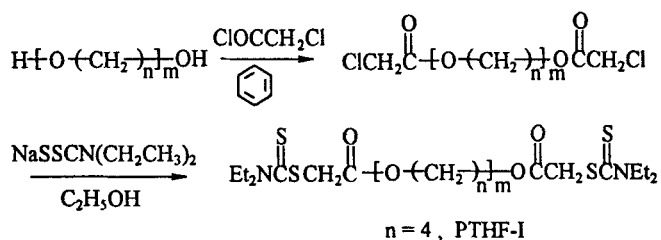
### Materials

Styrene (St), methyl methacrylate (MMA), butyl acrylate (BA), and vinyl acetate (VAc) were purified by vacuum distillation. Benzene, acetic anhydride, pyridine, tetrahydrofuran (THF), and benzoyl chloride were distilled. Acetic acid was recrystallized twice from benzene, mp 62–64°C. Polytetrahydrofuran (PTHF,  $M_n = 2900$ ) from DuPont Co.; sodium diethyldithiocarbamate trihydrate and 2-methyl-2-nitrosopropane (MNP) from Aldrich Co.; sodium hydroxide (NaOH) and sodium bicarbonate ( $\text{NaHCO}_3$ ) were used as received. Chloroacetyl chloride was prepared by the reaction of benzoyl chloride and acetic acid, bp 105–107°C.

The hydroxyl number of PTHF was determined by the titration method. The sample (200 mg), 1 mL acetic anhydride, and pyridine (v:v 1:4) were heated for 1 hour at 95–100°C. Then, 1 mL water was added and the mixture was heated for 10 minutes, cooled at room temperature, and titrated with 0.2 N NaOH using phenolphthalein indicator.

### Synthesis of Macroiniferters (PTHF-I)

PTHF (18 g), chloroacetyl chloride (3.5 mL), and benzene (100 mL) were refluxed for 20 hours under nitrogen. The excess chloroacetyl chloride and benzene were removed under vacuum. The residue was washed with 2%  $\text{NaHCO}_3$  aqueous solution and water, filtered, and dried. The resulting PTHF derivative was reacted with sodium diethyldithiocarbamate trihydrate (7.0 g) in 150 mL anhydrous ethanol, refluxed for 5 hours, and stirred overnight at room temperature. The resulting solution was filtrated, and ethanol was removed under vacuum. The residual solid was dissolved in THF and precipitated into petroleum ether in the cold. PTHF-I was characterized by NMR, UV, and GPC. The number of end groups ( $\text{Et}_2\text{NCSS}$ )



SCHEME 1.

was determined by UV spectroscopy using *n*-butyl diethyldithiocarbamylacetate as the standard ( $\lambda_{\text{max}} = 280 \text{ nm}$ ).

### ESR Study

The activity of the  $\text{Et}_2\text{NCSS}$  end group under UV light was investigated through ESR and a spin trapping technique using MNP as a trapping agent. A solution of sample (0.5 mL, 0.1 g/mL) in benzene and MNP (0.04 mL, 0.2 M) in acetonitrile in a flat quartz tube was irradiated and measured by an ESR instrument.

### Block Copolymerizations of Vinyl Monomers with PTHF-I

PTHF-I (0.5 g), monomers (St 0.5 mL, MMA 0.5 mL, BA 0.5 mL, or VAc 1.0 mL) and benzene (1.0 mL) were polymerized under irradiation of UV light with an 80-W UV lamp positioned 10 cm from sealed glass tubes at room temperature for 12–20 hours. The reaction product was washed with petroleum ether to remove the monomers and then dried under vacuum. The separation of polymers into homopolymers and block polymers was carried out by extraction with suitable

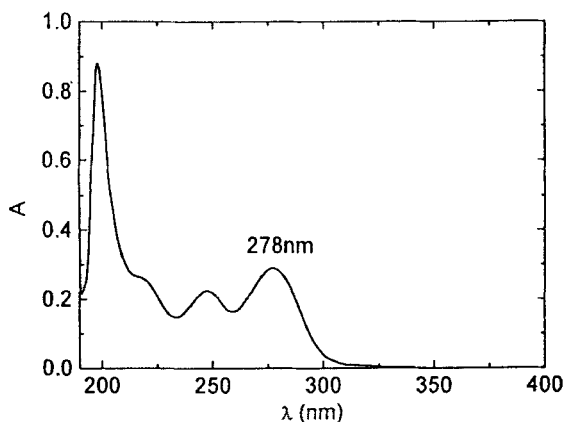


FIG. 1. UV spectrum of PTHF-I in THF,  $[\text{PTHF-I}] = 2.2 \times 10^{-4} \text{ g/mL}$ .

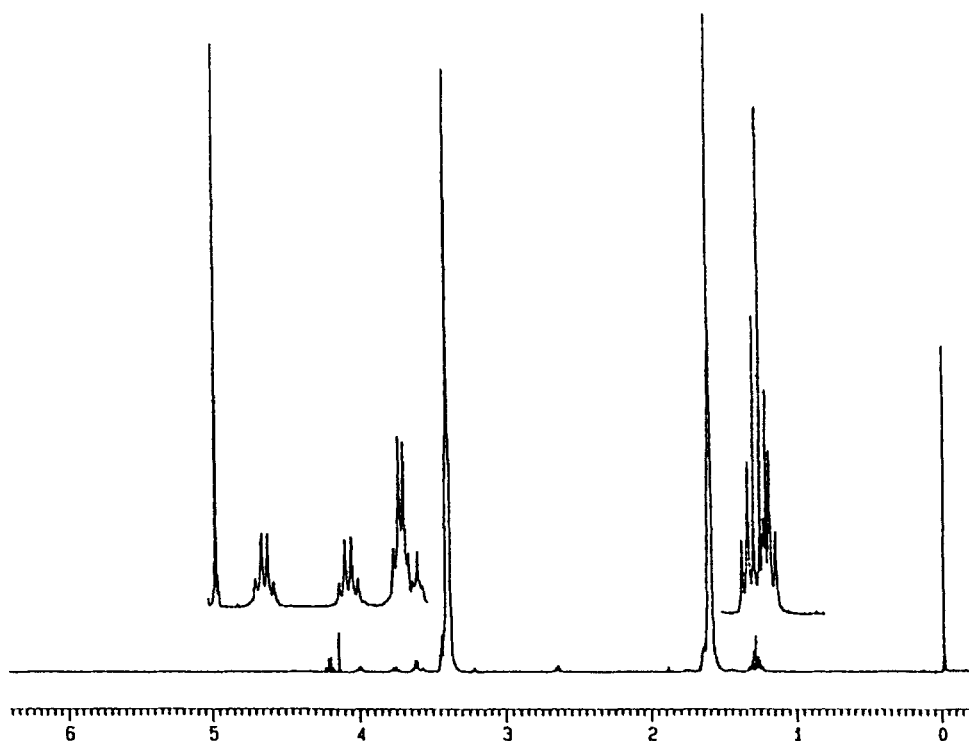


FIG. 2.  $^1\text{H-NMR}$  spectrum of PTHF-I in  $\text{CDCl}_3$ .

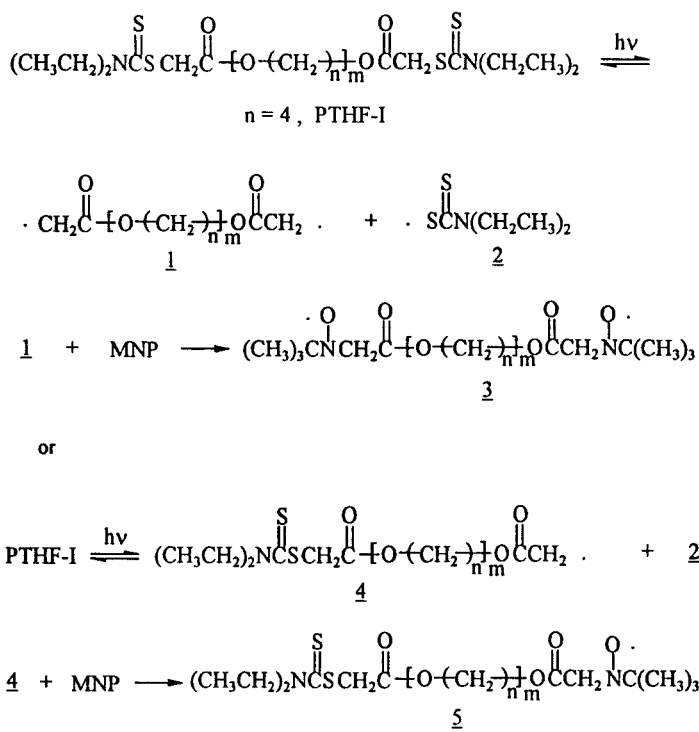
solvents: PTHF-I with anhydrous ethanol, PS with cyclohexane, PMMA and PBA with acetone, and PVAc with methanol. Then the fractions were examined by IR spectroscopy, and it was found that PTHF-I could be separated from the extract. However, no homopolymers, i.e., PS, PMMA, PBA, and PVAc, were observed after the extraction method. The resulting block copolymers were characterized by IR and  $^1\text{H-NMR}$  spectra, GPC analysis, and DSC.

### Measurements

IR and  $^1\text{H-NMR}$  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 col-

TABLE I. Data of the Molecular Weights and End Groups of PTHF-I

Sample	$M_n$ ( $10^{-4}$ )	$M_w$ ( $10^{-4}$ )	$M_w/M_n$	Number of end groups
PTHF	0.274	1.30	4.74	(OH) 1.99
PTHF-I	0.238	1.27	5.34	( $\text{Et}_2\text{NCSS}$ ) 2.20



SCHEME 2.

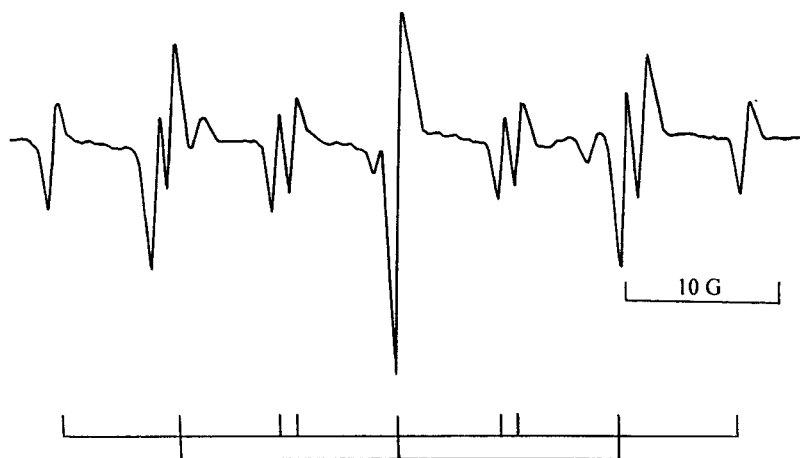


FIG. 3. ESR spectrum of PTHF-I/MNP system (1 mT = 10 G): [PTHF-I] = 0.12 g/mL, [MNP] =  $7.8 \times 10^{-3}$  M.

TABLE 2. Block Copolymerization of Second Monomers with PTHF-I in Benzene

No.	PTHF-I, g	SM, mL	<i>t</i> , hours	<i>P</i> <sub>total</sub> , g	Block copolymer	
					g	<i>M</i> <sub>n</sub> (10 <sup>-4</sup> )
1	0.500	St 0.55	20	0.594	0.214	0.290 <sup>a</sup>
3	0.503	MMA 0.54	14	0.751	0.334	0.377
6	0.209	VAc 1.10	10	0.547	0.180	0.349
7	0.502	BA 0.56	14	0.581	0.170	0.762

<sup>a</sup> <sup>1</sup>H-NMR.

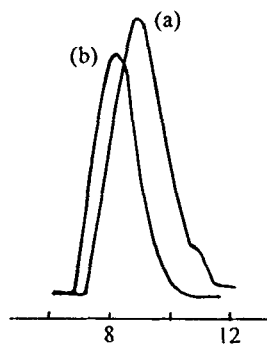
umns using tetrahydrofuran as the eluent and calibration with polystyrene standards. The UV spectra were recorded on Shimadzu UV-250 and UV-2100 instruments. The ESR spectrum was obtained on a Bruker ER 200D-SRC electron spin resonance spectrometer using the TM cavity at the X-band with 12.5 kHz modulation and 1.00 mW microwave power. The glass transition temperature (*T*<sub>g</sub>) was determined by a Shimadzu DSC-50 Differential Scanning Calorimeter at a heating rate of 20°C/min.

## RESULTS AND DISCUSSION

### Synthesis of Macroiniferters (PTHF-I)

For the synthesis, the hydroxyl groups on PTHF were first reacted with excess chloroacetyl chloride in benzene to fix the chloride groups on the chain ends. They were then transformed into diethyldithiocarbamyl groups by the reaction with sodium diethyldithiocarbamate trihydrate. The reaction is shown in Scheme 1.

The macroiniferter was characterized by NMR (Fig. 1) and UV (Fig. 2) spectra. In Fig. 1, 4.09 ppm (O=CCH<sub>2</sub>SSCNEt<sub>2</sub>), 3.98 and 3.75 ppm [SSCN-(CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>], and 1.27 ppm [SSCN(CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>] in PTHF-I are observed. The peak

FIG. 4. GPC curves of PTHF-I (a) and PBA-*block*-PTHF-*block*-PBA (b).

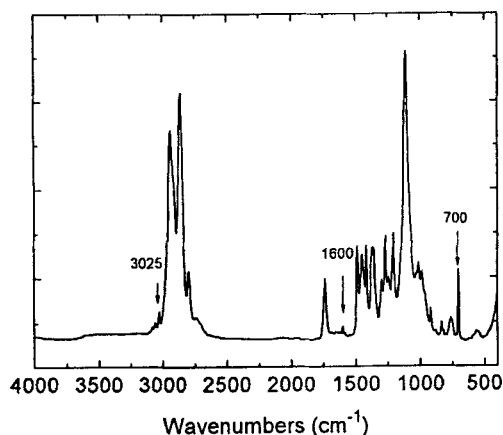


FIG. 5. IR spectrum of PS-*block*-PTHF-*block*-PS.

( $\lambda_{\max} = 278$  nm) in Fig. 2 corresponds to the  $\text{Et}_2\text{NCSS}$  group. Data about the molecular weight and number of end group are listed in Table 1, from which it can be seen that the molecular weight of the polyethers did not essentially change after reaction and that the number of  $\text{Et}_2\text{NCSS}$  groups is about 2.

### Mechanism of Copolymerization in the Presence of PTHF-I

Reghunadhan Nair [4] studied thermal iniferters with thiuram disulfide prepared by polyethylene oxide. Thermal polymerization of styrene in the presence of the macroiniferter at  $85^\circ\text{C}$  led to the formation of triblock copolymers. In thermal polymerization the S—S bond of thiuram disulfide cleaved irreversibly to form the radical  $\text{R}_2\text{NCSS}\cdot$ , which slowly initiated polymerization and rapidly scavenged growing radicals to produce the dithiocarbamyl end group. The dithiocarbamyl end group was quite stable thermally but cleaved homolytically under UV light. Photochemical cleavage of the C—S bond in the dithiocarbamyl group may provide a reversible system for controlling the photopolymerization of vinyl monomer in which the molecular weight of the resulting polymer increases linearly with reaction time and conversion [7–10]. PTHF-I could cleave to form macroradical *1* and radical  $\text{Et}_2\text{NCSS}\cdot$  under UV light due to its end groups being similar to *n*-butyl diethyl-dithiocarbamylacetate, which makes it a good photoiniferter as shown in Scheme 2. The adduct of macroradical *1* with MNP was radical *3* ( $a_\alpha^{\text{N}} = 14.5$  G,  $a_\beta^{\text{H}} = 7.7$  G) which is observed in Fig. 3 (ESR technique). In Fig. 3 another radical ( $a_\alpha^{\text{N}} = 15.6$  G) was the adduct of MNP and radical  $(\text{CH}_3)_3\text{C}\cdot$ , which was formed by the photolysis of MNP under UV light.

Theoretically speaking, PTHF-I also can form radical *4*, and the adduct of *4* with MNP is radical *5*. However, it is impossible to distinguish radical *3* from radical *5* by the ESR spectrum. Because of the same activities of the two end groups, we believe radical *1* is the predominant product from the photolysis of PTHF-I. Macroradical *1* can initiate the photopolymerization of vinyl monomers, and radical  $\text{Et}_2\text{NCSS}\cdot$  may essentially occur in the reversible reaction with the growing radical to control the chain length. PTHF-I containing about two  $\text{Et}_2\text{NCSS}$  end groups can



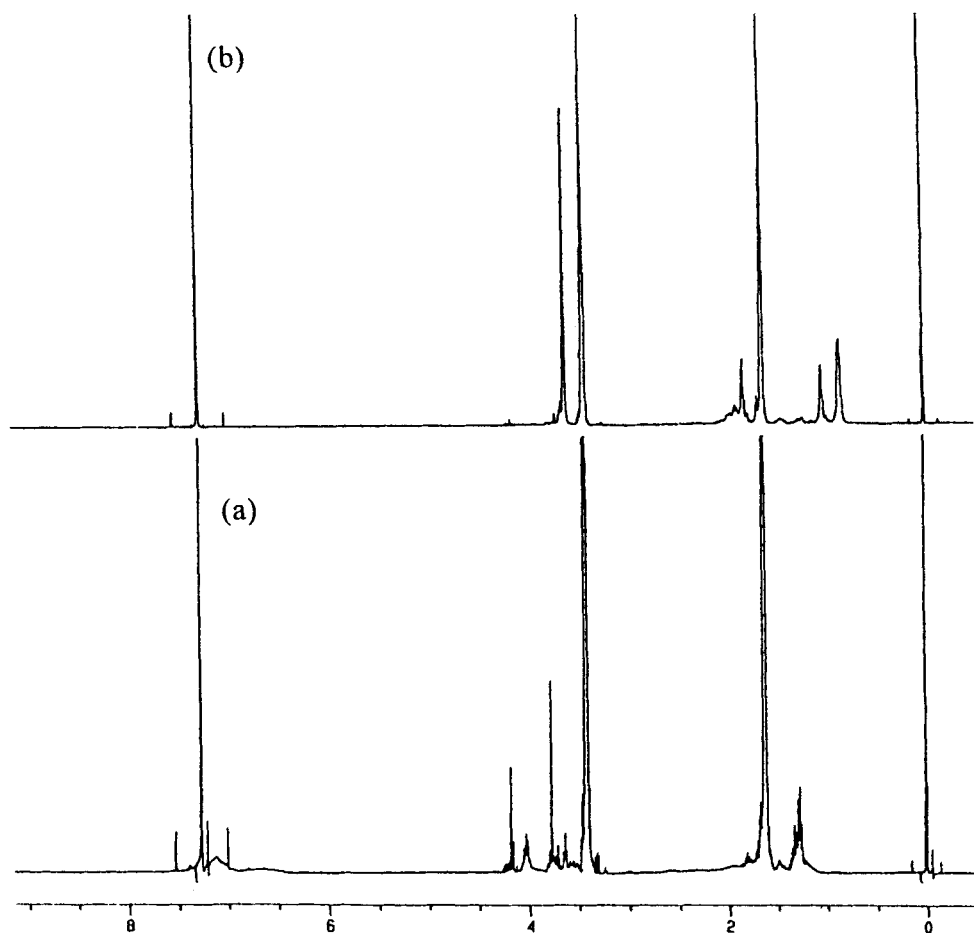


FIG. 6.  $^1\text{H-NMR}$  spectra of PS-*block*-PTHF-*block*-PS (a) and PMMA-*block*-PTHF-*block*-PMMA (b) in  $\text{CDCl}_3$ .

form radicals at two chain ends. Thus, block copolymers of the ABA type should be predominantly prepared by vinyl polymerization in the presence of PTHF-I.

### Synthesis and Characterization of Block Copolymers

As described above, PTHF-I can be used as a macroiniferter. Photopolymerizations of vinyl monomers (St, MMA, BA, and VAc) were carried out in the presence of PTHF-I. Block copolymers were obtained after purification, and the results are listed in Table 2. Figure 4 is GPC curves of PTHF-I and PBA-*block*-PTHF-*block*-PBA. It shows that the molecular weights of the block copolymer were larger than those of the original polymer (PTHF-I).

Block copolymers were characterized by IR, NMR, and UV spectroscopy and DSC analysis. Figure 5 is the IR spectrum of PS-*block*-PTHF-*block*-PS. The strong bands at 1112 (C—O—C), 3025 (benzene ring =C—H), 1601 (benzene ring C=C),

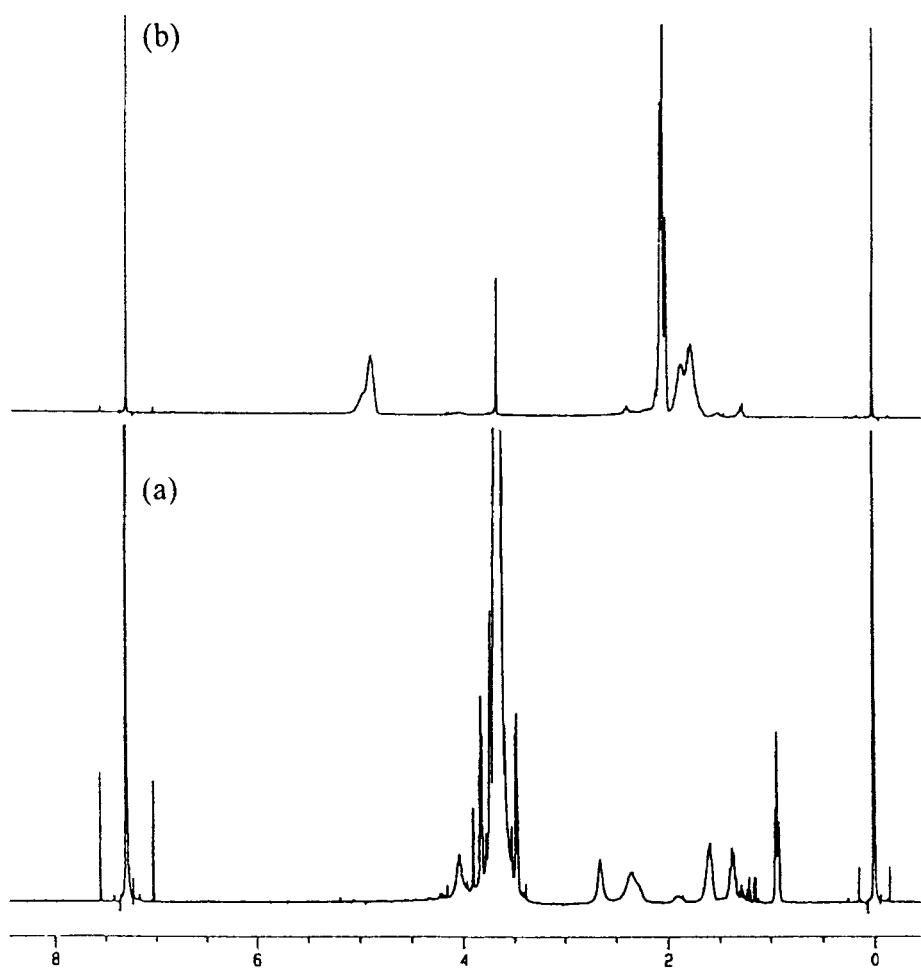


FIG. 7.  $^1\text{H-NMR}$  spectra of PBA-*block*-PTHF-*block*-PBA (a) and PVAc-*block*-PTHF-*block*-PVAc (b) in  $\text{CDCl}_3$ .

TABLE 3. Data of  $T_g$  and  $T_m$  Block Copolymer with PTHF-I

	PS- <i>block</i> -PTHF- <i>block</i> -PS		PMMA- <i>block</i> -PTHF- <i>block</i> -PMMA	
	PTHF	PS	PTHF	PMMA
$T_g$ ( $^{\circ}\text{C}$ )		73.0		114
$T_m$ ( $^{\circ}\text{C}$ )	48.7	23.7	32.3	

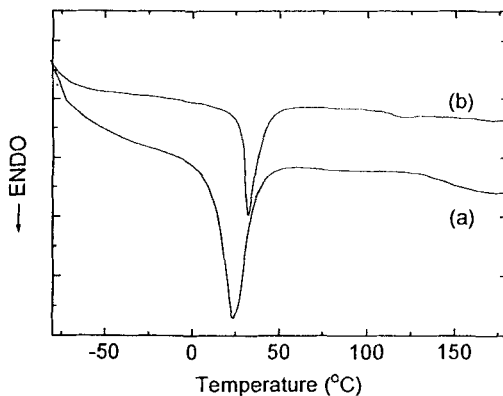


FIG. 8. The DSC traces of block copolymers with PTHF-I, (a) PS-*block*-PTHF-*block*-PS, (b) PMMA-*block*-PTHF-*block*-PMMA.

and  $700\text{ cm}^{-1}$  (monosubstituted of benzene) are attributed to PTHF and PS. From  $^1\text{H-NMR}$  (Figs. 6 and 7), the chemical shift of 3.38 ( $-\text{CH}_2\text{CH}_2\text{O}-$ ) and 1.62 ( $-\text{CH}_2\text{CH}_2\text{O}$ ) for PTHF, 7.09 (benzene ring) for PS, 3.60 ( $-\text{OCH}_3$ ) and 1.01 [ $-\text{CH}_2-\text{C}(\text{COOCH}_3)(\text{CH}_3)-$ ] for PMMA, 4.03 [ $-\text{CH}_2-\text{CH}(\text{CO}_2\text{C}_4\text{H}_9)-$ ] and 0.94 ( $\text{CH}_3$  in butyl) for PBA, and 4.87 [ $-\text{CH}_2-\text{CH}(\text{O}_2\text{CCH}_3)-$ ] and 2.04 ( $\text{CH}_3\text{COO}-$ ) for PVAc were observed. The results indicate that the block copolymers were synthesized from the polymerization of vinyl monomers with PTHF-I.

The result of DSC measurements are shown in Table 3. Figure 8 is DSC traces of block copolymers with PS and PMMA. The crystal melting temperature of the PTHF segments in block copolymers shifted from  $48^\circ\text{C}$  for pure PTHF homopolymer to  $24$  and  $32^\circ\text{C}$  for the block copolymers PS-*block*-PTHF-*block*-PS and PMMA-*block*-PTHF-*block*-PMMA, respectively. These shifts indicate that PS and PMMA affected the crystallinity of the PTHF chain.

## CONCLUSION

A polyether macroiniferter,  $\alpha$ -(diethyldithiocarbamylacetyl)- $\omega$ -(diethyldithiocarbamylacetoxo)-poly(oxytetramethylene) (PTHF-I), was synthesized and the end group was characterized by  $^1\text{H-NMR}$  and UV spectroscopy. The number of diethyldithiocarbamyl end groups measured was about two. The behavior of PTHF-I under UV light was investigated by ESR and a spin trapping technique, and the mechanism of photopolymerization of vinyl monomers in the presence of PTHF-I was deduced. Block copolymers of the ABA-type were prepared and characterized.

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