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SYNTHESIS OF BLOCK COPOLYMERS BY PHOTOCOPOLYMERIZATION OF VINYL MONOMERS WITH DIETHYLDITHIOCARBAMYL END-FUNCTIONAL POLYSTYRENE

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ABSTRACT

End-functional polystyrenes with the *N*,*N*-diethyldithiocarbamyl group were prepared by the photopolymerizations of styrene using alkyl diethyldithiocarbamylacetates as photoiniferters. Under UV light the end-functional polymers could initiate vinyl monomer to polymerize and form block copolymers, such as polystyrene-*block*-poly(methyl methacrylate), polystyrene-*block*-poly(vinyl acetate), and polystyrene-*block*-poly(*n*-butyl acrylate). According to end group analysis and EPR spectroscopy, AB-type block copolymers were produced. The glass transition temperatures and thermal stabilities of the block copolymers were investigated by means of thermal analysis.

INTRODUCTION

Radical polymerization is a very useful method either for preparation of vinyl polymers or for synthesis of block copolymers. In the past decades some papers have reported that block copolymers can be synthesized either by sequential polymerization of vinyl monomers using a living radical polymerization system [1–4], atom transfer radical polymerization [5], a polyfunctional initiator system [6–9], or by the radical polymerization of vinyl monomers initiated by a macroiniferter [10]. In addition, block copolymer can also be synthesized by the radical polymerization of end-functional polymer obtained from the photo-polymerization of vinyl monomer using the photoiniferter technique [11–13]. The end-functional polymer with a *N,N*-diethyldithiocarbamyl end group can form chain radical to initiate block copolymerization under UV light due to the homolytic cleavage of the C—S bond.

In a recent work we reported that ethyl *N,N*-diethyldithiocarbamylacetate and *n*-butyl *N,N*-diethyldithiocarbamylacetate were successfully used as photoiniferters in the polymerization of styrene in which the increase of molecular weight depended on time and conversion, and chain extension of the resulting polystyrene were observed, respectively [14]. This paper describes the synthesis of *N,N*-diethyldithiocarbamyl end-functional polystyrene of suitable molecular weight and the PS-*block*-PMMA, PS-*block*-PVAc, and PS-*block*-PBA diblock copolymers thereof.

EXPERIMENTAL

Materials

The monomers, styrene (St), methyl methacrylate (MMA), vinyl acetate (VAc), and *n*-butyl acrylate (BA), were distilled under vacuum. Benzene was washed by sulfuric acid and then by water, dried with anhydrous $CaCl_2$, and distilled. 2-Methyl-2-nitrosopropane (MNP) from Aldrich Chemical Co. was used as received. All other reagents were used after ordinary purification.

Ethyl diethyldithiocarbamyl acetate (EDCA) and *n*-butyl diethyldithiocarbamylacetate (BDCA) were prepared according to the method of References 15 and 16. The purified products were characterized by GPC, FT-IR, and ^{1}H-NMR spectra and elemental analysis [14].

Synthesis of End-Functional Polystyrene

The photopolymerizations of St were carried out in bulk. Styrene (2 mL) and *N,N*-diethyldithiocarbamyl compounds (0.1 M) were degassed for 5 minutes and sealed in glass tubes, respectively. They were polymerized at a distance of 10 cm from UV light (80 W) at room temperature for 12 hours. 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 and ^{1}H-NMR spectrometry. Photolysis of end-functional polystyrene was investigated by the spin trapping technique and electron paramagnetic resonance (EPR) spectroscopy.

Synthesis of Block Copolymers

End-functional polystyrene (0.2 g), second monomers (MMA 0.2 mL, BA 0.2 mL, or VAc 0.4 mL), and benzene (2.0 mL) were polymerized, respectively. The procedure is described above. The content was precipitated in an appropriate precipitant, methanol for MMA and petroleum either 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 FT-IR, and ^{1}H-NMR spectra and GPC analysis.

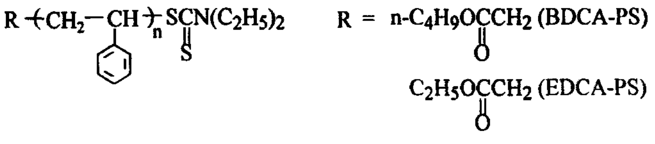
Measurements

FT-IR and ^{1}H-NMR spectra were recorded on Nicolet IR 750 spectrometers 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 using tetrahydrofuran as eluent, and calibration was with polystyrene standards. UV spectroscopy was recorded on Shimadzu UV-250 and UV-2100 instruments [the number of $(C_2H_5)_2NCSS$ end groups was examined by UV spectrum using benzyl *N*,*N*-diethyldithiocarbamate (272 nm) as the standard]. EPR spectra were obtained on a Bruker ER 200D-SRC electron spin resonance spectrometer using the TM cavity at the X-band in a quartz EPR tube with 100 kHz modulation and 1.00 mW microwave power, with MNP used as the spin trapping agent. The glass transition temperature (T_g) was determined with a Shimazu DSC-50 Differential Scanning Calorimeter at a heating rate of 20°C/min. The thermogravimetric analysis (TGA) was carried out with a Shimadzu DT-30 thermal analyzer in a nitrogen atmosphere at a rate of 20°C/min.

RESULTS AND DISCUSSION

Synthesis of End-Functional Polystyrene and Its Photolysis Reaction

Literatural reports on the mechanism of the free-radical polymerization of St and MMA initiated by monofunctional iniferters, such as 1-(*N*,*N*-diethyldithiocarbamyl)ethylbenzene (StDC) [13], ethyl 2-(*N*,*N*-diethyldithiocarbamyl)propionate (MADC) [13], benzyl *N*,*N*-diethyldithiocarbamate (BDC) [17], benzyl *N*-ethyldithiocarbamate (BEDC) [18], etc., indicated that the resulting polymers have one dithiocarbamate group in each polymer chain and that the end group is capable of further initiating chain extension and block copolymerization. We also found that BDCA and EDCA can initiate the photopolymerization of St in bulk, with the resulting polymers containing one $(C_2H_5)_2NCSS$ end group on a polymer chain [14]. Therefore, it is facile to obtain polymers with a suitable molecular weight (about 6000) and one dithiocarbamate group as shown in Scheme 1. The systemic names of the polymers are α-butoxycarbonylmethyl-ω-diethyldithiocarbamyl-polystyrene (BDCA-PS) and α-ethoxycarbonylmethyl-ω-diethyldithiocarbamyl-polystyrene (EDCA-PS).



SCHEME 1.

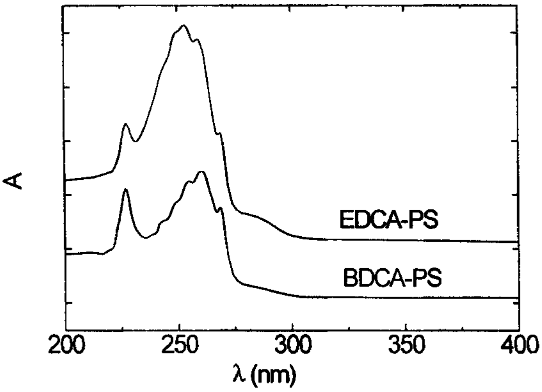


FIG. 1. UV spectra of BDCA-PS and EDCA-PS in tetrahydrofuran. [PDCA-PS] = 1.72 × 10^{-4} g/mL, [EDCA-PS] = 2.50 × 10^{-4} g/mL.

UV and ^{1}H-NMR spectra for BDCA-PS and EDCA-PS (Figs. 1 and 2) were in agreement with the formation of polymers containing two initiator fragments. In Fig. 1, 280 nm corresponds to the $(C_2H_5)_2NCSS$ group. The number of $(C_2H_5)_2NCSS$ end groups in BDCA-PS and EDCA-PS was about a unit, as summarized in Table 1.

Since it is difficult to differentiate the *n*-butyl group from the ethyl group in a UV spectrum, the ester group was identified by ^{1}H-NMR spectrum as shown in Fig. 2, from which CH_3 in the *n*-butyl group (δ = 0.87 ppm) and CH_3 and CH_2 in the

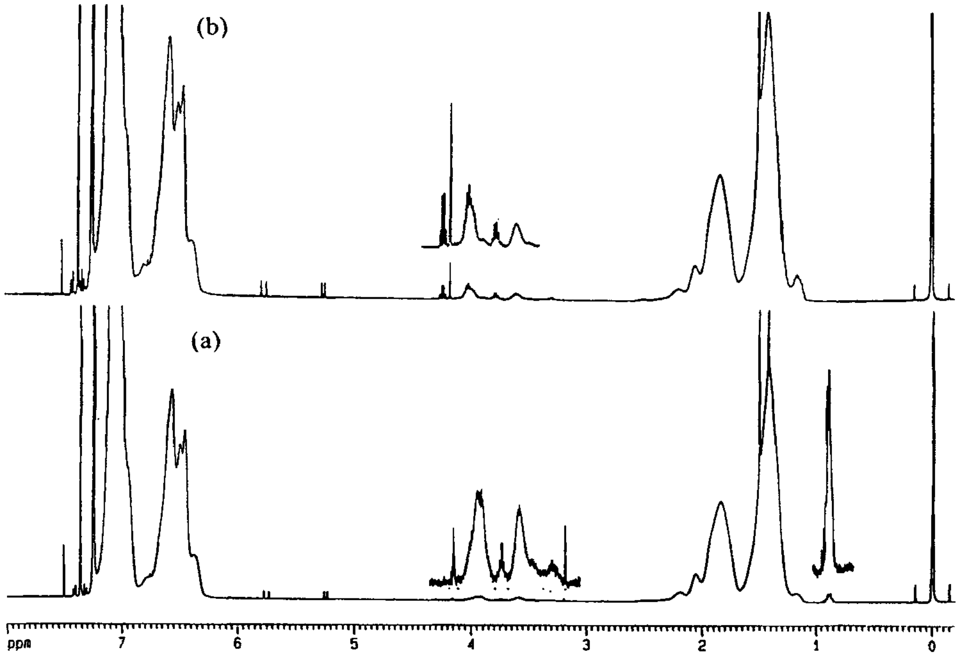


FIG. 2. ^{1}H-NMR spectra of BDCA-PS (a) and EDCA-PS (b) in $CDCl_3$.

TABLE 1. The Data of End-Functional Polymers[a]

Sample	M_n (10^{-4})	M_w (10^{-4})	M_w/M_n	Number of $(C_2H_5)_2NCSS$
BDCA-PS	0.586	2.31	3.94	0.98
EDCA-PS	0.689	1.97	2.86	1.01

[a] Polymerizations were carried out under an 80-W UV lamp at a distance of 10 cm at room temperature. [St] = 8.74 M, [BDCA] or [EDCA] = 0.1 M.

ethyl group (δ = 1.31, 4.23 ppm) were observed, respectively. The simultaneous $(C_2H_5)_2NCSS$ group was observed (δ = 3.7 and 4.0 ppm).

The reinitiation activity of the functional polymers was confirmed by EPR studies using MNP as a spin trapping agent. The EPR spectra of BDCA-PS/MNP and EDCA-PS/MNP systems under UV light are shown in Fig. 3, from which the observed spectra are assigned as radicals $\underline{3}$ (a_α^N = 14.7 G, a_β^H = 3.5 G) and $\underline{4}$ (a_α^N = 14.5 G, a_β^H = 3.3 G), respectively. The results indicate that in the polymerization the radical $(C_2H_5)_2NCSS\cdot$ can reversibly react with the growing chain radical. So $(C_2H_5)_2NCSS{-}C$ in BDCA-PS and EDCA-PS cleaved to form the radical $(C_2H_5)_2$-$NCSS\cdot$ and radicals $\underline{1}$ and $\underline{2}$, respectively, and these radicals adducted with MNP to produce radicals $\underline{3}$ and $\underline{4}$ as shown in Scheme 2. However, the other end groups (ester groups in BDCA-PS and EDCA-PS) were stable at the same conditions and could not cleave to produce radicals.

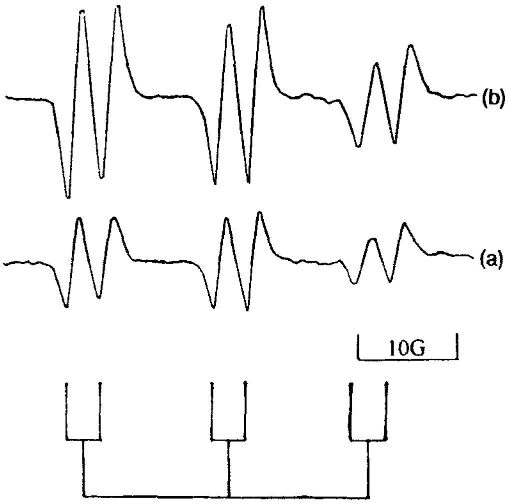
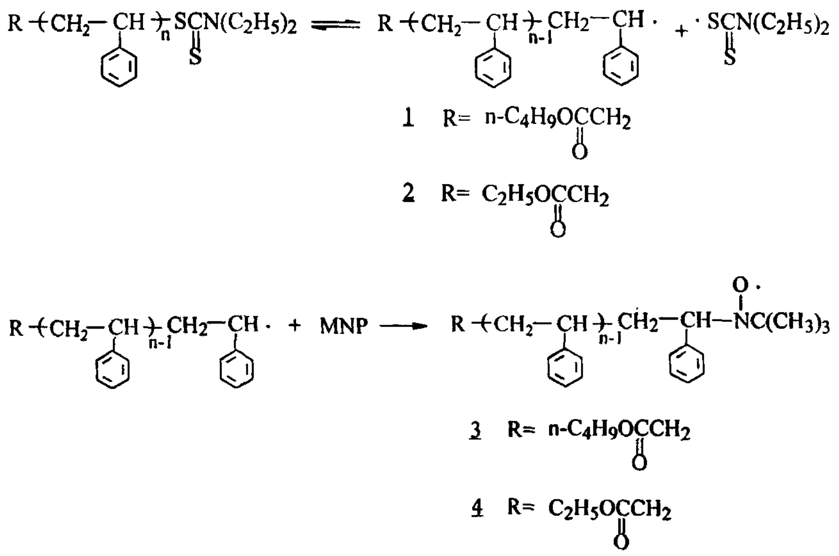


FIG. 3. EPR spectra of BDCA-PS/MNP and EDCA-PS/MNP systems obtained after irradiation at room temperature (1 mT = 10 G). (a) [BDCA-PS] = 0.1 g/mL, [MNP] = 2.94 × 10^{-3} M; (b) [EDCA-PS] = 0.1 g/mL, [MNP] = 2.94 × 10^{-3} M.



SCHEME 2.

Synthesis and Characterization of Block Copolymers

According to the above investigation, the photodissociation of the $(C_2H_5)_2$NCSS end group of functional polymers can initiate monomer to block copolymerization. Since these polymers contain a unit of the $(C_2H_5)_2$NCSS group, and terminations by coupling and disproportionation were neglected due to the reaction of radical $(C_2H_5)_2NCSS\cdot$ with the growing chain radical, AB-type block copolymers were obtained. The photo-copolymerizations of MMA, BA, and VAc with BDCA-PS and EDCA-PS were carried out in benzene solutions. The purified block copolymers were confirmed by FT-IR and ^{1}H-NMR spectra and GPC. Figures 4 and 5 show the GPC curves of the block copolymers and original polymers. The molecular

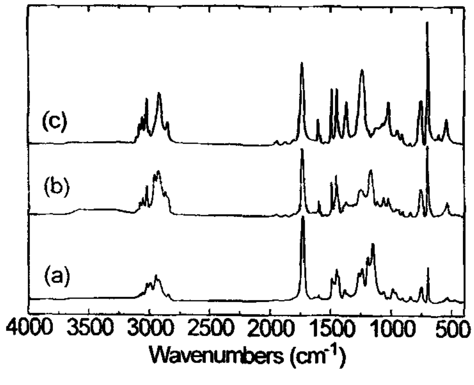


FIG. 4. FT-IR spectra of block copolymers. (a) B-PS-*block*-PMMA, (b) B-PS-*block*-PBA, (c) B-PS-*block*-PVAc.

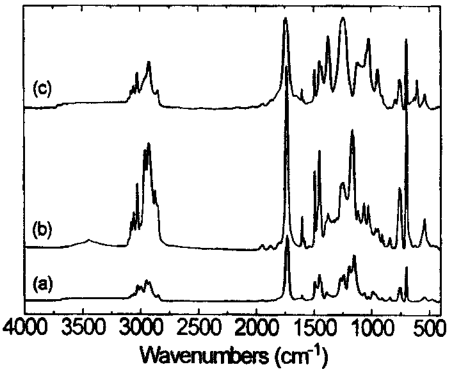


FIG. 5. FT-IR spectra of block copolymers. (a) E-PS-*block*-PMMA, (b) E-PS-*block*-PBA, (c) E-PS-*block*-PVAc.

weights of the block copolymers were larger than those of the original polymers as listed in Table 2. In FT-IR spectra (Figs. 6 and 7), the characteristic frequencies of the ester group (PMMA: C=O 1730 cm^{-1}, C—O 1150 cm $^{-1}$; PBA: C=O 1735 cm^{-1}, C—O 1164 cm^{-1}, PVAc: C=O 1740 cm^{-1}, C—O 1240 cm^{-1}) and phenyl group (PS: H—C=C 3082 cm^{-1}, C=C 1600 cm^{-1}, monosubstituted benzene 700 cm^{-1}) were observed, respectively. In ^{1}H-NMR spectra (Figs. 8 and 9), phenyl group (C_6H_5: δ = 6.57-7.05 ppm), $-COOCH_3$ (δ = 3.60 ppm), $-CH_3$ of butyl (δ = 0.93 ppm), and $-CH_2-CHOOC$ (δ = 4.87 ppm) were observed, respectively.

The glass transition temperatures (T_gs) of the end-functional polymers and block copolymers are also summarized in Table 3, and their DSC traces are shown in Figs. 10 and 11. Two T_gs indicated that two different chains were immiscible. Table 4 shows the comparative weight losses of block copolymers and homopoly-

TABLE 2. Block Copolymerization of Second Monomers with End-Functional Polymers[a]

	End-functional polymer		Second monomer, mL		Time, hours	Block copolymer	
	g	M_n (10^{-4})				g	M_n (10^{-4})
BDCA-PS	0.201	0.586	MMA	0.21	21	0.274	1.46
	0.200	0.586	VAc	0.44	40	0.235	1.06
	0.200	0.586	BA	0.22	21	0.359	1.30
EDCA-PS	0.200	0.689	MMA	0.21	21	0.332	1.02
	0.200	0.689	VAc	0.44	40	0.204	1.08
	0.200	0.689	BA	0.22	21	0.361	1.09

[a] Polymerization in benzene solution under irradiation of an 80-W UV lamp at a distance of 10 cm at room temperature.

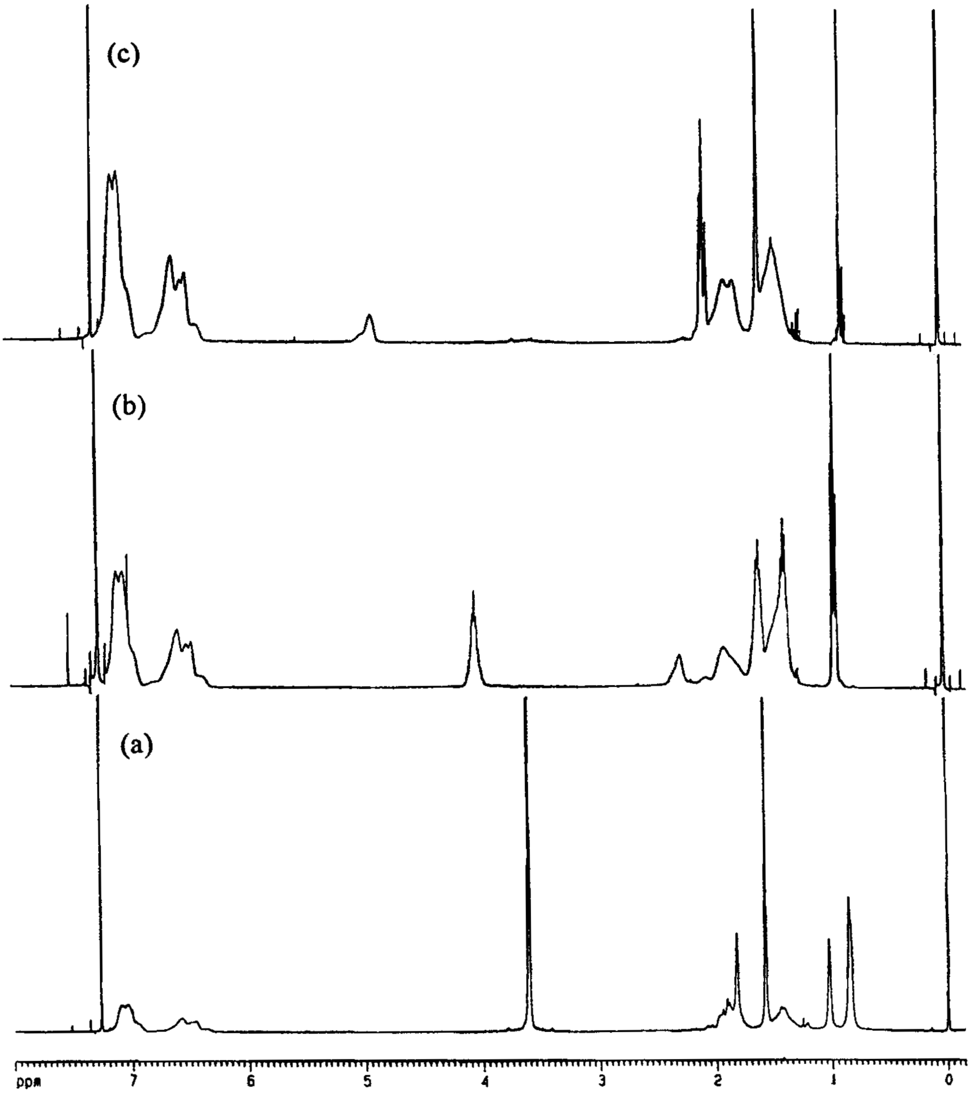


FIG. 6. ^{1}H-NMR spectra of block copolymers. (a) B–PS-*block*-PMMA, (b) B–PS-*block*-PBA, (c) B–PS-*block*-PVAc.

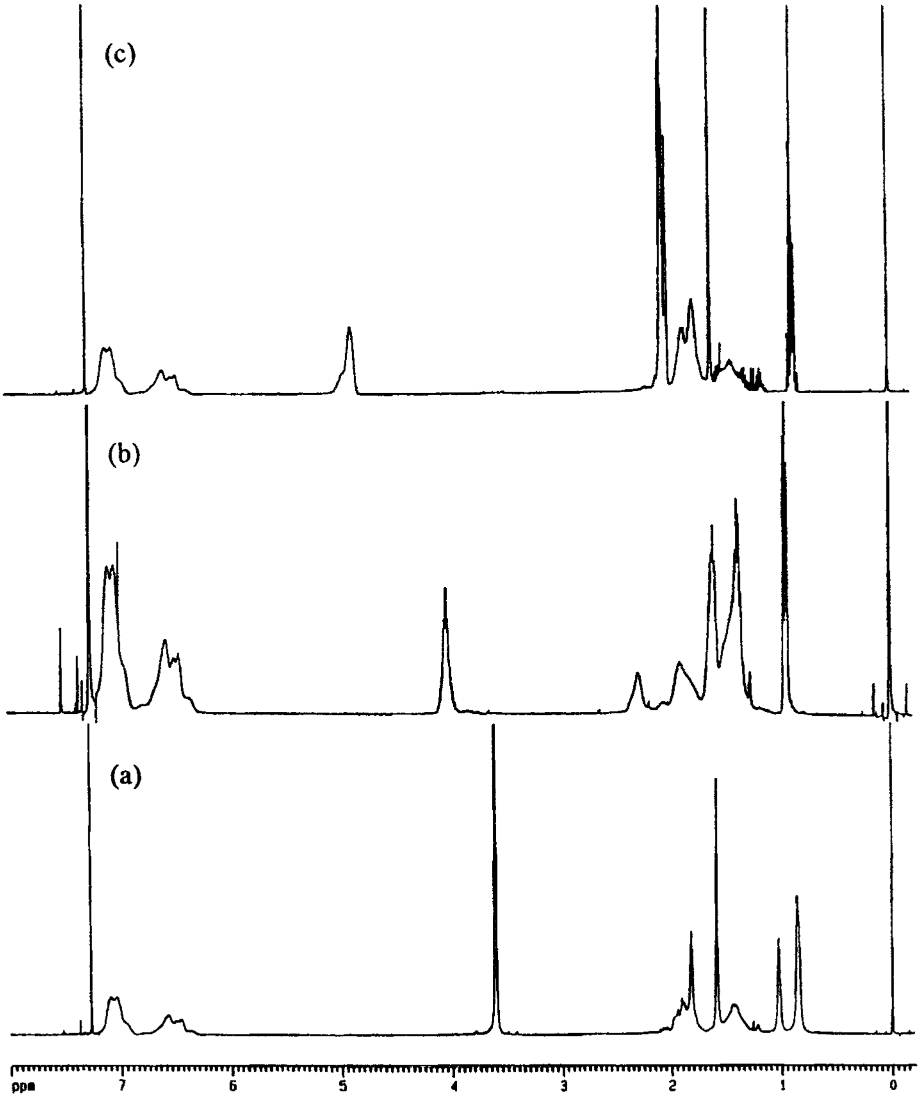


FIG. 7. ^{1}H-NMR spectra of block copolymers. (a) E-PS-*block*-PMMA, (b) E-PS-*block*-PBA, (c) E-PS-*block*-PVAc.

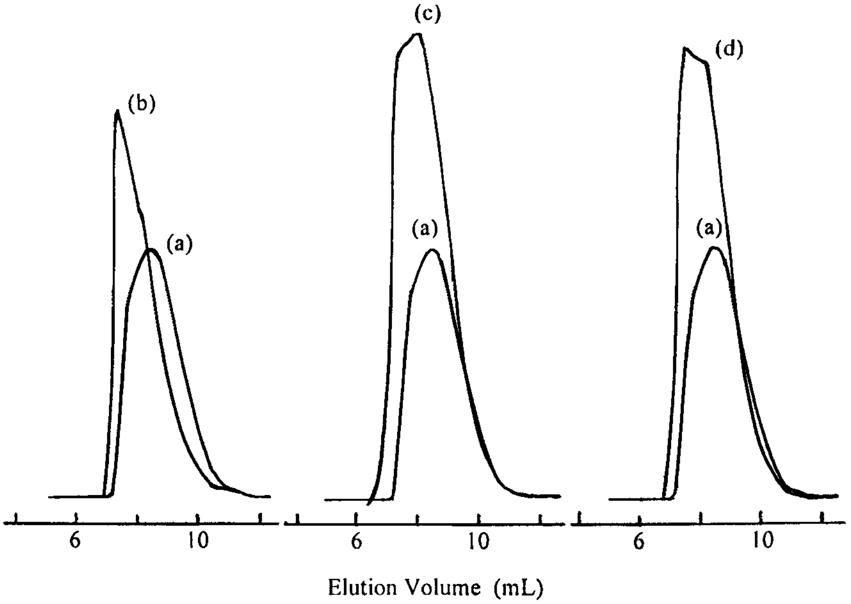


FIG. 8. GPC curves of block copolymers. (a) BDCA-PS, (b) B-PS-*block*-PMMA, (c) B-PS-*block*-PBA, (d) B-PS-*block*-PVAc.

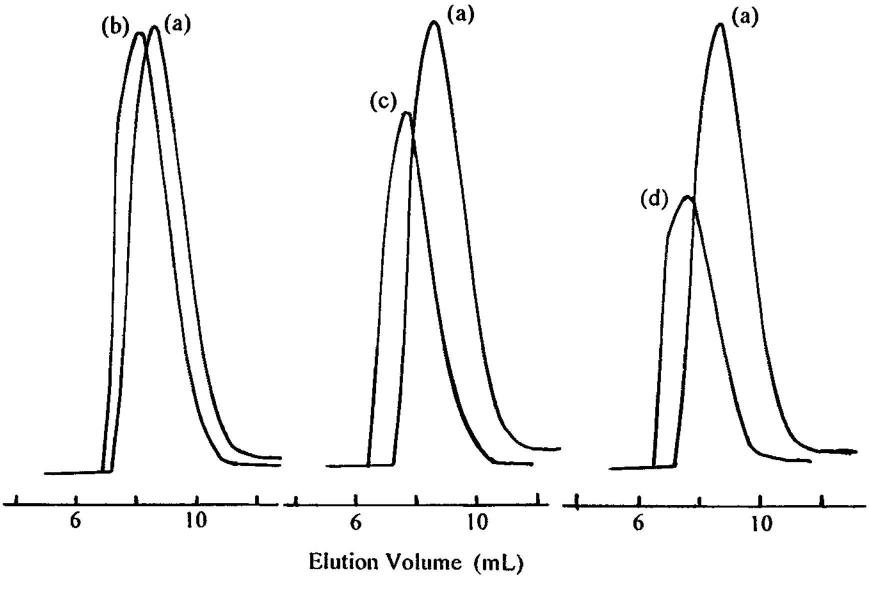


FIG. 9. GPC curves of block copolymers. (a) EDCA-PS, (b) E-PS-*block*-PMMA, (c) E-PS-*block*-PBA, (d) E-PS-*block*-PVAc.

TABLE 3. T_g Data of Block Copolymers

	T_g, °C		
Samples	PS	PMMA	PVAc
B-PS-*block*-PMMA[a]	72.7	114	–
B-PS-*block*-PVAc[a]	109	–	41.7
E-PS-*block*-PMMA[b]	70.7	110	–
E-PS-*block*-PVAc[b]	109	–	42.7

[a] Block copolymers were prepared in the presence of BDCA-PS.

[b] Block copolymers were prepared in the presence of EDCA-PS.

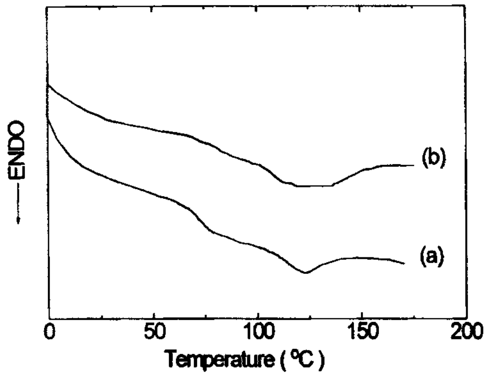


FIG. 10. DSC traces of (a) B-PS-*block*-PMMA and (b) E-PS-*block*-PMMA.

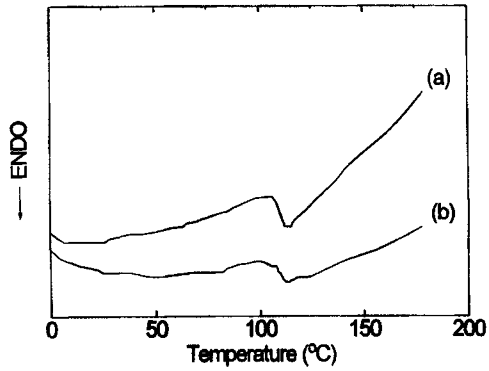


FIG. 11. DSC traces of (a) B-PS-*block*-PVAc and (b) E-PS-*block*-PVAc.

TABLE 4. Comparative Thermal Decomposition Characteristics of Block Copolymers

	Weight loss at temperature, °C					
Sample	10%	25%	50%	75%	90%	Complete
PS	356	390	410	425	445	460
PMMA	297	320	357	390	410	470
Block 1[a]	324	345	373	395	415	435
Block 2[b]	352	390	420	436	445	482

[a] Block 1: B-PS-*block*-PMMA.

[b] Block 2: E-PS-*block*-PMMA.

mers of St and MMA. The weight of PMMA in the block copolymers affected the stability of block copolymers.

CONCLUSION

End-functional polymers which can be used as macroiniferters were synthesized successfully by radical polymerization of styrene using novel photoiniferters, such as ethyl diethyldithiocarbamylacetate and *n*-butyl diethyldithiocarbamylacetate. AB-type block copolymers were obtained from the photocopolymerization of vinyl monomers in the presence of *N*,*N*-diethyldithiocarbamyl end-functional polystyrene. EPR studies confirmed that macroradical and $(C_2H_5)_2NCSS\cdot$ radical were formed from the homolytic cleavage of the C—S bond on end-functional polystyrene under UV light, and the other end group was stable in the same conditions. Block copolymers, such as PS-*block*-PMMA, PS-*block*-PVAc, and PS-*block*-PBA, were synthesized by this technique and characterized by FT-IR spectroscopy, DSC analysis, and so on.

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REFERENCES

[1] M. K. Georges, R. P. N. Veregin, and P. M. Kazmaier, *Polym. Prepr., 35*(2), 582 (1994).

[2] D. Greszta, D. Mardare, and K. Matyjaszewski, *Macromolecules, 27*, 638 (1994).

[3] D. Mardare and K. Matyjaszewski, *Macromol. Rep. Commun., 15*, 37 (1994).

[4] B. B. Wayland, G. Poszmik, and S. L. Mukerjee, *J. Am. Chem. Soc., 116*, 7943 (1994).
[5] J.-S. Wang and K. Matyjaszewski, *Ibid., 117*, 5614 (1995).
[6] I. Piirma and L. H. Chou, *J. Appl. Polym. Sci., 24*, 2051 (1979).
[7] S. N. S. John and I. Piirma, *Ibid., 33*, 727 (1987).
[8] U. Tunca, I. E. Serhatlv, and Y. Yagci, *Polym. Bull. (Berlin), 22*(516), 483 (1989).
[9] A. Onen and Y. Yagci, *J. Macromol. Sci.—Chem., A27*, 743 (1990).
[10] C. P. R. Nair and G. Clouct, *J. Macromol. Sci.—Rev. Macromol. Chem. Phys., C31*, 311 (1991).
[11] O. W. Webster, *Science, 251*(4996), 887 (1991).
[12] T. Otsu, M. Yoshida, and T. Tazaki, *Makromol. Chem., Rapid Commun., 3*, 127 (1982).
[13] T. Otsu, T. Matsunaga, T. Doi, and A. Matsunoto, *Eur. Polym. J., 31*(1), 67 (1995).
[14] X.-M. Yang and K.-Y. Qiu, *J. Macromol. Sci.—Pure Appl. Chem., A34*(2), 271 (1997).
[15] K. Krowichi and J. W. Lown, *J. Org. Chem., 52*(16), 3500 (1987).
[16] M. L. Kaplan, R. C. Haddon, and F. Wudl, *Ibid., 43*(24), 4642 (1978).
[17] T. Otsu, T. Matsunaga, and A. Kuriyama, *Eur. Polym. J., 25*, 643 (1989).
[18] T. Otsu and A. Kuriyama, *J. Macromol. Sci.—Chem., A21*(8&9), 961 (1984).

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