Radical Polymerization of Styrene Initiated with Alkyl N,N-Diethyldithiocarbamylacetate Photoiniferters

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RADICAL POLYMERIZATION OF STYRENE INITIATED WITH ALKYL *N,N*-DIETHYLDITHIOCARBAMYLACETATE PHOTOINIFERTERS

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ABSTRACT

Radical polymerization of styrene initiated with alkyl *N,N*-diethyl-dithiocarbamylacetate photoiniferter was studied in which the molecular weight of polymers increases with both reaction time and monomer conversion. A similar result was obtained when photopolymerization of styrene in the presence of polystyrene with the *N,N*-diethyldithiocarbamyl end group was carried out. The polystyrene with the *N,N*-diethyldithiocarbamyl end group was used as a macroiniferter to polymerize methyl methacrylate and vinyl acetate in the formation of block copolymers. The mechanism of photopolymerization was investigated via spin trapping and the electron paramagnetic resonance technique using 2-methyl-2-nitrosopropane as a trapping agent. The deviation in molecular weight distribution was ascribed to slow initiation and slow exchange between dormant and growing radical species.

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INTRODUCTION

In 1982 the word "iniferter" was first used by Otsu [1] to name those substances that acted as *initiator, transfer* agent and *terminator* in radical polymerization. The polymerization was characterized by a monotonous increase in molecular weight with conversion and a molecular weight distribution that remained fairly constant. Iniferters can be classified into thermal iniferters and photoiniferters. In addition to tetraethylthiuram disulfide, other sulfur compounds having N,N-diethyldithiocarbamate groups, such as benzyl N,N-diethyldithiocarbamate (BDC), p-xylylene bis(N,N-diethyldithiocarbamate) (XDC), benzyl N-ethyldithiocarbamate (BEDC), and p-xylylene bis(N-ethyldithiocarbamate) (XEDC), were found to serve as good photoiniferters [2–4]. Recently, some papers have reported that ethyl 2-(N,N-diethyldithiocarbamyl)isobutyrate (MMADC) and 2-(N,N-diethyldithiocarbamyl)propionate (MADC) [5–7] can be used as photoiniferters for the polymerization of styrene (St), methyl methacrylate (MMA), and butyl acrylate (BA), respectively. Thus, the similar compound alkyl N,N-diethyldithiocarbamylacetate should be an active photoiniferter although it has not been used in this way before. For our work, ethyl N,N-diethyldithiocarbamylacetate (EDCA) and n-butyl N,N-diethyldithiocarbamylacetate (BDCA) were prepared, and the photopolymerization of stryene with EDCA and with BDCA was carried out. The mechanism of polymerization is investigated by spin trapping and the electron paramagnetic resonance (EPR) technique, with end-group analysis of the resulting polystyrene as well. The chain extension and block copolymerization of the resulting polystyrene with the N,N-diethyldithiocarbamyl (Et$_2$NCSS) end group has also been studied.

EXPERIMENTAL

Materials

Chloroacetyl chloride and pyridine were used after distillation. n-Butanol, anhydrous ethanol, sodium N,N-diethyldithiocarbamate trihydrate, and 2-methyl-2-nitrosopropane (MNP, from Aldrich Chemical Company) were used as received. Styrene (St), methyl methacrylate (MMA), vinyl acetate (VAc), and other reagents were purified by common methods.

Preparation of BDCA and EDCA

To a three-necked round-bottomed flask (100 mL), equipped with magnetic stirrer and containing 0.05 mol n-butanol (or anhydrous ethanol), 4.2 mL pyridine, and 20 mL tetrahydrofuran (THF), 0.05 mol chloroacetyl chloride in 20 mL THF was added dropwise. The mixture was stirred for 2 hours at room temperature, then the solvent was removed, and the residual was washed by water, separated by separatory funnel, and dried. n-Butyl chloroacetate or ethyl chloroacetate was obtained (yield: 73 or 74%) and then it was reacted with an equal mole of sodium N,N-diethyldithiocarbamate trihydrate in a solvent mixture of anhydrous ethanol and acetone. The mixture was refluxed for 2 hours and then permitted to stand overnight at room temperature. After filtration, the filtrate solvent was removed under vacuum and the crude product was purified by distillation under reduced

pressure [or recrystallized from ethanol and water mixed solvent (2:1 v:v)]. BDCA was a liquid with bp 187–188°C/800 Pa (yield: 74%), and EDCA was a white needle crystal with mp 51–52.5°C (yield: 74%). ^{1}H NMR of BDCA (δ in ppm, in CDCl$_3$, 400 MHz): 0.93 [3H, CH_3—CH$_2$CH$_2$CH$_2$OOC], 1.27–1.33 [6H, (CH_3—CH$_2$)$_2$N], 1.41 [2H, CH$_3$—CH_2—CH$_2$CH$_2$OOC], 1.65 [2H, CH$_3$CH$_2$—CH_2—CH$_2$OOC], 3.79 [2H, (CH$_3$—CH_2)$_2$N], 4.02 [2H, (CH$_3$—CH_2)$_2$N], 4.15 [2H, OOC—CH_2—SSC], 4.16 [2H, CH$_3$CH$_2$CH$_2$—CH_2—OOC]. ^{1}H NMR of EDCA (δ in ppm, in CDCl$_3$, 400 MHz): 1.27–1.33 [9H, CH_3—CH$_2$OOC and (CH_3—CH$_2$)$_2$N], 3.77 [2H, (CH$_3$—CH_2)$_2$N], 4.02 [2H, (CH$_3$—CH_2)$_2$N], 4.16 [2H, OOC—CH_2—SSC], 4.23 [2H, CH$_3$—CH_2—OOC].

C$_{11}$H$_{21}$NO$_2$S$_2$ (BDCA). Calculated: C 50.15, H 8.05, N 5.32, S 24.34%. Found: C 48.86, H 8.00, N 5.35, S 25.70%.

C$_9$H$_{17}$NO$_2$S$_2$ (EDCA). Calculated: C 45.92, H 7.29, N 5.95, S 27.24%. Found: C 45.81, H 7.31, N 5.37, S 27.37%.

Polymerization

Photopolymerization of St was carried out in the presence of BDCA (or EDCA) in bulk under UV light with a 80-W high-pressure mercury lamp at 10 cm distance from sealed glass tubes and at ambient temperature (37°C). Polymers were precipitated into a large excess of methanol, twice reprecipitated from benzene with methanol, and dried under vacuum. Chain extension of the resulting polystyrene with St in benzene was also performed by a similar method, and the conversion of St was calculated with the increment of PSt. Block copolymerizations of MMA and VAc with PSt in benzene were carried out as well, using petroleum ether as precipitant. The separation of polymers into hompolymers and block copolymers was realized by extraction with suitable solvents, e.g., PSt with cyclohexane, PMMA with 95% EtOH, and PVAc with MeOH. Then the fractions were checked by IR and ^{1}H-NMR spectra and gel permeation chromatography (GPC).

EPR Studies

Photodissociation of BDCA, EDCA, and PSt with Et$_2$NCSS end group in the presence of 2-methyl-2-nitrosopropane (MNP) as a spin trapping agent was investigated. A solution of 0.50 mL 0.23 mol·L^{-1} BDCA (0.50 mL 0.22 mol·L^{-1} EDCA or 0.51 mL 0.1 g·mL^{-1} PSt) in benzene and 0.05 mL 0.2 mol·L^{-1} MNP in acetonitrile was degassed, irradiated, and measured by EPR spectroscopy.

Measurements

Molecular weights and molecular weight distributions were determined by GPC using a Waters 208 instrument equipped with a differential refractometer and Styragel 500 Å columns using THF as an eluent and a flow rate of 1.0 mL·min^{-1}. The molecular weight calibration curve was obtained using polystyrene standards. The number of Et$_2$NCSS end groups of polystyrene in THF was determined by UV spectroscopy recorded on a Shimadzu UV-250 model spectrophotometer [BDC as standard; its structure is similar to polystyrene with the Et$_2$NCSS group (272 nm)]. ^{1}H-NMR and IR spectra were recorded on a Bruker ARX400 spectrometer and a
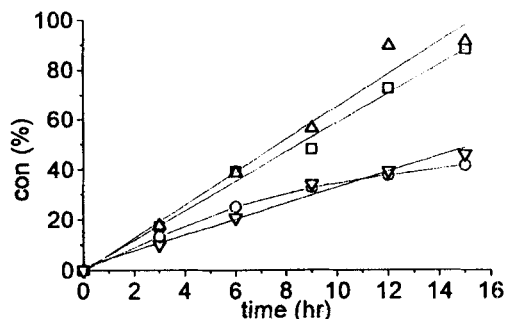
FIG. 1.   Time–conversion relations for polymerization of St with BDCA and EDCA at 37°C, [St] = 8.74 mol·L^{-1}, ($\square$) [BDCA] 0.05 mol·L^{-1}, ($\bigcirc$) [BDCA] 8.0 × 10^{-3} mol·L^{-1}, ($\triangle$) [EDCA] 0.05 mol·L^{-1}, (∇) [EDCA] 8.0 × 10^{-3} mol·L^{-1}.

Nicolet Magna-IR 750 spectrometer, respectively. EPR spectra were obtained on a Bruker ER200D-SRC electron spin resonance spectrometer using the TM cavity at the X-band in a quartz EPR tube with 100 kHz modulation frequency and 1.00 mW microwave power.

RESULTS AND DISCUSSION

Photopolymerization of St with BDCA and EDCA as Photoiniferters

In order to understand the behavior of BDCA and EDCA as photoinitiators, the conversion versus time, molecular weight ($\overline{M}_n$) versus time, and conversion were studied. The results of polymerization of St with BDCA and EDCA are shown in Figs. 1–3. From Fig. 1 the straight lines of conversion with time in the presence of BCDA and EDCA were observed. The increase of $\overline{M}_n$ with reaction time and conversion was also noticed in Figs. 2 and 3. The results revealed that BCDA and EDCA acted as iniferters. The data of $\overline{M}_n$, $\overline{M}_w/\overline{M}_n$, and the number of Et$_2$NCSS end groups of polystyrene obtained as a function of polymerization time are sum-
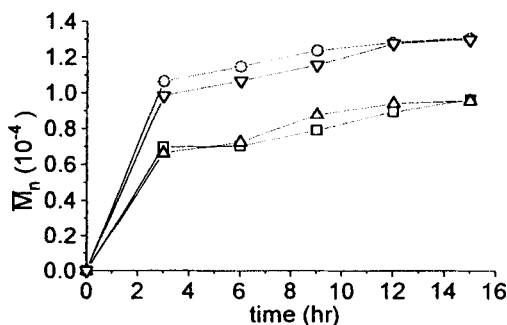

FIG. 2.   Time-$\overline{M}_n$ relations for polymerization of St with BDCA and EDCA at the same conditions as in Fig. 1.
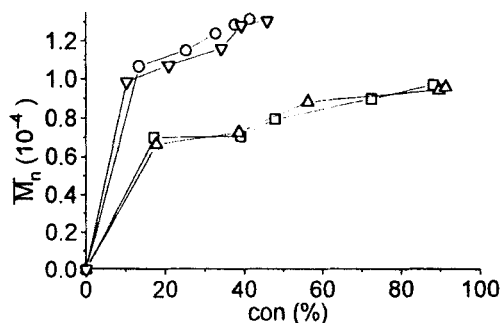
FIG. 3. Conversion-$\overline{M}_n$ relations for polymerization of St with BDCA and EDCA at the same conditions as in Fig. 1.

marized in Tables 1 and 2. Molecular weight distribution ($\overline{M}_w/\overline{M}_n$) remained essentially constant with time.

The Mechanism of Polymerization and EPR Studies

Matyjaszewski et al. [8] showed that a "living" radical polymerization requires a low stationary concentration of growing radicals which are in dynamic equilibrium with the dormant species—the reaction of growing radical and dormant species is reversible. There are three approaches to fulfill the requirement [8, 9]. System I is based on a reversible recombination of growing radicals with scavenging radicals, System II is based on the reaction of growing radicals to reversibly form persistent radicals, and System III is based on degenerative transfer. A good example of System I is photochemical polymerization with dithiocarbamate derivatives due to the reversible reaction between growing radicals and dormant species under photochemical conditions. The mechanism of photoiniferter ($R-SSCNEt_2$), such as BDC, MMADC, and MADC, was investigated by Otsu and coworkers [2, 3, 5] as shown in Scheme 1.

R· and RM$_n$· acted as reactive radicals, and Et$_2$NCSS· was a primary radical with low reactivity that reacted with growing radicals to form dormant species

TABLE 1. Photopolymerization of St in Bulk with BDCA at 37°C[a]

Sample	Time, hours	$\overline{M}_n$ (10^{-4})	$\overline{M}_w$ (10^{-4})	$\overline{M}_w/\overline{M}_n$	Number of end group (Et$_2$NCSS)
1	3	0.697	1.84	2.64	1.00
2	6	0.702	1.88	2.68	1.02
3	9	0.792	2.02	2.55	1.00
4	12	0.896	2.43	2.71	1.00
5	15	0.967	2.58	2.66	0.98

[a]Polymerization condition: [St] = 8.74 mol·L^{-1}, [BDCA] = 0.05 mol·L^{-1}.

TABLE 2.   Photopolymerization of St in Bulk with EDCA at 37°C[a]

Sample	Time, hours	$\overline{M}_n (10^{-4})$	$\overline{M}_w (10^{-4})$	$\overline{M}_w/\overline{M}_n$	Number of end group (Et_2NCSS)
1	3	0.662	1.82	2.75	0.97
2	6	0.724	1.94	2.68	0.99
3	9	0.880	2.21	2.51	1.01
4	12	0.942	2.52	2.68	1.00
5	15	0.956	2.57	2.69	0.99

[a]Polymerization condition: $[St] = 8.74 \; mol \cdot L^{-1}$, $[EDCA] = 0.05 \; mol \cdot L^{-1}$.

reversibly. Van Kerckhoven [10] also confirmed that photochemical cleavage of the $R_2NCSS-C$ bond may provide reversible systems.

In BDCA and EDCA systems the results indicated that BDCA and EDCA act similarly to BDC, MMADC, and MADC. The $Et_2NCSS-C$ bond in BDCA and EDCA cleaves to form $ROOCCH_2 \cdot$ and $Et_2NCSS \cdot$ radicals under UV light. The radical $ROOCCH_2 \cdot$ can initiate polymerization, and $Et_2NCSS \cdot$ can reversibly react with a growing radical. Polymer end-group analysis, which showed the presence of Et_2NCSS end groups on polystyrene, is assisted by this polymerization mechanism.

It is important to clarify the photodissociation behavior to BDCA, EDCA, and polystyrene chain end groups. Thus, the radical intermediates of the reaction were investigated by spin trapping and the EPR technique. The EPR spectra of BDCA/MNP and EDCA/MNP systems after UV irradiation are shown in Figs. 4 and 5, corresponding to radical $\underline{1}$ ($a_\alpha^N = 14.1$ G, $a_\beta^H = 7.6$ G) and $\underline{2}$ ($a_\alpha^N = 14.1$ G, $a_\beta^H = 7.5$ G), respectively. Under UV light, BDCA and EDCA react with MNP as shown in Scheme 2.

Figures 6 and 7 show the EPR spectra of the BDCA–PSt/MNP and EDCA–PSt/MNP systems (BDCA–PSt is PSt from the polymerization of styrene with BDCA as photoinitiator, and EDCA–PSt is that from the reaction with EDCA as photoinitiator). Theoretically speaking, these systems produce the same polystyrene radicals with different end groups, such as radicals $\underline{3}$ and $\underline{4}$. However, it is impossible to distinguish one end group from the other end group by EPR spectra since the

$$R-\overset{\overset{\displaystyle S}{\|}}{S}CNEt_2 \; \rightleftharpoons \; R\cdot \; + \; \cdot \overset{\overset{\displaystyle S}{\|}}{S}CNEt_2$$

$$R\cdot \; + \; M \; \longrightarrow \; RM\cdot$$

$$RM_n\cdot \; + \; M \; \longrightarrow \; RM_{n+1}\cdot$$

$$RM_n\cdot \; + \; \cdot \overset{\overset{\displaystyle S}{\|}}{S}CNEt_2 \; \rightleftharpoons \; RM_n\overset{\overset{\displaystyle S}{\|}}{S}CNE_2$$
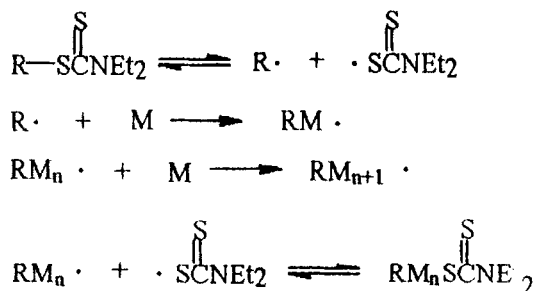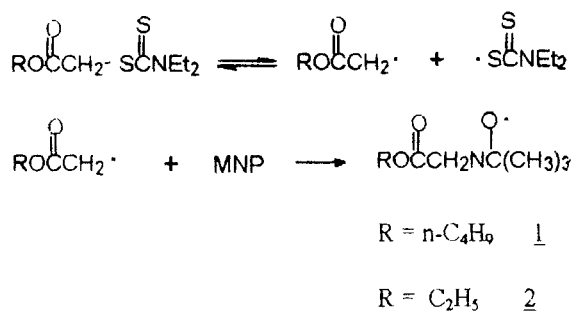
SCHEME 1.

FIG. 4. EPR spectrum of BDCA/MNP system obtained after irradiation at room temperature: $1 \, mT = 10 \, G$, [BDCA] $= 0.20 \, mol \cdot L^{-1}$, [MNP] $= 0.022 \, mol \cdot L^{-1}$.

FIG. 5. EPR spectrum of EDCA/MNP system obtained with similar conditions as in Fig. 4.

$$R = n\text{-}C_4H_9 \quad \underline{1}$$

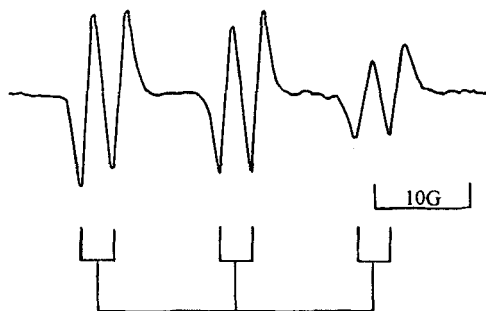$$R = C_2H_5 \quad \underline{2}$$

SCHEME 2.

FIG. 6. EPR spectrum of BDCA-PSt/MNP system obtained after irradiation at room temperature: 1 mT = 10 G, [BDCA-PSt] = 0.1 g·mL^{-1}, [MNP] = 2.94 × 10^{-3} mol·L^{-1}.

values of hyperfine splitting constants are the same, i.e., a_α^N = 14.7 G, a_β^H = 3.5 G. Using ^{1}H-NMR spectra of BDCA-PSt and EDCA-PSt, the ethyl group and the n-butyl group can be identified [the characteristic chemical shift for the ethyl group (δ = 4.23 ppm) and for the n-butyl group (δ = 0.93 ppm) are observed]. These results indicate that the expected Et$_2$NCSS—C bond in BDCA-PSt and EDCA-PSt cleaved to form the corresponding radicals (see Scheme 3).

The results of EPR studies, as mentioned above, indicated that the reaction of the C—S bond under UV light was reversible and confirmed that the mechanism of styrene polymerization with BDCA and EDCA as photoiniferters proceeds via the reversible reaction of C—S bonds of dormant species under UV light irradiation.

Chain Extension and Block Copolymerization of BDCA-PSt and EDCA-PSt

As described above, the photodissociation of the active chain end group of PSt can lead to chain extension and block copolymerization. The block copolymers are the AB-type copolymer since PSt contains one active end group (Et$_2$NCSS). Photopolymerization of St with BDCA-PSt or EDCA-PSt was carried out and the results are shown in Figs. 8 and 9, from which it can be seen that $\overline{M}_n$ increases with
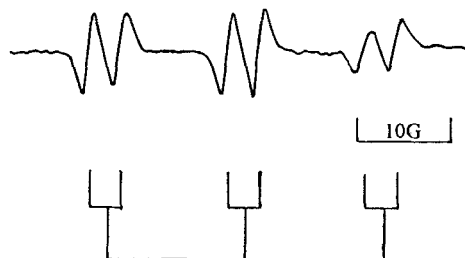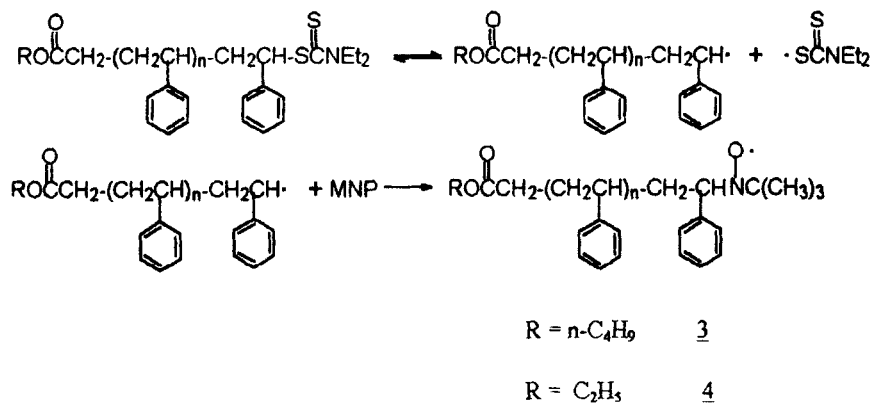

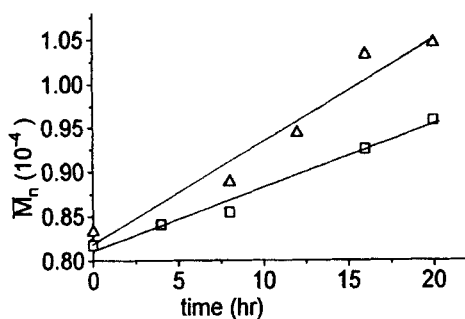FIG. 7. EPR spectrum of EDCA-PSt/MNP system obtained with similar conditions as in Fig. 6.

$$ROCCH_2\text{-}(CH_2CH)_n\text{-}CH_2CH\text{-}SCNEt_2 \rightleftharpoons ROCCH_2\text{-}(CH_2CH)_n\text{-}CH_2CH\cdot + \cdot SCNEt_2$$

$$ROCCH_2\text{-}(CH_2CH)_n\text{-}CH_2CH\cdot + MNP \longrightarrow ROCCH_2\text{-}(CH_2CH)_n\text{-}CH_2\text{-}CHNC(CH_3)_3$$

$$R = n\text{-}C_4H_9 \quad \underline{3}$$

$$R = C_2H_5 \quad \underline{4}$$

SCHEME 3.

FIG. 8. Time-$\overline{M}_n$ relations for polymerization of St in the presence of BDCA-PSt and EDCA-PSt at 37°C, [St] = 2.40 mol·L^{-1}, (□) [BDCA-PSt] = 0.05 g·mL^{-1}, (△) [EDCA-PSt] = 0.05 g·mL^{-1}.
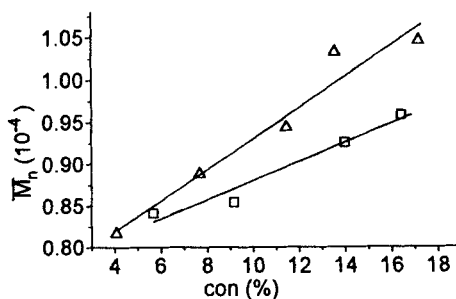

FIG. 9. Conversion-$\overline{M}_n$ relations for polymerization of St in the presence of BDCA-PSt and EDCA-PSt at the same conditions as in Fig. 8.

TABLE 3.   Block Copolymerization of Second Monomers with BDCA–PSt and EDCA–PSt

No.	B–PSt (M_1, g)	E–PSt (M_1, g)	M2, mL	Yield, g	Fractions extracted					
					M_1 polymer (%) ($\overline{M}_n$ 10^{-4})		M_2 polymer (%) ($\overline{M}_n$ 10^{-4})		Block polymer (%) ($\overline{M}_n$ 10^{-4})	
1	0.101	—	MMA 0.53	0.244	30.1	0.818	33.2	1.02	36.7	1.33
2	—	0.102	MMA 0.53	0.301	19.5	0.833	45.7	0.904	34.8	1.27
3	0.101	—	VAc 2.0	0.128	—	0.818	—	—	100	0.853
4	—	0.102	VAc 2.0	0.525	—	0.833	56.9	1.11	43.1	1.03

aPolymerization time: 20 hours for MMA, 41 hours for VAc.

both time and conversion. Block copolymers were also obtained by the same method using a second monomer instead of St. The formation of block copolymers (PSt-*block*-PMMA and PSt-*block*-PVAc) is confirmed by IR and ^{1}H-NMR spectra. The characteristic frequencies of the ester group of PMMA (1731 cm^{-1}) and PVAc (1739 cm^{-1}) and of the benzene of PSt (3082, 1601, and 698 cm^{-1}) are observed. In ^{1}H-NMR (CDCl$_3$) spectra, the presence of phenyl of PSt (δ = 7.05 and 6.57), —OCH_3 of PMMA (δ = 3.60), and —CHO— of PVAc (δ = 4.87) are observed. The block copolymer data are compiled in Table 3. However, the yield of block copolymers is low due to the difficult separation of block copolymer and homopolymer.

CONCLUSIONS

Photopolymerization of styrene initiated by alkyl *N,N*-diethyldithiocarbamylacetate has shown the nature of iniferter radical polymerization. Molecular weights increase with time and conversion, and molecular weight distribution remains substantially constant. Chain can be extended by new monomer addition, and block copolymers were prepared using BDCA–PSt and EDCA–PSt as macroiniferters. The EPR spectra results confirm that the reaction of the Et$_2$NCSS—C bond was reversible. However, the observed deviation of molecular weight distribution from typical living polymerizations is proposed to be due to slow initiation and a slow exchange reaction between the growing radical and the dormant species.

ACKNOWLEDGMENTS

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