for the radiotracer experiments were provided by the Oak Ridge National Laboratory with the help of W. Jack McDowell of the Separations Science Group to whom we are very grateful.

Registry No. Zinc, 7440-66-6; mercury, 7439-97-6; silver, 7440-22-4; gold, 7440-57-5.

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Synthesis, Reactivity, and Role of 4-Vinylbenzyl *N*,*N*-Diethyldithiocarbamate as a Monomer–Iniferter in Radical Polymerization

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ABSTRACT: For the synthesis and design of graft copolymers through radical polymerization, 4-vinylbenzyl *N*,*N*-diethyldithiocarbamate (VBDC) was prepared and used as a monomer–iniferter (initiator–transfer agent–terminator) which has two functions as a monomer and a photoiniferter. In the absence of light, VBDC polymerized easily with 2,2′-azobis(isobutyronitrile) via an ordinary radical polymerization mechanism, and its reactivity was similar to that of styrene (St). The homopolymer of VBDC and its copolymers with St were found to act as excellent photoiniferter of living radical polymerization in a homogeneous system to give graft copolymers consisting of benzene-soluble and -insoluble fractions, in which the amount of the latter increased when the VBDC units in the copolymer photoiniferter used increased. In the presence of UV light, VBDC polymerized without a radical initiator, leading to benzene-soluble and -insoluble polymers as a result of participation of the styryl double bond in the polymers produced. However, the photopolymerization of St with a catalytic amount of VBDC as a photoiniferter gave a benzene-soluble polymer that contains a styryl double bond and a *N*,*N*-diethyldithiocarbamyl group at the polymer chain ends, i.e., a macromer–iniferter.

Introduction

In previous papers,[1–6] monomeric and polymeric compounds with *N*,*N*-diethyldithiocarbamyl groups have been reported to serve as a photoiniferter of living radical polymerization in homogeneous systems. Therefore, the use of these iniferters (initiator–transfer agent–terminator) has been found to be effective for the synthesis and design of various functional and block polymers.[4–6]

If such iniferters having a polymerizable double bond, i.e., monomer–iniferter, are synthesized and used successively as both monomer and iniferter macromers and graft copolymers would be obtained according to Scheme I, where B is a *N*,*N*-diethyldithiocarbamyl (-SC(S)NEt$_2$) group.

Since St is a highly polymerizable monomer and benzyl *N*,*N*-diethyldithiocarbamate is an effective photoiniferter,[6] 4-vinylbenzyl *N*,*N*-diethyldithiocarbamate (VBDC) is also expected to serve as a monomer–iniferter. From these viewpoints, VBDC was prepared and its reactivities as both monomer and iniferter were evaluated. Moreover, the

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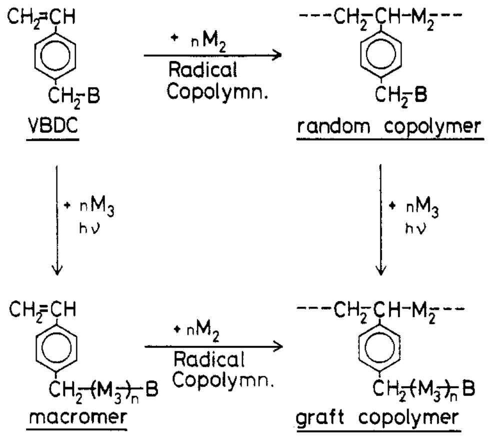
Scheme I



synthesis of macromers and graft polymers by using VBDC monomer–iniferter were attempted. The results obtained are described in this paper.

Experimental Section

Synthesis of VBDC Monomer–Iniferter. VBDC was synthesized from the reaction of *p*-chloromethylstyrene (*p*-CMS) with sodium diethyldithiocarbamate.[7] Namely, in a 500-mL three-necked flask equipped with a magnetic stirrer, a dropping funnel, and a reflux condenser were placed 41 g (0.24 mol) of sodium *N*,*N*-diethyldithiocarbamate and 200 mL of ethanol. A solution of 30 g (0.2 mol) of p-CMS in 50 mL of ethanol was added dropwise at 0 °C under a nitrogen atmosphere. During the reaction, sodium chloride was precipitated. The reaction continued under stirring for 20 h at room temperature. The solution was then poured into a large amount of water and extracted with ether. The extract was washed with water and dried on anhydrous sodium sulfate. The ether was removed under reduced pressure, and the residue was recrystallized three times from methanol; yield of VBDC: 42.5 g (80%); mp 56.5–57.5 °C; IR (KBr) 915, 985, 1415 cm^{-1} ($CH{=}CH_2$), 1210, 1485 cm^{-1} (CS–N); ^1H NMR (CCl_4) δ 7.31 (s, 4H, C_6H_4), δ 6.05 (m, 3H, $CH{=}CH_2$), δ 4.47 (s, 2H, C_6H_4–CH_2), δ 3.85 (broad, 4H, N–CH_2), δ 1.37 (t, 6H, CH_2CH_3). Anal. Calcd for $C_{14}H_{19}NS_2$: C, 63.34; H, 7.22; N, 5.28; S, 24.16. Found: C, 63.56; H, 6.95; N, 5.15; S, 24.34. From these results, VBDC thus obtained was confirmed to be pure.

Reagents. Pure *p*-CMS was prepared according to the method[8] reported previously and distilled before use. Styrene (St), methyl methacrylate (MMA), and vinyl acetate (VAc) were purified by distillation in a stream of nitrogen before use. 2,2′-Azobis(isobutyronitrile) (AIBN) was recrystallized twice from methanol. Solvents and other reagents were used after ordinary purification.

Polymerization. Radical polymerizations of VBDC were carried out in the dark in the presence of AIBN. The required amounts of VBDC, AIBN, and benzene were charged into a hard glass ampule, which was then degassed by conventional freezing and thawing techniques, and sealed off under vacuum. After polymerization for a given time, the contents of the tubes were poured into a large amount of *n*-hexane. The polymers precipitated were purified by a reprecipitation method from a benzene–methanol system.

A similar procedure was applied to the radical copolymerization of VBDC with St, which was performed with a low conversion (ca. 10%). Photopolymerizations were also carried out in the presence of VBDC or its copolymers as a photoiniferter under irradiation with a Toshiba SHL-100 UV lamp from a distance of 10 cm at room temperature.

Characterization of the Polymers. The polymers and copolymers obtained with St were purified by a reprecipitation method from a benzene–methanol system. The composition of the copolymers was determined by elemental analysis. The monomer reactivity ratios, r_1 and r_2, were calculated according to the nonlinear least-squares method.[9]

The separation of the polymers obtained from the graft copolymerization of MMA into graft and nongraft polymers was carried out by extracting them with suitable solvents, i.e., cyclohexane, acetonitrile, and benzene for the parent polymer (polymeric photoiniferter), the homopolymer of MMA, and the soluble graft copolymer, respectively.

Table I
Polymerization of VBDC in Benzene

[VBDC], mol/dm^3	[AIBN], mmol/dm^3	temp, °C	time, h	yield, %	10^{-2} [η], cm^3/g
0.98	1.62	60	5	13.6	0.16
0.98	1.62	60	9	28.4	0.20
0.38	0	30	6	0.8	
0.38	10.0	30	11[a]	19.7[b]	0.05[c]
0.38	0	30	11[a]	17.8[b]	0.04[c]

[a] Polymerized under UV irradiation. [b] Contained a small amount of benzene-insoluble polymer. [c] Indicates values for the benzene-soluble polymer.

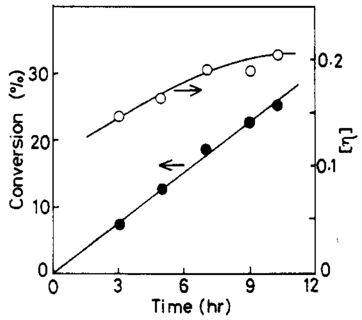
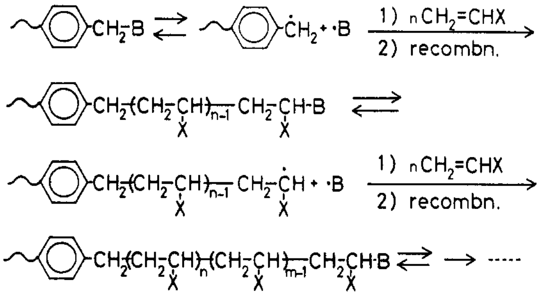


Figure 1. Radical polymerization of VBDC with AIBN in the dark at 60 °C: [VBDC] = 0.98 mol/dm^3; [AIBN] = 1.62 mmol/dm^3 in benzene; [η] in 10^{-2} cm^3/g.

Scheme II



The structures of the polymers were checked by their IR and NMR spectra. Intrinsic viscosities, [η], were determined by viscosity measurement in benzene at 30 °C.

Results and Discussion

Polymerization of VBDC. The results of the polymerization of VBDC in the absence or presence of UV light are shown in Table I.

As can be seen in this table, VBDC was found to polymerize easily with AIBN at 60 °C in the absence of light to give a colorless polymer. The IR and NMR spectra showed that the polymers consisted of ordinary chain structures polymerized by an opening of the double bond of VBDC. However, the [η] of the polymers was low compared with those of poly(St) produced under similar conditions.

Figure 1 shows time–conversion and time–[η] relations for the polymerization of VBDC with AIBN in the dark at 60 °C. The [η] of the polymers slightly increased with polymerization time, probably owing to a chain-transfer reaction of the propagating radical with the *N*,*N*-diethyldithiocarbamylmethyl group in the polymer produced.

As is also seen from Table I, in the presence of UV light, VBDC polymerized without AIBN to give polymers that contained a small amount of the benzene-insoluble polymer

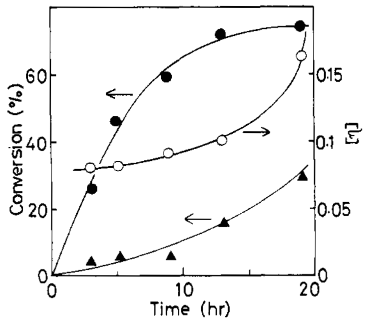


Figure 2. Photopolymerization of VBDC in benzene at 30 °C; [VBDC] = 3.77 mol/dm^3: (●) total yield; (▲) yield of the benzene-insoluble polymer; (○) [η] (in 10^{-2} cm^3/g) of the benzene-soluble polymer.

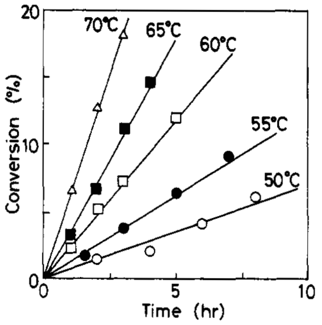


Figure 3. Time–conversion relations for the radical polymerization of VBDC at 50–70 °C: [VBDC] = 0.37 mol/dm^3; [AIBN] = 1.74 mmol/dm^3.

under these conditions. The [η] of the benzene-soluble polymers was very low, less than 10 cm^3/g. The addition of AIBN had no effect on polymer yield, indicating that the polymerization is mainly induced through photolysis of the C–S bond in VBDC[3,6] (see Scheme II). The time–conversion and time–[η] relations in the photopolymerization of VBDC in the absence of AIBN at 30 °C are shown in Figure 2. The yield of the benzene-insoluble polymers and the [η] of the benzene-soluble polymers produced increased as a function of reaction time, i.e., total yield. These results may suggest the participation of a part of the styryl double bond in the polymer produced into the polymerization.

Kinetic Study of the Radical Polymerization of VBDC. The polymerizations of VBDC were carried out with AIBN in benzene at 50–70 °C in the absence of light. The time–conversion relations are shown in Figure 3, from which the polymerizations at every temperature are found to proceed linearly with reaction time.

From the Arrhenius plot of the rates of polymerization (R_p) with reciprocal polymerization temperatures, the apparent activation energy for the overall polymerization of VBDC was calculated to be 95.8 kJ/mol. This value is comparable to that of St.

The dependency of the concentrations of VBDC monomer and AIBN initiator on R_p was then investigated. The rate equation for the polymerization of VBDC with AIBN at 60 °C was found to be expressed as follows:

$$R_p = k[\mathrm{AIBN}]^{0.55}[\mathrm{VBDC}]^{1.0}$$

where k is the overall rate constant. Although the observed order with respect to the AIBN concentration is slightly higher than 0.5 for bimolecular termination, it may be clear that the polymerization of VBDC in the dark proceeds principally via an ordinary radical mechanism.

Copolymerization of VBDC with St: Evaluation of Its Reactivity. The benzene-solution copolymerization of VBDC (M_1) with St (M_2) was performed with AIBN in the dark at 60 °C. The results are shown in Table II.

Table II
Radical Copolymerization of VBDC (M_1) with St (M_2) in the Dark[a]

monomer, mol %			copolymer	
[VBDC]	[St]	conversion, %	S, %	[VBDC], mol %
0	100	3.22	0	0
28.6	71.4	6.47	14.12	35.6
42.5	57.5	7.54	17.80	52.4
56.5	43.5	9.22	20.09	66.0
70.6	29.4	10.73	21.63	77.1
84.7	15.3	11.96	22.98	88.5
100	0	12.34	24.12	100

[a] Polymerized in benzene at 60 °C for 5 h; [AIBN] = 1.62 mmol/dm^3.

Table III
Copolymerization Parameters for VBDC and Related Styrenes (M_1)–St (M_2) Systems

M_1	r_1	r_2	$1/r_2$	Q_1	e_1
VBDC	1.44	0.68	1.47	1.31	−0.61
p-MBTS[a]	1.35	0.70	1.43	1.18	−0.56
p-CMS[b]	1.13	0.72	1.39	1.16	−0.58
p-MS[c]	1.15	0.82	1.22	1.48	−1.04

[a] Data of Otsu et al.[11] [b] Data of Tsuda et al.[8] [c] Data of Sianesi et al.[10]

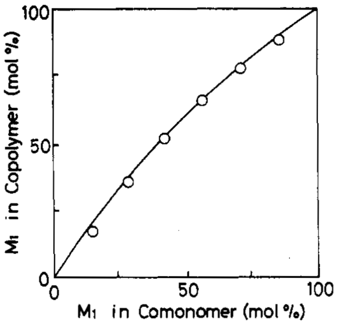


Figure 4. Monomer–copolymer composition curve for the radical copolymerization of VBDC (M_1) with St (M_2) at 60 °C; [AIBN] = 1.62 mmol/dm^3.

The yield of the copolymers was found to increase with the increase of the concentration of VBDC. The copolymer composition curve is shown in Figure 4, from which the reactivity of VBDC is observed to be somewhat higher than that of St. The determined r_1 and r_2 are summarized in Table III, in which those for the radical copolymerizations of *p*-CMS,[8] *p*-methylstyrene (*p*-MS),[10] and *p*-[((benzothiazolyl)thio)methyl]styrene (*p*-MBTS)[11] with St are also indicated.

Although all of these para-substituted Sts showed somewhat higher reactivity than St, it seems that their reactivities are almost identical with each other. The Q and e values for VBDC are also shown in Table III. It is clear that VBDC is regarded as an electron-donating conjugative monomer.

Photopolymerization of St or MMA with VBDC as Iniferter. Formation of Macromer. Figures 5 and 6 show the time–conversion and time–[η] relations in the photopolymerization of St and MMA, respectively, with VBDC as a photoiniferter at 30 °C. In both cases, the yield and [η] of the polymers produced increase with reaction time, the same as those observed in the photopolymerization with benzyl *N,N*-diethyldithiocarbamate as a monofunctional iniferter.[6] Therefore, these polymerizations are considered to proceed via a living radical mechanism in a homogeneous system, according to Scheme

Table IV
Graft Copolymerization of MMA with VBDC Homopolymer and St-VBDC Copolymers[a]

copolym					wt of homopoly(MMA) extract,[b] g	wt of parent VBDC copolym extract,[c] g	graft copolym[d]		
							sol fract		
[VBDC], mol %	10^{-2} [η], cm^3/g	wt, g	amt MMA, cm^3	tot yield, g			wt, g	10^{-2} [η], cm^3/g	insol fract, g
100	0.20	0.19	4	2.16	0.12	0.0	0.10	0.99	1.94
20.8	0.17	0.20	4	1.67	0.18	0.0	0.86	0.94	0.63
4.6	0.20	0.20	4	1.38	0.26	0.0	1.00	0.91	0.12
2.3	0.21	0.20	4	1.35	0.30	0.0	1.05	0.98	

[a] Polymerized in bulk at 30 °C for 2 h under UV irradiation. [b] Extracted by boiling acetonitrile from whole polymer obtained. [c] Extracted by boiling cyclohexane from the acetonitrile-insoluble polymer. [d] Separated with benzene into soluble and insoluble polymers.

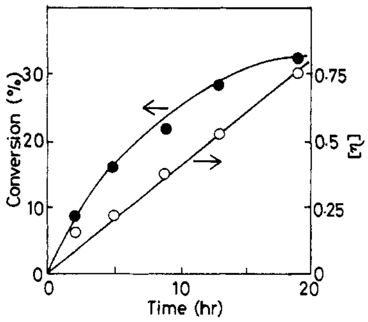


Figure 5. Photopolymerization of St with VBDC as the photoiniferter at 30 °C: [St] = 8.7 mol/dm^3; [VBDC] = 1 mmol/dm^3 in the dark; [η] in 10^{-2} cm^3/g.

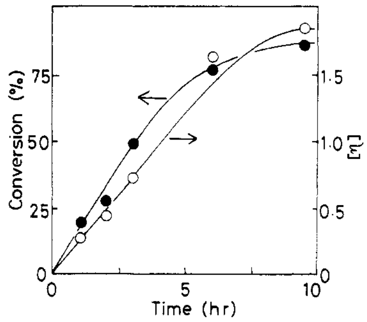


Figure 6. Photopolymerization of MMA with VBDC as the photoiniferter at 30 °C: [MMA] = 9.4 mol/dm^3, [VBDC] = 1 mmol/dm^3 in the dark; [η] in 10^{-2} cm^3/g.

II[2] where B is the $-SC(S)NEt_2$ group. The photodissociation of this C–B (i.e., C–S) bond gives a reactive propagating radical and a less reactive or nonreactive thio radical that undergoes primary radical termination.[1,5,12]

According to Scheme II, the polymer obtained is expected to always contain a styryl double bond and a *N*,*N*-diethyldithiocarbamyl group at its both ends if this double bond does not participate into the polymerization. Namely, this polymer is a macromer and strictly, in other words, a macromer–iniferter.

The ^{1}H NMR spectrum of the poly(St) obtained showed weak peaks due to the styryl double bond at 5–6 ppm that are similar to those observed in VBDC. Although weak peaks due to the styryl double bond and a somewhat strong peak of the diethyldithiocarbamyl group at 282 nm were also found in ^{13}C NMR and UV spectra, respectively, their number per one polymer molecule could not be determined because the molecular weight of the poly(St) used was greater than 50 000.

This polymer was recently observed to induce living radical polymerization of St, indicating that the diethyldithiocarbamyl group bonded at the polymer chain end. Moreover, it underwent radical copolymerization with diisopropyl fumarate, and the formation of a high molecular weight graft copolymer was confirmed by GPC data. These observations might suggest that the high molecular weight macromer, i.e., the macromer–iniferter shown in Scheme I, was produced at least from the photopolymerization of St with the VBDC monomer–iniferter.

Graft Copolymerization of MMA with VBDC Homopolymer and St Copolymer as a Photoiniferter. The results of the photopolymerization of MMA with VBDC homopolymer and St–VBDC copolymers at various compositions as a photoiniferter are shown in Table IV.

The VBDC homopolymer and copolymers used as photoiniferter were soluble in hot cyclohexane. From IR and ^{13}C NMR spectra, the polymer fractions extracted by acetonitrile and benzene were also confirmed to be poly(MMA) and the soluble graft copolymer, respectively. These polymerizations were performed easily, and the graft copolymers were obtained in high yield. The yields of whole polymers increased, but those of poly(MMA) extracted decreased, when the VBDC unit in the copolymers increased. In all polymerizations, the parent copolymer photoiniferter used was not extracted. The resulting graft copolymers consisted of benzene-soluble and -insoluble polymers, and the yield of the latter polymer increased with increasing content of the VBDC unit in the parent copolymer. The [η] of the benzene-soluble graft copolymers also increased about 5 times more than those of the parent photoiniferters used.

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Registry No. VBDC, 99798-43-3; *p*-CMS, 1592-20-7; VBDC (homopolymer), 99798-46-6; (VBDC)·(St) (copolymer), 99798-47-7; (MMA)·(VBDC) (copolymer), 99798-45-5; (St)·(VBDC)·(MMA) (copolymer), 99798-44-4; sodium diethyldithiocarbamate, 148-18-5.

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