

Polymerization of Styrene Using *N*-(*p*-Tolyl)-*N,N'*-diethyldithiocarbamoylacetamide as Photoiniferter

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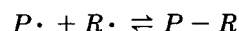
SYNOPSIS

N-(*p*-Tolyl)-*N,N'*-diethyldithiocarbamoylacetamide was prepared and used as a new photoiniferter for polymerization of styrene in bulk under UV light. This photopolymerization showed some specific character, i.e., molecular weights of resulting polymers increase with reaction time and monomer conversion, respectively. The reversible reaction between growing radical and dormant species was confirmed by electron spin resonance using 2-methyl-2-nitrosopropane as a spin trapping agent. Thus, the end functionalized polymer, *N,N'*-diethyldithiocarbamoyl-terminated polystyrene, reinitiated photopolymerization of methyl methacrylate and vinyl acetate to form block copolymers. The molecular weight distribution about 2.7 indicated that the polymerization is not a strictly living radical polymerization. © 1996 John Wiley & Sons, Inc.

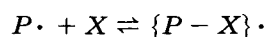
INTRODUCTION

Well-defined polymers are produced via living polymerization when chain growth is not disturbed by any chain-breaking reactions. In general, the high reactivity and nonselectivity of free radicals make it difficult to realize living radical polymerization. However, it is possible to adjust conditions of radical polymerization in a way that enables preparation of polymers with controlled molecular weights and relatively low poly-dispersities. There are three approaches summarized by Greszta et al.¹:

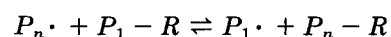
1. Deactivation of a growing radical with a stable radical by the reversible formation of a dormant covalent species, followed by their homolytic cleavage,



2. Reversible deactivation of a growing radical with a "nonradical" species by the formation of a dormant persistent radical,



3. Reversible degenerative transfer based on the thermodynamically neutral exchange reactions between growing radicals and transfer agents,



The example of the first approach is the photopolymerization with dithiocarbamate derivatives, i.e., benzyl *N,N'*-diethyldithiocarbamate (BDC), *p*-xylylene bis(*N,N'*-diethyldithiocarbamate) (XDC), and 1,2,4,5-tetrakis(*N,N'*-diethyldithiocarbamoyl) benzene (DDC).^{2,3} In the early 1980s, Otsu and colleagues^{4,5} reported a "living" radical polymerization of alkenes with these compounds and described their action as iniferter, which means that it acted as initiator, transfer agent, and terminator. In the polymerization of styrene with BDC, XDC, and DDC iniferters, a monotonous increase in molecular weight with conversion and formation of block copolymers were observed. In this paper, *N*-(*p*-tolyl)-*N,N'*-diethyldithiocarbamoylacetamide (TDCA) is used as a new photoiniferter for the polymerization of styrene, and the mechanism of polymerization is investigated by radical trapping and the electron spin resonance (ESR) technique and end group analysis of resulting polystyrene as well. The synthesis of block copolymers by this iniferter technique is discussed.

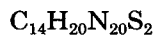
EXPERIMENTAL

Materials

Chloroacetyl chloride and triethylamine were distilled before use. *p*-Toluidine was recrystallized from alcohol and water-mixed solvent. Sodium *N,N*-diethyldithiocarbamate trihydrate reagent was used without further treatment. 2-Methyl-2-nitrosopropane (MNP) was purchased from Aldrich Chemical Company. Styrene (St), methyl methacrylate (MMA), vinyl acetate (VAc), and other reagents were used after ordinary purification.

Preparation of TDCA

N-(Chloroacetyl)-*p*-toluidine was synthesized by reaction of *p*-toluidine and chloroacetyl chloride in tetrahydrofuran in the presence of triethylamine at room temperature and recrystallized from ethanol, mp : 163°C.⁶ Then, TDCA was prepared via the reaction between *N*-(chloroacetyl)-*p*-toluidine and sodium *N,N*-diethyldithiocarbamate trihydrate in the mixture of anhydrous ethanol and acetone.⁷ The crude product was recrystallized from ethanol and water-mixed solvent and was a white needle crystal with mp : 96–97.5°C. ¹H-NMR (δ , ppm, in CDCl₃ 400 MHz): 1.3 [6H, N(CH₂CH₃)₂], 2.3 (3H, CH₃—C₆H₄), 3.7 [2H, N(CH₂CH₃)₂], 4.0 [2H, N(CH₂CH₃)₂], 4.2 (2H, NHCOCH₂), 7.2 (4H, C₆H₄), 9.1 (1H, NH).



Calcd C 56.76 H 6.76 N 9.46 S 21.62

Found 56.72 7.26 9.38 21.66

Photopolymerization

Photopolymerizations of St were carried out in the presence of TDCA in bulk under irradiation of UV light with an 80-W UV lamp at 10 cm from sealed glass tubes at 30°C. Polymers were collected at the given time by precipitation of the reaction solution into methanol and purified by redissolving in benzene and reprecipitating into methanol and drying in vacuum. Number- and weight-average molecular weights (M_n and M_w) were determined by gel permeation chromatography calibrated with polystyrene standards using a Waters 208 GPC instrument equipped with styragel 500 Å columns using tetrahydrofuran as an eluent. The number of the *N,N*-diethyldithiocarbamate (Et₂NCSS) end groups of the polystyrene was determined by UV spectroscopy [BDC as standard because structure is similar to

polystyrene with Et₂NCSS end group (272 nm)]. *p*-CH₃C₆H₄NHCOCH₂ group of polystyrene (PS) (253 nm) was also identified by UV spectrum recorded on a Shimadzu UV-250 model spectrophotometer at room temperature. The block copolymers were prepared in a similar manner. The separation of the polymers obtained into homopolymers and the block copolymer was carried out by extraction. PS was extracted with cyclohexane, PMMA with 95% EtOH, and PVAc with MeOH and then the fractions were checked by IR spectra and gel permeation chromatography (GPC).

ESR Analysis

Photodissociation of TDCA and Et₂NCSS-PS in the presence of MNP used as a spin trapping agent was investigated. An acetonitrile or benzene solution of MNP and TDCA or Et₂NCSS-PS was irradiated and measured by means of a Bruker ER 200 D-SRC ESR spectrometer using the TM cavity at the X-band, a microwave power of 1.00 MW, and a modulation frequency of 100 kHz.

RESULTS AND DISCUSSION

Photopolymerization of St using TDCA as photoiniferter

Polymerization of St was carried out via photochemical initiation with TDCA in bulk at 30°C. The time-conversion and time- M_n relations are shown in Figure 1, from which the yield and M_n of the polymers were observed to increase with time. In addition, the increase of M_n with conversion was also

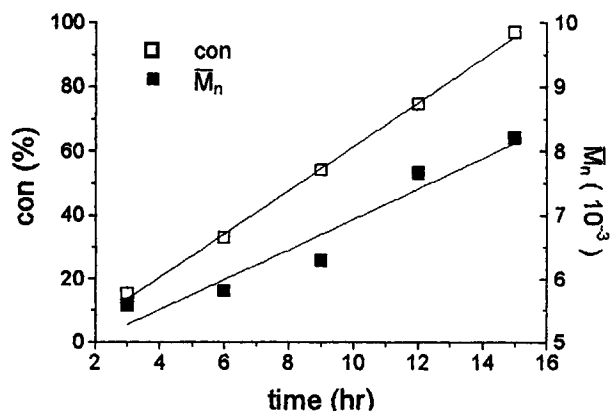


Figure 1 Time-conversion and time- M_n relations for bulk photopolymerization of St with TDCA at 30°C; [St] = 8.7M, [TDCA] = 0.1M.

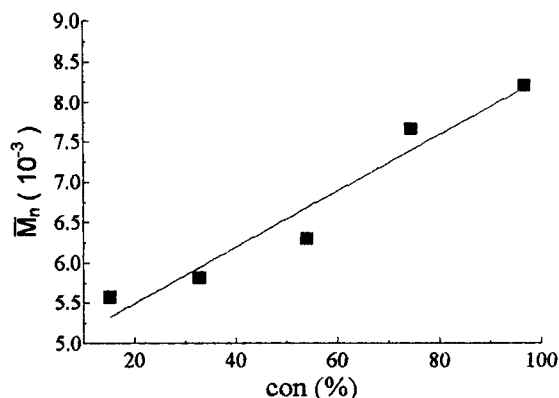


Figure 2 Conversion- M_n relation for bulk photopolymerization of St with TDCA at 30°C; [St] = 8.7M, [TDCA] = 0.1M.

found in conversion- M_n relation as shown in Figure 2. The result indicated that the polymerization proceeded quite differently from that of ordinary radical chain polymerization.

The data of M_n , dispersities (M_w/M_n), and the numbers of Et₂NCSS end group of polystyrene obtained as a function of polymerization time are summarized in Table I. From Table I, molecular weight distribution can be seen to be broad and not to change with time. This was not like that reported for living ionic polymerization,⁸ in which polymers with a narrow molecular weight distribution were found.

Initiation Mechanism of Photopolymerization and ESR Studies

The mechanism of dithiocarbamate iniferters was investigated by Otsu and coworkers² and is shown in Scheme 1. $R\cdot$ and $RM\cdot$ acted as a reactive radical and $R'\cdot$ is a low-reactive small radical that essentially reacts with growing radicals to form dormant covalent species (RMR') reversibly. Li and Shen⁹ also confirmed that $R'\cdot$ was more stable than the carbon radical and could be observed to exist in the

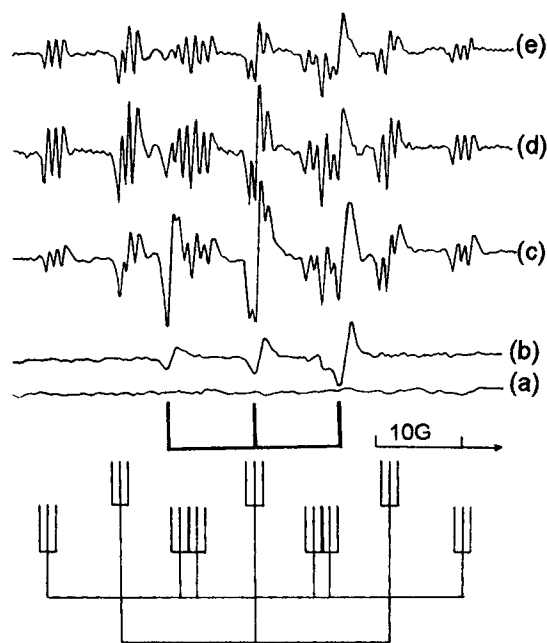
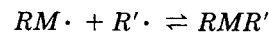
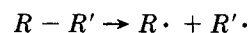


Figure 3 ESR spectrum obtained from photodissociation of TDCA in acetonitrile in the presence of MNP after irradiation at room temperature: [TDCA] = 0.184M, [MNP] = 0.0095M. (a) no light, (b) 0.5 min, (c) 2 min, (d) 3 min, (e) 5 min (1 mT = 10 G).

whole polymerization. A broader molecular weight distribution was ascribed to slow initiation and slow exchange between dormant and growing species. Thus, it was required to have high concentration of TDCA to control polymerization. The number of Et₂NCSS end group about 1 indicated that $R'\cdot$ reacts with the growing radical efficiently.

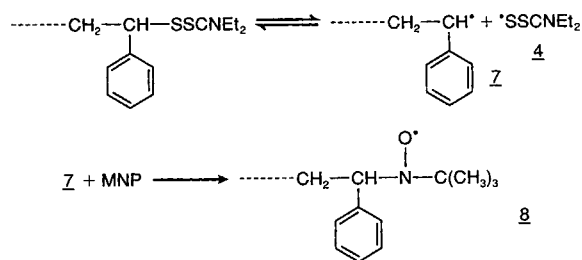


Scheme 1

Table I Photopolymerization of St with TDCA at 30°C^a

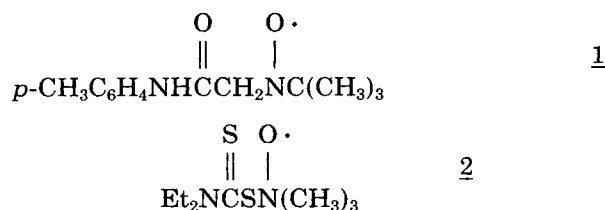
Sample	Time (h)	M_n (10^{-3})	M_w (10^{-3})	M_w/M_n	Number of End Group Et ₂ NCSS
1	3	5.57	15.4	2.77	1.04
2	6	5.81	16.2	2.78	1.05
3	9	6.29	17.5	2.78	1.09
4	12	7.66	20.8	2.72	0.95
5	15	8.21	22.9	2.79	0.96

^a Polymerization condition: [St] = 8.7M, [TDCA] = 0.1M, 80-W UV lamp at 10 cm.

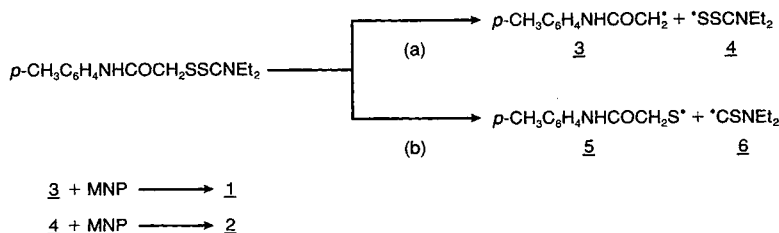


Scheme 2.

To reveal further this polymerization mechanism, it was important to clarify the photodissociation behavior of TDCA and polymer chain end group obtained from the polymerization of St with TDCA. Thus, the radical intermediates of the reaction were investigated by using the spin trapping technique.^{10,11} The ESR spectrum of the system TDCA/MNP after irradiation was shown in Figure 3 from which the observed spectrum is assigned as a mixture of two nitroxys: 1 ($a_\alpha^N = 15.5$ G, $a_\beta^H = 8.5$ G, $a_\gamma^N = 0.7$ G) similar to $\cdot\text{CH}_2\text{CONH}_2$ radical¹² and 2 ($a_\alpha^N = 10.0$ G).



Otsu and Kuriyama¹³ and Lambrinos et al.¹⁴ reported that $\text{PhCH}_2\text{SSCNEt}_2$ could dissociate at two different C—S bonds, e.g., (a) and (b) in Scheme 3. From the formation of the 1 and 2 radical, it revealed that 3 and 4 were produced by path (a) under UV light. 3 initiated the polymerization that was observed in the polystyrene end group and 4 acted



Scheme 3.

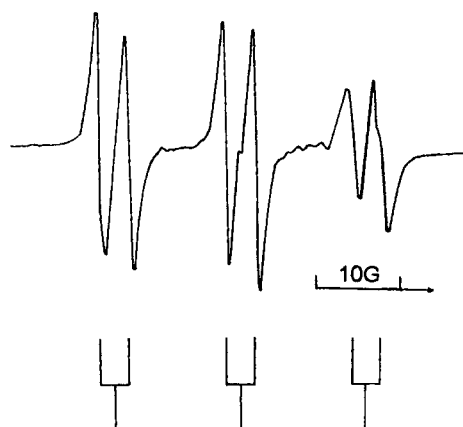


Figure 4 ESR spectrum of $\text{Et}_2\text{NCSS-PS}$ in benzene in the presence of MNP after irradiation at room temperature: $[\text{PSt}] = 0.15$ g/mL, $[\text{MNP}] = 0.0077$ M, 4 min under UV light (1 mT = 10 G).

as a low-reactive radical to couple with the growing radical. Radicals 5 and 6 were not observed; it showed that cleavage (b) was less important in this system.

Figure 4 shows the ESR spectrum of the $\text{Et}_2\text{NCSS-PS/MNP}$ system after irradiation. The spectrum is assigned to a radical, 8 ($a_\alpha^N = 14.5$ G, $a_\beta^H = 3.3$ G), from the reaction of MNP with 7 as shown in Scheme 3. The ESR results indicate that the C—S bond $\text{Et}_2\text{NCSS-PS}$ was weak and could cleave homolytically under UV light to reform growing radical 7 and radical 4.

Chain Extension and Block Copolymerization of $\text{Et}_2\text{NCSS-PS}$

As described above, TDCA can be used as photoiniferter to obtain end functionalized polymer, and the photodissociation of the active chain end group could lead to chain extension or block copolymer formation. Thus, photopolymerization of St in the presence of $\text{Et}_2\text{NCSS-PS}$ was carried out and the results

Table II Block Copolymerization of Vinyl Monomers with PS-SSCNET₂ at 30°C^a

PS (M ₁ , g)	Second Monomer (M ₂ , mL)	Time (h)	Total Yield (g)	Fractions Extracted					
				M ₁ Polymer		M ₂ Polymer		Block Copolymer	
				%	M _n 10 ⁻³	%	M _n 10 ⁻³	%	M _n 10 ⁻³
0.1	MMA (1.5)	9	0.280	18	9.45	46	10.2	36	12.8
0.1	VAc (2.0)	47	0.180	43	9.45	21	11.4	36	11.2

^a Polymerization under irradiation of an 80-W UV light from a distance of 10 cm.

are shown in Figures 5 and 6, from which it can be seen that M_n increased linearly with time and conversion. Block copolymers were also obtained by the same method. The formation of block copolymer (PS-*b*-PMMA and PS-*b*-PVAc) was confirmed by IR spectra, from which characteristic frequencies of

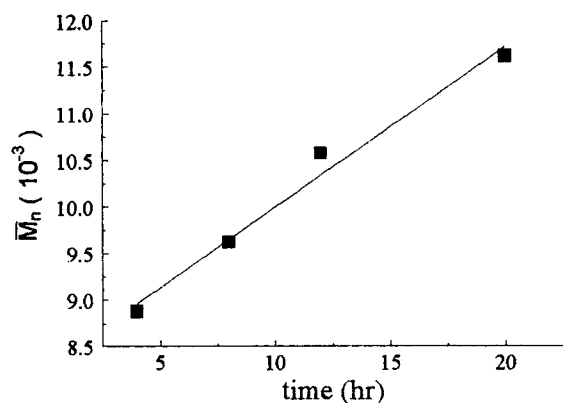


Figure 5 Time- M_n relation for photopolymerization of St in benzene in the presence of PS-SSCNET₂ at 30°C; [PSt] = 0.04 g/mL, [St] = 2.4M.

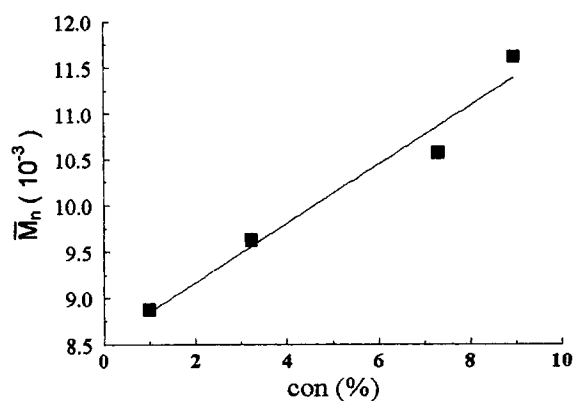


Figure 6 Conversion- M_n relation for photopolymerization of St in benzene in the presence of PS-SSCNET₂ at 30°C; [PSt] = 0.04 g/mL, [St] = 2.4M.

ester group of PMMA (1730 cm⁻¹) and PVAc (1740 cm⁻¹) and of benzene of PS (1600 and 700 cm⁻¹) were observed. At the same time, M_n of block copolymers larger than the original polymer (PS) are shown in Table II. However, the yields of block copolymers were low, which could be due to slow initiation.

CONCLUSION

Our results indicate that TDCA can be used as a photoiniferter for radical polymerization of styrene, and polymers containing Et₂NCSS end group, such as PS-SSCNET₂, could be used as macromolecular photoiniferter to realize chain extension and form block copolymers. Thus, block copolymers are prepared via this technique with MMA and VAc. However, the deviation, especially molecular weight distribution, from true living nature observed is due to slow initiation and slow exchange between dormant and growing radical species.

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