Polymer Bulletin 44, 123–128 (2000)

Polymer Bulletin

Radical polymerization of styrene initiate with a new multifunctional iniferter

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Received: 5 December 1999/Revised version: 17 January 2000/Accepted: 21 January 2000

Summary

A new multi-functional iniferter with photo-induced and thermal dissociation group in one molecule, diethyl 2,3-dicyano-2,3-di(p-*N*,*N*-diethyldithiocarbamylmethyl)phenyl-succinate(DDDCS), was successfully synthesized. The bulk polymerizations of styrene (St) with DDDCS were studied. The initiation can take place either under UV light irradiation by the reversible C-S bonds dissociation of DDDCS or under heating by the reversible hexa-substituted C-C bond thermally dissociation. The polymerizations have "living" polymerization characteristics under both cases, i.e., the yield and the molecular weight of the resulting polymer increased linearly with increasing reaction time, and the resultant polymers can act as macroiniferter for preparing block copolymer.

Introduction

In recent years, a number of systems based on reversible termination of growing radicals have been reported in order to realized "living"/controlled free radical polymerization.[1-9] Among them, the iniferter technique is a very useful and convenient method for the synthesis of polymers with well-designed structures, i.e., the molecular weight, molecular weight distribution, end groups. Since Otsu and his coworkers [1] proposed this concept and realized "living" radical polymerization of vinyl monomers in homogeneous system, many photoiniferters and thermal iniferters were prepared and used for vinyl monomers polymerizations to synthesize well-defined, block, graft, star and telechelic polymers efficiently, and there are many review articles were reported.[9-11] Our research group also reported some works on iniferters recently.[12-17]

In general speaking, photoiniferters are mainly the compounds bearing *N*,*N*-diethyldithiocarbamyl(DC) group,[1, 9-13, 15-17] and thermal iniferters, aside from phenylazotriphenylmethane (APT),[18] are hexa-substituted-ethane type structure compounds.[14,19-22] However, a compound containing both the DC group and hexa-substituted C-C bond, that can act as a photoiniferter as well as a thermal iniferter, has not been reported so far. In this article, we will report the synthesis and characterization of a new multi-functional iniferter bearing both the DC group and hexa-substituted C-C bond, such as diethyl 2,3-dicyano-2,3-di(*p*-*N*,*N*-diethyldithiocarbamylmethyl)phenyl-succinate (DDDCS), the C-S bond and hexa-substituted C-C bond of DDDCS can cleavage reversible under UV light irradiation and under heating, respectively(scheme 1). The radical polymerization behaviors of styrene initiated with DDDCS under UV light

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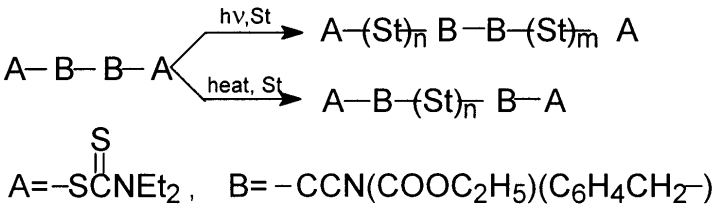
irradiation and under heating were studied.



Scheme 1

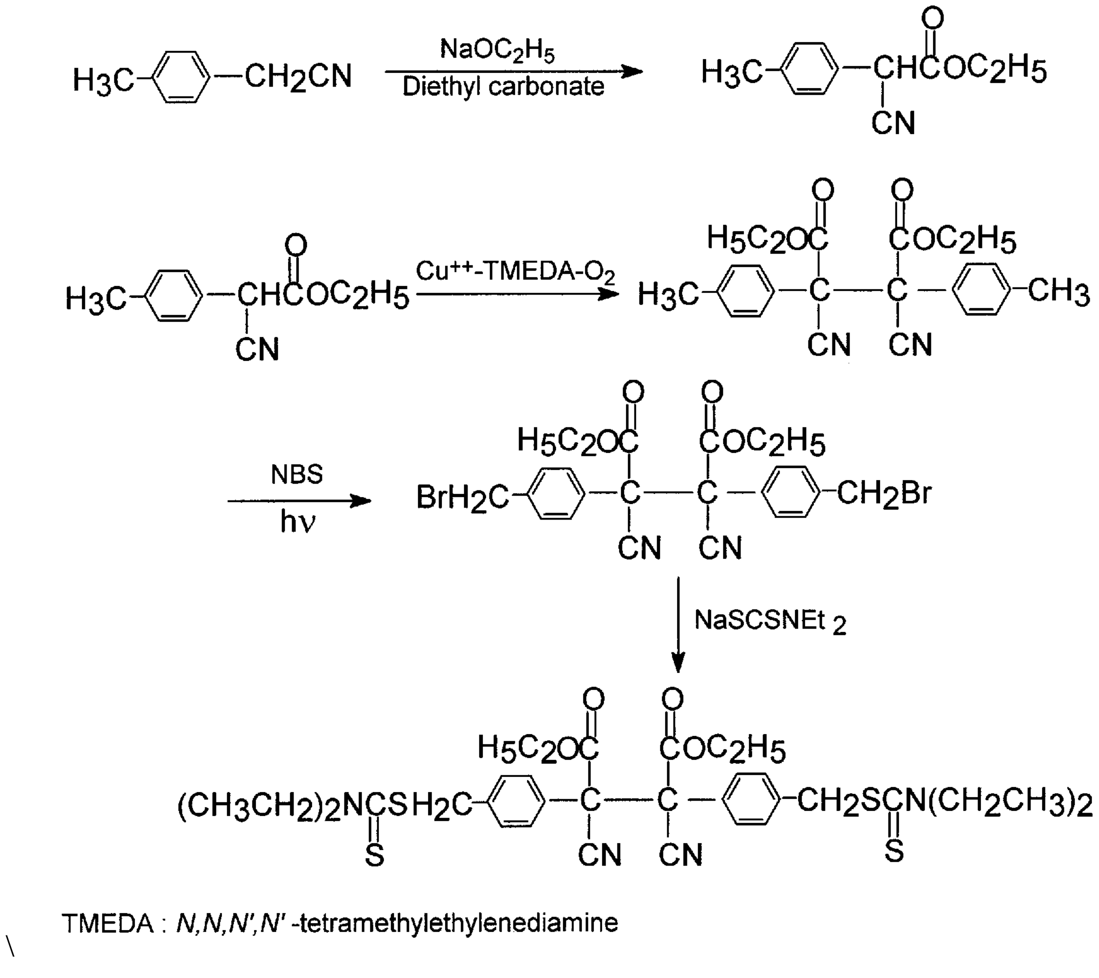
Experimental

Materials

Sodium diethyldithiocarbamate, *N*-bromosuccinimide (NBS), *p*-methylbenzyl cyanide from Acros Company were used as received without further purification. Diethyl carbonate and *N,N,N',N'*-tetramethylethylenediamine (TMEDA) were distilled before use. Styrene (St) was freshly distilled before use. Solvent and other reagents were purified by usual methods.

Preparation of DDDCS multi-functional iniferter

The new multi-functional iniferter DDDCS was synthesized from *p*-methylbenzyl cyanide in four steps as shown in scheme 2.



TMEDA : *N,N,N',N'*-tetramethylethylenediamine

Scheme 2

Diethyl 2,3-dicyano-2,3-di(*p*-toly)succinate(DCDTS) was synthesized by the process similar to that of 2,3-dicyano-2,3-diphenylsuccinate reported previously.[14] First, ethyl α-cyano-*p*-tolyacetate was prepared by the reaction of *p*-methylbenzyl cyanide and diethyl carbonate in toluene, bp: 145°C/2000Pa. Next DCDTS was synthesized by oxidative coupling reaction of ethyl α-cyano-*p*-tolyacetate with a Cu^{++}-TMEDA-O_2 system in chloroform. The crude product was recrystallized from methanol and four times from carbon tetrachloride. Then a white crystalline purified DCDTS was obtained. The yield was 64.2%, mp: 118.7-119.5°C. IR (KBr): 825, 1512, 2868 cm^{-1} ($-C_6H_4-$), 1156, 1234 cm^{-1} (C-O-C), 1750 cm^{-1} (C=O), 2257 cm^{-1} (-CN); ^1H NMR (δ, ppm, in $CDCl_3$, 400 MHz): 1.19-1.52 [6H, $-OCH_2C\mathbf{H}_3$], 2.34 [6H, $C\mathbf{H}_3C_6H_4-$], 4.23-4.41 [4H, $-OC\mathbf{H}_2CH_3$], 6.94-7.28 [8H, $CH_3C_6\mathbf{H}_4-$].

Elemental analysis for $C_{24}H_{24}N_2O_4$:

Calcd (%)	C	72.27	H	5.98	N	6.73
Found (%)	C	72.25	H	5.88	N	6.64

After that DCDTS was brominated by NBS under UV light irradiation, and finally reacted with sodium diethyldithiocarbamate. The crude product was recrystallized twice from carbon tetrachloride, a yellow crystalline purified DDDCS was obtained. The yield was 80.5%, mp: 149.5-150°C. IR (KBr): 827, 1510, 1633, 2871 cm^{-1} ($-C_6H_4-$), 1142, 1231 cm^{-1} (C-O-C), 1753 cm^{-1} (C=O), 2253 cm^{-1} (-CN), 1271 cm^{-1} (C=S); ^1H NMR (δ, ppm, in $CDCl_3$, 400 MHz) as shown in Figure 1: 1.21-1.25 [6H, $-OCH_2C\mathbf{H}_3$], 1.25-1.40 [12H, $-NCH_2C\mathbf{H}_3$] , 3.72-3.78 [4H, $-NC\mathbf{H}_2CH_3$], 4.02-4.07, [4H, $-NC\mathbf{H}_2CH_3$], 4.21-4.33 [4H, $-OC\mathbf{H}_2CH_3$], 4.54-4.58 [4H, $-C\mathbf{H}_2C_6H_4-$], 7.21-7.34 [8H, $-C_6\mathbf{H}_4-$]. UV (in tetrahydrofuran): 252 nm (NC=S), 282 nm [NC(S)S].

Elemental analysis for $C_{34}H_{42}N_4O_4S_4$:

Calcd (%)	C	58.42	H	6.06	N	8.02	S	18.35
Found (%)	C	58.40	H	6.11	N	8.08	S	18.26

From these results, the obtained compound was confirmed to be the target DDDCS.

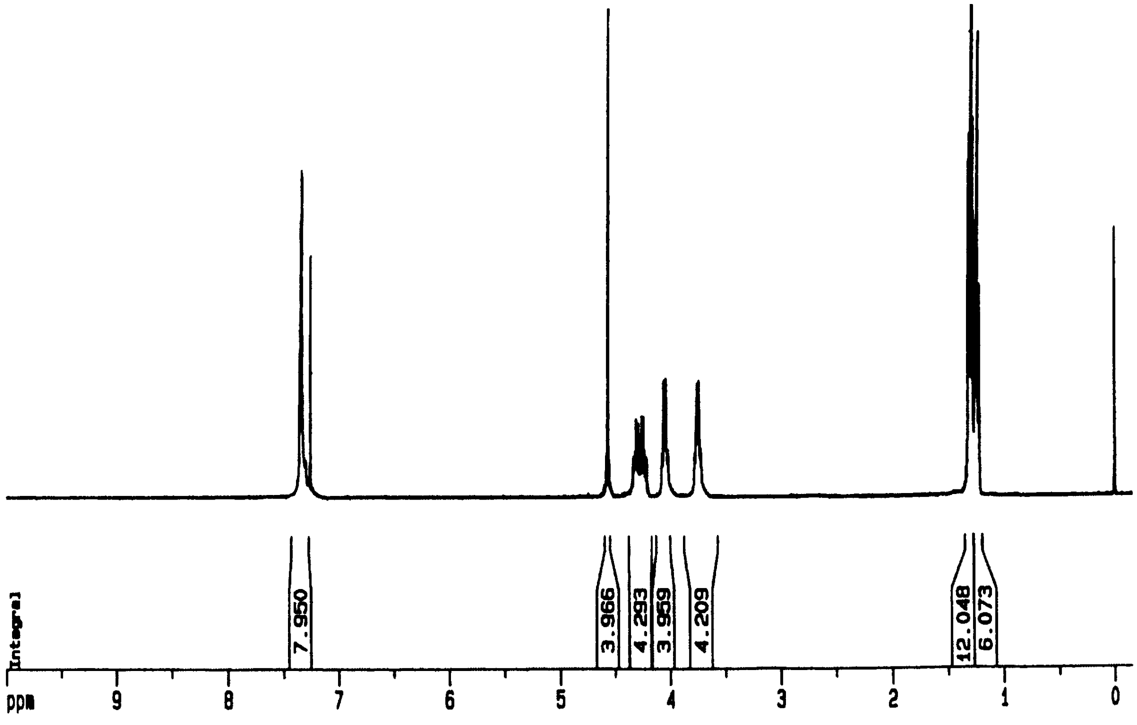


Figure 1 ^1H NMR spectrum of DDDCS in $CDCl_3$

Polymerization

Polymerizations of St with DDDCS multi-functional iniferter were carried out in sealed glass tubes at 85°C or under irradiation with a 250w UV lamp from a distance of 20 cm at ambient temperature. After polymerization for a specific time, the contents of the tubes were dissolved by tetrahydrofuran (THF) and then poured into a large amount of methanol, dried in vacuum, weighted, and calculated the conversion of polymerization.

Measurements

Monomer conversion was determinated by a gravimetric method. Molecular weights and molecular weight distributions of the polymers were determined at 35°C with Gel Permeation Chromatography (Waters Associates Model HPLC/GPC 515 liquid chromatography, equipped with a refractive index detector, HT2+HT3+HT4 μ-Styragel columns and calibrated with standard polystyrene), using THF as the eluent and a flow rate of 1.0 mL/min. IR and ^{1}H NMR spectra were recorded on a Nicolet IR 750 spectrometer and a Bruker ARX 400 spectrometer, respectively. UV spectrum was recorded on a Shimadzu UV-2101 PC spectrometer.

Results and discussion

"Living" Polymerization Characteristics of St with DDDCS as a Photoiniferter

Polymerizations of St initiated with DDDCS were carried out in bulk under UV light irradiation at ambient temperature. The time-conversion and time-M_n relations are shown in Figure 2, from which it can be seen that the conversion and M_n of the polymers increase with increasing reaction time, and the plots of conversion and M_n versus time gave linear relationships through the origin. In addition, increasing M_n with conversion through the origin was also found as shown in Figure 3, which is the "living" characteristics of St polymerization initiated by DC group containing photoiniferter as reported by Otsu *et al.*.[9] However, the polydispersities (M_w/M_n) of the resulting polymers were broad and ill controlled. Furthermore, the obtained PSt has an α- and an ω- DC end groups, which can polymerize other monomer to synthesize block copolymer. The results indicated that the "living" polymerization characteristics of St in the presence of DDDCS are similar with

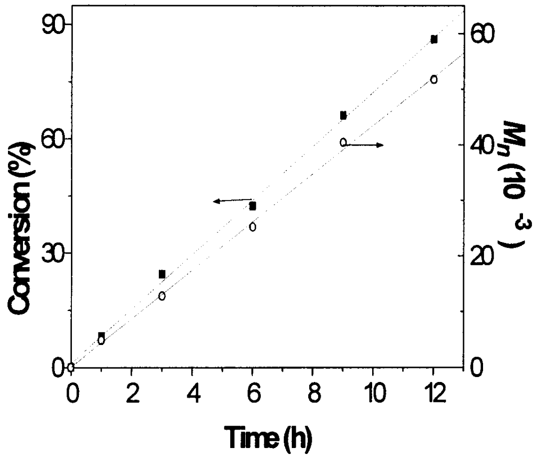


Figure 2 Relations of conversion and M_n versus time for photopolymerization of St with DDDCS under UV light irradiation; [St] = 8.7 mol/L, [DDDCS] = 1.74×10^{-2}mol/L

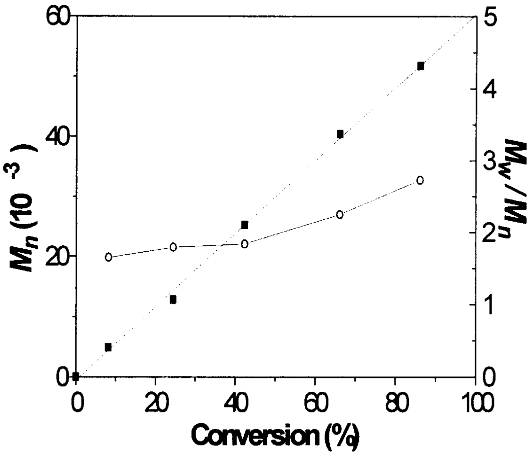


Figure 3 Relations of M_n and M_w/M_n versus conversion for photopolymerization of St with DDDCS under UV light irradiation; Conditions as Figure 2.

p-xylylene bis (*N*,*N*-diethyldithiocarbamate) photoiniferter.[23]

"Living" Polymerization Characteristics of St with DDDCS as a Thermal Iniferter

Polymerizations of St initiated with DDDCS were carried out in bulk at 85°C. The results of the polymerizations are shown in Figures 3 and 4. The data show that a 85% yield was obtained in 5 hours, and the resultant polymer possesses high molecular weight with polydispersity indices around 1.6. Also, the time-conversion and time-M_n relations in Figure 4 show that the conversion and M_n of the polymers increase linearly with increasing reaction time. In addition, linearly increasing M_n with conversion was also found as shown in Figure 5. At the same time, the numbers of Et_2NCSS end group of the resulting PSt are around 2.0, which confirmed the obtained PSt can act as a macroiniferter for further block copolymerization. These results revealed that the thermal polymerization of St with DDDCS also is a "living" polymerization.

From the comparison of the Figures 2 and 4, we can find that the plots of conversion and M_n versus time gave linear relationships through the origin, when DDDCS serve as a photoiniferter. While when DDDCS serve as a thermal iniferter, the plots of conversion and M_n versus time gave linear relationships but not through the origin. The diversity may be due to the difference of the termination groups that reversibly couple with propagating radicals at photo-induced and thermal polymerizations. In thermal decomposition initiated polymerization, the reversible termination group (BA as shown in scheme 1) is more larger and sterically hindered than in photoiniferter (A), this needs a little time to set up the reversible equilibrium of the propagating radicals and dormant species. In this case the termination by coupling and disproportionation will take place in the initial period of polymerization (Con. <10% generally). After the reversible equilibrium is set up, the polymerization proceeds by a "living" with reversible deactivation polymerization process. Interestingly, the polymers with higher molecular weight and lower polydispersity were obtained when DDDCS used as a thermal iniferter than as a photoiniferter, the investigations are in process and will report in the future.

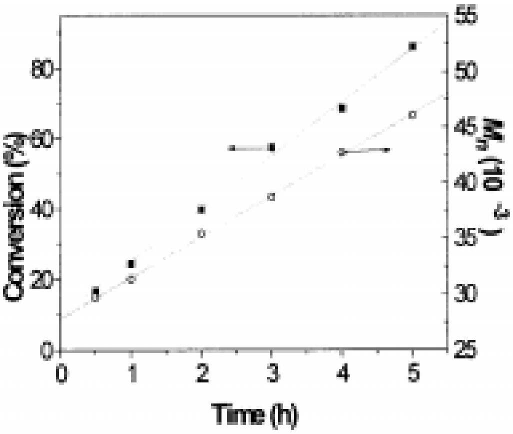


Figure 4 Relations of conversion and M_n versus time for polymerization of St with DDDCS at 85℃; [St] = 8.7 mol/L, [DDDCS] = 1.74 × 10^{-2}mol/L

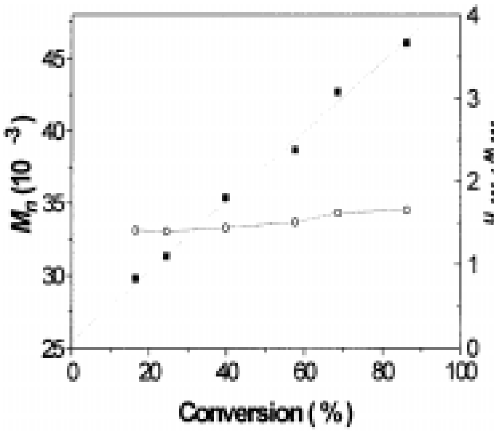


Figure 5 Relations of M_n and M_w/M_n versus conversion for polymerization of St with DDDCS at 85℃; Conditions as Figure 4.

Conclusions

A new compound, diethyl 2,3-dicyano-2,3-di(*p*-*N*,*N*-diethyldithiocarbamylmethyl)-phenylsuccinate(DDDCS), was successfully synthesized. It acted either as a photoiniferter or as a thermal iniferter for the polymerization of vinyl monomers. So called as a multi-functional iniferter. The bulk polymerizations of St initiated with DDDCS under UV light irradiation and under heating were studied. The polymerizations have "living" polymerization characteristics under UV light irradiation or heating, i.e., both the yield and the molecular weight of the resulting polymer increased linearly with increasing reaction time. Furthermore, the numbers of Et_2NCSS end group of the obtained PSt are almost the same around 2.0, this indicates that the PSt may used as macroiniferter for further preparation of block copolymers.

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