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Shu Hui Qin[a]; Dong Qi Qin[a]; Kun Yuan Qiu[a]; David G. Westmoreland; Willie Lau; Shuguang Wu; Graham Swift
[a] Department of Polymer Science and Engineering, Chemistry Building, Peking University, Beijing, China

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BULK POLYMERIZATION OF STYRENE WITH DIETHYL 2,3-DICYANO-2,3-DI(*p*-TOLYL)-SUCCINATE AS A THERMAL INIFERTER

Shu Hui Qin,[1] Dong Qi Qin,[1] Kun Yuan Qiu,[1,]* David G. Westmoreland,[2] Willie Lau,[2] Shuguang Wu,[2] and Graham Swift[2]

[1]Department of Polymer Science and Engineering, Chemistry Building,
Peking University, Beijing, 100871, China
[2]Rohm and Haas Company, Spring House, Pennsylvania 19477

ABSTRACT

The bulk polymerization of styrene (St) was investigated using diethyl 2,3-dicyano-2,3-di(*p*-tolyl)succinate (DCDTS), a hexa-substituted ethane compound, as an initiator. The polymerization data show that DCDTS behaves as a thermal iniferter, and the polymerization proceeds by a "living" radical polymerization mechanism with a reversible deactivation. The polymerization can be carried out at quite low temperatures (such as 65–85°C) and the final conversions are high. The PSt possessed high molecular weights and molecular weight distributions (M_w/M_n in the range of 1.4 to 1.6). End-group analysis by ^{1}H NMR spectroscopy reveals that the resultant PSt contains the fragments of DCDTS at its chain ends. This polymer with an ω-penta-substituted C–C bond end group could be used as a macroinitiator to carry out chain-extension reaction with St and could also block copolymerization with methyl methacrylate.

Key Words: Block copolymer; Diethyl 2,3-dicyano-2,3-di(*p*-tolyl)succinate (DCDTS); "Living" radical polymerization; Styrene; Thermal iniferter

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*To whom correspondence should be addressed.

INTRODUCTION

Since the report of living radical polymerization with the iniferter technique (1), significant attention has been paid to so-called “living”/controlled radical polymerization (2–5). This process is based on the reversible capping of the active site of the growing chains. Using this method many well-defined polymers, such as block, graft, and star copolymers, could be prepared (1–7). Among the present systems the iniferter technique is a useful and convenient method for synthesis of well-defined polymers in a homogenous system under mild reaction condition. The polymerization exhibits “living” characteristics, that is, the number-average molecular weight (M_n) increases with increasing conversion, the polymerization proceeds until all of the monomer has been consumed, and further addition of a second monomer result in block copolymerization. Although the molecular weight distribution is not well-controlled, the polymerization can be performed at much lower temperature than that of stable free radical polymerization (SFRP), and the resultant polymers do not need purification as in the case of atom transfer radical polymerization (ATRP). Moreover, a large number of monomers, such as styrene, methyl methacrylate, *n*-butyl acrylate, vinyl acetate, acrylonitrile, and methylacrylonitrile, can be polymerized in a “living” manner with this method (7). Also, the iniferter technique provides a useful means for surface chemical modification with controlled layer thickness (8,9).

Various compounds have been found to serve as iniferters for vinyl polymerization. Compounds containing N,N-diethyldithiocarbamyl and tetraphenyl substituted ethane functionality have been reported in the literatures (1,6,7,10–19), and compounds with a P–P bond (20) or hexa-substituted C–C bond (21) have been recently introduced, which can polymerize MMA and St at a lower temperature. Some macroiniferters based on polyurethane have also been synthesized (22,23). In this work, we used diethyl 2,3-dicyano2,3-di(*p*-tolyl) succinate (DCDTS) as a thermal iniferter for the polymerization of styrene, and a mechanism for the polymerization is proposed based on end group analysis of the resultant PSt. In addition, chain extension and block copolymerization of the PSt obtained have also been investigated.

EXPERIMENTAL

Materials

DCDTS was prepared according to a previously reported procedure (24). Styrene and methyl methacrylate were purified by washing with 5% sodium hydroxide solution, then with water, and drying over magnesium sulfate over night. Then, they were fractionally distilled in vacuum over CaH_2 and stored in a refrigerator. Tetrahydrofuran (THF) was dried by refluxing over the deep purple sodium benzophenone complex and distilled. Other regents and solvents were used as received.

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Polymerization

Polymerizations of styrene with DCDTS thermal iniferter were carried out using the following procedure. Deaerated styrene (with DCDTS dissolved) was added via a syringe to a glass tube under nitrogen atmosphere. After three freeze-pump-thaw cycles, the glass tube was sealed under vacuum, and the reaction mixture was heated in an oil bath thermostat. Periodically the tube was removed from the bath, and the reaction mixture was dissolved in THF and then poured into a large amount of methanol, filtered, dried, and weighed; monomer conversion was then calculated. Block copolymers were prepared by copolymerization of MMA with the resultant PSt using a similar procedure. Separation of the mixture of homopolymers and block copolymer was carried out by solvent extraction. PSt was extracted with cyclohexane and PMMA with 95% ethanol.

Measurements

Molecular weights and molecular weight distributions of the polymers were determined on a Waters gel permeation chromatograph equipped with a 515 HPLC pump, 2410 refractive index detector, and three μ-Styragel columns (HT2 + HT3 + HT4). All samples were run in THF at 35°C at a rate of 1.0 mL/min. Linear polystyrene standards were used for calibration. The data were analyzed on a Waters Millennium 32 system. IR and ^{1}H NMR spectra were recorded on a Nicolet IR 750 spectrometer and a Bruker ARX 400 spectrometer, respectively. The glass transition temperature (T_g) was determined with a TA DSC-2010 Differential Scanning Calorimeter at a heating rate of 10°C/min.

RESULTS AND DISCUSSION

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

The results of St polymerization with DCDTS thermal iniferter are compiled in Table 1. From the Table, we can see that conversion and M_n increased with reaction time. After 6 h, a PSt with high conversion (>80%) and high molecular weight (up to 59,700) was obtained. The plot of M_n versus conversion in Figure 1 shows that M_n increased linearly with conversion. GPC traces of the corresponding polymers are shown in Figure 2. These results demonstrate the "living" behavior of St polymerization with DCDTS. However, the linear plot in Figure 1 did not pass through the origin, the molecular weight distribution (MWD) values of the resulting polymers increased slightly with reaction time, and the M_n values did not agree well with the theoretical ones, $M_{n(th)}$, which calculated from $M_{n(th)} = [St]/[DCDTS] \times M_{w(St)} \times$ Conv. indicating that the polymerization of St was not well-controlled with DCDTS.

St polymerization with DCDTS thermal iniferter can be carried out at different temperatures. The data for the effect of temperature on polymer molecular weight

Table 1. Bulk Polymerization of St with DCDTS as a Thermal Iniferter at 85°C

Time (h)	Conversion (%)	M_n (10^{-3})	M_w/M_n
1	13.6	34.3	1.44
2	25.4	38.7	1.42
3	42.3	44.0	1.50
4	54.4	49.0	1.55
5	68.5	53.4	1.57
6	83.8	59.7	1.60

Polymerization conditions: $[St] = 8.7\ mol \cdot L^{-1}$, $[DCDTS] = 4.4 \times 10^{-2}\ mol \cdot L^{-1}$.

and conversion are compiled in Table 2. The data show that within the same reaction time interval (3 h), conversion increased from 9.2 to 96.2% with increasing temperature from 65°C to 105°C, while the molecular weight decreased from 88,200 to 39,800. This indicates that the polymerization follows the principle of conventional radical polymerization, that is, the polymerization carried out at lower temperature, lower monomer conversion, and higher molecular weight is obtained.

Polymerization Mechanism and End-Group Analysis

The proposed mechanism for the "living" radical polymerization of St with DCDTS iniferter is shown in Scheme 1, which is similar to that for other carbon–carbon bond structure thermal iniferters proposed by Otsu et al. (17,18) and Braun et al. (15,16). According to the mechanism, DCDTS first thermally dissociates into 2 carbon-centered radicals $R^{\cdot}$, which can initiate St to polymerize or terminate

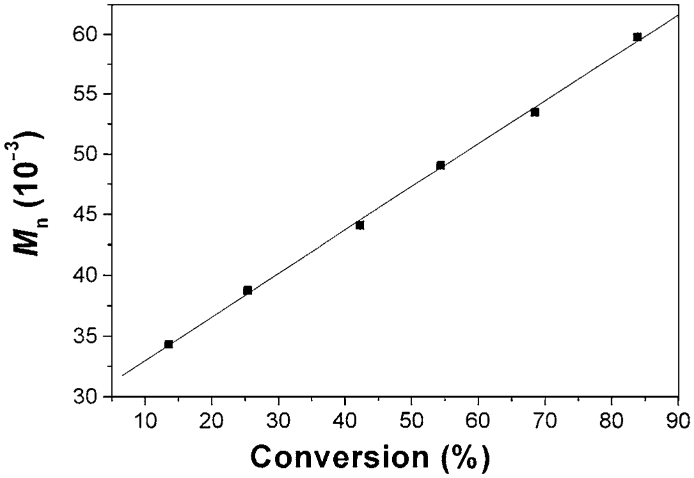


Figure 1. M_n-conversion relation for bulk polymerization of St with DCDTS at 85°C; $[St] = 8.7\ mol \cdot L^{-1}$, $[DCDTS] = 4.4 \times 10^{-2}\ mol \cdot L^{-1}$.

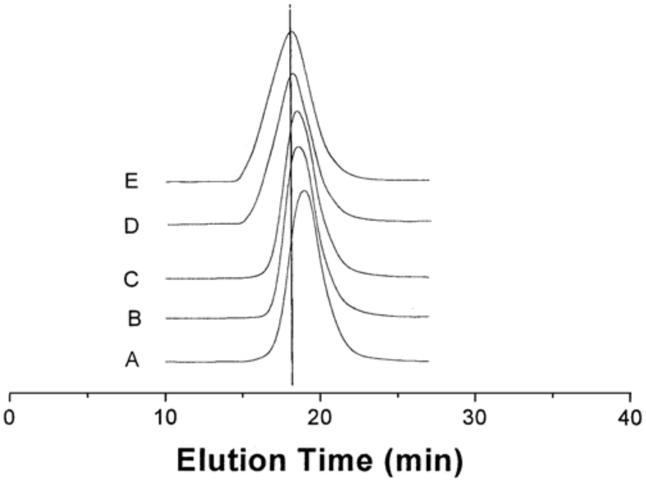


Figure 2. GPC elution curves of PSt prepared by bulk polymerization of St with DCDTS at 85°C, [DCDTS] = 4.4×10^{-2} mol · L^{-1}. Polymerization time: A), 1; B), 2; C), 3; D), 4; and E), 5 h.

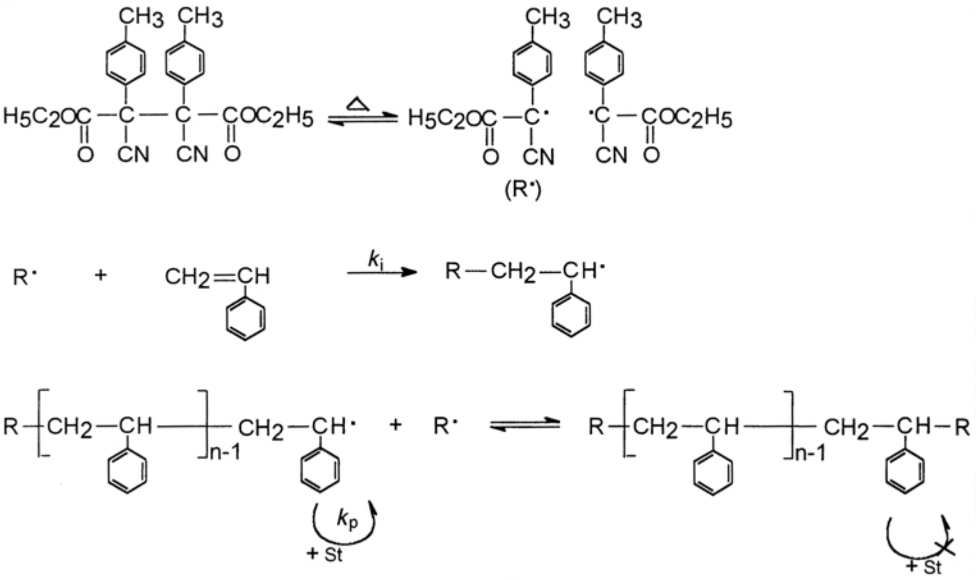
reversibly with the propagating chain radical to form a dormant species. By thermal decomposition of the end of the polymer with the penta-substituted C–C bond, the dormant species can dissociate into an active chain radical and a radical R$^\cdot$. The active chain radical can add St to polymerize, and R$^\cdot$ mainly deactivates the propagating radical to form a penta-substituted C–C bond end group. The polymerization then continues via this "living" process with reversible deactivation.

Figure 3 shows a representative ^{1}H NMR spectrum of the resultant PSt. Besides the characteristic chemical shifts of the repeat units of St, there are characteristic signals originating from DCDTS. The methyl (e) and methylene (d) protons of the ethyl ester group, the methyl (f) protons of the tolyl group, and the protons of the phenyl (c) group, which come from DCDTS, are seen at 1.24, 4.22, 2.24, and 7.26 ppm, respectively. The data indicate that the end group of the polymer contains a fragment of DCDTS but cannot distinguish the fragments of the α-end from those of the ω-end.

Table 2. The Data of St Polymerization with DCDTS at Different Temperatures

Temperature (°C)	Conversion (%)	M_n (10^{-3})	M_w/M_n
65	9.2	88.2	1.64
75	24.4	52.7	1.57
85	42.3	44.0	1.50
95	62.1	41.3	1.52
105	96.2	39.8	1.56

Polymerization conditions: [St] = 8.7 mol · L^{-1}, [DCDTS] = 4.4×10^{-2} mol · L^{-1}, $t = 3$ h.



Scheme 1.

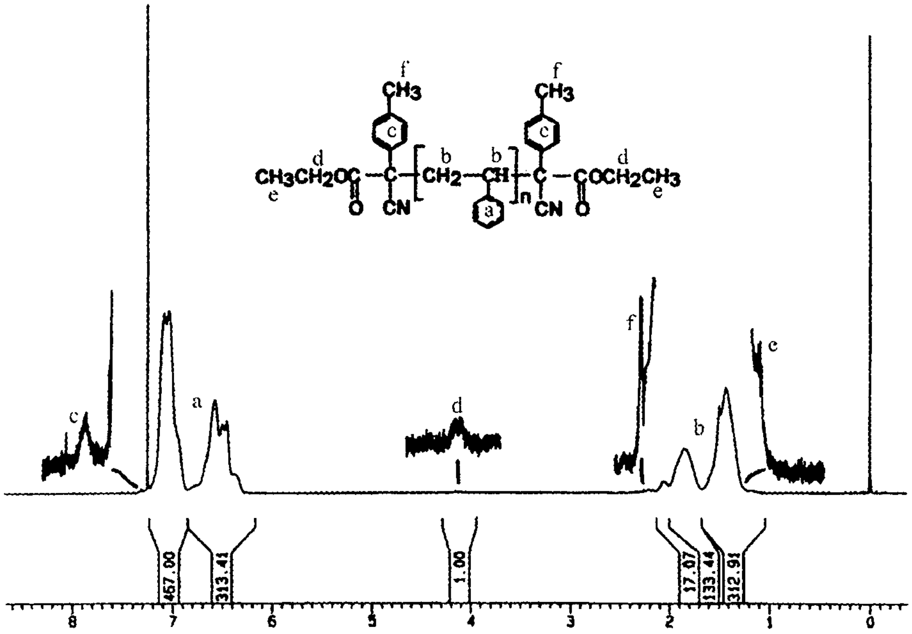


Figure 3. ^{1}H-NMR spectrum of DCDTS-PSt, $M_n = 65{,}900$, $M_w/M_n = 1.46$ (in $COCl_3$, 400 MHz).

Chain Extension and Block Copolymerization

As described above, PSt prepared with DCDTS (DCDTS-PSt) has two fragments of the iniferter as end groups. It is expected that the end group having a penta-substituted C–C bond can act a thermal macroiniferter for chain extension with fresh St or block copolymerization with other monomers. A chain extension polymerization of PSt was carried out in bulk at 85°C in the presence of DCDTS-PSt with $M_n = 34{,}300$ and $M_w/M_n = 1.44$; a conversion of 62% was achieved after 4 h. The M_n of chain-extended PSt increased to 91,600 and the polydispersity index (M_w/M_n) increased slightly to 1.51. The increase in molecular weight can be clearly demonstrated by the GPC curves as shown in Figure 4.

Block copolymers were also obtained with the same method. Formation of a PSt-*b*-PMMA copolymer was also confirmed by GPC analysis and IR and DSC spectroscopies. Figure 5 shows the GPC traces of the DCDTS-PSt and PSt-*b*-PMMA; it shows no additional peak, and the molecular weight increased from 34,300 to 135,100, confirming that block copolymer has been formed. The IR spectrum of PSt-*b*-PMMA had the characteristic adsorption peaks of PSt at 700 cm^{-1}, 1600 cm^{-1}, 3082 cm^{-1} ($-C_6H_5$), and PMMA at 1731 cm^{-1} (C=O), and 1150 cm^{-1} (C–O–C), respectively. The DSC curve of PSt-*b*-PMMA shows two T_g transitions at 105 and 119°C; whereas in a comparison experiment the T_g values of PSt and PMMA homopolymers were determined to be 95 and 126°C, respectively.

The chain extension reaction and block copolymerization reveal that the penta-substituted C–C bond in the end group of DCDTS-PSt can thermally dissociate. It also indicates that the polymerization of St with DCDTS thermal iniferter is "living" polymerization process.

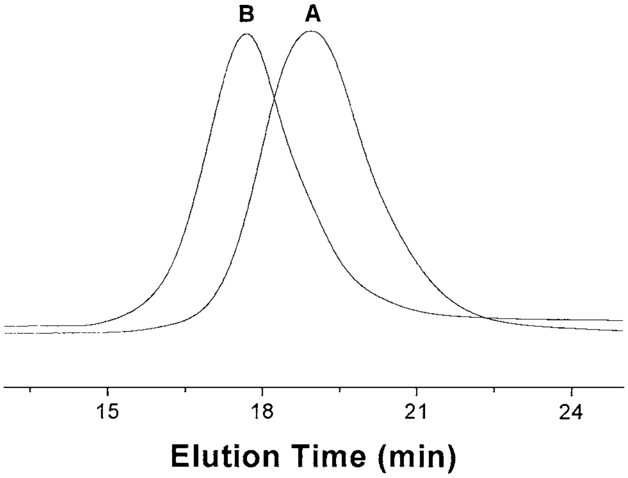


Figure 4. GPC curves of PSt before and after chain-extension reaction at 85°C. A), DCDTS-PSt; B), chain-extended product.

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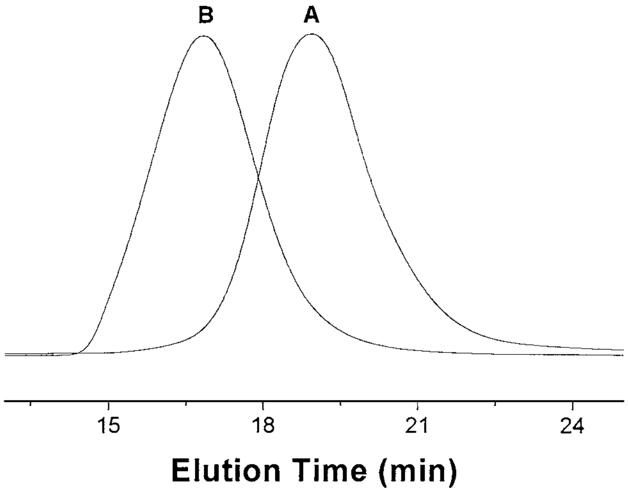

Figure 5. GPC curves of PSt before and after copolymerization with MMA at 85°C. (A) DCDTS-PSt; (B) PSt-*b*-PMMA.

CONCLUSION

DCDTS, a hexa-substituted ethane compound, was used as a thermal iniferter for St polymerization. The polymerization demonstrates the characteristics of a "living" process, that is, both the conversion and the molecular weight of the resultant polymer increased with increasing reaction time. Furthermore, the chain-extension reaction and block copolymerization confirmed that the PSt bearing an ω-penta-substituted C–C bond functional end group can be used as a macroinitiator.

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