

Controlled Radical Polymerization of Styrene Initiated by Diethyldithiocarbamate-Mediated Iniferters

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ABSTRACT: We demonstrated that density functional theory calculations provide a prediction of the trends in C-S bond dissociation energies and atomic spin densities for radicals using two model compounds as diethyldithiocarbamate (DC)-mediated iniferters. On the basis of this information, we synthesized 2-(*N,N*-diethyldithiocarbamyl)isobutylic acid (DTCA) and (4-cyano-4-diethyldithiocarbamyl)pentanoic acid (CDPA) as DC-mediated iniferters. Free-radical polymerizations of styrene (St) were carried out in benzene initiated by DTCA or CDPA under UV irradiation. The first-order time-conversion plots showed the straight line for the UV irradiation system initiated by CDPA indicating the first order in monomer. The number-average molecular weight (M_n) of the polystyrene (PSt) increased in direct proportion to monomer conversion. The molecular weight distribution (M_w/M_n) of the PSt was in the range of

1.3–1.7. It was concluded this polymerization system proceeded with a controlled radical mechanism. However, photopolymerization of styrene initiated by DTCA showed nonliving polymerization consistent with UV initiation. Theoretical predictions supported these experimental results. Methacrylic acid (MA) could also be polymerized in a living fashion with such a PSt precursor as a macroinitiator because PSt exhibited a DC group at its terminal end. This system could be applied to the architecture of block copolymers. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 95: 413–418, 2005

Key words: styrene; density functional theory; controlled radical polymerization; dithiocarbamate-mediated iniferter; block copolymer

INTRODUCTION

The synthesis of polymers via living radical polymerization has gained importance because of its great versatility with a wide range of monomers, the control of the molecular weights, and the low polydispersities of the resulting polymers. The photochemical reactions and initiation polymerization of *N,N*-diethyldithiocarbamate derivatives have been extensively studied by Otsu.¹ Generally, this type of compounds is used as an iniferter. Among these iniferters, the well-designed dithiocarbamates (DC) are most efficient photoinitiators, including living radical polymerization, which leads to various functional, block, graft, star, and crosslinked polymers that have a normal molecular weight distribution (M_w/M_n). The field of living radical polymerization has expanded rapidly in recent years, being used in a nitroxide-mediated process^{2–6} and in atom transfer radical polymerization (ATRP) procedures.^{7–12} Moreover, DC compounds are

also useful reversible addition-fragmentation chain transfer (RAFT) agents in which the nitrogen lone pair is part of an aromatic ring.¹³

We have an interest in realization for living radical polymerization in aqueous media. Up to now, the ATRP is one of the best methods to achieve living radical polymerizations in an aqueous solution. However, this method is not useful for the polymerization of methacrylic acid or acrylic acid monomers, because such systems need basic ligands such as bipyridyl compounds. The RAFT process is also a convenient method for the architecture of hydrophilic polymers using water-soluble chain transfer reagents such as 4-cyanopentanoic acid dithiobenzoate.^{14–16} More recently, we demonstrated that density functional theory calculations provide a reliable and quantitative prediction of the trends in C-S bond dissociation energies for several model compounds as photoinitiator. On the basis of this information, we designed the photoinitiator 2-(*N,N*-diethyldithiocarbamyl)isobutyric acid (DTCA) to polymerize hydrophilic vinyl monomers (2-hydroxyethyl methacrylate and *N*-isopropylacrylamide) with living radical mechanisms.^{17,18} Kwak et al.¹⁹ also prepared carboxylic acid mono functional poly(methyl methacrylate) (PMMA)

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by emulsion photopolymerization using 4-diethylthiocarbamylsulfanylmethyl benzoic acid as an iniferter.

In this article, we prepared DC-mediated iniferters, that is, DTCA and (4-cyano-4-diethylthiocarbamyl)pentanoic acid (CDPA). Free-radical polymerizations of styrene (St) were carried out in benzene using DTCA or CDPA as an initiator under UV irradiation. We performed the kinetic analysis to understand the radical mechanisms of initiation and propagation. We also prepared PSt-*block*-poly(methacrylic acid) (PMA) by copolymerization of methacrylic acid (MA) with PSt precursor as a macroinitiator via a living fashion.

EXPERIMENTAL PROCEDURES

Materials

4,4'-Azobis(4-cyanopentanoic acid) (V-501; Wako Pure Chemical Ind. Ltd.), tetraethylthiuram disulfide (TD), methanol, chloroform, benzene, 1,4-dioxane, *N,N*-dimethylformamide (DMF), diethyl ether, *n*-hexane, and tetrahydrofuran (THF; Tokyo Kasei Kogyo Co. Ltd.) were used as received. Styrene (St) and methacrylic acid (MA; Tokyo Kasei Kogyo Co. Ltd.) were purified by vacuum distillation.

DTCA was synthesized by the reaction of 2-bromoisobutyric acid with *N,N*-diethylthiocarbamate sodium salt. Details concerning the synthesis and purification have been given elsewhere.¹⁷

Synthesis of iniferter (4-cyano-4-diethylthiocarbamyl)pentanoic acid (CDPA)

To a solution of V-501 (1 g, 3.57 mmol) in dioxane (70 mL) was added TD (1.06 g, 3.57 mmol), and the reaction mixture was stirred at 88°C for 24 h in a sealed glass ampoule under high vacuum. The reaction mixture was concentrated and the residue subjected to column chromatography on silica with chloroform/methanol (3 : 1) as eluent; $R_f = 0.62$ and yield 54%.

Free-radical polymerizations of styrene

Typical radical polymerizations of styrene (50 vol % benzene solution) were carried out initiated by CDPA ($[St]_0/[CDPA]_0 = 60$ mol/mol) at 30°C varying the UV irradiation time (250 W high-pressure mercury lamp, Ushio Denki SX-UI 250 HAMQ; UV intensity 42 mW/cm², irradiation distance 15 cm). After polymerization, the polymer was recovered by precipitation with methanol. The conversion was estimated by gravimetric measurements.

Synthesis of block copolymers

To prove the existence of the DC group at the terminal end of PSt, we synthesized block copolymers with a

PSt precursor as a macroinitiator. Photopolymerization of MA (0.5 mL) was carried out in DMF (5 mL) initiated by a PSt macroinitiator ($M_n = 7000$, 0.05 g) at 30°C under UV irradiation for 2 h. After polymerization the PSt-*block*-poly(methacrylic acid) (PMA) was recovered by precipitation with diethyl ether.

Characterization

The number-average molecular weights (M_n) and molecular weight distribution (M_w/M_n) of polystyrene (PSt) were determined by gel permeation chromatography equipped with a refractive index (RI) recorder (GPC; Tosoh high-speed liquid chromatography HLC-8120), which was operated with two TSK gel columns, GMH_{XL} (excluded-limit molecular weight $M_{EL} = 4 \times 10^8$) and G2000H_{XL} ($M_{EL} = 1 \times 10^4$), in series with THF as eluent (flow rate 1.0 mL/min) at 38°C. The calibration curve was performed with PS standards. The chemical shifts of CDPA were determined by ¹H-NMR (500 MHz JEOL GSX-500 NMR spectrometer) in CD₃OD.

The composition of the block copolymers was determined by FT-IR spectroscopy (Shimadzu FTIR-8500). A calibration curve was constructed using a mixture of PSt and PMA (characteristic absorbance of aromatic ring of PSt; 1497 cm⁻¹, and carbonyl moiety of PMA; 1700 cm⁻¹). To prove the formation of PSt-*block*-PMA, the turbidimetric measurement of the block copolymer and corresponding PSt precursor was carried out at the wavelength of 500 nm. 10 mg of each polymer sample was dissolved in 70 mL DMF, and *n*-hexane was added stepwisely with vigorous stirring in cell (Pyrex cylinder, 150 mL) for turbidimetric measurement at 25°C (Corona Front Scatter Method Turbidimeter UF-11).

Density functional theory calculations

To design the DC-mediated iniferters, we performed density functional theory calculations (B3LYP functional using the 6-31G-(d) basis set) for the model compounds CDPA and DTCA. The C-S bond energies were calculated assuming a homolytic bond cleavage corrected with zero-point energy. Details concerning the calculations have been given elsewhere.¹⁷

RESULTS AND DISCUSSION

Figure 1a shows the results of C-S bond dissociation energies and bond lengths for CDPA and DTCA. Steric factors are important in determining bond dissociation energies. It can be anticipated that this should be reflected in longer lengths of the breaking C-S bond in the ground state for which steric factors are greater. The calculations predict that the value of the C-S bond length (1.873 Å) of CDPA is longer than

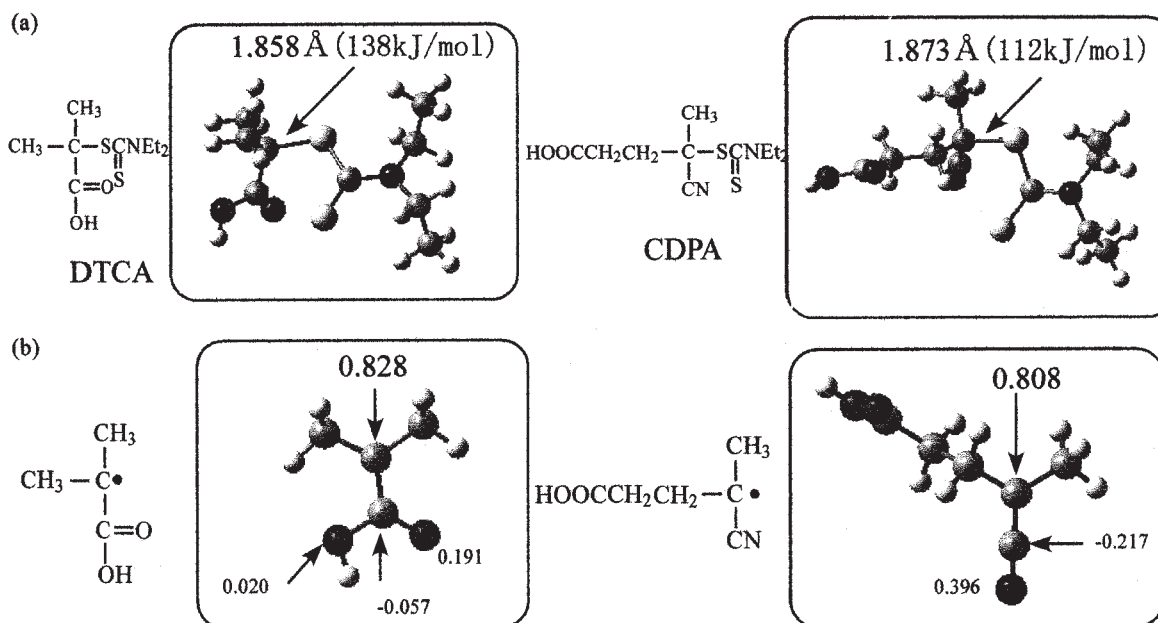


Figure 1 Results of density functional theory for model iniferters calculated assuming a homolytic bond cleavage at 3L YP/6-31G(d) corrected with zero-point energy: (a) C-S bond lengths and bond energies, (b) atomic spin densities for radicals.

that (1.858 Å) of DTCA. On the other hand, Figure 1b shows atomic spin densities for corresponding produced radicals. It is also found that the 4-cyanopentanoic acid radical is more stable than the isobutyric acid radical due to the electron-attracting of the CN substituent group. Based on the above information, we prepared CDPA as an iniferter. The CDPA was provided by the transfer reaction of the 4-cyanopentanoic acid radical to the TD compound. The $^1\text{H-NMR}$ spectrum of CDPA is shown in Figure 2. This spec-

trum indicates the expected resonances for the methyl protons (e: δ 1.20 and 1.29 ppm) and methylene protons (d: 3.79 and 3.94 ppm) of the DC group, the methyl protons (c: 1.72 ppm), and the ethylene protons (b: 2.21 and 2.50 ppm, a: 2.40 ppm). Photolysis of the iniferter CDPA leads to initiating a 4-cyanopentanoic acid radical with a less active DC radical (see Scheme 1). This 4-cyanopentanoic acid radical can add to the vinyl group of a styrene monomer. Propagating radicals always take the equilibrium with the DC rad-

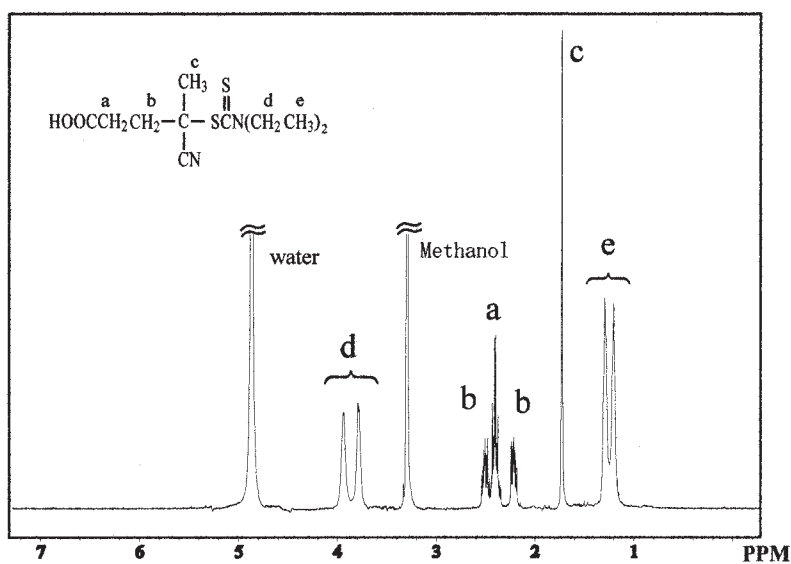
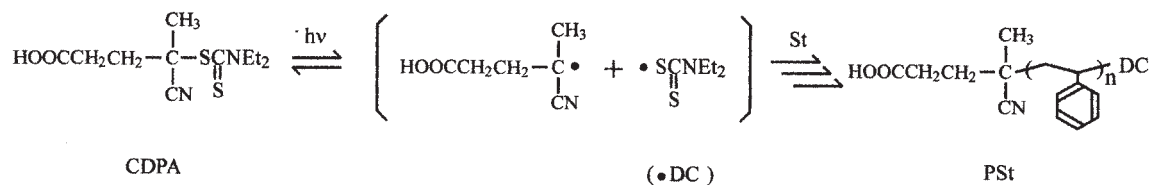


Figure 2 $^1\text{H-NMR}$ spectrum of (4-cyano-4-diethyldithiocarbamyl)pentanoic acid (CDPA) in CD_3OD .



Scheme 1

icals. By repeating these elementary reactions, this polymerization system proceeds to form PSt.

To demonstrate this concept, photopolymerizations of St were carried out in benzene initiated by CDPA (50 vol % benzene solution, $[\text{St}]_0/[\text{CDPA}]_0 = 60$), varying the UV irradiation times. Typical GPC profiles of these polymerization series are shown in Figure 3. All the GPC curves show a unimodal distribution. The elution peaks shift to the high-molecular weight-side increasing with reaction times. The conversion was estimated by gravimetric measurements for the recovered polymers.

We performed the first-order time conversion plot in this polymerization system (see Fig. 4), where $[\text{M}]_0$ is the initial concentration of the monomer St. The straight line in the semilogarithmic coordinates indicates not only the first order in the monomer but also a constant for the active species.

Figure 5 shows the plot of M_n or M_w/M_n against conversion, where the dotted line indicates the calculated values ($M_{n,\text{calcd}}$) assuming that one molecule of the initiator generates one polymer chain. The M_n of the obtained polymers increased in direct proportion to monomer conversion through the origin. However,

the M_n values were higher than the calculated values. This means that the initiator efficiency of CDPA ($f = \sim 0.3$) was not so high. The polydispersity increased gradually with an increment of conversion ($M_w/M_n = 1.3\text{--}1.7$). Therefore, this polymerization system seems to proceed with a controlled radical mechanism. Sigwalt et al.^{20–22} and Turner et al.²³ reported the mechanism of polymerization of *n*-butyl acrylate and block copolymer formation using dithiocarbamate free-radical chemistry. They proposed a photochemical cleavage of the thiocarbonyl-nitrogen bond and subsequent elimination of CS_2 as the decomposition pathway. In this work, such side reactions do not seem to take place during polymerization of St. These problems will be mentioned later in the section on block copolymer synthesis.

Subsequently, photopolymerization of St was carried out initiated by DTCA under UV irradiation (50 vol % benzene solution, $[\text{St}]_0/[\text{DTCA}]_0 = 30$). The elution peaks of GPC scarcely shifted regardless of polymerization time, though all the GPC curves showed a unimodal distribution. Figure 6 shows the plot of M_n or M_w/M_n against conversion. The M_n of the obtained polymers showed almost constant value (~ 5000). This system showed nonliving polymerization consistent with UV initiation. The iniferter CDPA was profitable for the polymerization of St compared to DTCA as predicted by density functional theory.

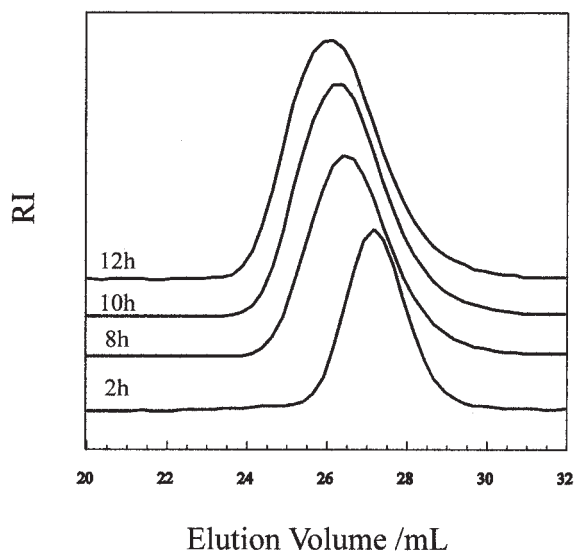


Figure 3 GPC profiles of photopolymerizations of styrene in benzene initiated by CDPA (50 vol % benzene solution, $[\text{St}]_0/[\text{CDPA}]_0 = 60$) in THF as eluent at 38°C , varying UV irradiation time.

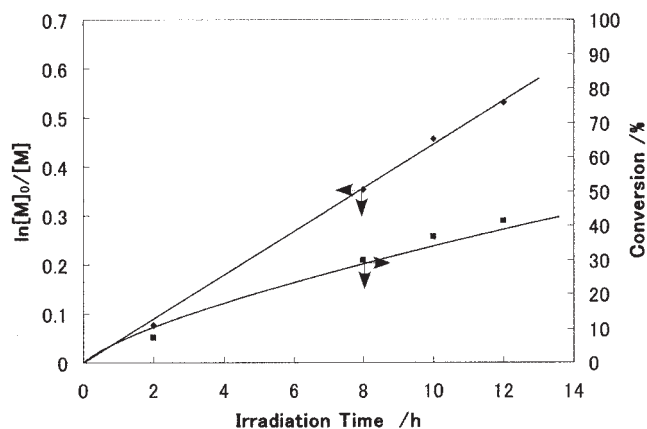


Figure 4 First-order time-conversion plots for photopolymerizations of styrene in benzene initiated by CDPA (50 vol % benzene solution, $[\text{St}]_0/[\text{CDPA}]_0 = 60$) under UV irradiation.

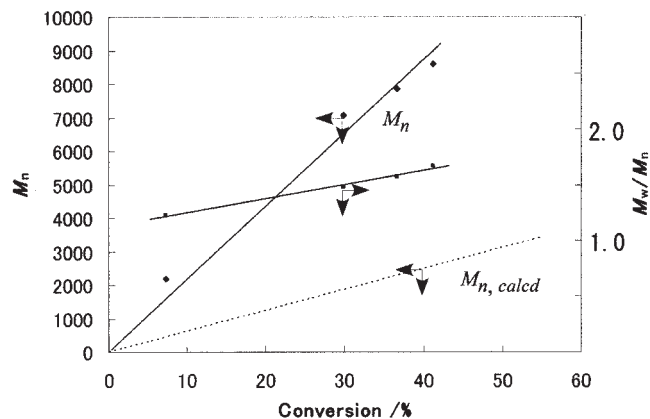


Figure 5 Plots of number-average molecular weight (M_n) or molecular weight distribution (M_w/M_n) against conversion for photopolymerizations of styrene in benzene initiated by CDPA (50 vol % benzene solution, $[St]_0/[CDPA]_0 = 60$) under UV irradiation; the dotted line indicates calculated values of M_n ($M_{n,calcd}$).

Such different reactivities of propagating radicals for vinyl monomers have been left unsolved in this work.

We performed the block copolymer synthesis by photopolymerization of MA with the PSt precursor (sample initiated by CDPA under UV irradiation; $M_n = 7000$, $M_w/M_n = 1.5$) as a macroinitiator. This precursor corresponds to the sample at 30% conversion (see Fig. 5). The FTIR spectrum of the copolymer produced showed the expected absorbance for the carbonyl group (1700 cm^{-1}) and aromatic ring (1497 and 840 cm^{-1}). To determine the composition of the copolymer, a calibration curve was constructed using a mixture of PSt and PMA (aromatic absorbance at 1497 cm^{-1} , and carbonyl groups at 1700 cm^{-1}). The composition of the PSt block was determined to be 59 mol

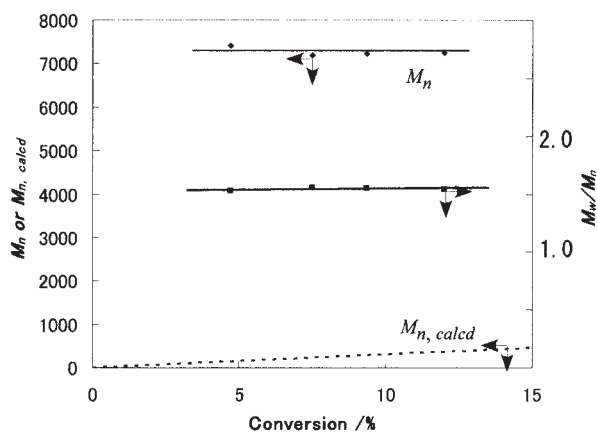


Figure 6 Plots of M_n or M_w/M_n against conversion for photopolymerizations of styrene in benzene initiated by DTCA (50 vol % benzene solution, $[St]_0/[DTCA]_0 = 30$) under UV irradiation; the dotted line indicates calculated values of M_n ($M_{n,calcd}$).

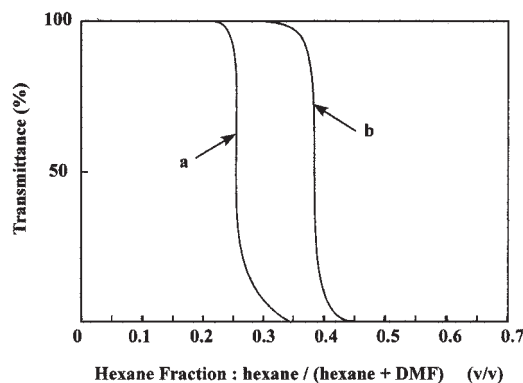


Figure 7 Turbidity curves of PSt-*block*-PMA (a) and PSt precursor (b).

%. Therefore, the M_n of the PMA block was estimated to be 4000, that is, $86[0.41 \times 7000 / (104 \times 0.59)]$. The turbidity curves of the block copolymer and PSt precursor are shown in Figure 7. Curves a and b indicate the turbidities of PSt-*block*-PMA and the PSt precursor, respectively. Beyond the *n*-hexane fraction of 0.22, *n*-hexane works as precipitant for PSt-*block*-PMA (curve a). On the other hand, turbidity for curve b (PSt precursor) shifts to the high fraction side (0.30–0.45) of *n*-hexane due to small molecular weight. These results support not only the formation of the block copolymer but also good functionality of the PSt precursor, that is, PSt exhibited a DC group at its terminal end.

In this work, we studied the living nature of free-radical polymerization of the hydrophobic styrene monomer initiated by DC-mediated iniferters. The density functional theory calculations for iniferters supported strongly the experimental data. The PSt precursors obtained in this work can be used widely as macroinitiators in the architecture of block copolymers. Moreover, the CDPA sodium or ammonium salt was soluble in water. We are using this initiator for living free-radical polymerization of hydrophilic methacrylic acid in aqueous media. The results obtained will be reported in the near future.

CONCLUSIONS

We have explored the approach to living free-radical polymerization of styrene using the DC-mediated iniferters CDPA and DTCA. The first-order time-conversion plot for the polymerization system initiated by CDPA under UV irradiation showed a straight line. The M_n of the obtained PSt increased in direct proportion to monomer conversion. The polydispersity indices increased gradually with an increment of conversion, and the polymerization seemed to proceed with a controlled radical mechanism. However, the radical system initiated by DTCA showed nonliving polymer-

ization consistent with UV initiation. The density functional theory calculations for DC-mediated iniferters supported strongly such experimental data. MA could be polymerized in a living fashion with such a PSt precursor as the macroinitiator. It will be possible to apply this system to the architecture of block copolymers.

The density functional theory calculations were carried out at the Computer Center of the Tokyo Institute of Technology and the Computer Center of the Institute for Molecular Science, and we thank them for their generous permission to use the SG1 Origin 2000 and Compaq Alpha Server GS320 and IBM SP2, respectively.

References

- Otsu, T. *J Polym Sci Polym Chem Ed* 2000, 38, 2121.
- Georges, M. K.; Veregin, R. P. N.; Kazmaier, P. M.; Hamer, G. K. *Macromolecules* 1993, 26, 2987.
- Hawker, C. J.; Barclay, G. G.; Orellana, A.; Dao, J.; Devonport, W. *Macromolecules* 1996, 29, 5245.
- Li, I. Q.; Howell, B. A.; Koster, R. A.; Priddy, D. B. *Macromolecules* 1996, 29, 8554.
- Puts, R. D.; Sogah, D. Y. *Macromolecules* 1996, 29, 3323.
- Emrick, T.; Hayes, W.; Fréchet, J. M. J. *J Polym Sci Part A: Polym Chem* 1999, 37, 3748.
- Wang, J. S.; Matyjaszewski, K. *J Am Chem Soc* 1995, 117, 5614.
- Patten, T. E.; Xia, J.; Abernathy, T.; Matyjaszewski, K. *Science* 1996, 272, 866.
- Kato, M.; Kamigaito, M.; Sawamoto, M.; Higashimura, T. *Macromolecules* 1995, 28, 1721.
- Percec, V.; Barboiu, B. *Macromolecules* 1995, 28, 7970.
- Granel, C.; DuBois, P.; Jérôme, R.; Teyssie, P. *Macromolecules* 1996, 29, 8576.
- Ando, T.; Kamigaito, M.; Sawamoto, M. *Macromolecules* 1998, 31, 6708.
- Chiefari, J.; Chang, Y. K.; Ercole, F.; Kristina, J.; Jeffrey, J.; Le, T. P. T.; Mayadunne, R. T. A.; Meijs, G. F.; Moad, G.; Rizzardo, E.; Thang, S. H. *Macromolecules* 1998, 31, 5559.
- Lowe, A. B.; McCormick, C. L. *Aust J Chem* 2002, 55, 367.
- McCormick, C. L.; Lowe, A. B. *Acc Chem Res* 2004, 37, 312.
- Yusa, S.; Shimada, Y.; Yamamoto, T.; Morishima, Y. *Polym Prepr Jpn* 2002, 51, 1578.
- Ishizu, K.; Khan, R. A.; Ohta, Y.; Furo, M. *J Polym Sci Part A: Polym Chem* 2004, 42, 76.
- Ishizu, K.; Khan, R. A.; Furukawa, T.; Furo, M. *J Appl Polym Sci* 2004, 91, 3233.
- Kwak, J.; Lacroix-Desmazes, P.; Robin, J. J.; Boutevin, B.; Torres, N. *Polymer* 2003, 44, 5119.
- Lambrinos, P.; Tardi, M.; Polton, A.; Sigwalt, P. *Eur Polym Mater* 1990, 26, 1125.
- Manga, J. D.; Polton, A.; Tardi, M.; Sigwalt, P. *Polym Int* 1998, 45, 14.
- Manga, J. D.; Tardi, M.; Polton, A.; Sigwalt, P. *Polym Int* 1998, 45, 243.
- Turner, S. R.; Blevins, R. W. *Macromolecules* 1990, 23, 1856.