

Iniferter Concept and Living Radical Polymerization

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ABSTRACT: Iniferters are initiators that induce radical polymerization that proceeds via initiation, propagation, primary radical termination, and transfer to initiator. Because bimolecular termination and other transfer reactions are negligible, these polymerizations are performed by the insertion of the monomer molecules into the iniferter bond, leading to polymers with two iniferter fragments at the chain ends. The use of well-designed iniferters would give polymers or oligomers bearing controlled end groups. If the end groups of the polymers obtained by a suitable iniferter serve further as a polymeric iniferter, these poly-

merizations proceed by a living radical polymerization mechanism in a homogeneous system. In these cases, the iniferters (C—S bond) are considered a dormant species of the initiating and propagating radicals. In this article, I describe the history, ideas, and some characteristics of iniferters and living radical polymerization with some iniferters that contain dithiocarbamate groups as photoiniferters and several compounds as thermal iniferters. From the viewpoint of controlled polymer synthesis, iniferters can be classified into several types: thermal or photoiniferters; monomeric, polymeric, or gel iniferters; monofunctional, di-

functional, trifunctional, or polyfunctional iniferters; monomer or macromonomer iniferters; and so forth. These lead to the synthesis of various monofunctional, telechelic, block, graft, star, and crosslinked polymers. The relations between this work and other recent studies are discussed. © 2000 John Wiley & Sons, Inc. *J Polym Sci A: Polym Chem* 38: 2121–2136, 2000

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TAKAYUKI OTSU

Dr. Takayuki Otsu is a Professor Emeritus, Osaka City University. He was born in Osaka in 1929 and received his B.Sc. degree from the Osaka Institute of Science and Technology in 1951. He then was appointed as an instructor at Osaka City University and started his research work on radical polymerization under the late Professor Minoru Imoto. In 1956, he found that polymers derived from thiuram disulfides could induce photopolymerization to give block and graft copolymers. This discovery became the foundation for this highlight. For his work, he was awarded a D.Sc. degree from Osaka University in 1959 and went to the United States of America to work as a research associate with Professor Carl S. Marvel at the University of Illinois for a year. Then, he returned to Osaka City University and was appointed Associate Professor. In 1965, he accepted the position of Full Professor of Polymer Chemistry of the

Department of Applied Chemistry, Faculty of Engineering, Osaka City University, and worked there for 26 years. In the meantime, he served as a senator for Osaka City University from 1977 to 1979. After his retirement in 1992, he moved to Kinki University, Wakayama, as Professor until his retirement in 1999.

The main topics of his research are the various fields of radical polymerization: basic studies of rates and mechanisms, new monomers and initiators, monomer structure–reactivity relationships, syntheses of head-to-head polymers, controlled polymer syntheses with the iniferter and living radical polymerization techniques, and syntheses of new acrylic polymers from maleic, fumaric, and itaconic derivatives. He is the author or coauthor of more than 550 original papers, 120 review articles, 10 books, 30 book chapters, and more than 100 patents. Dr. Otsu was invited abroad to more than 40 International Symposia, universities, and laboratories to give various lectures. He has served as a member of the organizing committee of the International Symposia held in Japan. He was also a chairman of the Japanese side of the Japan–China Symposium on Radical Polymerization (now the Asia Polymer Symposium) from 1980 to 1990. He has served on the editorial boards of several journals and edited a number of monograph series on polymer and experimental sciences. Dr. Otsu also served as Vice President of the Society of Polymer Science, Japan from 1986 to 1988. He was given the Chemical Society of Japan Award for Young Chemists in 1961, and he was also the recipient of the Award for Distinguished Service in the Advancement of Polymer Science in 1990 from the Society of Polymer Science, Japan.

In 1951, I started to work under Professor M. Imoto at the newly established Institute of Polytechnics, Osaka City University, on the radical polymerization of vinyl chloride (VC) with benzoyl peroxide (BPO)/dimethylaniline as an initiator, and I published two articles¹ on the initiation mechanism in 1955. In those days, two new polymers, high-density polyethylene and isotactic polypropylene, were discovered with novel initiators, and the initiation mechanism for radical polymerization was also discussed by several workers.² In 1953, the definition of block and graft copolymers was clarified by Mark,³ who emphasized that some physical properties were different from those of random and alternating copolymers. After that, the synthesis of these polymers has been attempted with several methods⁴ in which the block copolymer of styrene (St) and methyl methacrylate (MMA) is prepared with polymeric radical initiators⁵ and the living polymer discovered by Szwarc⁶ in 1956.

This being the case, I had an interest in new initiators and their mechanisms, and I focused my attention on the unique reaction behavior of organic sulfur compounds, which have been used as a thiyl radical source, an accelerator, a modifier, a terminator for vinyl or diene polymerization, and an accelerator for mastication and vulcanization in the rubber industry.

In 1954, we began to examine the initiating ability of these compounds in radical polymerization of St and MMA and found in 1956 that various sulfides and disulfides (e.g., phenyl, benzoyl, benzothiazoyl, xanthogene, thiuram, and dithiocarbamate derivatives) could serve as efficient photoinitiators.^{7,8} Among thiuram disulfides,⁹ tetraethylthiuram disulfide (**1**; R = C₂H₅) was the most excellent photo- and thermal initiator. However, for other monomers such as vinyl acetate (VAc), acrylonitrile, and VC, **1** served as a weak initiator or terminator, depending on the reactivities of the monomers.^{8,10}

From kinetic studies,^{10–12} **1** was found to act not only as an initiator but also as a retarder, terminator, and transfer agent. Data on sulfur analysis indicated that the resulting polymers had nearly two initiator fragments (**5** in eq 4) at the chain ends, as is shown in Table I.¹³ Therefore, the polymerization of the monomer (M) with **1** proceeds via the dissociation of **1**, initiation, propagation, primary radical (PR) termination, and chain transfer (CT) to **1**, according to eqs 1–5,¹² respectively:

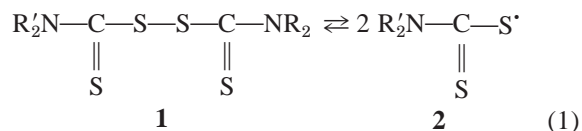
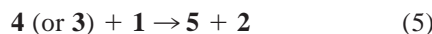
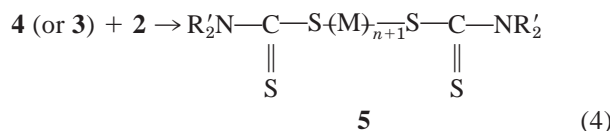
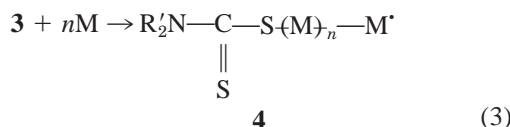
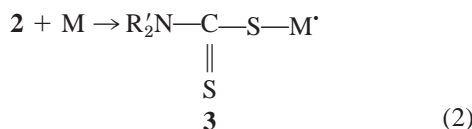
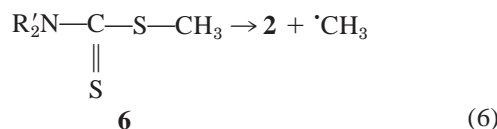


Table I. Polymerization of St with **1**^a

1 (g)	Yield (%) ^b	$M_n \times 10^{-4}$	S (%) ^f	N^g	Reference
1.0	20	3.3 ^d	0.40	2.2	13
0.15	25	1.6 ^d	0.78	1.7	13
0.20	32	1.2 ^d	0.78	1.5	13
0.25	38	0.96 ^d	0.74	2.2	13
0.15	28	8.2 ^e	—	2.0	22
0.30	35	5.3 ^e	—	2.0	22
0.45	39	4.2 ^e	—	2.3	22
0.10	23 ^c	6.4 ^e	—	1.7 (2.1) ^h	22
0.18	10 ^c	4.5 ^e	—	1.7 (2.1) ^h	22
0.25	18 ^c	5.9 ^e	—	1.7 (2.1) ^h	22

^a 10 mL of St, 4 h, 80 °C.^b 27 h (St) and 20 h (MMA).^c MMA was used.^d Determined by viscometry.^e Determined by membrane osmometry in toluene.^f Determined by the Carius method.^g Number of (C₂H₅)₂NC(S)S— end groups per polymer determined by S (%) or UV spectrometry and M_n .^h Calculated with M_n determined by viscometry.

The ordinary bimolecular termination is neglected because PR **2** is less reactive for initiation and more reactive for PR termination. The CT to **1** also occurs because the CT constants are high values,²² 0.72 for St and 0.48 for MMA at 60 °C, yielding a relatively low molecular weight (MW) polymer, **5**, with two sulfide end groups similar to those in methyl *N,N*-diethyldithiocarbamate (**6**) that can act as a photoinitiator, as is shown in eq 6:¹⁰



After purification by reprecipitation twice, polymer **5**, obtained from St, was found in 1957 to initiate the photopolymerization of MMA^{13,14} and VAc to give block copolymers (**12** in eq 9). Alkaline hydrolysis of the latter provided a new block copolymer consisting of a hydrophobic poly(St) and a hydrophilic poly(vinyl alcohol).¹⁵

Moreover, when the polymers of St were allowed to react with **1** in the presence or absence of BPO in benzene at 60–100 °C, an appreciable amount of fragments of **1** was introduced. These polymers also induced the photopolymerization of MMA, leading to graft copolymers.¹⁴ By this method, several graft copolymers were prepared.¹⁶ At that time, however, the idea of polymer design was not taken into consideration, but this method has been applied for the preparation of various block and graft copolymers.

After we published these results in several journals, the study was interrupted because I worked with Professor Carl S. Marvel at the University of Illinois (Urbana, Illinois). At that time, a new thermally stable polymer, polybenzimidazole, was prepared by Vogel¹⁷ in the next room. My research work on the synthesis of a ladder polyquinoline was unsuccessful, and I felt an urge to study the synthesis of new polymers.

RELATED WORKS AND THE PROLOGUE TO NEW RADICAL POLYMERIZATION

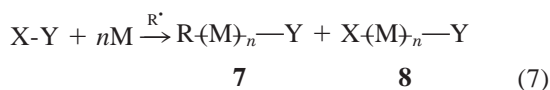
After I returned to Osaka in 1960, we began to study together with more than 10 coworkers. We went on from

sulfide initiators to various other synthetic studies, including the synthesis and polymerization of various vinyl sulfide monomers, copolymerization of vinyl sulfides and olefins with maleic anhydride, stereospecific radical polymerization with metal peroxides and metal-containing initiator systems (e.g., reduced nickel, metal chelates, or metallocenes with various halides), monomer structure–reactivity relationship with the generalized Hammett equation (Yamamoto–Otsu equation), initiation and propagation mechanism by sector, spin trapping and electron spin resonance techniques, and monomer-isomerization polymerization of internal olefins to poly(1-olefins) with Ziegler–Natta catalysts.

The early work with disulfide initiators did not have a chance to develop further until 1978, but we continued to consider how to control the polymer end structure and build a model for living radical polymerization. In 1968, 1971, and 1977, I published three text books¹⁸ on radical polymerization, from which I learned that radical chain polymerization has a number of advantages arising from the characteristics of intermediate radicals, which are formed from the monomer and initiator used; for example, many monomers can polymerize with excellent reproducibility, easy prediction of their reactivities from the accumulated data on the elementary reaction mechanism and monomer structure–reactivity relationship, utilization of water, and so on. From these advantages, more than 70% of vinyl polymers (more than 50% of all plastics) are produced industrially by radical polymerization.

As shown in a recent article with almost the same title,¹⁹ these advantages of radical polymerization result in some disadvantages, one of which is the difficulty in preparing polymers with well-controlled MWs, molecular weight distributions (MWDs), and primary structures; these are now the most important problems.¹⁹ However, the precision synthesis of these polymers through living radical polymerization, without some new idea, had been considered impossible until 1982.

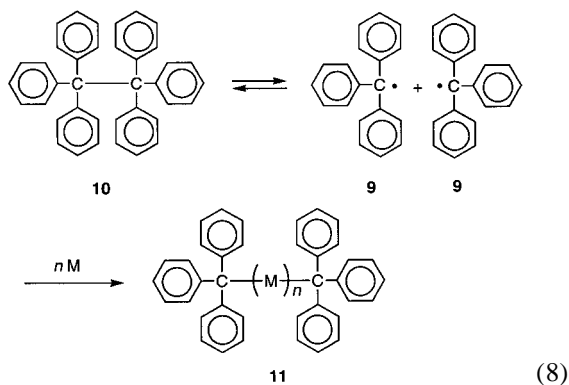
As is known, the MW and end groups can be controlled with a CT reaction. When an appropriate X–Y CT agent is used in the presence of a radical initiator, two types of oligomers or telomers, **7** and **8**, are formed, as in eq 7, depending on the CT constant, C_{tr} :



If C_{tr} is very high, telomer **8** is mainly formed, and a negligible amount of telomer **7** is also formed, as is known for the telomerization of ethylene with carbon tetrachloride. In these polymerizations, bimolecular termination is negligible, and the polymerization proceeds

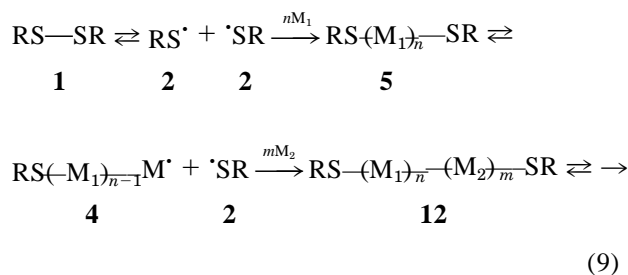
by an insertion of monomers in the X–Y bond, as shown in eqs 1–5. When CT agents with a relatively low C_{tr} are used, the amount of oligomer **8** decreases, and that of oligomer **7** increases, so that the end structure of the oligomers is difficult to control by this method. However, if the initiator or R^{\cdot} produced reacts more easily with the CT agent than the monomers, the yield of oligomer **8** increases (see eqs 21 and 22).

In 1975–1979, I paid attention to the work of Gomberg's²⁰ first discovery of stable radicals. He found that trityl radical **9** exists in an equilibrium mixture with its dimer, **10** (see **58** in eq 29),^{20(c)} as shown in eq 8:



Marvel et al.²¹ reported that when **10** was allowed to react with St, a telomer mixture, **11** ($n = 1-2$), was isolated, similar to **8** in eq 7, indicating that **9** scarcely initiates polymerization and then reacts with **9** to give **11**, which has two trityl end groups.

At that time, I realized that the scheme of eq 8 is quite similar to our scheme shown in eqs 1–6, which can be rewritten as eq 9:



where RS is $R_2^{\cdot}\text{NC(S)S}$. **1** and **5** are the monomeric and polymeric initiators, respectively, which can dissociate into PR **2** and propagating radical **4**, respectively. **12** is the resulting block copolymer.^{27,28} These results seem to provide the possibility of breaking through unsolved problems for designing a living radical polymerization (discussed later).

In 1979, we started the reexamination of old data using new equipment and confirmed that the polymers obtained from St and MMA with different amounts of **1**

Table II. MW, MWD, and Number of End Groups (N) of Poly(St) Obtained by **1**, **18**, and **21**

Iniferter (mol · L ⁻¹)	Time (h)	M_n	MWD	N
1 (7.7×10^{-3})	3	1.3	2.2	1.7
	6	2.5	2.5	1.9
	10	2.8	2.8	2.0
	15	3.3	3.2	2.0
18 (7.8×10^{-3})	3	2.1	2.1	0.9
	6	3.2	2.1	0.9
	10	4.5	2.3	1.0
	15	6.3	2.9	1.0
21 (3.8×10^{-3})	3	3.8	—	1.8
	6	6.3	—	1.7
	10	9.5	—	1.7
	15	15.4	—	2.0

have two dithiocarbamate end groups like **5** (see Tables I and II).^{22–25} The polymers isolated could further initiate photopolymerization to give block copolymers,^{21–25} and the MW of the polymers increased with increased reaction time,^{23–31} as shown in Figure 1. These radical polymerizations seem to be a new radical polymerization, different from those initiated by BPO or 2,2'-azobisisobutyronitrile (AIBN).

When we consider polymer formation by radical polymerization, there are two extreme cases in regard to the activity of the initiators used:

Case 1 is radical polymerization with the usual strong initiators leading to high-MW polymers without controlled end groups because bimolecular termination occurs by combination or disproportionation. However, the bulk polymerization of St with BPO or AIBN gives a polymer with two initiator fragments, because the termination for St occurs only by combination, which is a special case. In these polymerizations, MW does not change principally with reaction time, and these polymers have been used for synthesizing various commodity materials.

Case 2 involves weak initiators such as **1** or CT agents (eq 7) in which bimolecular termination is negligible and the polymers with controlled ends are formed by PR termination and CT reaction. These polymerizations proceed by an insertion of monomers (see eqs 7–9), and the MWs of the polymers do not change or increase with reaction time. These polymerizations might provide a new route for preparing specialty polymers or oligomers.

INIFERTER CONCEPT

Definition and Classification

As described in Case 2, if initiators such as **1** induce such radical polymerization, polymers with two initiator fragments at their ends, such as **5**, are obtained (see Tables I and II) as the result of the monomer insertion (eq 9). The use of well-designed initiators gives various polymers or oligomers with controlled end groups, such as telechelic and block polymers.^{19,22,24,28} The basic principles of polymer synthesis with the iniferter technique are described here, and some characteristics of polymerization are discussed later.

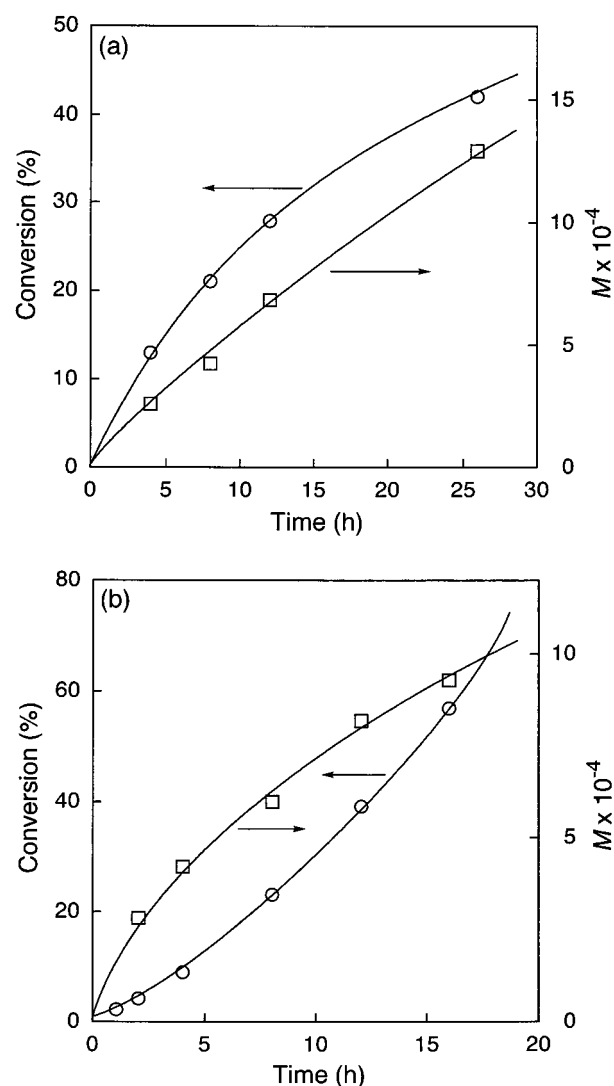
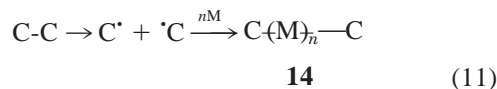
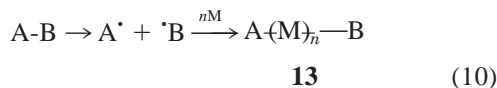


Figure 1. Time–conversion and time–molecular weight (M) relationships for the photopolymerization of (a) St in bulk ($[I] = 7.7 \times 10^{-3}$ mol/L) and (b) MMA in benzene ($[MMA] = 4.7$ mol/L, $[I] = 4.6 \times 10^{-3}$ mol/L) with **1** at 30 °C (from ref. 19).

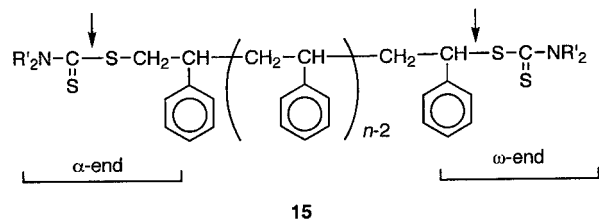
In 1982, we proposed for these initiators the name *iniferter* (initiator–transfer agent–terminator),²² and we set forth a model for living radical polymerization in a homogeneous system²³ with some iniferters. Several weak initiators, including sulfides, phenylazo compounds, amines, alkoxyamines, halides, and thiols for the A–B type (see eq 10), and peroxides, disulfides and tetraphenylethanes for the C–C type (see eq 11) are used as iniferters.^{19,22–24,28}

Similar to initiators, there are thermal or photoiniferters, monomeric or polymeric iniferters, and single or two-component (e.g., redox) iniferters. The iniferters are divided from the structure of their bonds into A–B-type and C–C-type iniferters, which serve as follows:

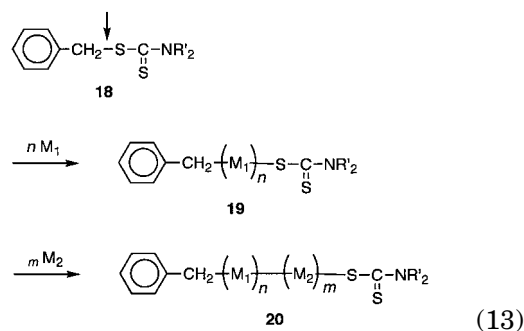
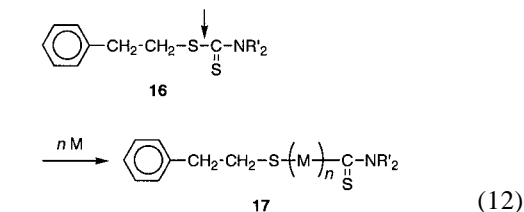


where A^{\cdot} in eq 10 is a reactive radical that participates in initiation and then propagation, and B^{\cdot} is a less reactive or nonreactive radical that principally enters into PR termination to give polymer **13**. In the case of C–C-type iniferters (eq 11), two C^{\cdot} are less reactive radicals that participate in both initiation and PR termination, leading to polymer **14**, in which n is the total number of inserted monomer molecules. In the beginning of our reexamination in 1979, we used some thiuram and other disulfides as a C–C-type photoiniferter to prepare various block copolymers.^{25–27}

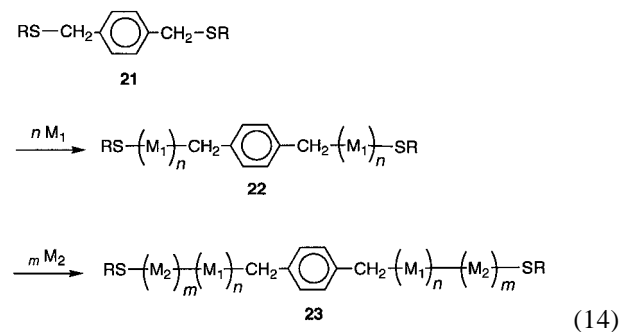
As understood from eq 11, however, the C–C type has several disadvantages compared with the A–B type, including the inability to control the reactivity of C^{\cdot} toward M or PR and the iniferter function changing from the C–C type to the A–B type during polymerization. Another disadvantage is that, for example, polymer **5** produced from **1** of the C–C type is unfavorable for preparing the controlled block copolymers because two dithiocarbamate end groups are bonded to the different carbon atoms of the terminal monomer units to form the α and ω ends, as is rewritten by **15**. That is, the C–S bond, shown by an arrow, at the ω end would be more easily dissociated photochemically than that at the α end, as was pointed out by Okawara et al.³²



where the structures of the α and ω end groups bonded to the terminal monomer units correspond to those of 2-phenethyl *N,N*-diethyldithiocarbamate (**16**) and benzyl *N,N*-diethyldithiocarbamate (**18**), respectively, as A–B-type model compounds. Therefore, radical dissociation in **15**, **16**, and **18** occurs at different bonds, as shown by the arrows in eqs 12 and 13:

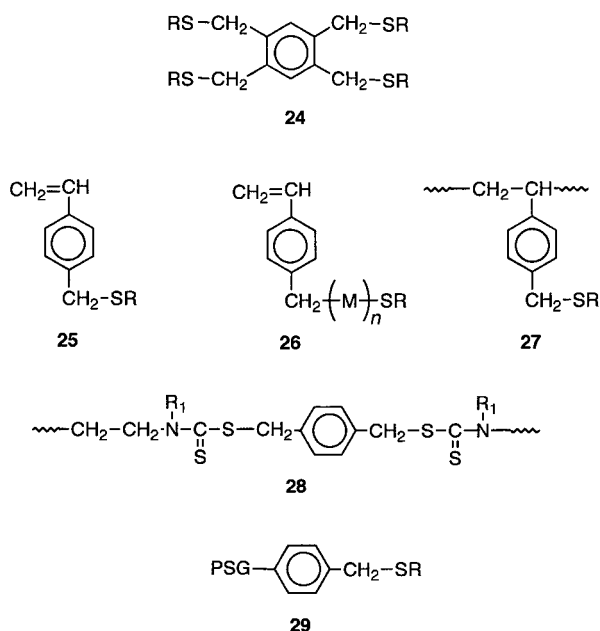


where **16** acts as a weaker photoiniferter than **18**, which serves as an excellent photoiniferter because a benzyl radical similar to the propagating radical of St is produced.²⁵ If **18** is used as a monofunctional photoiniferter to yield the monofunctional end-reactive polymer **19**, AB-type block copolymer **20** is obtained.^{25,27–30} Similarly, if *p*-xylylene bis(*N,N*-diethyldithiocarbamate) (**21**) is used as a difunctional photoiniferter, difunctional polymer **22** is obtained, from which ABA block copolymer **23** is also precisely prepared, according to eq 14.^{27–30} However, block copolymers with a narrow MWD are not obtained with dithiocarbamate iniferter (discussed later):



Thus, the A–B-type iniferters are further classified, from the viewpoint of controlled synthesis, that is, the number of iniferter bonds (functionality) or double bonds intro-

duced into the benzene nucleus of **16**, into several types: monofunctional (**16**),^{25,29,30} difunctional (**21**),^{29,30} trifunctional, tetrafunctional (**24**),³¹ pentafunctional, or hexafunctional iniferters; monomer iniferter 4-vinylbenzyl *N,N*-diethyldithiocarbamate (**25**);³³ macromonomer iniferter **26**;³³ polyfunctional iniferter **27**;³³ multifunctional iniferter **28**;³⁴ and poly(St) gel (PSG) iniferter **29**,^{35,36} in which RS is $(C_2H_5)_2NC(S)S$ as follows:



With **18** (or **19**), **21** (or **22**), **24**, **25** (or **27**), **26**, and **28** as photoiniferters, various monofunctional polymers, including AB block (**20**), ABA block (**23**), star, graft (or crosslinked), comb, and multiblock copolymers, respectively, were prepared.³⁸

Synthesis and Design of Block Copolymers

As shown before, it is a characteristic of the iniferter technique that radical polymerization using an iniferter with a definite functionality gives a polymer with the same functionality. Therefore, various AB and ABA block copolymers consisting of poly(St), poly(MMA), and poly(VAc) were synthesized in good yields with **18** and **21** as monofunctional and difunctional photoiniferters, respectively, as shown in eqs 13 and 14.^{28–30}

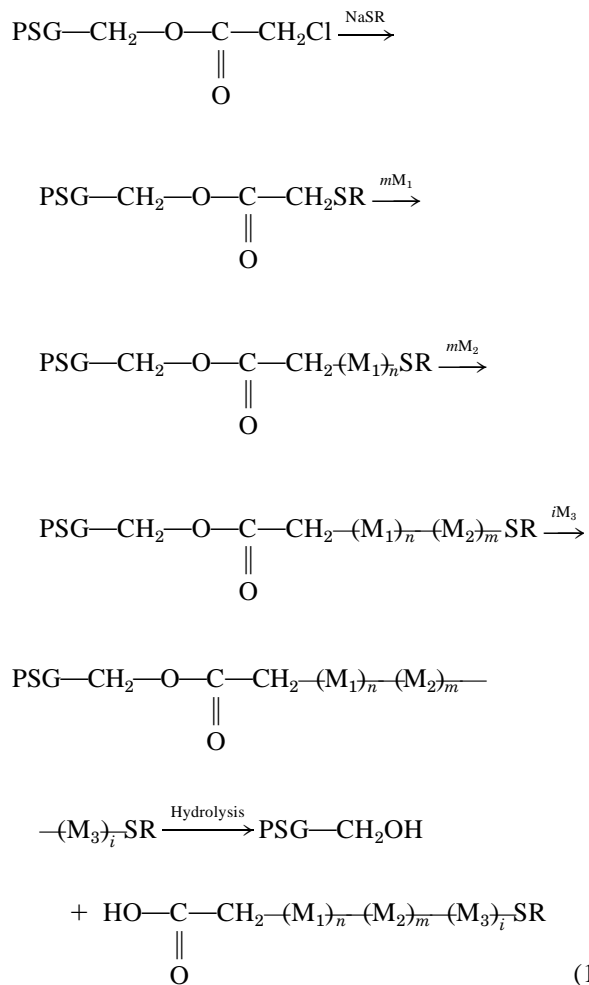
When a similar technique was applied to copolymerization, several AB and ABA block copolymers containing random and alternating copolymer sequences were synthesized, including poly(St-*co*-MMA)-*b*-poly(VAc), poly(VAc)-*b*-poly(St-*co*-MMA)-*b*-poly(VAc), poly(St)-*b*-poly-(DiPF-*alt*-IBVE), and poly(St)-*b*-poly(St-*co*-MMA)-*b*-poly(VAc), and poly(St)-*b*-poly(St-*co*-MMA)-*b*-poly(VAc),³⁰ in which DiPF,

IBVE, and MAn are diisopropyl fumarate, isobutyl vinyl ether, and maleic anhydride, respectively.

Some multiblock copolymers can be synthesized by successive polymerization and isolation with the iniferter technique, but pure tri- or tetra-block copolymers free from homopolymers could not be isolated because no suitable solvents for separation were found.²⁶ To break through this point, we attempted to use a solid-phase synthesis.³⁵

Solid-Phase Block Copolymer Synthesis

In 1963, Merrifield³⁷ reported a brilliant solid-phase synthesis with a reagent attached to the polymer support. If a similar idea can be applied to the iniferter technique, pure block copolymers might be synthesized by radical polymerization. The dithiocarbamate group attached to a PSG through a hydrolyzable ester spacer was used as a PSG photoiniferter (**29**), as shown in eq 15:



According to this scheme, after the photopolymerization of the M_1 monomer, the whole polymer was isolated and

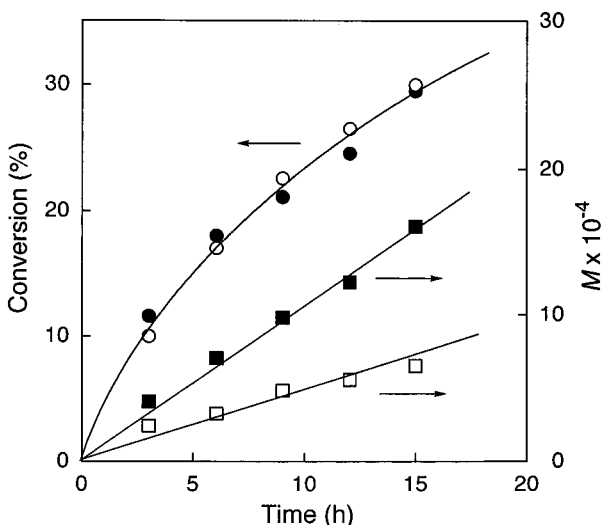


Figure 2. Time–conversion and time–molecular weight (M) relationships for the photopolymerization of St with **18** (○, □) and **21** (●, ■) in benzene at 30 °C. [St] = 6.9 mol/L; [**18**] = 7.8×10^{-3} mol/L; [**21**] = 3.8×10^{-3} mol/L (from ref. 19).

extracted with benzene to separate a homopolymer of M_1 . The poly(St) grafted onto PSG was used for the photopolymerization of M_2 in the presence of **1** as a source of **2**. After the extraction and hydrolysis of the graft–block copolymer attached to PSG **30**, a block copolymer, poly(St)-*b*-poly(MMA), was isolated. Further photopolymerization of M_3 in the presence of **1** with **30** as a PSG photoiniferter was undertaken. After hydrolysis and extraction, a pure triblock copolymer, poly(St)-*b*-poly(MMA)-*b*-poly(St), was isolated.³⁵ In a similar way, poly(St)-*b*-poly(MMA)-*b*-poly-(ClSt) as a triblock copolymer and poly(St)-*b*-poly(MMA)-*b*-poly(St)-*b*-poly(MMA) and poly(St)-*b*-poly(MMA)-*b*-poly(EMA)-*b*-poly(MOST) as tetrablock copolymers,^{35,36} in which ClSt, EMA, and MOST are *p*-chlorostyrene, ethyl methacrylate, and *p*-methoxystyrene, respectively, were also prepared in good yields.

Synthesis and Design of Star, Graft, and Crosslinked Polymers

1,2,4,5-Tetrakis(*N,N*-diethyldithiocarbamylmethyl)benzene (**24**) was prepared as a tetrafunctional photoiniferter.³¹ The polymerization of St with **24** was accompanied by the formation of benzene-insoluble polymers, which decreased with the addition of **1** as a generator of **2** to avoid mutual termination, but the reactivities of **24** through an iniferter bond were the same as those in **18** and **21** (see Fig. 2).

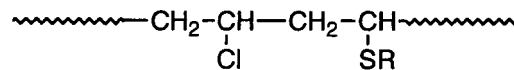
A similar polymerization of MMA was performed to give benzene-soluble polymers that contained more than

24% star polymers with more than three functionalities. These polymers also served as a polyfunctional photoiniferter for St to give a star–block copolymer,²¹ which then converted to a crosslinked polymer. From methyl acrylate (MA) polymerization with **24** in the presence of **1**, a benzene-soluble star polymer was obtained.⁶²

To synthesize graft, comblike, and crosslinked polymers, monomer iniferter **25**,³³ $\text{CH}_2=\text{CHCH}_2\text{—SR}$, and $\text{CH}_2=\text{C}(\text{CH}_3)\text{COOCH}_2\text{CH}_2\text{—SR}$ were prepared.³⁹ In the absence of light, **25** easily homopolymerized and copolymerized with St in benzene by AIBN to give benzene-soluble polymer **27**, which also served as a polyfunctional photoiniferter leading to graft and crosslinked polymer formations. When the **25** unit in the copolymers with St decreased, the yield of the soluble graft polymers increased.³³

In the presence of light, **25** polymerized without AIBN to give low-MW benzene-soluble polymer **26**, which contained a small amount of crosslinked polymer. The photopolymerization of MMA with **25** gave the benzene-soluble polymers containing a styryl double bond and a dithiocarbamate group at both polymer ends. Macromonomer iniferter **26** was copolymerized with MMA in the presence of AIBN, and various designed graft copolymers were synthesized.

Polymers with a dithiocarbamate photoiniferter group in a side-chain end were also synthesized by a chemical reaction. For example, when poly(VC) reacted with sodium dithiocarbamate (NaSR) in dimethylformamide, the polymer that was 15 wt % SR group was prepared, as with **31**,⁴⁰ which was then used as a photoiniferter for preparing new antithrombogenic heparized polymers,⁴¹ which were commercialized. These iniferter techniques have been used for the surface grafting of hydrophilic monomers onto hydrophobic polymer surfaces.⁴² Recently, surface grafting techniques using a dithiocarbamate photoiniferter were applied to a precision processing technology of polymer surfaces.⁴³



31

Synthesis of Polymers with Thermal Iniferters

Some thermal iniferters have been known since 1939, when Schulz⁴⁵ used first 1,2-dicyanotetraphenylethane (see **36**, $X = \text{CN}$) and phenylazotriphenylmethane (see **32**) as an initiator.

Asymmetric Azo Compounds

Phenylazotriphenylmethane (**32**), which is known as a phenyl radical source, has been used as an A–B-type thermal iniferter^{22,44,45(b)} (see Fig. 3), as in eq 16:

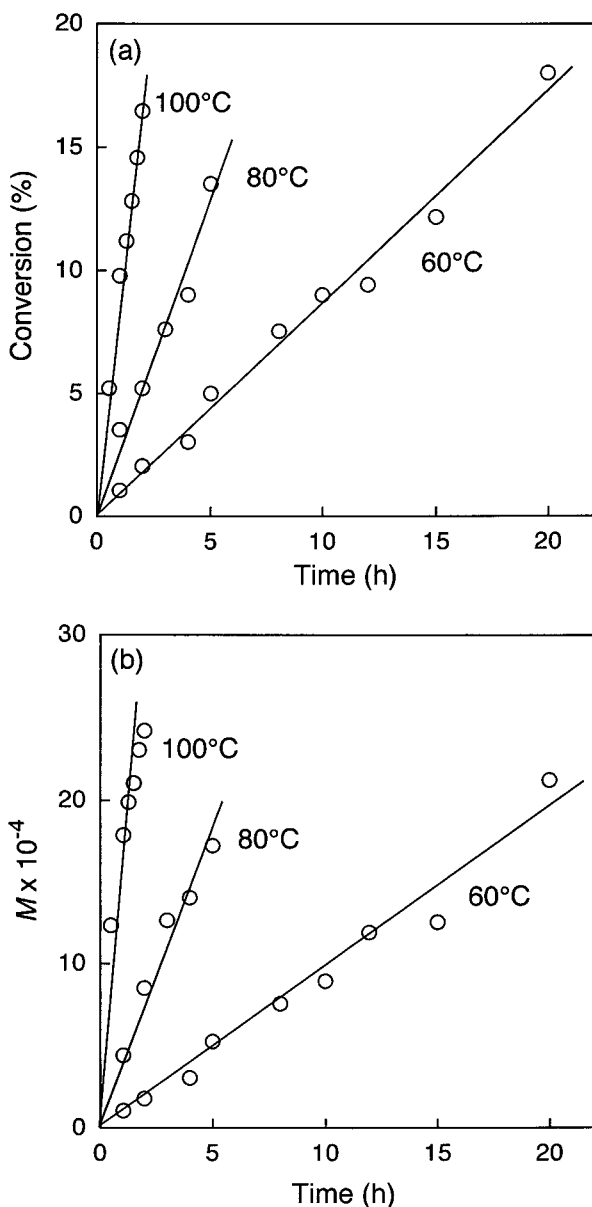
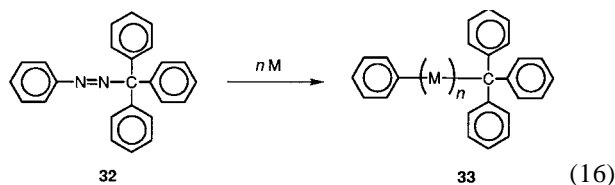


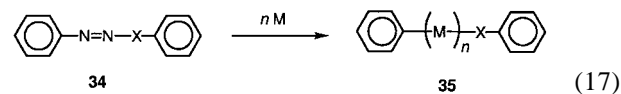
Figure 3. (a) Time–conversion and (b) time–molecular weight (M) relationships for the bulk polymerization of MMA with **32** at 60–100 °C. $[32] = 1.0 \times 10^{-2}$ mol/L (from ref. 19).



By the thermal decomposition of **32** in St, a reactive phenyl radical and a stable trityl radical, which participate in initiation and PR termination, respectively, lead-

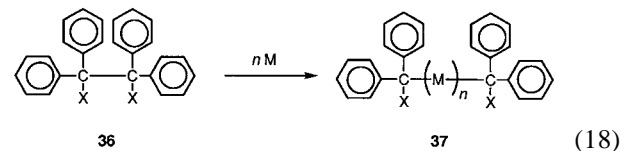
ing to poly(St) (**33**), are produced, similar to **1** (eq 10) and **10** (eq 9), which does not serve below 80 °C as a polymeric iniferter. When MMA, a 1,1-disubstituted monomer, was used, however, poly(MMA) (**33**), with a thermally weak bond at the ω end to lead a living radical polymerization, similar to **36** and **38** (see eqs 18 and 19, respectively), was obtained (see the Living Radical Polymerization in Homogenous Systems section). **33** was found to dissociate further to induce an ordinary radical polymerization. The yield of block copolymers was not so high because some undesirable side reactions might occur (see the Features in Living Radical Polymerization with Iniferters section).⁴⁴

The other phenylazo compounds are phenylphenylazosulfide (**34**; X = S)^{63(a)} and 1,3-diphenyltriazene (**34**; X = NH),^{63(b)} which also serve as A–B-type thermal iniferters leading to polymer **35** (eq 17), in which **35** (X = S) may serve as a polymeric photoiniferter, providing a block copolymer:



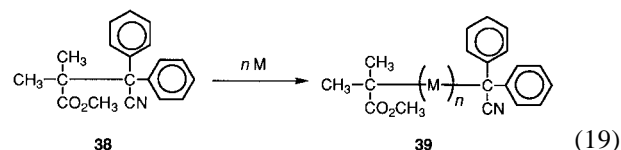
Tetraphenylethanes

1,2-Disubstituted tetraphenylethane (**36**) also serves as a C–C-type thermal iniferter leading to polymer **37**, as in eq 18:



where X is CN,^{45(a),48} C₂H₅,⁴⁶ $-(CH_2)_3-$,⁴⁶ OC₆H₅,⁴⁷ and OSi(CH₃)₃.

Because substituted diphenylmethyl radicals produced are less reactive for initiation but more reactive for PR termination, **36**^{46–48} can induce the living radical polymerization of MMA. The resulting polymer **37**, which has a weak bond at ω end, similar to **33** (eq 16), leading to the block copolymerization of St.⁴⁸ A model compound for this bond, **38** was prepared and was found to serve as a A–B-type thermal iniferter for the living radical polymerization of MMA to give a polymer with the same terminal group as **39** (eq 19):

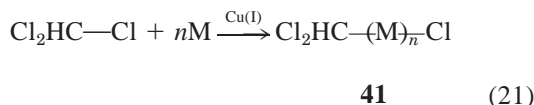
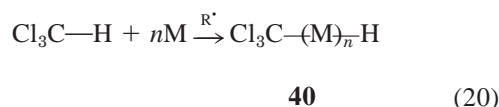


Sulfides

Some sulfides and disulfides have been expected to act as a thermal iniferter.²² Endo et al.⁵³ in our laboratory found that some cyclic alkylene disulfides could induce the living radical polymerization of St at 120 °C. The MW and MWD of the polymers increased with reaction time, and the block copolymers with MMA were also obtained with the resulting poly(St) as a polymeric iniferter.

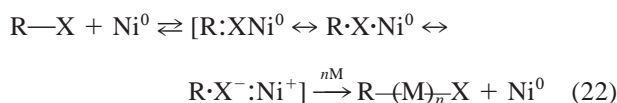
Halides

As shown in eq 7, telomerization proceeds by an insertion of monomer molecules into an X–Y bond in the telogen. When chloroform is used, monomer molecules are inserted into C–H and C–Cl bonds in CHCl₃, in the presence of AIBN and amine low-valent metal chlorides such as CuCl (amine) as initiators, to give **40** and **41**, respectively (eqs 20 and 21):^{50(a)(b),51}



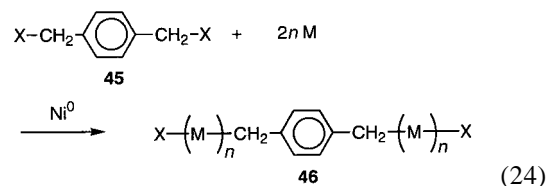
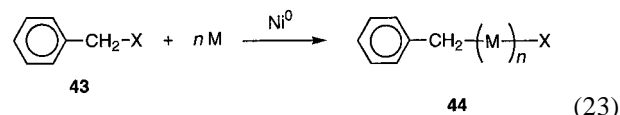
In the latter case (eq 21),^{50,51} it seems to serve as a redox iniferter; that is, Cl₂HC[·] and Cl[·], produced by one electron transfer in a metal complex with CHCl₃, participate in initiation and PR termination, respectively, to give a telomer.^{19,50,51}

Similarly, we have been studying since 1967 various metal-containing initiator systems⁵² of reduced nickel (50% Ni on Kieselguhr for the hydrogenation catalyst) and many type of halides, RX (X = Cl or Br), and found that polymer **42** was produced according to eq 22,^{53(e)} in which a halogen atom transfer occurs:



If benzyl halides (**43**) and *p*-xylylene dihalids (**45**) were used together with reduced nickel as A–B-type monofunctional and difunctional redox iniferters^{54,55} for St, respectively, polymers that had monofunctional and difunctional benzylic halide end groups bonded to one end of **44** and both ends of **46**, respectively, were obtained. These polymers of St, **44** and **46**, served as monofunc-

tional and difunctional polymeric iniferters (eqs 23 and 24) that induced the living radical polymerization of MMA, in the presence of nickel, to give block copolymers poly(St)-*b*-poly(MMA) and poly(MMA)-*b*-poly(St)-*b*-poly(MMA), respectively:



where X is chloride and bromide. Therefore, in a fashion similar to the case of dithiocarbamate photoiniferters, various type of polymers might be prepared. Recently, some binary systems, similar to redox iniferter, transition-metal compounds, and alkyl halides, were reported to induce living radical polymerization (discussed later).^{65,66}

LIVING RADICAL POLYMERIZATION WITH INIFERTERS^{56–60}

Characteristics of Radical Polymerization with Iniferters

As shown previously, various functional polymers have been synthesized with dithiocarbamate photoiniferters, which can principally induce further radical polymerization. Because radical polymerization proceeds by the low selectivity of a reactive propagating radical, it seems that relatively low-temperature (e.g., room temperature) photopolymerization is better for the controlled synthesis. Therefore, we mainly used photoiniferters in which dithiocarbamate compounds were adopted to easy preparation and functionalization. However, the iniferters cannot always induce living radical polymerization, from which the end groups of polymers produced from some iniferters should further dissociate thermally or photochemically into radicals, which can function as polymeric iniferters.

Similar to the relations in Figure 1, for example, time–conversion or time–molecular weight relations in the photopolymerization of St with **18** and **21**, as monofunctional and difunctional iniferters, respectively, and relations in the polymerization of MMA, not St, with **32** as a thermal iniferter, are shown in Figures 2 and 3,

respectively. There are some characteristic phenomena in radical polymerizations using these iniferters:¹⁹

1. The MW of the polymers increases as a function of reaction time (Figs. 1–3, Table II).
2. The MWD of the polymers also increases with time from a value of 2, which is obtainable for ordinary radical chain polymerization (Table II).
3. The number of iniferter fragments bonded to the polymer end is independent of reaction time (Table II).
4. The block copolymers are synthesized with polymers isolated from various stages of the polymerization.

These results, except an item (2) that is discussed later, are in agreement with the results of living anionic polymerization, discovered by Szwarc,⁶ and other ionic or coordination polymerizations; accordingly, these polymerizations seem to be performed via a living radical polymerization.

Living Radical Polymerization in Homogeneous Systems

History (~1981)

As is well-known, free radicals are classified from their lifetimes into long-lived, stable (less reactive) radicals and short-lived, unstable (reactive) radicals. Trityl radical **9** (eq 8) is long-lived radical that scarcely reacts with a monomer,²¹ but it readily reacts with short-lived reactive radicals such as the initiating or propagating radicals that exist in concentrations as low as 10^{-7} – 10^{-9} mol · L⁻¹.

These stable radicals have been used as a terminator of radical polymerization. However, some 1,2-disubstituted tetraphenylethanes (**36**; eq 18) were found early on (e.g., 1939) by Schulz^{45(a)} to serve as a weak initiator to give a polymer that was later confirmed to be **37** (X = CN; eq 18).^{47,48}

In 1967, Borsig et al.⁴⁶ reported that **36** [X = C₂H₅ and —(CH₂)₃—] induced the radical polymerization of MMA and that both the yield and MW of the resulting polymers increased with increased conversion. These observations might suggest a possibility for living radical polymerization. On the basis of these results and kinetic results, they pointed out that this compound has two functions: initiator and terminator.

In 1981, Bledzki and Braun⁴⁷ also found that 1,2-dicyano- and 1,2-diphenoxy-tetraphenylethanes (**36**) could initiate the oligomerization of MMA to give a functional oligomer (eq 18) that can further induce radical polymerization.

Our Model

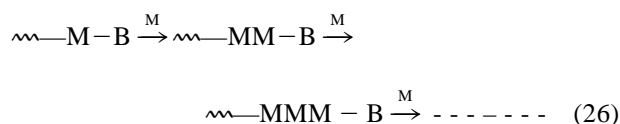
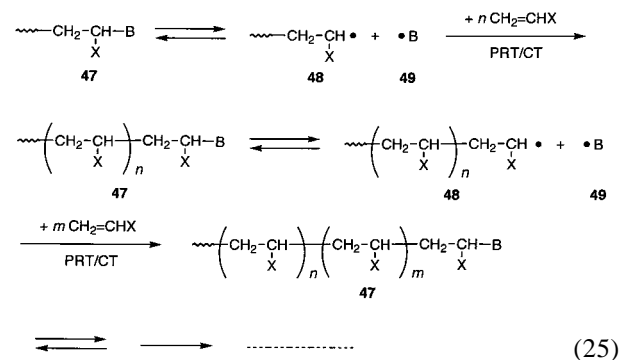
As pointed out in eq 8, the trityl radicals (**9**) exist in equilibrium with the dimer, hexaphenylethane (**10**).²⁰

This means that a precursor of radical **9** is **10**, which is a covalent compound, that is, a dormant species of **9**. Similarly, for eq 9 the dormant species (precursor) of intermediate radicals **2** and **4** are the stable covalent compounds **1** and **5**, respectively.

On the basis of these considerations and several experimental results shown previously, we proposed in 1982 a model for living radical polymerization using some iniferters,²³ as is shown in eqs 25²⁵ and 26. In our original article,²³ we wrote the following:

In order to find a system of living radical polymerization in homogeneous solution, one must try to form propagating polymer chain ends which may dissociate into a polymer A with a radical chain end and small radical B, which must be stable enough not to initiate a new polymer chain. Such a radical polymerization would proceed via a living mechanism, according to Scheme 1.

As an extreme case, if the polymerization proceeds via a stepwise insertion of one monomer molecule into the C—B bond (eq 1), (i.e. repeated cycles of slow dissociation, fast one monomer addition and fast recombination), it would result in a successive polymerization in which the propagating radical is represented by an intermediate radical paired with a stable small radical.



where eq 26 is the same with eq 1.²³ **47** is a polymeric iniferter that is a dormant species of propagating radical **48** (A in Scheme 1²³), which reacts competitively with monomers and the less reactive or nonreactive radical **49** (B in scheme 1²³ to reproduce **47**. The number of inserted monomer molecules is determined by the reactivity of radical **49** because in the case of dithiocarbamate photoiniferters, **49** (i.e., **2**) is a less (not non-) reactive radical that can react with a monomer to initiate polymerization. The probability of entering into PR termination seems to be not so high compared with stable

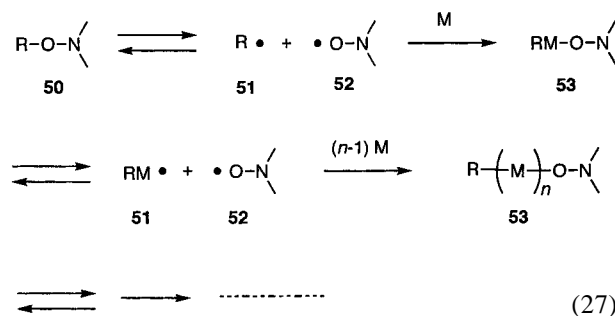
nitroxide (see eq 27), although CT to the iniferter does occur, as shown previously. From the results of no formation of the polymers with a narrow MWD under various conditions, and the MW of the polymers produced initially, more than 30 of St monomers seem to be inserted, by a chain mechanism, every dissociation of C—B bond (eq 25). This insertion reaction is greatly dependent on the reactivities of the intermediate radicals, **48** and **49**, and the concentrations of monomer and iniferter used.

As shown in eq 16, phenylazotriphenylmethane (**32**), which decomposes into a reactive phenyl radical and a nonreactive and stable trityl radical (**9**), as a thermal iniferter could induce the living radical polymerization of MMA, not St, as is described in the Features in Living Radical Polymerization with Iniferters section, with a good living nature (Fig. 3) to give poly(MMA) with a **9** end⁴⁴ (i.e., **56**). Similar results were also observed for **36**⁴⁸ and **38**.⁴⁹ In these cases, a dormant species is a sterically hindered, bulky hexasubstituted ethane bond (**56**; see the Features in Living Radical Polymerization with Iniferters section) at a terminal end.^{44,48,49} However, the poly(St) end, which has a less sterically hindered pentasubstituted ethane bond (**57**; see the Features in Living Radical Polymerization with Iniferters section), cannot decompose further below 100 °C.

Because the polymerizations of MMA with **36** and **38** proceeded with a relatively low living nature, some side reactions, such as disproportionation and substitution to a benzene nucleus in **9** (see the Features in Living Radical Polymerization with Iniferters section), seem to have occurred during the recombination between the propagating MMA radical and **9**,^{44,48} as is seen from a model (eq 25).

Other Models and a Comparison

In 1984, Rizzardo⁶⁴ reported a living radical polymerization with some alkoxyamines (**50**) at temperatures greater than 100 °C that dissociate into reactive alkyl or propagating radical (**51**) and stable nitroxide (**52**), which participates only in PR termination to give polymer **53** as an iniferter, according to eq 27:



In this case, a dormant species is a C—O bond. The reaction scheme in eq 27 interested us because it was

quite similar to our model but superior in its results. This technique was developed by Georges et al.⁶⁷ in 1993 from the recent nitroxide technique using 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO), by which nitroxide groups can easily be introduced into various polymers. These nitroxide compounds, as thermal iniferters, induce living radical polymerization of St at temperatures greater than 100 °C, according to eq 27, to give polymers with the controlled MW and MWD of poly(St) chains. This technique was the first successful example of preparing poly(St) with a narrow MWD by radical polymerization.

The other initiators for living radical polymerization are systems consisting of transition-metal compounds. In 1984, Mun and Sato⁶⁸ in our laboratory pointed out the possibility of a living radical mechanism for the polymerization of MMA using cobaltocene-bis(ethylacetoacetonato) copper(II), but more detailed results were not obtained. In 1993–1995, some promising initiator systems were found independently by three groups.

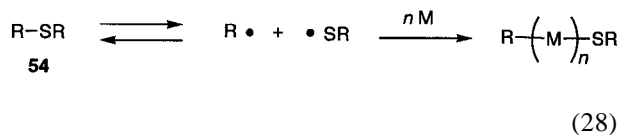
In 1994, Wayland's^{69(a)} group discovered the living radical polymerization of acrylates mediated by organocobalt porphyrin complexes. Davis et al.^{69(b)} both predicted and used some cobalt complexes for acrylate polymerization and obtained polymers with narrow MWDs (~1.2). They assumed, as Wayland's group demonstrated, that the C—Co(III) bond is a dormant species. Sawamoto⁶⁶ and Matyjaszewski^{65,70} independently reported that the binary systems of alkyl halides and transition-metal compounds, RuCl₂(PPh₃)₃ and CuCl(dipy), respectively, induce living radical polymerization in which a dormant species is a C—X bond, which can dissociate via one electron transfer in the metal complexes with X. For this polymerization, Matyjaszewski⁷⁰ coined in 1995 the term *atom transfer radical polymerization*, which was applied to the preparation of various functional block and graft polymers with narrow MWDs. In the same year, Percec's⁷¹ group discovered that aryl and alkyl sulfonyl halides act as universal initiators for the living radical polymerization of methacrylates, acrylates, and styrenes.

Features in Living Radical Polymerization with Iniferters

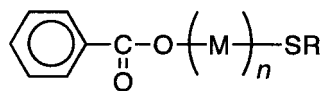
Dithiocarbamate Photoiniferters

As stated previously, dithiocarbamate compounds, which have a diethylthiocarbamyl-thiyl group [RS in R = (C₂H₅)₂NC(S)] including thiuram disulfides (**1**) and sulfides (**54**) and can easily be prepared, purified, and handled, have several advantages and a few disadvantages as iniferters in radical polymerization as follows.^{(61)a}

First, **1** (RS-SR) and **54** (R-SR) can serve as C-C and A-B-type thermal and photoiniferters for block copolymer synthesis, as in eqs 1 and 28, respectively:



In the presence of **1** and BPO without light, oligomer **55** is produced, similar to **7** in eq 7, which can act as an A-B-type polymeric photoiniferter and is also applied for the AB block polymer synthesis:



55

These results show that **1** is an efficient CT agent, and the derived RS serves as a PR terminator, an inhibitor for a bimolecular termination or crosslinking reaction, and a crossrecombinator to reform the RS end group (see the Living Radical Polymerization in Homogeneous Systems section).

Second, the RS group in dithiocarbamates, which has a λ_{max} value of 282 nm and an ϵ value of 10,500, functions as an A-B-type iniferter under the irradiation of light. RS' shows the same reactivity toward the monomer.^{29,31} When suitable RS compounds were used as monofunctional iniferter **18**, difunctional iniferter **21**, and tetrafunctional iniferter **24**, the observed rates by **21** and **24**³¹ were two and four times faster than those by **18**, respectively, as shown in part in Figure 2. For example, when the concentrations per one iniferter were kept constant, that is, $[\mathbf{18}] = [\mathbf{21}]/2 = [\mathbf{24}]/4$, all of the yields observed were on the same yield-time curve, but the MW of the polymers by **21** were two times higher than those by **18**.

These results strongly suggest that **18** and **21** induced living monoradical and diradical polymerizations to give AB and ABA block copolymers, respectively. When **24** was used for St, gelation occurred; however, the MW for the MMA polymerization by **24**, which proceeded without gelation, was 2.7 times higher, but not 4 times, than those by **18**, because of uncertainties in the formation of microgel and in the MW determination.³¹ From these results, the iniferter techniques using a selected dithiocarbamate are very useful method for various controlled polymer syntheses.

Third, an important disadvantage is no polymer being formed with a narrow MWD, as discussed previously

(see the Living Radical Polymerization in Homogeneous Systems section).

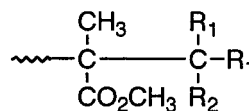
Fourth, a typical A-B photoiniferter such as **18** dissociates into a RS' and benzyl radical similar to the propagating poly(St) radical, but 1-phenethyl radical derived from the photolysis of the respective dithiocarbamate is more similar to this. Therefore, several photoiniferters, which give radicals quite identical to the respective propagating radicals produced from some monomers (St, MMA, MA, VAc), were prepared.⁶¹ All these photoiniferters induced the living radical polymerization of St. The observed results were almost the same as those with **18**.

Fifth, another limitation of this technique is the structure of the monomers. St and MMA and their derivatives can easily be polymerized by a living radical mechanism, but VAc and MA are polymerized with a low living nature or no living nature. The addition of **1**, as a source of RS', greatly improved the living nature.^{61,62}

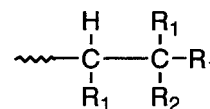
Thermal Iniferters

As stated in the Synthesis of Polymers with Thermal Iniferters and Living Radical Polymerization in Homogeneous Systems sections, some thermal iniferters, **32**, **36**, and **38**, induced the living radical polymerization of 1,1-disubstituted ethylenes such as MMA to give poly(MMA), **33**, **37**, and **39**, respectively, which can serve as polymeric iniferters for the living radical polymerization of MMA or the radical polymerization of St. However, these iniferters and **34** initiated the radical chain polymerization of monosubstituted ethylenes such as St to give poly(St), **33**, **37**, **39**, and **35**, respectively, which cannot induce polymerization.

The dormant species for the living radical polymerization of MMA is a C-C bond (**56**). However, **57**, produced from the radical polymerization of St, is not a dormant species that does not decompose (see the Living Radical Polymerization in Homogeneous Systems section):



56

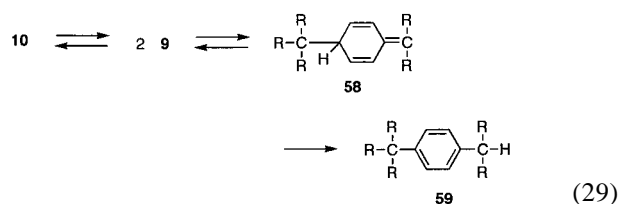


57

where $R_1 = \text{C}_6\text{H}_5$ and $R_2 = \text{C}_6\text{H}_5$ or CN. Therefore, in these thermal iniferters, the use of 1- or 1,1-substituted ethylenic monomer would control whether ordinary or living radical polymerization occurs.

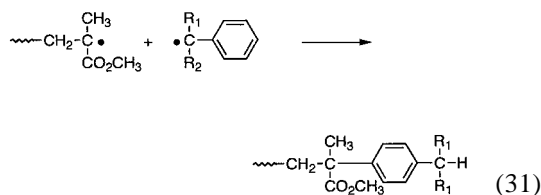
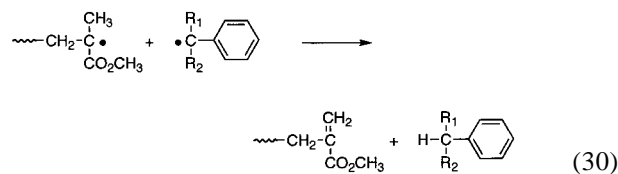
The polymerization of MMA with **36** and **38** proceeded with a relatively low living nature to give poly-

mers **37** and **39**, respectively, which led to block copolymer formation with St, even if in a low yield. From these observations, we remembered that the dormant species of trityl radicals (**9**) is not only hexaphenylethane (**10**) but 1-diphenylmethylene-4-triphenylmethyl-2,5-cyclohexadiene (**58**), as was pointed out by Lankamp et al.^{20(c)} in 1968, which then converts to **59** by an intramolecular or intermolecular hydrogen transfer (substitution), as in eq 29:



where R is C₆H₅.

Therefore, in the cases in which these thermal iniferters are used, some undesirable side reactions such as the disproportionation (eq 30) and substitution of the propagating poly(MMA) radical into the benzene nucleus of **9** (eq 31) seem to occur:



where R₁ = C₆H₅ and R₂ = C₆H₅ or CN. In the case of redox iniferters, these reactions seem unlikely.

These thermal iniferters have several disadvantages: preparation and functionalization are difficult, the block polymer yield is not so high because of side reactions, and 1,1-disubstituted monomers are only effective for living radical polymerization.

CONCLUSION

The history, ideas, and some characteristics of iniferters and living radical polymerization using some iniferters, which was proposed in 1982^{22,23} for controlled polymer synthesis, have been described. Three types of iniferters, dithiocarbamates, phenylazo or tetraphenylethanes, and

binary systems of halide-reduced nickel, have also been proposed and used as photo-, thermal, and redox iniferters, respectively. Among these iniferters, the well-designed dithiocarbamates are the most efficient photo-iniferters, inducing living radical polymerization that leads to various functional, block, graft, star, and crosslinked polymers with a normal MWD. For several years, some excellent iniferters and their systems of nitroxides,⁶⁴ using TEMPO⁶⁷ and containing some transition-metal complexes,^{65,66,70,71} have been developed for a precise living radical polymerization to synthesize various vinyl polymers with controlled MWDs and end structures.

More than 40 years have passed since the discovery of living polymers by Szwarc⁶ in 1956. Living radical polymerization, in which a living radical exists as a dormant species, that is, an iniferter, has now been established.

Moreover, 100 years have also passed since Gomberg's²⁰ first discovery of long-lived stable trityl radical, whose dormant species is its dimer hexaphenylethane (**10**), which is an iniferter. Thereafter, phenylazotriphenylmethane and tetraphenylethanes, which are derivatives of **10**, were used as the first initiators in 1939 by Schulz.⁴⁵ Therefore, the discovery of free radicals by Gomberg²⁰ was that of a weak initiator, that is, an iniferter, and the origin of a new radical polymerization, as stated in Case 2, which seems to be making a breakthrough and is now advancing into controlled specialty-polymer synthesis.

However, because ordinary radical polymerization, as shown in Case 1, has a number of advantages arising from the characteristics of intermediate radicals, which are electrically neutral and short-lived radicals, these radical polymerizations are the most effective technique for large-scale preparation, which may indicate a mature radical polymerization. More than 70% of the various vinyl polymers have been prepared industrially to be used as commodity materials.

The author is deeply indebted to his coworkers for this work, too many to be cited here, but whose names appear in the references. He also thanks his many coworkers who collaborated on other radical polymerization projects in the polymer laboratory of Osaka City University. This article and a recent review article (ref. 19) were made possible by a grateful collaboration with Associate Professor Akikazu Matsumoto, Osaka City University.

REFERENCE AND NOTES

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