Living Cationic Polymerization Toward Macromolecular Design: Synthesis of End-Functional Multiarmed Polymers

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LIVING CATIONIC POLYMERIZATION TOWARD MACROMOLECULAR DESIGN: SYNTHESIS OF END-FUNCTIONAL MULTIARMED POLYMERS

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ABSTRACT

A series of multiarmed polymers with terminal functional groups have been synthesized on the basis of living cationic polymerizations of vinyl ethers and p-alkoxystyrenes. The syntheses were performed by two methods, one via living polymerizations with new multifunctional initiating systems followed by endcapping of the resultant multifunctional living polymers, and the other using designed silyl enol ethers as multifunctional terminators (coupling agents) that combine two to four end-functionalized linear living polymers. These two methodologies thus led to telechelic and 3- or 4-arm star polymers and macromonomers with hydroxyl, acetate, methacrylate, and styryl end functionalities.

INTRODUCTION

The most fundamental requirement in macromolecular design is the precise control of polymerization reactions by which one can design and synthesize well-defined polymers. In chain-growth polymerizations there can be no doubt that "living" polymerizations offer the best methods to fulfill such requirements in the

†Present address: Chemical Laboratory, Sekisui Chemical Company, 2-1 Hyakuyama, Shimamoto-cho, Mishima-gun, Osaka 618, Japan.
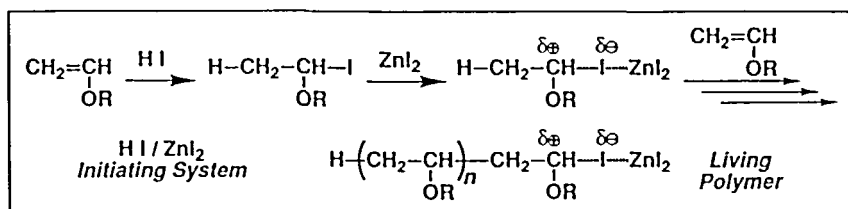
FIG. 1.   Living cationic polymerization of vinyl monomers: features and examples.

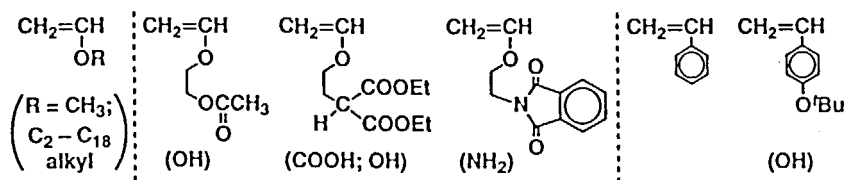precise control of macromolecular architectures. As briefly summarized in Fig. 1, we have been developing a series of living cationic polymerizations of vinyl monomers [1], which have long been considered very difficult because of the inherent instability of the growing carbocations involved therein. Most typically, living cationic polymerization can be induced by a binary mixture (initiating system) of hydrogen halide and a weak Lewis acid, such as the HI/ZnI$_2$ system illustrated in Fig. 1.

In addition to the control of polymer molecule weight and its distribution, the advantages and features of living cationic polymerizations may be summarized as follows:

(a)   Highly convenient, to be carried out simply under dry nitrogen without an elaborate vacuum-line technique and in some cases even above room temperature

(b)   Widely applicable to a variety of vinyl monomers, including those with polar pendant functional groups (Fig. 1)

(c)   Especially suited for functionalization, i.e., a variety of functional groups can be introduced into specific positions in controlled polymer architectures, such as chain ends and pendant substituents

(d)   Synthetically versatile, allowing the syntheses of not only linear but also multiarmed and other polymers with unique and controlled three-dimensional structures (spherical, cylindrical, etc.), as schematically illustrated below.
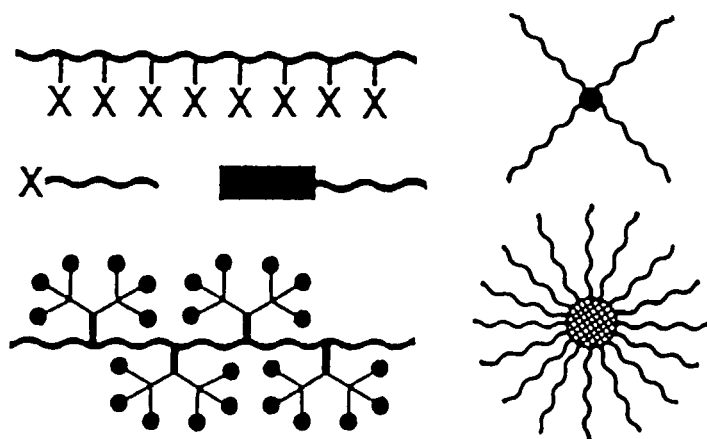
This paper describes a part of our recent study focused specifically on Features (c) and (d): the synthesis of end-functional multiarmed star polymers with uniform arm lengths, controlled molecular weights, and terminal functionalities.

END-FUNCTIONAL MULTIARMED POLYMERS: METHODOLOGY

End-Functionalized Polymers by Living Cationic Polymerization

In general, living polymerizations provide at least two methods for the synthesis of end-functionalized polymers, and this, of course, is the case for living cationic processes (Fig. 2). The two methods are based either on the initiation with a functionalized initiator (e.g., 1 in Fig. 2) or on the termination (endcapping) with a functionalized terminator (2). By judicious selection and combinations of these methods, a variety of end-functionalized polymers have been synthesized by living cationic polymerization [1, 2], including monofunctional, telechelic, and multiarmed polymers. As also summarized in Fig. 2, the versatility of the living cationic polymerizations can be attested by the wide variety of not only polymer structures to be prepared but also functional groups to be attached (hydroxyl, ester, vinyl, etc.) and monomers to be applied (vinyl ethers and styrenes, both nonpolar and polar or functionalized).

End-Functionalization of Multiarmed Polymers

The primary focuses of this article are how to construct multiarmed structures in a controlled fashion through living cationic polymerization and how to incorporate various functional groups therein. These can be accomplished by at least two methods, as Fig. 3 shows schematically for 4-arm star polymers. Both involve combinations of initiation and termination reactions and the use of multifunctional reagents: (A) multifunctional initiation and monofunctional termination (endcapping of multiarmed living polymers); (B) monofunctional initiation and multifunctional termination (coupling of linear living polymer chains). The following parts
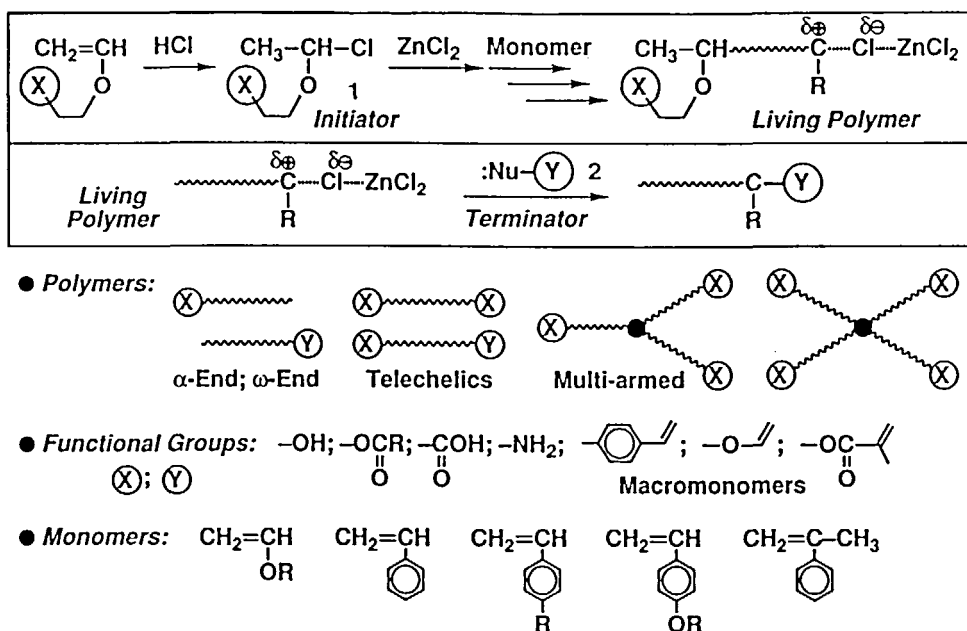
FIG. 2.   End-functionalized polymers by living cationic polymerization: methodologies and examples.

($\otimes$; $\circ{Y}$: Functional Groups)

● *Multifunctional Initiation – Termination*
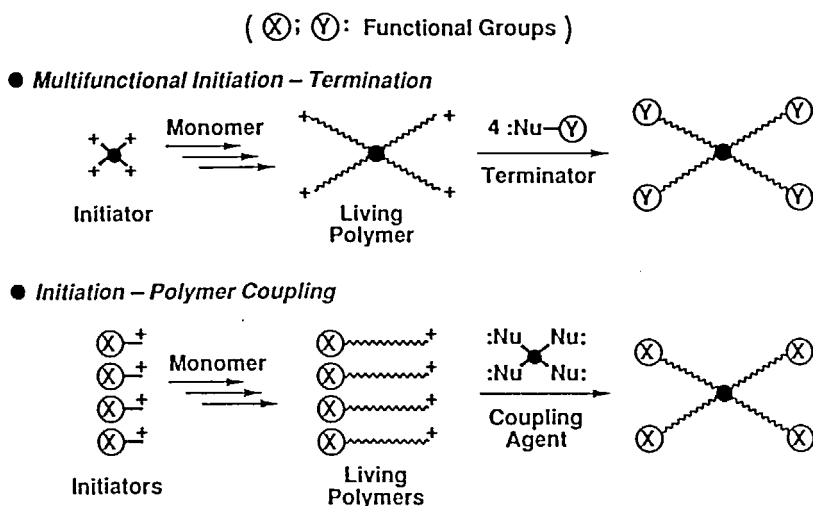
● *Initiation – Polymer Coupling*

FIG. 3.   End-functionalization of multiarmed polymers in living cationic polymerization: methodologies.

discuss examples for the syntheses via the two methods that have recently been used in our laboratories.

SYNTHESIS BY MULTIFUNCTIONAL INITIATION

Design of Multifunctional Initiating Systems

Evidently the key to this method is the development of multifunctional initiating systems that can induce living cationic polymerizations. We have recently developed tri- and tetrafunctional initiating systems (Fig. 4) for the living polymerizations of vinyl ethers and p-alkoxystyrenes [3–5]. The endcapping of the resulting multifunctional living polymers with suitable nucleophiles then permits the synthesis of end-functional multiarmed polymers, where the terminal groups include carboxylic acids (for vinyl ethers) [3, 5] and methacrylate (for p-alkoxystyrenes) [4]. The synthesis and application of the trifunctional initiating systems have been described in our recent papers [3, 4].

More recently, a tetrafunctional initiator has been developed as illustrated in Fig. 5 [5]. Thus a tetrafunctional phenol (3) is treated with an excess of 2-chloroethyl vinyl ether in the presence of sodium hydroxide in dimethyl sulfoxide to give the corresponding tetrafunctional vinyl ether (4). Subsequent addition of trifluoroacetic acid to each of the four vinyl groups in 4 leads to a tetraester (5) that is the target tetrafunctional initiator. As with the trifunctional counterpart (cf. Fig. 4) [3], 5 initiates living cationic polymerization of isobutyl and other vinyl ethers when it is coupled with ethylaluminum dichloride (EtAlCl$_2$) as an activator (Lewis acid) in the presence of an excess of 1,4-dioxane as a carbocation stabilizer (added base) [6]; Eq. (1) shows this initiation process.

$$\text{(1)}$$
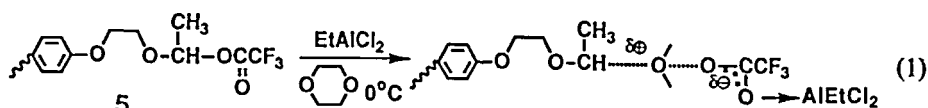
Importantly, in designing multifunctional initiators such as 5, a critical factor is the spatial separation of the multiple initiation sites (e.g., the four carboxylates in 5). Inspection of space-filling models for 4 and 5 demonstrates that the four functional groups therein are attached to the end of the four spacer arms that are radially connected to the cyclohexane core. Such separation apparently prevent intramolecular side-reactions during the addition of the carboxylic acid to the vinyl ether moiety.

This proposition is supported by the fact that a calix[4]arene derivative (6), another tetrafunctional phenol, can give the corresponding vinyl ether which, however, cannot be further transformed into a tetrakis(trifluoroacetate) similar to 5. In this case the cyclic structure arising from 6 brings the four vinyl ether groups into close vicinity and thereby facilitates intramolecular side-reactions in the presence of the acid.

End-Functionalization

The 5/EtAlCl$_2$ initiating system induces, for example, living cationic polymerization of isobutyl vinyl ether (IBVE) in the presence of 1,4-dioxane to give polymers with narrow molecular weight distributions (MWDs) and controlled molecular
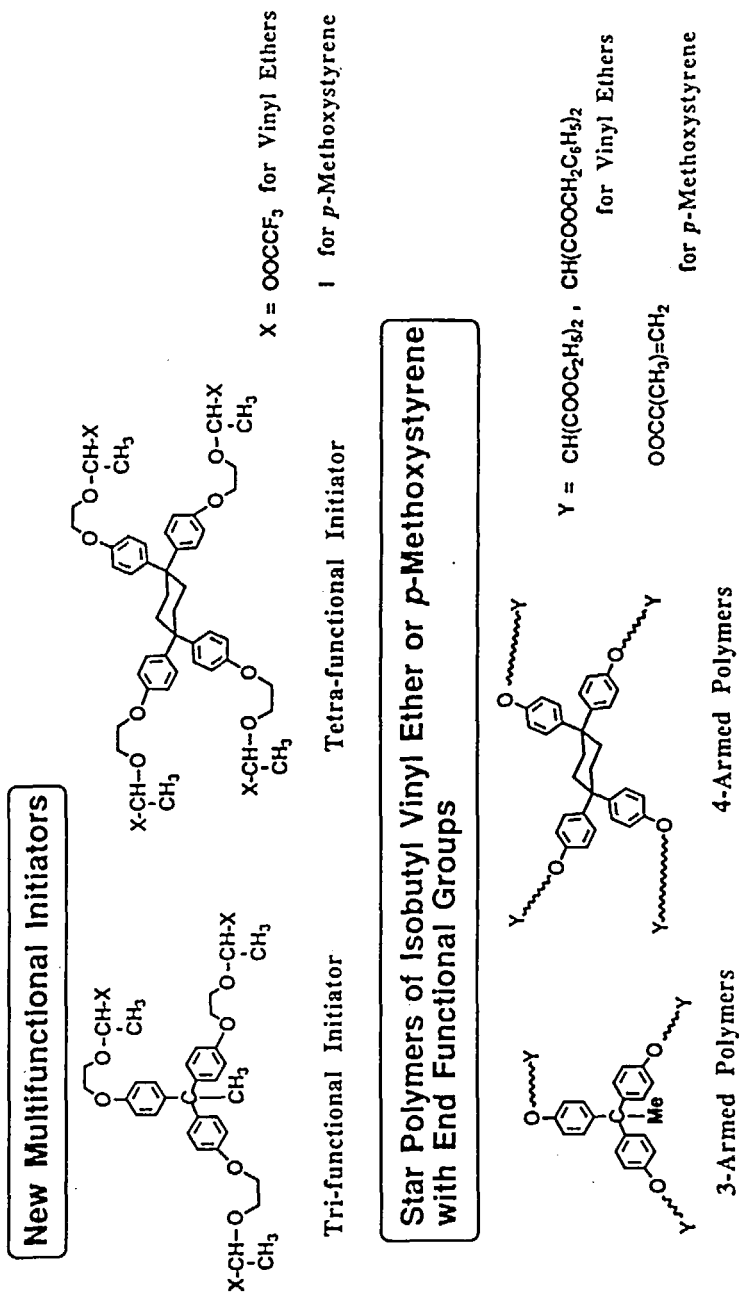
FIG. 4. Synthesis of 3- and 4-arm star polymers by living cationic polymerizations with multifunctional initiators.
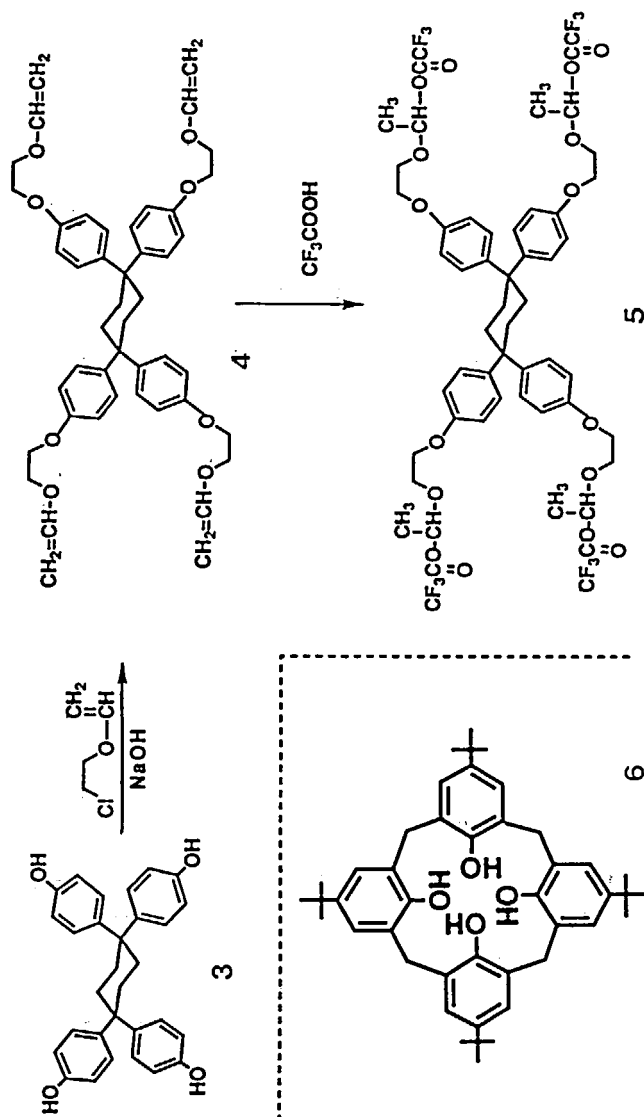
FIG. 5. Synthesis of a tetrafunctional intiator (5) for living cationic polymerization.

weights [5]. When unquenched, the resulting polymer (7) thus carried four living sites attached to four polymer chains of uniform lengths. These living sites can be endcapped by nucleophiles, most typically by the sodium salt of ethyl malonate (Eq. 2), into end-functionalized 4-arm star polymers such as 8 [7, 8]. NMR structural analysis shows the attachment of nearly four malonate functions per molecule.
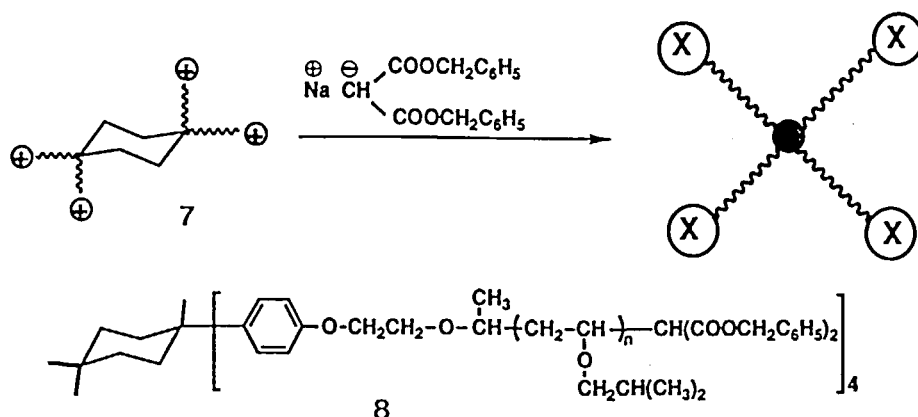
SYNTHESIS BY MULTIFUNCTIONAL TERMINATION

Design of Multifunctional Terminators

Although the endcapping reaction with the malonate anion (Eq. 1) is highly efficient and quantitative, its multifunctional versions [e.g., tris(malonate) sodium salt] are much less efficient as terminators for the synthesis of multiarmed polymers by polymer coupling reactions (cf. Fig. 3) [9]. The major reason for this is the low solubility of the multiple anions in organic solvents.

Noting this fact, we turned our focus to neutral and highly soluble terminating functions (nucleophiles) and have recently found that certain silyl enol ethers, both mono- and multifunctional, are highly efficient terminating agents for living cationic polymers [10]. Figure 6 shows examples of such enolate quenchers and their reactions with living poly(vinyl ethers). For example, monofunctional silyl enol ether 9 selectively and quantitatively attacks the chain end of the living poly(IBVE) (10) generated by the hydrogen chloride/zinc chloride initiating system [10]. The quenching reaction gives polymer 11 where the enolate is connected to the chain end through a ketone linkage.

Very similarly, the corresponding tetrafunctional silyl enol ether (12) cleanly and efficiently couples four linear living polymers (10) to form 4-arm star polymers (13) [11]. In contrast to the multiple malonates, enolate 12 and its bi- and trifunctional analogs are highly soluble in methylene chloride and other polymerization solvents and serve as excellent multifunctional terminators (chain couplers) for living cationic polymerizations. It is mandatory, by definition, that they must be added to living polymer solutions at the strict stoichiometry of [living end] = [silyl enolate group], and even under these conditions the enolates in 12 and its analogs

FIG. 6. Multifunctional silyl enol ethers for coupling reaction of living cationic polymers: reaction pathway and examples.

FIG. 7. Telechelic and end-functional 4-arm star polymers by polymer coupling reactions in living cationic polymerization.

are active and selective enough to undergo fast and quantitative termination to give 4-arm star polymers in high yields.

End-Functionalization

The development of multifunctional silyl enol ethers (12, etc.) permits us to synthesize end-functionalized, multiarmed polymers [12]. Thus, as shown in Fig. 7, the first step is the living polymerization of IBVE with a functionalized initiator (14) in conjunction with zinc chloride (activator) to yield a living polymer (15) carrying the α-end functional group (X) derived from 14. Functionality X may include acetate, methacrylate, and styryl.

These end-functionalized living polymers (15) are then terminated (chain-coupled) with 12 into 4-arm star polymers (16) that carry four terminal functions (X) at the end of each arm chain. Similar coupling reactions of 15 with the bifunctional counterpart of 12 lead to a series of telechelic polymers (Fig. 7). Among these end-functionalized polymers, those with methacrylate or styryl terminal groups are particularly interesting as novel multifunctional and star-shaped or telechelic macromonomers.

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