

TELECHELIC POLYMERS

Introduction

Telechelic polymers are defined as macromolecules that contain two reactive end groups. A pioneering work on the synthesis functional polymers and their conversion to the final products with specific properties by reacting with functional groups may be dated back to 1947 (1). However, the concept was not fully recognized until 1960 (2). Significant contributions to the development of this class of polymeric materials are still found in the current literature. In the last decade there has been a rapid growth in the development and understanding of new controlled radical polymerizations (3). Precise control of functionality, molecular weight, and uniformity (molecular weight distribution) can now be made not only by ionic polymerization routes but also by newly developed living radical polymerization (qv) techniques. Another striking development has been achieved in the metathesis polymerization. Many new catalysts have been developed and applied to preparation of advanced materials (4–8). The range of monomers and functional groups used in the preparation of telechelic polymers has been expanded in recent years as a result of such developments.

This article describes the general techniques for the preparation of telechelics. A special emphasis has been placed on controlled radical and metathesis polymerization methods.

A polymer can be considered to be telechelic if it contains end groups that react selectively to give a bond with another molecule. Depending on the functionality, which must be distinguished from the functionality of the end group itself, telechelics can be classified as mono-, di-, tri-, and multifunctional telechelics (polytelechelics) (9). The functionality is defined as

$$f = \frac{\text{Number of functional groups}}{\text{Number of polymer chains}} \quad (1)$$

Telechelic polymers can be used as cross-linkers, chain extenders, and precursors for block and graft copolymers. Moreover, star and hyper-branched or dendritic polymers are obtained by coupling reactions of monofunctional and multifunctional telechelics with appropriate reagents. Various macromolecular architectures obtained by the reactions of telechelics are represented in Figure 1.

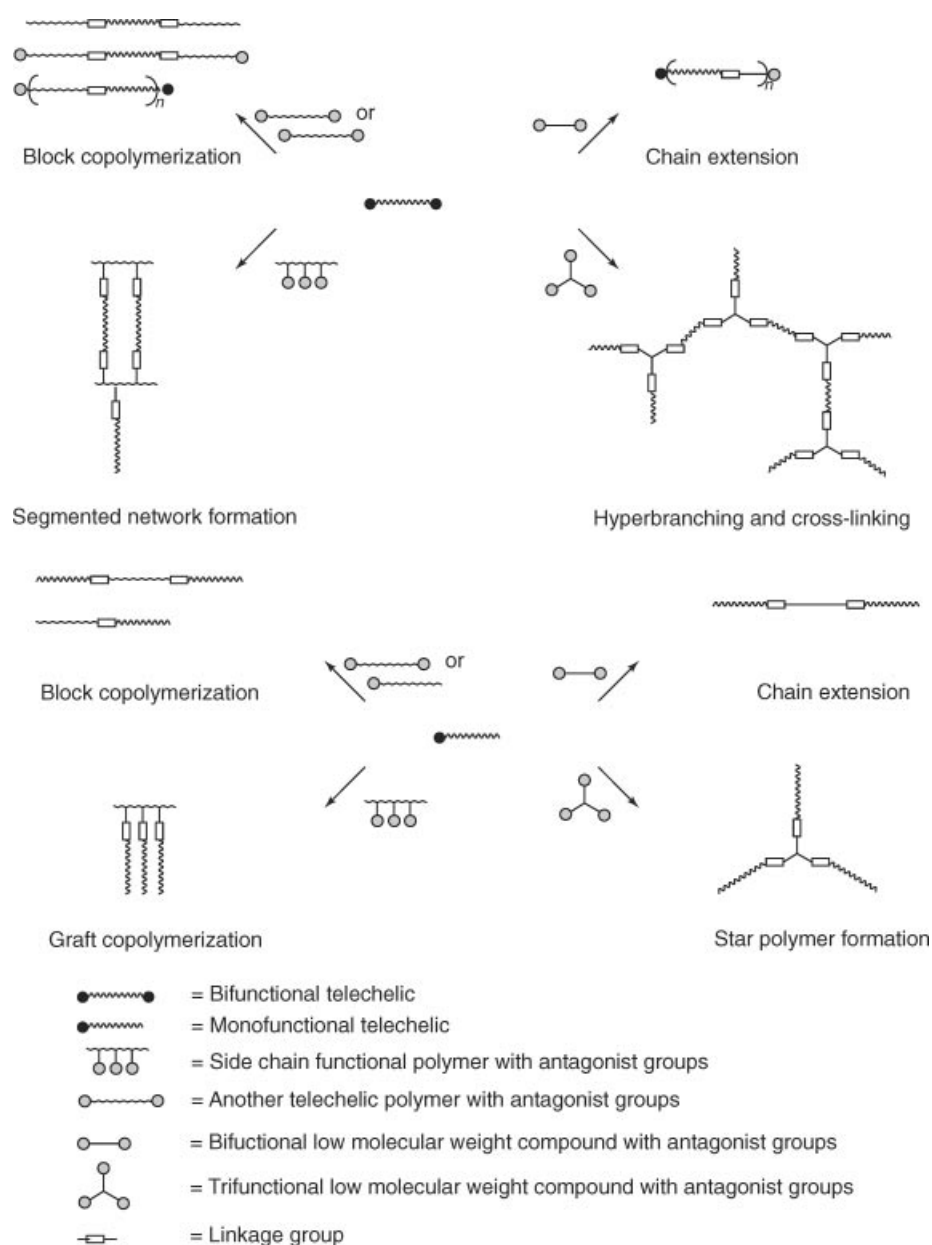


Fig. 1. Various architectures obtained by the reactions of telechelics.

The functionality of the end group itself is important. When such groups are bifunctional (eg, vinyl groups) they can participate in polymerization reactions, yielding graft copolymers or networks; such telechelic polymers are called macromolecular monomers, macromonomers, or macromers.

Industrial interest in telechelics was stimulated by the development of thermoplastic elastomers, which consist of ABA block and multiblock copolymers. Liquid telechelic polymers are the basis for reaction injection molding. Liquid telechelics that can be used for network formation offer processing advantages and may result in materials with improved properties (10).

Radical Polymerization

Free radical polymerization, is the most widely used methodology in synthetic polymer chemistry owing to its simplicity, applicability to many monomers, and relatively high tolerance to impurities and functional groups.

Conventional Radical Polymerization. Telechelics can be synthesized by radical polymerization (qv) in two ways: End groups can be controlled using a large concentration of (functional) initiator (dead-end polymerization), or polymerization can be conducted in the presence of suitable transfer agents (telomerization) (10–14).

The first method has serious limitations because well-defined end groups can be observed only if not more than one type of primary radical is formed that does not cause side reactions such as transfer. Moreover, a propagating radical will readily react with another radical, primary or macroradical, either through disproportionation or through coupling reactions (termination) (Fig. 2). The former will produce monofunctional telechelics with both a saturated and an unsaturated chain end, while only the latter will yield bifunctional telechelics.

Table 1 shows the percentage of termination by coupling (combination) for some common monomers (15).

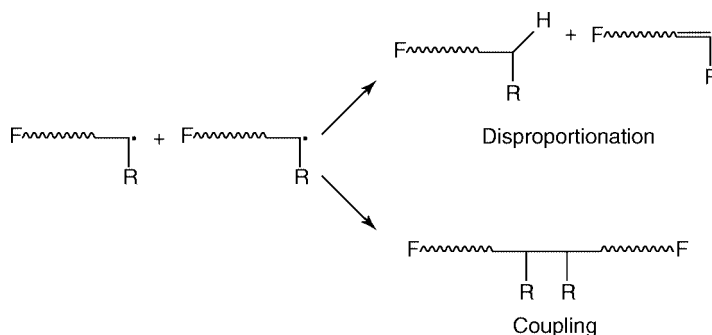


Fig. 2. Termination reactions.

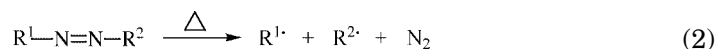
Table 1. Percentage of Termination by Combination of Different Monomers at 25°C^a

Monomer	Percent	Monomer	Percent
styrene	100	methyl methacrylate	33
<i>p</i> -chlorostyrene	100	ethyl methacrylate	32
<i>p</i> -methoxystyrene	81	<i>N</i> -butyl methacrylate	25
methyl acrylate	100	acrylonitrile	100
ethyl acrylate	100	methacrylonitrile	35

^aRef. 15.

Functional Initiators

Azo Initiators. In this section we report the preparation of telechelics involving thermally labile azo compounds. Upon heating, aliphatic azo compounds evolve nitrogen, thus forming two carbon-centered free radicals (see Initiators, Free-Radical).



The activation energies for this reaction are, supposing R¹ and R² are aliphatic, between 60 and 160 kJ·mol^{−1}. Azo groups are, therefore, a highly suitable radical source with respect to the energy required. Despite being thermally labile, azo groups are photoactive, too. Aliphatic azo groups evolve nitrogen with quantum yields as high as Φ = 0.44 (AIBN 16). However, the absorbance is relatively low, being ε = 13 cm²·mol^{−1} at λ_{max} = 350 nm (AIBN 17). In order to obtain telechelics, the initiating azo compound has to be at least bifunctional: it must carry one or more functional sites other than the azo function itself. Because of the potential variability in the chemical nature of the azo initiators it is possible to prepare telechelics with a wide variety of functional groups (Table 2).

Telechelics with certain functional groups can be prepared directly from the precursor initiators or, alternatively, via modification of the available telechelics. For instance, hydrolysis of nitrile groups yields carboxyl-terminated oligostyrene while isocyanate end groups are obtained directly from the azide telechelics or by treatment of amino-terminated polymers with phosgene (19). The functional group approach to synthesize amino telechelics causes some complications since amino compounds participate in chain-transfer reactions. Yagci and co-workers (37,38) proposed a convenient and simple synthetic route for the preparation of amino telechelics via free radical polymerization using (acyloxy) imino azoinitiator and subsequent photolysis and hydrolysis.

Table 2. Azo Initiators Used for the Synthesis of Telechelic Polymers

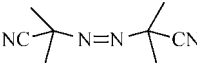
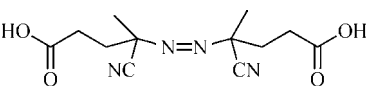
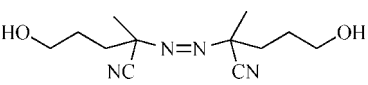
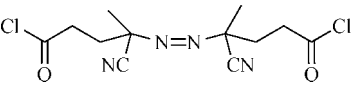
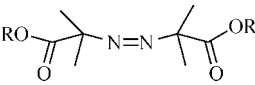
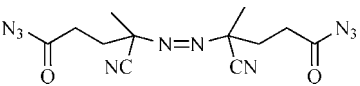
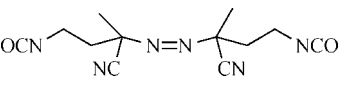
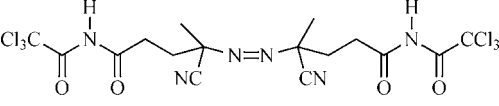
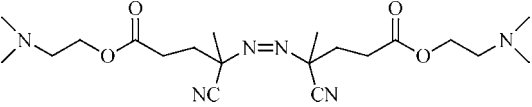
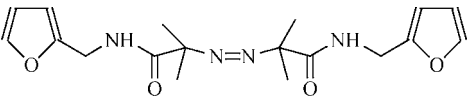
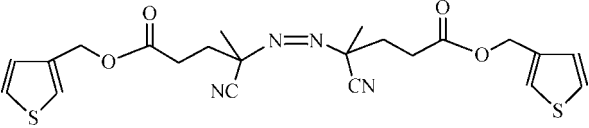
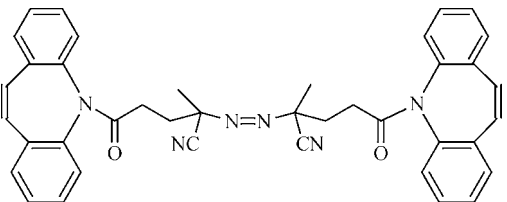
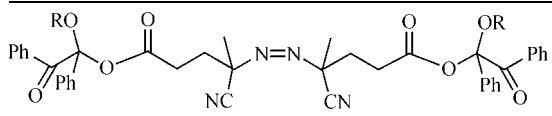
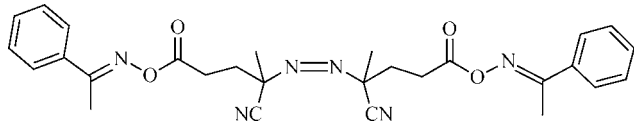
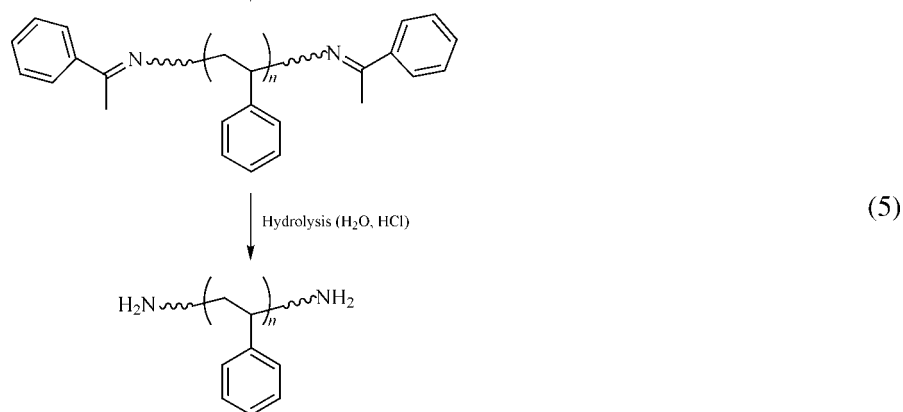
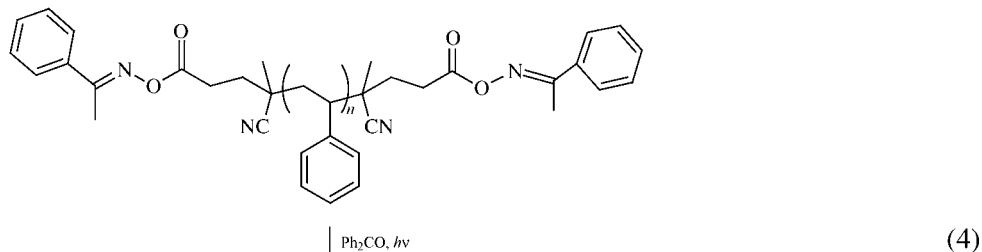
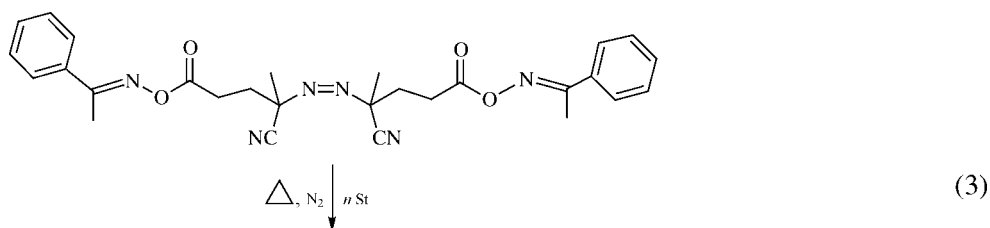
Structure of the initiator	Reference
	18–20
	21–27
	21–23,28
	29
	19
	30
	30
	31
	32
	33
	34
	35

Table 2. (Continued)

Structure of the initiator	Reference
	36
	37



Peroxide Initiators. Hydroxyl radicals formed by a redox reaction with H_2O_2 are highly reactive, and have not been reported for the small-scale preparation of telechelics. However, the industrial preparation of hydroxy-terminated butadiene oligomers probably involves such process (39).

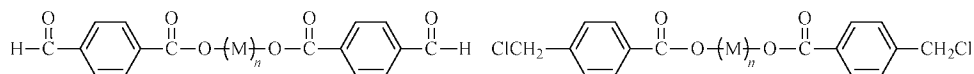
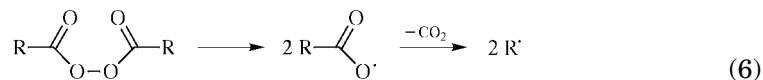


Fig. 3. Structure of telechelics obtained by functional benzoyl peroxide initiators.

Diacyl peroxide decomposition can yield two types of radicals ($\text{RCOO}^\bullet$, $\text{R}^\bullet$):

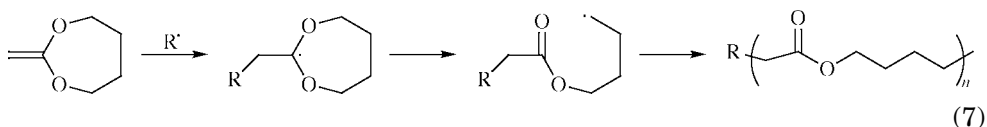


However, these peroxides have not been utilized for the preparation of telechelics. The less reactive aroyl peroxides give styryl telechelics (40). When employing benzoyl peroxides p-substituted with chloromethyl or aldehyde groups, the telechelics require no further modification before being used as prepolymers (Fig. 3).

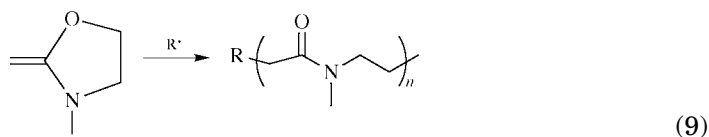
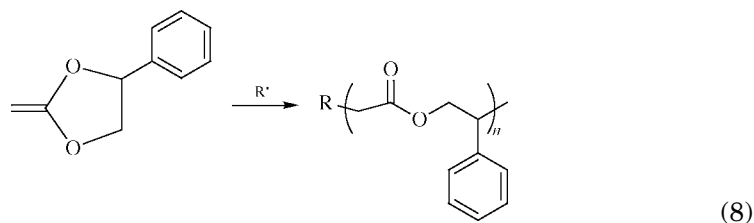
Ethylene polymerized with diethyl peroxydicarbonate contains terminal ester groups (41). Using ^{14}C -labeled cyclohexane peroxydicarbonate, the fate of the primary radicals during the polymerization of methyl methacrylate (MMA) and styrene has been studied (42). Although this reference includes no detailed analysis of the products, it indicates that ROOCO -terminated polystyrene telechelics may be obtained by this technique. A similar method has been used for the preparation of telechelic polybutadiene (43). The carbonate end groups are easily modified into terminal hydroxyl groups by hydrolysis. Hydrogenation of the carbonate functionalized telechelic polybutadiene, followed by hydrolysis, yields hydroxy-terminated polyethylene telechelics.

Free Radical Copolymerization of Alkenes with Unsaturated Heterocyclic Compounds

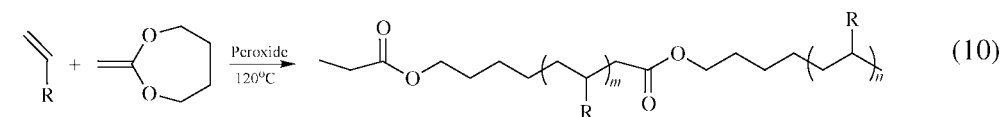
Free radical ring-opening polymerizations of unsaturated heterocyclic compounds are driven by formation of a carbon-oxygen double bond at the expense of a less stable carbon-carbon double bond. By the reaction mechanism outlined in reaction 7, the seven-membered keten acetals, such as 2-methylene-1,3-dioxepane, undergo essentially complete ring opening, leading to the corresponding polyester (44–51).



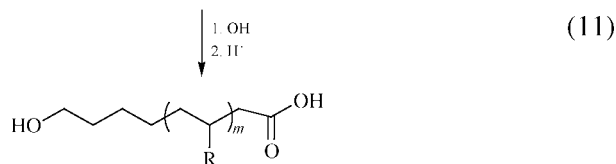
Similarly, the five-membered phenyl-substituted and nitrogen analogue monomers yield the corresponding polyester and polyamide.



Telechelic polystyrene and polyethylene containing a hydroxyl and a carboxylic end group are obtained by copolymerizing a small quantity of 2-methylene-1,3-dioxepane with a large quantity of styrene or ethylene, and then hydrolyzing the resulting polymers (reactions 10 and 11).

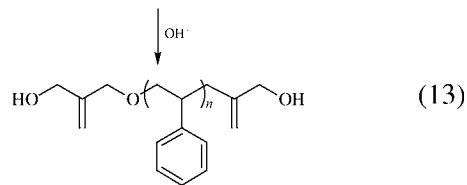
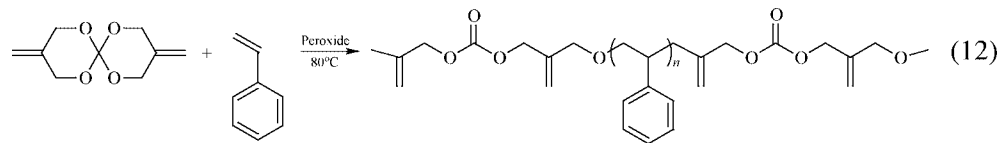


R = H or Ph



Copolymerization (qv) of common monomers with cyclic ketene thioacetals result in telechelics containing a thiol and a carboxylic acid group as chain ends.

Finally, the unsaturated spiro-*ortho*-carbonate shown in reactions 12 and 13 undergoes double ring opening during free radical copolymerization so as to introduce carbonate groups into the backbone of an addition polymer. Therefore, telechelic polystyrene containing two primary hydroxy chain ends is obtained by hydrolysis of the copolymer from styrene and the spiro monomer.



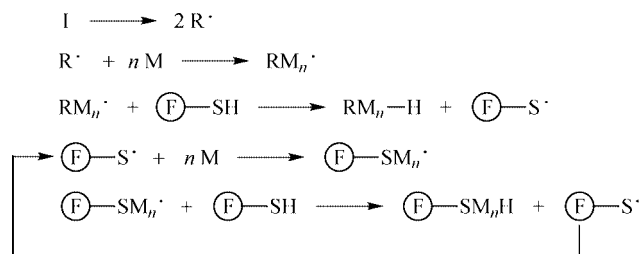
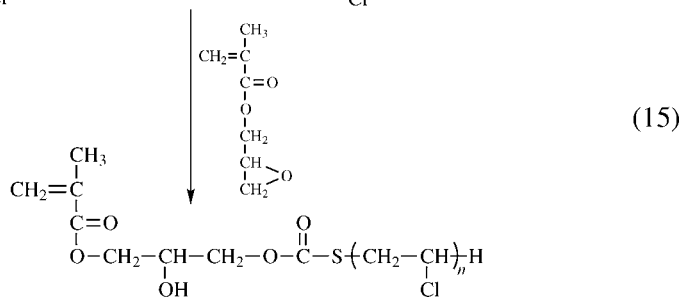
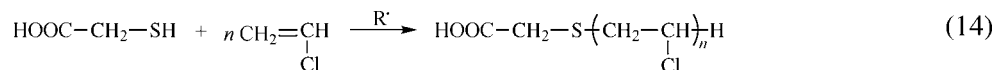


Fig. 4. Functionalization of polymers by chain transfer agents.

Transfer Techniques

Transfer Agents. In free radical polymerization, thiols are often employed as chain transfer agents. Chain transfer reactions involving thiols proceed via hydrogen atom abstraction as illustrated in Figure 4.

Consequently, these molecules do not offer any scope for introducing functionalities at both ends. However, monofunctional telechelics have been successfully prepared by using thiols. For example, Boutevin and co-workers (52,53) introduced polymerizable vinyl groups to poly(vinyl chloride) (PVC) according to that strategy. 3-Mercaptopropionic acid has been used as functional chain transfer agent producing a PVC with one carboxylic acid end group (reaction 14). This monofunctional telechelic was converted into a macromonomer according to reaction 15.



Polystyrene macromonomers (54) with molecular weight of 10^3 – 10^4 were also prepared. Polymerization of methacrylate or vinyl chloride in the presence of 2-mercaptoethanol (55,56) and subsequent treatment of the resulting polymer with methacryloyl chloride led to methacryl end capped polymethacrylates and PVC.

Free radical polymerization in the presence of a chain transfer agent (telogen) is often called *telomerization reaction*. Many different telogens have been reported (57); the most studied and well-documented telogen is CCl_4 (Fig. 5).

CBr_4 and CHI_3 are not suitable owing to their very high transfer constant, which yields only oligomeric materials.

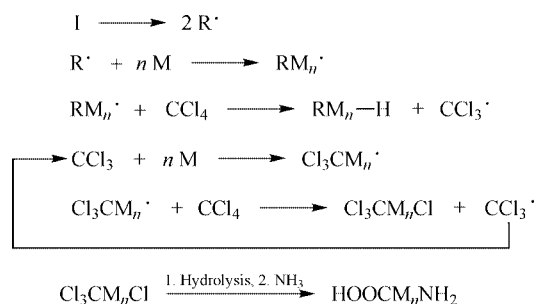
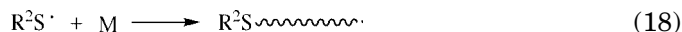
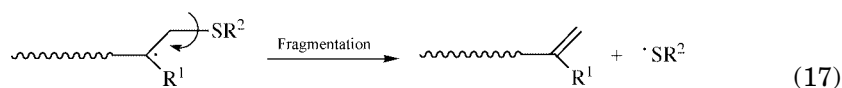
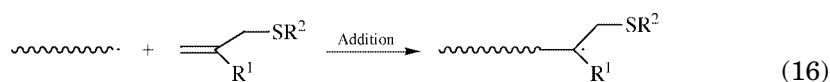


Fig. 5. Telomerization: Synthesis of α,ω -aminoacids.

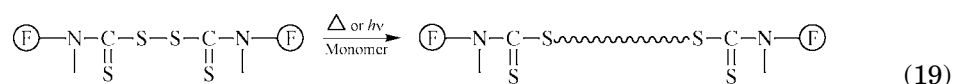
Addition–Fragmentation Agents. In recent years, addition–fragmentation reactions turned out to be a versatile and exceptionally interesting tool for polymer synthesis. These reactions aim at gaining control over molecular weight and make it possible to synthesize end-functionalized polymers, often macromonomers, which may further be employed in block or graft copolymerization (58–60). The principle of addition–fragmentation type reactions can be described briefly as follows: Free radicals, macro radicals, add to olefinic double bonds of a specially designed addition–fragmentation agent. The intermediate thus produced is relatively unstable and prone to fragmentation, what mostly means β -fragmentation. In this step a new radical is generated, which initiates polymerization. As a result, a growing radical chain has been terminated and a new chain initiated (chain transfer) (61). addition–fragmentation reactions combine the advantage of high efficiency in chain transfer with the possibility of end-functionalizing the polymer. Thus, macromonomers and mono- and bifunctional polymers are prepared when functionality is introduced into one or both of the substituents R^1 and R^2 , as illustrated in the example of allylic sulfides.



Other allylic compounds which participate in addition fragmentation reactions and yield telechelics analogous to allylic sulfides include allylic bromides, allylic phosphonate, allyl peroxides, and allylic stannane and vinyl ethers (62).

Iniferters. The peculiar behavior of thiuram disulfides in free radical polymerization was first identified by Tobolsky (63,64). These molecules can act simultaneously as an *initiator*, chain transfer agent, and *terminator* in a polymerization reaction and generally referred as *iniferters* by analogy to their role (65,66). Photochemically and thermally activated iniferter characteristics of thiuram disulfides

led to the derivation of telechelics. Telechelic preparation is based on the concept of locating the required function on the alkyl group of the thiuram disulfide and using it in the photo or thermal polymerization. Since end groups are introduced via initiation and transfer and common bimolecular termination between two growing chains are negligible, perfect bifunctional telechelics are available along this route.



Several functional disulfides and substituted tetraphenylethylenes were also used as iniferters in free radical polymerization. Table 3 shows various functional iniferters used for deriving telechelics.

The functionalities of the telechelics prepared by iniferter method were reported to be close to 2, within experimental error. The formation of the nonfunctional polymers was claimed to be negligible because of the triple function of the iniferter.

Controlled Radical Polymerization

Accurate control of polymerization process is an important aspect for the preparation of well-defined telechelics and end-functionalized macromolecules. Such control of chain ends was traditionally accomplished using living ionic polymerization techniques. But it is well known that the ionic processes suffer from rigorous synthetic requirements and in some cases they are sensitive to the functional groups to be incorporated. As described above in detail, free radical polymerization is flexible and less sensitive to the polymerization conditions and functional groups. However, conventional free radical processes yield polydisperse polymers without control of molecular weight and chain end. Competing coupling and disproportionation steps and the inefficiency of the initiation steps lead to functionalities less than or greater than those theoretically expected. Recent developments in controlled/living radical polymerization provided the possibility to synthesize well-defined telechelic polymers with controlled functionality also with radical routes (75). As it will be shown below, all the three standard methods for controlled/living radical polymerization, namely atom transfer radical polymerization (ATRP) (76,77), stable free radical mediated polymerization (SFRP), also called as nitroxide mediated polymerization (NMP) (78), and reversible addition-fragmentation chain transfer polymerization (RAFT) (79), were used for the preparation of telechelic polymers.

Atom Transfer Radical Polymerization. Atom transfer radical polymerization (ATRP) (80,81) involves reversible homolytic cleavage of a carbon-halogen bond by a redox reaction between an organic halide (R-X) and a transition metal, such as copper(I) complexed with 2,2'-bipyridine (bpy), as illustrated in reaction 20:

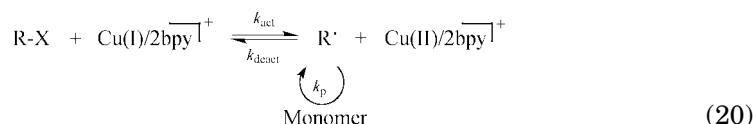
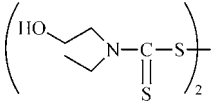
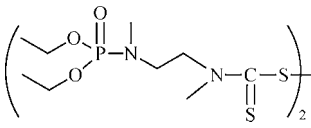
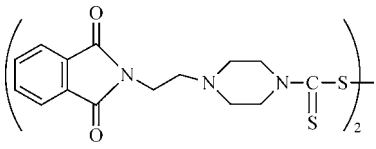
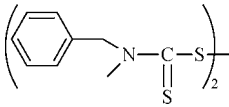
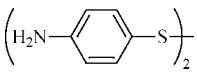
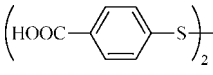
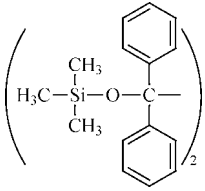
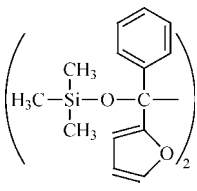
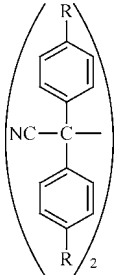


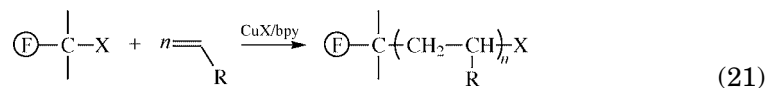
Table 3. Iniferters and End Groups

Iniferter	Monomer ^a	Functional group	Reference
	MMA	OH	67
	MMA, St	Phosphorylamide	68
	Isoprene	NH ₂	69
	MMA, St	Phenyl	70
	St, <i>t</i> -BA	NH ₂	71
	St	COOH	71
	MMA	OH	72
	MMA, BA, STA, St	Furanyl	73
	MMA	R = Cl, C(CH ₃) ₃	74

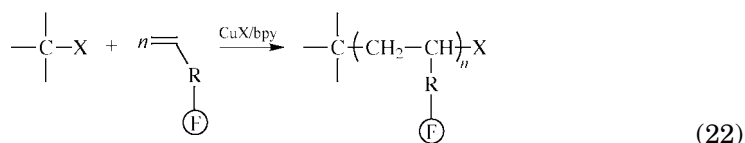
^aMMA: methyl methacrylate, St: styrene, *t*-BA: *tert*-butyl acrylate, STA: stearyl acrylate.

Polymer functionalization by ATRP can be achieved by using functional initiators and monomers and the chemical transformation of the halogen end groups. These routes are summarized in reactions 21-23.

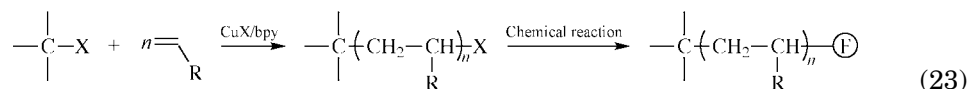
Through Initiator Functionality



Through Monomer Functionality



Through Chemical Reaction of Halide End Groups



Quite a number of functional initiators were successfully used in ATRP to prepare functional styrene and acrylate type polymers (82). For this purpose initiators should be equipped with the desired functional groups as well as with a radical stabilizing group on the α -carbon atom such as aryl, carbonyl, nitrile, and multiple halogens to ensue successful ATRP. Notably, direct bonding of halogen to aryl or carbonyl group does not facilitate radical generation. In this connection, it should also be pointed out that any functionalities in the initiator should not interfere with ATRP, ie, should be inert to catalyst. The telechelic polymers prepared by using functional initiator approach in ATRP are presented in Table 4, along with the functional groups. Carboxylic acid functionalization by ATRP is rather difficult since the acid functionality poisons the catalyst. However, ATRP of MMA by using 2-bromoisobutyric acid was reported to proceed. Various protected initiators were also reported for carboxylic acid functionalization (113,114). Hydrolysis of the protecting groups yields polymers with the desired carboxylic acid functionalities.

Some other functionalities including bifunctionalities (115–117) were introduced to polymers by ATRP. Substituted aromatic and aliphatic sulfonyl chlorides were shown to be efficient initiators for ATRP and were used as initiators for the incorporation of functionalities to polystyrenes and polyacrylates (118). In these applications heterogeneous $\text{CuCl}(\text{bpy})_3$ systems were utilized.

Obviously, ATRP leads to the formation of monofunctional telechelics since the other chain always contains halogen as a result of the fast deactivation process. These polymers could be called *heterotelechelic* since halogen is also a functional group. Therefore, α,ω -telechelics can only be prepared by transformation of the

Table 4. Monofunctional Telechelic Polymers Prepared by Using Functional Initiators in ATRP

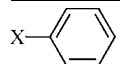
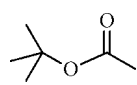
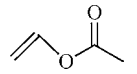
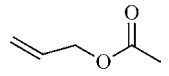
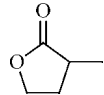
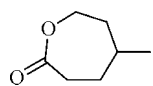
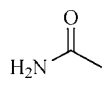
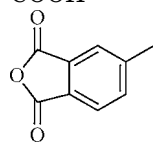
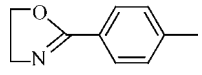
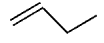
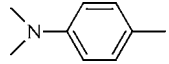
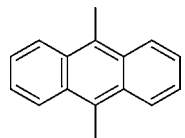
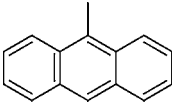
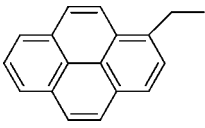
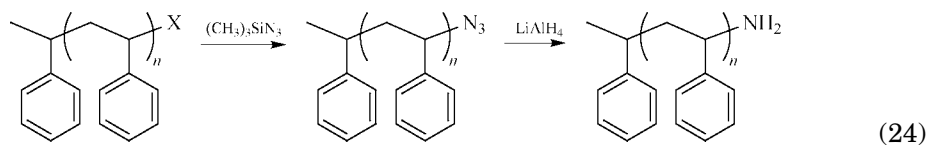
Functional group	Polymer ^a	Reference
		
X = H, CH ₃ , Br, CN, NH ₂ , CHO, NO ₂ , OCH ₃	PSt, PMA	83–87
CN	PSt, PMA	88–90
	PSt, PMA, PtBA	
	PSt, PMA	85
OH	PSt, PMA, PBA PMMA	87,91–98
	PSt	99
	PSt, PMA	100
	PSt, PMA	85
		87
	PSt	85
COOH	PMMA	101
	PSt	102
	PSt	102
	PMA	103–105
	PSt	106
	PSt	107

Table 4. (Continued)

Functional group	Polymer ^a	Reference
	PMMA	108
	PSt	109,110
	PMMA	111
	PSt, PMMA	112

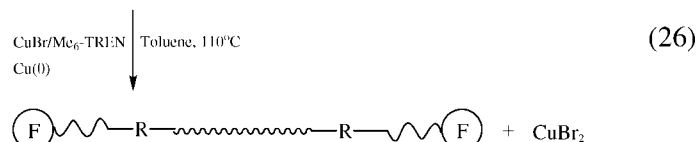
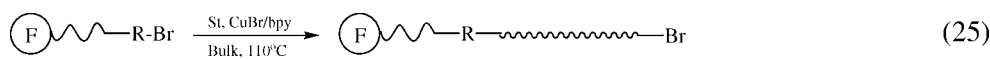
^aPMMA: poly(methyl methacrylate), PSt: polystyrene, PBA: poly(butyl acrylate), PtBA: poly(*tert*-butyl acrylate), PMA: poly(methyl acrylate).

halide end group by means of nucleophilic substitution, free radical chemistry, or electrophilic addition catalyzed by Lewis acids (119). Typical example of such displacement is represented in reaction 24, which illustrates the reactions used to replace the halogens with azides and consequently leading to amino-functional telechelics (120,122).



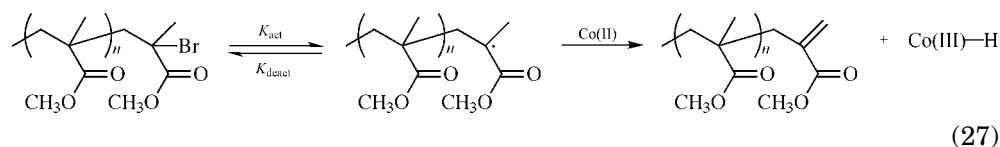
Other examples of halogen atom displacement to produce alcohol, C₆₀, epoxy, maleic anhydride, triphenylphosphine, and ketone functionalized polymers are described in the literature (123–125). The halide displacement is particularly important to prepare bifunctional hydroxy telechelics, which find application in the preparation of segmented polyester and polyurethanes (126). In such applications the first hydroxyl group can be incorporated by using hydroxy-functional initiator derivatives (127). The second hydroxyl group functionalization can then be achieved by direct displacement of halogen group with an amino alcohol or utilizing allyl alcohol. Diols can also be prepared by coupling of monohydroxy functional polymeric halides. In this connection it is noteworthy to mention the recent work (106) regarding atom transfer coupling process for the synthesis of bifunctional telechelics. Polymers monofunctionalized with aldehyde, aromatic hydroxyl, dimethyl amino groups were obtained by ATRP of styrene using functional initiators in the presence of the CuBr/bpy catalytic complex. Bifunctional

telechelics with double molecular weights as compared to the starting materials were prepared by coupling of monofunctional polymers in atom transfer radical generation conditions, in the absence of monomer, using CuBr as catalyst, tris[2-(dimethylamino)ethyl]amine (Me₆TREN) as ligand, Cu(0) as reducing agent, and toluene as solvent. The overall process is depicted in reactions 25 and 26.

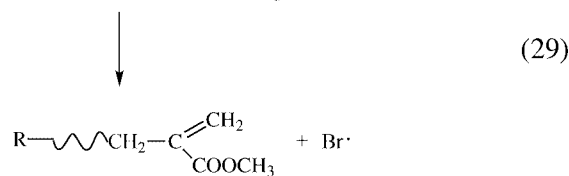
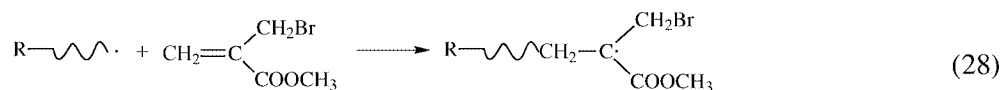


where $\text{(F)} = \text{CHO, OH, COOH, N(CH}_3)_2$

Incorporation of unsaturated end groups to polymers by ATRP is limited to certain groups. Only allyl and vinyl acetate groups were successfully incorporated (Table 4). Other polymerizable groups such as epoxides and oxazolines are not reactive toward radicals. In order to produce polymers with a more reactive unsaturated end groups such as methacrylates, a combined ATRP and catalytic chain transfer process was proposed (128). In this methodology, the catalytic chain transfer agent was added to the ATRP of MMA near to the end of polymerization, leading to the formation of ω -unsaturated PMMA macromonomer with low polydispersity and controlled molecular weight (reaction 27).

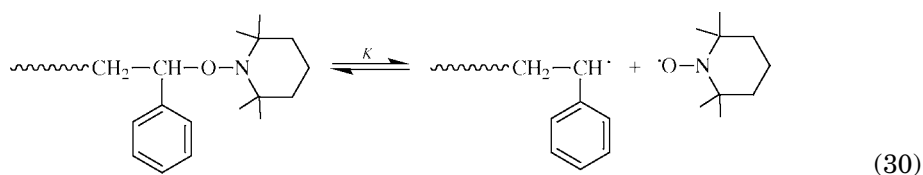


Here, the CTC agent acts as a chain transfer terminator but does not initiate new chain in the classical manner. Similarly, Haddleton and co-workers (129) used methyl(2-bromomethyl)acrylate in transition-metal-mediated controlled radical polymerization to replace the ω -halogen end group via addition–fragmentation to yield a methacrylate-based macromonomer.

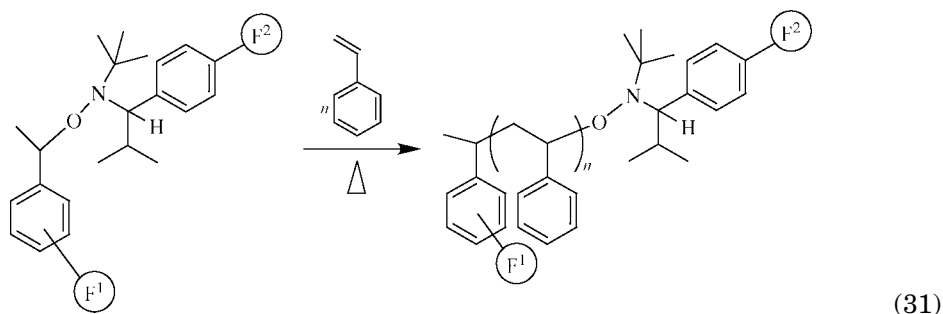


More recently, a convenient, one-pot synthesis of telechelic polymers with unsaturated end groups was developed (130). Addition of excess ethyl(2-bromomethyl)acrylate to ATRP of acrylate monomers after 80–90% conversion resulted in the formation of mono- and bifunctional polymers. The average degree of end functionality was almost quantitative ($f = 1$ for a monofunctional and $f = 2$ for a bifunctional initiator).

Nitroxide Mediated Living Radical Polymerization. Another controlled radical polymerization developed in recent years is stable free radical mediated polymerization (SFRP), also called as nitroxide mediated radical polymerization (NMP) (78,131). This type polymerization can be realized through reversible deactivation of growing radicals by stable radical such as 2,2,6,6-tetramethylpiperidinyloxy (TEMPO).



It is possible to prepare telechelic polymers by NMP procedure since it tolerates a wide variety of functional groups (78). For the synthesis of telechelics by NMP there are two general methods, ie, functional groups can be placed at the initiating chain end, F^1 , or the nitroxide mediated chain end, F^2 .



Telechelics with a variety of functional groups can essentially be prepared by using functional nitroxides (Table 5).

It was reported that high degree of functionalization, ie, greater than 95%, is possible even at molecular weights up to 50,000–75,000 by NMP method (152).

A wide variety of functional groups including polynuclear aromatic pyrene group can also be introduced by taking advantage of monoaddition of maleic anhydrides and maleimide derivatives to alkoxy amine end group followed by elimination of mediating nitroxide radical (153). The thermal stability of the telechelics was increased as the alkoxyamine group was removed.

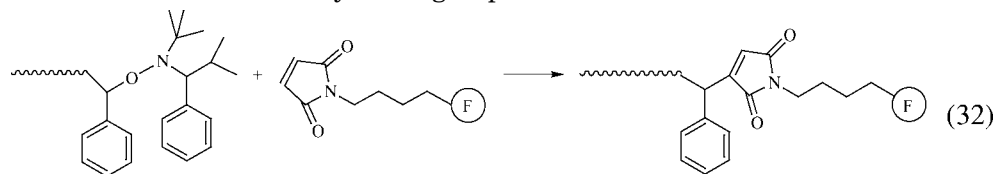
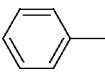
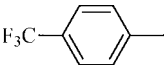
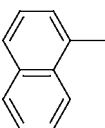


Table 5. Functional Groups Attached to Polymers by Nitroxide Mediated Living Free Radical Procedures

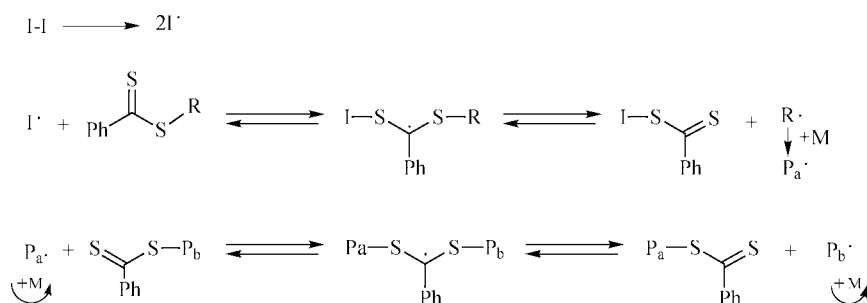
Functional group	Reference
OH	132–140
	141,142
	140
	143,144
	137,144–147
CN	141,148
PO(OR) ₂	141,149–151
P(O) ₂ OH	140
NH ₂	78
COOH	78

Reversible Addition–Fragmentation Chain Transfer Polymerization.

Controlled radical polymerization can also be achieved by reversible addition–fragmentation chain transfer polymerization (RAFT) (79). In this technique, after the initiation, the RAFT agents reversibly deactivate the polymer chains as the rate constant of chain transfer is faster than the rate constant of propagation (Fig. 6).

Telechelics can be prepared by RAFT process by selecting suitable RAFT agents (79).

Among the controlled radical polymerization methods discussed here, ATRP is the most applied route for the preparation of telechelics since besides the initiator functionalization, the terminal halogen produced in ATRP can easily be converted to many useful functionalities, eg by nucleophilic substitution (82).

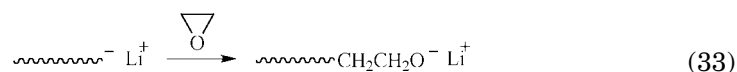
**Fig. 6.** Reversible addition–fragmentation chain transfer polymerization (RAFT).

Displacement of nitroxides and dihydroesters is more difficult in respective NMP and RAFT processes.

Anionic Polymerization

Anionic Polymerization (qv) (154–159) and, in particular, living polymerization can be used for the synthesis of telechelics. Living polymerization is characterized by the absence of termination and transfer and, when initiation is rapid and quantitative, by narrow dispersity that can be described by a Poisson distribution, and by linear increase of molecular weight with conversion. The propagating species are carbanions or other negatively charged species. Bivalent growing chains allow the generation of two terminal end groups and the facile synthesis of telechelic polymeric materials, depending on the monomer, initiator, solvent, and termination agent (160).

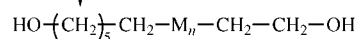
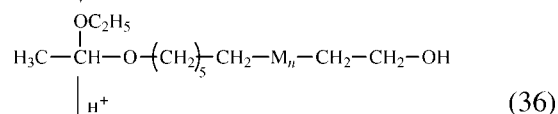
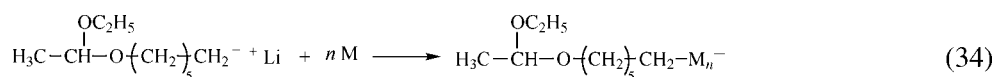
Hydroxyl End Groups. Living polystyrene is terminated by the addition of oxirane, which generates hydroxylate end groups (161,162).



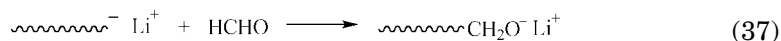
The alcoholate ion can initiate the polymerization of ethylene oxide, but the rate is low enough so that polyether formation can be avoided by quenching immediately after termination (163).

Other monomers, such as butadiene (164) and isoprene (165), have been polymerized and hydroxylated by the reaction of the corresponding living polymers with ethylene oxide. Bifunctional living polybutadiene has been generated in hexane using living oligomeric isoprene or 2,3-dimethylbutadiene as initiator (166). The hydroxyl functionality varies between 1.7 and 2.0.

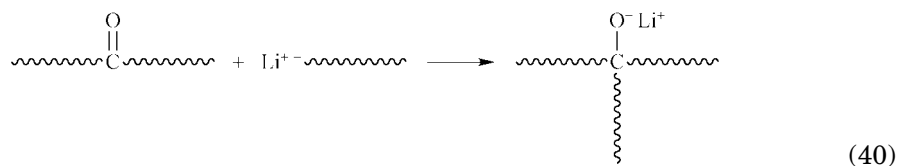
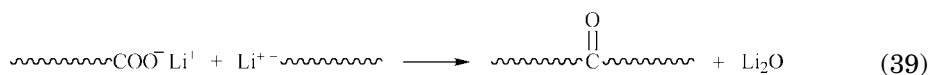
Organolithium initiators with blocked hydroxyls increase the functionality of the products since one OH function is introduced with the initiator and the other one via termination, eg with oxirane (167).



Formaldehyde can also be used as termination agent yielding OH end groups (159).

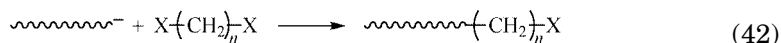


Mercapto End Groups. Living polystyrene reacts quantitatively with thiirane to form terminal mercapto groups (168). Termination with thiirane was also used for the formation of telechelic polyisoprene containing SH end groups.

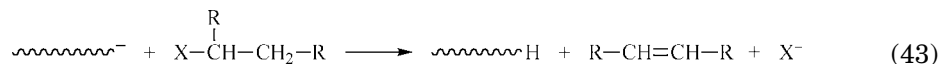
$$\text{~~~~~}^{-} \text{Li}^{+} + \text{CO}_2 \longrightarrow \text{~~~~~COO}^{-} \text{Li}^{+} \quad (38)$$

$$\sim\text{Li}^+ + \text{Cyclopentanone} \longrightarrow \sim\text{C(=O)}(\text{CH}_2)_2\text{C(=O)O}^-\text{Li}^+ \quad (41)$$

Halide End Groups. The most direct route for the preparation of halide terminal groups is the reaction of living polymers with a halogen, eg, chlorine (174,175) or iodine (176). Quantitative reaction is prevented by the occurrence of Wurtz coupling reactions. The percentage of halide end groups is increased by an intermediate Grignard step. For example, in this way, bromine gives an excellent yield of bromine-terminated telechelics.

A more general route employs an excess of primary α,ω -dihalides (175).

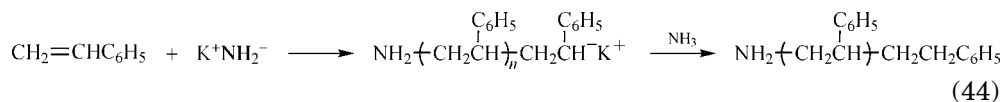


Secondary and tertiary halides lead to side reactions by β -elimination (177).



α,α -Dihaloxylenes or 1,4-dihalo-2-butanones give primary benzylic and allylic halides. Yields are increased by first converting the polymer into a Grignard salt. This process has been applied to prepare halogen-terminated telechelics from polybutadiene (178).

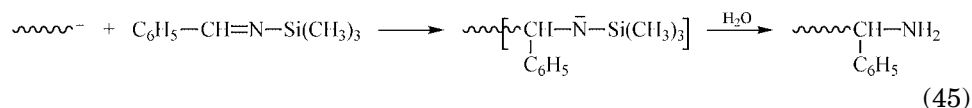
Amino End Groups. The polymerization of styrene initiated by potassium amide in liquid ammonia yields polymers with one primary amine group per chain (179).



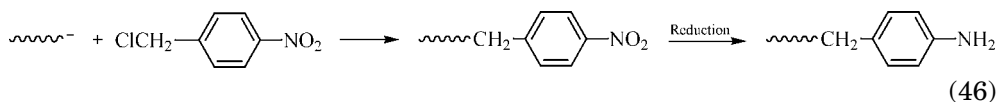
Initiators with the blocked amino groups, such as *p*-thio-*N,N*-bis(trimethylsilyl)aniline, have been used for anionic polymerization (Fig. 7).

Bifunctionality is achieved by coupling with dimethyldichlorosilane. The primary amine end groups are regenerated by acid hydrolysis (180).

An alternative route for the introduction of amine end groups by reaction with blocked functional terminating agents (181) is as follows:



An indirect route for the introduction of amine end groups on aromatic ring has been described (182).



Secondary amine groups are generated by reaction with *N*-alkyl aziridines (176).

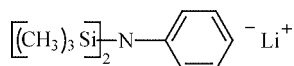
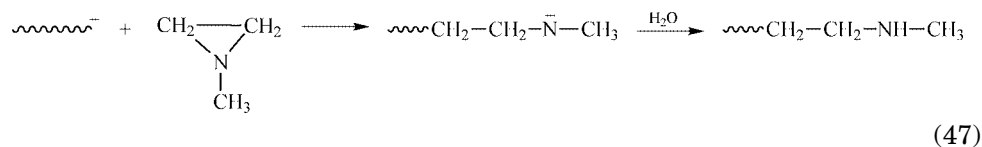
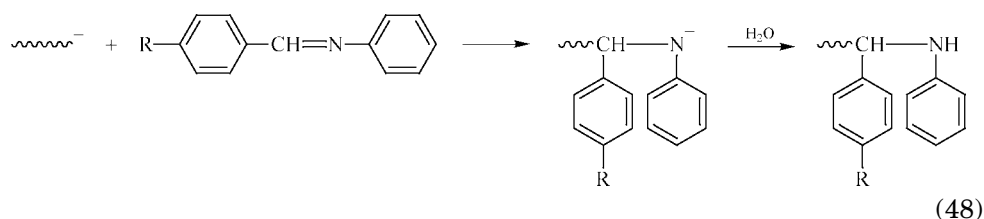


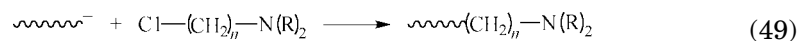
Fig. 7. Initiator with the blocked amino group.



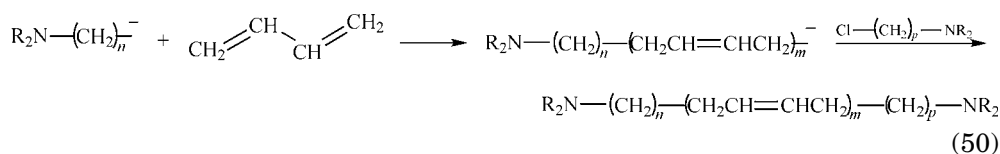
An interesting alternative is shown below (183):



Tertiary amine terminated polymers are made by reaction with α -chloro- ω -amino-alkanes (184).

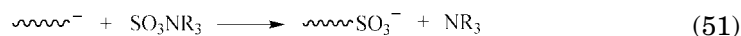


Living polybutadiene prepared with a tertiary amine functionalized alkyl lithium initiator is terminated by an α -chloro- ω -amino-alkane (185).

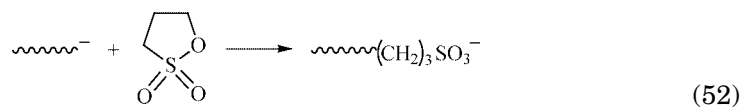


Ionic End Groups. Telechelics with quaternary ammonium end groups are prepared by quaternization of telechelic tertiary amines with organic halides (184). Unstable salts are formed by the reaction of living polymers with boron and aluminum alkyls. Only the triphenylboron derivatives are stable enough to be examined spectroscopically.

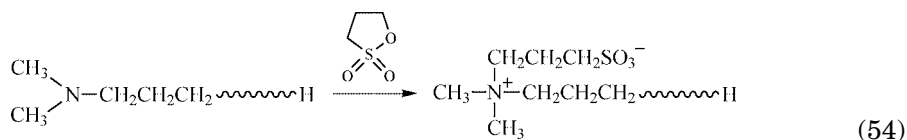
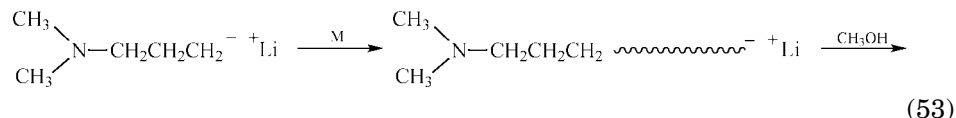
Reaction of living polymers with sulfur trioxide gives sulfonate salts. The reactivity of such salts as well as side reactions is reduced by complexation with a tertiary amine (185).



Termination of living polymers with sultones yields sulfonates. This reaction has been claimed to be quantitative in tetrahydrofuran at -78°C (186).



The synthesis and dilute and bulk solution properties of end-functionalized polymers with zwitterionic end groups have recently been reviewed (187). Reportedly, such polymers with different architectures (linear, block, and star copolymers) can be prepared by means of anionic polymerization. First, dimethylamine groups were introduced by using 3-dimethylaminopropyllithium as functional initiator. This group was then switched to sulfozwitterionic one by reaction with propanesultone.



Organometallic Groups. The reaction of living polymers with $\text{Pb}(\text{C}_4\text{H}_9)_3\text{Cl}$ yields polymers containing $\text{Pb}(\text{C}_4\text{H}_9)_3$ end groups. These end groups undergo homolytic scission at the carbon–lead bond, giving terminal free radicals (188).

Dipolystyryl aluminum chloride, prepared by stoichiometric reaction of 1 mol of AlCl_3 and 2 mol of living polystyrene, is used together with titanium halide catalyst to synthesize styrene–ethylene block copolymers (189).

Recently, new methods for preparation of telechelic polymers with better functionalization using alkyl aluminum initiated anionic polymerization were described (190–193).

Recent Trends in Functionalization of Telechelics. As described before, the direct carboxylation of polymeric organolithium with carbon dioxide in hydrocarbon solution often results in inefficient functionalization (170). Alternatively, an *ortho*-ester functionalized alkyl chloride, namely 4-chloro-1,1,1-trimethoxy butane, was used to prepare *ortho*-ester functionalized polymers (194).



The *ortho*-ester functionalized polymers can be hydrolyzed to the corresponding carboxyl functionalized polymers. Similarly, functionalization with the oxiranes, glycidylpropyltrimethoxysilane, 3,4-epoxy-1-butene, and 1,1,1-trifluoro-2,3-epoxypropane has been investigated (195) to prepare trimethoxysilyl functionalized polymers, 1,3-diene functionalized macromonomers, and trifluoromethyl functionalized polymers, respectively. Secondary amine functionalized polymers were prepared by termination with *N*-(benzylidene)methylamine and also using an *N*-benzyl tertiary amine functionalized alkyl lithium initiator followed by hydrogenolysis of the benzyl group.

The preparation of telechelics by carbocationic polymerization (qv) of vinyl monomers (196,197) has received little attention because of the high reactivity and low selectivity of growing species. The synthesis of useful telechelics requires the control of molecular weight and end groups; this was not possible until the discovery of living cationic polymerization.

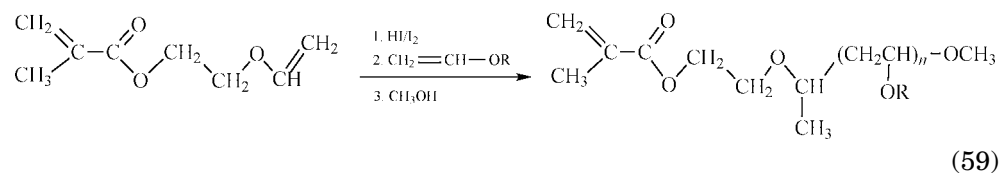
$$\begin{array}{c}
 \text{CH}_2=\text{CH} + \text{HI} \longrightarrow \text{CH}_3-\underset{\text{OR}}{\text{CH}}-\text{I} \xrightarrow[\text{CH}_2=\underset{\text{OR}}{\text{CH}}]{\text{I}_2} \begin{array}{c} \text{H}_3\text{C}-\underset{\text{CH}}{\text{CH}}-\text{OR} \\ \text{H}_2\text{C}=\underset{\text{CH}}{\text{CH}}-\text{OR} \end{array} \xrightarrow{\text{I}_2} \begin{array}{c} \text{H}_3\text{C}-\underset{\text{CH}}{\text{CH}}-\text{OR} \\ | \\ \text{CH}_2-\underset{\text{CH}}{\text{CH}}-\text{I}-\text{I}-\text{I}_2 \\ | \\ \text{OR} \end{array} \xrightarrow{\text{Polymer}} \text{Polymer}
 \end{array}
 \quad (56)$$

$$\quad (57)$$
$$\text{CH}_2=\text{CHOXOCH}=\text{CH}_2 \xrightarrow{\text{HI}} \begin{array}{c} \text{CH}_3\text{CHOXOCHCH}_3 \\ | \quad | \\ \text{I} \quad \text{I} \end{array} \xrightarrow[\text{monomer}]{\text{I}_2} \text{I}-\underset{\text{OR}}{\underset{|}{(\text{CH}-\text{CH}_2)_m}}-\overset{\text{CH}_3}{\underset{|}{\text{CHOXOCH}}}-\overset{\text{CH}_3}{\underset{|}{(\text{CH}_2)_n}}-\text{I}$$

where $\text{X} = (\text{CH}_2)_4, \text{CH}_2\text{CH}_2\text{O}-\text{C}_6\text{H}_4-\text{C}(\text{CH}_3)_2-\text{C}_6\text{H}_4-\text{OCH}_2\text{CH}_2$

(58)

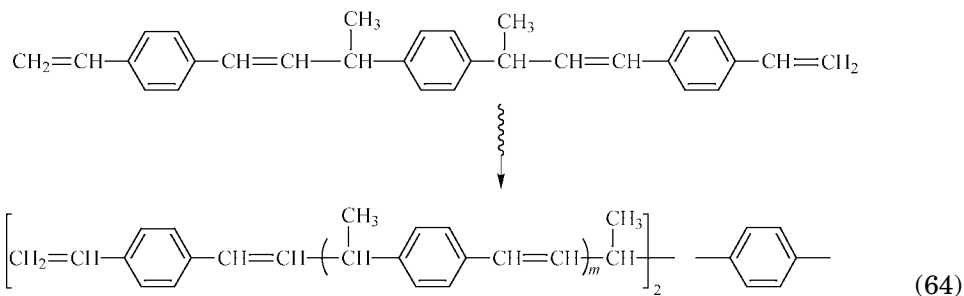
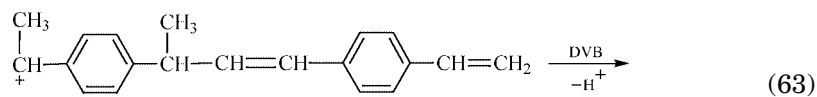
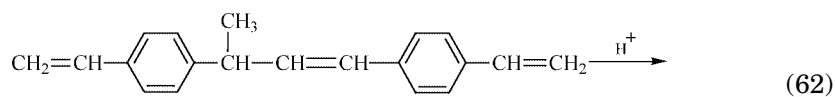
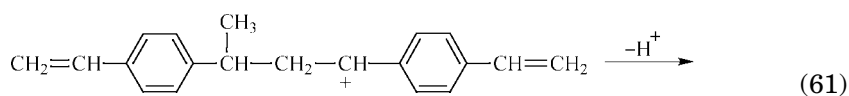
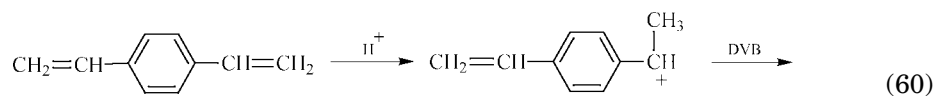
Treatment of living poly(EVE) with mono- or diamines yields telechelics with amino end groups (201). Vinyl ether based macromonomers have been prepared by a one-pot method (203–205).



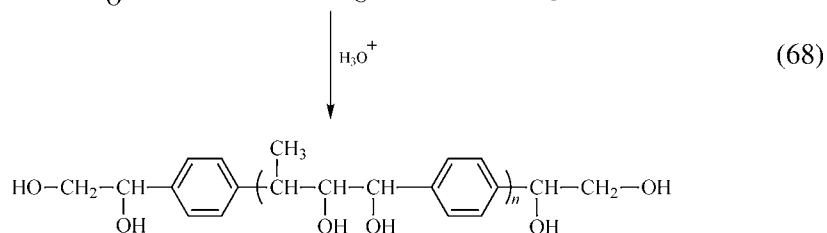
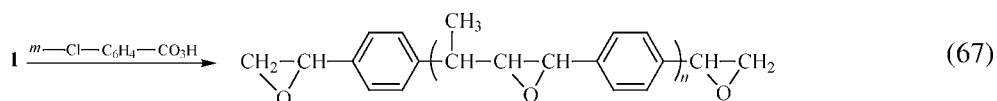
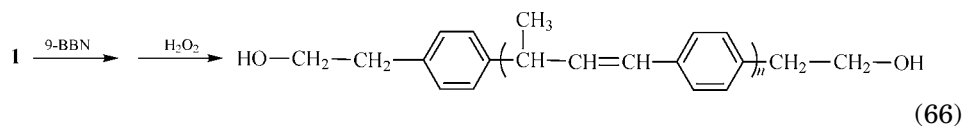
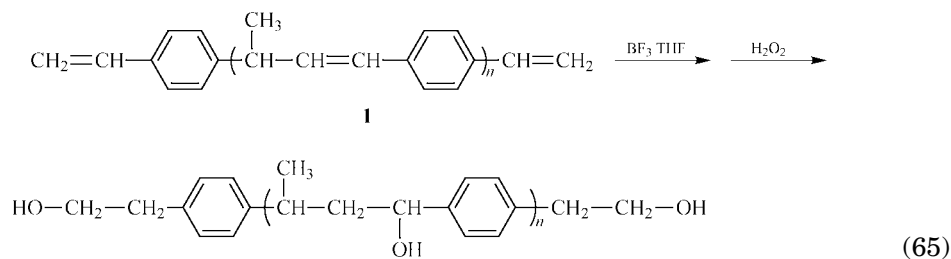
Polydivinylbenzene. Linear unsaturated polymers are obtained by a selective reaction between divinylbenzene (DVB) and cationic initiators such as $\text{CF}_3\text{SO}_3\text{H}$ or $\text{CH}_3\text{COCLO}_4$ (210–213). A sequence of protonation, propagation, and transfer steps yields telechelics with α,ω -vinyl end groups.

Table 6. Telechelic Poly(alkyl vinyl ethers)

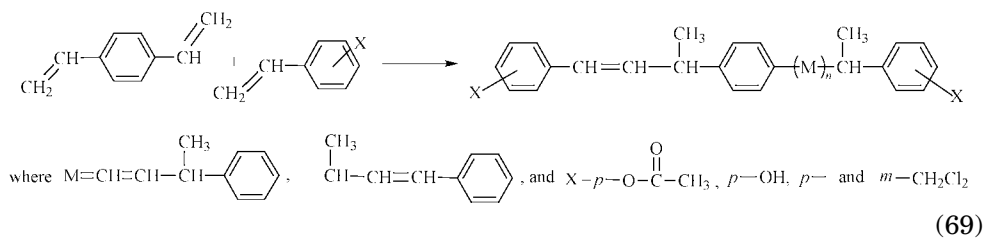
Functionality	Polymer	Reference
Hydroxyl	Poly(2-chloroethyl vinyl ether)	206
Aldhyde	Poly(2-chloroethyl vinyl ether)	206
Malonic ester	Poly(isobutyl vinyl ether)	207
Malonic ester	Poly(methyl vinyl ether)	207
Azo	Poly(isobutyl vinyl ether)	208
Imide	Poly(isobutyl vinyl ether)	209
Amino	Poly(isobutyl vinyl ether)	209



Reactions with 9-borabicyclo[3.3.1]nonane (9-BBN) and H_2O_2 yield hydroxyl-terminated telechelics (211).



Although one keeps control over the end groups the final product may not be called a pure telechelic but a chain functionalized polymer. $\alpha\omega$ -Acetoxy-poly(DVB) was synthesized from *p*-DVB, *p*-acetyl styrene, and $\text{CH}_3\text{COClO}_4$ in benzene at 70°C (212,213).



Polyisobutylene. On the basis of the reaction sequence shown in Figure 8, the conditions under which telechelics form can be predicted.

Head groups are controlled by initiation; propagation, termination, and transfer control the molecular weight and terminal groups. This method was first used for the synthesis of telechelics from isobutylene (214,215). The technique has been refined and is then called the inifer technique (216–221).

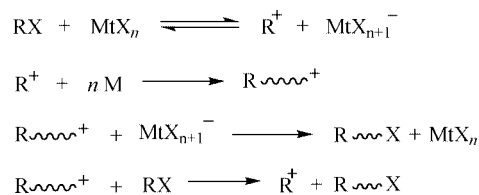


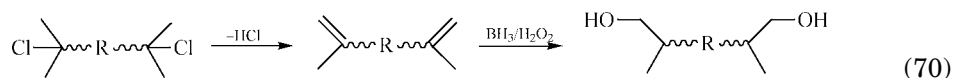
Fig. 8. Telechelics by inifer process. Here Mt is metal, M is monomer, and X is halide.

The compounds shown in Figure 9 act as both initiator and transfer agents, which led to the term inifer.

Notably, the number of functionality of the telechelics thus formed is related to the number of chloro groups present in the inifer. Preparation of telechelics by this method requires low temperatures and highly pure starting materials.

Quenching of living carbocationic polymerization also leads to *tert*-chlorine-telechelic polyisobutylenes (222). Synthesis of mono- (223–226), di- (227–235), tri- (236), and tetrafunctional (237) polyisobutylenes carrying Cl termini was reported.

The chloro end group is easily converted to olefinic or primary alcohol end groups (238–242).



One-pot dehydrochlorination–metalation of *tert*-chloro-telechelic polyisobutylenes (PIB) by combinations of *n*- with *sec*-butyl lithium (243) and of *n*-butyl lithium with *tert*-butoxide (244) leads to terminally lithiated polyisobutylenes. Oxyethylation and reaction with CO₂ of the latter yielded primary alcohols and carboxylate termini, respectively (244).

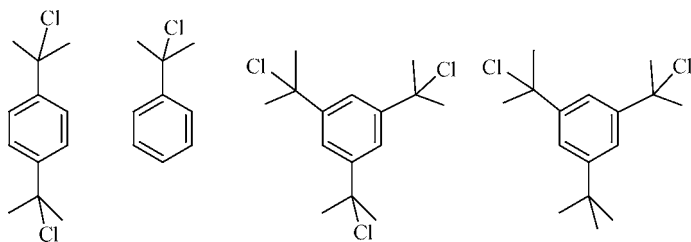
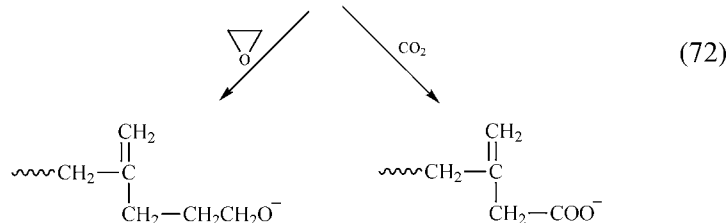
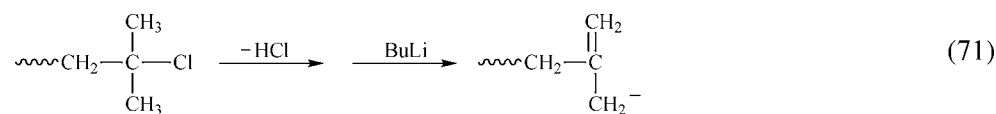
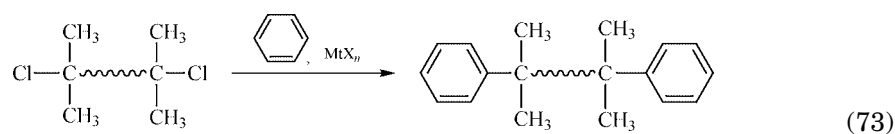


Fig. 9. Examples of inifers.

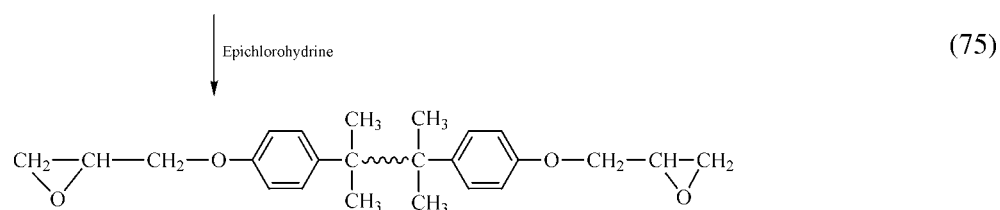
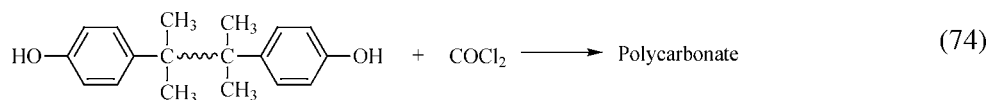


Friedel–Crafts alkylation of benzene, toluene, or phenol gives a variety of diaryl products (245):

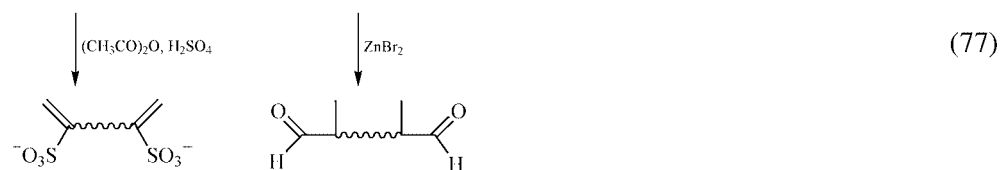


Nitration of the aromatic units followed by reduction yields an amine telechelic (245,246).

A phenol end group formed by Friedel–Crafts alkylation can be used for further derivatives (247,248).

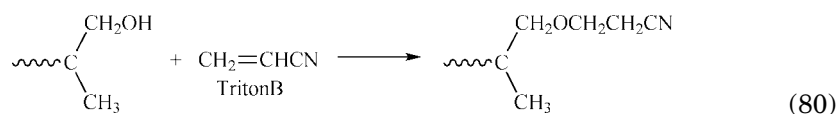
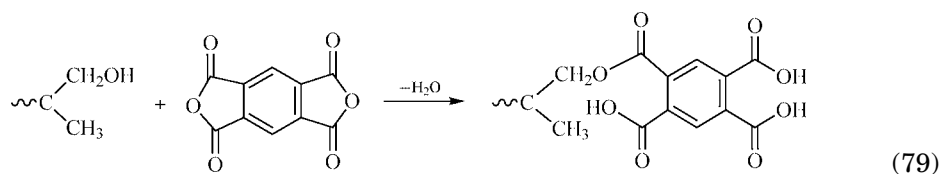
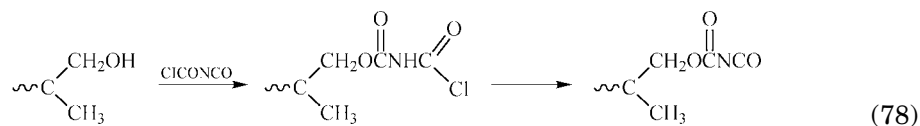


α,ω -Olefin telechelics can be converted into diepoxides and further to dialdehydes. Sulfonation of polyisobutylene with acetyl sulfate yields the corresponding sulfonate (249,250).



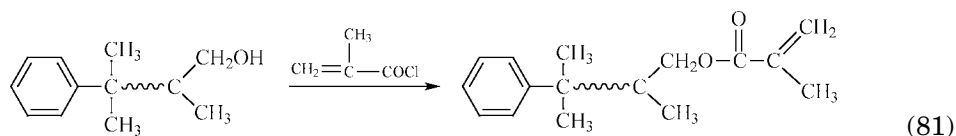
Similarly, di- and triallyl telechelic polyisobutylenes have been converted to di- and triepoxy telechelics (241,242). Hydrosilation of olefinic telechelics in the presence of suitable catalysts gives telechelics with reactive SiCl groups (251).

The hydroxy-terminated telechelics were used as starting material for numerous derivatives (252,253):



An improved Gabriel synthesis was used for amino-terminated telechelics (254).

Macromonomers can be synthesized from a hydroxy-terminated polymer by reaction with methacryloyl chloride (255).



Instead of RCl, tertiary esters were used in combination with BCl₃ for the synthesis of telechelics from isobutylene. The polymerization mechanism shown in Figure 10 was suggested (256,257):

Various other initiator systems for the controlled/living polymerization of isobutylene have been reported (222). The capping reaction of living polyisobutylene with 1,1-diphenylene ethylene (DPE) results in the formation of a stable and fully ionized diarylcarbenium ion, which can be used for chain-end functionalization by quenching with appropriate nucleophiles as shown in reactions 82 and 83 (258–261).

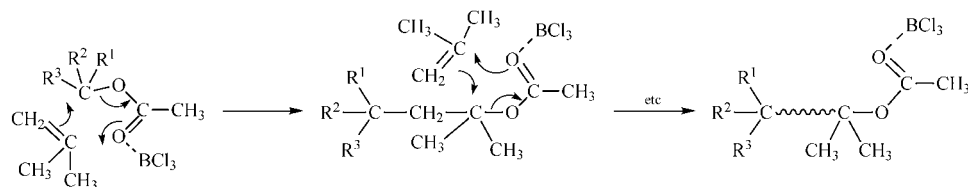
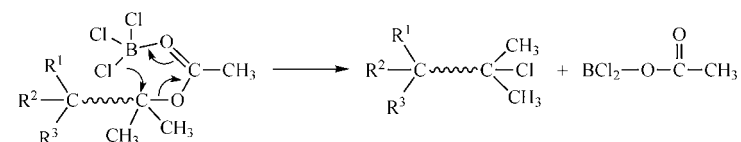
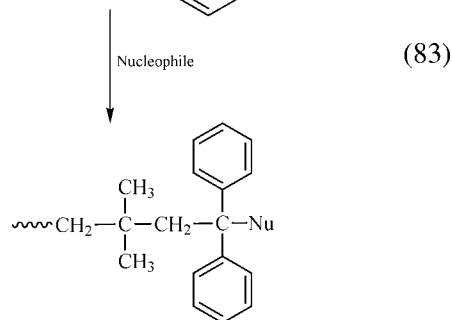
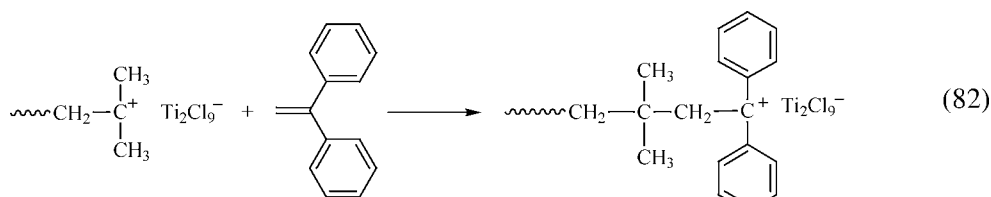
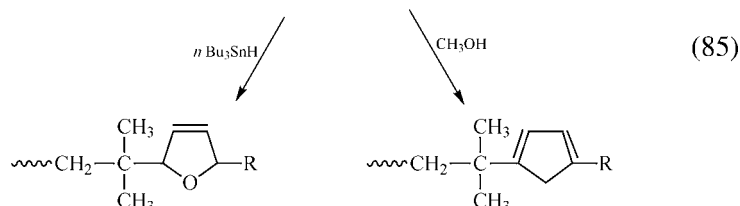
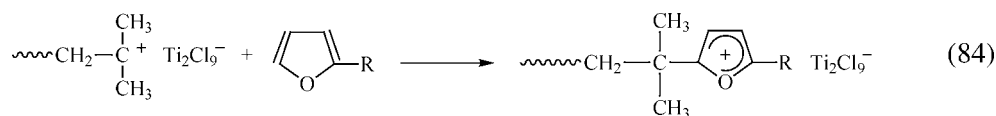
Insertion*Termination and End Group Control*

Fig. 10. Function of $(R_1R_2R_3)COOCH_3/BCl_3$ in the polymerization of isobutylene.

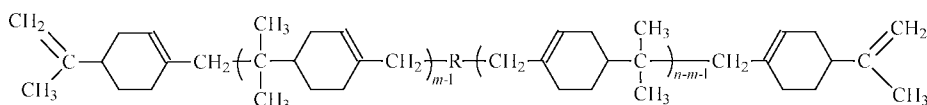
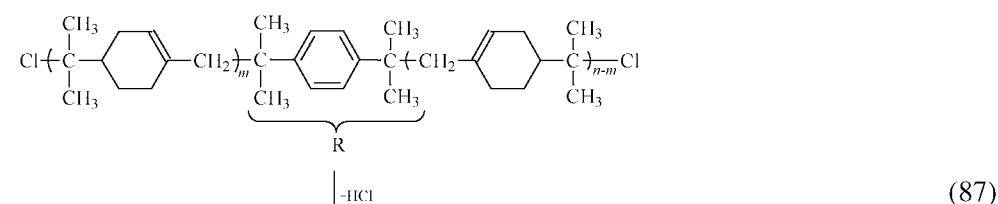
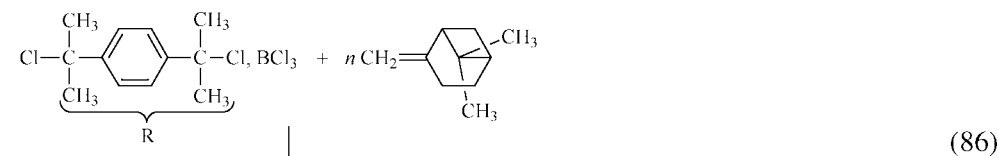


Using this strategy, a variety of chain-end functional polyisobutylenes including methoxy, amine, carbonyl, and ester end groups, have been prepared (262). By the rational combination of initiation and capping techniques, a series of α,ω -asymmetrically functionalized PIBs have also been obtained (262–264). It was shown that living polyisobutylene could also be end-capped with 2-alkylfurans. Quenching the resulting cation with tributyltin hydride and methanol yielded polyisobutylene with dihydrofuran and furan functionality, respectively (265,266).



It appears that 2-alkylfurans are more suitable capping agents when subsequent functionalizations at elevated temperatures are required.

Polypinene. β -Pinene is converted into telechelics with 1,4-diisopropylchlorobenzene and BCl_3 as initiator (267).



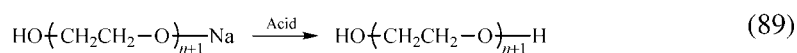
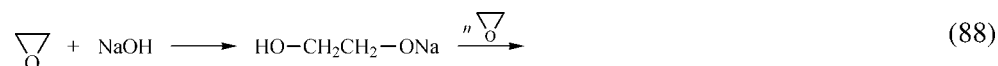
Polystyrene and Derivatives. Telechelic polystyrene, poly(2,4,6-trimethylstyrene), poly(*p*-methylstyrene), and poly(*p*-chlorostyrene) can be prepared by living carbocationic polymerization (269–271) or by inifer method (272). While end-quenching the living carbocationic polymerization gave quantitatively polymers with *sec*-benzylic termini, the dicumyl chloride/ BCl_3 inifer system yielded α,ω -dichloro telechelics. Telechelics with olefine end groups were also prepared by dehydrochlorination (272,273).

Ring-Opening Polymerization

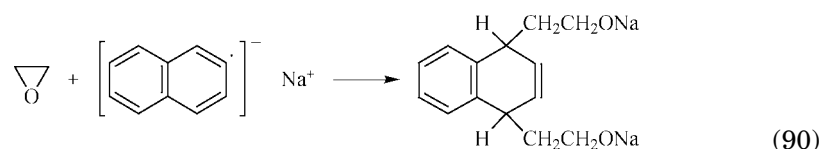
The synthesis of telechelics by ring opening has attracted great interest because of the commercial potential of the resulting compounds, such as polyether polyols. The end groups are introduced by initiation, end capping, or transfer reactions.

Cyclic Ethers.

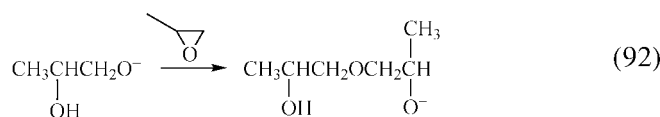
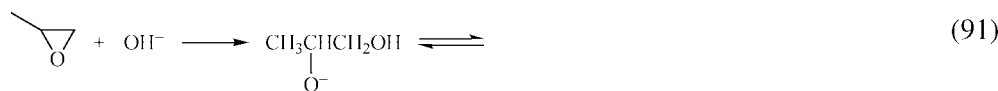
Oxiranes. Both anionic and cationic polymerization can be used to synthesize telechelics from oxiranes. Anionic polymerization of oxirane (ethylene oxide) yields α,ω -dihydroxy poly(ethylene oxide) (274,275).



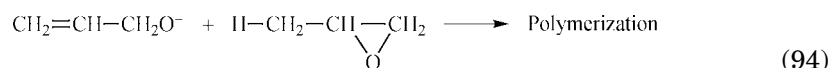
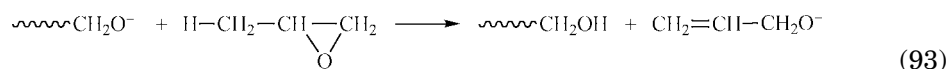
Polymerization with sodium naphthalene yields a chain with two simultaneously growing ends (276,277).



The anionic polymerization of methyl oxirane occurs predominantly by breaking of the oxygen-methylene bond, yielding terminal secondary alcohol functionality.



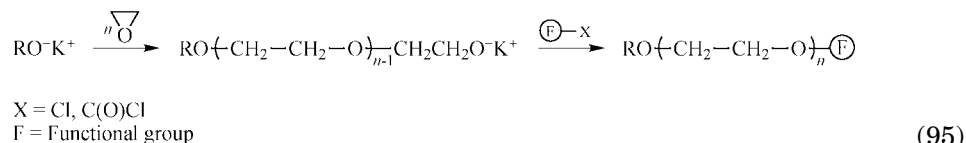
It should be mentioned that an important transfer reaction is occurring, leading to an allylic chain end:



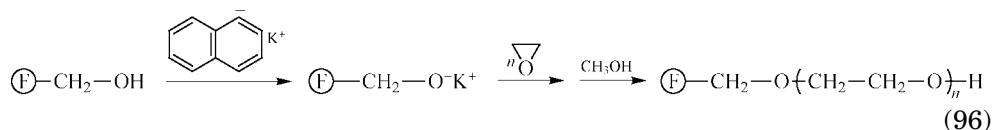
Hydroxyl end groups can be converted to various other functional groups (278). Generally, oxirane telechelics are synthesized either by one of the following methods: (1) end-capping of the living polymerization (termination method), (2) initiation of living polymerization (initiation method), and (3) transformation of hydroxyl end groups (279,280). Methods (1) and (2) are simple and usually afford most well-defined telechelics of a controlled degree of polymerization with a

narrow polydispersity, but critically depend on the proper combination of anionic living polymerization with an effective terminator or initiator carrying desired functionality. Suitable terminators include alkyl and acid chlorides possessing functional groups.

Termination



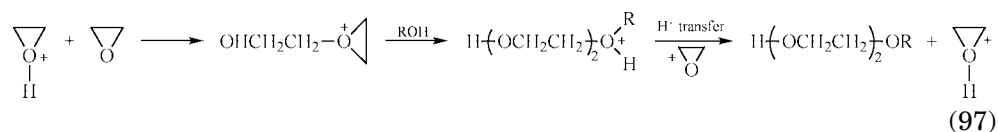
Initiation



This way many poly(ethylene oxide)s with various functional groups including photo- and electroactive, and polymerizable groups were prepared (280–283). Moreover, suitable combinations of termination and initiation methods yield heterofunctional telechelics.

Although living anionic polymerization seemed to be the versatile method for the preparation of telechelic from oxiranes, with substituted oxiranes some side reactions leading to unsaturated species occur (reaction 93). An alternative initiating system based on aluminum complexes of Schiff bases was proposed for the preparation of α,ω -telechelics from differently substituted oxiranes (284–286).

The usual cationic polymerization of oxiranes cannot be used to synthesize telechelic polymers owing to a high tendency of backbiting resulting in cyclic oligomers (287). However, a process involving the addition of a hydroxyl end group to an activated (protonated) monomer has been described (287–289).



The polymer chain contains the less reactive (nucleophilic) hydroxyl end group. The driving force for this reaction comes from the protonated monomer, and no cyclic oligomers are formed. Similar results have been obtained from the polymerization of methyloxirane (290) and chloromethyloxirane in the presence of ethylene glycol (291). Photo- and azo-functional telechelics were also prepared by the so-called activated monomer polymerization (292,293).

Tetrahydrofuran. The cationic polymerization of tetrahydrofuran (THF) is living in the sense that, under certain conditions, the concentration of oxonium

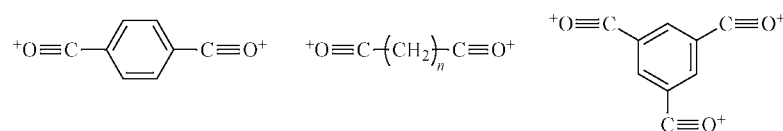
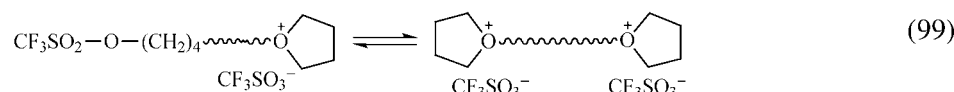
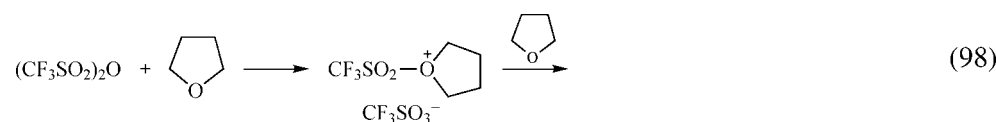


Fig. 11. Examples of bi- and trifunctional initiators with BF_4^- , PF_6^- , or SbF_6^- as counterions.

ions remains constant (294). The species is highly reactive and can be transformed into end groups by reaction with suitable nucleophiles. Polytetrahydrofuran (PTHF) with one functional end group is thus obtained after end capping of the living polymers produced with a monofunctional initiator. For the synthesis of bi- or trifunctional telechelics, initiators with corresponding functionality must be used (Fig. 11) (295,296).

Independent activity of all initiator functions of these bi- and trifunctionalized initiators has been reported. Copolymers can be formed if 10–20% of the THF is replaced by methyloxirane (297).

Anhydrides of super acids such as trifluoromethane sulfonic acid or fluoro-sulfonic acid yield two active ends (298,299).



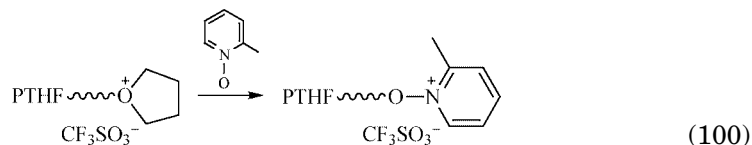
Molecular weight and functionality are controlled only at low initiator concentration because of the low solubility of the initial bisoxonium salt (299).

Because of the reversibility of the polymerization and the high reactivity of the oxonium functions, bi- and trifunctional PTHFs are not easy to use. However, addition of a nucleophile to a solution of living polymer yields telechelics that are easier to handle (300). End-capping reagents and the resulting end groups are shown in Table 7.

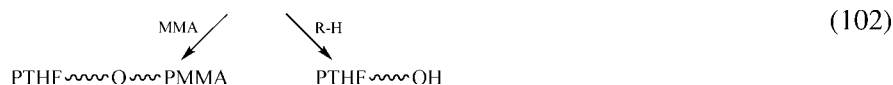
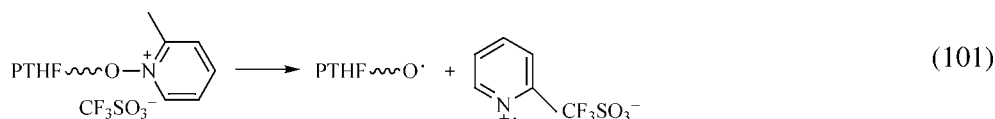
Table 7. End-Capping Reagents and End Groups

End-capping reagent	End group
NH_3 (liquid)	$-\text{NH}_2$
KOCN	$-\text{NCO}$
H_2S	$-\text{SH}$
$\text{HOOC}(\text{CH}_2)_2\text{COOH}$	$-\text{COOH}$
$\text{C}_2\text{H}_5\text{NH}_2$	$-\text{NHC}_2\text{H}_5$
$\text{CH}_2=\text{CHCH}_2\text{NH}_2$	$-\text{NHCH}_2\text{CH}=\text{CH}_2$
LiBr	$-\text{Br}$

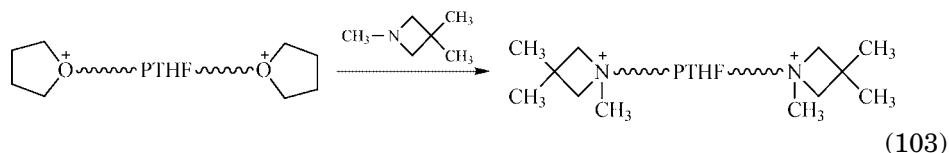
Some other functionalities such as photosensitive benzoin (301) and alkoxy pyridinium (reaction 100) (302), pyrrole (303), methacrylate groups (304) can also be introduced to PTHF by selecting suitable nucleophiles.



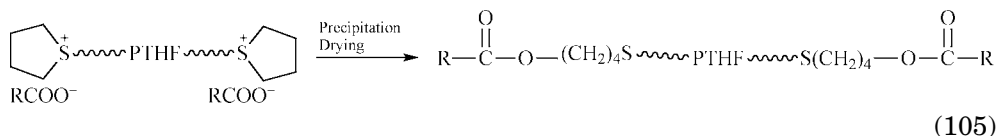
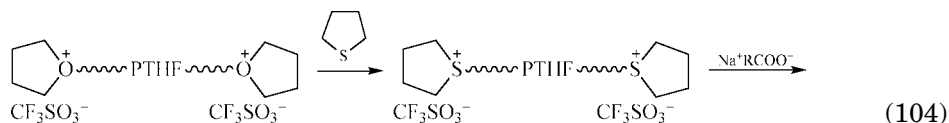
The pyridinium salt end-functionalized PTHFs can be used as polymeric initiators for photoinduced reactions. Upon photolysis the pyridinium moiety decomposes and polymeric radicals are formed. Depending on the additives present in the system, hydroxy telechelics (305) or block copolymers (302) are thus formed.



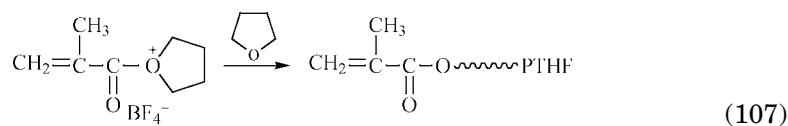
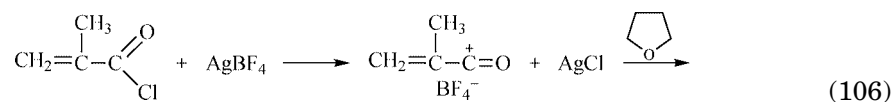
An interesting reaction is the so-called active species exchange (306).



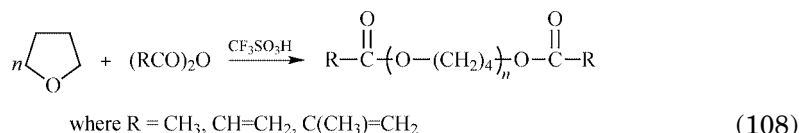
The less reactive, weak electrophilic azetidinium ions undergo ring-opening reactions with charged nucleophiles such as carboxyl ions. The reaction of PTHF with thiolane gives similar results (307).



End groups have also been introduced by using a functionalized initiator (308,309).

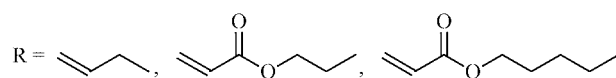
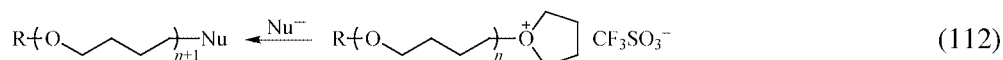
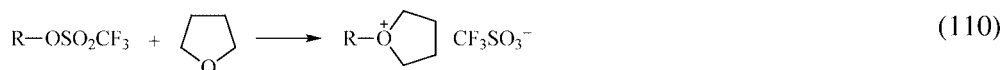
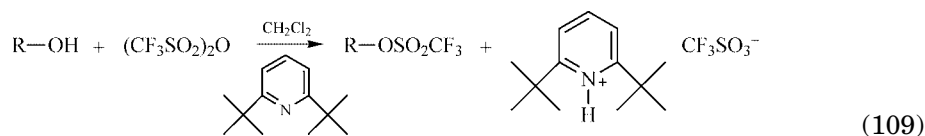


Proton-initiated polymerization of THF in the presence of carboxylic acid anhydrides gives ester-terminated end groups.

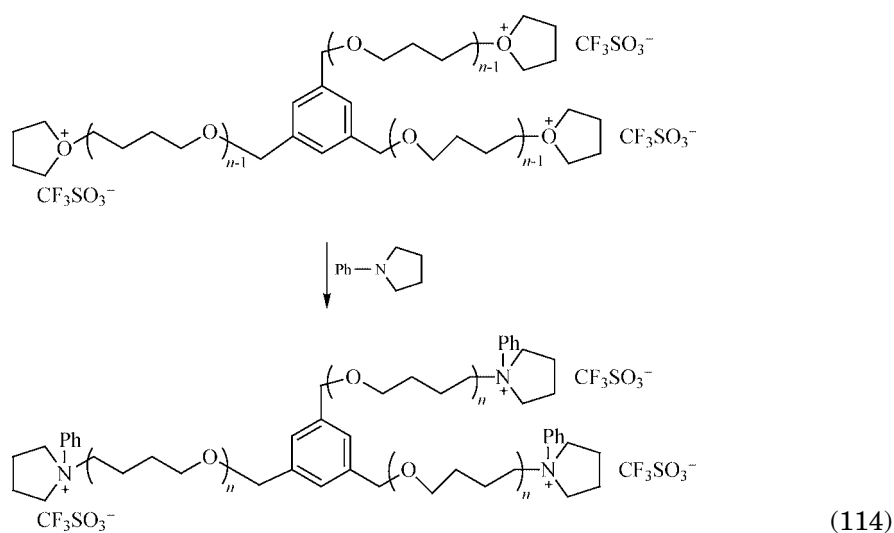
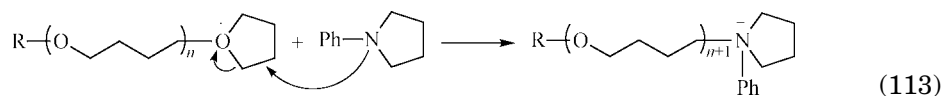


Hydrolysis results in the corresponding hydroxy-terminated PTHF.

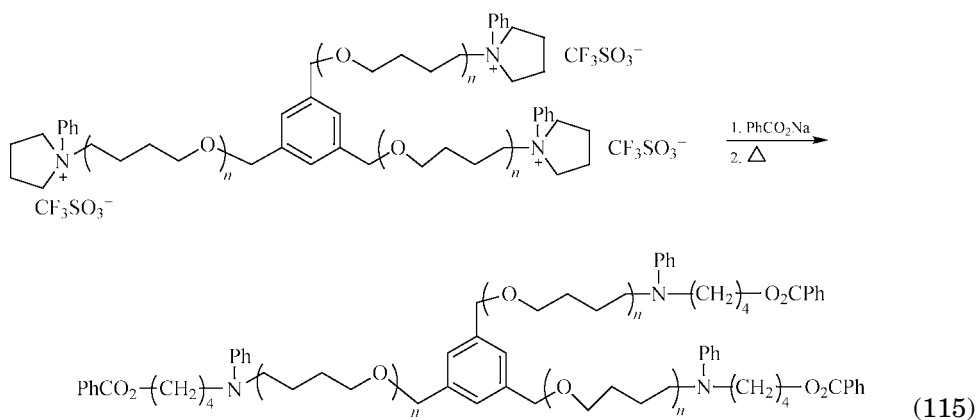
Recently, it was shown that hydroxyl groups can be transformed *in situ* to a triflate ester in the presence of a proton trap for the initiation of the cationic ring-opening polymerization of THF. Providing that suitably functionalized hydroxyl groups are selected and the hydroxyl group is not attached to a bulky alkyl group (310), PTHF telechelics with narrow molecular weight distribution and quantitative functionalization can be obtained. Macromonomers with acrylate, methacrylate, and allyl functional groups have been successfully synthesized (311).



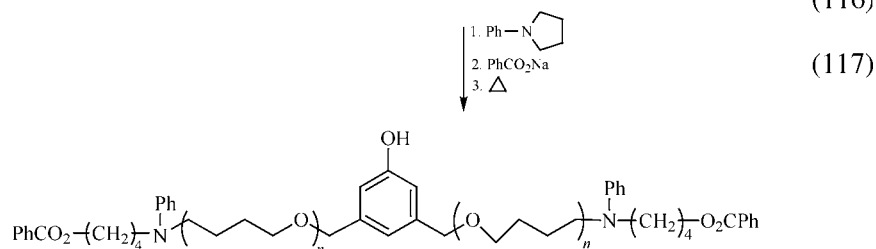
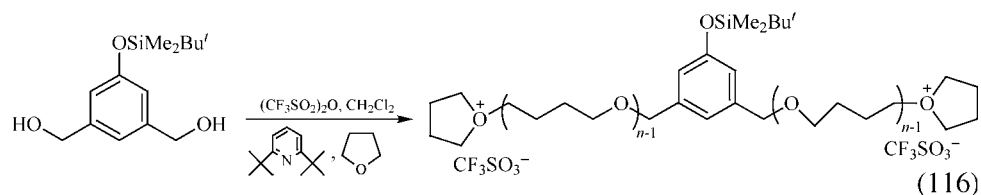
Interesting variation of end-capping reaction with *N*-phenylpyrrolidine (reaction 113) can be used to prepare mono-, bi-, and trifunctional star-shaped, telechelic PTHF having *N*-phenylpyrrolidinium salt groups as illustrated in the example of trifunctional living PTHF.



Heat treatment of the polymers carrying carboxylate anions results in a quantitative ring-opening reaction.

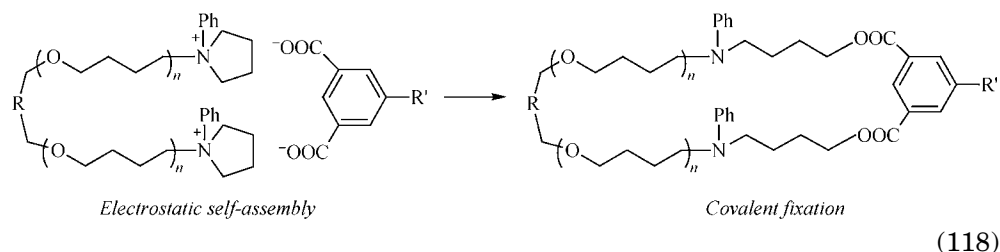


Another class of telechelic PTHFs has also been prepared, in which functional groups were located not only at the chain ends but also at the interior desired position. In this case, the *tert*-butyldimethylsilyl-protecting group was removed during the precipitation to yield α,ω -*kentro*-telechelic polymers (312).



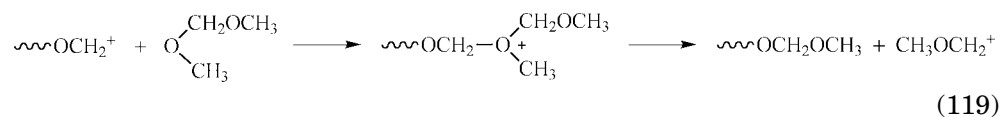
Moreover, *eso*-telechelic PTHF having pyrrolidinium salt groups at the prescribed inner positions were also prepared (313).

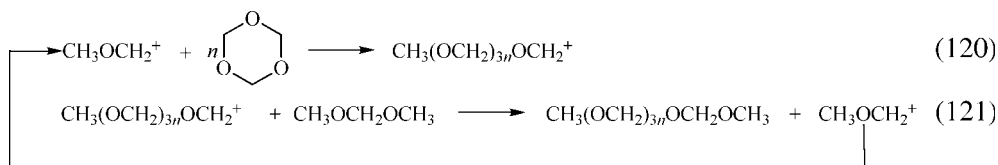
Cyclic polymers, having one or two functional groups, are termed as *kyklo*-telechelics with analogy to the Greek word *kyklos* (which means cyclic). Such telechelics can be prepared again by the electrostatic self-assembly and covalent fixation process as depicted in reaction (118).



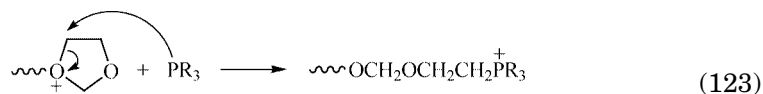
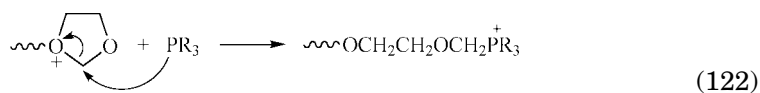
By suitably selecting R and R' groups, various mono- and bifunctional telechelics having hydroxyl and allyl groups were prepared (314).

Cyclic Acetals. A number of cyclic acetals of varying ring size have been polymerized with cationic initiators (315); trioxane and dioxolane are the most important. Polymerization of trioxane in the presence of a transfer agent such as dimethyl formal or an anhydride yields polyoxymethylene with ether and ester end groups, respectively (316).





Triflic acid or anhydrides initiates polymerization of 1,3-dioxolane (DXL) and 1,3-dioxepane (DXP) (317). After transformation of the active ends into phosphonium salts, the functionality of these polymers was determined with ^{31}P NMR ($f = 2$).

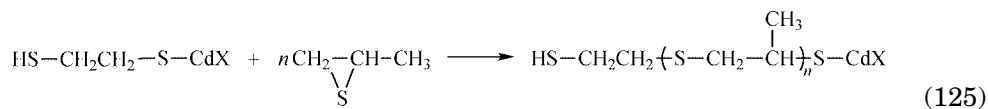
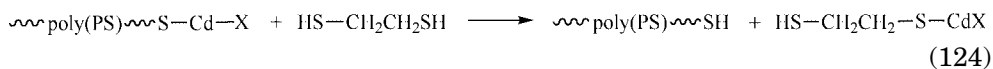


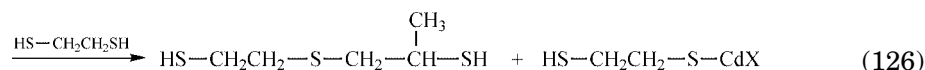
Another pathway yields a thermodynamically more stable product, but is kinetically less favorable. Because of extensive chain transfer the polymerization of DXL is not living. However, if a functionalized acetal is added to the monomer, telechelic polymers, eg α,ω -bisacrylate of poly(DXL) (318), are obtained. Similarly, addition of trimethylamine to growing poly(DXL) initiated with triethyloxonium hexafluoroantimonate yields telechelics with one trimethylammonium and one ethoxy end group (319).

An activated monomer mechanism similar to that described for oxiranes has been proposed to account for the formation of hydroxy-terminated poly(DXL) (320).

Cyclic Sulfides. The three-membered cyclic thiiranes can be polymerized cationically, anionically, or by a coordination mechanism. The four-membered cyclic thietanes can be polymerized by cationic and anionic mechanisms, but five-membered rings cannot be polymerized. Polymerization of propylenesulfide initiated with sodium naphthalene yields telechelics with naphthalene groups on both ends, if the living chain is terminated 1-chloromethylnaphthalene (321).

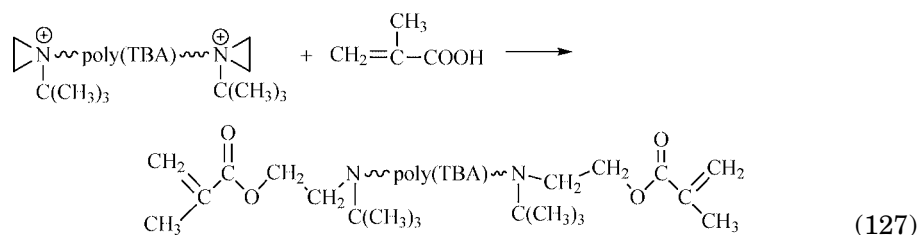
The propagating species in the anionic polymerization of propylene sulfide are thiolate anions, and therefore, reactions 124-126 can be used for the synthesis of α,ω -mercaptopoly(propylene sulfide)s (321,322).





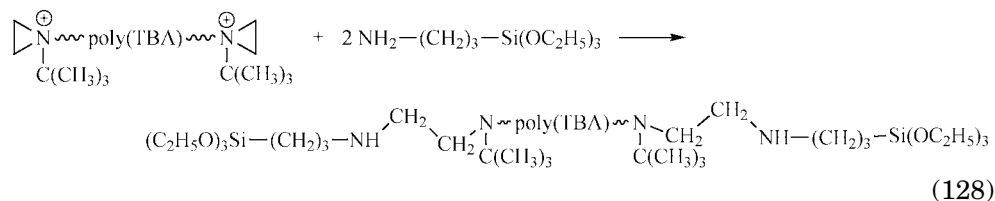
The cationic polymerization of thiiranes has not been reported as a method for the synthesis of telechelics, because of the rapid chain transfer to polymer and degradation of the active polymer to low molecular weight cyclic products (323).

Cyclic Amines. The three-membered cyclic amines and the four-membered cyclic amines can be polymerized only by cationic mechanism (324). Monofunctional initiators, such as methyl triflate (325), produce monofunctional telechelics from *t*-butylaziridine (TBA). Addition of the monomer to a bifunctional living PTHF solution (326) gives bifunctional poly(TBA). This is a method of making ABA block copolymers. The aziridinium end groups react with acrylic acids to form the corresponding esters (327).



Reactions with pyromellitic acid or with polyamines such as diethylenetriamine give cross-linked products (328).

End capping with γ -aminopropyltriethoxysilane groups yields telechelics that form networks after hydrolysis (328).

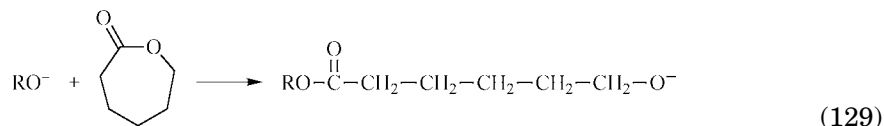


Lactones. Lactones are polymerized by anionic and cationic initiators (329). Nearly all four-, seven-, and eight-membered rings polymerize, but the five-membered rings do not, nor do many of six-membered rings (see RING-OPENING POLYMERIZATION).

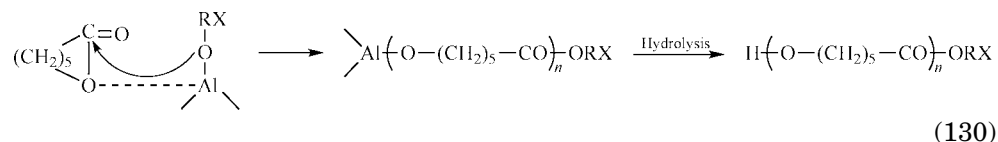
The anionic initiators for the polymerization of β -lactones are usually organic bases such as tertiary amines (330). The chain transfer reactions involving a proton abstraction from the α -position and α,β -unsaturation can be avoided with α,α -disubstituted-propiolactones such as pivalactone (331–333).

Pivalactone (α,α -dimethyl- β -propiolactone) (PVL) can be converted to telechelics and used for the preparation of block copolymers (331,332). An asymmetrical telechelic is prepared from PVL (334) with cyclic amine initiators. These telechelics have α -cycloammonium and ω -carboxyl end groups.

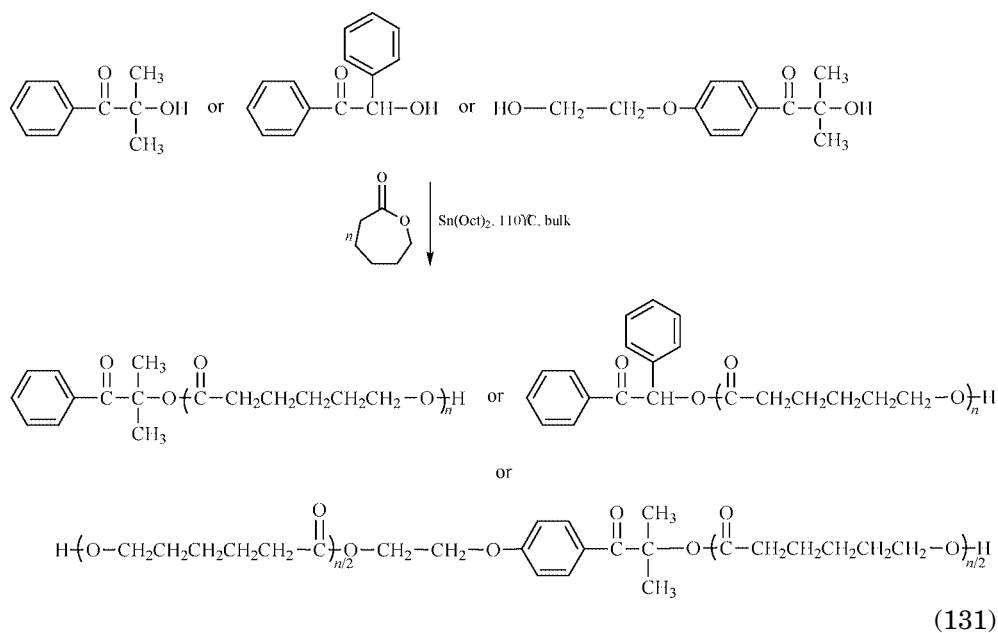
ϵ -Caprolactone can be polymerized by alcoholates.



An alcoholate end group can, however, attack the ester groups of the chain, broadening the molecular weight distribution (335,336) and forming cyclic monomers. Living polymers of ϵ -caprolactone have been obtained with bimetallic oxoalkoxides and porphionato aluminum alcoholates (337). The selective end group functionalization of poly(ϵ -caprolactone) (PCL) was investigated by using aluminum alkoxides carrying functional alkoxy groups as initiators (338–341). Aluminum alkoxides carrying functional alkoxy groups ($\text{X} = \text{Br}$, $-\text{CH}_2\text{N}(\text{Et})_2$, $-\text{CH}_2-\text{CH}=\text{CH}_2$, $-\text{CH}_2\text{OC}(\text{O})\text{C}(\text{CH}_3)=\text{CH}_2$, etc) provide asymmetrical telechelic polyesters (342–344).



It was also shown that functional zinc alkoxides are also effective initiators for the ring-opening polymerization of ϵ -caprolactone under very mild conditions via a polymerization mechanism described for aluminum alkoxides (345). Tin octoate, $\text{Sn}(\text{O}(\text{O})\text{CCH}(\text{C}_2\text{H}_5)\text{C}_4\text{H}_9)_2$, is another type of initiator to synthesize telechelics based on PCL. In particular, when it is used in conjunction with hydroxyl functional compounds or prepolymers, telechelics, linear and star-shaped block copolymers, or networks can be obtained via corresponding alkyl octoate formation (346–354). More recently, novel end-chain and mid-chain telechelics functionalized with photoactive groups of PCL were synthesized (355).



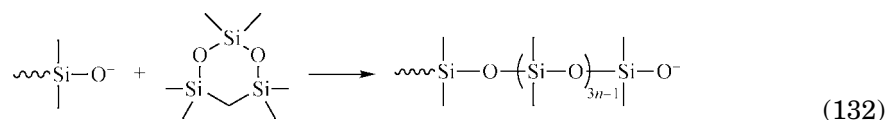
It was also reported that macromonomers based on end-functionalized PCL were prepared by different strategies using lipase enzymes as the catalysts (356–359). In the first strategy, an alcohol containing the target end-functionality initiated the ring-opening polymerization of ϵ -caprolactone. Alternatively, acids and esters containing the target end-functionality were added to prepolymerized ϵ -caprolactone. Either or both strategies yielded mono- and ditelechelics (359).

Hydroxy telechelics of PCL can be transformed to thiol functionalized polymers under mild conditions by using 2,4-dinitrophenylthioacetic acid as the protecting group (360).

ϵ -Caprolactone polymerization initiated with trialkyloxonium salt in combination with an alcohol (361) is easily controlled. A similar reaction has been described for cyclic ethers (288).

Siloxanes. Polysiloxanes are used as segments in block copolymers because of their low temperature flexibility, high gas permeabilities, excellent electrical properties, biocompatibility, and surface properties.

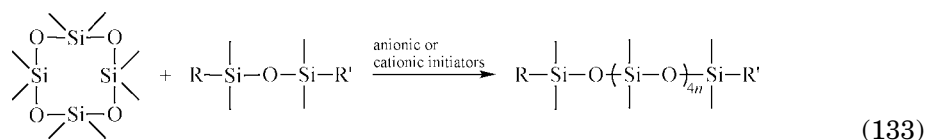
Linear polysiloxanes are prepared by anionic and cationic polymerization of cyclosiloxanes (362), such as hexamethylcyclotrisiloxane (D_3) and octamethylcyclotetrasiloxane (D_4). Anionic polymerization is initiated by hydroxides, alcoholates, phenolates, silanolates, and siloxanolates. The active species is the silanolate anion.



Cationic polymerization is initiated by strong protonic acids, such as sulfuric acid, trifluoromethane sulfuric acid, or trifluoroacetic acid.

Both anionic and cationic species undergo backbiting during polymerization, creating equilibrium between chains and rings (363,364).

Bifunctional polysiloxanes with a variety of end groups are obtained by using end blockers with different end groups R (365–367).



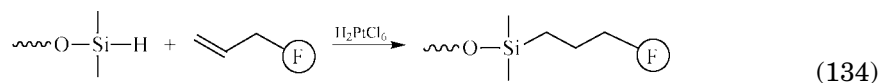
End groups include amino, dimethylamino, piperazine, carboxyl, ethylene oxide, and hydroxymethylene (Table 8).

A large number of polysiloxanes with functional end groups are commercially available (368).

The hydrosilation of unsaturated functional compounds with polysiloxanes containing Si–H end groups can also be used for the preparation of polysiloxane telechelics (369).

Table 8. Commercial Telechelic Polydimethylsiloxanes^a

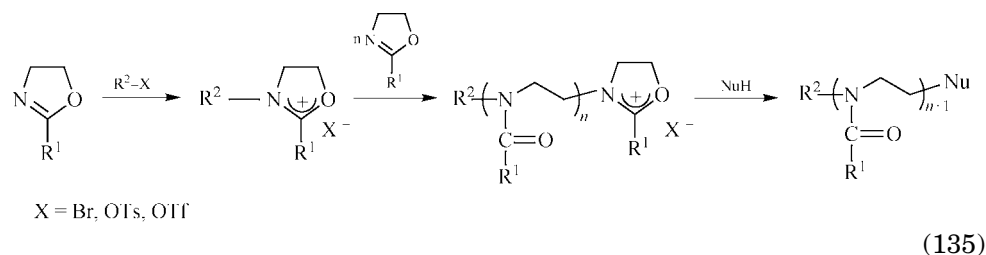
End group R	Molecular weight
$\begin{array}{c} \\ \text{---Si---OH} \\ \end{array}$	400–310,000
$\begin{array}{c} \text{O} \\ \\ \text{---O---C---CH}_3 \end{array}$	36,000
---Cl	425–600
$\text{---N(CH}_3)_2$	36–450
$\text{---OC}_2\text{H}_5$	
$\begin{array}{c} \text{O} \\ \\ \text{---O---C---(CH}_2\text{)}_{17}\text{CH}_3 \end{array}$	
$\begin{array}{c} \\ \text{---Si---CH=CH}_2 \\ \end{array}$	
$\begin{array}{c} \diagup \\ \text{Si(CH=CH}_2\text{)}_2 \\ \diagdown \end{array}$	
$\begin{array}{c} \\ \text{---Si---H} \\ \end{array}$	400–62,00
$\begin{array}{c} \text{---(CH}_2\text{)}_3\text{NH}_2 \\ \text{---(CH}_2\text{)}_2\text{O---C---C=CH}_2 \\ \quad \quad \quad \quad \\ \quad \quad \quad \text{O} \quad \text{CH}_3 \end{array}$	

^aRef. 368.

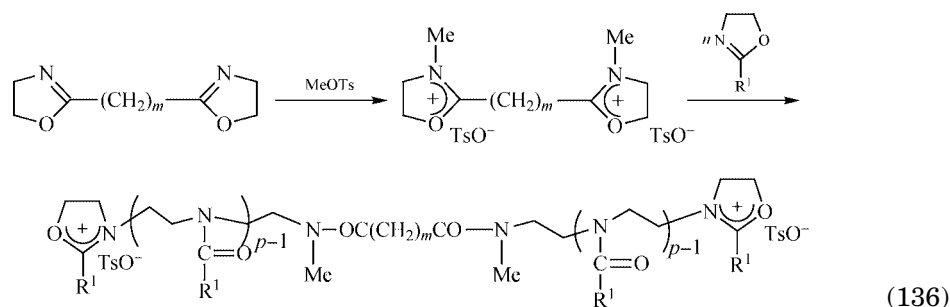
Synthesis of chain or end-functional polysiloxanes with methacrylate (370), hydroxy propyl (371), epoxy (372), benzoin (373), carboxyl ester or carboxyl amido (374), and chloromethylphenethyl (375) groups were described.

Alternatively, the chemical transformation of functional groups attached to the siloxane prepolymers by reacting with appropriate reagents provides desired functionalization. For example, electroactive pyrrole functional polysiloxanes were prepared from the corresponding amino telechelics (375).

Oxazolines. Cationic polymerization of 2-alkyl-2-oxazolines provides an excellent methodology for the easy introduction of functional end groups (376). Polymerization proceeds via oxazolinium species and functional groups can be incorporated at both initiation and termination steps by using functional initiator and nucleophile, respectively.



Poly(oxazoline) telechelics with hydroxyl, amino, triphenylphosphonium, piperidine, pyrrole, styryl, acrylamide, acrylate, methacrylate, and butadiene end groups were successfully synthesized (377–387). Reaction of methyltosylate (MeOTs) with bisoxazolines gives rise to the formation of bis(oxazolinium tosylate) (387). Living polymerization of monofunctional oxazolines having propagating species at both ends can be initiated by the addition of the monomer.



Termination of the living ends with suitable nucleophiles yields difunctional thiol, vinylbenzyl, carboxylic acid, *t*-butylmalonate, benzyl and unsaturated ester telechelics (387–389).

Metathesis Polymerization

Olefin metathesis has been of interest both industrially and academically because of its great synthetic utility (4). Mechanistically related metathesis reactions include ring opening metathesis (ROM), ring-closing metathesis (RCM), cross-metathesis (CM), acyclic diene metathesis (ADMET) polymerization, and ring-opening metathesis polymerization (ROMP) (Fig. 12) (5–8,390,391).

Acyclic Diene Metathesis Polymerization. Acyclic diene metathesis (ADMET) and the other metathesis polymerization methods are closely related to the catalyst system employed. Besides classical catalysts, Schrock-type alkylidenes and Grubbs-type carbenes can be used in ADMET polymerization.

ADMET polymerization and depolymerization methods have been used in the synthesis of telechelic oligomers. The metathesis depolymerization of 1,4-polybutadiene is accomplished in the presence or absence of a monofunctional diene by using either of the catalysts presented in Figure 13. Telechelic oligomers with terminal alkene, ester, and silyl ether and imide functional groups may be

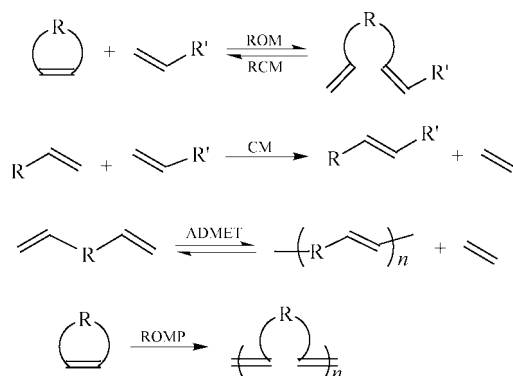


Fig. 12. Metathesis pathways.

prepared (392,393). Amine and alcohol functions are not well tolerated with the current catalysts and can be incorporated to polymers by using protecting group strategy. Telechelics with both of these types of end groups were synthesized using direct ADMET polymerization of dienes in the presence of a functional group protected α -olefin (394,395).

Ring-Opening Metathesis Polymerization. In ring-opening metathesis polymerization (ROMP), the use of functionalized acyclic alkenes as chain transfer agents not only permits the regulation of the polymer molecular weight but also opens a simple and efficient route to telechelics (4). Because of their higher reactivity, *cis*-alkenes are preferably employed for this purpose.

A broad variety of difunctional allylic olefins have been used for the synthesis of amino-, carboxyl-, and halide-terminated polybutadienes by means of the Grubbs catalyst **I** (396–398). With the same catalyst, commercially interesting hydroxy telechelic polybutadienes could be obtained by the cleavage of the acetyl end-capped polymer or the copolymer, as depicted in Figure 14 (399,400).

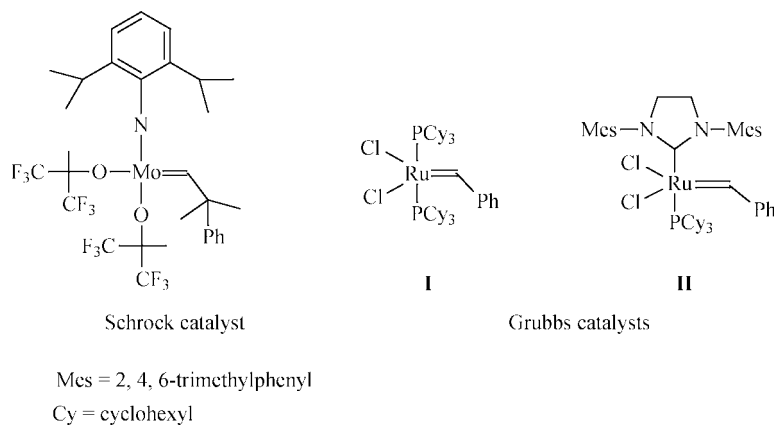


Fig. 13. Well-defined metathesis catalysts.

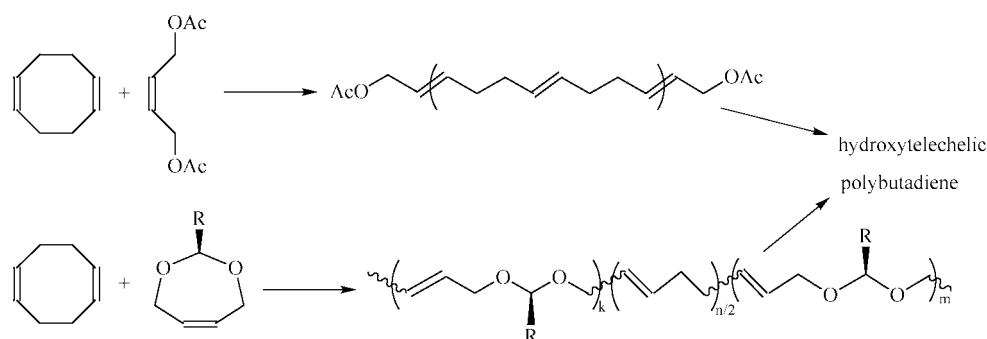


Fig. 14. Hydroxytelechelic polybutadiene by ROMP and hydrolysis.

ROMP in the presence of unprotected alcohols led to decreased yields and significant amounts of aldehyde end groups due to isomerization (399–401). However, ROMP with the addition of 1,4-bis(acetoxy)-2-butene (43) or even the related unprotected diols was performed successfully with the highly active Grubbs catalyst **II**. In the latter case, THF was added to minimize isomerization to aldehydes (401). Br- and Cl-telechelic poly(butadiene)s were employed for the synthesis of ABA triblock copolymers by subsequent grafting from the ROM polymers with methyl methacrylate (MMA) or styrene via ATRP (398). The preparation of poly(butadiene)s with cross-linkable end groups, such as epoxides or methacrylates, was reported by Grubbs and co-workers (402). Related syntheses of acetoxy end-terminated polymers with Grubbs-type catalysts were performed not only for cyclooctadiene but also for norbornene and 7-oxanorbornene derivatives (403,404).

End-functionalized poly(norbornene)s capped with one or two acetoxy or alcohol groups were prepared with the Grubbs catalyst **I** and mixed NHC/phosphine catalysts (405). Acetoxy and hydroxyl end-capped polymers were prepared by Gibson and Okada from bis(*tert*-butylester)-substituted norbornene by means of the Grubbs catalyst **I**. Subsequent hydrogenation of the hydroxy functionalized polymer gave the corresponding poly(norbornene) (406).

A further interesting approach for chain-end functionalization was reported. The treatment of a living ROM polymer Grubbs catalyst **I** with molecular oxygen led to monoaldehyde-end-capped polymers in high yields (407). With W- or Mo-based catalysts, the analogous synthetic protocol would partially lead to a coupling reaction, thereby yielding polymers with doubled molecular weight (6,407,408).

The synthesis of a homologous series of unsaturated oligomeric esters by cross-metathesis of cyclopentene and MMA is reported (409,410). Ozawa and co-workers (411) reported on the polymerization of norbornene in the presence of various functionalized terminal olefins as chain-transfer agents. Mechanistic considerations let them assume that the obtained polymers each bore one vinyl end group and one functional end group.

Nomura and co-workers reported that norbornene-based macromonomers of the following structure (Fig. 15) containing ring-opened poly(norbornene) derivatives in the side chain can be prepared efficiently by the ROMP using well-defined molybdenum catalysts and subsequent end-group reactions (412,413).

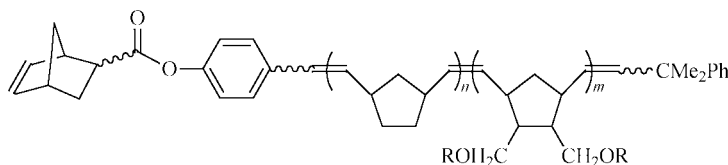


Fig. 15. Structure norbornene-based macromonomers.

Interestingly, these macromonomers were copolymerized with norbornene derivatives via ROMP to yield various macromolecular architectures (414).

ROMP approach was also applied by several groups to prepare polymers having functional groups reactive toward ATRP (398,414,415).

Chain Scission

Telechelics can also be prepared by the cleavage of high molecular weight moieties by oxidation, reduction, rearrangements, and irradiation (Table 9).

Oxidation. Treatment of PVC with ozone (416–418) gives telechelics; the attack probably starts at the vinyl double bonds.

Ozonolysis can be used as an analytical method for polymers containing carbon–carbon double bonds (438–441).

Acid, acid chlorides, and hydroxy-functionalized telechelics have been described (418). The reaction of polybutadiene with controlled amounts of ozone can be used to prepare hydroxy-terminated telechelic polybutadienes (419). The oxidative cleavage of copolymers of isobutylene with dienes has been studied

Table 9. Telechelics Prepared by Chain Scission

Structure	End group	References
$-(\text{CH}_2-\text{CHCl})_n-$	COOH	416–418
	COCl	418
	OH	
$-(\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2)_n-$	OH	419
$-\left[\text{CH}_2-\text{C}(\text{CH}_3)_2\right]_n-$	COOH	420–423
	COCH ₃	424,425
	CH ₂ OH	426–430
	CHOHCH ₃	
$-(\text{CH}_2-\text{CH}_2)_n-$	COOH	431
$-\left[\text{CH}_2-\text{CH}(\text{C}_6\text{H}_5)\right]_n-$	OH	432,433
$-(\text{CH}_2-\text{CH}_2-\text{O}-\text{CH}_2\text{CH}_2\text{S}_x)_n-$	SH	434–436
$-\left[(\text{CH}_2\text{CH}_2)_n(\text{CH}_2-\underset{\text{CH}_3}{\text{CH}})_p\right]_q-$	OH	437

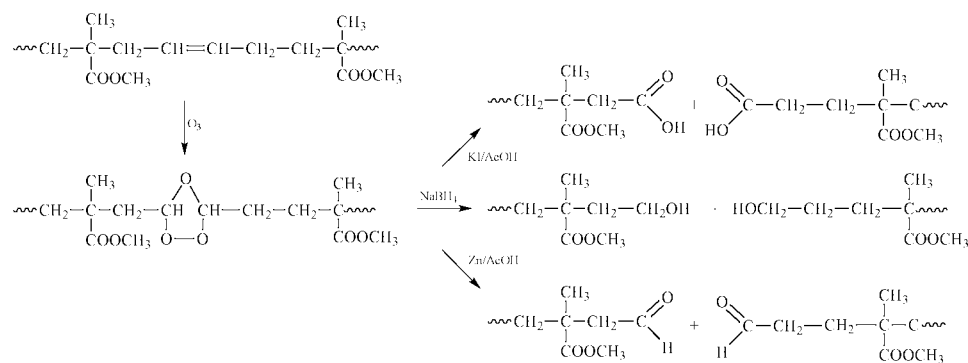


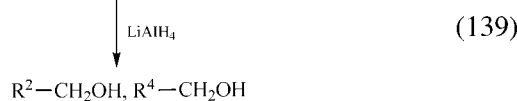
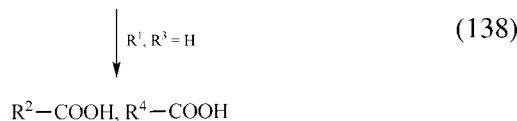
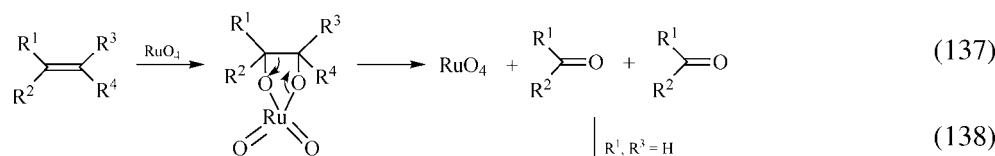
Fig. 16. Telechelic oligomers by ozonolysis.

extensively (442–444), in particular the formation of carboxyl-terminated telechelics

(424–427). Ebdon and co-workers (445–451) prepared a variety of telechelic oligomers with terminal aldehyde, hydroxyl, ketone, or carboxylic end groups by ozonolysis of suitable copolymers of MMA or St containing small amounts of C=C bonds (Fig. 16). These bonds were introduced using either a diene or acetylene as comonomer.

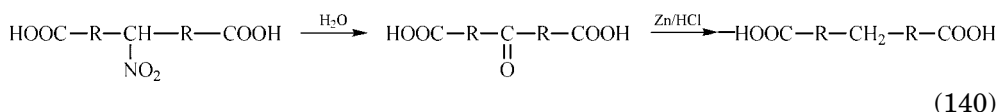
Polystyrene and a poly(styrene-*stat*-butadiene) have been reacted with ozone in various solvents to establish conditions necessary for the production of telechelics having high and controllable end group functionalities. Workup with sodium borohydride or Zn/acetic acid gives dihydroxy- or dialdehyde-ended oligostyrenes, respectively. Oxidative workup with $\text{SeO}_2/\text{H}_2\text{O}_2$ yields carboxyl end groups. Side reactions associated with the synthesis of telechelic oligostyrenes by the ozonolysis route, ie, attack of the α -position of the backbone but also of the aromatic unit, can be minimized by the use of *N*-dialkyl amides as ozone scavenger (452).

Side reactions can be avoided with a selective oxidizing agent such as ruthenium tetroxide (453) which is soluble in many solvents. It can be used in catalytic quantities in combination with another oxidizing agent, eg, peracetic acid (454). Ruthenium dioxide in combination with periodate can be used in water or in organic solvents in the presence of a phase transfer catalyst (424,425).

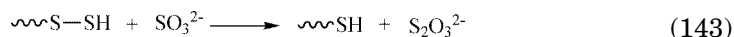
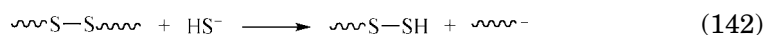
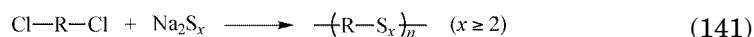


Butyl rubber yields asymmetrical α -carboxyl- ω -ketone telechelics with RuO_4 , whereas poly(isobutylene-*co*-2,3-dimethylbutadiene) yields symmetrical α,ω -ketone and α,ω -carboxyl telechelics (426–429). If the incorporation of the diene is sterically specific, ideal functionalization ($f = 2$) can be obtained with these methods, provided that high molecular weight starting materials are employed (430). Cleavage of partially hydrogenated polybutadiene with RuO_4 gives α,ω -carboxypolyethylene (431).

Many other oxidizing agents can be used to cleave polymer chains. For example, fuming nitric acid cleaves polyethylene to yield carboxyl telechelic polyethylene (455–459). However, nitration of the polymer chain is a side reaction. The nitro groups can be converted to ketones without further reduction of molecular weight (460).

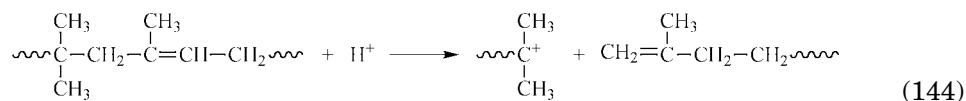


Reduction. Liquid thiokols are telechelics produced commercially by a reductive cleavage reaction (434–438).

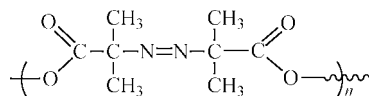
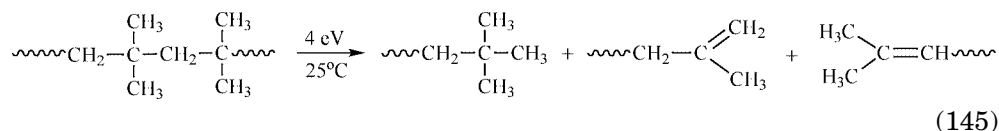


Other Degradation Methods. Ethylene–propylene telechelics with hydroxyl end groups (437) are prepared by thermal degradation followed by ozonolysis and reduction of the end group by an alkylaluminum compound. Products with molecular weights of approx 1000 with a functionality $f = 1.7$ were obtained (437).

Degradation of polyisobutylene or poly(isobutylene-*co*-isopropylene) at low temperature in the presence of a Lewis acid yields α,ω -diolefin telechelics (461).

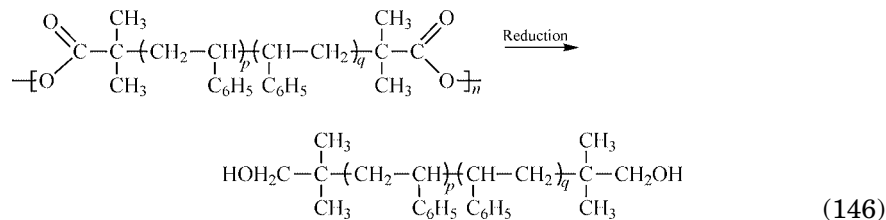


The radiolysis of polyisobutylene also gives α,ω -olefin telechelics (462).

**Fig. 17.** Polyazoester.

An interesting pathway to telechelics is the synthesis of polymers containing heat- or light-sensitive groups in the main chain, for example, azo groups (432, 433,463). Thus, polycondensation of AIBN with diols yields polyesters (Fig. 17).

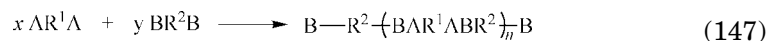
Decomposition of the azo function in the presence of styrene yields AB block copolymers, which can be converted into α,ω -dihydroxyl polystyrene by a reductive cleavage of the ester bonds.



Another potential photochemical route to prepare telechelics is the photolysis of copolymers of MMA with various vinylketones. Upon irradiation these copolymers undergo chain scission almost entirely by a Norrish Type I process, giving oligomers with allylic end groups (464,465).

Step-Growth Polymerization

Step-growth polymerization is a simple method of preparing reactive oligomers (466), many of which cannot be prepared by the methods described previously. Increasing commercialization of thermoplastic elastomers, based on tri- or multi-block copolymers, has led to a growing interest in telechelics of polymers with high glass-transition temperatures, which may be used as rigid blocks. Polymers with high glass-transition temperatures are frequently prepared by a step-growth polymerization. Almost all functional groups can, in principle, be utilized for step-growth polymerization. However, side reactions such as cyclization and decarboxylation limit the molecular weight, functionality, and yield. AR^1A and BR^2B are followed to react ($x < y$),



and the molecular weight of the products is given by

$$\bar{DP}_n = \frac{(1+r)}{(1+r-2p)}$$

where $\bar{DP}_n$ is the number-average degree of polymerization, $r = (\text{AR}^1\text{A}):(\text{BR}^2\text{B})$ with $(\text{AR}^1\text{A}) < (\text{BR}^2\text{B})$, and p = conversion of AR^1A .

At 100% conversion of the minor reactant, the molecular weight of the product is determined by the following equation:

$$\bar{DP}_n = \frac{(1+r)}{(1-r)}$$

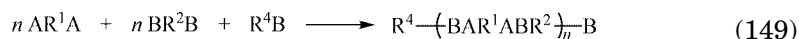
and the end groups are those of the major component.

This method can be applied for the preparation of α,ω -dicarboxyoligoesters, α,ω -dicarboxyoligoamides. It has also been applied to the preparation of α,ω -diphenol oligocarbonates and epoxy resins (467–472).

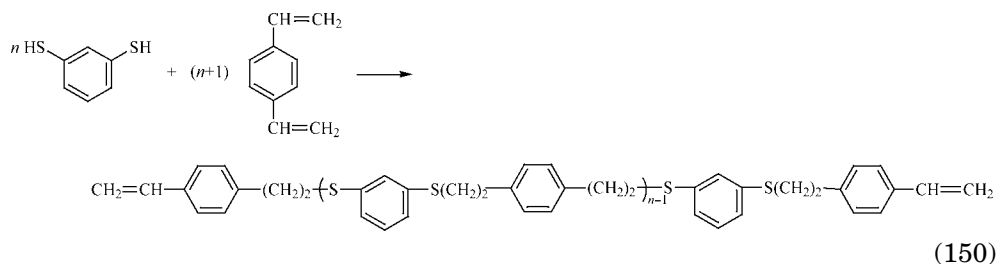
In an alternative method of achieving nonstoichiometry, AR^3X or BR^4X (where X represents a functional group which does not react with A or B) is added to the reaction system. At complete conversion, X forms the end groups of the polymer:



The latter method is also useful for preparing monofunctional telechelics. In this case a monofunctional reactant is used. For example, R^4B gives

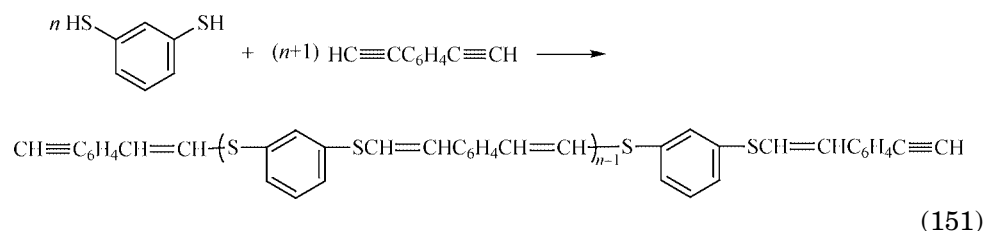


Nonstoichiometric Reactions. This addition of an SH group to a carbon-carbon double bond involves radical intermediates, but nevertheless exhibits the typical features of a polycondensation reaction. The end group and molecular weight are controlled by stoichiometry of the reactants (473).

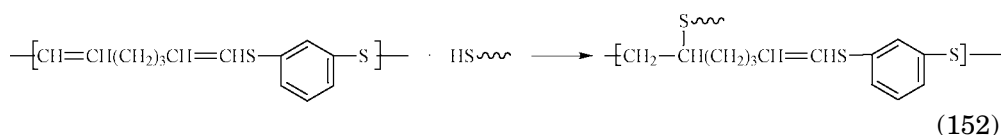


Thus an excess of the divinyl reactant yields products with olefinic end groups, whereas an excess of the dithiol component yields products with mercapto end groups. For products of molecular weight below 5000, end group analysis can be used to determine the molecular weight. Similar addition reactions have also

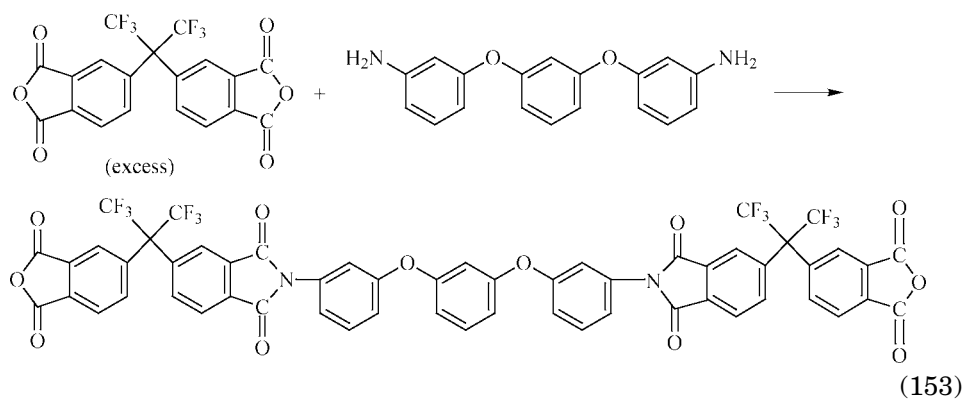
been carried out with triple bonds (474,475), ie using 1,4-diethynylbenzene in place of DVB.



Aliphatic α,ω -dialkynes give telechelics only when the alkyne is used in excess. If the dithiol is in excess, the SH end groups react with the double bonds of the polymer backbone to produce branched or finally cross-linked products.



Telechelics can also be prepared by conventional polycondensation (476).



The acid anhydride end groups can subsequently be modified by reaction with substituted aromatic amines.

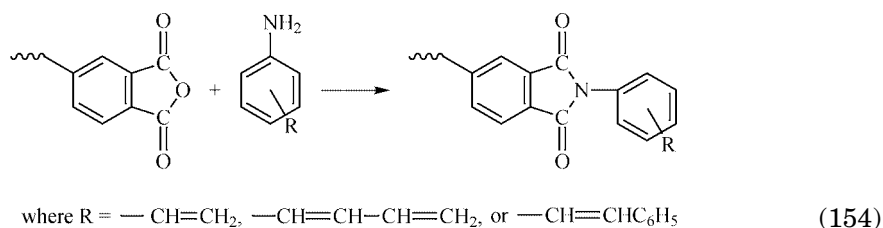


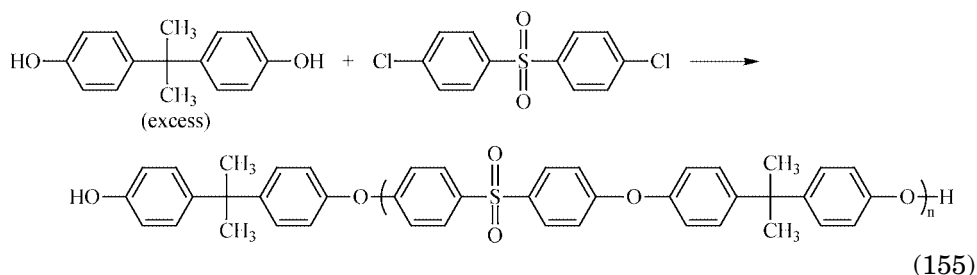
Table 10. Reactions of Bisphenol A with *p*-Dichlorophenyl Sulfone^a

DP _n ^b	Molecular weight			
	Theoretical	By IR	By ¹ H NMR	By UV
1	670	785	680	720
2	1110	1175	1110	1110
4	2000	1950	2040	2100
7	3320	3600		3380

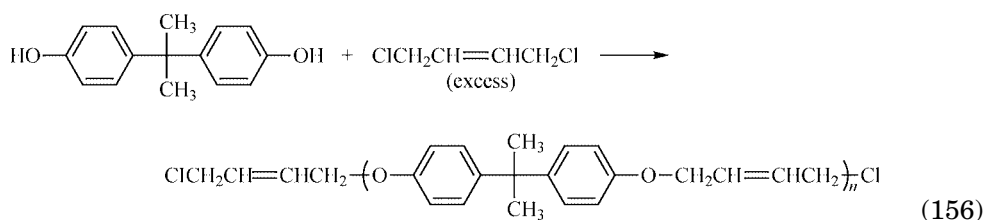
^aRef. 482.^bNumber-average.

Other examples of telechelic synthesis by polycondensation reactions involving an excess of one of the reactants, followed by modification of the resulting end groups, have also been described (477–481).

Studies (482,483) of the polycondensation of bisphenol A and *p*-dichlorodiphenyl sulfone show that molecular weight and end groups can be controlled by using nonstoichiometric ratios of the reactants; agreement with theory is excellent (Table 10).

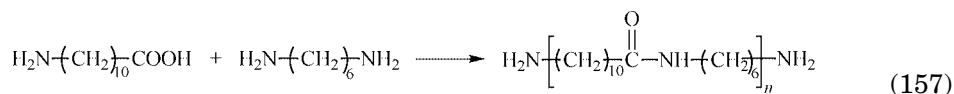


With the aid of phase-transfer catalysts, several polycondensates can be obtained under mild conditions. An example is given in reaction 156:

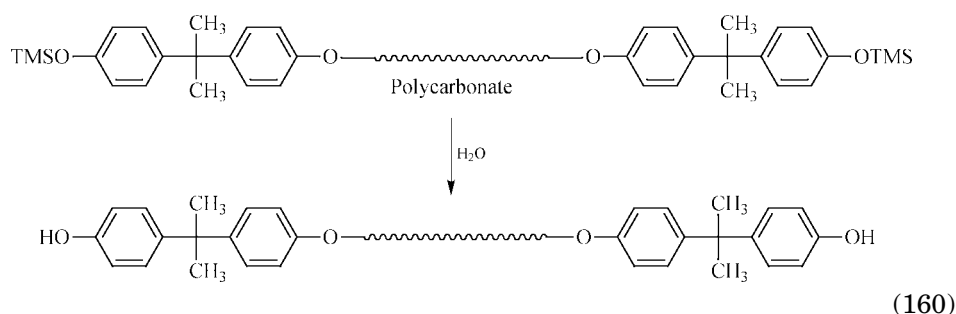
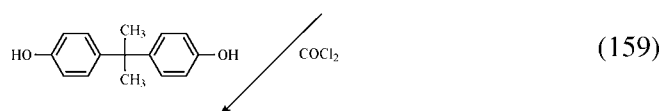
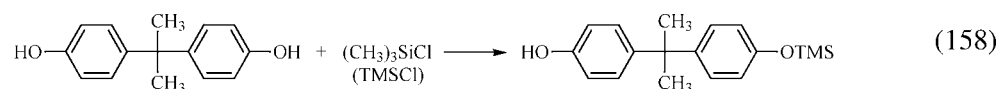


This reaction was carried out in a water–chlorobenzene mixture in the presence of NaOH and tetrabutyl ammonium hydrogen sulfate (484).

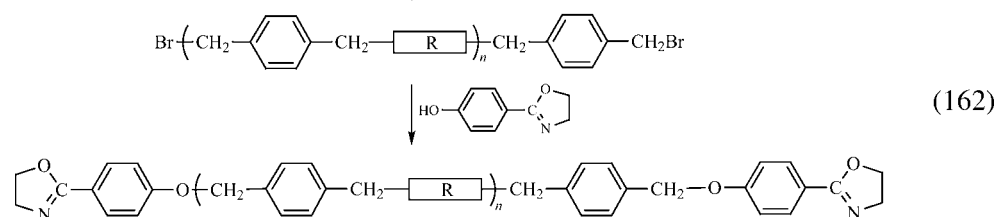
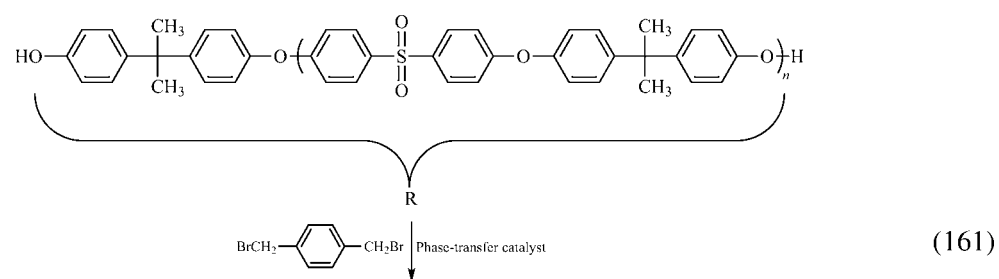
For polycondensation where a single reactant contains both functional groups, an additional reactant can achieve the necessary nonstoichiometry:



End groups and molecular weight are controlled by the diamine concentration (485). The introduction of protecting groups results in the following reactions (486):



Phase-transfer catalysts have also been used for the modification of telechelics (487).



Macromonomers

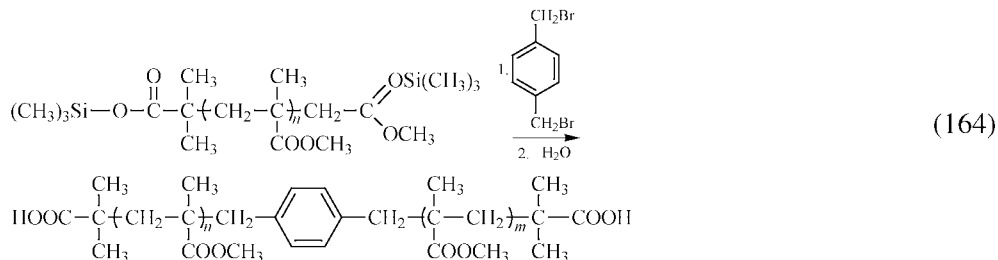
Macromolecular monomers, called *macromonomers* or *macromers*, can be defined as oligomers or polymers with a polymerizable end group. Such groups may be

vinyl, acrylic, heterocyclic (ring opening polymerization), dicarboxylic, or dihydroxylic (step-growth polymerization). The increasing interest in these materials stems from the growing need for well-defined graft copolymers for which macromonomers often are ideal starting materials (488–496). The length and number of branches of the graft copolymers can be controlled by the molar mass and feed ratio of macromonomers to comonomers. In the previous sections, the synthesis of macromonomers has been described particularly when the chemistry involved is similar to that for the telechelics with other functional groups. The principal focus of the following part will be to describe well-established general approaches for the synthesis of macromonomers. For a wider view, the reader's attention should be directed to the review articles (279,280,497,498) and a book (499) solely devoted to macromonomers.

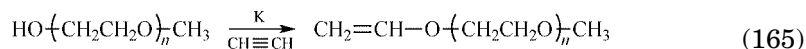
Anionic Polymerization. Anionic methods for the synthesis of macromonomers can be divided into initiation and end-capping (Table 11).

Although the initiation method is widely used, side reactions of the unsaturated head groups often lead to low functionality.

Polar monomers, such as MMA, rarely give high yields of macromonomers by straightforward anionic polymerization. However, group-transfer polymerization (517–522), which is a special case of Anionic Polymerization (qv), gives macromonomers with perfect functionality.



The reaction of the alcoholate of polyoxyethylene with acetylene yields a macromonomer (523).



Cationic Polymerization. Both initiator and end-capping methods can be used to obtain macromonomers by cationic polymerization (see CARBOCATIONIC POLYMERIZATION). Telechelics can be made this way from PTHF (Table 12). A typical reaction is given below:

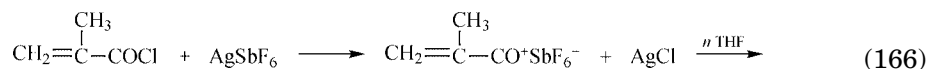
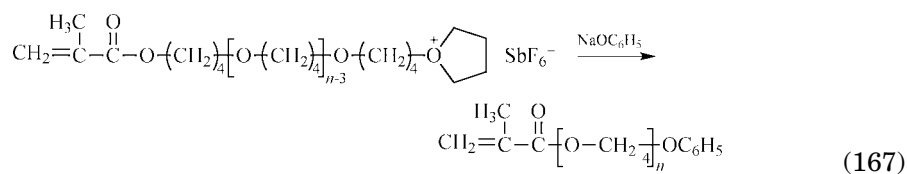


Table 11. Macromonomers by Anionic Polymerization

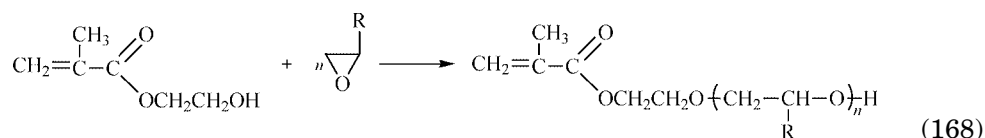
Initiator	References	End capping	References
<i>Styrene</i>			
$\text{CH}_2=\text{CH}_2\text{Li}$	500, 501	$\text{CH}_2=\underset{\text{CH}_3}{\text{CH}}-\text{COCl}$	488
$\text{CH}_2=\text{CH}_2\text{CH}_2\text{Li}$	501	$\text{ClCH}_2\text{CH}_2-\text{O}-\underset{\text{CH}_3}{\text{CH}}=\text{CH}_2$	488
		$\text{CH}_2=\underset{\text{CH}_3}{\text{CH}}-\text{Si}(\text{CH}_3)_2-\text{CH}_2\text{Cl}$	502
		$\text{CH}_2=\underset{\text{R}}{\text{C}}-\text{C}_6\text{H}_4-\text{CH}_2\text{Cl}$	503
		$\text{CH}_2=\text{CH}-\text{C}_6\text{H}_4-\text{CH}_2\text{Cl}$	488
<i>Methyl methacrylate</i>			
$\text{CH}_2=\text{CH}-\text{C}_6\text{H}_4-\text{MgCl}$	504	$\text{CH}_2=\text{CH}_2-\text{CH}_2\text{Br}$	505
		$\text{CH}_2=\text{CH}-\text{C}_6\text{H}_4-\text{CH}_2\text{Br}$	505
		$\text{CH}_2=\underset{\text{CH}_3}{\text{C}}-\text{C}_6\text{H}_4-\text{CH}_2\text{Br}$	506
<i>Ethylene oxide</i>			
$\text{CH}_2=\underset{\text{CH}_3}{\text{C}}-\text{C}_6\text{H}_4-\text{CH}_2\text{OK}$	507	$\text{CH}_2=\underset{\text{CH}_3}{\text{CH}}-\text{COCl}$	507,508
	509	$\text{CH}_2=\text{CH}-\text{C}_6\text{H}_4-\text{CH}_2\text{Cl}$	510
<i>Vinylpyridine</i>			
$\text{CH}_2=\text{CH}-\text{C}_6\text{H}_4-\text{MgCl}$	504	$\text{CH}_2=\underset{\text{CH}_3}{\text{CH}}-\text{C}_6\text{H}_4-\text{CH}_2\text{Cl}$	511
		$\text{CH}_2=\underset{\text{CH}_3}{\text{CH}}-\text{COCl}$	512
		$\text{CH}_2=\underset{\text{CH}_3}{\text{C}}-\text{C}_6\text{H}_4-\text{CH}_2\text{Br}$	513

Table 11. (Continued)

Initiator	References	End capping	References
<i>Hexamethylcyclo-trisiloxane</i>			
		$\text{CH}_2=\text{CH}-\text{C}_6\text{H}_4-\text{Si}(\text{CH}_3)_2\text{Cl}$	514
		$\text{CH}_2=\text{CH}-\text{Si}(\text{CH}_3)_2\text{Cl}$	515
		$\text{CH}_2=\text{C}(\text{CH}_3)-\text{COO}(\text{CH}_2)_3-\text{Si}(\text{CH}_3)_2\text{Cl}$	516



Oxiranes also polymerize under similar conditions.



This macromonomer is sold under the trade name Blendmer (530).

Termination of the cationic ring-opening polymerization of *N*-*t*-butylaziridine with methacrylic acid yields macromonomers (531).

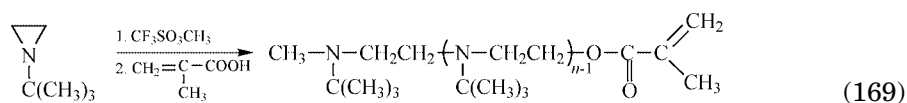
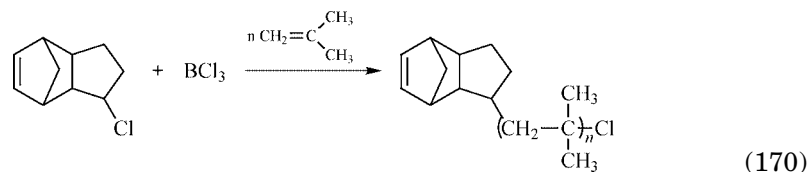


Table 12. Macromonomers from PTHF

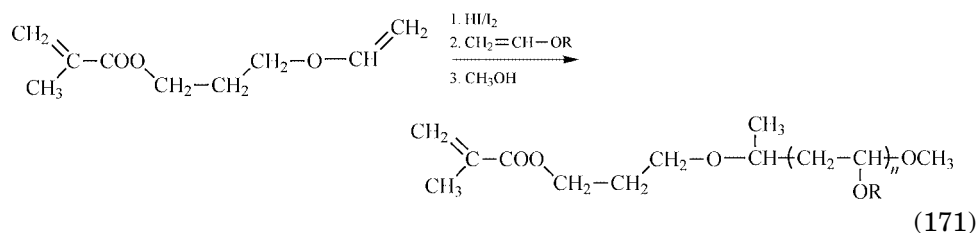
Initiator	References	End capping	References
$\text{CH}_2=\text{C}(\text{CH}_3)-\text{CO}^+ \text{SbF}_6^-$	524	$\text{CH}_2=\text{CH}-\text{C}_6\text{H}_4-\text{ONa}$	526
$\text{C}_6\text{H}_5-\text{CH}=\text{CH}-\text{CH}_2^+ \text{PF}_6^-$	525	$\text{CH}_2=\text{CH}-\text{C}_6\text{H}_4-\text{CH}_2\text{ONa}$	527
$\text{CH}_2=\text{CH}-\text{C}_6\text{H}_4-\text{CH}_2^+ \text{PF}_6^-$	525	$\text{CH}_2=\text{C}(\text{CH}_3)-\text{C}_6\text{H}_4-\text{CH}_2\text{OK}$	528
		$\text{C}_6\text{H}_5-\text{CH}=\text{CH}-\text{CH}_2-\text{OLi}$	529

Macromonomers from 2-isobutylene have been prepared by the inifer method (532,533).



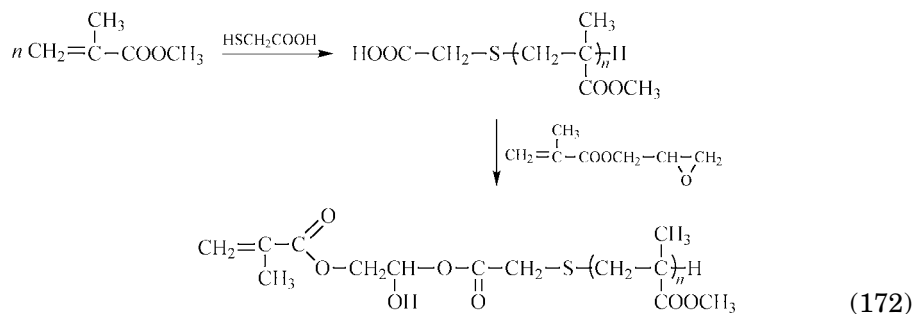
This macromonomer has been copolymerized with ethylene and propylene in the presence of Ziegler–Natta catalysts.

The living polymerization of vinyl ethers using the HI/I_2 (534,535) or the acetal/TMST method (536) can be used for macromonomer synthesis.



These macromonomers are characterized by narrow molecular weight distribution and excellent functionality.

Radical Polymerization. Macromonomers can also be synthesized by radical polymerization (537,538).



With thioglycolic acid as a chain-transfer agent, macromonomers are prepared from dimethylaminoethyl methacrylate and other acrylate and methacrylate derivatives (539). Iodoacetic acid is used as the transfer agent for polystyrene macromonomers (540).

3-Mercaptopropionic acid can be used as a transfer agent for preparing telechelics from acrylamide and *N*-vinylpyrrolidone (541).

All these reactions first lead to simple COOH -terminated (monotelechelic) polymers and are converted into macromonomers by a glycidylmethacrylate (eg reaction 172).

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