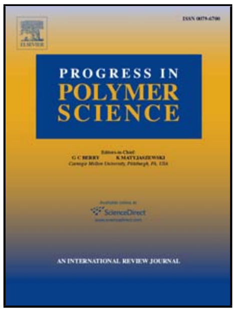

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The Synthesis of Modified Polyethylene via Coordination Polymerization Followed by ATRP, RAFT, NMRP or ROP

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Abstract

Research on the synthesis of modified polyethylene (PE) is of great significance to both academic study and industrial applications. The synthesis of modified polyethylene has experienced remarkable and significant progress in the control over the microstructure, composition, molecular weight and molecular weight distribution of the polymeric products. This review summarizes the achievements in the synthesis of modified polyethylene via combining coordination polymerization with atom transfer radical polymerization (ATRP), reversible addition-fragmentation chain transfer (RAFT) polymerization, nitroxide-mediated radical polymerization (NMRP) or ring-opening polymerization (ROP) for the last decade. In addition, the mechanisms of the aforementioned polymerization techniques are expounded in this contribution.

Keywords

Modified Polyethylene; ATRP; RAFT; NMRP; ROP

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1. Introduction

As the largest volume and the most widely used commodity polymers, polyolefins have become the indispensable materials to our society with a worldwide production exceeding 100 million tons per year [1-3]. Polyolefins are widely used in commercial fields due to the combination of excellent physical and chemical properties, such as mechanical strength, flexibility, chemical stability, superior processability and recyclability, along with low cost [3,4].

Polyethylene (PE) is deemed as one of the most useful polyolefins for its impact resistance along with the aforementioned properties [5]. However its inherent shortcomings, for example poor adhesion and incompatibility with other materials due to its nonpolar character impede its application in many areas, where more expensive and less environmentally friendly materials are used [4]. The modified polyethylene containing polar groups possess both improved surface and bulk properties, such as barrier properties, toughness, adhesion, printability, wettability, miscibility with other polar polymers and so on [6-8]. Modified polyethylene may act as an effective compatibilizer for mixtures of polyolefins with other materials [9,10]. For example, copolymers of ethylene with 5-hexen-1-ol or 10-undecen-1-ol were used to improve the miscibility of polyethylene with polar natural polymers [11].

For more than half an century, modification of polyethylene has been an academic challenge as well as an industrially important area [2]. Based on previous literature, three common approaches for the modification of polyethylene can be summarized: (a) copolymerizing functional monomers with ethylene, (b) modifying preformed polyethylene chemically, (c) introducing reactive functional groups which can be used directly as or converted into initiating sites for the subsequent polymerization, such as ring-opening polymerization (ROP) or reversible-deactivation radical polymerization (RDRP) [2,4].

As one of the most significant research field developed in the past decades, RDRP provides a versatile access to well-defined polymers with topology and components, designed to develop predetermined, desirable properties [12-14]. Hence the RDRP technique is a promising methodology to afford modified polyethylene.

There has been debate over the terminology for the depiction of radical polymerizations, such as atom transfer radical polymerization (ATRP), reversible addition fragmentation chain transfer polymerization (RAFT) and nitroxide mediated radical polymerization (NMRP) [15]. It is not rational to employ “living” to depict these polymerizations since International Union of Pure and Applied Chemistry (IUPAC) has defined a living polymerization as “a chain polymerization in which irreversible chain termination and irreversible chain transfer are absent” [15,16]. Moad et al. thought it improper to use the term “controlled” which has an established and broader usage, to indicate a particular form of polymerization [17]. Recently, reversible-deactivation radical polymerization (RDRP) was recommended by IUPAC as the preferred term to describe a radical polymerizations in which active-dormant equilibria exist [18].

This paper summarizes recent progress in the synthesis of modified polyethylene by combining coordination polymerization with reversible-deactivation radical polymerization, including ATRP, RAFT and NMRP. In addition, ring-opening polymerization (ROP) also plays an important role in the synthesis of modified PE containing polar segments, hence efforts in this aspect are also traced. The general procedures for this strategy are shown as Fig. 1.

Fig. 1

2. Synthesis of modified PE containing polar segments employing ATRP

2.1. ATRP

Since the concept of ATRP was first brought forward by Matyjaszewski et al. in 1995 [19,20], this synthetic strategy has been intensively studied, with significant advances owing to its ability to mediate a reversible-deactivation radical polymerization for a wide range of monomers, to result in well-defined polymers and copolymers [21,22]. At present, ATRP is the most extensively studied RDRP method due to both its excellent control and ability to afford polymeric materials with various topologies, functionalities and compositions [23-25]. Furthermore, self-organization of copolymers into regular nano-structured morphologies has been achieved through ATRP based on its accurate supramolecular control [25-28]. ATRP has become a very versatile approach to prepare various block and graft copolymers [22,29].

Matyjaszewski et al. [30] have depicted the mechanism, monomers, initiators, transition metal complexes and ligands of ATRP. A typical catalytic system of ATRP consists of a transition metal complex with an alterable oxidation number, a ligand compound and an initiating alkyl halide [30-32]. ATRP can be successfully mediated by several metals, with Cu proven to be the most efficient. Phosphorus ligands and nitrogen ligands including various derivatives of bidentate bipyridine (bpy), phenanthroline (phen), tetradentate tris[2-aminoethyl]amine (tren) ,etc., are used as ligands [30,31].

The mechanism of ATRP (Fig. 2) comprises the generation of a radical R· through the homolytic cleavage of an alkyl halide bond R-X by a transition metal complex Mt^n, which reaches a higher oxidation state Mt^{n+1}. Then R· may propagate with vinyl monomers or become a dormant species reversibly by Mt^{n+1}. Due to the persistent radical effect [33] in reversible conversion between the propagating radicals and corresponding dormant species, the radical concentration is kept low, so that irreversible radical termination is diminished.

Fig. 2

2.2. Synthesis of modified PE by combining coordination polymerization and ATRP

To develop a versatile RDRP method to synthesize polymers with various topologies and compositions, ATRP was employed in combination with coordination polymerization to produce polyolefin based block and graft copolymers with polar segments, such as polypropylene based copolymers [34-37].

The synthesis of modified polyethylene via ethylene polymerization or copolymerization followed by a subsequent ATRP has been studied extensively, and many copolymers with various architectures and compositions have been obtained. The first report for the synthesis of ethylene graft copolymers containing polystyrene or polyacrylate segments via atom transfer radical polymerization appeared in 1999 by the Matyjaszewski group [38].

The same group prepared poly(*n*-butyl acrylate)-*g*-polyethylene (PBA-*g*-PE)) through combining Pd-mediated living olefin polymerization and ATRP [1]. Branched polyethylene with a methacrylate-functionalized end group, polyethylene macromonomer (PE-MM), was first prepared by living olefin polymerization mediated by Pd(II) α-diimine catalyst (Fig. 3). A low temperature (6 •) and high ethylene pressure (400 psi) were chosen as the reaction conditions to ensure a living polymerization. Thus PE-MMs with uniform molecular weight ($M_n \sim 11000$) and low polydispersity (PDI < 1.05) were successfully prepared.

Through the atom transfer radical copolymerization of PE-MM with *n*-butyl acrylate (*n*BA), PBA-*g*-PEs with different compositions (PE-MM wt % = 34.7, 59.2 and 70.2, respectively) were obtained in the presence of CuBr/PMDETA (*N,N,N’,N”,N”*-pentamethyldiethylenetriamine) (Fig. 4). The relatively low PDI ($M_w/M_n \sim 1.4$) suggested a controlled copolymerization. However the conversions of the PE-MM and *n*BA were not very high due to the high viscosity of the polymerization medium and the intrinsic incompatibility between PE segments and the polar backbone [1].

Fig. 3 and Fig. 4

Graft copolymers containing highly crystalline polyolefin segments, e.g. linear polyethylene, have received less attention than that bearing noncrystalline polyolefin. A main contributor to this disparity is the poor solubility of crystalline polyolefins in RDRP systems [12].

Matyjaszewski et al. [12] synthesized polyethylene-*g*-poly(*n*-butyl acrylate) (PE-*g*-P*n*BA) and polyethylene-*g*-poly(methyl methacrylate) (PE-*g*-PMMA) from linear polyethylene macroinitiators. Ethylene copolymers bearing pendent hydroxyl groups were synthesized through the copolymerization of ethylene with 10-undecen-1-ol using zirconocene catalyst. Then through the reaction of *α*-bromoisobutyryl bromide with the hydroxyl groups attached to the preformed copolymers, linear polyethylene based multifunctional macroinitiators were prepared and used in the following ATRP of *n*-butyl acrylate (*n*BA) and methyl methacrylate (MMA) (Fig. 5). For the graft polymerization, a catalytic system of $CuCl/CuCl_2$/ BA_6TREN (*tris*(2-(*di*(2-(*n*-butoxycarbonyl)ethyl)amino)ethyl)amine) with high activity was employed to obtain a high enough polymerization rate with a dilute monomer concentration. Both the linear increase of the molecular weight of detached poly(*n*-butyl acrylate) (PBA) with the monomer conversion and the low PDI (1.28, after 3 h polymerization) indicated that the graft polymerization of *n*BA was well controlled. However, the graft polymerization of MMA was not as well controlled as that of *n*BA. A subsequent study showed that the prepared PE-*g*-P*n*BA displayed a microphase separation and unique thermomechanical behavior due to the existence of both crystalline PE and amorphous P*n*BA segments [39].

Fig. 5

Kallitsis et al. [40] studied the synthesis of ethylene copolymers possessing polystyrene segments through the reactive blending of end-functionalized polystyrene with polyethylene-*g*-poly(glycidyl methacrylate) (PE-*g*-PGMA). Polystyrenes bearing one carboxyl group per chain end were synthesized via ATRP of styrene and a subsequent hydrolysis reaction using commercially available haloesters as initiators. Then *α*-carboxyl polystyrenes were grafted to PE-*g*-PGMA through the reaction of carboxyl group with the epoxy groups in PE-*g*-PGMA. And the obtained graft copolymers can be used as compatibilizers for the immiscible polyethylene/polystyrene blend.

It is well known that benzylic protons are reactive and that various functional groups can be introduced at benzylic position through corresponding chemical reactions, such as halogenation and metallation [41]. This fact highlights the incorporation of *p*-methylstyrene into polyethylene as another promising method to achieve the modification of polyethylene.

Jiang et al. [42] reported the graft polymerization of MMA and *n*BA from functionalized poly[ethylene-*co*-(*p*-methyl styrene)] via ATRP. Copolymerizations of ethylene with *p*-methylstyrene (*p*-MS) were first conducted with several metallocene catalysts. The results showed that the copolymer obtained with *rac*-Et(Ind)$_2$ZrCl$_2$ contained more *p*-MS comonomer (4.9 mol %), indicating that the bridge catalyst is more favorable for incorporation of the comonomer. Through bromination of poly[E-*co*-(*p*-MS)] with *N*-bromosuccinimide (NBS), macroinitiators were obtained for the subsequent graft polymerization of polar monomers (such as MMA and BA) using CuCl/2,2-bipyridine as the catalytic system (Fig. 6). The contents of polar segments in the graft copolymers showed a remarkable increase with the polar monomer concentration, indicating control of the graft polymerization for the two cases. Due to a steric effect, the side chains of PMMA are much longer than that of PBA under the same polymerization conditions.

Fig. 6

Polyethylene with a terminal initiating site for ATRP prepared by catalytic coordination polymerization of ethylene in the presence of chain transfer agent (CTA) followed by subsequent conversions, facilitated the preparation of block copolymers.

Kaneyoshi et al. [43] reported the synthesis of block and graft copolymers with polyacrylate and linear polyethylene segments by combining degenerative transfer (DT) ethylene polymerization and ATRP. The mechanism of DT polymerization is shown schematically in Fig. 7. Low molecular weight Zn-terminated polyethylene (PE-Zn) with was synthesized through a well controlled DT ethylene polymerization mediated by a catalyst system of bis(imino)-pyridineiron/diethylzinc/methylaluminoxane(MAO) (Fig. 8 shows the structure of bis(imino)pyridine-iron complex). The PE-Zn was converted into monohydroxyl-terminated polyethylene (PE-OH) with end functionality of 77% by ordinal oxidation and hydrolysis reactions (Fig. 9). Through the reaction of the hydroxyl groups of the PE-OH with *α*-bromoisobutyryl bromide, polyethylene *α*-bromoisobutyrate macroinitiators (PE-MI) were accomplished for the subsequent ATRP of *n*-butyl acrylate and *t*-butyl acrylate. Thus, well-defined PE-*b*-P*n*BA and PE-*b*-P*t*BA copolymers were prepared successfully with narrow polydispersities (PDI < 1.2). The M_n of block copolymers showed a linear increase with the conversion of comonomer during the ATRP process.

Fig 7, Fig 8 and Fig 9

A PE macromonomer with a terminal *α*-methacrylate group was obtained from dehydrobromination of the prepared PE-MI. Utililzing a 'grafting-through' ATRP with PE-MM and butyl acrylate, well-defined P*n*BA-*g*-PE and P*t*BA-*g*-PE copolymers with low polydispersities ($M_w/M_n < 1.5$) were synthesized (Fig. 10) [43].

Fig. 10

Vinyl groups in polymer chains can be converted into different functionalities through certain chemical reactions and can then be used to prepare block or graft copolymers.

Inoue et al. [44] reported the preparation of well-controlled ethylene block copolymers via ATRP from linear polyethylene terminated with a vinyl group. The ATRP macroinitiators were synthesized through the addition reaction of *α*-halocarboxylic acid with the vinyl groups at PE (M_n = 1800) chain ends (Fig. 11). The ATRP of *n*-butyl acrylate, methyl methacrylate, and styrene from PE macroinitiators showed high conversions, exceeding 75% after 44 h, 29 h and 120 h, respectively. All the three polymerizations proceeded in a controlled fashion in the presence of a suitable ATRP catalyst system, and block copolymers were synthesized with narrow polydispersities, especially polyethylene-*b*-polystyrene (PDI = 1.17).

Fig. 11

Matyjaszewski et al. [45] synthesized polyethylene-*g*-polystyrene copolymers utilizing ATRP with vinyl-terminated linear polyethylene (PE-vinyl), which was synthesized through ethylene polymerization. First, the vinyl-terminated linear polyethylene was converted into monohydroxy-terminated polyethylene (PE-OH) through a series of sequential reactions (Fig. 12). The preformed PE-OH was esterified by *α*-bromoisobutyryl bromide in the presence of triethylamine, followed by dehydrobromination of the *α*-bromoisobutyrate group to prepare *α*-methacrylate terminated polyethylene (PE-MM) (Fig. 13). A series of well-defined polystyrene-*g*-polyethylene copolymers (PDI < 1.2) were prepared through the copolymerization of PE-MM with styrene using CuBr/Me$_6$TREN catalyst.

Fig. 12 and Fig. 13

Park [46] explored the synthesis of ethylene graft copolymers via ATRP from polyethylene containing unreacted vinyl groups, obtained through the copolymerization of ethylene and 1,7-octadiene (Fig. 14). A macroinitiator PEOD-Br was obtained for the subsequent ATRP through the bromination of poly(ethylene-*co*-1,7-octadiene) with HBr/Br$_2$ at room temperature. The graft polymerization of styrene (St), butyl methacrylate (BMA) and glycidyl methacrylate (GMA) were performed at 120°C with PEOD-Br/CuBr/bpy as the initiator. The molecular weights of PEOD-*g*-PSt and PEOD-*g*-PBMA increased linearly with the monomer conversion and polymerization time, however the grafting rate of GMA was much lower for ST than for BMA. Additionally, the wide molecular weight distribution (PDI > 3) of the obtained copolymers implied that the ATRP was ill-controlled.

Fig. 14

The synthesis of polyolefin block or graft copolymers by combiningcoordination polymerization with ATRP typically includes three steps: (a) preparing polyolefins with certain groups, (b) converting the groups into active sites, (c) the ATRP of polar comonomers from the active sites [7]. Recently, some groups reported the synthesis of polyethylene macroinitiators in one step through the direct copolymerization of ethylene with ATRP inimer [7,47-49].

Guan et al. [47] were the first to report the synthesis of dendritic nanoparticles via a tandem chain walking polymerization (CWP) and ATRP. As shown in Fig. 15, the copolymerization of ethylene with comonomer **2** using α-diimine Pd complex **1** as the chain walking catalyst resulted in two dendritic macroinitiators, with different molecular weights. Then, a range of dendritic copolymers with core-shell structure were prepared by tuning the polymerization time in the ATRP of oligo(ethylene glycol) methacrylate (OEGMA, M_n = 300) from the initiating sites of the macroinitiators, in the presence of CuBr/$CuBr_2$/dNbpy (4,4'-(*di*-5-nonyl)-2,2'-bipyridine). The M_n of dendritic copolymers increased linearly with the monomer conversion, indicating that ATRP proceeded in a controlled fashion. Under low monomer conversions, the M_n of the polymers showed a linear increase with polymerization time (< 8 h), meaning the molecular weight and size of the dendritic copolymers could be controlled simply by the polymerization time.

Fig. 15

Ye et al. [7] studied the synthesis of hyperbranched polyethylene possessing ATRP initiating sites via Pd-diimine catalyst mediated copolymerization of ethylene with inimer 2-(2-bromoisobutyryloxy) ethyl acrylate (BIEA). ^{1}H-NMR analysis indicated that the polar comonomer content in the resultant polymers increased with the concentration of BIEA, and that the branching densities were similar. The macroinitiators were used to synthesize copolymers possessing core-shell structure and PMMA side chains through ATRP of methyl methacrylate (MMA) (Fig. 16).

Fig. 16

Using the strategy shown in Fig. 16, Xiao [48] synthesized polyethylene-*g*-poly(*t*-butyl methacrylate) copolymer using ATRP to graft *t*-butyl methacrylate via the macroinitiator. A hydrolysis reaction of the methacrylate units of the graft copolymers yielded a pH-responsive polyethylene-*g*-poly(acrylic acid) (PE-*g*-PAA) with a relatively narrow polydispersity (PDI = 1.47~1.59) (Fig. 17). The hydrodynamic diameter of the resultant PE-*g*-PAA showed a reversible change with the solution pH.

Fig. 17

Ferrocene is one of the electrochemically active groups used in anion recognition [49,50]. Xiao [48] studied the synthesis of ethylene graft copolymer containing ferrocene units, and the possible application of the graft copolymer in anion recognition. The copolymerization of ethylene with BIEA using Pd catalyst produced hyperbranched polyethylene macroinitiators, from which ATRP of ferrocenyloxy ethyl acrylate (FcEA) (synthesized according to the procedures in Fig. 18) was initiated in the presence of CuBr/$CuBr_2$/PMDETA to prepare the graft copolymer polyethylene-*g*-poly(ferrocenyloxy ethyl acrylate) (PE-*g*-PFcEA) (Fig. 19). The cyclic voltammetry (CV) curves of the ethylene graft copolymer solution showed a clear response to the addition of $H_2PO_4^-$, indicating the ability of anion recognition by

PE-*g*-PFcEA.

Fig. 18 and Fig. 19

Bazan et al. [51] prepared a well confined PE macroinitiator for subsequent ATRP through the copolymerization of ethylene with compound **3** using nickel α-iminocarbaxamidato complex as catalyst and Ni(COD)$_2$ (bis(1,5-cyclooctadiene)-nickel) as the coactivator, based on the procedures shown in Fig. 20. In the polymerization, a mixture of **1/2** is first exposed to ethylene for a time t_1 before the addition of **3** to avoid the appearance of precipitate produced by **2** in the presence of **3**. The M_n of the obtained copolymers showed a linear increase with reaction time t_2, indicating the copolymerization proceeded in a controlled manner. Furthermore, the mole percentage of **3** in the copolymers did not vary with t_2 but increased with the decrease of ethylene pressure. When t_1 = 3 min and t_2 = 2 min, the molecular weight of the copolymer reached to 45K with PDI of 1.3. Then the ATRP of MMA was carried out and semicrystalline graft copolymers with a narrow polydispersity (PDI = 1.2~1.3) were obtained. In a subsequent publication, PE-*g*-P*n*BA with varying compositions were synthesized using the same strategy. The examination of mechanical properties showed that the resultant PE-based graft copolymers possessed excellent elastomeric performance [52].

Fig. 20

With functionalized Pd-diimine catalysts, polyethylene can be afforded with an end group, which may act as an initiating site for a following polymerization. Ye et al. [53] prepared polyethylene block copolymers via a two-step tandem strategy combining "living" ethylene polymerization with ATRP. Via a "living" ethylene polymerization in the presence of functionalized Pd-diimine catalyst (see Fig. 21) under typical conditions of 400 psi ethylene pressure and 5 °C, a highly branched PEs with narrow polydispersities (PDI = 1.08~1.21) were provided with an end-capping 2-bromoisobutyryl group. ATRP of styrene and *n*-butyl acrylate in the presence of these polyethylene macroinitiators and CuBr/$CuBr_2$/PMDETA provided polyethylene-*b*-polystyrene and polyethylene-*b*-poly(*n*-butyl acrylate) copolymers, respectively, with narrow polydispersities (PDI ~ 1.3) as shown in Fig. 22. The length of the functional block could be regulated conveniently through the polymerization time.

Fig. 21 and Fig. 22

2.3. Modification of preformed polyethylene and ethylene copolymers through ATRP

ATRP has also been widely used to graft from or graft onto solid surfaces, such as silicone substrate [54,55]. ATRP was applied to modify preformed polyethylene subsequently pretreated chemically or radiatively.

Matyjaszewski's group made broad research on the synthesis of graft copolymers by ATRP employing both "grafting from" and "grafting through" techniques. They reported the synthesis of polyethylene graft copolymers employing ATRP from commercially available poly(ethylene-*co*-glycidyl methacrylate) (P[E-*co*-GMA]) [56]. Chloroacetate functional macroinitiator (PE-Cl) and 2-bromoisobutyrate functional macroinitiator (PE-Br) were prepared through the reaction of the oxirane rings of

P(E-*co*-GMA) with chloroacetic acid and 2-bromoisobutyric acid, respectively (Fig. 23). Then the ATRP in the presence of CuCl/dNbpy of styrene (St) initiated by macroinitiator PE-Cl and methyl methacrylate (MMA) initiated by PE-Br were completed. The molecular weight of the cleaved PS chains showed a linear increase with the conversionwith a polydispersity of (PDI < 1.4). DSC analysis implied the existence of phase separation of the graft copolymers for both cases. St and MMA contents in the obtained graft copolymer reached 74 wt % and 81 wt %, respectively.

Fig. 23

Yamamoto et al. [57] studied the graft polymerization of MMA from high density polyethylene (HDPE) films modified by 2,2,2-tribromoethanol or benzophenone (Fig. 24). The process employed typical ATRP mediated by a nickel complex and reverse ATRP mediated by an iron complex. In the typical ATRP of MMA, SEC profiles showed that the graft PMMA chain cleaved from the substrate had a narrow polydispersity (<1.4), almost the same as that of free PMMA produced simultaneously during grafting polymerization. The characteristics of free PMMA and graft PMMA were assumed the same. The grafting ratio showed a linear relation with the molecular weight of the free PMMA. Its increase was attributed to the growing chain length of the graft PMMA, suggesting that the grafting of PMMA from the surfaces of HDPE processed in a controlled fashion. The highest grafting ratios reached 1.31 wt % for typical ATRP and 16.7 wt % for reverse ATRP, respectively.

Fig. 24

Although ATRP and stable free radical polymerization (SFRP) permit “controlled” or “living” polymerizations, the initiators, mediators and ligands required in these processes are quite expensive [5]. Different from typical ATRP, the reverse ATRP mentioned above may utilize conventional radical initiators, for example α,α'-azobisisobutylonitrile (AIBN) [58,59], benzoyl peroxide (BPO) [60] and 1,1,2,2-tetraphyenyl-1,2-ethandiol (TPED) [61], etc., for the initiation process, together with transition-metals in a higher oxidation state, and potentially can be applied in industry.

Yamamoto et al. [5] studied the graft polymerization of MMA on to polyethylene via reverse ATRP. The reverse ATRP of MMA was found to proceed in a controlled manner with different peroxides in the presence of Fe catalyst. To produce peroxides on the polymer, PE was irradiated by γ-rays in air. Then PMMA-grafted PE was prepared through the reverse ATRP of MMA using FeCl3/PPh3/AIBN as the catalytic system (Fig. 25). A well defined grafting polymerization of MMA onto PE film was not obtained in an inhomogeneous (bulk) grafting system, nevertheless a controlled grafting process was obtained in a homogeneous grafting system (in *o*-xylene solution)This was supported by the narrow polydispersity (PDI < 1.4) of the PMMA side chains and a linear increase of M_n of grafted PMMA with monomer conversion.

Fig. 25

To enhance the surface hydrophilicity of poly(ethylene-*co*-acrylic acid) (PEAA) film, Husson et al. [62] studied the preparation of polyacrylamide-grafted PEAA copolymer film employing ATRP. The process consisted of two steps: immobilization of initiators and graft polymerization of acrylamide. In the first step, after converting the carboxylic acid groups of the copolymer into acid chloride groups, two different ethanolamines were anchored onto the PEAA films (shown as Fig. 26). When diethanolamine was used, the initiator density of the functionalized PEAA film was 1.64 times that with ethanolamine. Then the graft polymerization was performed in acrylamide aqueous solution in the presence of CuCl/Me$_6$TREN. The hydrophilicity of grafted films was shown to have a remarkable increase in comparison with unfunctionalized films, indicated by a decrease of the static water contact angle.

Fig. 26

3. Synthesis of modified PE containing polar segments employing RAFT polymerization

3.1. RAFT polymerization

Reversible addition fragmentation chain transfer (RAFT) polymerization was inaugurated by Moad's group [63-65] as a new living radical polymerization with excellent effectiveness and versatility in the presence of thiocarbonylthio compounds (**Fig. 27**). Surveys of the development and guidelines for selection of RAFT agents are available in the literature [66,67]. Since RAFT polymerization is applicable for various polar and nonpolar monomers under a broad range of polymerization conditions, it was thought to be one of the most robust and versatile polymerization techniques [17,29,67-72].

Fig. 27

The general mechanism of RAFT polymerization is shown as Fig. 28 [17,70-72]. A unique feature of the RAFT polymerization mechanism is the reversible addition-fragmentation when thiocarbonylthio compounds are used as the RAFT agent; initiating radicals are released though chain transfer and reversible addition fragmentation. The process provides a living radical polymerization as identified by a linear increase of molecular weight with conversion, low polydispersity and pseudo-first-order kinetics.

Fig. 28

3.2. Synthesis of modified PE by combining coordination polymerization and RAFT polymerization

RAFT polymerization is widely employed to synthesize various stimuli-responsive block copolymers [68,73-75]. The preparation of modified polyolefin utilizing RAFT polymerization has attracted considerable interest [76-78]. Kawahara et al. [79] reported the synthesis of polyethylene-poly(methyl methacrylate) (PE-PMMA) polymer hybrid by RAFT polymerization. A sequential functionalization of hydroxyl-capped polyethylene, afforded by the copolymerization of ethylene with allyl alcohol, yielded polyethylene-based RAFT agent bearing a dithiobenzoate group. Subsequent RAFT polymerization of MMA was performed with the polyethylene-based RAFT agent and AIBN initiator in a 60℃ bath of toluene (Fig. 29). ^{1}H NMR analysis showed that 80 % of copolymer chain ends contained hydroxyl groups. Polymers hybrid containing PMMA segment (PDI < 2.4; M_n = 38,500 and 40,000, respectively) were prepared after 24 hrs polymerization. A nanometer level microphase separation morphology between the PE and PMMA segments was revealed by TEM images of the purified polymer hybrid.

Fig. 29

Making use of the reactive carbon-metal bonds in polyolefin chains obtained based on the “catalyzed chain growth” (CCG) mechanism [80,81] is another promising strategy to prepare terminally modified polyolefins, which can serve as building blocks for multi-segmented polymers [82].

Through the reaction of dipolyethylenyl magnesium (PE-Mg-PE) with a range of thiocarbonylated compounds (Fig 30), D’Agosto et al. [82] synthesized thio thiocarbonylate-terminated polyethylene, called macroRAFT agents. These were designed to mediate subsequent RAFT polymerizations to provide polyethylene-based block copolymers. A PE-Mg-PE based on a CCG mechanism was obtained through ethylene polymerization mediated by $(C_5Me_5)_2NdCl_2Li(OEt_2)_2$/butyloctylmagnesium (BOMg). The macroRAFT agent was synthesized by adding a solution of RC(S)S-SC(S)R in toluene at the end of ethylene polymerization (molar ratio RC(S)S-SC(S)R/Mg = 2:1 or 4:1). The functionalization rates of the resultant polymers were calculated ranging from 22.0 to 90.7% based on the NMR analysis.

Fig 30

Based on the previously reported research, D’Agosto et al. [83] successfully synthesized polyethylene-*b*-poly(*n*-butyl acrylate) through a combination of catalyzed chain growth polymerization and RAFT polymerization (Fig 31). Iodine-terminated polyethylene (PE-I) was prepared with functionalization degrees ranging from 73.0% to 96.8%. The procedure involved the addition of iodine at the end of ethylene polymerization process of catalyzed chain growth on magnesium. Through the reaction of PE-I with NaN_3 and following hydrogenation, modified polyethylene with an amine end group (PE-NH_2) was produced. Then PE based RAFT agent was prepared through the reaction of PE-NH_2 with an ester containing moiety that can mediate a RAFT polymerization. Polyethylene block copolymers were produced after the final RAFT polymerization of *n*-butyl acrylate mediated by the RAFT agent. .

Fig. 31

Though RAFT polymerization is capable of preparing block copolymers due to the living character, many polymerization steps are necessary for the preparation of multiblock copolymer using a monofunctional RAFT agent. Koning et al. [69,84] studied the preparation of multiblock copolymers using the difunctional and multifunctional RAFT agents shown in Fig. 32. When a difunctional RAFT agent based on 'Kraton', a monohydroxyl end capped poly(ethylene-co-butylene), was used, a triblock copolymer poly(ethene-*co*-butene)-*b*-PBA-*b*-poly(ethene-*co*-butene) was obtained in one polymerization step.

Fig. 32

4. Synthesis of modified PE containing polar segments employing NMRP

4.1. NMRP

A subclass of stable free radical polymerization that belongs to reversible-deactivation radical polymerization, nitroxide-mediated radical polymerization (NMRP), was first reported in 1986 [85]. It facilitates accurate control over the molecular weight and chain ends of vinyl polymers with narrow polydispersity [86,87]. Compared with other reversible-deactivation radical polymerization methods, NMRP possesses several advantages, such as easier product purification and an excellent functional group tolerance since no metal complex is used [86].

Though NMRP was restricted to a limited scope of monomers in its early versions, notable advances have been accomplished with the appearances of novel nitroxides. Polymerizations possessing RDRP characteristics of various monomers including styrene, alkyl acrylates, acrylamides, dienes, and so on, can be achieved with the aid of advanced NMRP techniques [29,88-90].

Stable nitroxide free radicals, such as 2,2,6,6-tetramethylpiperidinyl-l-oxy (TEMPO), are used as thermally labile “capping” agents, to permit reversible trapping of growing radicals to form dormant species (alkoxyamines) with a thermally cleavable C-ON covalent bond [2,91]. The irreversible chain termination reactions are limited by the equilibrium between dormant and active radicals, which shifts strongly toward the dormant species at a proper polymerization temperature (Fig. 33) [2,14,**92**]. There are two ways to initiate nitroxide-mediated radical polymerizations, by employing either (a) a radical initiator and a nitroxide for a bimolecular system or (b) a alkoxyamine acting as an initiator and a control agent for a monomolecular system [2,29].

Fig. 33

4.2. Synthesis of modified PE by combining coordination polymerization and

NMRP

Efforts have been made to synthesize well-defined olefin copolymers possessing polar segments with the assistance of NMRP [93,94]. Waymouth et al. [10] studied the synthesis of polyethylene graft block copolymers using alkoxyamines as the initiators via a two-step strategy as shown in Fig. 34. Polyethylene backbone possessing initiators was obtained through the copolymerization of ethylene with alkoxyamine and butene. Butene was employed to improve the solubility of the resultant copolymers. Homopolymers and graft copolymers were obtained simultaneously through free radical grafting reactions using initiator **2**. The molecular weights and polydispersities of the grafts and the homopolymers are very similar, indicating that the initiation and propagation from **2** occurred as efficiently as from the alkoxyamine units contained in copolymers. The number of grafts per backbone was calculated to be in the range 0.20~1.13, and the PDI of the grafts were around 1.20. Then copolymers with grafts of block polymers were synthesized through a continuous addition of a second monomer.

Fig. 34

The reactivity of carbon-metal bonds can be used to prepare end-functionalized polyethylene bearing an initiator for the subsequent NMRP. D'Agosto et al. [95,96] reported the preparation of macroalkoxyamine based on polyethylene and polyethylene-*b*-poly(*n*-butyl acrylate) (PE-*b*-P*n*BA) via the NMRP of *n*-butyl acrylate, initiated by alkoxyamine-terminated polyethylene. To incorporate an alkoxyamine that can initiate a controlled radical polymerization at a lower temperature, two novel alkoxyamines 4-[(2,2-dimethyl-4-(N-tert-Butyl-N-(1-diethoxyphosphoryl-2,2-dimethylpropyl)aminoxy)-4-n-butoxycarbonyl)butanoyloxyl]-2,2,6,6-tetramethylpiperidinyl-1-oxy (DD1) and 4-[(2,2-dimethyl-4-(N-tert-Butyl-N-(1-diethoxyphosphoryl-2,2-dimethylpropyl)aminoxy)-4-phenyl)butanoyloxyl]-2,2,6,6-tetramethylpiperidinyl-1-oxy (DD2) were designed and synthesized as shown in Fig 35. By adding solutions of DD1 and DD2 in toluene at the end of ethylene polymerization, PE-DD1 and PE-DD2 were obtained with functionalization rates of 17.1 mol % and 40 mol %, respectively. PE-DD2 was employed to initiate the NMRP of *n*-butyl under controlled radical polymerization conditions to afford PE-*b*-P*n*BA block copolymers with relatively low PDI (1.19~1.35).

Fig 35

Mohajery et al. [97] reported the synthesis of polyethylene-*g*-polystyrene (PE-*g*-PS) copolymers via nitroxide-mediated radical polymerization. Poly(ethylene-*co*-*m,p*-methyl styrene) was first obtained through the copolymerization of ethylene with *m,p*-methyl styrene (*m,p*-MS) employing metallocene catalyst $Et(Ind)_2ZrCl_2$. Both the activity of the catalyst and *m, p*-methyl styrene content in copolymers increased with the concentration of the comonomer, suggesting an excellent incorporation of *m,p*-methyl styrene with ethylene. After the introduction of bromine at the benzylic position through bromination, macroinitiators were prepared by the reaction of brominated copolymer with 1-hydroxyl-2,2,6,6-tetramethylpiperidine for the following graft polymerization (as shown in Fig. 36). Based on ^{1}H-NMR, the bromination degree of the copolymer was 0.92 mol % and 55.43 % of bromomethyl styrene units were converted into TEMPO macroinitiators. Polyethylene graft copolymers containing 22.6 mol % and 3.9 mol % of polystyrene were obtained via the graft polymerization of styrene initiated from the macroinitiators.

Fig. 36

5. Synthesis of modified PE containing polar segments employing ROP

5.1. ROP

Ring-opening polymerization (ROP) is a useful method to prepare microstructure-controlled polymers and polymers with novel structures, which may not be available through conventional polymerization techniques [98]. The initiation of ROP can be achieved by thermal, anionic and transition metal-catalyst. Among these, ionically catalyzed ROP has been well investigated, but currently, thermally induced ROP is the most general polymeric method [98,99].

5.2. Synthesis of modified PE by combining coordination polymerization and ROP

Ring-opening polymerization is also capable of providing ethylene copolymers with polar segments. The common segments incorporated into polyolefins are poly(ε-caprolactone), poly(L,L-lactides), poly(propylene glycol). and so on. To obtain these block or graft copolymers through ROP, polyethylene bearing hydroxyl groups is generally a necessary precursor.

In-situ chain transfer during the polymerization is an effective method to introduce functional groups to polymer chains and afford terminally functionalized polyolefins [100-102]. Several compounds, including organoborane [103,104], alkyl aluminum [105,106] and alky zinc [107-109] are reported to be effective chain transfer agents

(CTA) in olefin polymerizations.

9-Borabicyclononane (9-BBN) possessing a B-H group has proven to be a very effective chain transfer agent in metallocene-mediated olefin polymerization or copolymerization [100,101]. Chung et al. [110] reported the synthesis of amphiphilic polyethylene-*b*-poly(ethylene oxide) (PE-*b*-PEO) via the combination of ethylene polymerization in the presence of CTA with subsequent ROP of ethylene oxide (Fig. 37). In the presence of dialkylborane (H-BR$_2$), metallocene-catalyzed ethylene polymerization produced borane-terminated polyethylene, which was converted into an anionic macroinitiator for a succeeding ring opening polymerization through a subsequent oxidation and metalation. The ring opening polymerization of ethylene oxide with the polyethylene based initiator yielded the target diblock copolymers with ethylene oxide incorporation ranging from 40 mol % to 80 mol %.

Fig. 37

Polyethylene-*b*-poly(ε-caprolactone) (PE-*b*-PCL) was successfully prepared using a similar method (Fig. 38) [111]. In a deviation from the previous report [110], diethyl aluminum chloride was used to metalate the hydroxy groups of the resultant hydroxyl-terminated polyethylene. Then the ROP of ε-caprolactone produced the target block copolymer with ε-caprolactone incorporation ranging from 7 mol % to 41 mol %.

Fig. 38

Kim’s group [9] reported the synthesis of hydroxyl-terminated polyethylene (PE-OH) through sequential oxidation and hydrolysis of Al-terminated polyethylene, which was obtained using a controlled chain transfer reaction during the ethylene polymerization with $Cp^*_2ZrCl_2$/MAO as the catalyst system (Fig. 39). The ^{1}H-NMR results showed that at least 85% of the polymer chains had a hydroxyl end group. Polyethylene-*b*-poly(ε-caprolactone) (PE-*b*-PCL) copolymer was synthesized through the ring-opening polymerization of ε-caprolactone, using stannous octoate as a catalyst in the presence of the preformed PE-OH.

Fig. 39

Using a similar method, Dubois et al. [112] successfully prepared polyethylene-*b*-poly(L,L-lactides) (PE-*b*-PLA) combining catalytic ethylene oligomerization and the ring-opening polymerization of lactide (LA) (Fig. 40**)**. Zinc-ended PE was synthesized via ethylene oligomerization with zirconocene/MAO as the catalytic system with the presence of diethyl zinc as chain transfer agent and was oxidized by synthetic air to give hydroxyl-terminated PE with a functionalization degree of 67 %. Then ROP of LA conducted in the presence of the preformed PE-OH and $Sn(Oct)_2$ occurred in a controlled fashion: the experimental molecular weight values of the block copolymers where in good agreement with the theoretical values, implying the ROP involved a “coordination-insertion” mechanism [113].

Fig. 40

Hydroxyl groups can be introduced into polyethylene chains, e.g., through saponification of the copolymer of ethylene with vinyl acetate. Kojoh et al. [3] reported the synthesis of polyethylene-*g*-poly(propylene glycol) (PE-*g*-PPG) and polyethylene-*g*- poly(ε-caprolactone) (PE-*g*-PCL) through a combination of coordination polymerization and ROP. It was determined that the positions of hydroxy groups in the polymer chains could be adjusted by masking allyl alcohol by different AlR_3 in the copolymerization of ethylene with allyl alcohol using zirconocene as the catalyst (Fig. 41). The macroinitiator for the subsequent ring opening polymerization was prepared through the copolymerization of ethylene with 10-undecen-1-ol alike to the aforementioned. Two graft copolymers PE-*g*-PPG and PE-*g*-PCL were prepared through the ROP of propylene glycol and *ε*-caprolactone, respectively using poly(ethylene-*co*-10-undecen-1-ol) as (Fig. 42). All the hydroxyl groups were consumed for propylene oxide polymerization to give PE-*g*-PPG and 36~80 mol % of the hydroxyl groups worked as initiators in the case of *ε*-caprolactone during the synthesis of PE-*g*-PCL.

Fig. 41 and Fig. 42

From commercially available poly(ethylene-*co*-vinyl acetate) (PEVAc), Yoon et al. [114] prepared polyethylene graft copolymers through the ring-opening polymerization of *ε*-caprolactone (CL) (Fig. 43). PEVAc containing 10 and 20 wt % of vinyl acetate (VAc) units were converted into poly(ethylene-*co*-vinyl alcohol) (PEVOH) with vinyl alcohol contents of 1.7 mol % and 6.3 mol %, respectively through saponification in ethanol/KOH solution for 3 days. Then through the following ring-opening polymerization of CL, a series of graft copolymers (M_w/M_n = 4.06 ~ 6.61) were obtained.

Fig. 43

6. Synthesis of modified PE containing polar segments employing ATRP together

with ROP

Wang's group made advances in the synthesis of modified polyethylene by incorporating ROP and ATRP. Xiao [48] synthesized a novel hyperbranched-star polyethylene-*g*-poly(hydroxyethyl acrylate)-*g*-poly(*ε*-caprolactone) (PE-*g*-PHEA-*g*-PCL) by a combination of coordination polymerization, ATRP and ROP (**Fig. 44**). Copolymerization of ethylene with BIEA using a Pd catalyst was performed to provide hyperbranched polyethylene macroinitiators, from which the ATRP of 2-hydroxyethyl acrylate was initiated in the presence of CuBr/$CuBr_2$/PMDETA. From this, dentrimers possessing hydroxyl groups at the end of side chains were obtained. The dentrimer was used to synthesize a hyperbranched-star PE-*g*-PHEA-*g*-PCL through the ring-opening polymerization of *ε*-caprolactone, initiated by the hydroxyl groups, using stannous 2-ethylhexanoate as catalyst. The dendrimers possess a core of amorphous morphology and comb-like side chains. The side chains of the resultant dendrimers tended to crystallize, suggesting the copolymers may exhibit elastomeric characteristics.

Fig. 44

7. Summary

Polyethylene is one of the most valuable commercial polymers and has been used widely across the world. Improving its properties through the introduction of polar segments in a controlled fashion makes a great significance. Various kinds of modified polyethylene have been prepared through the combination of coordination polymerization and reversible-deactivation radical polymerization or ring-opening polymerization.

Though remarkable success has been achieved in the synthesis of modified polyethylene, substantial work is necessary in this field. For the future, efforts for the synthesis of modified polyethylene should be made in the following four aspects: **(1)** synthesis of modified polyethylene by incorporating RDRP or ROP into coordination polymerization mediated not only by zirconocene or Pd-diimine catalyst systems, but also by other metallocenes, Ni-based and Fe-based catalyst systems; **(2)** synthesis of functionalized polyethylene, for example pH-responsive and thermo-sensitive polyethylene, through the introduction of novel polar or functional segments into polyethylene chains; **(3)** synthesis of modified polyethylene with better-defined architectures by combining RDRP technique (or ROP) with living ethylene polymerization, which allows for a precise control over the polyethylene structure [115]; **(4)** synthesis of modified polyethylene involving the process of catalyzed chain growth; and **(5)** further explorations for the applications of the resultant polyethylene copolymers.

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Poly(olefin) Graft Copolymers by a Combination of Metallocene and “Living” Free Radical Polymerization Techniques. Macromolecules 1998;31:4396-4398

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Figure captions

Fig. 1. General procedures for the synthesis of modified PE by combining coordination polymerization and RDRP or ROP.

Fig. 2. Mechanism for atom transfer radical polymerization [20,30]

Fig. 3. Pd (II) α-diimine catalyst [1]

Fig. 4. ATRP of *n*BA with PE-MM to prepare PBA-*g*-PE [1]

Fig. 5. Synthesis of PE multifunctional macroinitiator [12]

Fig. 6. Synthesis of grafted poly[ethylene-*co*-(*p*-methylstyrene)] graft copolymers via ATRP [42]

Fig. 7. Reaction mechanism for DT polymerization in a binary catalyst system [43]

Fig. 8. Structure of bis(imino)pyridine-iron complex [43]

Fig. 9. Reaction pathway for the synthesis of polyethylene macroinitiators (PE-MI)

[43]

Fig. 10. Preparation of P*n*BA-*g*-PE and PtBA-*g*-PE via atom transfer radical polymerization [43]

Fig. 11. One-step synthesis of PE-MI from vinyl-ended PE [44]

Fig. 12. Procedures for the synthesis of PE-OH from PE-vinyl [45]

Fig. 13. Synthetic pathway for PE-MM from PE-OH [45]

Fig. 14. Copolymerization of ethylene with 1,7-octadiene (OD) [46]

Fig. 15. Tandem CWP-ATRP for the synthesis of dendritic nanoparticles [47]

Fig. 16. Synthetic procedures of core-shell structured copolymer [7]

Fig. 17. Synthetic procedures of pH-responsive poly(ethylene-*g*-acrylic acid) [48]

Fig. 18. Synthesis of ferrocenyloxy ethyl acrylate from ferrocenecarboxylic acid [48]

Fig. 19. Synthesis of PE-*g*-PFcEA by combining coordination polymerization and ATRP [48]

Fig. 20. Synthesis of PE macroinitiators and their subsequent ATRP [49]

Fig. 21. Synthesis of functionalized Pd catalyst [53]

Fig. 22. Tandem strategy for synthesis of functionalized polyethylene block copolymers (PE: Polyethylene; PBA: Poly(n-butyl acrylate); PS: Polystyrene) [53]

Fig. 23. Synthesis of macroinitiators PE-Cl and PE-Br for the following ATRP [56]

Fig. 24. Introduction of initiation groups: (a) 2,2,2-tribromoethanol for typical ATRP and (b) benzophenone for reverse ATRP to HDPE films [57]

Fig. 25. Graft polymerization of MMA to irradiated PE with a reverse ATRP [5]

Fig. 26. Reaction procedures for preparing initiator-functionalized PEAA films [62]

Fig. 27. Various types of thiocarbonylthio compounds [63-65]

Fig. 28. Mechanism of reversible addition-fragmentation chain transfer (RAFT) polymerization [17,71,72]

Fig. 29. Synthetic route for PE-PMMA polymer hybrid via RAFT polymerization [79]

Fig. 30. Synthesis of macroRAFT agents through the reaction of disulfide compounds with $Mg(PE)_2$ [82]

Fig. 31. Strategy for the preparation of various end-functionalized polyethylenes [83]

Fig. 32. Difunctional or multifunctional RAFT agents [69]

Fig. 33. Reversible termination between propagating radicals and stable nitroxides [2,14]

Fig. 34. Synthesis of graft block copolymers via copolymerization and subsequent NMRP [10]

Fig. 35. Synthesis of alkoxyamines bearing a free nitroxide moiety [96]

Fig. 36. Total synthesis of polyethylene graft copolymer employing NMRP [97]

Fig. 37. Synthesis of PE-*b*-PEO via coordination polymerization and ROP [110]

Fig. 38. Synthesis of PE-*b*-PCL via coordination polymerization and ROP [111]

Fig. 39. Synthesis of PE-*b*-PCL[9]

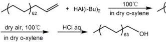
Fig. 40. Sequential ROP of LA initiated by PE-OH/$Sn(Oct)_2$ [112]

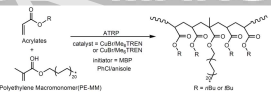
Fig. 41. Copolymerization of ethylene with allyl alcohol protected by different trialkyl aluminums [3]

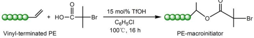
Fig. 42. Synthetic route for polyethylene-*g*-poly(propylene glycol)

Fig. 43. Synthesis of graft copolymers via ring-opening polymerization [114]

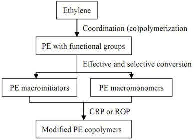
Fig. 44. Synthetic route of PE-*g*-PHEA-*g*-PCL via a combination of coordination polymerization, ATRP and ROP [48]

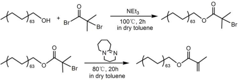

62
+ HAl(i-Bu)2
100℃
in dry o-xylene
62
Al(i-Bu)2
dry air, 100℃
in dry o-xylene
HCl aq.
63
OH

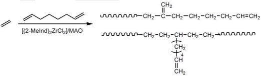

O
O
R
Acrylates
+
OH
O
20
Polyethylene Macromonomer(PE-MM)
ATRP
catalyst = CuBr/Me$_6$TREN
or CuBr/Me$_6$TREN
initiator = MBP
PhCl/anisole
O
R
20
R = *n*Bu or *t*Bu

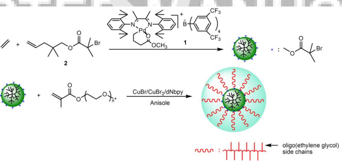


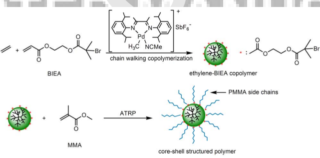
+
HO
O
Br
15 mol% TfOH
C6H5Cl
100℃, 16 h
O
O
Br
Vinyl-terminated PE
PE-macroinitiator

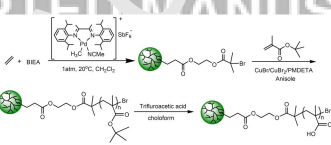

Ethylene
Coordination (co)polymerization
PE with functional groups
Effective and selective conversion
PE macroinitiators
PE macromonomers
CRP or ROP
Modified PE copolymers

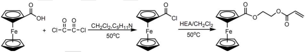

63
OH
+
O
Br
Br
NEt3
100℃, 2h
in dry toluene
63
O
O
Br
63
O
O
Br
N
N
80℃, 20h
in dry toluene
63
O
O

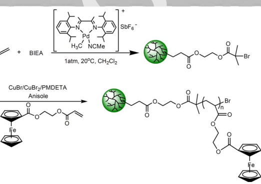

[(2-MeInd)2ZrCl2]/MAO
CH2
CH2–C–CH2–CH2–CH2–CH2–CH2–CH=CH2
CH2–CH2–CH–CH2–CH2–CH2
CH2
4
CH
CH2

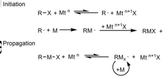

Pd
OCH3
N
N
+
B
CF3
CF3
4
1
2
Br
*
:
Br
+
O
n
*
CuBr/CuBr2/dNbpy
Anisole
:
oligo(ethylene glycol)
side chains

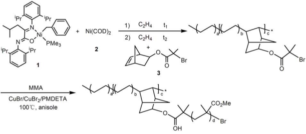

+
SbF6⁻
N
Pd
N
H3C
NCMe
chain walking copolymerization
BIEA
Br
ethylene-BIEA copolymer
:
Br
PMMA side chains
ATRP
MMA
core-shell structured polymer


BIEA
+
SbF_6^-
N
Pd
H_3C
NCMe
1atm, 20°C, CH_2Cl_2
Br
CuBr/$CuBr_2$/PMDETA
Anisole
Br
n
Trifluroacetic acid
choloform
Br
n
HO

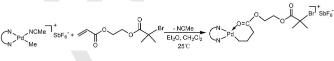

OH
O
Fe
+
Cl
CH2Cl2,C5H11N
50°C
HEA/CH2Cl2
50°C

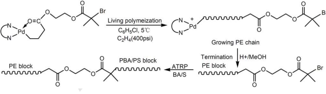

+
BIEA
SbF$_6^-$
Pd
H$_3$C
NCMe
1atm, 20^{o}C, CH$_2$Cl$_2$
Br
CuBr/CuBr$_2$/PMDETA
Anisole
Fe
n
Br
Fe

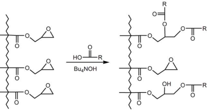

Initiation
R−X + Mt^n ⇌ R· + Mt^{n+1}X
R· + M → RM· → RMX + Mt^n
+ Mt^{n+1}X
Propagation
R−M−X + Mt^n ⇌ RM_x· + Mt^{n+1}X
+M



iPr
iPr
N
Ni
O
PMe3
N
iPr
iPr
1
+
Ni(COD)2
2
1) C2H4 t1
2) C2H4 t2
+
O
O
Br
3
a
b
c
*
O
O
Br
MMA
CuBr/CuBr2/PMDETA
100℃, anisole
a
b
c
*
O
OH
CO2Me
d
Br

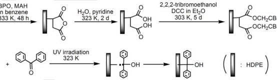

N
N
Pd
NCMe
Me
+
SbF6-
+
O
O
O
O
Br
- NCMe
Et2O, CH2Cl2
25℃
N
N
Pd
O=C
O
O
O
Br
+
SbF6-

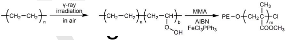

Br
Living polymeization
C6H5Cl, 5℃
C2H4(400psi)
Br
Growing PE chain
Termination
H+/MeOH
PE block
Br
PE block
PBA/PS block
ATRP
BA/S

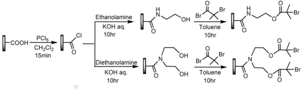


R=CH_2Cl Chloroacetate

R=$C(CH_3)_2Br$ 2-Bromoisobutyrate


(a)
BPO, MAH
In benzene
333 K, 48 h
H2O, pyridine
323 K, 2 d
OH
OH
2,2,2-tribromoethanol
DCC in Et2O
303 K, 5 d
OCH2CBr3
OCH2CBr3
(b)
H
+
UV irradiation
323 K
OH
OH
: HDPE


$-(CH_2-CH_2)_n-$
γ-ray
irradiation
in air
$-(CH_2-CH_2)_a-(CH_2-CH)_b-$
O-OH
MMA
AIBN
$FeCl_3PPh_3$
$PE-O-(CH_2C)_m-Cl$
CH_3
$COOCH_3$

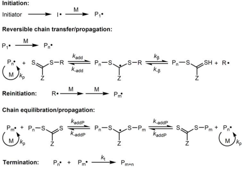

COOH
PCl5
CH2Cl2
15min
Cl
Ethanolamine
KOH aq.
10hr
OH
Br
Toluene
10hr
Diethanolamine
KOH aq.
10hr
OH
Toluene
10hr
Br

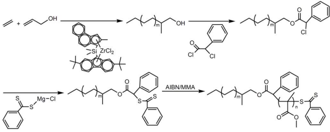
a

Z: Ph or CH_3

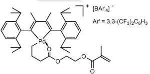
R: $C(CH_3)_2Ph$, $CHCH_3Ph$, CH_2Ph, $C(CH_3)_2CN$,

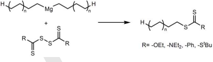
$C(CH_3)(CN)CH_2CH_2CO_2Na$, $C(CH_3)(CN)CH_2CH_2CH_2OH$, etc.

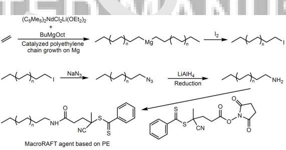

Initiation:
Initiator
I•
M
P1•
Reversible chain transfer/propagation:
P1•
M
Pn•
Pn•
M
kp
S
S—R
Z
kadd
k-add
Pn—S
S—R
Z
kβ
k-β
Pn—S
SH + R•
Z
Reinitiation:
R•
M
M
Pm•
Chain equilibration/propagation:
Pm•
M
kp
Pn—S
S
Z
kaddP
k-addP
Pn—S
S—Pm
Z
k-addP
kaddP
S
S—Pm
Z
Pn•
M
kp
Termination:
Pn• + Pm•
kt
Pm+n

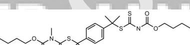

OH
Si
ZrCl2
m
OH
O
Cl
O
Cl
Cl
Mg−Cl
S
S
m
O
O
S
S
AIBN/MMA
m
O
O
S
S
n
O
O

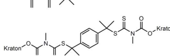
ag



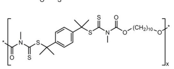

H
n
Mg
n
H
+
R
S
S
S
S
R
H
n
S
S
R
R= -OEt, -NEt$_2$, -Ph, -S^{t}Bu


$(C_5Me_5)_2NdCl_2Li(OEt_2)_2$
+
BuMgOct
Catalyzed polyethylene chain growth on Mg
Mg
n
I_2
I
NaN_3
N_3
$LiAlH_4$
Reduction
NH_2
NH
O
NC
S
CN
N
MacroRAFT agent based on PE

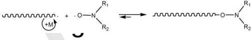


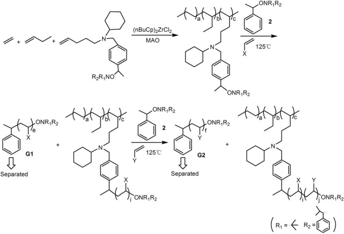


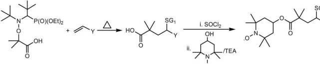
Kraton
Kraton



(CH2)10
x

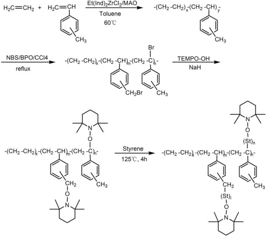

+M
O
N
R$_1$
R$_2$
O
N
R$_1$
R$_2$

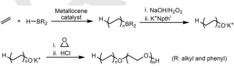

(nBuCp)2ZrCl2
MAO
R2R1NO
a
b
c
ONR1R2
2
X
125℃
G1
e
Separated
G2
f
Y
Separated
i
j
R1 =
R2 =

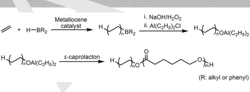


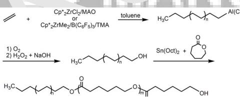
DD1: Y = C(O)O*n*-BuPh DD2: Y = Ph

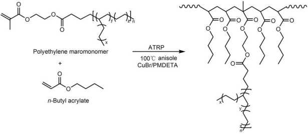
SG1: *N*-(2-methyl-2-propyl)-*N*-(1-diethylphosphono-2,2-dimethylpropyl)-N-oxyl)

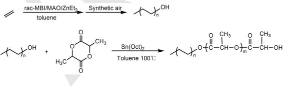

Et(Ind)2ZrCl2/MAO
Toluene
60℃
NBS/BPO/CCl4
reflux
TEMPO-OH
NaH
Styrene
125℃, 4h

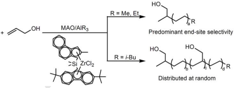

H—BR$_2$
Metallocene catalyst
i. NaOH/H$_2$O$_2$
ii. K$^+$Npth$^-$
i.
ii. HCl
(R: alkyl and phenyl)

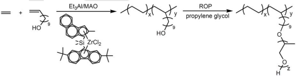

H−BR₂
Metallocene catalyst
i. NaOH/H₂O₂
ii. Al(C₂H₅)₂Cl
ε-caprolacton
(R: alkyl or phenyl)

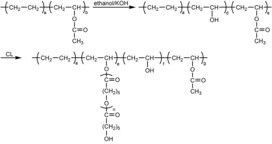

Cp*2ZrCl2/MAO
or
Cp*2ZrMe2/B(C6F5)3/TMA
toluene
H3C
n
Al(CH3)2
1) O2
2) H2O2 + NaOH
H3C
n
OH
Sn(Oct)2 +
O
O
H3C
n
O
O
O
m
O
OH

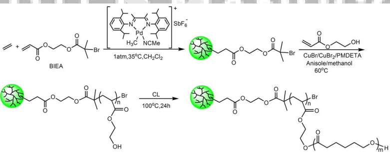

Polyethylene maromonomer
+
n-Butyl acrylate
ATRP
100℃ anisole
CuBr/PMDETA
x
y
z
n

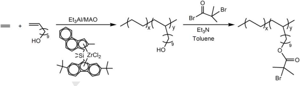

rac-MBI/MAO/ZnEt2
toluene
Synthetic air
OH
n
Sn(Oct)2
Toluene 100℃
CH3
H3C
O
m

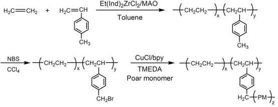

MAO/AlR3
R = Me, Et
Predominant end-site selectivity
R = i-Bu
Distributed at random


+
HO
9
Et$_3$Al/MAO
Si
ZrCl$_2$
x
y
HO
9
ROP
propylene glycol
x
y
9
O
O
H
z

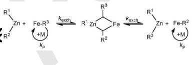

ethanol/KOH
CL


+
SbF6-
Pd
N
N
H3C
NCMe
Br
BIEA
1atm,35°C,CH2Cl2
OH
CuBr/CuBr2/PMDETA
Anisole/methanol
60°C
CL
100°C,24h
n
m
H


Et$_3$Al/MAO
HO
9
Si
ZrCl$_2$
x
y
HO
9
Br
O
Br
Et$_3$N
Toluene
x
y
9
O
O
Br



PM(polar monomer): MMA or *n*-BA


R1
Zn +
R2
Fe-R3
+M
kp
kexch
R3
R1 Zn
Fe
R2
kexch
R1
Zn +
R3
Fe-R2
+M
kp