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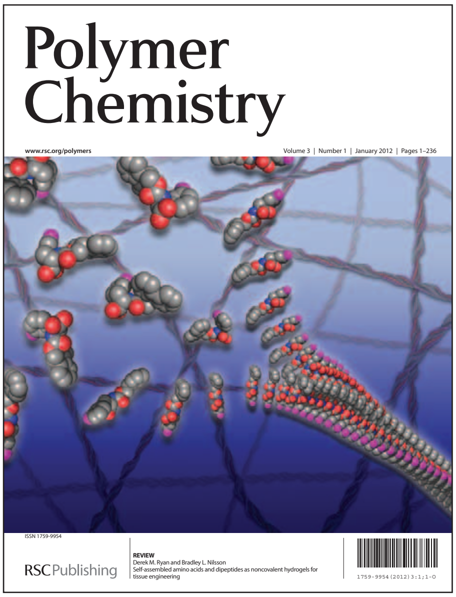
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# Recent progress in chemical modification of syndiotactic polystyrene

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## Abstract

It is an unquestionable fact that syndiotactic polystyrene (sPS) has stimulated great interest on the basis of its importance in basic scientific research and potential industrial applications, because it is regarded as a new low-cost engineering polymer with various desirable properties, such as high melting temperature (270 °C), fast crystallization rate, low dielectric constant, excellent mechanical properties, low permeability to gases, outstanding dimensional stability, excellent processing characteristics at a very low melt viscosity, and good chemical resistance. However, some drawbacks of sPS restrict its practical use: its brittleness, a disadvantage in applications where mechanical properties are important; the absence of polar groups for adhesion to substrates and compatibility with polar polymers; and the need to process sPS at high temperatures due to its high melting points. Thus modification of sPS is necessary for expanding its application fields and has been the subject of investigation. This review provides a snapshot of recent progress in chemical modification of syndiotactic polystyrene including *in situ* functionalization of sPS (syndiospecific copolymerization of styrene with a second monomer and catalytic chain transfer to a chain transfer agent), post-functionalization of sPS (introduction of polar groups into sPS, graft or block copolymerization onto sPS, and hydrogenation of sPS or its copolymers) and monomer modification.

**Keywords**: Syndiotactic polystyrene, Chemical modification, Materials properties

## Contents

## 1. Introduction

There are three different structural of polystyrene that can be prepared from styrene monomer: atactic, isotactic and syndiotactic [1-4]. In atactic polystyrene (aPS), the phenyl rings are randomly placed on both sides of the extended carbon chains. Atactic polystyrene is a thermoplastic amorphous resin due to the high degree of random distribution of the phenyl rings relative to the backbone. Since the introduction of atactic polystyrene in the 1930s by a number of companies including BASF in Germany and Dow in the United States, this type of polystyrene has been emerged as the most common and well known polymer. Owing to its low cost and good processability, aPS has versatile applications in many fields, such as the packaging and durable goods. In isotactic polystyrene (iPS) all the phenyl rings are located on the same side of the stretched carbon chain. Isotactic polystyrene has been synthesized using a Ziegler-Natta catalyst system. This type of polystyrene is semi-crystaline material with a high melting point (240 °C). Isotactic polystyrene is not commercially viable to its slow crystallization rate. In syndiotactic polystyrene (sPS) phenyl rings regularly alternate from side to side with respect to the extended carbon chains. This type of polystyrene has attracted increasing attention due to its excellent physicochemical properties and potential for various practical and technological applications. Syndiotactic polystyrene can be crystallized into two different chain conformations, helical and trans. Helical ($T_2G_2$) conformations are formed in solution-recovered sPS, whereas the more favorable all-trans ($T_4$) conformations are formed either from the melt or annealing at elevated temperatures [5-8].

Syndiotactic polystyrene is regarded as a new low-cost engineering polymer with various desirable properties, such as high melting temperature (270 °C), fast crystallization rate, a high glass transition temperature (100 °C), low dielectric constant, low permeability to gases, low moisture absorption, low viscosity, good chemical and temperature resistance, the good dimensional stability and an improved mechanical strength [4,9,10]. Half-sandwich titanocene and methylaluminoxane (MAO) catalyst system has been proposed as the favor precursors to catalyze syndiospecific polymerization of styrene [11-14]. Several drawbacks can, however, restrict the practical application of syndiotactic polystyrene: its brittleness, a disadvantage in applications where mechanical properties are important; the lack of polar groups for adhesion and compatibility with other polymers; and the need to process sPS at high temperatures. Recently, several attempts have been made to improve the physical properties and processability of sPS by several procedures. One involves the syndiotactic copolymerization of styrene with a second monomer in order to produce a styrene/olefin copolymer [15-17]. Another modification procedure involves the preparation of functionalized sPS polymers, such as sulfonated sPS [18,19], acetylated and/or benzoylated sPS [20] and maleic and/or succinic anhydride-*grafted* sPS [21,22]. In addition, polymer blends also provide a way to modify sPS. However, because sPS usually lacks compatibility with a second polymer, blending sPS with other polymers produces weak interfacial adhesion and leads to poor mechanical properties. This problem can be circumvented through using compatibilizers, which are usually block, graft and functionalized polymers. However, it is difficult to prepare a copolymer containing a sPS block. In this respect, a graft or functionalized sPS has been proposed as the first choice to serve as compatibilizer [23-25].

This review highlights the some major developments in chemical modification of syndiotactic polystyrene including *in situ* functionalization of sPS (syndiospecific copolymerization of styrene with a second monomer and catalytic chain transfer to a chain transfer agent), post-functionalization of sPS (introduction of polar groups into sPS, graft or block copolymerization onto sPS and hydrogenation of sPS or its copolymers) and monomer modification. The different techniques used to modification of sPS, and materials properties of the modified syndiotactic polystyrenes will be discussed.

## 2. *In situ* functionalization

Introduction of functional groups into polymer backbone in the reactive medium is known the *in situ* functionalization pathway. This method has been emerged as one of the most powerful approach for chemical modification of syndiotactic polystyrene. This approach is divided into two main categories: statistical syndiospecific copolymerization of styrene with a second monomer, and catalytic chain transfer to a chain transfer agent. The selected procedures around the *in situ* functionalization of sPS are discussed in the following sections.

### 2.1. Syndiospecific copolymerization of styrene with a second monomer

The incorporation of a co-monomer during the syndiospecific polymerization of styrene has a marked effect on the properties and polymorphic behavior of resultant syndiotactic polystyrene copolymers [26-45]. Many of the traditional catalytic systems capable of producing sPS have been assessed in the copolymerization of styrene with a second monomer (especially ethylene), however, usually resulting atactic or alternating structures, scarce performances and/or often mixtures of homopolymers [46,47]. Recently, highly versatile homogeneous catalytic systems have been discovered for syndiotactic copolymerization of large variety of monomers with styrene [48-54]. In this respect, single-site catalysts based on group 3 metals (yttrium, scandium, and the lanthanide series) have been developed for syndiotactic copolymerization of styrene with dienes and α-olefins [55,56]. The binary group 3 metal catalyst systems has been developed by Hou group [57,58]. These systems are very active and can be compared in this respect to the "classic" $CpTiCl_3$/MAO catalyst system. They suggested that this high activity may be expected, taking into account the similar nature of active cationic species in those two systems. They established that these binary cationic systems are obviously among the most effective catalysts to date for copolymerizing styrene with ethylene, considering productivities, stereoselectivities and the possibility to prepare copolymers with very high styrene content.

Recently, Hou et al. [58] reported the syndiospecific copolymerization of 1,5-hexadiene (HD) with styrene and ethylene by a series of half-sandwich scandium dialkyl complexes bearing various auxiliary ligands. They demonstrated that the THF-free aminobenzyl scandium complex with a sterically demanding ligand, such as $(C_5Me_4SiMe_3)Sc(CH_2C_6H_4NMe_2\text{-o})_2$, in combination with an equivalent of $[Ph_3C][B(C_6F_5)_4]$, can serves as an excellent catalyst for the cyclocopolymerization of 1,5-hexadiene with styrene to produce a new family of polymer materials containing methylene-1,3-cyclopentane (MCP) units, vinyltetramethylene (VTM) units, and unique syndiotactic styrene-styrene sequences. Moreover, they found that with use of this catalyst system, the terpolymerization of HD, styrene (St), and ethylene (Et), has also lead to synthesis of cyclopolymer materials containing the five-member ring MCP units, ethylene-ethylene blocks, and syndiotactic styrene-styrene sequences. They concluded that the copolymer compositions can be controlled in a wide range simply by changing the co-monomer feeding ratios. Most of the synthesized copolymers exhibited high melting points originating from the syndiotactic polystyrene (sPS) blocks and polyethylene (PE) blocks well as in the case of the terpolymers. A schematic of the copolymerization and terpolymerization procedures utilized by Hou et al. are shown in Schemes 1 and 2.

**(Scheme 1)**

**(Scheme 2)**

In 2010 Jian et al. [59] reported the synthesis of a linked-half-sandwich lutetium allyl complex that bears a pyridyl-functionalized cyclopentadienyl ligand $[(C_5Me_4\text{-}C_5H_4N)Lu(\eta^3\text{-}C_3H_5)_2]$ for catalysis of highly syndiospecific and *cis*-1,4-selective copolymerizations of styrene and butadiene. Activating with $[Ph_3C][B(C_6F_5)_4]$, the complex showed excellent dual catalysis and outstanding activities for syndiotactic (rrrr>99%) styrene polymerization, and for *cis*-1,4-selective butadiene polymerization (99%) accordingly. Moreover, in the copolymers, the styrene incorporation rate varied from 4.7 to 85.4 mol%, whereas the polybutadiene (PB) block was highly *cis*-1,4-regulated (95%) and the polystyrene segment remained purely syndiotactic (rrrr>99%). The results obtained in syndiospecific homo and copolymerization's of styrene (St) and butadiene (Bd) in the presence of $[(C_5Me_4\text{-}C_5H_4N)Lu(\eta^3\text{-}C_3H_5)_2]/[Ph_3C][B(C_6F_5)_4]$ catalyst system are summarized in Tables 1 and 2.

**(Table 1)**

**(Table 2)**

The first example of a group-4-based catalytic system to synthesis of ethylene-styrene interpolymers (ESIs) containing syndiotactic styrene-styrene sequences (syndiotactic polystyrene blocks) with a high styrene content was reported by Yoon et al. [60] in 2011. They synthesized a novel titanium complex, $\{[C_5(CH_3)_5]ClTi\}_2O_2C_2(CH_3)_4(\mu\text{-}O)$, which has two titanium metal centers linked by heteroleptic bridges, *oxo* and pinacolato. These two titanium metal centers complex was employed for syndiospecific copolymerization of styrene and ethylene in the presence of modified methylaluminoxane (MMAO). The syndiospecific copolymerizations of styrene and ethylene using the mentioned catalyst system were carried out at various polymerization temperatures with different ratios of monomers. They concluded that the highest polymerization activity was obtained at a high polymerization temperature of 90 °C. Table 3 is summarized the results obtained by Yoon et al. in ethylene-styrene copolymerization using the $\{[C_5(CH_3)_5]ClTi\}_2O_2C_2(CH_3)_4(\mu\text{-}O)$/MMAO catalyst system.

**(Table 3)**

Rodrigues et al. [61] reported the stereocontrolled styrene-isoprene copolymerization and styrene-ethylene-isoprene terpolymerization with a single-component allyl *ansa*-neodymocene catalyst [$(CpCMe_2Flu)Nd(C_3H_5)(THF)$]. They obtained copolymers having high molecular weights ($\overline{M}n$ = 12,000-91,000 gmol$^{-1}$) and unimodal, relatively narrow molecular weight distributions ($\overline{M}w/\overline{M}n$ = 1.3-2.8). The results obtained for styrene-isoprene copolymerization and styrene-ethylene-isoprene terpolymerization catalyzed in the presence of $(CpCMe_2Flu)Nd(C_3H_5)(THF)$ complex in various reaction conditions are summarized in Tables 4 and 5, respectively.

**(Table 4)**

**(Table 5)**

The cationic half-sandwich scandium-based catalyst system such as binary system $[Sc(CH_2SiMe_3)_2(C_5Me_4SiMe_3)(thf)]/[Ph_3C][B(C_6F_5)_4]$ shows unique activity and selectivity for the syndiospecific copolymerization of styrene with ethylene [57]. After completing the styrene polymerization reaction, injection of ethylene (1 atm) into the mixture produces the diblock styrene-ethylene copolymer having a sPS block. While, the copolymerization is carried out in the presence of styrene and ethylene monomers, multi-block styrene-ethylene copolymers with sPS blocks connected by polyethylene units are obtained selectively (Scheme 3) [62].

**(Scheme 3)**

Zinck et al. [63] reported the insertion of single styrene units into polyisoprene (PI) using $Nd(BH_4)_3(THF)_3$, $La(BH_4)_3(THF)_3$, and $Cp^*Nd(BH_4)_2(THF)_2$ combined with butylethylmagnesium catalyst systems. The resulting poly[(1,4-*trans*-isoprene)-*co*-styrene] exhibits quite narrow dispersity index, up to 30% inserted styrene, and a 96–98% 1,4-*trans*-microstructure. They investigated that the presence of a bulky and electron-rich ligand in the coordination sphere of the metal leads to an increasing amount of styrene inserted and narrower chemical composition and molecular weight distributions. The presence of significant quantities of styrene in the medium does not alter the selectivity of the reaction, in contrast with *cis*-specific polymerizations [63].

Ban et al. [64] described the synthesis of highly stereoregular styrene (St)/1,3-butadiene (Bd) block copolymers (sPS-*b*-*cis*-PB), composing of syndiotactic polystyrene (sPS) segments chemically bonded with *cis*-polybutadiene (*cis*-PB) segments, through a stereospecific sequential block copolymerization of St with Bd in the presence of a $C_5Me_5TiMe_3/B(C_6F_5)_3/Al(Oct)_3$ catalyst system. For this purpose, firstly they polymerized styrene in toluene at -25 °C, via syndiospecific living polymerization method in the presence of a $C_5Me_5TiMe_3/B(C_6F_5)_3/Al(Oct)_3$ catalyst system. Afterwards, *cis*-specific living polymerization of Bd was carried out in toluene at -40 °C, by adding of a toluene solution of Bd to the polymerization medium. The livingness of the whole polymerization system was confirmed through a linear increase in the weight-average molecular weights of the copolymers *versus* the polymer yields in both steps, whereas the molar mass distributions remained constant. They analyzed that the presence of crystallizable sPS segments is the basis of high melting temperatures (up to 270 °C) in synthesized copolymers. Scanning electron microscopy images of a binary sPS/*cis*-PB blend with or without the addition of the sPS-*b*-*cis*-PB copolymers showed that it could be used as an effective compatibilizer for non-compatibilized sPS/*cis*-PB binary blends.

Son et al. [65] employed a series of monocyclopentadienyl titanium complexes containing a pendant amine donor on a Cp group (A = $CpTiCl_3$, B = $CpNTiCl_3$, C = $CpNTiCl_2TEMPO$, for Cp = $C_5H_5$, CpN = $C_5H_4CH_2CH_2N(CH_3)_2$, and TEMPO = 2,2,6,6-tetramethylpiperidine-*N*-oxyl) for styrene homopolymerization and ethylene-styrene (Et-St) copolymerization. They found that activated by methylaluminoxane (MAO) at 70 °C, complexes with the amine group (B and C) are active for styrene homopolymerization and products syndiotactic polystyrene (sPS). The copolymerizations of ethylene and styrene with B and C yields highmolecular weight ethylene-styrene copolymer, whereas complex A yields mixtures of sPS and polyethylene, revealing the critical role that the pendant amine has on the polymerization behavior of the complexes. Table 6 summarized the results obtained for ethylene-styrene copolymerization catalyzed by complexes A-C at 70 °C. After investigation, it was revealed that the complex C having a TEMPO ligand produces higher molecular weight ethylene-styrene copolymer with narrower dispersity index compared to complex B under the same reaction conditions. Moreover, they concluded that the behavior of copolymerization with complexes B and C is strongly affected by the reaction temperature; at 120 °C complexes B and C generate blends of ethylene-styrene copolymers and aPS, whereas at 70 °C these complexes afford ethylene-styrene copolymers and sPS, either as blocky sequences in the ethylene-styrene copolymers or as reactor blends.

**(Table 6)**

### 2.2. Functionalization of sPS via catalytic chain transfer

The developments of selective chain transfer technologies permit the syntheses of end-functionalized polyolefins with well-defined architecture. An efficient and versatile method for syntheses of end-functionalized sPS is catalytic chain transfer to a chain transfer agent. In this respect, main group metal alkyl (aluminum and magnesium alkyls) [66,67], functional silanes [68,69], and boranes [70,71] are the most common known examples of chain transfer agents. These chain transfer agents are introduced in the reactive medium at the beginning of the polymerization process and leads to end-functionalized sPS. Since the efficiency of this method has been extensively discussed elsewhere [12,50,70], we discuss briefly about some of the new conducted researches in this area.

Huang et al. [72] reported the synthesis of well-defined syndiotactic polystyrene-*g*-isotactic polypropylene (sPS-*g*-iPP) graft copolymers. For this purpose, a chain transfer reaction was initiated by a chain transfer complex composed of 1,2-bis(4-vinylphenyl)ethane (BVPE), and hydrogen in propylene polymerization mediated by *rac*-$Me_2Si[2\text{-}Me\text{-}4\text{-}Ph(Ind)]_2ZrCl_2$ and MAO, which produce iPP macromonomer bearing a terminal styryl group (iPPt-St). Afterwards, syndiospecific graft copolymerization of styrene onto macromonomer (iPPt-St) was carried out by mono-titanocene catalyst ($CpTiCl_3$/MAO) to yield sPS-*g*-iPP graft copolymers. They found that the graft copolymers were generally possessed dual melting and crystallization temperatures, which were related respectively to the sPS backbone and iPP graft segments. However, it was approved that the two segments displayed largely different melting and crystallization behaviors than sPS homopolymer. Besides, from a non-isothermal melt crystallization study, they concluded that the individually taking place crystallizations of the sPS and iPP segments intervened in each other. This might be related to the strong interaction between sPS and iPP segments in the graft copolymer, causing the graft copolymer to exhibit distinctively different crystalline morphology in contrast with sPS and iPP homopolymers. A schematic of synthetic procedures of sPS-*g*-iPP graft copolymers utilized by Huang et al. is shown in Scheme 4.

**(Scheme 4)**

Hsiao and Tsai [69] reported the synthesis of structurally well-defined end-functionalized syndiotactic polystyrene by vinylsilane inducing selective chain transfer reactions during the syndiospecific polymerization of styrene in the presence of vinylsilanes. They found that the addition of dimethylphenylvinylsilane (DMPVS) led to a drastic reduction of polymer yields (entries 8-12 of Table 7). Moreover, they noted that conducting the polymerization under hydrogen (entries 2-7 of Table 7) can improve the polymer yields but it does not lead to a significant reduction in molecular weight of the resulting polymers. They concluded that the terminal vinylsilane groups can be easily converted into various functional groups that permit further structural modification of sPS to produce end-functionalized sPS containing a broad variety of reactive terminal groups (Scheme 5).

**(Table 7)**

**(Scheme 5)**

## 3. Post-functionalization of syndiotactic polystyrene

Another effective and versatile method to chemical modification of syndiotactic polystyrene is post-functionalization of sPS. This includes introduction of polar groups into syndiotactic polystyrene backbone, synthesis of syndiotactic polystyrene graft or block copolymers, and hydrogenation of syndiotactic polystyrene or its copolymers. This pathway for the chemical modification of sPS leads to the fabrication of a wide variety of surface functionalities without changing polymerization kinetics and enables incorporation of chemical moieties or creation of polymer architectures which cannot tolerate by the polymerization process.

### 3.1. Introduction of polar groups into syndiotactic polystyrene

Syndiotactic polystyrene has attracted both academic and industrial attention because of its excellent performance, which is claimed to be comparable to that of engineering resins like polyesters, polyamides and nylon-66. Thus, sPS has become a promising engineering plastic material for application in various fields, such as automotive, electronic and packaging industries. However, the absence of polar groups in this polymer restricts its end uses, especially where adhesion to substrates and compatibility with polar polymers and low impact strength are desired [73-77]. Therefore, modification of sPS by introduction of polar groups is of interest. Most of these problems can be circumvented through the polarizing of sPS itself or copolymerization with a polymer having polar groups. Some of the main methods to introduction of polar groups into sPS backbone are discussed in the following

### 3.1.1. Post-functionalization of sPS via transition-metal catalyzed cross-coupling reaction

The transition metal catalyzed cross-coupling reaction such as Kumada, Suzuki–Miyaura, Heck, Stille, Negishi, Hiyama, and Sonogashira has emerged as one of the most powerful carbon–carbon bond formation protocols available to practitioners of chemical synthesis [78,79]. The cross-coupling reactions such as Suzuki-Miyaura reaction can be used to introduce polar groups into syndiotactic polystyrene backbone. As an example, Shin et al. [80] reported the post-functionalization of high-molecular-weight syndiotactic polystyrene (sPS) via combination of electrophilic bromination at the *para*-position of the polymer aromatic ring and subsequent Suzuki-Miyaura cross-coupling reactions with functionalized phenylboronic acids. A schematic of the post-functionalization of syndiotactic polystyrene by Shin et al. is shown in Scheme 6. They examined the surface energy change of the sPS, sPS-Br and functionalized syndiotactic polystyrenes by water contact angles study**.** The results obtained are shown in Figure 1. Pure sPS has a contact angle of 102.5º, while the sPS-Br (8.5 mol %) has a contact angle of 101.4º, which suggests that incorporation of bromine group has an insignificant effect on surface polarity. After the introduction of polar groups via Suzuki-Miyaura cross-coupling reactions, however, water contact angles of the polar-functionalized sPS materials were much lower (93-96º) than that of sPS. Due to the functionalization, these results indicated that hydrophilicity was increased in the polymer.

**(Scheme 6)**

**(Figure 1)**

### 3.1.2. Sulfonated syndiotactic polystyrene (SsPS)

The functionalization of syndiotactic polystyrene by sulfonate groups has been studied extensively [81-84]. It was shown that sulfonated sPS can be obtained by treating sPS with sulfonating reagent such as acyl sulfate complexes prepared from acetic anhydride, lauric acid or caproic anhydride associated to sulfuric acid [19,85,86]. Sulfonated syndiotactic polystyrene (SsPS) have many different properties compared with pure sPS and can be used as the compatibilizer for blend of sPS and other polar polymers. For example, increase in modulus, melt and solution viscosity, glass transition temperature ($T_g$) and decrease in melting point are some of the major changes would be occurred after sulfonation of syndiotactic polystyrene [18,87]. The decrease in the melting temperature of the SsPS is occurs due to the formation of ionic aggregates which reduce the mobility of the polymer chain during the crystallization process and lead to the formation of smaller crystallites which melt at lower temperatures than the pure sPS. The increase in the glass transition temperature of the SsPS originates from the formation of ionic aggregates as well which restricted segmental motion of the polymer chains may traverse both ionic and amorphous regions of the ionomer.

Govindaiah et al. [18] reported the synthesis of sulfonated syndiotactic polystyrene in mixture of 1,1,2-trichloroethane and chloroform and investigated the effect of sulfonation on the crystallization behavior of syndiotactic polystyrene. The studies on the thermal properties of sulfonated sPS ionomers by differential scanning calorimetry (DSC) showed that thermal behavior of the synthesized SsPS depends on the sulfonation level. Moreover, incorporation of sulfonic acid groups into the syndiotactic polystyrene backbone was found to affect the crystallization behavior of sPS. The results obtained from DSC data are summarized in Table 8. As shown in Table 8, melting temperature ($T_m$), heat of fusion ($\Delta H$), and crystallization temperature ($T_c$) were lowered by the incorporation of sulfonic acid groups on the syndiotactic polystyrene backbone.

**(Table 8)**

Selective functionalization of the polymer surfaces have attracted significant attention in recent years because of their wide range of potential applications in various fields such as membranes [88,89] and biomedical polymers [90,91]. Musto et al. [92] described the selectively sulfonation of the sPS (the $\delta$-form) film by soaking of sPS film in a solution of chlorosulfonic acid in chloroform at room temperature (Scheme 7). The results exhibited comparatively large diffusivity and solubility values for low-molecular weight compounds such as chloroform, which can be effectively used as a carrier solvent. The results of sulfonation of the $\delta$-form are compared with those obtained with a *trans-planar* crystalline modification of sPS ($\beta$-form). It is found that the $\delta$-form is suitable for obtaining sulfonated films with a high degree of surface selectivity.

**(Scheme 7)**

Li et al. [85] reported the synthesis of sulfonated syndiotactic polystyrene using a mixed solvent containing 1,1,2-trichloroethane (TCE) and chloroform (CF) (60/40 v/v) and acetyl sulfate as sulfonating agent. Efficiency of the sPS sulfonation reaction in different solvents and different amount of sulfonating agent is summarized in Table 9.

**(Table 9)**

Furthermore, they synthesized sodium, potassium, zinc (II), manganese (II), and cobalt (II) salt of the sulfonated syndiotactic polystyrene. The FTIR and DSC data showed that the roles of the cation-anionic site interaction in the alkali form and transition metal form ionomers are somewhat different. The DSC data also showed that the alkali metal cations had more pronounced effect on the $T_g$ then did the transition metal cations. They reported that the crystallization behavior of the ionomers with low degree of sulfonation also exhibited considerable differences in comparison with the pure sPS. Then melting points ($T_m$) and the degree of crystallization ($X_c$) were significantly lowered by the presence of the sulfonic acid groups or the sulfonate metal groups. In addition, the synthesized ionomers were more thermally stable and more hygroscopic then the neat sPS. The obtained data such as melting point ($T_m$), melting enthalpy ($\Delta H_m$), crystallinity ($X_c$), crystallization temperature ($T_c$), and crystallization enthalpy ($\Delta H_c$) from DSC curves is summarized in Table 10. Furthermore, the glass transition temperature ($T_g$), of the synthesized ionomers with 1.7% and 11.9% degree of sulfonation is also summarized in Table 11. They concluded that the synthesized sulfonated syndiotactic polystyrenes were soluble in chloroform and methanol mixed solvent.

**(Table 10)**

**(Table 11)**

In the further work, Li et al. [86] utilized the sulfonated syndiotactic polystyrene with the sulfonation degree of 11.9 mol% (SsPS-H-12) as a compatibilizer in the blend of syndiotactic polystyrene/polyamide-6 (sPS/PA6). They suggested that, due to strongly acid-base interaction of sulfonic acid groups of the SsPS-H with the amine end-groups of

PA6 the addition of SsPS-H to sPS/PA6 blends would reduce the dispersed phase size and improve the adhesion between the phases. The glass transition temperatures of the PA6 component in the compatibilized sPS/PA6 blends shifted significantly towards higher temperature with increasing the content of SsPS-H-12. This investigation with lower melting point and crystallization temperatures of PA6 in the sPS/PA6 blends containing higher SsPS-H contents compared to the incompatibilized blend might indicate the enhanced compatibility and provide some insight into the level of interaction between the PA6 and SsPS-H. Accordingly, the compatibilized blends, compared to the blends without SsPS-H, had significantly higher impact strength. The best improvement in the impact strength of the blends was achieved with the content of the SsPSH (11.9 mol%) about 5 wt.%.

Wang et al. [93] studied the effect of the potassium salt of sulfonated syndiotactic polystyrene (SsPS-K) on compatibility, crystallization behavior, and mechanical properties of the syndiotactic polystyrene (sPS)/polyester (PET)/potassium salt of sulfonated syndiotactic polystyrene (SsPS-K) alloys prepared by melt blending method. The yielded alloys were characterized with DSC and dynamic mechanical analysis (DMA). Results demonstrated that all the alloys exhibited one glass transition temperature ($T_g$) and the half-peak width of the sPS/PET/SsPS-K alloys became narrower compared with that of sPS/PET alloys, which decreased with an increasing content of the SsPS-K ionomer. According to the DSC data, they also reported that $T_m$ of sPS and PET of the alloys were similar to those of the pure polymers and did not change with the content of the SsPS-K ionomer, while the initial crystallization temperature ($T_0$) and crystallization temperature at peak ($T_p$) was increased. In addition, the thermal mechanical analysis (TMA) results showed that the alloys could retain the perfect heat proof property of sPS. Finally, they concluded that, the ternary alloys had better mechanical properties and significantly higher unnotched Izod impact strength than those of the alloys without SsPS-K. When the weight ratio of sPS/PET/SsPS-K was 85/15/4, the impact strength reached to the maximum of 11.5 kJ/m$^2$, which was about three times that of pure sPS, and still had a higher tensile strength, flexural strength, and storage modulus, which were 38.8, 54.2, and $1.55 \times 10^4$ MPa, respectively. Table 12 summarized the mechanical properties of each prepared alloys by Wang and his coworkers.

**(Table 12)**

### 3.1.3. Acetylated or benzoylated syndiotactic polystyrene

Selective and controlled incorporation of polar functional groups into sPS backbone has been suggested as an efficient way to improve its surface properties and overcome the certain deficiencies. It is found that syndiotactic polystyrene is acetylated quantitatively to poly(4-acetylstyrene) using the Friedel-Crafts reaction in a heterogeneous process. Acetylation reaction of sPS was conducted in a heterogeneous process by using acetyl halides and anhydrous aluminum chloride as acetylating agents and catalyst, respectively.

Gao and Li [20] developed a acetylation procedure of sPS in a heterogeneous process by using carbon disulfide as the dispersing medium, acetyl chloride as the acetylating agent and anhydrous aluminium chloride as the catalyst. The resultant acetylated syndiotactic polystyrene (AsPS) was characterized by means of FTIR and NMR spectroscopy. They found that the incorporation of acetyl groups into sPS has a marked effect on the thermal properties of the obtained materials. In their experiments, the degree of crystallinity was decreased by the presence of acetyl groups, while the glass transition temperature was increased. The reported data such as glass transition temperature ($T_g$), melting point ($T_m$), melting enthalpy ($\Delta H_m$), crystallinity ($X_c$), and the crystallization temperature ($T_c$) for the synthesized acetylated sPS with different degrees of acetylation is summarized in Table 13.

**(Table 13)**

Another method for modification of syndiotactic polystyrene is benzoylation of its phenyl groups via Friedel-Crafts reaction. It has been well established that benzoylation is an effective way to enhance the thermal stability of the sPS ($\delta_e$ form) and can be carried out by both solution and solid procedures [94].

Gao et al. [95] synthesized benzoylated syndiotactic polystyrene in a heterogeneous process by using carbon disulfide as the dispersing medium, and benzoyl chloride and anhydrous aluminum chloride as benzoylating agent and catalyst, respectively. The resultant polymer was characterized by FTIR and $^1$H NMR spectroscopy. They found that the incorporation of benzoyl groups into sPS was effect on the thermal properties of these materials. In addition, melting point and the degree of crystallinity decreased by the presence of benzoyl groups, while the glass transition temperature increased. The reported data such as glass transition temperature ($T_g$), melting point ($T_m$), melting enthalpy ($\Delta H_m$), crystallinity ($X_c$), and the crystallization temperature ($T_c$) for the synthesized benzoylated sPS with different degrees of benzoylation is summarized in Table 14.

**(Table 14)**

### 3.1.4. Maleic or succinic anhydride-*grafted* syndiotactic polystyrene

Maleic anhydride (MA) and succinic anhydride (SA), are polar monomers, is usually used in polyolefins grafting modification. Another classic and efficient method for introduction of polar groups into sPS is the preparation of maleic and succinic anhydride-*grafted* syndiotactic polystyrene [96,97]. The improved adhesion of maleic and succinic anhydride-functionalized sPS to polar materials such as polyamide (PA), metals, and glass fibers are originated a large interest. The maleic and succinic anhydride-*grafted* polyolefines is often used as compatibilizers in polymer blends [97-99]. Therefore, the preparation of MA and SA-functionalized sPS is very attractive and challenging. Because of the unfavorable reaction between MA or SA and the catalyst or co-catalysts, however, the copolymerization of styrene with MA and SA by syndiospecific polymerization is not practical. According to previously reports, MA-functionalized sPS could be synthesized by Friedel-Crafts acylation reaction [21], free radical-induced grafting reaction in solution grafting process [100], or solid reaction method [22].

Chen et al. [21] reported the synthesis of maleic anhydride-*grafted* syndiotactic polystyrene by Friedel-Crafts acylation reaction in the presence of anhydrous aluminium chloride ($AlCl_3$) as catalyst and carbon disulfide ($CS_2$) as dispersing agent in a heterogeneous process. The incorporation of carboxyl groups and double bonds onto pendant aromatic groups of sPS confirmed by FTIR spectroscopy and $^1H$ NMR studies. The obtained expected MA contents (*i.e.* degrees of acetylation) in the various condition reactions of sPS-*g*-MA are summarized in Table 15. Furthermore, the thermal properties of MA-modified sPS were also studied by means of differential scanning calorimetric (DSC). They found that the thermal behavior of the MA-modified sPS exhibits considerable differences in comparison to the neat sPS. The melting temperature ($T_m$), crystallization temperature ($T_c$), and degree of crystallinity of the maleated polymers decrease with increasing content of carboxyl groups, while the glass transition temperature ($T_g$) increases. The obtained data from DSC study is summarized in Table 16.

**(Table 15)**

**(Table 16)**

The maleic anhydride-*grafted* syndiotactic polystyrene can be prepared by a solution grafting process at 110 °C using 1,1,2-trichloroethane as solvent and dicumyl peroxide as free radical initiator. Using this method Li et al. [100] synthesized MA-functionalized sPS. The $^1$H nuclear magnetic resonance (NMR) and infrared spectroscopy studies showed that the attachment of maleic anhydride onto sPS was in the form of single succinic anhydride rings as well as short oligomers. The degree of grafting with this method goes up to 1.16 wt%. Compared to the pure sPS, the maleic anhydride functionalized sPS crystallized at a higher rate. On the other hand, in the presence of grafts, both the degree of crystallinity and the melting point ($T_m$) goes down to 254 °C for the polymer functionalized at 1.16 wt%.

Using solid reaction method, Lim et al. [22] synthesized maleic anhydride-*grafted* syndiotactic polystyrene (sPS-*g*-MA) via free radical-induced grafting reaction. They used azobisisobutyronitrile (AIBN) and dicumylperoxide (DCP) as the radical initiators. The formation of sPS-*g*-MA was directly confirmed by Fourier transform infrared (FTIR) spectroscopy and the expected MA contents in sPS-*g*-MA from various conditions reactions are summarized in Table 17.

**(Table 17)**

In another study, Li et al. [97] reported the functionalization of syndiotactic polystyrene with succinic anhydride (SA) by use of Friedel-Crafts acylation reaction in the presence of anhydrous aluminum chloride in carbon disulfide (Scheme 8). They proved that an optimum reaction should be carried out at 30 °C with a molar ratio of aluminum chloride to succinic anhydride of 3/1. The degree of succinoylation corresponding to carboxylic acid value of the polymers was determined by chemical titration, and the data is summarized in Table 18. They found that the crystallization temperature, melting temperature, and degree of crystallinity of the modified polymer decreased with increasing the degree of succinoylation, while the glass transition temperature increased. Table 19 summarized the obtained data from differential scanning calorimetry (DSC). They concluded that the succinic anhydride (SA) functionalized sPS offers possibility for the development of sPS based polymer blends and composites, thus extending the application field of sPS.

**(Scheme 8)**

**(Table 18)**

**(Table 19)**

### 3.2. Graft or block copolymerization onto syndiotactic polystyrene

It is well established that desired properties are not usually attainable by the properties of a single homopolymer; thus, modification of some polymers such as sPS by anchoring several functional groups is necessary for obtaining desired physicochemical properties [101-104]. Graft or block copolymerization of a second monomer onto syndiotactic polystyrene is one of the most effective ways to overcome the certain deficiencies of sPS, since the polymer surfaces can be modified without compromising bulk properties. In this section, we briefly review the some new conducted researches around the graft or block copolymerization onto syndiotactic polystyrene via living radical polymerization techniques, macromonomer technique, melting graft copolymerization, anionic grafting reaction, and ring-opening polymerization.

### 3.2.1. Graft or block copolymerization onto syndiotactic polystyrene via living radical polymerization

Copolymerization is a powerful tool for preparing polymers with specific properties through the proper selection of monomers and architectural designing by manipulation of constituent monomers of copolymers. Copolymers in general exhibit physical and mechanical properties far different from those of blends of the same corresponding homopolymers [105-108]. There are many synthetic approaches than can be used to prepare block or graft copolymers. In this respect, “living” free-radical polymerization (LFRP) techniques such as atom transfer radical polymerization (ATRP) [109-112], nitroxide-mediated polymerization (NMP) [113-115], and reversible addition of fragmentation chain transfer (RAFT) [116-118], have been developed for synthesizing tailor-made polymers with well-defined architecture and predictable molecular weights.

Gao et al. [119] synthesized syndiotactic polystyrene-*graft*-poly(glycidyl methacrylate) (sPS-*g*-PGMA) copolymer by a heterogeneous atom transfer radical polymerization (ATRP) using 2-bromo-2-methylpropanoyl bromide modified syndiotactic polystyrene (BMPsPS) as macroinitiator and copper bromide combined with 2,2'-bipyridine (bpy) as catalyst in anisole at room temperature. To aim this purpose, they firstly synthesized BMPsPS macroinitiator with 7.0 mol% bromine content via Friedel-Crafts acylation reaction of sPS with 2-bromo-2-methylpropanoyl bromide in a heterogeneous process. The obtained macroinitiator was subsequently used in copolymerization with glycidyl methacrylate monomer via ATRP technique in a heterogeneous process to yield a graft copolymer (sPS-*g*-PGMA). They also inducted that in the presence of the functional groups, the degree of crystallinity and the melting temperature were significantly lowered, while the glass transition temperature ($T_g$) was increased. Table 20 lists the degree of crystallinity and thermal data for each of the samples synthesized by Gao and his coworkers.

**(Table 20)**

In 2009 Brownell et al. [25] described the synthesis of syndiotactic polystyrene-*graft*-poly(methyl methacrylate) (sPS-*g*-PMMA), syndiotactic polystyrene-*graft*-poly(*tert*-butyl acrylate) (sPS-*g*-P*t*BA), and syndiotactic polystyrene-*graft*-poly(acrylic acid) (sPS-*g*-PAA) using a combination of iridium-catalyzed C-H activation/borylation and atom transfer radical polymerization (ATRP). In the first step, the syndiotactic polystyrene was functionalized by pinacolboronate ester (sPS-Bpin). Next, by hydrolysis of sPS-Bpin, hydroxy-functionalized syndiotactic polystyrene (sPS-OH) was obtained. Afterwards, a macroinitiator (sPS-Br) suitable for ATRP was synthesized by the esterification of 2-bromo-2-methylpropionyl bromide and sPS-OH. Finally, the graft copolymerizations of methyl methacrylate, *tert*-butyl acrylate, and acrylic acid from the macroinitiator using ATRP technique afforded polar block grafted sPS materials. The schematic demonstrations of their procedures are shown in Schemes 9 and 10. Brownell et al. utilized differential scanning calorimetry (DSC) to study the thermal properties of the synthesized samples. The obtained results are shown in Table 21.

**(Scheme 9)**

**(Scheme 10)**

**(Table 21)**

Annunziata et al. [120] synthesized well-defined syndiotactic polystyrene-*block*-atactic polystyrene (sPS-*b*-aPS) stereoblock polymers in a two-step process using a combination of ‘‘pseudo-living’’ Ziegler-Natta and atom transfer radical polymerizations. For this purpose, styrene syndiospecific polymerized by $Cp^*Ti(CH_2Ph)_3/B(C_6F_5)_3/Al(n\text{-}Oct)_3$ (1:1:1) followed terminated by adding *N*-bromosuccinimide (NBS) to produce sPS-Br polymers almost perfectly (97%) end-capped with bromine atoms. These synthesized sPS-Br were used as macroinitiators in the atom transfer radical polymerization of styrene affording sPS-*b*-aPS with a broad range of compositions. A schematic of the sequential preparation of sPS-*b*-aPS stereoblock polymers by Annunziata et al. is shown in Scheme 11. The results obtained for styrene polymerization and bromination end-capping and synthesis of sPS-*b*-aPS via ATRP are summarized in Tables 22 and 23, respectively. They concluded that studies on the crystallization behavior by differential scanning calorimetry (DSC) under non-isothermal and isothermal conditions rather unexpectedly showed that the synthesized stereoblock polymers crystallized faster than the corresponding aPS/sPS blends with comparable compositions.

**(Scheme 11)**

**(Table 22)**

**(Table 23)**

The controlled graft and block copolymerization onto sPS backbone using nitroxide-mediated polymerization (NMP) method and the preparation of its polymer/layered doublehydroxide (LDH) nanocomposite was reported for the first time by Jaymand [76], in 2011. For this purpose, firstly 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) was coupled with α-phenyl-chloro-acetylated sPS and then the controlled graft and block copolymerization of styrene (St) and *p*-methylstyrene (MSt) monomers onto the sPS backbone were initiated by the sPS and sPS-*g*-aPS carrying TEMPO groups as macroinitiators, respectively. A schematic of the grafting procedures utilized by Jaymand are shown in Schemes 12 and 13. The structures of the obtained graft and block copolymers were determined by $^1$H nuclear magnetic resonance and Fourier transform infrared spectroscopy. The $^1$H NMR spectra of both sPS-*g*-aPS and sPS-*g*-(aPS-*b*-aPMS) copolymers showed that the functional groups of the TEMPO were retained at the end of the polymer chains, which provided strong evidence of NMP reaction occurrence. By these evidences, the possibility of homopolymer formation in the grafting reaction can be excluded in mentioned study as well as living characteristic of polymerization. Providing additional evidence on the effectiveness of graft copolymerization, the thermal properties of the copolymers were examined by DSC. According to his investigations, the presence of graft segments affected on the melting behavior of the sPS backbone. Table 24 provides series of DSC results for neat sPS and sPS-*g*-(aPS-*b*-aPMS) copolymer synthesized by Jaymand.

**(Scheme 12)**

**(Scheme 13)**

**(Table 24)**

In further work Jaymand [122] brominated the obtained sPS-*g*-(aPS-*b*-aPMS) copolymer by *N*-boromosuccinimide (NBS) as brominating agent to obtain a multicentre macroinitiator [(sPS-*g*-(aPS-*b*-aPMS))-Br]. This multicentre macroinitiator was used to polymerize of methyl mthacrylat monomer to produce the [sPS-*g*-(aPS-*b*-aPMS)]-*g*-PMMA copolymer using the ATRP technique in the presence of the CuBr/2,2'-bipyridyl (bpy) catalyst system. The topology followed is shown in Figure 2. The calculated grafting parameters for sPS-*g*-aPS, sPS-*g*-(aPS-*b*-aPMS) and [sPS-*g*-(aPS-*b*-aPMS)]-*g*-PMMA are summarized in Table 25. Because of relatively wide scope of monomers which could be employed (especially in the ATRP technique), stability of catalyst, the simple polymerization procedure, and controllability of graft structure, these employed methods (NMP and ATRP) to preparation of sPS graft and block copolymers has become an attractive method.

**(Figure 2)**

**(Table 25)**

Since the first report of radical addition-fragmentation chain transfer (RAFT) processes in 1970s [123,124] it has been well demonstrated that these processes are versatile approaches to synthesis of polymers with controlled molecular weight, narrow dispersity index, and complex macromolecular architectures [125-127]. Unfortunately, to the best of our knowledge, this approach was neglected definitely for the synthesis of sPS copolymers.

### 3.2.2. Synthesis of syndiotactic polystyrene copolymers via macromonomer technique

Synthesis of graft copolymers can manage not only to tune the properties of the surface, but also the molecular structure and chemical composition of the resultant polymer for expanding utilizations. Using macromonomer techniques [77,128,129], graft copolymers are generally synthesized either by the linkage of two different polymers through a coupling reaction [105,130] or polymerization of a monomer from active sites on a polymer backbone [131,132]. Macromonomers are relatively new category of functionalized polymer materials having one or more reactive polymerizable groups. Macromonomers can be synthesized by various methods, including anionic, cationic and radical polymerization, as well as the chemical modification of polymer ends. The use of macromonomers provides an efficient route to control the molecular architecture of polymers, including crosslinked and branched copolymers such as comb, star, brush and graft types [133-135].

On the basis of earlier studies, Jaymand [77] could develop a general method for the synthesis of vinyl-terminated syndiotactic polystyrene multicenter macromonomer (VsPSM) for the graft copolymerization of methyl methacrylate (MMA) monomer onto sPS backbone using free-radical polymerization. For this purpose, the chlorine groups of α-phenyl-chloro-acetylated sPS were converted to 9-decen-1-oxy groups by a substitution nucleophilic reaction in the presence of a solvent composed of 9-decen-1-ol moiety, sodium hydride (NaH), and dry *N*,*N*-dimethylformamide (DMF). The obtained VsPSM was used in free-radical copolymerization with MMA monomer in a heterogeneous process to yield a graft copolymer (sPS-*g*-PMMA). The grafting procedure utilized by Jaymand is shown schematically in Scheme 14. The structure of VsPSM and sPS-*g*-PMMA were determined by $^1$H nuclear magnetic resonance and Fourier transform infrared (FTIR) spectroscopy. The extent of the presence of the vinyl terminal group for sPS, was calculated 20.58% from $^1$H NMR and the volume of the two parts (sPS and PMMA) of the graft copolymer were calculated 36 wt.% and 64 wt.% from thermogravimetric analysis (TGA). Furthermore, as he reported, both melting point ($T_m$) and glass transition temperature ($T_g$) of the graft copolymer were affected by the side chains. DSC results, however, showed that the melting temprature ($T_m$) was significantly lowered by the presence of the PMMA segments, while the glass transition temperature ($T_g$) was increased. Table 26 summarized the DSC results for neat sPS and sPS-*g*-PMMA copolymer synthesized by Jaymand.

**(Scheme 14)**

**(Table 26)**

Endo and Sugita described the synthesis of graft copolymer from copolymerization of styrene-terminated poly(ethylene oxide) macromonomer (SEOM) and styrene (St) with $CpTiCl_3$/methylaluminoxane catalyst in toluene [136]. Copolymerization of styrene and SEOM ($\overline{Mn} = 1.00\times10^3$) with $CpTiCl_3$/MAO was conducted in toluene at 30 °C for 3 hours, and the results are summarized in Table 27. Other additional important contribution of Endo and Sugita study was the observation of the reactivity of SEOM. As they concluded, in $CpTiCl_3$/MAO catalyst system, the reactivity of SEOM possessed a low molecular weight in syndiospecific copolymerization with styrene was higher than that of styrene-terminated polyisoprene macromonomer (SIPM) or styrene-terminated aPS macromonomer (SSTM). Also, the reactivity of high molecular weight SEOM was lower than that of low molecular weight SEOM.

**(Table 27)**

### 3.2.3. Graft copolymerization onto sPS via melting graft copolymerization

Another effective and versatile method to modification of sPS is graft copolymerization of a second monomer onto sPS via melting graft copolymerization. For example, Cao et al. [137] described the synthesis of sPS graft copolymers by melting graft copolymerization. For this purpose, the mixture of sPS, itaconic acid and dibutyl maleate monomers and dicumyl peroxide (DCP) as an initiator was heated at 280 °C into a small-type injector. A schematic of the copolymerization procedure utilized by Cao et al. is shown in Scheme 15. Thermal property study indicated that the glass-transition temperature ($T_g$) and melting temperature ($T_m$) decreased with increasing addition of monomer. However, the enthalpy and the corresponding crystallinity ($X_c$) of *grafted*-sPS first decreased and then increased. The obtained data from DSC is summarized in Table 28. They concluded that the synthesized *grafted*-sPS with polar poly(dibutyl maleate-*block*-itaconic acid) can be used as a compatibilizer for syndiotactic polystyrene/polyadimide 66 blends due to increased hydrophilicity in the polymer.

**(Scheme 15)**

**(Table 28)**

### 3.2.4. Synthesis of syndiotactic polystyrene graft copolymers by anionic grafting and ring-opening reactions

The modification of polymer properties through the synthesis of its graft or block copolymers has been studied for decades. Synthesis of sPS graft copolymers can be achieved via anionic grafting and ring-opening reactions.

Srinate et al. [138] described the synthesis of syndiotactic polystyrene-*graft*-polybutadiene by anionic grafting reaction. For this purpose, poly(styrene-*co*-4-

methylstyrene), was firstly synthesized by the copolymerization of styrene and 4-methylstyrene monomers with a trichloro(pentamethyl cyclopentadienyl) titanium (IV)/modified methylaluminoxane system as a metallocene catalyst at 50 °C. Afterwards, the methyl group of 4-methylstyrene units in syndiotactic poly(styrene-*co*-4-methylstyrene) (sPSMS) was deprotonated by butyl lithium (BuLi) and further reacted with polybutadiene to graft polybutadiene (PB) onto the deprotonated methyl of the sPSMS backbone. Table 29 summarized the obtained results of various reaction conditions. As they concluded, the sPSMS-*g*-PB/pure sPS blend had higher strength and toughness than pure sPS. Therefore, sPSMS-*g*-PB might be used as a compatibilizer in sPS blends to modify their mechanical properties.

**(Table 29)**

Rahmani and Entezami [139] reported the synthesis of syndiotactic polystyrene-*graft*-polydimethylsiloxane copolymers using a two-stage process. In the first step, they synthesized syndiotactic polystyrene copolymer [poly(styrene-*co*-*p*-methylstyrene) (sPSMS)] by the copolymerization of styrene and *p*-methylstyrene with cyclopentadienyltitanium trichloride/methylaluminoxane catalyst system. Then, the yielded copolymer was grafted with polydimethylsiloxane by the anionic ring-opening polymerization of hexamethylcyclotrisiloxane with a metallation reagent in cyclohexane or tetrahydrofuran (THF) (Scheme 16). The effect of the solvent on the degree of grafting in the copolymers was investigated. It was demonstrated that the degree of grafting in the copolymer was higher in THF. Moreover, thermal property study by DSC indicated that the melting, crystallization and glass transition temperatures of the synthesized graft copolymers decreased with increasing degree of graft in the copolymers. The thermal data for each of the samples synthesized by Rahmani and Entezami is summarized in Table 30.

**(Scheme 16)**

**(Table 30)**

### 3.3. Hydrogenation of syndiotactic polystyrene or its copolymers

Another method for post functionalization of syndiotactic polystyrene is hydrogenation of sPS or its copolymers. Partially hydrogenation of sPS can lead to syndiotactic poly(styrene-*co*-vinylcylohexane) containing styrene-styrene syndiotactic sequences while fully hydrogenation of sPS is leaded to syndiotactic poly(vinylcylohexane). Hydrogenation of sPS can be carried out using Pd (5 wt%)-$BaSO_4$ as the catalyst [140,141]. Moreover, sPS-*block*-polybutadiene copolymer can be converted to sPS-*block*-polyethylene copolymer via hydrogenation of sPS-*block*-polybutadiene in the presence of *p*-toluenesulfonhydrazide [142].

## 4. Homo and copolymerization of substituted styrenic monomers

Another effective and versatile method to prepare modified syndiotactic polystyrene is homo and copolymerization of substituted styrenic monomers. It has been well established that the substituted styrenic monomers with higher electron donating groups (such as *p*-*n*-alkylstyrenes) leads to the highest yields among the monomers [143-146].

Rabagliati et al. [147] employed binary metallocene-MAO and ternary diphenylzinc-metallocene-MAO (metallocene = titanocene, zirconocene, hafnocene) as initiators systems in the homopolymerization of styrene as well as its copolymerization with several diverse co-monomers including substituted styrenes, styrene derivatives, α-olefins and dienes. On the basis of their investigations, titanocenes were more effective than zirconocenes and hafnocenes in the homopolymerization of styrene while zirconocenes performed better in α-olefin polymerization. It was found that titanocenes generated mainly syndiotactic polystyrene while zirconocenes yielded atactic polystyrene or, depending on the zirconocene, a low percentage of sPS. The results obtained in the homopolymerization of styrene with various binary and ternary metallocene systems are summarized in Table 31. For mentioned binary and ternary metallocene initiators the polymerization process depended largely on the inductive effect of the substituents linked to the benzene ring of styrene and on its position (*ortho*, *meta* or *para*). Substituent multiplicity reduced the effectiveness of these initiator systems markedly. The results obtained from styrene copolymerization with styrene derivatives, α-olefins and dienes, using ternary and binary initiator systems are shown in Tables 32 and 33, respectively.

**(Table 31)**

**(Table 32)**

**(Table 33)**

In addition, recently Sago et al. [148] reported the synthesis of syndiotactic poly(*p-tert*-butylstyrene) (sPTBS), and investigated its physical gelation with some organic solvents. The temperature-concentration phase diagram of sPTBS/*trans*-decalin gel clearly indicated that sPTBS formed a polymer-solvent molecular compound with a ratio of 2.7 *trans*-decalin per monomer unit.

Kawabe and Murata [149] reported the synthesis of syndiotactic poly(4-hydroxystyrene) (PHOST) with narrow molecular weight distribution (1.05-1.15) by syndiospecific living polymerization of silyl-protected hydroxystyrene derivatives in the presence of (trimethyl)pentamethylcyclopentadienyltitanium ($Cp^*TiMe_3$), trioctylaluminium

(Al(Oct)$_3$), and tris(pentafluorophenyl) borane (B($C_6F_5$)$_3$) catalyst system at a polymerization temperature of about -25 °C followed by the deprotection reaction of silyl group with concentrate hydrochloric acid (HCl). They found that the use of bulky trialkylsilyl protective groups was an effective way to control the stereoregularity and molecular weight distribution (MWD) of resulting polymer. Moreover, they concluded that the obtained syndiotactic PHOST had a good solubility in polar solvents such as methanol, ethanol, THF, and DMF and a high glass transition temperature ($T_g$) of 194°C.

In their further work [150] syndiospecific living block copolymerizations of 4-(*tert*-butyldimethylsilyloxy) styrene (TBDMSS) and 4-methylstyrene (4MS) were reported in the presence of (trimethyl)pentamethylcyclopentadienyltitanium (Cp*TiMe$_3$), trioctylaluminium (Al(Oct)$_3$) and tris(pentafluorophenyl) borane (B($C_6F_5$)$_3$) catalyst systems at a polymerization temperature of about -25 °C. By the deprotection reactions of silyl group with concentrate hydrochloric acid (HCl), syndiotactic poly{(4-hydroxystyrene)-*block*-[(4-methylstyrene)-*co*-(4-hydroxystyrene)]} (poly[HOST-*b*-(4MS-*co*-HOST)]) with narrow molecular weight distribution (1.05-1.18) was successfully prepared.

Kim and Do [151] synthesized syndiotactic poly(4-*tert*-butyldimethylsilyloxystyrene) and poly(4-hydroxystyrene) with high molecular weight using a (pentamethylcyclopentadienyl)titanatrane/MMAO catalyst system. For this purpose, they initially synthesized 4-*tert*-butyldimethylsilyloxybenzaldehyde from methylene chloride and 4-hydroxybenzaldehyde in the presence of triethylamine. Afterwards, 4-*tert*-butyldimethylsilyloxystyrene was synthesized through Witting reaction. The syndiospecific polymerization of 4-*tert*-butyldimethylsilyloxystyrene results syndiotactic poly(4-*tert*-butyldimethylsilyloxystyrene) and syndiotactic poly(4-hydroxystyrene) produced by acidic hydrolysis of *tert*-butyldimethylsilyl groups from poly(4-*tert*-butyldimethylsilyloxystyrene) in diethyl ether as the solvent. They stated that syndiotactic poly(4-*tert*-butyldimethylsilyloxystyrene) is soluble in polar organic solvents such as THF, $CHCl_3$, methylene chloride and shows good thermal stability. Moreover, it is found that syndiotactic poly(4-hydroxystyrene) is well soluble in methanol.

## 5. Summary and conclusion

Since the discovery of the syndiotactic polystyrene (sPS) in 1985, the synthesis of this polymer has attracted much attention, because in the last decades it is regarded as a new low-cost engineering polymer with various desirable properties, such as high melting temperature (270 °C), fast crystallization rate, low dielectric constant, excellent mechanical properties, low permeability to gases, outstanding dimensional stability, excellent processing characteristics at a very low melt viscosity, and good chemical resistance. Nevertheless, some drawbacks of sPS restrict its practical use: sPS similar to atactic polystyrene (aPS) has poor impact strength, inherent brittleness, and low surface energy. Moreover, the absence of polar groups for adhesion to substrates and compatibility with polar polymers, and the need to process sPS at high temperatures due to its high melting temperature. Therefore, modification of sPS is necessary for expanding the application fields of sPS and has been the subject of investigation.

This review provided an overview of recent developments in chemical modification of sPS including *in situ* functionalization of sPS (syndiospecific copolymerization of styrene with a second monomer and catalytic chain transfer to a chain transfer agent), post-functionalization of sPS (introduction of polar groups into sPS, graft or block copolymerization onto sPS and hydrogenation of sPS or its copolymers) and monomer modification. . It has been proved that these methods are efficient and powerful tools to improve the physical and chemical properties of syndiotactic polystyrene.

In conclusion, we propose that the introduction of polar groups or synthesis of sPS copolymers with conventional polymers possessing functional polar groups may be the best and first choice for the modification of sPS. In this respect, introduction of polar groups such as sulfonic acid, succinic and maleic anhydride groups into sPS might be attended in industrial applications due to the low expense and high simplicity of these methods. This intense interest originates from the improved adhesion and compatibility of polar groups-functionalized sPS to polar materials such as polyamide (PA), metals, and glass fibers. If the catalyst and polymerization process could be developed in such a way that the manufacturing costs were kept down, it would be expected that syndiotactic polystyrene represents further applications in coming decades and becomes an alternative engineering plastic with its own advantages.

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## Abbreviations

sPS, syndiotactic polystyrene; aPS, atactic polystyrene; iPS, isotactic polystyrene; MAO, methylaluminoxane; MMAO, modified methylaluminoxane; TMA, trimethylaluminum; Cp, $C_5H_5$; HD, 1,5-hexadiene; MCP, methylene-1,3-cyclopentane; VTM, vinyltetramethylene; Et, ethylene; PE, polyethylene; St, styrene; PB, polybutadiene; Bd, butadiene; GPC, gel permeation chromatography; $^1H/^{13}C$ NMR, $^1H/^{13}C$ nuclear magnetic resonance; FTIR, Fourier transform infrared; DSC, differential scanning calorimetry; ESI, ethylene-styrene interpolymer; DMA, dynamical mechanical analysis; TEMPO, 2,2,6,6-tetramethylpiperidine-*N*-oxyl; ES copolymer, ethylene-styrene copolymer; iPP, isotactic polypropylene; BVPE, 1,2-bis(4-vinylphenyl)ethane; DMPVS, dimethylphenylvinylsilane; SsPS, sulfonated syndiotactic polystyrene; $T_m$, melting temperature; $T_c$, crystallization temperature; $\Delta H_m$, melting enthalpy; $\Delta H_c$, crystallization enthalpy; $X_c$, degree of crystallization; PA6, polyamide-6; PET, poly (ethylene terephthalate); TMA, thermal mechanical analysis; AsPS, Acetylated syndiotactic polystyrene; MA, maleic anhydride; SA, succinic anhydride; AIBN, azobisisobutyronitrile; DCP, dicumylperoxide; LFRP, living free-radical polymerization; ATRP, atom transfer radical polymerization; NMP, nitroxide-mediated polymerization; RAFT, reversible addition of fragmentation chain transfer; PGMA, poly(glycidyl methacrylate); bpy, 2,2'-bipyridine; PMMA, poly(methyl methacrylate); P*t*BA, poly(*tert*-butyl acrylate); PAA, poly(acrylic acid); *NBS*, *N*-bromosuccinimide; DMF, *N*,*N*-dimethylformamide; TGA, thermogravimetric analysis; sPSMS, syndiotactic poly(styrene-*co*-4-methylstyrene); THF, tetrahydrofuran; sPTBS, syndiotactic poly(*p*-

*tert*-butylstyrene); PHOST, poly(4-hydroxystyrene); TBDMSS, 4-(*tert*-butyldimethylsilyloxy) styrene.

## Schemes and Figures Captions:

**Scheme 1.** Copolymerization of 1,5-hexadiene (HD) with styrene (St) by half-sandwich scandium dialkyl-scandium complex [58].

**Scheme 2.** Terpolymerization of 1,5-hexadiene (HD) with styrene (St) and ethylene (Et) by half-sandwich scandium dialkyl-scandium complex [58].

**Scheme 3.** Scandium-catalyzed syndiospecific copolymerization of styrene with ethylene [62].

**Scheme 4.** Synthetic route of the sPS-*g*-iPP copolymer [72].

**Scheme 5.** Functional group transformations in vinylsilane end-capped syndiotactic polystyrene [69].

**Scheme 6.** Electrophilic bromination and subsequent Suzuki-Miyaura cross coupling reactions of syndiotactic polystyrene [80].

**Figure 1.** Water contact angles of (a) sPS (102.5º), (b) sPS-Br (101.4º), (c) sPS-CHO (95.6º), (d) sPS-$NH_2$ (95.4º), and (e) sPS-$CONH_2$ (93.7º) [80]. Copyright 2010 WILEY–VCH Verlag GmbH & Co. KGaA.

**Scheme 7.** Sulfonation of the sPS by chlorosulfonic acid [92].

**Scheme 8.** Functionalization of syndiotactic polystyrene with succinic anhydride (SA) by using Friedel-Crafts acylation reaction in the presence of anhydrous aluminum chloride [97].

**Scheme 9.** Synthesis of syndiotactic polystyrene macroinitiator (sPS-Br) [25].

**Scheme 10.** Synthesis of polar graft copolymers of syndiotactic polystyrene [25].

**Scheme 11.** Sequential preparation of sPS-*b*-aPS stereoblock polymers [120].

**Scheme 12.** Synthesis of the sPS-TEMPO macroinitiator [76].

**Scheme 13.** Graft and block copolymerization of styrene and *p*-methylstyrene monomers onto the sPS backbone via nitroxide-mediated polymerization (NMP) [76].

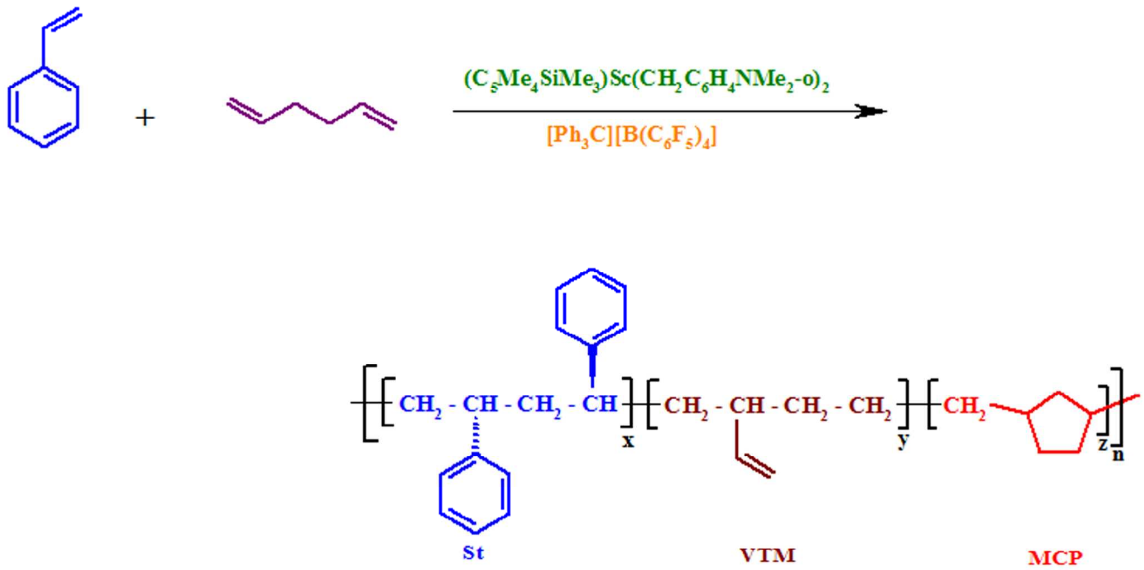
**Figure 2.** Graft and block copolymerization onto syndiotactic polystyrene via NMP and ATRP techniques [122].

**Scheme 14.** Synthetic route of the vinyl-terminated syndiotactic polystyrene multicentre macromonomer (VsPSM) and graft copolymerization of methyl methacrylate onto syndiotactic polystyrene [77].

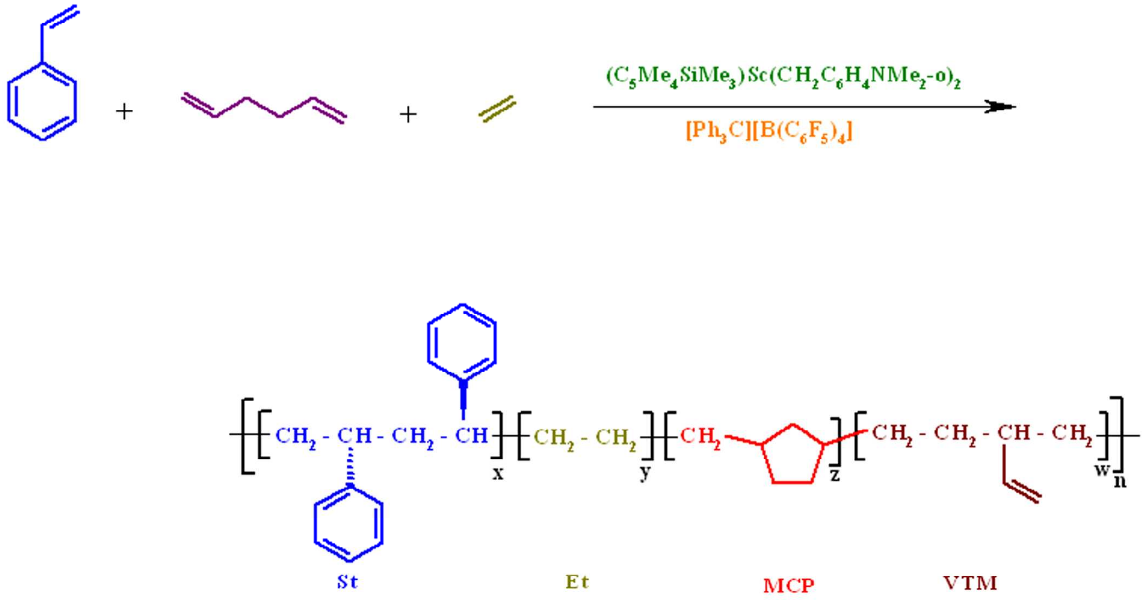
**Scheme 15.** Graft copolymerization of itaconic acid and dibutyl maleate monomers onto sPS via melting graft copolymerization [137].

**Scheme 16.** Synthesis of syndiotactic poly(styrene-*co*-*p*-methylstyrene)-*graft*-polydimethylsiloxane [139].

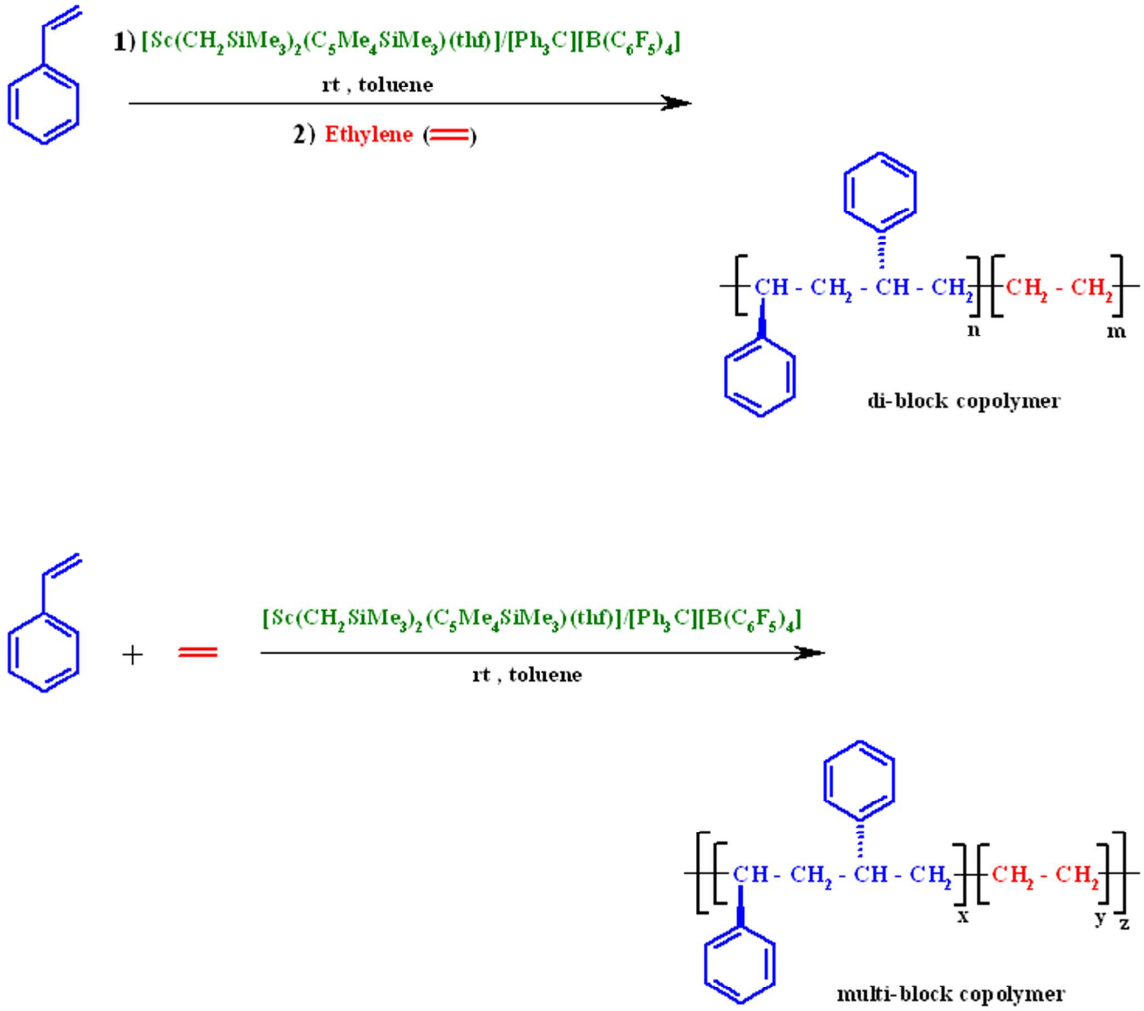
# Schemes and Figures:



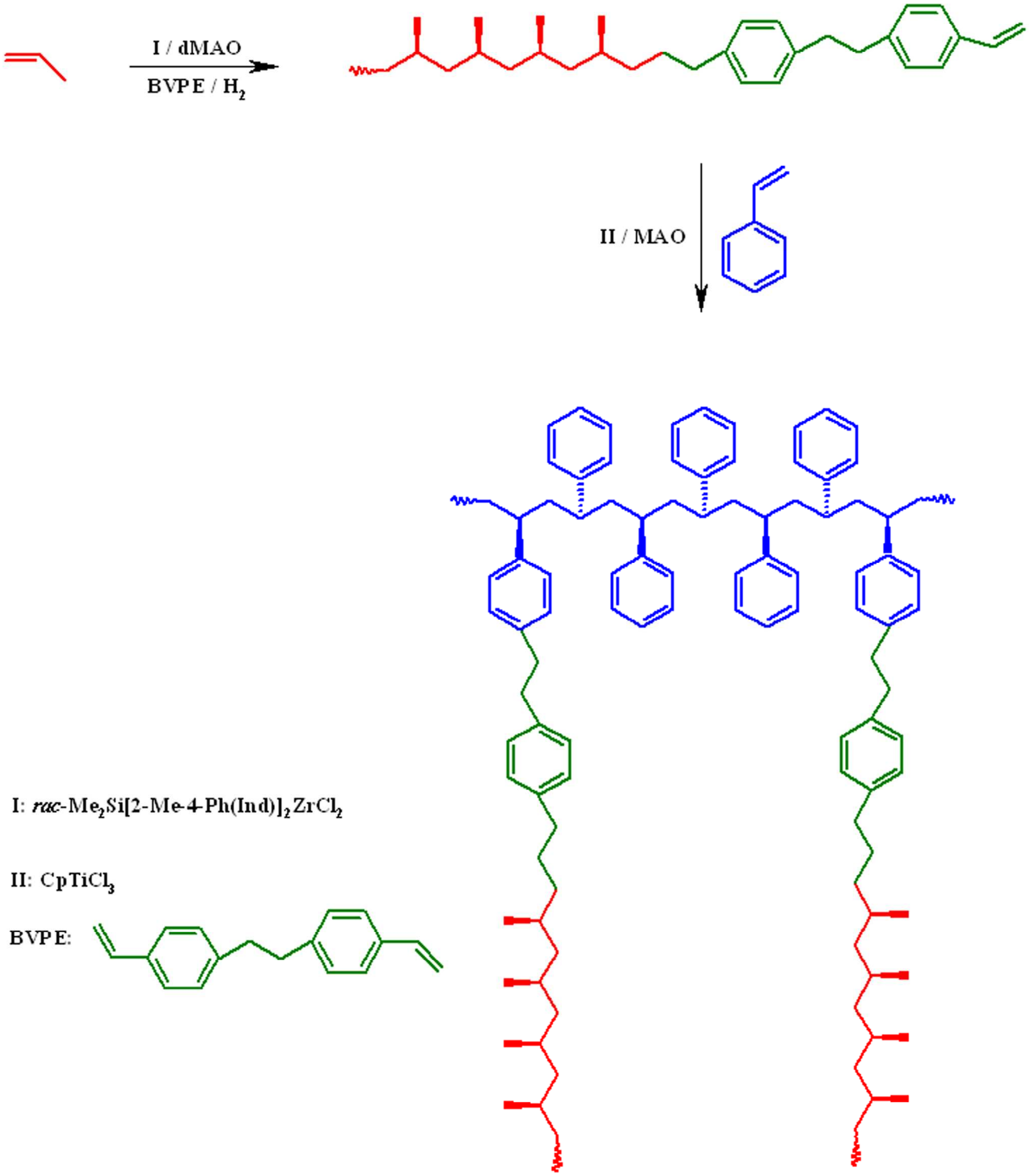
**Scheme 1.** Copolymerization of 1,5-hexadiene (HD) with styrene (St) by half-sandwich scandium dialkyl-scandium complex [58].



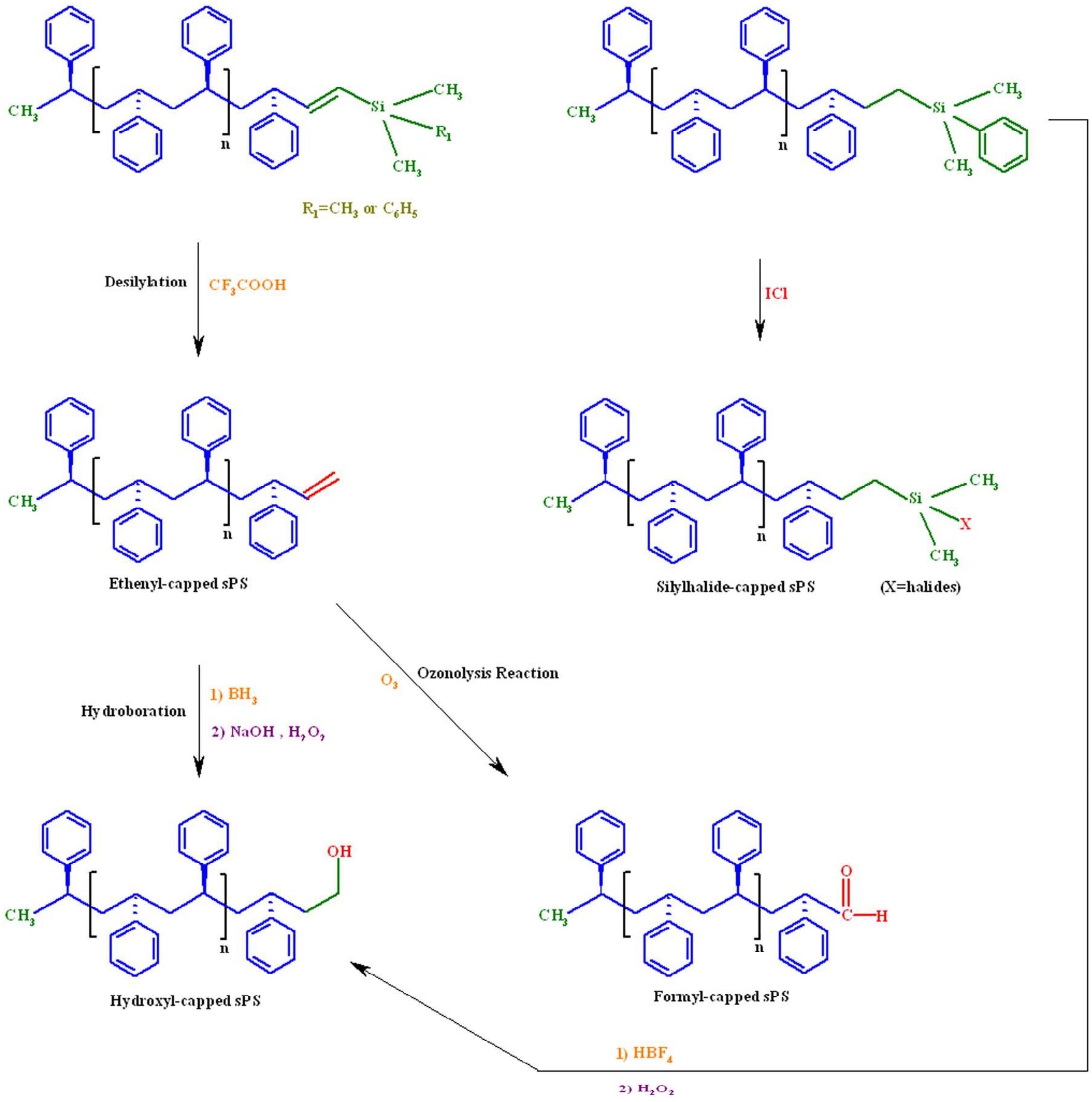
**Scheme 2.** Terpolymerization of 1,5-hexadiene (HD) with styrene (St) and ethylene (Et) by half-sandwich scandium dialkyl-scandium complex [58].



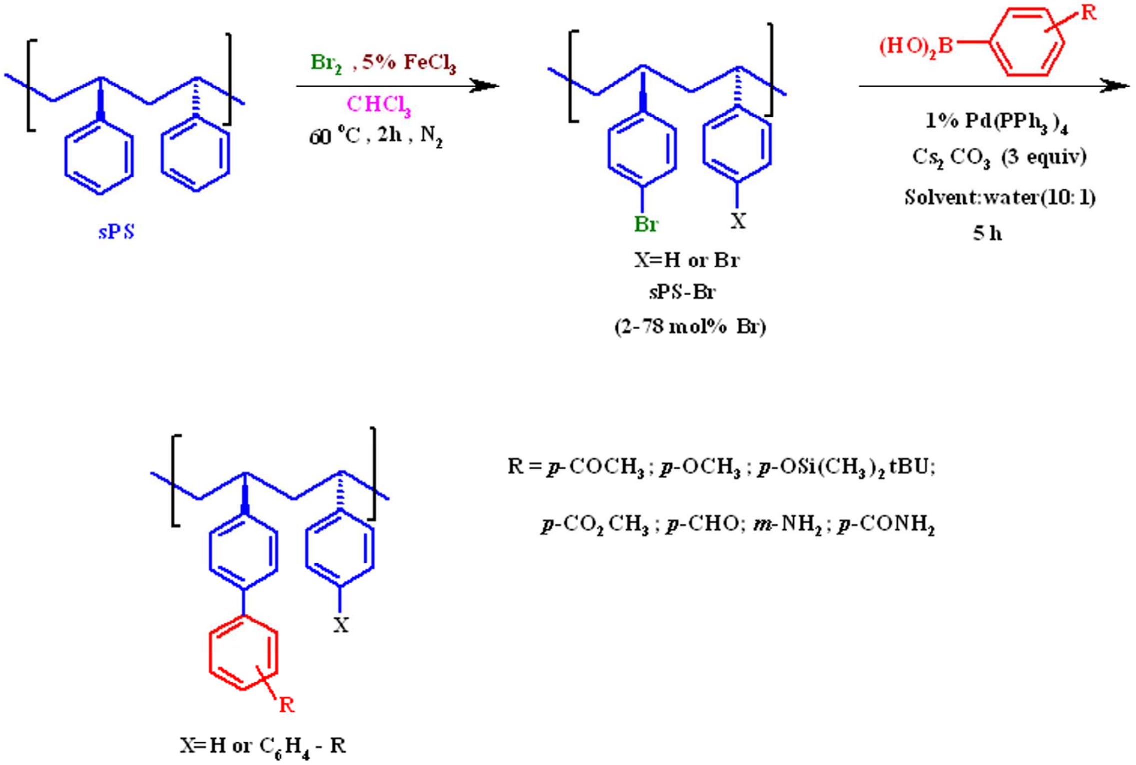
**Scheme 3.** Scandium-catalyzed syndiospecific copolymerization of styrene with ethylene [62].



**Scheme 4.** Synthetic route of the sPS-*g*-iPP copolymer [72].



**Scheme 5.** Functional group transformations in vinylsilane end-capped syndiotactic polystyrene [69].



**Scheme 6.** Electrophilic bromination and subsequent Suzuki-Miyaura cross coupling reactions of syndiotactic polystyrene [80].

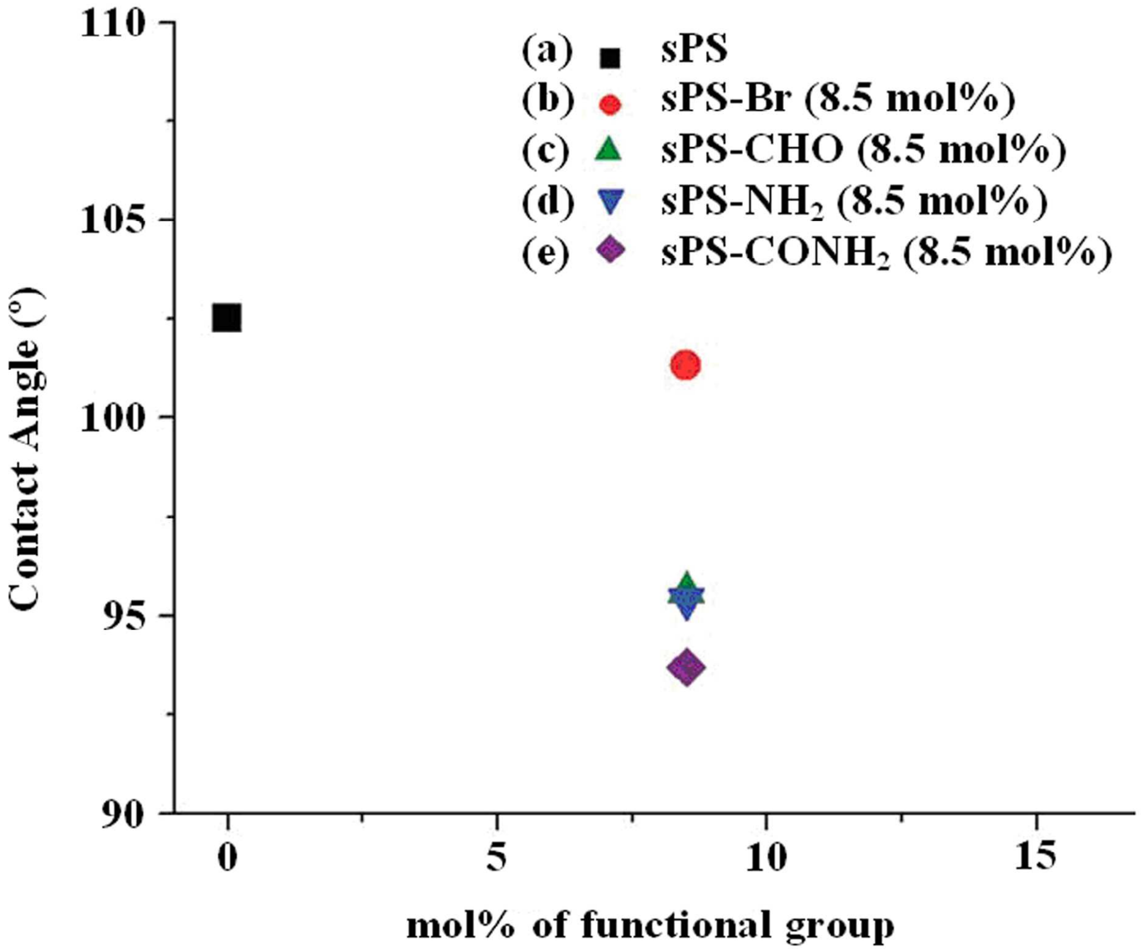
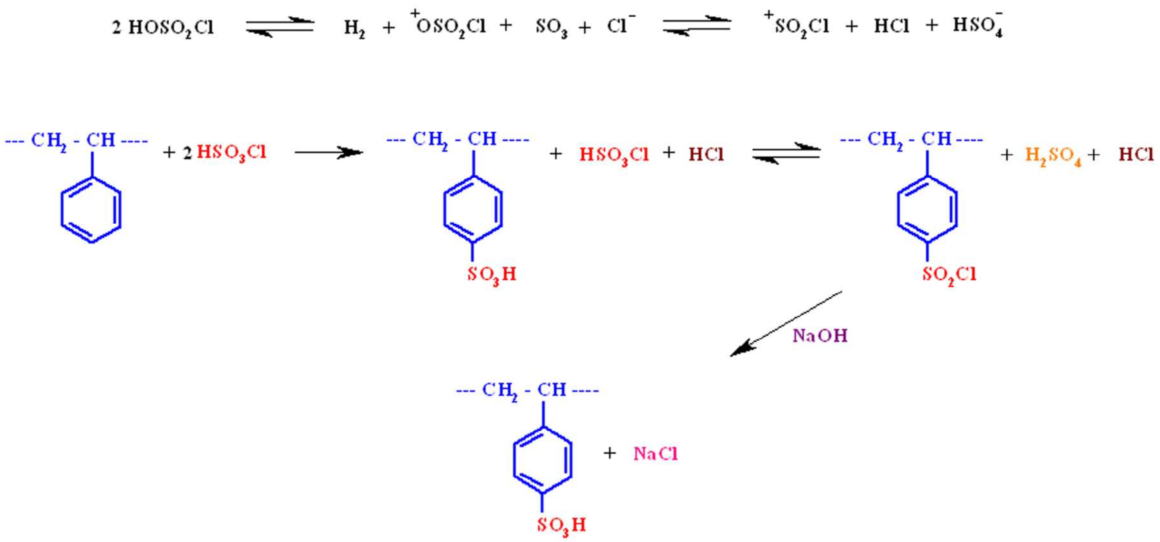
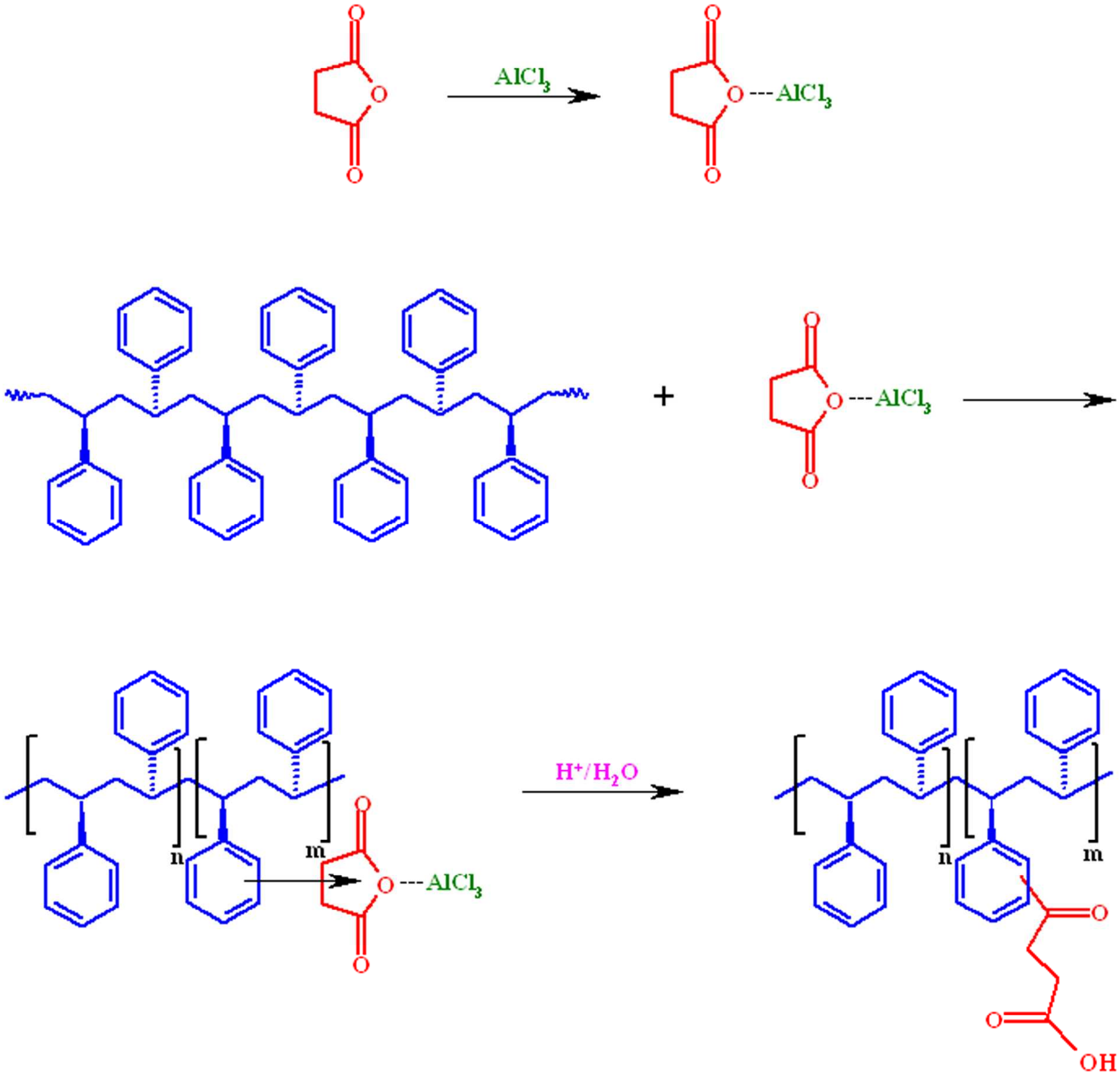


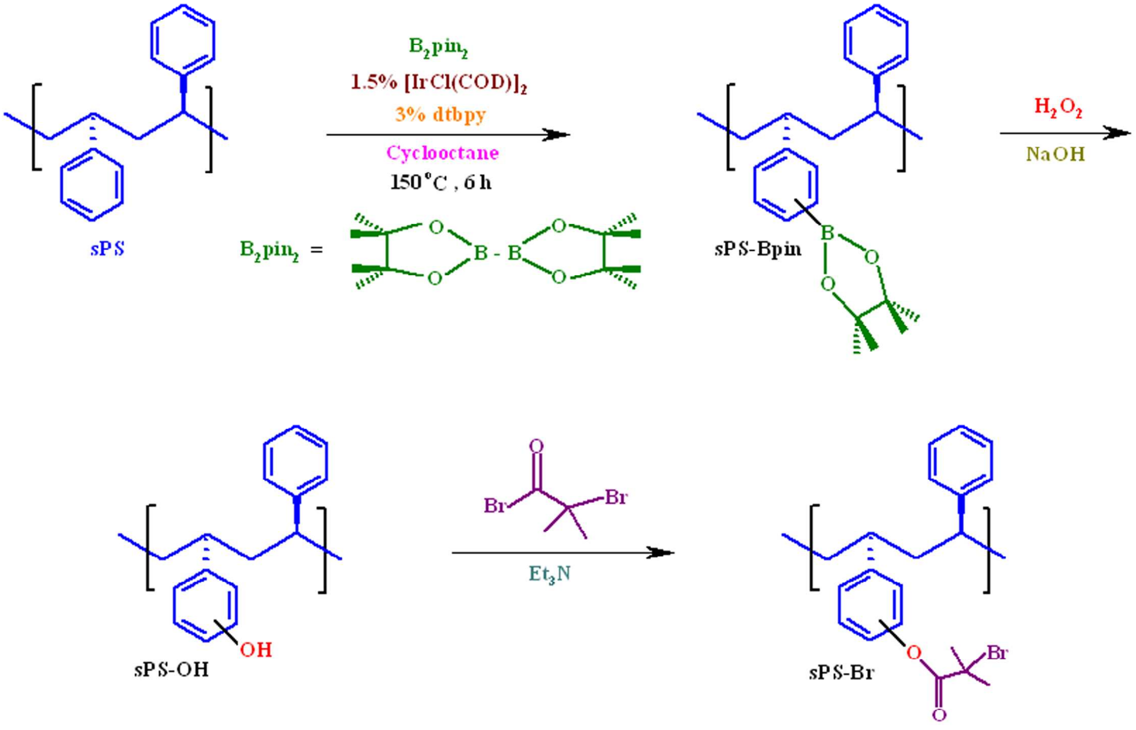
**Figure 1.** Water contact angles of (a) sPS (102.5º), (b) sPS-Br (101.4º), (c) sPS-CHO (95.6º), (d) sPS-NH$_2$ (95.4º), and (e) sPS-CONH$_2$ (93.7º) [80]. Copyright 2010 WILEY–VCH Verlag GmbH & Co. KGaA.



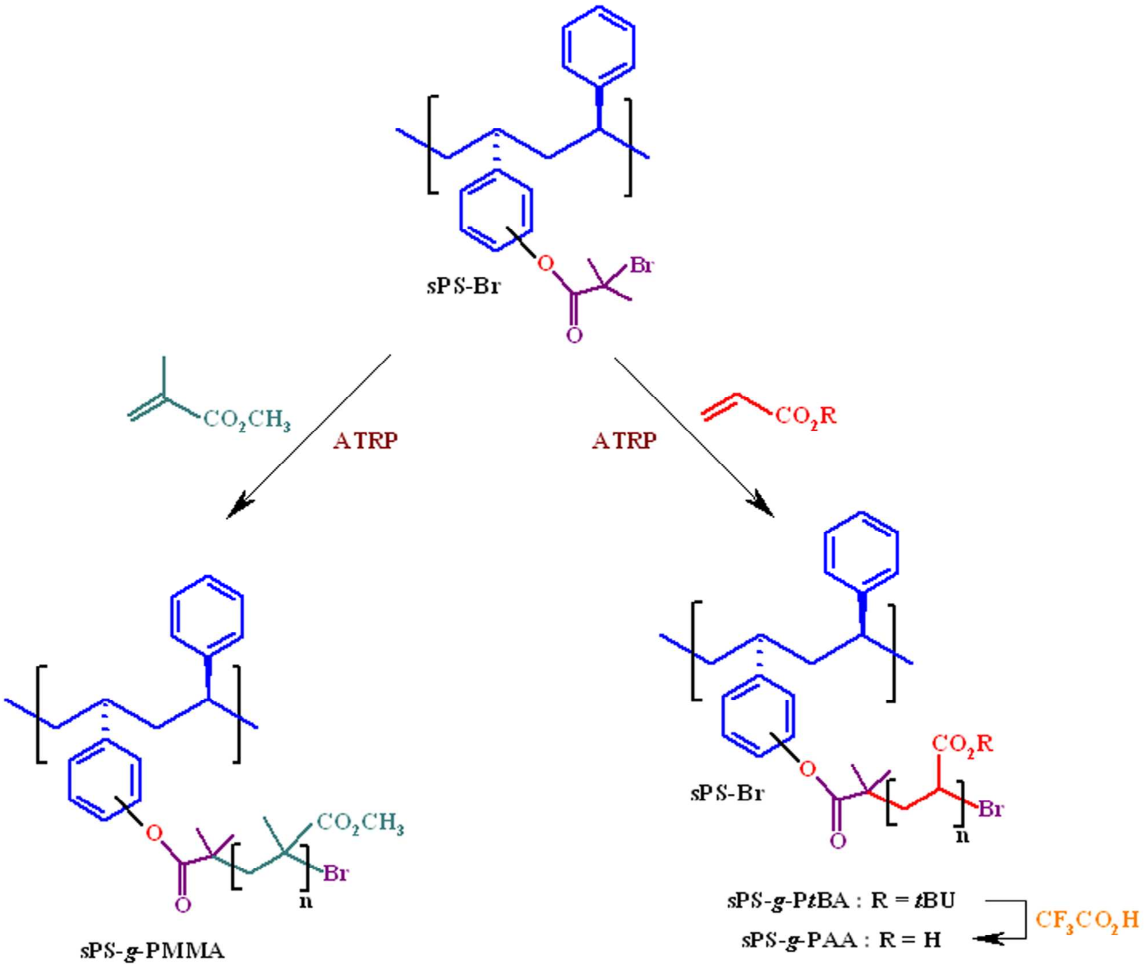
**Scheme 7.** Sulfonation of the sPS by chlorosulfonic acid [92].



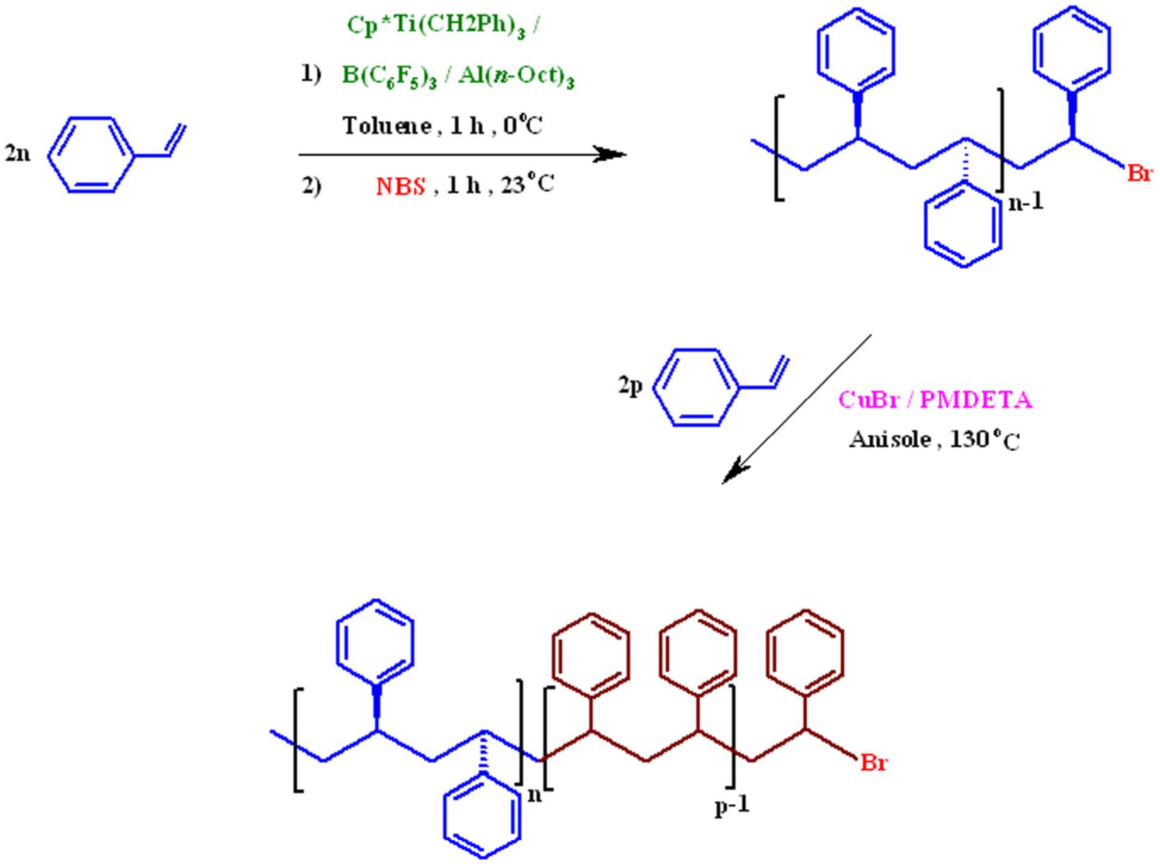
**Scheme 8.** Functionalization of syndiotactic polystyrene with succinic anhydride (SA) by using Friedel-Crafts acylation reaction in the presence of anhydrous aluminum chloride [97].



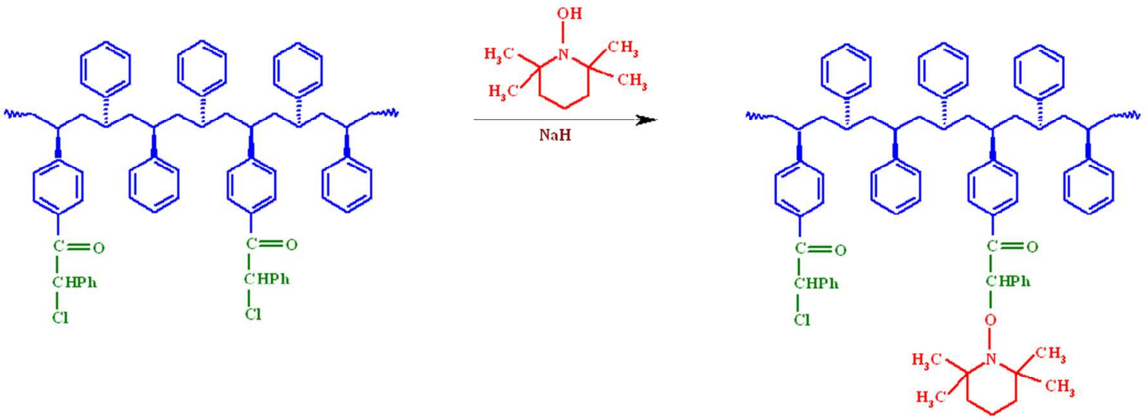
**Scheme 9.** Synthesis of syndiotactic polystyrene macroinitiator (sPS-Br) [25].



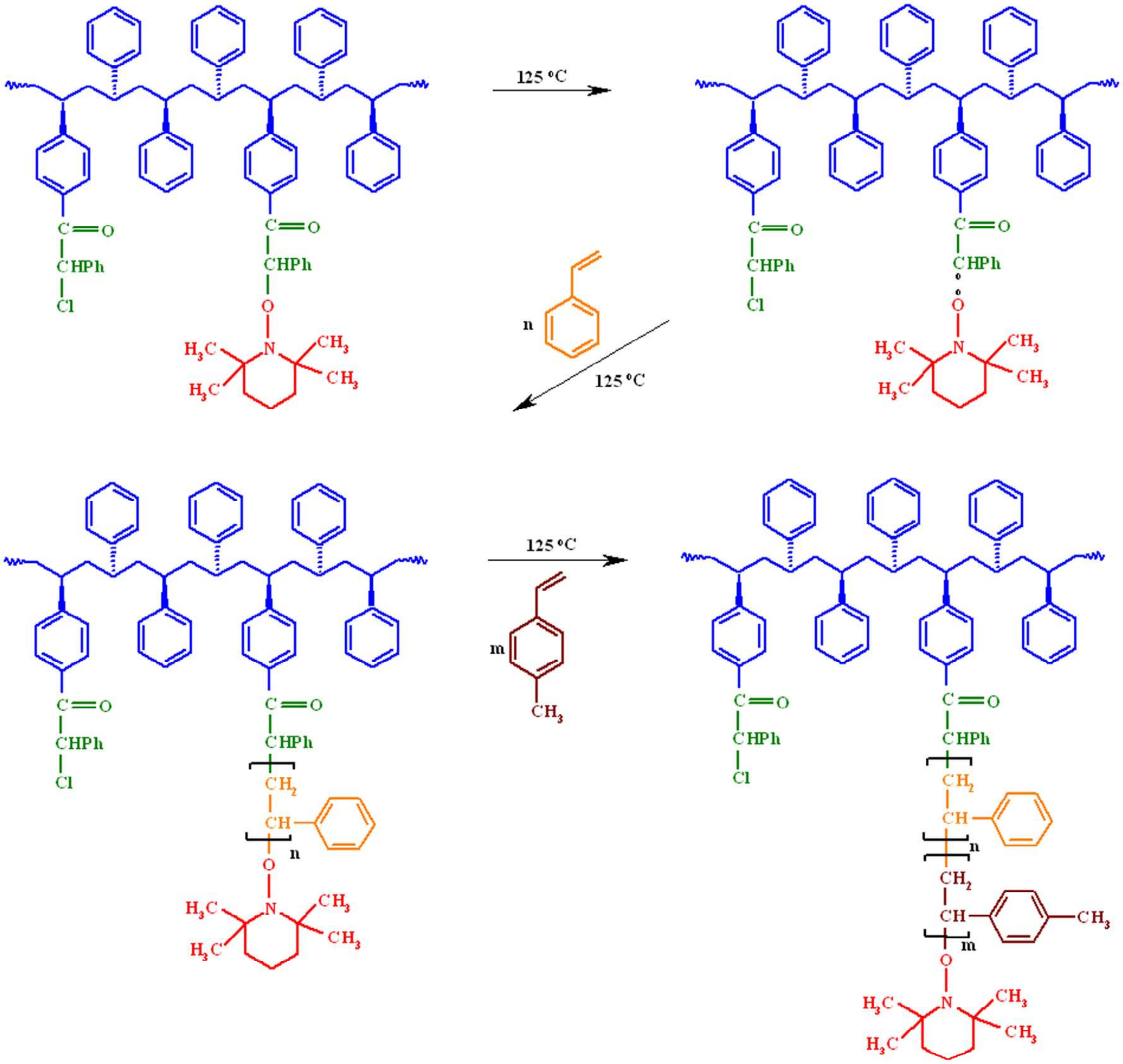
**Scheme 10.** Synthesis of polar graft copolymers of syndiotactic polystyrene [25].



**Scheme 11.** Sequential preparation of sPS-*b*-aPS stereoblock polymers [120].



**Scheme 12.** Synthesis of the sPS-TEMPO macroinitiator [76].



**Scheme 13.** Graft and block copolymerization of styrene and *p*-methylstyrene monomers onto the sPS backbone via nitroxide-mediated polymerization (NMP) [76].

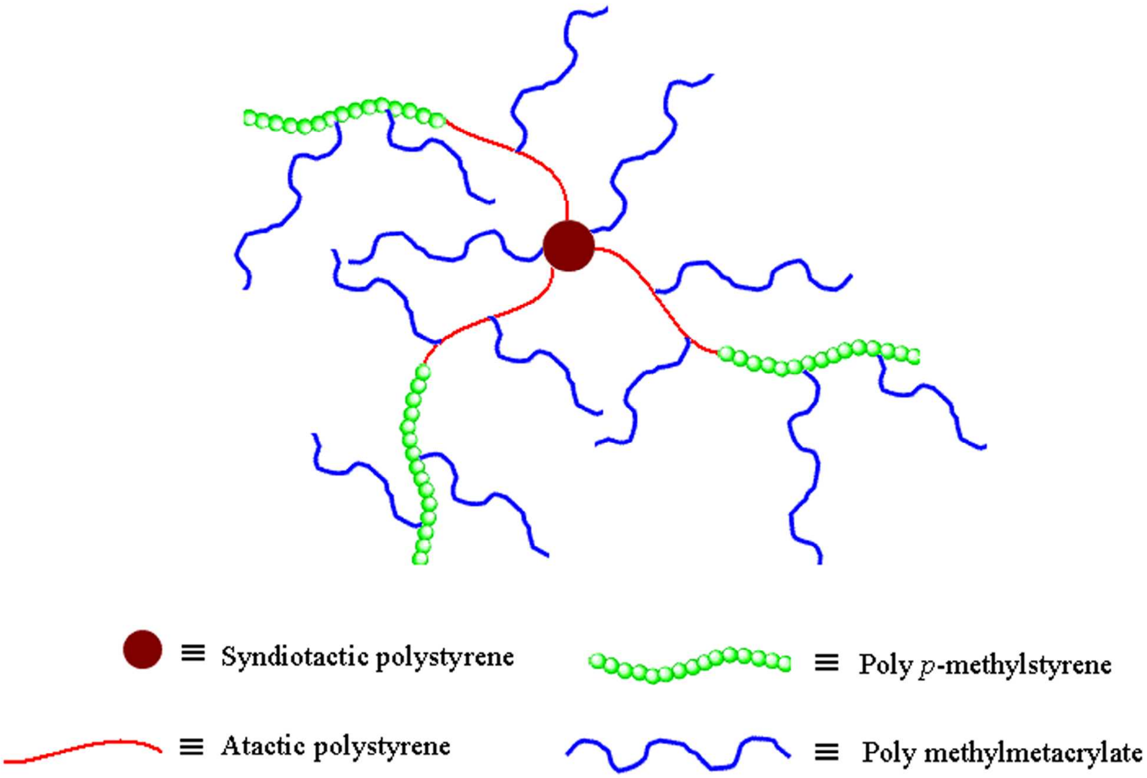
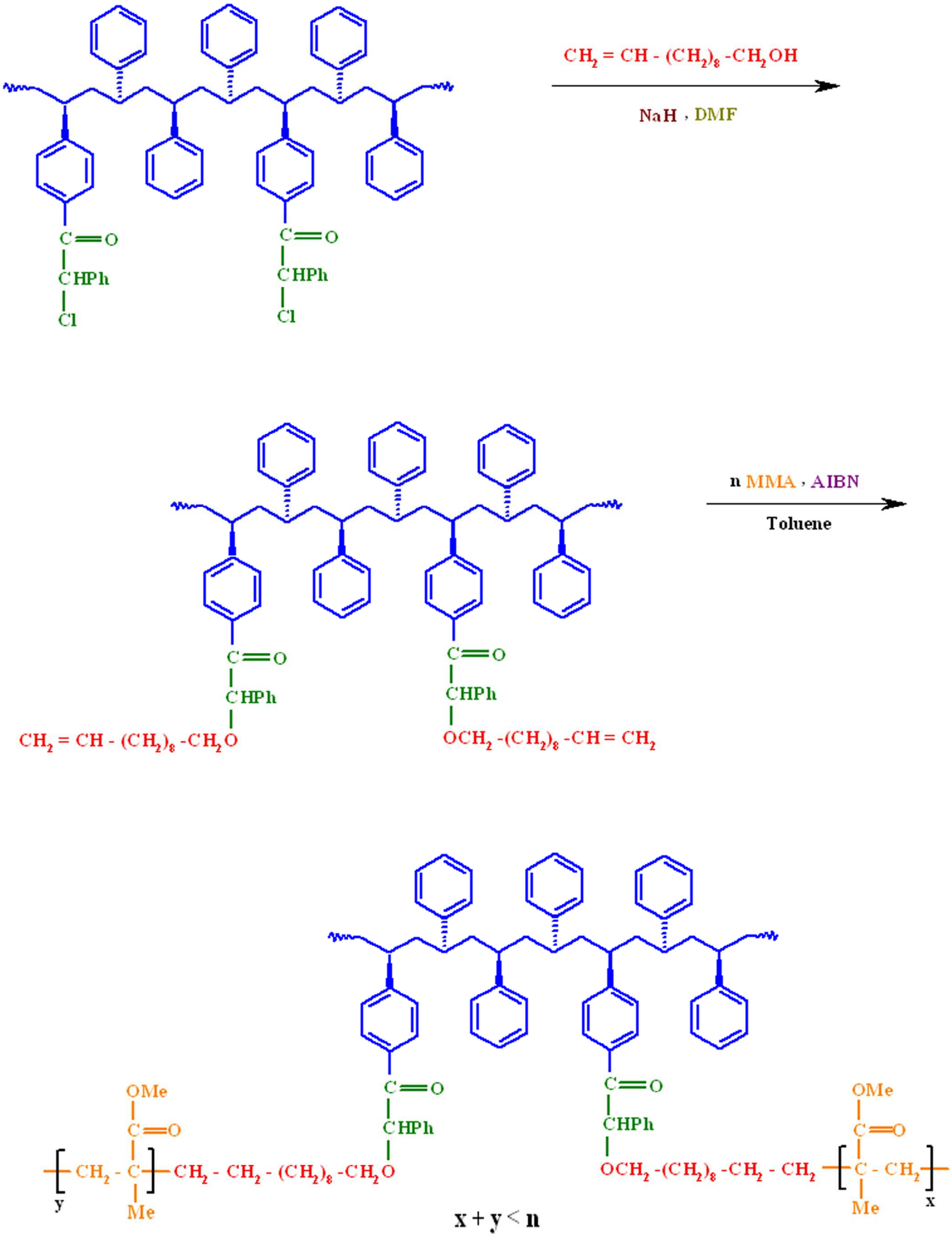
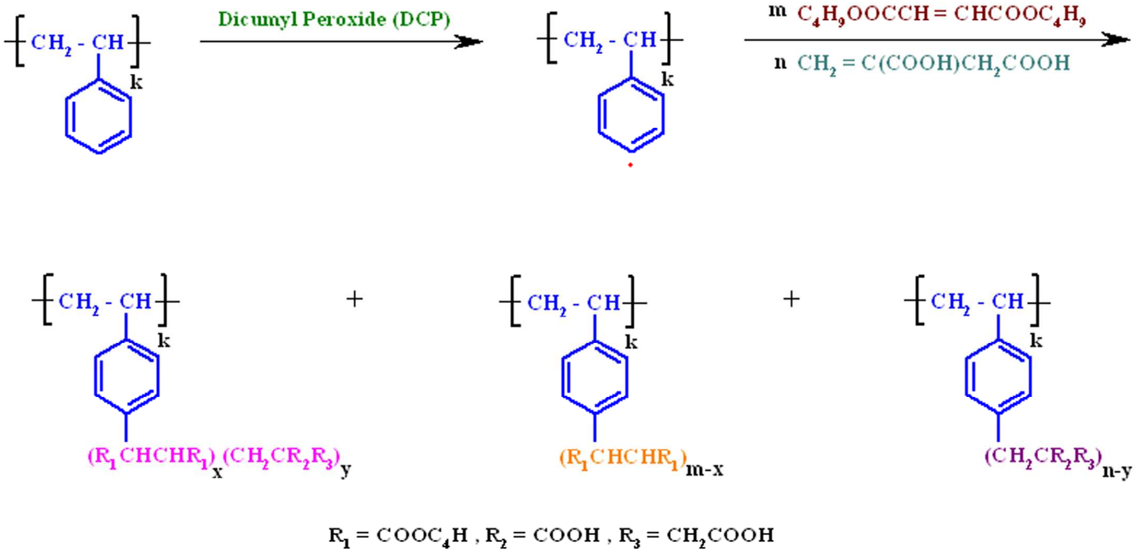


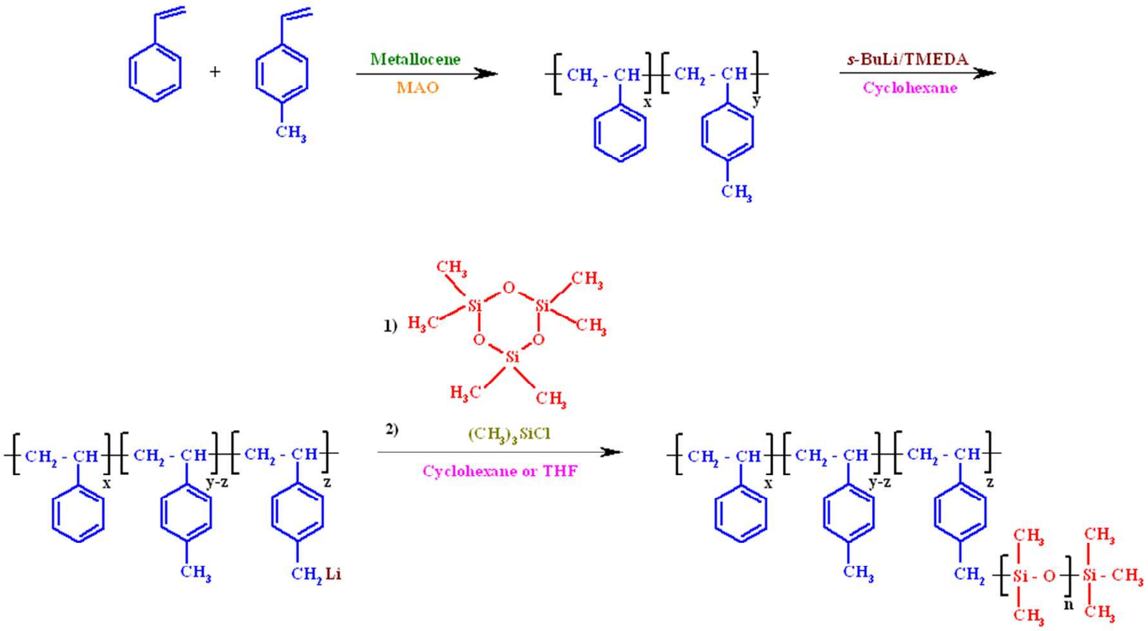
**Figure 2.** Graft and block copolymerization onto syndiotactic polystyrene via NMP and ATRP techniques [122].



**Scheme 14.** Synthetic route of the vinyl-terminated syndiotactic polystyrene multicentre macromonomer (VsPSM) and graft copolymerization of methyl methacrylate onto syndiotactic polystyrene [77].



**Scheme 15.** Graft copolymerization of itaconic acid and dibutyl maleate monomers onto sPS via melting graft copolymerization [137].



**Scheme 16.** Synthesis of syndiotactic poly(styrene-*co*-*p*-methylstyrene)-*graft*-polydimethylsiloxane [139].

# Recent progress in chemical modification of syndiotactic polystyrene

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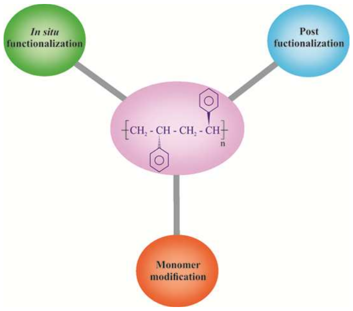
Tabriz, Iran



This review provides a snapshot of recent progress in chemical modification of syndiotactic polystyrene.

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## Tables Captions:

**Table 1.** Syndiospecific homopolymerization of styrene (St) and *cis*-1,4-selective homopolymerization of butadiene (Bd) catalyzed by [($C_5Me_4$-$C_5H_4N$)Lu($\eta^3$-$C_3H_5$)$_2$]/[$Ph_3C$][B($C_6F_5$)$_4$] [59].[a]

**Table 2.** Butadiene (Bd)-styrene (St) diblock copolymerization catalyzed by [($C_5Me_4$-$C_5H_4N$)Lu($\eta^3$-$C_3H_5$)$_2$]/[$Ph_3C$][B($C_6F_5$)$_4$] [59].[a]

**Table 3.** Ethylene-styrene copolymerization using the {[$C_5(CH_3)_5$]ClTi}$_2O_2C_2(CH_3)_4$($\mu$-O)/MMAO system. Polymerization conditions: Al/Ti=2000, Ti=4µmmol, $t_p$=20 min, solvent = toluene $V_{total}$ = 30 ml, ethylene pressure = 1 atm [60].

**Table 4.** Styrene-isoprene copolymerization in various reaction conditions catalyzed by complex [(CpCMe$_2$Flu)Nd($C_3H_5$)(THF) [61].[a]

**Table 5.** Styrene-ethylene-isoprene terpolymerization in various reaction conditions catalyzed by complex [(CpCMe$_2$Flu)Nd($C_3H_5$)(THF) [61].[a]

**Table 6.** Ethylene-styrene copolymerization catalyzed by complexes A-C at 70 °C [65].[a]

**Table 7.** Preparations of end-functionalized sPS by conducting syndiospecific styrene polymerization in the presence of dimethylphenylvinylsilane (DMPVS) [69].[a]

**Table 8.** Summary of DSC data for SsPS [18].

**Table 9.** Efficiency of the syndiotactic polystyrene sulfonation in different solvents and different amount of sulfonating agent [85].

**Table 10.** Summary of DSC results for neat sPS and SsPS ionomers with 1.7% sulfonation degree [85].

**Table 11.** Glass transition temperature ($T_g$) of sPS and SsPS-M-Y ionomers [85].[a]

**Table 12.** Mechanical properties for each of the prepared alloys by Wang and his coworkers [93].

**Table 13**. Summary of DSC results for sPS and AsPS [20].

**Table 14.** Summary of DSC results for sPS and partial benzoylated samples [95].

**Table 15.** The Degree of acetylation in the sPS-*g*-MA prepared at various conditions reactions [21].[a]

**Table 16.** Summary of DSC results for sPS and MA-modified sPS [21].

**Table 17.** The maleic anhydride content in the sPS-*g*-MA prepared at different conditions reactions [22].

**Table 18.** Synthesis of succinic anhydride fanctionalized syndiotactic polystyrene (SA-sPS) by Friedel-Crafts reaction [97].[a]

**Table 19.** Summary of DSC results for sPS and SA-sPS [97].

**Table 20.** DSC results of pure sPS, BMPsPS and sPS-*g*-PGMA with different degree of graft [119].

**Table 21.** Thermal properties of sPS and its graft copolymers synthesized by Brownell and his coworkers [25].

**Table 22.** Results of styrene polymerization and bromination end-capping [120].[a]

**Table 23.** Synthesis of sPS-*b*-aPS via ATRP [120].[a]

**Table 24.** DSC results for neat sPS and sPS-*g*-(aPS-*b*-aPMS) synthesized by Jaymand [76].

**Table 25.** Grafting parameters for sPS-*g*-aPS, sPS-*g*-(aPS-*b*-aPMS) and [sPS-*g*-(aPS-*b*-aPMS)]-*g*-PMMA [122].

**Table 26.** DSC results for neat sPS and sPS-*g*-PMMA synthesized by Jaymand [77].

**Table 27.** Copolymerization of SEOM and styrene with $CpTiCl_3$/MAO catalyst in toluene at 30 °C for 3 h [136].[a]

**Table 28.** Thermal properties of *grafted*-sPS with various monomer additions [137].

**Table 29.** Results of the anionic grafting reaction of sPSMS with PB [138].[a]

**Table 30.** Thermal properties of pure sPSMS and poly(styrene-*co*-*p*-methylstyrene)-*graft*-polydimethylsiloxane [139].

**Table 31.** Homopolymerization of styrene using binary initiator systems, metallocene MAO and ternary systems, diphenylzinc-metallocene-MAO, including various metallocenes, in toluene at 60 °C for 48 hours [147].[a]

**Table 32**. Styrene copolymerization using $Ph_2Zn$ -$CpTiCl_3$-MAO ternary initiator system in toluene at 60 °C for 6 hours. Styrene/Comonomer = 50/50 (mol/mol) [147].[a]

**Table 33.** Styrene copolymerization using $CpTiCl_3$-MAO binary initiator system, in toluene at 60 °C for 6 hours. Styrene/Comonomer=50/50 (mol/mol) [147].[a]

## Tables:

**Table 1.** Syndiospecific homopolymerization of styrene (St) and *cis*-1,4-selective homopolymerization of butadiene (Bd) catalyzed by $[(C_5Me_4\text{-}C_5H_4N)Lu(\eta^3\text{-}C_3H_5)_2]/[Ph_3C][B(C_6F_5)_4]$ [59].[a]

| Run | Monomer | [M]/[Ln] | Tim [min] | Conv. [%] | Activity[b] | *syn*-PS[c] [%] | *cis*-1,4[d] [%] | $\overline{Mn}$ [e] $\times 10^{-4}$ | $\overline{Mw}/\overline{Mn}$ [e] | $T_g$ [f] [°C] | $T_m$ [f] [°C] |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | St | 250 | 1 | >99 | 1560 | >99 | | 5.3 | 1.97 | | 270 |
| 2 | St | 500 | 1 | >99 | 3120 | >99 | | 9.7 | 1.94 | | 270 |
| 3 | St | 750 | 1 | >99 | 4680 | >99 | | 15.3 | 1.98 | | 271 |
| 4 | St | 1000 | 1 | >99 | 6240 | >99 | | 22.3 | 1.88 | | 270 |
| 5 | Bd | 500 | 1 | >99 | 1620 | | 97.1 | 3.1 | 1.24 | -107 | |
| 6 | Bd | 1000 | 1 | >99 | 3240 | | 97.0 | 6.4 | 1.26 | -106 | |
| 7 | Bd | 2000 | 1 | >99 | 6480 | | 97.0 | 13.2 | 1.25 | -105 | |
| 8[g] | Bd | 1000 | 2 | >99 | 1620 | | 97.1 | 6.3 | 1.28 | -106 | |
| 9[h] | Bd | 500 | 10 | 70 | 114 | | 99.0 | 3.6 | 2.13 | -109 | |

[a] Polymerization conditions: Lu (10 µmol), [Lu]/[Bd] = 1:1 (mol/mol), toluene/monomer = 5:1 (v/v), $T_p$ = 20 °C, unless otherwise noted; [b] Given in kg of polymer $(mol_{Lu}\ h)^{-1}$; [c] Measured by $^1H$ and $^{13}C$ NMR spectroscopy in $[D_4]$1,2-dichlorobenzene at 125°C; [d] Determined by $^1H$ and $^{13}C$ NMR spectroscopy in $CDCl_3$ at 25°C; [e] Determined by GPC in 1,2,4-trichlorobenzene at 150 °C against a polystyrene standard for *syn*-PS and in THF at 40°C against polystyrene standard for PB; [f] Determined by DSC; [g] After polymerization of 5 mmol of butadiene for 1 min, another 5 mmol of butadiene were added and the reaction mixture was stirred for another 1 min; [h] Chlorobenzene (5 ml).

**Table 2.** Butadiene (Bd)-styrene (St) diblock copolymerization catalyzed by [($C_5Me_4$-$C_5H_4N$)Lu($\eta^3$-$C_3H_5$)$_2$]/[$Ph_3C$][B($C_6F_5$)$_4$] [59].[a]

| Run | St fed | Time | Conv. | Activity[b] | St found[c] | Microstructures[c] | | | $\overline{Mn}$ [d] | $\overline{Mw}/\overline{Mn}$ [e] | $T_g$[e] | $T_m$[e] |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | [mol%] | [min] | [%] | | | *cis*-1,4[%] | *trans*-1,4 [%] | 1,2 [%] | ×$10^{-4}$ | | [°C] | [°C] |
| 1 | 10 | 10 | 86 | 306 | 4.7 | 95.5 | 2.8 | 1.7 | 8.8 | 1.43 | -104 | n.d. |
| 2 | 20 | 10 | 81 | 312 | 12.7 | 95.3 | 2.7 | 2.0 | 10.4 | 1.41 | -103 | n.d. |
| 3 | 40 | 10 | 77 | 342 | 29.1 | 95.2 | 3.0 | 1.8 | 11.5 | 1.29 | -104 | 263 |
| 4 | 50 | 10 | 73 | 348 | 39.0 | 95.2 | 2.6 | 2.2 | 11.7 | 1.36 | -105 | 264 |
| 5 | 60 | 10 | 67 | 336 | 46.4 | 95.3 | 3.1 | 1.8 | 12.1 | 1.34 | -105 | 264 |
| 6 | 80 | 10 | 63 | 354 | 69.9 | 95.2 | 2.4 | 2.4 | 10.3 | 1.55 | n.d. | 265 |
| 7 | 90 | 10 | 67 | 396 | 85.4 | 95.1 | 2.4 | 2.5 | 9.8 | 1.68 | n.d. | 266 |
| 8[f] | 50 | 5/5[g] | 100/75 | 396 | 42.8 | 95.8 | 2.5 | 1.7 | 13.5 | 1.31 | -105 | 268 |
| 9[h] | 50 | 10/10[g] | 100/46 | 306 | 31.5 | 95.7 | 2.4 | 1.9 | 22.5 | 1.39 | -106 | 266 |

[a] Polymerization conditions: Lu (10 μmol), [Lu]/[Bd] = 1:1 (mol/mol), toluene (5 ml), [Bd+St]/[Lu] = 1000:1 (mol/mol), $T_p$ = 20 °C, unless otherwise noted; [b] Given in kg of copolymer ($mol_{Lu}$ h)$^{-1}$; [c] Measured by $^1H$ and $^{13}C$ NMR spectra in $C_2D_2Cl_4$; [d] Determined by GPC in 1,2,4-trichlorobenzene at 150 °C against a polystyrene standard; [e] Determined by DSC; [f] Sequential copolymerization. Butadiene (5 mmol) was added first followed by styrene (5 mmol); [g] Sequential polymerization time; [h] Sequential copolymerization. Butadiene (10 mmol) was added first followed by styrene (10 mmol).

**Table 3.** Ethylene-styrene copolymerization using the $\{[C_5(CH_3)_5]ClTi\}_2O_2C_2(CH_3)_4(\mu\text{-}O)$/MMAO system. Polymerization conditions: Al/Ti=2000, Ti=4μmmol, $t_p$=20 min, solvent = toluene $V_{total}$ = 30 ml, ethylene pressure = 1 atm [60].

| Run | $T_p$ (°C) | Ethylene Pressure (atm) | Styrene (ml) | Yield[a] (mg) | Activity: $10^{-2}$ kg ESI. (mol Ti)$^{-1}$. h$^{-1}$ | $\overline{Mw}$ $\times10^{-4}$[b] | PDI[b] | PS cont.[c] (mol%) | $T_m$[c] (°C) |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 50 | 1 | 5 | 216 | 1.6 | 5.82 | 1.60 | 64 | 260 |
| 2 | 70 | 1 | 5 | 586 | 4.4 | 1.36 | 1.61 | 70 | 265 |
| 3 | 90 | 1 | 5 | 1 203 | 9.0 | 1.20 | 1.66 | 80 | 265 |
| 4 | 90 | 1 | 3 | 727 | 5.5 | 0.66 | 1.93 | 69 | 254 |
| 5 | 90 | 1 | 0 | trace | n.d.[e] | n.d.[e] | n.d.[e] | n.d.[e] | n.d.[e] |
| 6[f] | 90 | 0 | 5 | 2 506[g] | 15.0[h] | 2.9 | 2.03 | 100 | 270 |

[a] Extracted copolymer yield; [b] Determined by means of GPC; [c] Styrene content in copolymers according to $^1$H NMR ($CDCl_3$); [d] Determined by means of DSC; [e] Not determined; [f] Polymerization conditions: Al/Ti = 2000, Ti = 5μmmol, $t_p$ = 20 min, toluene = 45 ml, styrene = 5 ml, ethylene pressure = 0 atm; [g] Yield of 2-butanone insoluble portion having a syndiotacticity index of 98%; [h] Activity $10^{-2}$ kg sPS.(mol Ti)$^{-1}$. h$^{-1}$.

**Table 4.** Styrene-isoprene copolymerization in various reaction conditions catalyzed by complex [(CpCMe$_2$Flu)Nd(C$_3$H$_5$)(THF) [61].[a]

| Run | [St]/[Nd] | [St][b] | [Ip][b] | T (°C) | Time (min) | Yield[c] (g) | Activity[d] kg/(mol h) | St[e] (mol%) | [f] $\overline{Mn}$ ×10$^3$ (g/mol) | [f] $\overline{Mw}/\overline{Mn}$ | T$_m$[g] (°C) | T$_g$[g] (°C) | T$_g$[h] (°C) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 600 | 8.7 | - | 60 | 5 | 2.3 | 1710 | 100 | 54 | 1.73 | 264 | - | nd |
| 2 | -[i] | 0 | 10 | 60 | 35 | 2.0 | 122 | 0 | 27 | 1.09 | 49 | - | nd |
| 3 | 600 | 4.7 | 4.0 | 60 | 6 | 2.4 | 550 | 70 | 55 | 1.54 | - | - | 63 |
| 4 | 600 | 6.0 | 3.0 | 60 | 15 | 3.8 | 165 | 85 | 91 | 1.25 | - | 62 | 67 |
| 5 | 600 | 7.9 | 0.9 | 60 | 10 | 9.6 | 380 | 94 | 63 | 1.62 | 218 | 77 | nd |
| 6 | 600 | 8.3 | 0.5 | 60 | 4 | 9.2 | 957 | 97±2 | 12 | 3.25 | 228 | 77 | 84 |
| 7 | 600 | 8.3 | 0.5 | 80 | 3.5 | 8.8 | 1025 | 97±2 | 20 | 2.95 | 227 | 83 | 91 |
| 8 | 1700 | 8.3 | 0.5 | 80 | 7 | 1.8 | 309 | 97±2 | 73 | 1.33 | 245 | - | 112 |

[a] General conditions: 0.05–0.15 mmol Ln; total volume 10 ml; reactions were conducted in neat monomers; [b] Styrene and isoprene concentration in mol/l; [c] Mass of copolymer recovered; [d] Catalytic activity in kg/(mol(Ln) h); [e] Amount of styrene incorporated in the copolymer, as determined by $^1$H NMR; ''±2'' refers to the experimental uncertainty in determining the isoprene content in styrene-rich copolymers; [f] Number average molecular weight and polydispersity determined by GPC in 1,3,6-trichlorobenzene at 135 °C *vs*. PS standards; [g] Melting and glass transition temperatures determined by DSC; [h] Glass transition determined by DMA; [i] [Ip]/[Nd]=1800.

**Table 5.** Styrene-ethylene-isoprene terpolymerization in various reaction conditions catalyzed by complex [(CpCMe$_2$Flu)Nd(C$_3$H$_5$)(THF) [61].[a]

| Run | [St]/[Nd] | [St][b] | [Ip][b] | P (bar) | T (°C) | Time (min) | Yield[c] (g) | Activity[d] | St[e] (mol%) | Ip (mol%) | Et (mol%) | $\overline{Mn}$ [f] ×10$^3$ (g/mol) | $\overline{Mw}/\overline{Mn}$ [f] | T$_m$[g] | T$_g$[g] | T$_g$[h] |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 1800 | - | 10 | 4 | 60 | 15 | 11.4 | 138 | - | 76 | 24 | 112 | 1.61 | - | - | nd |
| 2 | 600 | 2.2 | 2.2 | 5 | 60 | 60 | 7.2 | 33 | 41 | 34 | 25 | 73 | 2.41 | - | - | 35 |
| 3 | 600 | 7.9 | 0.9 | 1 | 60 | 15 | 8.9 | 244 | 96±2 | 3 | <1 | 41 | 2.84 | 204 | 76 | nd |
| 4 | 600 | 4.1 | 0.5 | 4 | 60 | 15 | 25.6 | 235 | 71 | 6 | 23 | 83 | 1.18 | 219 | 56 | 55 |
| 5 | 600 | 4.1 | 0.5 | 4 | 80 | 15 | 40.5 | 375 | 71 | 6 | 23 | nd | nd | nd | nd | nd |
| 6 | 600 | 4.1 | 0.5 | 1 | 60 | 30 | 18.7 | 86 | 81 | 3 | 16 | nd | nd | - | 60 | 84 |

[a] General conditions: 0.02–0.35 mmol Ln; total volume 1-60 ml; [b] Styrene and isoprene concentration in mol/l; [c] Mass of copolymer recovered; [d] Catalytic activity in kg/(mol(Nd) h); [e] Amount of styrene incorporated in the copolymer, as determined by $^1$H NMR; ‘‘±2’’ refers to the experimental uncertainty in determining the isoprene and ethylene contents in styrene-rich terpolymers; [f] Number average molecular weight and polydispersity determined by GPC in 1,3,6-trichlorobenzene at 135 °C vs. PS standards; [g] Melting and glass transition temperature determined by DSC; [h] Glass transition determined by DMA.

**Table 6.** Ethylene-styrene copolymerization catalyzed by complexes A-C at 70 °C [65].[a]

| Run | Cat | St (g) | $P_E$ (psig) | MAO (mg) | Tim (h) | Yield (g)[b] | Acetone-sol (wt %) | THF-sol (wt %) | St mol %[c] | $T_g$ (°C)[d] | $T_m$ (°C)[d] | $\Delta H_m$ (J/g)[d] | $\overline{Mn}$[f] | $\overline{Mw}$[f] | PDI[f] |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | A | 5 | 20 | 116 | 1.5 | 2.15 | 17 | | 17 | | 124, 251 | 2.82, 2.34 | | | |
| 2 | A | 10 | 5 | 116 | 4 | 4.78 | 15 | | 100 | 99 | 247 | 20.3 | 10K | 19K | 2.0 |
| 3 | B | 5 | 20 | 116 | 1.5 | 0.23 | 10 | 80 | 39 | 17 | 120 | 0.42 | | | |
| 4 | B | 10 | 20 | 116 | 2 | 2.43 | 12 | 76 | 46 | 28 | 129 | 2.19 | | | |
| 5 | B | 10 | 5 | 116 | 2 | 0.70 | 21 | 72 | 52 | 41 | 260 | 2.66 | 46K | 112K | 2.4 |
| 6 | B | 10 | 5 | 116 | 4 | 0.62 | 32 | 64 | 62 | 40 | 261 | 4.06 | 38K | 118K | 3.1 |
| 7 | B | 10 | 5 | 232 | 4 | 1.44 | 33 | 52 | 66 | 40, 99 | 260 | 8.28 | 28K | 94K | 3.4 |
| 8 | B | 20 | 5 | 116 | 2 | 1.19 | 26 | 40 | 63 | 43 | 262 | 2.79 | 47K | 96K | 2.0 |
| 9 | C | 5 | 15 | 116 | 1.5 | 0.22 | 10 | 81 | | 19 | n.o.[g] | n.o.[g] | | | |
| 10 | C | 5 | 10 | 116 | 2 | 0.28 | 18 | 76 | 48 | 31 | n.o.[g] | n.o.[g] | | | |
| 11 | C | 10 | 10 | 116 | 4 | 0.40 | 16 | 75 | 51 | 31, 95 | 260 | 2.88 | 28K | 71K | 2.6 |
| 12 | C | 10 | 5 | 116 | 4 | 0.58 | 47 | 35 | 71 | 33, 99 | 253 | 4.66 | 136K | 189K | 1.4 |

[a] All polymerizations were performed with 8 µmol catalyst in a toluene solution (total volume of 30 ml); [b] Yield before solvent fractionation; [c] Styrene content (mol%) in polymer after acetone (and THF) fractionation, estimated by $^{13}C$ NMR; [d] Determined by DSC after solvent fractionation. $T_g$, glass transition temperature; $T_m$, melting temperature; $\Delta H_m$, heat of melting; [e] 4 µmol catalyst was applied; [f] Determined by GPC after solvent fractionation; [g] Not observed.

**Table 7.** Preparations of end-functionalized sPS by conducting syndiospecific styrene polymerization in the presence of dimethylphenylvinylsilane (DMPVS) [69].[a]

| Run | Styrene (mmol) | DMPVS (mmol) | $H_2$ (atm) | Activity[b] ($10^4$) | Conv. (%) | $\overline{Mn}$ [c] ($10^3$) | PDI[c] | $T_m$[d] (°C) | Tacticity[e] |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 27.0 | - | 2.0 | 52.9 | 97.8 | 323.6 | 2.6 | 265 | |
| 2 | 27.0 | 6.8 | 2.0 | 28.9 | 53.5 | 20.5 | 2.1 | 261 | |
| 3 | 27.0 | 6.8 | 1.0 | 28.4 | 52.6 | 20.8 | 2.2 | 262 | |
| 4 | 27.0 | 12.8 | 1.0 | 11.3 | 20.9 | 11.2 | 2.1 | 261.2 | - |
| 5 | 27.0 | 20.4 | 1.0 | 9.7 | 18 | 5.8 | 1.8 | 257.1 | |
| 6 | 27.0 | 28.0 | 1.0 | 8.0 | 14.8 | 4.9 | 1.8 | 253.2 | 92 |
| 7 | 27.0 | 35.6 | 1.0 | 7.3 | 13.5 | 3.1 | 1.6 | 239.8 | 90 |
| 8 | 27.0 | 6.8 | - | 18.1 | 33.5 | 21.7 | 2.21 | 262.7 | |
| 9 | 27.0 | 12.8 | - | 9.2 | 17 | 11.5 | 2.15 | 262.5 | |
| 10 | 27.0 | 20.4 | - | 7.9 | 14.6 | 6.3 | 1.8 | 257.3 | 91 |
| 11 | 27.0 | 28.0 | - | 6.7 | 12.4 | 5.2 | 1.8 | 256.1 | 90 |
| 12 | 27.0 | 35.6 | - | 5.8 | 10.7 | 3.3 | 1.7 | 237.5 | |

[a] Polymerization conditions: 50 ml of toluene; 5.0 µmol of Cp*Ti(OMe)$_3$; 1.5 mmol of MAO; reaction temperature 20°C; reaction time = 2 h; [b] Catalytic activity = g of polymer/(mol of catalyst); [c] $\overline{Mn}$ (number average molecular weight) = g/mol and PDI (polydispersity, $\overline{Mw}/\overline{Mn}$) were determined by high-temperature GPC (solvent 1,2,4-trichlorobenzene; temperature 135°C); [d] $T_m$ (melting temperature) was determined by DSC; [e] Tacticity (syndiotacticity in rrrrr) was determined via $^{13}C$ NMR analyses.

**Table 8.** Summary of DSC data for SsPS [18].

| Sulfonation level (mol %) | $T_g$ (°C) | $T_m$ (°C) | $\Delta H_m$[a] (J/g) | $T_c$ (°C) | $\Delta H_c$[b] (J/g) |
|---|---|---|---|---|---|
| 0 | 99 | 270 | 35.7 | 240 | 27.2 |
| 0.5 | 100 | 269 | 34.8 | 234 | 23.6 |
| 2.0 | 102 | 263 | 33.9 | 224 | 24.3 |
| 4.2 | 104 | 259 | 27.2 | 213 | 21.6 |
| 5.0 | 104 | 249 | 19.4 | 188 | 10.1 |
| 10.5 | 110 | - | - | - | - |

[a] heat of fusion melting; [b] heat of fusion of crystallization.

**Table 9.** Efficiency of the syndiotactic polystyrene sulfonation in different solvents and different amount of sulfonating agent [85].

| | Reaction condition[a] | | | Degree of sulfonation (mol%) | | |
|---|---|---|---|---|---|---|
| Run | Solvent[b] | sPS (g) | Acetyl sulfate (mmol) | Theorical | Practical | Sulfonation efficiency (%) |
| 1 | CF | 3.0 | 2.16 | 8.0 | 1.7 | 21 |
| 2 | TCE | 3.0 | 2.16 | 8.0 | 2.2 | 26 |
| 3 | TCE/CF | 3.0 | 2.16 | 8.0 | 4.1 | 51 |
| 4 | TCE/CF | 3.0 | 4.55 | 18.0 | 9.3 | 52 |
| 5 | TCE/CF | 3.0 | 5.83 | 24.0 | 11.9 | 50 |

[a] All sulfonation rections were conducted at 60°C for 3 hours with acetyl sulfat as sulfonating reagent. The total volum of the reaction mixture was calibrated at 280 ml; [b] The solvents used are 1,1,2-trichloroethane (TCE), chloroform (CF) and the mixed solvent TCE/CF (60/40 v/v).

**Table 10.** Summary of DSC results for neat sPS and SsPS ionomers with 1.7% sulfonation degree [85].

| Samples | $T_m$ (°C) | $\Delta H_m$ (J/g) | $X_c$ (%) | $T_c$ (°C) | $\Delta H_c$ (J/g) |
|---|---|---|---|---|---|
| SsPS | 273.6 | 24.7 | 47 | 234.0 | 23.3 |
| SsPS-h-1.7 | 270.4 | 21.3 | 40 | 227.2 | 19.2 |
| SsPS-Na-1.7 | 265.0 | 19.2 | 36 | 226.4 | 18.4 |
| SsPS-Zn-1.7 | 273.0 | 14.4 | 27 | 232.1 | 6.83 |

**Table 11.** Glass transition temperature ($T_g$) of sPS and SsPS-M-Y ionomers [85].[a]

| | $T_g$ (°C) for various M | | | | | |
|---|---|---|---|---|---|---|
| Y | H | Na | Zn | Mn | Co | sPS |
| 1.7 | 101.4 | 1.3.7 | - | - | - | 98.6 |
| 11.9 | 119.8 | 123.6 | 125.1 | 111.4 | 109.3 | - |

[a] M and Y denoted the counterion and sulfonation degree, respectively.

**Table 12.** Mechanical properties for each of the prepared alloys by Wang and his coworkers [93].

| sPS/PET/SsPS-K (wt %) | Unnotched Izod impact strength ($kJ/m^2$) | Tensile strength (MPa) | Flexural strength (MPa) | Storage modulus ($10^4$ MPa) |
|---|---|---|---|---|
| 100/0/0 | 4.1 | 33.6 | 42.8 | 1.89 |
| 90/10/0 | 4.4 | 30.8 | 39.3 | 1.10 |
| 85/15/0 | 5.1 | 29.2 | 37.8 | 1.06 |
| 80/20/0 | 5.4 | 21.4 | 29.4 | - |
| 75/25/0 | 5.5 | 19.6 | 25.3 | - |
| 70/30/0 | 6.3 | 17.6 | 19.4 | 1.03 |
| 60/40/0 | 3.2 | 15.4 | 16.5 | 0.91 |
| 0/100/0 | 13.9 | 50.3 | 68.7 | 1.91 |
| 85/15/2 | 8.2 | 41.5 | 55.4 | 1.53 |
| 85/15/4 | 11.5 | 38.8 | 54.2 | 1.55 |
| 85/15/6 | 6.6 | 36.5 | 45.5 | 2.33 |
| 85/15/8 | 4.9 | 31.2 | 41.3 | 1.52 |

**Table 13**. Summary of DSC results for sPS and AsPS [20].

| Run | Degree of acetylation (mol%) | $T_g$ (°C) | $T_m$ (°C) | $X_c$ (%) | $\Delta H_m$ (J/g) | $T_c$ (°C) |
|---|---|---|---|---|---|---|
| 1 | 17.8 | 103.7 | 266.8/253.6 | 19.8 | 10.5 | 222.1 |
| 2 | 25.3 | 104.7 | 266.9/256.2 | 22.4 | 11.9 | 218.9 |
| 3 | 33.2 | 106.6 | 267.4/256.2 | 17.7 | 9.4 | 216.9 |
| 4 | 38.4 | 108.2 | 267.2/260.1 | 10.8 | 5.7 | 213.9 |
| 5 | 42.6 | 110.9 | 265.9/256.8 | 10.4 | 5.5 | 198.5 |
| sPS | - | 100.9 | 269.7/260.8 | 52.0 | 27.6 | 235.5 |

**Table 14.** Summary of DSC results for sPS and partial benzoylated samples [95].

| Run | Degree of benzoylation (mol%) | $T_g$ (°C) | $T_m$ (°C) | $X_c$ (%) | $\Delta H_m$ (J/g) | $T_c$ (°C) |
|---|---|---|---|---|---|---|
| 1 | 7 | 101 | 250/261 | 43 | 23 | 216 |
| 2 | 16.8 | 101 | 248/259 | 36 | 19 | 208 |
| 3 | 24.5 | 104 | 246/256 | 27 | 14 | 201 |
| 4 | 33.4 | 106 | 237 | 4.5 | 2 | 199 |
| sPS | - | 101 | 251/271 | 52 | 28 | 239 |

**Table 15.** The Degree of acetylation in the sPS-*g*-MA prepared at various conditions reactions [21].[a]

| Run | $AlCl_3$ (mmol) | Tim (h)[b] | Temprature (°C) | Degree of acetylation (mol%) |
|---|---|---|---|---|
| 1 | 10 | 2 | 15 | 1.0 |
| 2 | 10 | 2 | 25 | 2.2 |
| 3 | 10 | 2 | 30 | 5.2 |
| 4 | 10 | 2 | 35 | 7.6 |
| 5 | 15 | 2 | 25 | 4.0 |
| 6 | 20 | 2 | 25 | 6.2 |
| 7 | 15 | 4 | 25 | 4.5 |

[a] Conditions: sPS, 0.52 g (5.0 mmol); MA, 0.49 g (5.0 mmol); $CS_2$, 50 ml; [b] The reaction time is referred to duration of reaction between the $AlCl_3$-MA charge-transfer complex and sPS polymer.

**Table 16.** Summary of DSC results for sPS and MA-modified sPS [21].

| Run | DA[a] | $T_g$ (°C) | $T_m$ (°C)[b] | $\Delta H_m$ ($J.g^{-1}$) | $X_c$[c] (%) | $T_c$[b] (°C) | $\Delta H_c$ ($J.g^{-1}$) |
|---|---|---|---|---|---|---|---|
| 1 | 0.0 | 92.7 | 270.7 | 29.5 | 55.7 | 239.5 | 30.4 |
| 2 | 0.7 | 96.9 | 268.3 | 32.8 | 61.9 | 234.7 | 29.4 |
| 3 | 1.3 | 101. 4 | 265.4 | 23.7 | 44.7 | 232.5 | 23.6 |
| 4 | 4.0 | 101.4 | 261.5 | 13.9 | 26.2 | 219.0 | 11.3 |
| 5 | 7.6 | 103.2 | 260.3 | 3.9 | 7.4 | 212.7 | 1.2 |

[a] DA is referred to the content of carboxyl groups (mol%); [b] The glass transition temperatures, $T_g$s, were determined as the mid-point of the step change in the heat flow. The melting, $T_m$, and crystallization, $T_c$, temperatures were selected as the peak maximum or minimum in endothermic or exothermic transition, respectively; [c] The degree of crystallinity, $X_c$, is determined by the equation: $X_c = (\Delta H_m / \Delta H_m^0) \times 100\%$, where $\Delta H_m$ is the melting enthalpy of the sample and $\Delta H_m^0$ is the melting enthalpy of 100% crystalline sPS (53 $J.g^{-1}$).

**Table 17.** The maleic anhydride content in the sPS-*g*-MA prepared at different conditions reactions [22].

| sPS (g) | MA (g) | DCP (g) | AIBN (g) | Temprature (°C) | Grafted MA content (wt.%) |
|---|---|---|---|---|---|
| 1000 | 500 | 30 | 0 | 70 | 1.09 |
| 1000 | 500 | 30 | 0 | 100 | 1.47 |
| 1000 | 500 | 0 | 30 | 70 | 0.13 |
| 1000 | 500 | 0 | 30 | 100 | 0.20 |

**Table 18.** Synthesis of succinic anhydride fanctionalized syndiotactic polystyrene (SA-sPS) by Friedel-Crafts reaction [97].[a]

| Run | [AlCl3]/[SA] (molar ratio) | Time[b] (h) | Temperature (°C) | DS[c] (mol%) |
|---|---|---|---|---|
| 1 | 2 | 2 | 20 | 0.5 |
| 2 | 2 | 2 | 30 | 1.5 |
| 3 | 2 | 2 | 40 | 4.1 |
| 4 | 3 | 2 | 30 | 2.8 |
| 5 | 4 | 2 | 30 | 4.6 |
| 6 | 3 | 4 | 30 | 3.7 |
| 7 | 3 | 6 | 30 | 5.9 |

[a] Conditions: sPS, 0.52 g (5 mmol); SA, 0.50 g (5 mmol); $CS_2$, 50 ml; [b] The reaction time are refereed to duration of reaction between the $AlCl_3$-SA charge-ransfer complex and sPS polymer, [c] DS referred to the degree of succinoylation obtained by titration analysis.

**Table 19.** Summary of DSC results for sPS and SA-sPS [97].

| Run | DS[a] (mol%) | $T_g$[b] (°C) | $T_m$[b] (°C) | $\Delta H_m$ (J/g) | $X_c$[c] (%) | $T_c$[b] (°C) | $\Delta H_c$ (J/g) |
|---|---|---|---|---|---|---|---|
| 1 | 0 | 92.7 | 270.7 | 29.5 | 55.7 | 239.5 | 30.4 |
| 2 | 0.5 | 97.2 | 269.8 | 27.5 | 51.9 | 236.7 | 26.9 |
| 3 | 1.5 | 97.1 | 268.0 | 19.6 | 37.0 | 225.8 | 20.3 |
| 4 | 3.7 | 98.3 | 263.8 | 16.0 | 30.2 | 213.0 | 16.7 |
| 5 | 5.9 | 95.1 | 255.6 | 13.4 | 25.3 | 197.6 | 16.0 |

[a] DS referred to the degree of succinoylation; [b] The glass transition temperatures ($T_g$) were determined as the midpoint of the step change in the heat flow. The melting ($T_m$) and crystallization ($T_c$) temperatures were selected as the peak maximum or minimum in endothermic or exothermic transition, respectively; [c] The $X_c$ = degree of crystallinity in the sample.

**Table 20.** DSC results of pure sPS, BMPsPS and sPS-*g*-PGMA with different degree of graft [119].

| Samples | Degree of graft (%) | $T_m$ (°C) | $T_g$ (°C) | $T_c$ (°C) | $\Delta H_f$ (J/g) | $X_c$ (%) |
|---|---|---|---|---|---|---|
| Neat sPS | - | 273.0 | 99.3 | 238.5 | 27.5 | 52.0 |
| BMPsPS | - | 232.4 | 76.7 | 165.5 | 14.7 | 27.9 |
| sPS-g-PGMA | 44 | - | 102.4 | - | - | - |
| sPS-g-PGMA | 175 | - | 100.1 | - | - | - |
| sPS-g-PGMA | 250 | - | 96.8 | - | - | - |

**Table 21.** Thermal properties of sPS and its graft copolymers synthesized by Brownell and his coworkers [25].

| Polymer | Functional Group | $T_g$ (°C) | $T_m$ (°C) | ΔHf (J/g)[a] | Crystallinity (%)[b] |
|---|---|---|---|---|---|
| sPS | None | 110 | 270 | 17.8 | 33 |
| sPS-Bpin | 2 mol % Bpin | 116 | 243 | 5.6 | 11 |
| sPS-OH | 2 mol % OH | 103 | 268 | 16.9 | 32 |
| sPS-Br | 2 mol % Br | 115 | 253 | 17.0 | 32 |
| sPS-*g*-PMMA | 6 mol % PMMA | 108 | 247 | 11.7 | 22 |
| sPS-g-PMMA | 13 mol % PMMA | 106 | 250 | 8.4 | 16 |
| sPS-g-PMMA | 26 mol % PMMA | 103 | 246 | 5.4 | 10 |
| sPS-*g*-P*t*BA | 13 mol % P*t*BA | 108 | -[c] | -[c] | -[c] |
| sPS-*g*-P*t*BA | 17 mol % P*t*BA | 108 | -[c] | -[c] | -[c] |
| sPS-*g*-PAA | 13 mol % PAA | 107 | -[c] | -[c] | -[c] |
| sPS-*g*-PAA | 17 mol % PAA | -[c] | -[c] | -[c] | -[c] |

[a] Obtained after calibration of instrument with Indium standards; [b] Calculation based off of reported $\Delta H_f^{\circ}$ of 100% crystalline sPS, 53.2 J/g; [c] Not detected.

**Table 22.** Results of styrene polymerization and bromination end-capping [120].[a]

| Run | [Ti]/[Al]/[St] | Time [min] | Yield [g] | Conv. [%] | sPSBr[b] [%] | $\overline{Mn}_{,\mathrm{Theo}}$[c] [×10$^3$] | $\overline{Mn}_{,\mathrm{NMR}}$[d] [×10$^3$] | $\overline{Mn}_{,\mathrm{GPC}}$[e] [×10$^3$] | $\overline{Mw}/\overline{Mn}$[e] |
|---|---|---|---|---|---|---|---|---|---|
| PS-1 | 1:1:65 | 7 | 0.2 | 22 | 96 | 1.5 | 9.5 | 8.9 | 1.8 |
| PS-2 | 1:1:65 | 15 | 0.4 | 44 | 97 | 3.0 | 9.4 | 11.1 | 1.7 |
| PS-3 | 1:1:65 | 30 | 0.7 | 80 | 97 | 5.5 | 17.0 | 14.9 | 2.0 |
| PS-4 | 1:1:65 | 45 | 0.9 | 100 | 98 | 6.7 | 12.5 | 13.5 | 1.9 |
| PS-5 | 1:1:325 | 15 | 0.6 | 13 | 97 | 4.5 | 35.0 | 52.3 | 1.7 |
| PS-6 | 1:1:325 | 30 | 1.2 | 27 | 94 | 9.0 | 44.4 | 58.2 | 1.7 |
| PS-7 | 1:1:325 | 60 | 1.8 | 40 | 87 | 13.6 | 43 | 61.5 | 2.0 |
| PS-8 | 1:1:325 | 90 | 2.7 | 60 | 86 | 20.4 | 38.1 | 77.5 | 1.8 |
| PS-9 | 1:1:325 | 120 | 3.4 | 75 | 85 | 25.5 | 53.6 | 79.4 | 1.7 |
| PS-10 | 1:1:325 | 150 | 4.3 | 95 | 89 | 32.5 | 69.0 | 84.0 | 1.9 |
| PS-11 [f,g] | 1:1:100 | 30 | 0.3 | 35 | 80 | 3.6 | 10.0 | 16.9 | 1.8 |
| PS-12[f] | 1:5:100 | 30 | 0.6 | 64 | 78 | 6.6 | 17.1 | 12.7 | 2.2 |
| PS-13[f] | 1:20:100 | 30 | 0.2 | 22 | 80 | 2.3 | 8.2 | 7.7 | 2.4 |

[a] All experiments were duplicated at least once, polymerization conditions unless otherwise stated: Cp*Ti(CH$_2$Ph) = 132µmol, B(C$_6$F$_5$)$_3$ = 1 equiv., Al(*n*-Oct)$_3$ = 1 equiv., temperature = 0 °C, toluene = 38 ml, NBS (50 equiv. vs. Ti); [b] % of polystyrene chains end-capped with Br as determined from $^1$H NMR spectroscopy, from the integral values of signals for brominated end-groups over the sum of integrals for unsaturated end-groups and brominated one; [c] Calculated from [styrene]/[Ti] × conversion × M$_{\mathrm{styrene}}$; [d] Determined by NMR, according to: [integrals for the methine hydrogen in the chain]/[sum of integrals for all chain-end-groups] × M$_{\mathrm{styrene}}$; [e] $\overline{Mn}$ [10$^3$

g.mol$^{-1}$] and $\overline{Mw}/\overline{Mn}$ determined by GPC in TCB at 150 °C *versus* PS standards; [f] Cp*Ti($CH_2Ph$)$_3$ = 88mmol; B($C_6F_5$)$_3$ = 1 equiv; [g] Same conditions as those reported by Grassi et al. (Ref. [121]).

**Table 23.** Synthesis of sPS-*b*-aPS via ATRP [120].[a]

| Run | [sPS-Br]/[Cu]/ [PMDETA]/[St] | Time [h] | Yield [g] | $\overline{Mn}_{,GPC}$[b] [$\times 10^3$] | $\overline{Mw}/\overline{Mn}$[b] | aPS[c] [%] | sPS[c] [%] |
|---|---|---|---|---|---|---|---|
| PS-3-Cop1 | 1:3:3:650 | 4 | 0.247 | 17.7 | 1.9 | 16 | 84 |
| PS-3-Cop2 | 1:3:3:650 | 24 | 0.344 | 23.6 | 2.0 | 37 | 63 |
| PS-3-Cop3 | 1:3:3:650 | 65 | 0.553 | 32.8 | 2.3 | 55 | 45 |
| PS-4-Cop1 | 1:3:3:650 | 144 | 0.994 | 51.5 | 2.4 | 80 | 20 |
| PS-14-Cop1[d] | 1:3:3:250 | 4 | 0.178 | 10.7 | 2.1 | 25 | 75 |

[a] Copolymerization conditions unless otherwise stated: sPS-Br 96-98% brominated = 0.200 g, CuBr = 3 equiv., PMDETA = 3 equiv., styrene = 1 m1, anisole = 10 ml, temperature = 130 °C; [b] $\overline{Mn}$ [$10^3$ g.mol$^{-1}$] and $\overline{Mw}/\overline{Mn}$ determined by GPC in TCB at 150 °C *versus* PS standards; [c] Composition calculated from the $\overline{Mn}$ values of the starting sPS-Br and the resulting copolymer; [d] sPS-Br=0.150 g.

**Table 24.** DSC results for neat sPS and sPS-*g*-(aPS-*b*-aPMS) synthesized by Jaymand [76].

| Samples | $T_m$ (°C) | $T_g$ (°C) |
|---|---|---|
| Neat sPS | 270 | 98.4 |
| sPS-*g*-(aPS-*b*-aPMS) | - | 99.2 |

**Table 25.** Grafting parameters for sPS-*g*-aPS, sPS-*g*-(aPS-*b*-aPMS) and [sPS-*g*-(aPS-*b*-aPMS)]-*g*-PMMA [122].

| Samples | Mass of Grafting ($W_g$) | Weight Gain (%WG) | Grafting Efficiency (%GE) | Grafting Yield (%G) |
|---|---|---|---|---|
| sPS-*g*-aPS | 0.92 | 13.00 | 28.48 | 45.65 |
| sPS-*g*-(aPS-*b*-aPMS) | 0.84 | 10.62 | 26.25 | 40.47 |
| [sPS-*g*-(aPS-*b*-aPMS)]-*g*-PMMA | 0.98 | 13.37 | 27.30 | 48.98 |

**Table 26.** DSC results for neat sPS and sPS-*g*-PMMA synthesized by Jaymand [77].

| Samples | $T_m$ (°C) | $T_g$ (°C) |
|---|---|---|
| Neat sPS | 270 | 98.4 |
| sPS-*g*-PMMA | 247 | 102.6 |

**Table 27.** Copolymerization of SEOM and styrene with $CpTiCl_3$/MAO catalyst in toluene at 30 °C for 3 h [136].[a]

| | | MEK Insoluble | | | |
|---|---|---|---|---|---|
| [SEOM] (g) | Yield (%) | (wt %) | $\overline{Mn}\times10^{-4}$ | $\overline{Mw}/\overline{Mn}$ | No. Grafts/Chain[b] |
| 0 | 31.0 | 80 | 6.4 | 2.02 | - |
| 0.5 | 7.8 | 76 | 3.2 | 2.53 | 2.7 |
| 0.2 | 5.4 | 75 | 1.9 | 3.15 | 4.9 |
| 0.3 | 3.5 | 65 | 1.8 | 2.14 | 5.1 |

[a] SEOM, $\overline{Mn}\times1.0\times10^{3}$, [styrene] = 2.6 mol/l, [$CpTiCl_3$] = $6.8\times10^{-4}$ mol/l, MAO/Ti = 500 (mole ratio); [b] Calculated from the $^1$H NMR spectrum of the copolymer and $\overline{Mn}$ of the copolymer.

**Table 28.** Thermal properties of *grafted*-sPS with various monomer additions [137].

| Monomer Addition (%) | $T_g$ (°C) | $T_m$ (°C) | ΔH (J/g) | $X_c$ (%) |
|---|---|---|---|---|
| 0 | 129.03 | 271.37 | 21.23 | 40.1 |
| 3.28 | 117.32 | 270.98 | 20.05 | 37.8 |
| 5.39 | 116.62 | 269.75 | 19.29 | 36.4 |
| 7.16 | 115.08 | 269.76 | 19.21 | 36.2 |
| 10.37 | 111.77 | 269.75 | 19.89 | 37.5 |
| 13.41 | 108.59 | 269.95 | 22.75 | 42.9 |
| 15.24 | 106.18 | 269.57 | 22.84 | 43.1 |

**Table 29.** Results of the anionic grafting reaction of sPSMS with PB [138].[a]

| Sample | sPSMS (g) | PB (g) | Reaction time (h) | Yield (g) | PB (%) | [η] (g/dL) | $\overline{Mw}\times10^4$ |
|---|---|---|---|---|---|---|---|
| PB[b] | 0.0 | 1.0 | - | - | 100.00 | 0.24 | 35.35 |
| PS-0[c] | 1.0 | 0.0 | - | - | 0.00 | 0.07 | 0.48 |
| PS-1 | 0.5 | 1.0 | 0.5 | 0.85 | 3.94 | 0.11 | 2.17 |
| PS-2 | 0.5 | 1.0 | 1.0 | 1.26 | 11.50 | 0.19 | 17.28 |
| PS-3 | 0.5 | 1.0 | 2.0 | 1.38 | 34.47 | 0.28 | 66.31 |

[a] The grafting reaction conditions were 2 mmol of *n*-BuLi, 0.01 mol of potassium *tert*-butoxide, and 25 °C; [b] *cis*-PB (commercial); [c] sPSMS (non-grafted copolymer).

**Table 30.** Thermal properties of pure sPSMS and poly(styrene-*co*-*p*-methylstyrene)-*graft*-polydimethylsiloxane [139].

| Run | X[a] (mol %) | $T_m$[b] (°C) | $T_c$[b] (°C) | $T_g$[c] (°C) |
|---|---|---|---|---|
| 1 | 0 | 220 | 161 | 86 |
| 2 | 3.8 | 217 | 152 | 85 |
| 3 | 8.5 | 212 | 140 | 70 |

[a] X referred to the degree of graft; [b] The crystallization ($T_c$) and melting ($T_m$) temperatures were determined from DSC cooling and heating scans, respectively; [c] The glass transition temperatures ($T_g$) were determined as the midpoint of the step change in the heat flow.

**Table 31.** Homopolymerization of styrene using binary initiator systems, metallocene MAO and ternary systems, diphenylzinc-metallocene-MAO, including various metallocenes, in toluene at 60 °C for 48 hours [147].[a]

| | Metallocene-MAO | | $Ph_2Zn$-Metallocene-MAO | |
|---|---|---|---|---|
| Metallocene | Conversion (%) | Tacticity | Conversion (%) | Tacticity |
| $Cp_2TiCl_2$ | 1.8 | Syndiotactic | 6.7 | Syndiotactic |
| (*n*-BuCp)$_2$TiCl$_2$ | 11.0 | Syndiotactic | 11.4 | Syndiotactic |
| $CpTiCl_3$ | 30.5[b] | Syndiotactic | 42.0[b] | Syndiotactic |
| $Cp_2ZrCl_2$ | 1.0 | Atactic | 1.1 | Atactic |
| (i-BuCp)$_2$ZrCl$_2$ | 2.5 | Atactic | 2.7 | Atactic |
| $Ind_2ZrCl_2$ | 7.8 | Atactic | 8.4 | Atactic |
| (H$_4$-Ind)$_2$ZrC$_{l2}$ | 1.6 | Atactic | 2.1 | Atactic |
| Et(Ind)$_2$ZrCl$_2$ | 3.1 | Atactic | 3.3 | Atactic |
| i-Pr(Flu)(Cp)ZrCl$_2$ | 8.2 | Atactic | 8.5 | Atactic |
| (n-BuCp)$_2$HfCl$_2$ | not performed | Atactic | 0.6 | Atactic |

[a] Polymerization conditions: Total volume 40 ml, [styrene] = 2 mol/l, [metallocene] = $4\times10^{-4}$ mol/l, [MAO] = 0.33 mol/l for binary initiator systems. The same concentrations for ternary systems, but [metallocene] = [$Ph_2Zn$] = $2\times10^{-4}$ mol/l; [b]After 6 hours polymerization.

**Table 32**. Styrene copolymerization using $Ph_2Zn$ -$CpTiCl_3$-MAO ternary initiator system in toluene at 60 °C for 6 hours. Styrene/Comonomer = 50/50 (mol/mol) [147].[a]

| Run | Comonomer | Yield | $\vert\eta\vert$[b] | DSC[c] | | Insoluble Fraction |
|---|---|---|---|---|---|---|
| | | (%) | (dl/g) | $T_g$(°C) | $T_m$ (°C) | (%) |
| 1 | Only St | 42.0 | 0.20 | 100.7 | 262.3 | 99.3 |
| 2 | *p*-MeOSt | 75.1 | 0.47 | 110.1 | n.s. | 4.6 |
| 3 | *p*-Bu$^t$St | 70.2 | 0.23 | 129.6 | n.s. | 13.5 |
| 4 | *p*-MeSt | 47.3 | 0.18 | 108.8 | n.s. | 28.0 |
| 5 | *p*-$NH_2$St | 47.0 | n.d. | 97.6 | 257.6 | n.d. |
| 6 | *p*-ClSt | 26.3 | n.d. | 92 | 226.8 | n.d. |
| 7 | *p*-FSt | 27.0 | n.d. | 92.4 | 252.8 | n.d. |
| 8 | *p*-BrSt | 7.7 | n.d. | 93.0 | 231.4 | n.d. |
| 9 | α-MeSt | 14.4 | n.d. | 94.1 | 238.1 | n.d. |
| 10 | 2,4-$Me_2$St | 6.8 | n.d. | 112.4 | n.s. | n.d. |
| 11 | 2,4,6-$Me_3$St | 3.6 | n.d. | 91.6 | 251 | n.d. |

[a] Polymerization conditions: Total volume 60 ml; [St]+[comonomer] = 2 mol/l; [MAO] = 0.33 mol/l; [metallocene] = [$Ph_2Zn$] = $2\times10^{-4}$ mol/l; [b] Intrinsic viscosity: measured in o-DCB at 35 °C, 1 point determination; [c] Second heating, crude polymer.

n.d. = not determined; n.s. = no signal; *48 h run; **40 °C, and 1.5 h run.

**Table 33.** Styrene copolymerization using $CpTiCl_3$-MAO binary initiator system, in toluene at 60 °C for 6 hours. Styrene/Comonomer=50/50 (mol/mol) [147].[a]

| Run | Comonomer | Yield | $\|\eta\|^b$ | DSC[c] | | Insoluble Fraction |
|---|---|---|---|---|---|---|
| | | (%) | (dl/g) | $T_g$(°C) | $T_m$ (°C) | (%) |
| 1 | Only St | 30.5 | 0.25 | 93.5 | 255 | 99.2 |
| 2 | *p*-MeSt | 32.8 | 0.35 | 97.1 | 255 | 99.9 |
| 3 | 2,4-$Me_2$St | 6.8 | n.d. | 112.4 | n.s. | n.d. |
| 4 | α-MeSt | 25.1 | 0.12 | 91.4 | 239 | n.d. |
| 5 | 1-$C_{10}H_{20}$ | 3.8 | 0.25 | 96.9 | 261 | n.d. |
| 6 | 1-$C_{16}H_{32}$ | 11.6 | 0.1 | n.s. | 248 | 81.9 |

[a] Polymerization conditions: Total volume 60 ml; [St]+[comonomer] = 2 mol/l; [MAO] = 0.33 mol/l [metallocene] = $2\times10^{-4}$ mol/l; [b] Intrinsic viscosity: measured in o-DCB at 35 °C, 1 point determination; [c] Second heating, crude polymer.

n.d. = not determined; n.s. = no signal; *48 h run.