Preparation and Application of Sulfonated Poly(1-octene-*co*-styrene)

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ABSTRACT: In this article, 1-octene and styrene was copolymerized by the supported catalyst ($TiCl_4$/ID/$MgCl_2$). Subsequently, by sulfonation reaction, sulfonated poly(1-octene-*co*-styrene)s which were amphiphilic copolymers were prepared. The copolymerization behavior between 1-octene and styrene is moderate ideal behavior. Copolymers prepared by this catalyst contain appreciable amounts of both 1-octene and styrene. Increase in the feed ratio of styrene/1-octene leads to increase in styrene content in copolymer and decrease in molecular weight. As the polymerization temperature increases, the styrene content in the copolymers increases, however, the molecular weight decreases. Hydrogen is an efficient regulator to lower the molecular weights of poly(1-octene-*co*-styrene)s. The sulfonation degree of the sulfonated poly(1-octene-*co*-styrene)s increased as the styrene content in copolymer increased or the molecular weight decreased. Thirty-six hour is long enough for sulfonation reaction. The sulfonated poly(1-octene-*co*-styrene)s can be used as effective and durable modifying agent to improve the wettability of polyethylene film and have potential application in emulsified fuels and for the stabilization of dispersions. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 119: 677–684, 2011

Key words: Ziegler-Natta polymerization; polyolefins; functionalization of polymers; copolymerization

INTRODUCTION

Polyolefins are widely used in a wide range of applications since they provide an excellent combination of mechanical and chemical properties as well as processability. Nevertheless, deficiencies such as lack of reactive functional groups in the polymer structure have limited some of their end uses particularly those in which adhesion, dyeability, paintability, printability, or compatibility with other functional polymers is paramount. This disadvantage can be overcome by introducing suitable functional groups in polyolefins.[1–3] Generally, there are three approaches to the functionalization of polyolefins. The most traditional one is the chemical modification of the preformed polyolefins. However, due to the inert nature of polyolefins, this approach has to resort to high-energy sources to break the stable C—H bonds to form polymeric radicals, usually accompanied by undesirable side reactions, such as degradation and corss-linking.[4–6] The second approach is the direct copolymerization of olefins with functional monomers, and it has been regard as the most ideal methods. Unfortunately, some fundamental chemical difficulties, namely catalyst poisoning and side reactions, have prevented the direct process for commercial application.[7,8] Late-transition-metal catalysts, for example, Pd and Ni-based complexes,[9–11] which have better tolerance to functional groups, have been reported as the best catalysts for the copolymerization of olefins with functional monomers. However, the stereotacticity of polyolefins produced by the catalysts is poor. The reactive polyolefin intermediate approach[12–14] provides another effective way to access functionalized polyolefins by first designing a reactive copolymer "intermediate" that can be effectively synthesized and subsequently interconverted to functional polymer. Obviously, the key factor in this approach is the design of a comonomer containing a reactive group. Usually, three kinds of reactive comonomers, borane monomers, para-methylstyrene and divinyl-benzene, were used to copolymerize with olefins.

As styrene is readily available in a pure state and commercial polystyrene has very reliable properties, the copolymerizations of olefinic monomers with styrene have been extensively studied.[15,16] However, most of the literatures were about the copolymerizations of styrene and olefins catalyzed by homogeneous single-site catalysts.[17–21] There was few article

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on the copolymerization of styrene and ethylene or propylene catalyzed by heterogeneous Ziegler-Natta catalysts because of relatively low activity of styrene.[22–24] Heterogeneous Ziegler-Natta catalysts are not suitable for the synthesis of styrene-ethylene or styrene-propylene copolymers. The incorporation of styrene in styrene-ethylene copolymer and styrene-propylene copolymer was usually less than 1 mol % and 4 mol %, respectively. Despite the economical importance of polyethylene (PE) and polypropylene and the large number of relevant academic and industrial studies, the polymerization of higher α-olefins remains a relatively unexplored field. It is possible to find some reports on the preparation of poly(α-olefin) by metallocene catalysts, but for the other catalysts, the sources are very scarce, even there are predictions for oversupply in linear α-olefins for the forthcoming years.[25] To our knowledge there is no study on the copolymerization of styrene and α-olefin higher than propylene catalyzed by heterogeneous Ziegler-Natta catalysts. But heterogeneous Ziegler-Natta catalysts are commonly used throughout the polymer industry. And the steric hindrance of higher α-olefin is much higher than that of ethylene and propylene. This maybe suppresses the catalyst's ability to discriminate between higher α-olefin and styrene for binding, thus enhances the incorporation of styrene. In addition, the sulfonation of polystyrene is a common procedure in the manufacture of ion-exchange materials, membranes and plasticizers. The sulfonating agents used include sulfuric acid, oleum, sulfur trioxide, chlorosulfonic acid and acetyl sulfate. The sulfonic acid group (—SO_3H) is added to the aromatic ring by electrophilic substitution. Therefore, in this article, styrene was used as a comonomer containing a reactive group to copolymerize with 1-octene. Subsequently by sulfonation, a series of amphiphilic sulfonated poly(1-octene-*co*-styrene) was prepared. The influence of reaction conditions on the composition of the sulfonated poly(1-octene-*co*-styrene) and its potential application were investigated.

EXPERIMENTAL

Materials

Nitrogen (99.999%, N_2) was purified by passing through two columns of deoxygen catalyst and preactivated 4 Å molecular sieves to remove the residual moisture and oxygen. 1-Octene was purchased from Aldrich, purified by refluxing and distilled over sodium, and kept under a dry N_2 atmosphere. Styrene (>98%) was purified by washing with 10% NaOH and then distilling under reduced pressure. The supported catalyst $TiCl_4$/ID/$MgCl_2$ (Ti content = 3 wt %) was donated by Beijing Research Institute of Chemical Technology. Triisobutylaluminium (Aldrich, Ali-Bu_3) was used as received. An external electron donor diphenyl dimethoxysilane (Hubei Huabang Chemical, $Ph_2(MeO)_2Si$ or DDS) was dried over CaH_2 and distilled before use. *n*-Heptane as solvent was purified over sodium/benzophenone ketyl and distilled under a dry N_2 atmosphere before use.

Copolymerization procedures of 1-octene and styrene

All manipulations were carried out under a nitrogen atmosphere with standard Schlenk techniques. A typical copolymerization was conducted as follows. The designated amounts of *n*-heptane (40 mL), styrene, 1-octene, Al(i-Bu) (2.5 mmol) and DDS (0.25 mmol) were injected into a 100 mL glass flask connected to a Schlenk line and equipped with a magnetic stirrer under N_2 atmosphere. Then, the flask was immersed in a thermostat at designated temperature. Finally, the supported catalyst $TiCl_4$/ID/$MgCl_2$ (ID = internal donor) (about 40 mg) was added into the mixture to initiate the copolymerization. In all reactions, Al/Ti (molar ratio) = 100 and Al/Si (molar ratio) = 10 were used. After 2 h, copolymerization was terminated by the addition of HCl acidified methanol. The resulting copolymer was precipitated by adding isopropanol, washed with methanol and dried in vacuum at 50°C. The copolymer was placed in a Soxhlet extractor and allowed to undergo extraction in ethyl acetate for 24 h to remove homopolystyrene. Finally, the copolymer was dried in vacuum at 50°C for 12 h.

Sulfonation of poly(1-octene-*co*-styrene)

Poly(1-octene-*co*-styrene) was sulfonated by attaching —SO_3H group at the paraposition of the benzene ring in styrene unit. A 1% (w/v) solution of poly(1-octene-*co*-styrene) (0.5 g) in ortho-dichlorobenzene (50 mL) was prepared. The solution was stirred and refluxed at ~ 100°C, while 50 mL 50 wt % concentrated sulfuric acid was slowly added to begin the sulfonation reaction. After a designated reaction time, the reaction was terminated by slowly adding 100 mL methanol. The reacted copolymer solution was then precipitated with deionized water. The precipitate was washed several times with water and methanol, separately, and then dried in a vacuum oven at 50°C for 24 h. This washing and drying procedure was repeated until the pH of the wash water was neutral.

Preparation of micelles

About 0.1 g sulfonated poly(1-octene-*co*-styrene) dissolved in 8 g toluene. 2 g ethanol was slowly added

into the solution at 40°C. Then the mixture was gently stirred for 3 h, followed by sonication for 2 h. As a consequence, reverse micelles were formed in the solution, where the hydrophilic $-SO_3H$ groups constituted the core and the hydrophobic backbone and hexyl side chains constituted the outer shell.

Measurements

Sulfonation degree (SD) of sulfonated poly(1-octene-*co*-styrene) was determined by titration procedure. Sulfonated poly(1-octene-*co*-styrene)s were dissolved in a mixed solvent of chloroform/ethanol (90/10, v/v) with concentrations ranging from 1 to 2% (w/v). The solution was titrated immediately with 0.015–0.020 mol/L sodium methoxide/methanol solution using three to four drops of phenolphthalein (1%) as the indicator. The exact concentration of sodium methoxide was determined by titrating with benzonic acid. The SD was determined by the following equation:

$$\mathrm{SD} = \frac{V_{\mathrm{NaOCH_3}} \times C_{\mathrm{NaOCH_3}}}{M} \times 100$$

where $V_{\mathrm{NaOCH_3}}$ is the volume (mL) of the sodium methoxide/methanol solution consumed in the titration. $C_{\mathrm{NaOCH_3}}$ is the concentration (mol/mL) of the sodium methoxide/methanol solution. M is the mole summation of 1-octene and styrene in the sample which is calculated from the ^{1}H-NMR integrals.

All NMR spectra were recorded in deuterated chloroform on a Varian Mercury 300 Plus instrument. The composition of poly(1-octene-*co*-styrene)s were calculated from the ^{1}H-NMR integrals of methyl in 1-octene units and phenyl in styrene units. Molecular weight and polydispersity index (PDI) were measured with gel permeation chromatography on a PL-GPC220 at 150°C with 1, 2, 4-$C_6H_3Cl_3$ as the eluent and using narrow dispersity polystyrene as calibration standards. Differential scanning calorimetry (DSC) was performed under a N_2 atmosphere on a Perkin–Elmer DSC-7 at a heating rate of 10°C/min. The hydrodynamic diameter and size distribution of micelles were determined by dynamic light scattering (DLS) using a Brookhaven 90 Plus particle size analyzer. The scattered light of a vertically polarized He-Ne laser (632.8 nm) was measured at an angle of 90° and was collected on an autocorrelator. Each analysis lasted for 3 min and performed at 25°C. Before the light scattering measurements the sample solutions were filtered using Millipore Teflon filter with a pore size of 0.45 μm. Transmission electron microscopy (TEM) was performed on a JEOL JEM-1230 electron microscopy operating at an acceleration voltage of 80 kV. A drop of emulsion was placed onto a 200-mesh copper grid coated with a thin film of carbon. Solvent evaporated at room temperature under atmospheric pressure for 24 h. After that, the grids were negatively stained by 2 wt % phosphor-tungstic acid. Energy dispersive X-ray analysis (EDAX) was recorded and evaluated with a Noran Voyager X-ray spectrometer attached to a Zeiss DSM 982 Gemini (5-Kv acceleration voltage). Noran Voyager uses top hat filtering for background subtraction and reference spectra for peak deconvolution. All specimens were coated with a thin carbon layer to obtain an electrically conductive surface. The contact angles to water of the samples were measured on the Dataphysics OCA20 Optical Contact Angle Goniometer at ambient temperature. The probe liquid was distilled water with a surface tension of 72 mN/m. A liquid droplet was carefully placed on a film using a syringe. A drop volume of 1 μL was used for every measurement. The average contact angle value was obtained by measuring five different positions of the same sample.

TABLE I
Copolymerization Results Under Different Feed Ratios at 50°C

Run	[C8]/[St]	Conversion (%)	St incorporation (mol %)	y
1	4	8.7	5.5	17.18
2	2.33	7.4	9.6	9.42
3	1.5	6.2	18.8	4.32
4	1	5.5	33.1	2.02
5	0.67	4.9	45.6	1.19
6	0.43	4.3	62.3	0.61

y = ratio between the content of C8 and St in poly(1-octene-*co*-styrene).

RESULTS AND DISCUSSION

Effect of monomer feed ratio on the copolymerization of 1-octene and styrene

One of the best ways to investigate a copolymerization system is to determine its reactivity ratios of the comonomers. To get meaningful results, a series of copolymerization were carried out by changing monomer feed ratio and comparing the resulting copolymer's compositions under conversion of 10%. The experimental results were summarized in Table I. As the feed ratio of styrene/1-octene increased, the catalyst efficiency for the copolymerization of styrene and 1-octene decreased, while the styrene content in the copolymers increased. The reactivity ratios of 1-octene (r_1) and styrene (r_2) are estimated by Kelen-Tüdös linearization method.[26]

The obtained values of reactivity ratios are $r_1 = 2.05$ and $r_2 = 0.44$. Since the product of r_1 and r_2 is 0.902 which is a little less than unity. Meanwhile, r_1

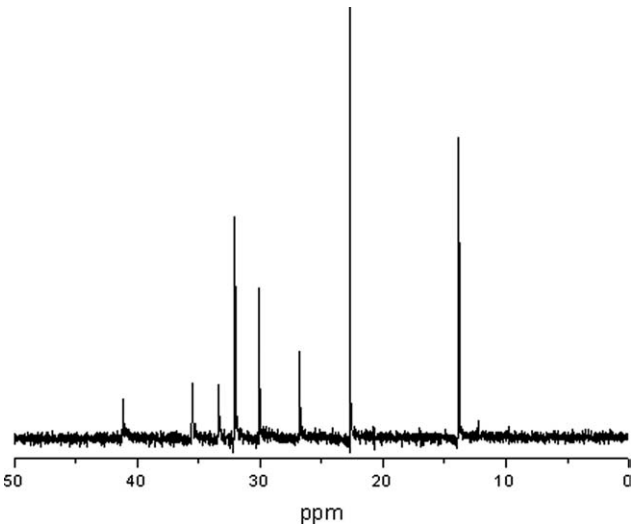

Figure 1 ^{13}C-NMR of poly(1-octene-*co*-styrene) containing 5.5 mol % styrene units.

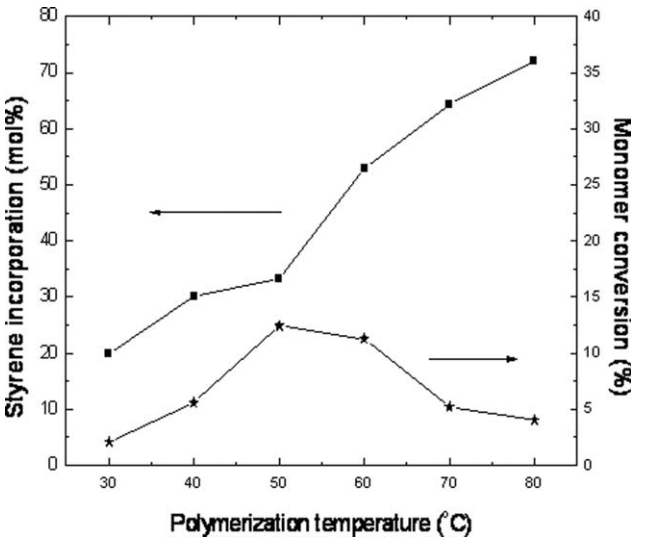

Figure 2 Effect of polymerization temperature on copolymerization: [1-octene] 0: [styrene] 0 = 1.

and r_2 are not too different. The copolymerization behavior between 1-octene and styrene is moderate ideal behavior. It indicates that there will exist a large range of comonomer feed compositions, which yield copolymers containing appreciable amounts of both 1-octene and styrene.

The chain structure of poly(1-octene-*co*-styrene)s was influenced by the copolymer composition. When the styrene content in copolymer was low, e.g., 5.5 mol %, styrene units distributed along the copolymer backbone separately. Because according to the ^{13}C-NMR spectrum (as shown in Fig. 1) there was only resonance at 42.5 ppm which arose from the methylene in the isolated styrene units. And there was only one glass transition temperature (T_g) at about −60°C which indicated the block 1-octene sequences in this copolymer. However, when the styrene content in copolymer was high, e.g., 62.5 mol %, there were block styrene sequences on the copolymer backbone. According to the ^{13}C-NMR spectrum, there was not only resonance at 42.5 ppm (arose from the methylene in the isolated styrene units) but also resonance at 44.5 ppm (arose from the methylene in the block styrene units). And there were two T_g at about −60°C and 110°C, respectively. The latter was the glass transition temperature of block styrene sequences on this copolymer.

TABLE II
The Effect of Monomer Feed Ratio on Copolymers' Molecular Weight and its Distribution

C8: St (molar ratio)	4	7 : 3	1	3 : 7
$\overline{M}_n$ ($\times 10^4$)	32.2	30.9	28.6	18.4
PDI	6.4	5.3	4.5	5.5

C8 = 1-octene; St = styrene; polymerization temperature = 50°C.

The influence of monomer feed ratio on the molecular weight and its distribution was summarized in Table II. As the feed ratio of styrene/1-octene increased, the number-average molecular weight of the copolymers decreased. Variation of monomer feed ratio could not change the nature of the catalyst. Hence it did not impact the copolymers' molecular weight distribution to a major extent.

Effect of polymerization temperature on the copolymerization of 1-octene and styrene

From Figure 2, the monomer conversion (or the catalytic efficiency of the supported catalyst $TiCl_4$/ID/$MgCl_2$) for copolymerization of 1-octene and styrene is highly sensitive to temperature. It decreased rapidly when the temperature exceeded 50°C. However, the styrene content in the copolymers increased gradually.

The influence of polymerization temperature on the copolymers' molecular weight and its distribution was summarized in Table III. As the polymerization temperature increased, the number-average molecular weight of poly(1-octene-*co*-styrene)s decreased gradually. In the range of 40– 70°C, PDI of poly(1-octene-*co*-styrene)s was similar to each other. However, when poly(1-octene-*co*-styrene) was prepared at 30 or 80°C, PDI of these two copolymers

TABLE III
The Effect of Polymerization Temperature on Copolymers' Molecular Weight and its Distribution

Temperature (°C)	30	40	50	60	70	80
$\overline{M}_n$ ($\times 10^4$)	40.0	31.1	28.6	26.6	15.2	10.5
$\overline{M}_w/\overline{M}_n$	3.6	4.5	4.5	4.7	5.0	3.3

[1-octene] $_0$: [styrene] $_0$ = 1.

TABLE IV
The Effect of Polymerization Temperature on Copolymers' Molecular Weight and its Distribution Using H_2 as Molecular Weight Regulator

Temperature (°C)	50	70	80
$\overline{M}_n$ ($\times 10^4$)	14.8	12.4	10.4
$\overline{M}_w/\overline{M}_n$	4.1	4.0	3.6

[1-octene] $_0$: [styrene] $_0$ = 1; The volume of H_2 is 20 vol % of the gas phase over the reaction solution.

were similar to each other but lower than that of those copolymers mentioned above.

The same conclusion could be drawn when hydrogen (H_2) was used as molecular weight regulator (listed in Table IV).

Effect of hydrogen on the copolymerization of 1-octene and styrene

Poly(1-octene-*co*-styrene)s with high molecular weight cannot dissolve in solvent conveniently. That is not propitious to the subsequent functionalization of poly(1-octene-*co*-styrene). Hydrogen is commonly used as an important regulator to lower the molecular weights of polyolefins produced with heterogeneous catalysts. The chain transfer reaction with hydrogen may activate some dormant species. So addition of hydrogen into the copolymerization of 1-octene and styrene may increase the monomer conversion. Under the identical conditions, when the volume of H_2 was 20 vol% of the gas phase over the reaction solution, the monomer conversion was as high as 40% which was much higher than the monomer conversion (less than 10 %) in absence of hydrogen. The influence of hydrogen on copolymers' molecular weight and its distribution was shown in Figure 3. Copolymers' molecular weight could be efficiently regulated by hydrogen. Introduction of hydrogen into the copolymerization lowered the resulting copolymers' molecular weight gradually. When the ratio of hydrogen exceeded 10 vol%, copolymers' molecular weight leveled off. Addition of a small amount of hydrogen narrows down the distribution of copolymers' molecular weight. Further increasing in the amount of hydrogen did not impact the copolymers' polydispersity to a major extent. In addition, there was no influence of hydrogen on the styrene content in the copolymers.

Effect of the styrene content in copolymer on the SD

From Table V, the higher the styrene content in copolymer, the higher the probability of the colliding of —SO_3H and styrene to capture one another to form sulfonated poly(1-octene-*co*-styrene).

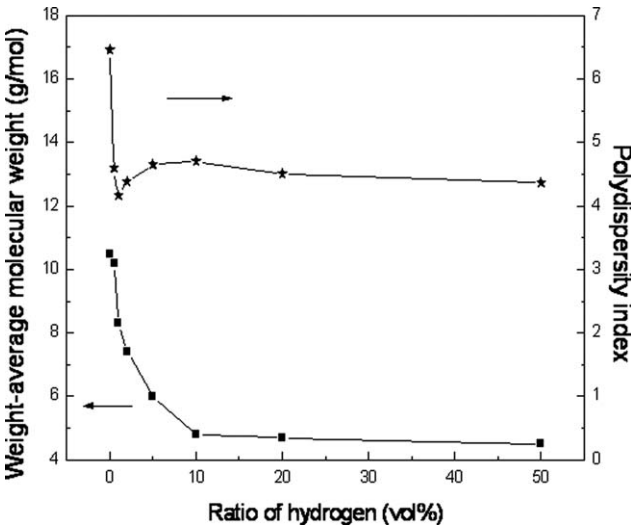

Figure 3 Effect of hydrogen on the copolymers' molecular weight and its distribution: the amount of H_2 is the volume percentage of H_2 in the gas phase over the reaction solution.

Effect of the copolymers' molecular weight on the SD

From Figure 4, as copolymers' molecular weight decreased, SD increased. Usually polymers with low molecular weight can relatively easily dissolve in solvent. The higher the solubility of polymer, the higher the conformation freedom of the polymer chain is. This is propitious to introduce —SO_3H into poly(1-octene-*co*-styrene).

Effect of sulfonation reaction time on the SD

From Figure 5, when the sulfonation reaction time was shorter than 36 h, the SD of the sulfonated copolymers increased as the reaction time increased. However, when the reaction time was longer than 36 h, the SD decreased slightly. That arose from the carbonization of copolymers because of contact with concentrated sulfuric acid for a long time. And those carbonization product remained in the resulting sulfonated product since it was difficult to separate them from sulfonated poly(1-octene-*co*-styrene)s.

TABLE V
Effect of the Styrene Content in Copolymer on the Sulfonation Degree

Run	$\overline{M}_n$ ($\times 10^5$)	Styrene incorporation (mol %)	Sulfonation degree (mol %)
1	3.1	5.5	1.2
2	2.8	33.1	3.3
3	2.7	52.9	4.9

Sulfonation reaction time = 3 h.

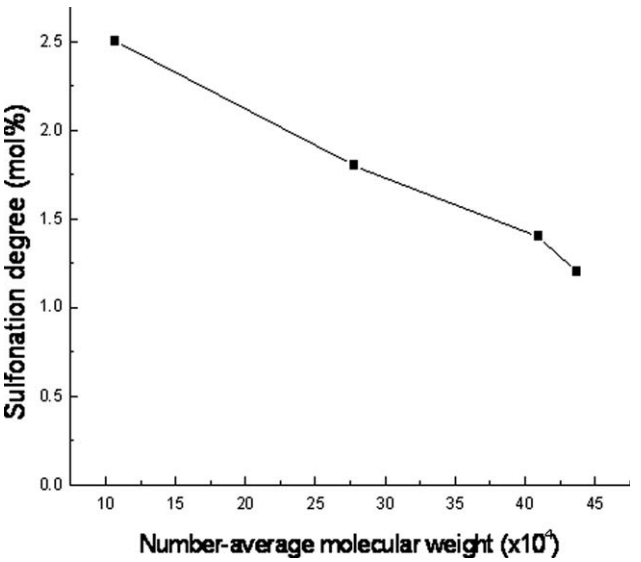

Figure 4 Effect of the copolymers' molecular weight on the sulfonation degree: styrene content in copolymer = 5.5 mol %; sulfonation reaction time = 3 h.

Using sulfonated poly(1-octene-*co*-styrene)s as surface modifying agent for PE

PE is one of the most widely used polymeric materials for its high specific modulus and strength. But the hydrophobic surface of PE causes some problems in practical applications, for instance, poor wettability, poor adhesion and biocompatibility. Surface modification of PE film by coating modifying agent on the surface of PE film is a minor technologically difficult and lower cost method. And this method does not damage PE film itself. Since the side chain of poly(higher α-olefin) is similar to the chain structure of PE, it can be forecasted that the adhesion between poly(higher α-olefin) and PE film

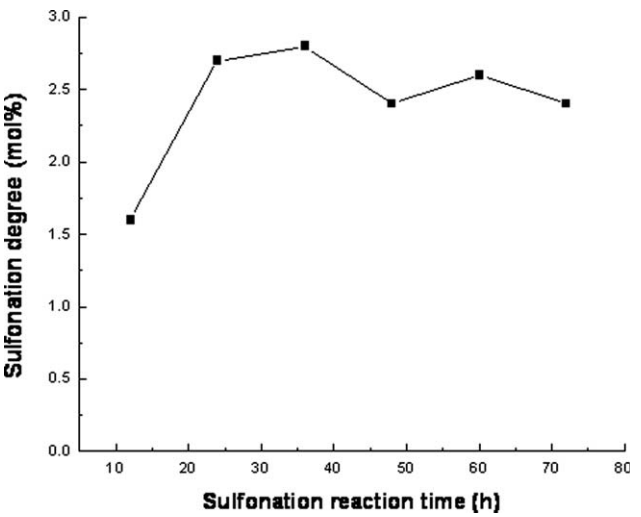

Figure 5 Effect of sulfonation reaction time on the sulfonation degree: styrene content in copolymer = 5.5 mol %; = 10.5×10^4.

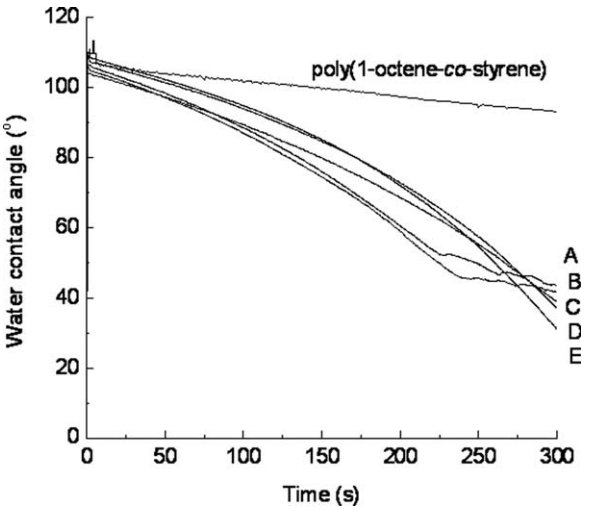

Figure 6 Water contact angle of modified PE film versus aging time: (A) SD = 1.2 mol %; (B) SD = 1.4 mol %; (C) SD = 1.6 mol %; (D) SD = 1.8 mol %; (E) SD = 2.5 mol %; SD = sulfonation degree of the sulfonated poly(1-octene-*co*-styrene)s.

is strong. And sulfonated poly(1-octene-*co*-styrene) can assemble orderly to some extent on the PE surface. Consequently, the wettability of PE film can be improved as $-SO_3H$ enrich to the interface between sulfonated poly(1-octene-*co*-styrene) and air. The coating procedure and treatment of PE film were mentioned in our previous work.[27] The static water droplet contact angles of modified PE film were measured from 0 to 5 min aging at room temperature. The results were shown in Figure 6. The pristine poly(1-octene-*co*-styrene) did not impact the wettability of PE surface. Coated by sulfonated poly(1-octene-*co*-styrene)s, the water droplet contact angles of modified PE film dropped sharply. When the aging time was 5 min, the water droplet contact angle of the modified PE film was as low as 30°, namely, the water droplet well spread on the PE surface. As the SD of the sulfonated poly(1-octene-*co*-styrene)s increased, the decrement of contact angle increased gradually.

To mimic the scour of water vapor and water droplets on the PE surface in the airtight and humid circumstance when PE film is used as agriculture film, the hot-fog test[27] of modified PE film were performed and the results were shown in Figure 7. After being tested by hot-fog, the initial contact angle of PE film coated by sulfonated poly(1-octene-*co*-styrene) decreased from 114° to 97°. Meanwhile, the obvious decreasing in water contact angle showed earlier (at about 1 min) and the decrement was much higher than that of modified PE film untested by hot-fog. The hot-fog test results illustrate that, after contact with water vapor, sulfonated poly(1-octene-*co*-styrene) can improve the wettability of PE film more effectively. At the same time, the adhesion between PE film and sulfonated poly(1-octene-*co*-styrene) is very strong. Sulfonated poly(1-octene-*co*-styrene) cannot be washed

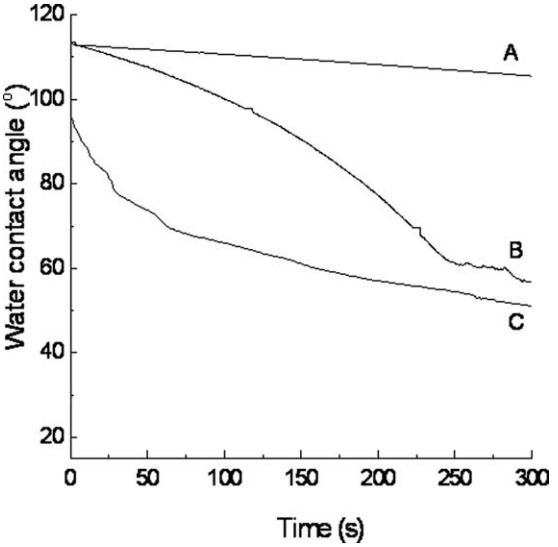

Figure 7 Water contact angle of modified PE film versus aging time: (A) coated by poly(1-octene-*co*-styrene); (B) coated by sulfonated poly(1-octene-*co*-styrene); (C) coated by sulfonated poly(1-octene-*co*-styrene) and tested by hot-fog.

away from PE surface by water vapor. Because poly(1-octene-*co*-styrene)s are random copolymers, their glass transition temperature (T_g) are about −60°C. Induced by water vapor the chain of sulfonated poly(1-octene-*co*-styrene) would rearrange, namely, the hydrophilic units (—SO_3H) immigrated and enriched to the interface between sulfonated poly(1-octene-*co*-styrene) and water. This was proved by the measurement of elemental composition on the modified surface of PE film (as listed in Table VI). After hot-fog test, oxygen and sulfur enriched on the surface of the modified PE film. And the similarity of chain structure between PE and the hexyl side chains of 1-octene units make PE and sulfonated poly(1-octene-*co*-styrene) adhere to each other tightly.

TABLE VI
The Hydrodynamic Diameter of the Micelles of Sulfonated Poly(1-octene-*co*-styrene) in Ethanol/Toluene

Entry	$\overline{M}_n$ ($\times 10^4$)	Styrene incorporation (mol %)	SD (mol %)	Diameter (nm)
1	37.4	62.5	3.8	49.3
2	18.1	62.5	4.1	54.9
3	13.5	62.5	4.5	51.4
4	10.0	62.5	5.1	62.5
5	43.7	5.5	1.2	96.1
6	41.0	5.5	1.4	129.9
7	27.8	5.5	1.8	170.6
8	10.5	5.5	2.5	239.1
9	10.5	5.5	2.5	239.1
10	10.5	5.5	2.8	290.3

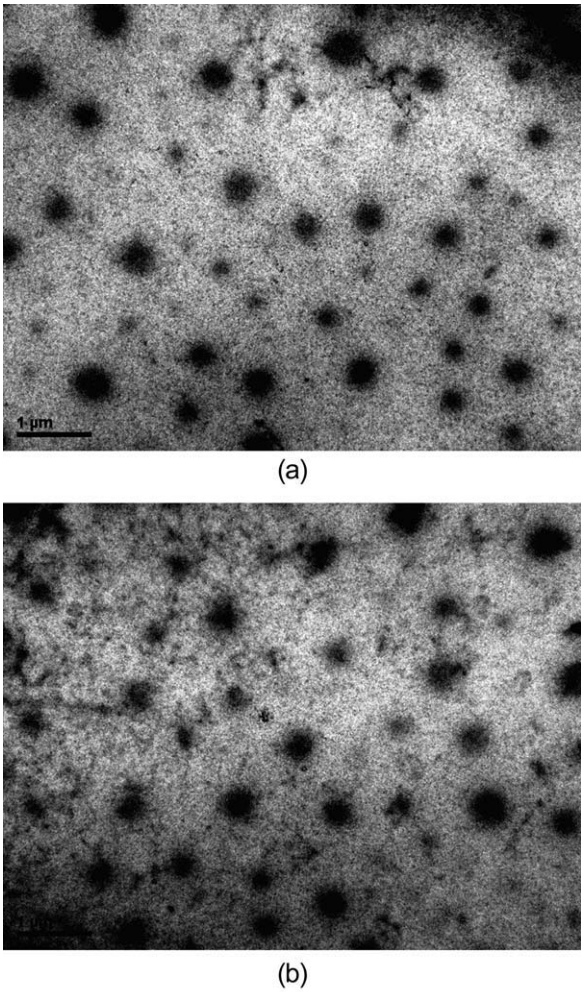

Figure 8 TEM images of the micelles of sulfonated poly(1-octene-*co*-styrene) in ethanol/toluene: (a) SD = 2.8 mol %; (b) SD = 2.4 mol %; SD = sulfonation degree of the sulfonated poly(1-octene-*co*-styrene)s.

Micellization behavior of sulfonated poly(1-octene-*co*-styrene)

A proper amount of sulfonated poly(1-octene-*co*-styrene) dissolved in the mixture of toluene and ethanol. Consequently, reverse micelles were formed in the solution, where the hydrophilic —SO_3H groups constituted the core and the hydrophobic backbone and hexyl side chains constituted the outer shell. The morphology of the micelles of sulfonated poly(1-octene-*co*-styrene) in ethanol/toluene was observed by TEM. As show in Figure 8, the micelles were spherical but unequal in size. The hydrodynamic diameter of these micelles were measured and listed in Table VI. The hydrodynamic diameter of these micelles was in the range of 50–290 nm. In Entry 1–4, although the molecular weight of these four sulfonated poly(1-octene-*co*-styrene)s were different from each other, they yielded micelles with almost the same hydrodynamic diameter. This may

be due to the same styrene content in copolymer and similar SD of these four copolymers. In Entry 5–10, as the SD of the sulfonated poly(1-octene-*co*-styrene)s increased, the hydrodynamic diameter of the micelles increased. The styrene content in copolymer of the sulfonated poly(1-octene-*co*-styrene)s in Entry 5–10 was low which made them easily soluble in ethanol/toluene. Hence the higher the SD of the sulfonated poly(1-octene-*co*-styrene)s, the higher the compatibility between ethanol phase and toluene phase. As a result, the sulfonated poly(1-octene-*co*-styrene) with higher SD could adopt more free chain conformation in the interface which gave rise to bigger micelles. Although the SD of the sulfonated poly(1-octene-*co*-styrene)s in Entry 1–4 were higher than that in Entry 5–10, the hydrodynamic diameter of the micelles in Entry 1–4 were smaller than that in Entry 5–10. This should be attribute to the high styrene content in copolymer of the sulfonated poly(1-octene-*co*-styrene)s in Entry 1–4 which resulted in relatively poor solubility of these copolymers in ethanol/toluene. Therefore, the conformation freedom of these copolymers' chain was low. Consequently, micelles prepared by these copolymers were relatively small. Since this family of amphiphilic copolymers can form reverse micelles in nonpolar solvent, they have potential application in emulsified fuels and for the stabilization of dispersions. More detailed study is under the way.

CONCLUSIONS

To prepare amphiphilic copolymers, sulfonation of poly(higher α-olefin-*co*-styrene)s is a simple but high-performance method. Catalyzed by the supported catalyst ($TiCl_4$/ID/$MgCl_2$), the copolymerization behavior between 1-octene and styrene is moderate ideal behavior. Copolymers prepared by this catalyst contain appreciable amounts of both 1-octene and styrene. Increase in the feed ratio of styrene/1-octene leads to increase in styrene content in copolymer and decrease in molecular weight. As the polymerization temperature increases, the styrene content in the copolymers increases, however, the molecular weight decreases. Hydrogen is an efficient regulator to lower the molecular weights of poly(1-octene-*co*-styrene)s. The SD of the sulfonated poly(1-octene-*co*-styrene)s increased as the styrene content in copolymer increased or the molecular weight decreased. 36 h is long enough for sulfonation reaction. The sulfonated poly(1-octene-*co*-styrene)s can be used as effective and durable modifying agent to improve the wettability of PE film and have potential application in emulsified fuels and for the stabilization of dispersions.

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