Isotactic-Polypropylene/Atactic-Polystyrene Miktoarm Star Copolymers: Synthesis and Aggregation Morphology

Yuanjie Wang, Xinzhi Liu, Liying Liu and Hui Niu *

State Key Laboratory of Fine Chemicals, Department of Polymer Science and Engineering, School of Chemical Engineering, Dalian University of Technology, Dalian 116024, China; yuanjiewang@iccas.ac.cn (Y.W.); wolong@mail.dlut.edu.cn (X.L.); lxhn@mail.dlut.edu.cn (L.L.)
* Correspondence: hniu@dlut.edu.cn
Received: 5 September 2019; Accepted: 25 September 2019; Published: 27 September 2019

Abstract: In this work, a series of isotactic-polypropylene/atactic-polystyrene (iPP/aPS) miktoarm star copolymers, P_xS_y, was synthesized via an arm-first approach. Varied star macromolecule architectures were fabricated by designing the arm length and the arm numbers (x and y). These miktoarm stars were able to form micelles in selective solvent (N,N′-dimethylformamide (DMF)), in which the insoluble iPP arms formed the core and the soluble aPS arms formed the shell. The miktoarm polymers aggregated to micro-nanoscale binary structures (MNBSes) in the casting process, and their morphologies, including the MNBS shape and size, were greatly influenced by the P_xS_y architectures. The MNBSes endowed the material surface with superhydrophobic performance with a water contact angle of 157.0° and a sliding angle of 1.5°.

Keywords: miktoarm star copolymer; isotactic-polypropylene; atactic-polystyrene; aggregation morphology

1. Introduction

The design of polymer topology provides convenient ways to control the properties of materials. In the past decades, the self-assembly of linear block copolymers in selective solutions has been a very important area in both experimental and theoretical research [1–6]. This interest is mainly due to the application of block copolymer self-assembly in functional materials and nanoscale devices. For instance, amphiphilic diblock copolymers performing various self-assembly behaviors in selective solvents have offered opportunities for novel bionic applications, imitating the vast extraordinary morphologies on biological surfaces in nature that exhibit peculiar performances such as super-water-repellent properties [7–9]. Xu et al. [10] easily fabricated a superhydrophobic surface with a bionic micro-nanoscale binary structure (MNBS) from a common isotactic-polypropylene/poly(methyl methacrylate) diblock copolymer (iPP-b-PMMA) based upon the principle of micelles, where diblock copolymers usually form in selective solvent. In N,N′-dimethylformamide (DMF), the iPP-b-PMMA formed a micelle solution, and each micelle was composed of an insoluble iPP core and a soluble PMMA shell; thus, through a one-step casting process, a material surface with bionic superhydrophobicity was obtained. The surface possessed an MNBS similar to that of a lotus leaf, where every microscale papilla (1–2 µm) is covered by nanoscale papillae (50–200 nm) [8,11,12]. This strategy provided a replacement for traditional complex superhydrophobic surface preparation technology, which combines surface energy reduction [13] with surface roughness improvement [14,15].

Star-like copolymers are branched macromolecules that are connected by several linear arms jointed at one junction point. They have hydrodynamic radii smaller than those of linear copolymers.
with similar molecular weights [1,5]. They have a compact and three-dimensional structure with a large surface area. Heteroarm star copolymers, including block-arm copolymers ((AB)x) and miktoarm copolymers (ABC or A,B,y) exhibit many unique micellar properties different from block copolymers, which has been discussed in a series of experimental studies [16–18]. Take miktoarm stars A,B,y, for example: compared to the linear diblock copolymer AB, A,B,y exhibits more complicated behaviors. Pispas et al. [19,20] compared the polystyrene/polysoprene (SxI) miktoarm stars S12 and S21 to diblock SI and found that the aggregation numbers of their micelles in n-decane increased in the order S12 < S21 < SI, indicating that the influence of star architecture on micellization is more complex than in the corresponding linear block copolymer.

Since Xu’s pioneering work [10] proved that by benefiting from the crystallinity and solvency resistance of iPP, even an ordinary diblock copolymer (iPP-b-PMMA) could display advantages in MNBS surface fabrication, we could expect that iPP miktoarm star copolymers would exhibit a more diversified performance due to the complexity of the miktoarm star copolymer architecture. Although a series of well-defined iPP block and graft copolymers are emerging from progress in propylene coordination polymerization technology [21–23], the synthesis of miktoarm star-shaped iPP has not been reported. This is mainly due to an unavoidable chain transfer reaction at the iPP initiating end and an inert feature at the iPP “arm” fabrication.

Recently, we reported an efficient route to synthesize iPP star-like homopolymers through an arm-first approach via a designed styril-capping procedure in propylene polymerization. In this approach, a reactive iPP precursor containing a methoxysilane terminal end was fabricated for the first time [24]. Based upon this technique, in the present work a series of isotactic-polypropylene/atactic-polystyrene (iPP/aPS) miktoarm star copolymers PxaSy (x and y represent the arm numbers) were synthesized for the first time, and the influence of iPP/aPS miktoarm star copolymer architecture on their aggregation morphology and surface superhydrophobic properties was investigated in detail.

2. Materials and Methods

2.1. Materials and Measurements

All O2 and moisture-sensitive manipulations were carried out inside an argon-filled vacuum atmosphere dry-box. Chemical pure-grade tetrahydrofuran (THF), hexane, and toluene were refluxed over Na/benzophenone. N,N’-dimethylformamide (DMF), 4-chlorostyrene and SiCl4 were purchased from Aladdin Company (Shanghai, China). The metalloocene catalyst rac-C2H4(Ind)2ZrCl2 was from J&K Chemical (Beijing, China). Methylaluminoxane (MAO) was purchased from Energy Chemical (Shanghai, China) and was dried under vacuum to remove trimethylaluminum (TMA). The resulting dry MAO (dMAO) was diluted in toluene. The free radical initiator 2,2′-azobis(isobutyronitrile) (AIBN) from Energy Chemical was purified through recrystallization twice from methanol. Bromobenzene, CS2, and stannous octoate (SnOct2) were obtained from Energy Chemical and were used as received; and 4-(chloromethyl)phenyl trimethoxysilane (90%) was purchased from Alfa Aesar (Tianjin, China) and was used as received. Styrene was purified by distillation under reduced pressure to remove the inhibitor. Polymerization-grade propylene was purchased from Dalian Guomgming Gas Company (Liaoning, China).

All ambient-temperature 1H-NMR spectra were measured in chloroform-d at 25 °C with a Bruker Avance III-500 instrument (Karlsruhe, Germany). All high-temperature 1H-NMR and 13C-NMR spectra were recorded in 1,1,2,2-tetrachloroethane-d2 at 100 °C with a Vaian DLG 400 instrument (PaloAlto, CA, USA). Polymer characterizations with high-temperature gel permeation chromatography (GPC) were carried out on PL-GPC220 equipment (South Queensferry, UK). A differential refractive index detector, a capillary viscometer, and a two-angle light-scattering (LS) detector were equipped. The detecting angles of the light-scattering detector were 15° and 90°. Here, 1,2,4-trichlorobenzene was used as the eluent, and the test was carried out at 150 °C with a flow rate of 1.0 mL/min. Narrow
molecular-weight-distributed polystyrene samples were used for calibration as standards. The melting curves of the polymers were measured by differential scanning calorimetry (DSC, TA Q2000, New Castle, PA, USA) with a heating and cooling rate of 10 °C/min under a nitrogen atmosphere. The second-scan data were collected to remove any heat history. The polymer morphology was examined by scanning electron microscopy (SEM, Hitachi SU8200 instrument, Tokyo, Japan), and the acceleration voltage was 5 kV. All samples were Pt-coated before SEM investigation. TEM images were collected using a transmission electron microscopy Hitachi HT7700 EXALENS (Tokyo, Japan) operating at 100 keV. The specimens were prepared by drop-casting the polymer dispersion onto a carbon-coated copper grid. The water contact angle (WCA) was measured with a contact angle detector (Powereach JC2000 D2W, Shanghai Zhongchen Digital Technology Apparatus Co. Ltd, Shanghai, China). The WCA value was obtained with a constant volume of water (4 μL) by averaging five results at different positions on the same sample. The water contact angle was measured by inclining the specimen on an inclinable platform.

2.2. Synthesis of iPP and aPS Arm Precursors

Propylene polymerization was conducted in a 250-mL round-bottomed flask with 50 mL of toluene. A typical reaction involved the sequential addition of 15 mmol of (p-vinylphenyl)trichlorosilane (the synthesis route was shown in a previous work [24]), 8 mmol of dMAO, and 4 μmol of metallocene catalyst (rac-C2H4(Ind)2ZrCl2) into the reaction flask. The polymerization temperature and propylene gas pressure were set at 30 °C and 1 atm, respectively. After 15 min, the polymerization was terminated by pouring the polymer solution into absolute methanol: then iPP with a methoxysilane terminal group was obtained. The resulting polymer was washed with methanol, filtered, and dried under vacuum for 24 h at 50 °C. Finally, methoxysilane-terminated iPP was obtained.

Atactic polystyrene (aPS) was synthesized by reversible addition-fragmentation chain transfer (RAFT) polymerization of styrene in toluene solvent with a monomer volume concentration of 50%. AIBN was used as the initiator and 4-(trimethoxysilyl)benzyl dithiobenzoate (TBDB) (synthesis route is shown in Chart 1 according to the literature [25]) as the RAFT agent. The molar ratio of St/TBDB/AIBN was set as 50/1/0.2, 100/1/0.2, and 150/1/0.2 for the synthesis of PS-1, PS-2, and PS-3, respectively. The reaction was allowed to proceed at 80 °C for 48 h, and the resulting solution was precipitated, washed with methanol, filtered, and dried under vacuum for 24 h at 50 °C. Finally, aPS pink powder was obtained.

![Chart 1. Synthetic route of RAFT agent TBDB.](image)

2.3. Synthesis of iPP/aPS Miktoarm Star Copolymers

Copolymerization was conducted in a 50-mL round-bottomed flask. In a typical miktoarm copolymer (run S-1 in Table 2) synthesis procedure, a mixture of 0.18 g (0.042 mmol) methoxysilane-terminated aPS and 0.82 g (0.125 mmol) methoxysilane-terminated iPP with 5 wt% stannous octoate (SnOct2) [26] was dissolved in 5 mL of toluene under nitrogen. The mixture was stirred for 3 h at 120 °C (the reaction mechanism is shown in Chart 2). The resulting product, the miktoarm star copolymer iPP/aPS, was precipitated with methanol, then washed with ethanol, and finally dried under vacuum at 50 °C for 24 h: 1.0 g polymer was obtained. The possible aPS and star-aPS homopolymers were removed through THF-dialyzing at room temperature for 24 h, and the possible iPP and star-iPP homopolymers were removed by Soxhlet extraction with boiling THF over 10 h (collecting the soluble part to get the miktoarm star copolymer, as shown in Table S1). Finally, the miktoarm star polymer S-1 was obtained.
Chart 2. Reaction mechanism of intermolecular elimination catalyzed by SnOct₂.

3. Results and Discussion

The methoxysilane-capped iPP (iPP arm) was synthesized through a facile “two-in-one” approach, as shown in Scheme 1, in which a steric jamming phenomenon (during the styril 2,1-insertion) was utilized in propylene polymerization, which we successfully implemented in previous work on the synthesis of star-iPP [24]. By using TMA-free dMAO, the chain transfer to aluminum was restrained, and thus the terminal groups included two kinds of structures, i.e., vinyl and methoxysilane ends. The $^1$H-NMR spectrum of the methoxysilane-terminated iPP obtained is shown in Figure 1. The peak at $\delta = 4.73$–4.80 ppm (peak e) was assigned to a vinyl chain end deriving from $\beta$-H elimination, and the signals attributed to the terminal methoxyl and phenyl groups can be observed at $\delta = 3.63$ ppm (peak a), $\delta = 7.24$ ppm (peak b), and 7.60 ppm (peak c). Then the terminal composition could be analyzed quantitatively. The methoxysilane capping ratio was evaluated quantitatively as 70.4%, and the stereoregularity (presented by the $mmm$ pentad content calculated by $^{13}$C-NMR [27]) of the iPP arm was 82% (Figure S1). The average molecular weight of the iPP arm precursor was determined to be 6500 g/mol by GPC.

The methoxysilane-terminated aPS (aPS arm) was synthesized through a RAFT reaction. AIBN was used as the initiator and TBDB as the RAFT agent, as depicted in Scheme 1. In the TBDB, the $C_6H_5-(C=S)-S-$ and $-C_6H_4-$ moiety exhibited characteristic $^1$H-NMR resonances (in Figure 2) at $\delta = 8.01$–7.40 ppm originating from the protons d and e. Peaks at 4.62 ppm (g) and 3.61 ppm (f) represent the protons of the methylene adjacent to the S atom and methoxy groups adjacent to the Si atom, respectively. For the polymers, the $^1$H-NMR spectra presented signals ascribed to proton c at around 7.10 and 6.59 ppm and to protons a and b around 1.2–2.0 ppm, which belonged to the styrene units. Moreover, due to the living feature of RAFT polymerization, three Si(OCH₃)₃-terminated aPSES with varied number average molecular weights of 4400 (aPS-1), 8300 (aPS-2), and 11700 (aPS-3) were synthesized easily, as displayed in Table 1.

Scheme 1. Synthetic route of iPP/aPS miktoarm star copolymers via arm-first approach.
Having fabricated the iPP and aPS arms, an intermolecular elimination reaction was carried out to synthesize the miktoarm star copolymers in toluene solution at 120 °C catalyzed with SnOct2. A series of miktoarm star copolymers was synthesized by changing the aPS arm length and adjusting the feeding ratio of the aPS arm and the iPP arm, as shown in Table 2. Figure 3 exhibits $^1$H-NMR spectra of the resulting miktoarm star copolymers. The disappearance of iPP’s terminal methoxyl group at $\delta = 3.63$ ppm (peak a in Figure 1) and the disappearance of aPP’s terminal methoxyl group at 3.61 ppm

![Figure 1](image1.png)

**Figure 1.** $^1$H-NMR spectrum of methoxysilane-terminated iPP (iPP arm). Solvent (*): 1,1,2,2-tetrachloroethane-$d_2$.

![Figure 2](image2.png)

**Figure 2.** $^1$H-NMR spectra of TBDB and methoxysilane-terminated aPSes (aPS arms). Solvent (*): 1,1,2,2-tetrachloroethane-$d_2$.

| Samples | $M_n$ a (g/mol) | $M_{peak}$ a (g/mol) | $D$ |
|---------|----------------|----------------------|-----|
| aPS-1   | 4400           | 6800                 | 1.9 |
| aPS-2   | 8300           | 12,500               | 1.8 |
| aPS-3   | 11,700         | 20,700               | 1.7 |

*a The average molecular weight $M_n$, and the peak molecular weight $M_{peak}$ were determined by high-temperature GPC with a light-scattering detector.
(peak f in Figure 2) indicated the elimination reaction. Since the possible byproducts (star-aPS and star-iPP homopolymers) and the unreacted arms were removed by ambient temperature THF-dialysis (to remove the aPS) and by boiling THF-Soxhlet extraction (to remove the iPP), the composition of the miktoarm star copolymers could be calculated from the $^1$H-NMR results.

Table 2. Synthesis and characterization of iPP/aPS miktoarm star copolymers.

| Sample | aPS Precursors | aPS/iPP (mol/mol) | aPS/iPP (%) | iPP (%) | $M_n$ (g/mol) | $M_{peak}$ (g/mol) | $D$ | $AN_{aPS}$ | $AN_{iPP}$ | $AN_{total}$ | $T_m$ (°C) | $\Delta H_m$ (J/g) | $T_c$ (°C) | $\Delta H_c$ (J/g) | $X_{c,iPP}$ (%) |
|--------|----------------|-------------------|-------------|---------|---------------|-------------------|-----|------------|-------------|--------------|-----------|-----------------|---------|-----------------|-------------|
| S-1    | aPS-1          | 1/3               | 52.9        | 9.7     | 6600          | 13,100           | 2.0 | -          | -           | -            | 131.3     | 64.0           | 102.5   | 69.1            | 38.8       |
| S-2    | aPS-2          | 1/3               | 56.1        | 4.3     | 6600          | 13,100           | 2.0 | -          | -           | -            | 131.3     | 64.0           | 102.5   | 69.1            | 38.8       |
| S-3    | aPS-3          | 1/3               | 52.9        | 9.7     | 6600          | 13,100           | 2.0 | -          | -           | -            | 131.3     | 64.0           | 102.5   | 69.1            | 38.8       |
| S-4    | aPS-4          | 1/3               | 56.1        | 4.3     | 6600          | 13,100           | 2.0 | -          | -           | -            | 131.3     | 64.0           | 102.5   | 69.1            | 38.8       |

*Condition of synthesis of miktoarm star copolymers: SnOct$_2$ = 5 wt%, $T = 120$ °C, $t = 3$ h. $^b$ aPS-arm/iPP-arm feeding ratio; $^c$ iPP/aPS is the aPS-arm/iPP-arm ratio incorporated into the miktoarm star copolymers determined by $^1$H-NMR, and iPP is the propylene content in the miktoarm star copolymers determined by $^1$H-NMR; $^d$ the average molecular weight $M_n$, and the peak molecular weight $M_{peak}$ were determined by high-temperature GPC with a light-scattering detector; $^e$ in the miktoarm star copolymers, the aPS arm number $AN_{aPS}$ and the iPP arm number $AN_{iPP}$ were calculated by combining the $^1$H-NMR and GPC data, and the total arm number was $AN_{total} = AN_{aPS} + AN_{iPP}$; $^f$ determined by DSC (Figure S2); $T_m$, the melting point; $T_c$, the crystalline point; $\Delta H_m$, the melting enthalpy; $\Delta H_c$, the crystalline enthalpy; $X_{c,iPP}$, crystallinity of iPP calculated by calorimetry.

A detailed structure in the miktoarm star copolymers was detected by GPC equipped with light-scattering detector GPC-LS (Figure 4). The polymer absolute molecular weights are summarized in Table 2. Combined with the $^1$H-NMR results, the average arm number of aPS and iPP in each miktoarm star copolymer, $AN_{aPS}$ and $AN_{iPP}$, respectively, was calculated according to the following formulae (Equations (1) and (2)):

$$M_{aPS} \times AN_{aPS} + M_{iPP} \times AN_{iPP} = M_{peak-star},$$

$$\frac{(M_{iPP} \times AN_{iPP})/42}{(M_{iPP} \times AN_{iPP})/42 + (M_{aPS} \times AN_{aPS})/104} \times 100 = iPP \text{ (mol%)},$$

in which $M_{aPS}$ and $M_{iPP}$ are the peak molecular weights ($M_{peak}$ in Tables 1 and 2) of aPS and iPP, respectively; $M_{peak-star}$ is the peak molecular weight of the miktoarm star polymer determined by GPC; and iPP (mol%) is the propylene content (data shown in Table 2) in the miktoarm star copolymers determined by $^1$H-NMR. In order to give relatively proximate and unified results, the average molecular weight was calculated from the peak molecular weight ($M_{peak}$). The total arm number $AN_{total}$ was the
sum of $AN_{aPS}$ and $AN_{iPP}$. The schematics of all of the miktoarm star copolymers are summarized in Table 3.

![GPC-LS curves of iPP/aPS miktoarm star copolymers](image)

**Figure 4.** GPC-LS curves of iPP/aPS miktoarm star copolymers (elucent: 1,2,4-trichlorobenzene; temperature: 150 °C).

**Table 3.** Schematics of miktoarm star copolymers $P_x S_y$ with different lengths of soluble aPS arms in selective solvent DMF.

| Miktoarm Stars Synthesized in This Work |  |
|----------------------------------------|--|
| iPP: ![iPP](image)                     | aPS: ![aPS](image)  |
| $S-1$ ($P_2 S_1$)                      | $S-2$ ($P_3 S_1$)  |
| ![S-1](image)                         | ![S-2](image)  |
| $S-3$ ($P_2 S_2$)                      | $S-4$ ($P_2 S_2$) |
| ![S-3](image)                         | ![S-4](image)  |

The weak interaction between selective solvents and insoluble blocks in polymers is the cause of micelle formation. These insoluble blocks are far away from the solvent and aggregate with each other to form micelles [28–30]. In this work, DMF was chosen as the selective solvent. The direct dissolution of iPP/aPS miktoarm star copolymers in DMF was not easy and can be attributed to the crystallinity of iPP and the high glass transition temperature ($T_g$) of aPS. The star polymer was first dispersed in DMF, and the mixture was heated to 60 °C to accelerate dissolution. The stock solution was further dispersed by ultrasonic treatment in ambient atmosphere for an additional 2-h period to ensure complete dispersion of the sample. Using the above sample preparation protocol, semitransparent micelle solution was obtained. No polymer precipitation was observed in the miktoarm star solutions after standing for 3 days. A Tyndall effect was observed in the miktoarm star copolymer solutions (Figures 5 and S3).
The MNBS surfaces were able to be formed through casting of the polymer micelles at relatively low concentrations (C = 0.5 mg/mL in selective solvent DMF, much lower than in the iPP-/PMMA system, which was reported as 50 mg/mL [10]). Using a dropper to absorb the dispersion, they were dropped on the slide and dried under vacuum at room temperature for 12 h. As the images show in Figure 6, the interplay between the soluble and insoluble parts in these systems, which influence the aggregation morphology, seemed to be rather complex. Polymers S-1 and S-4 presented granular particles with diameters of 100–200 nm, and polymers S-2 and S-3 exhibited a rod-like shape, in which S-2 aggregated to dumbbell-like rods with a diameter of ~3 μm and a length of ~6 μm, whereas S-3 formed tiny rods about 100 nm in diameter and 1 μm in length.

Figure 5. Photographs of iPP/aPS miktoarm star polymer solutions irradiated by a laser beam after three days.

Figure 6. The first and second rows: SEM images of surfaces cast from the iPP/aPS miktoarm star copolymer solutions; the bottom row: TEM images of the iPP/aPS miktoarm star copolymers drop-cast from the DMF solution.
When we compared three miktoarm star polymers with single but different lengths of soluble arms, that is, S-1, S-2, and S-3, an aggregation size order of S-1 (S_{short}) < S-3 (S_{long}) < S-2 (S_{medium}) was observed. This trend was contrary to the common rule of block copolymers. In block copolymers, the aggregation number depends mainly on the insoluble block length rather than the soluble block length [28]. In P$_3$S$_3$ miktoarm stars, however, as equal numbers (AN$_{aPS}$ = 1) of the corona segment were connected to two or three iPP chains at the same junction point, as depicted in Figure 7a, a short aPS arm (S-1) resulted in not only a considerable reduction of the corona thickness and overall size of the micelles, but also the isolation of the particles from each other without apparent entanglement. The formation of an iPP core in DMF resulted in the curvature of the core–corona interface toward the two iPP arms of the miktoarm copolymer. This is not a comfortable situation for the iPP arms, as they have to be accommodated in a small space. Increasing the length of aPS improved the solubility of the copolymer and thus favored more elongated structures, as shown in Figure 7b,c. A more elongated/bigger core released some of the crowding [20]. In this way, a larger size of the whole micelle was produced in S-2. However, further extension of the aPS length (or volume) contrarily compressed the iPP core space and reduced the micelle size (S-3); thus, medium-sized aggregation formed. The coronal chain stretching and copolymer topology around the junction point are important factors that determine micellar size, as well as the aggregation morphology.

Figure 7. Schematics of iPP/aPS miktoarm star copolymers with different lengths of soluble aPS arms in selective solvent DMF: (a) S-1, (b) S-2, and (c) S-3.

Comparing S-2 (P$_3$S$_1$) and S-4 (P$_2$S$_2$), which possessed approximately equal overall molecular weights and arm numbers, their aggregation sizes (diameters) increased in the order S-4 (P$_2$S$_2$) < S-2 (P$_3$S$_1$). This order was similar to that observed in polystyrene/polyisoprene miktoarm stars (S$_x$I$_y$) in Pispas’s work [20]. That work compared S$_1$I$_2$ and S$_2$I to diblock SI and found that all samples formed spherical micelles in selective solvent, n-decane (for polyisoprene). Aggregation numbers increased in the order S$_1$I$_2$ < S$_2$I < SI. Borisov et al. [17] examined how the A$_x$B$_y$ miktoarm polymer parameters affect the equilibrium morphology of self-assembling aggregates and the stability range of classical morphologies (sphere, cylinder, and lamella). According to their prediction, an increase in the number of soluble arms in the miktoarm star (keeping the total number of monomer units in soluble blocks constant) would stabilize the spherical geometry of self-assembled micelles, which is coincident with sample S-4 presenting a smaller and more compact spherical morphology than sample S-2 did.

Overall, the most probable cause for the observed surface morphology was a complex combination of copolymer composition, macromolecular architecture, and the solvent. The self-assembly of miktoarm star copolymers in selective solvent is often dominated by competition between the chain-stretching energy in the core, the interfacial energy, and the repulsion energy among the coronal chains [6,31]. Moreover, iPP/aPS miktoarm star copolymers, to some extent, belong to rod–coil copolymers [16], which contain crystallizable rod-like iPP and flexible coil-like aPS moieties. Their assembly behaviors might be different from coil–coil S$_x$I$_y$ miktoarm stars in morphology because of the geometric disparity between the rod and coil segments and the anisotropic interactions between rod blocks, which form crystalline structures.

The rough surfaces of the iPP/aPS miktoarm star copolymers presented superhydrophobicity. The contact angles of 4-μL water drops on the surfaces S-1, S-2, S-3, and S-4 were 153.0°, 153.5° 152.8°, and 134.5°, respectively. Although their aggregation sizes varied in orders of magnitude, they all possessed a MNBS morphology of nanoscale papillae covered on each microscale particle: the miktoarm star polymer micellar stacking formed microscale roughness, while the curvature of micelles on the surface...
of the aggregates provided nanoscale roughness, which endowed these surfaces with a bionic structure similar to a lotus leaf. The MNBS minimized the contact area and created more air space trapped between the water and the surface, which induced the improvement of surface hydrophobicity [13,14]. With the increase of aPS arms, the contact angles on the surfaces decreased to 134.5° (S-4), accompanied by adhesion between the microscale particles. However, a surface of S-2/S-3 mixture (1:1, w/w) cast from DMF exhibited a multilevel scale structure with a high contact angle of 157.0° and a very low sliding angle (α) of 1.5° (sample S-(2 + 3) in Figures 8 and S4), indicating a superhydrophobic and self-cleaning surface was achieved.

![Contact angle of water drops on the surfaces cast from the iPP, aPS, and iPP/aPS miktoarm star copolymer solutions](image)

**Figure 8.** Contact angle of water drops on the surfaces cast from the iPP, aPS, and iPP/aPS miktoarm star copolymer solutions and the sliding angle (α) of the surface of the S-2/S-3 mixture S-(2 + 3).

### 4. Conclusions

In summary, in this work, a series of iPP/aPS miktoarm star copolymers (P_xS_y) were synthesized via an arm-first approach, and the polymer architectures were fabricated by designing the arm length and the arm number. The polymer morphologies, including the MNBS shape and size, were greatly influenced by the P_xS_y architecture, indicating that the aggregation mechanism for miktoarm star copolymers is a complex combination of polymer composition, molecular architectural effects, and the solvent. The very preliminary nature of the results based on the limited set of experiments became clear. Multilevel bionic MNBS could be obtained from iPP/aPS miktoarm star copolymer micelles, which produced superhydrophobic properties even though the surface morphology varied with the macromolecular architecture. The experimental results will help in understanding the principles governing the organization of miktoarm star structures constructed in solution and will provide suggestions for designing polymers for specific applications such as super-water-repellent materials or anisotropic particles.

**Supplementary Materials:** The following are available online at http://www.mdpi.com/2073-4360/11/10/1574/s1.

**Author Contributions:** Y.W. and X.L. performed the experiments, analyzed the experimental results, and wrote the paper; L.L. also contributed to the analysis of the experimental results; H.N. supervised the whole procedure, analyzed the data, and wrote the paper.

**Funding:** This work was financially supported by the National Natural Science Foundation of China (No. 21374121) and the Fundamental Research Funds for the Central Universities (No. DUT17LAB14).

**Conflicts of Interest:** The authors declare no conflicts of interest.
References

1. Riess, G. Micellization of block copolymers. *Prog. Polym. Sci.* 2003, 28, 1107–1170. [CrossRef]
2. Li, Z.; Kesselman, E.; Talmor, Y.; Hillmyer, M.A.; Lodge, T.P. Multicompartment Micelles from ABC Miktoarm Stars in Water. *Science* 2004, 306, 98–101. [CrossRef] [PubMed]
3. Moughton, A.O.; Hillmyer, M.A.; Lodge, T.P. Multicompartment Block Polymer Micelles. *Macromolecules* 2012, 45, 2–19. [CrossRef]
4. Zhulina, E.B.; Borisov, O.V. Theory of Block Polymer Micelles: Recent Advances and Current Challenges. *Macromolecules* 2012, 45, 4429–4440. [CrossRef]
5. Zhang, Q.; Fan, G.; Zhao, N.; Guo, X.; Xu, J.; Dong, J.; Zhang, L.; Zhang, Y.; Han, C.C. Facile Screening of Various Micellar Morphologies by Blending Miktoarm Stars and Diblock Copolymers. *ACS Macro Lett.* 2017, 6, 711–715. [CrossRef]
6. Nakajima, A.; Fujishima, A.; Hashimoto, K.; Watanabe, T. Preparation of Transparent Superhydrophobic Boehmite and Silica Films by Sublimation of Aluminum Acetylaceionate. *Adv. Mater.* 1999, 11, 1365–1368. [CrossRef]
7. Youngblood, J.P.; McCarthy, T.J. Ultrahydrophobic Polymer Surfaces Prepared by Simultaneous Ablation of Polyprrylene and Sputtering of Poly(tetrafluoroethylene) Using Radio Frequency Plasma. *Adv. Mater.* 2003, 15, 1174 11 of 12. [CrossRef]
8. Feng, L.; Li, S.; Li, Y.; Li, H.; Zhang, L.; Zhai, J.; Song, Y.; Liu, B.; Jiang, L.; Zhu, D. Super-Hydrophobic Surfaces: From Natural to Artificial. *Adv. Mater.* 2002, 14, 1857–1860. [CrossRef]
9. Xie, Q.; Xu, J.; Deng, L.; Jiang, L.; Tang, W.; Luo, X.; Han, C.C. Facile Creation of a Super-Amphiphobic Coating Surface with Bionic Microstructure. *Adv. Mater.* 2004, 16, 302–305. [CrossRef]
10. Xie, Q.; Fan, G.; Zhao, N.; Guo, X.; Xu, J.; Dong, J.; Zhang, L.; Zhang, Y.; Han, C.C. Facile Creation of a Bionic Super-Hydrophobic Block Copolymer Surface. *Adv. Mater.* 2004, 16, 1830–1833. [CrossRef]
11. Neinhuis, C.; Barthlott, W. Characterization and Distribution of Water-repellent, Self-cleaning Plant Surfaces. *Ann. Bot.* 1997, 79, 667–677. [CrossRef]
12. Barthlott, W.; Neinhuis, C. Purity of the sacred lotus, or escape from contamination in biological surfaces. *Planta* 1997, 202, 1–8. [CrossRef]
13. Youngblood, J.P.; McCarthy, T.J. Ultrahydrophobic Polymer Surfaces Prepared by Simultaneous Ablation of Polypropylene and Sputtering of Poly(tetrafluoroethylene) Using Radio Frequency Plasma. *Adv. Mater.* 2003, 15, 1365–1368. [CrossRef] [PubMed]
14. Miwa, M.; Nakajima, A.; Fujishima, A.; Hashimoto, K.; Watanabe, T. Effects of Surface Roughness on Sliding Angles of Water Droplets on Surperhydrophobic Surfaces. *Langmuir* 2000, 16, 5754–5760. [CrossRef]
15. Erbil, H.Y.; Demirel, A.L.; Avcı, Y.; Mert, O. Transformation of a Simple Plastic into a Superhydrophobic Surface. *Science* 2003, 299, 1377–1380. [CrossRef]
16. Zhang, J.; Chen, X.F.; Wei, H.B.; Wan, X.H. Tunable assembly of amphiphilic rod-coil block copolymers in solution. *Chem. Soc. Rev.* 2013, 42, 9127–9154. [CrossRef]
17. Zhulina, E.B.; Borisov, O.V. Effect of Block Copolymer Architecture on Morphology of Self-Assembled Aggregates in Solution. *ACS Macro Lett.* 2013, 2, 292–295. [CrossRef]
18. Tsiamantas, C.; Psarros, C.; Mays, J.W.; Pitsikalis, M. Micellization behavior of model asymmetric miktoarm star copolymers of the AA′B type, where A is polysisoprene and B is polystyrene. *Polym. J.* 2013, 45, 1216–1223. [CrossRef]
19. Pispas, S.; Hadjichristidis, N.; Potemkin, I.; Khokhlov, A. Effect of Architecture on the Micellization Properties of Block Copolymers: A2B Miktoarm Stars vs AB Diblocks. *Macromolecules* 2000, 33, 1741–1746. [CrossRef]
20. Sotiriou, K.; Nannou, A.; Velis, G.; Pispas, S. Micellization Behavior of PS(PI)3 Miktoarm Star Copolymers. *Macromolecules* 2002, 35, 4106–4112. [CrossRef]
21. Huang, H.; Niu, H.; Dong, J.Y. Synthesis of Azide End-functionalized Isotactic Polypropylene Building Block and Renewed Modular Synthesis of Diblock Copolymers of Isotactic Polypropylene and Poly(ε-caprolactone). *J. Polym. Sci. Part. A Polym. Chem.* 2011, 49, 2222–2232. [CrossRef]
22. Hustad, P.D. Frontiers in Olefin Polymerization: Reinventing the World’s Most Common Synthetic Polymers. *Science* 2009, 325, 704–707. [CrossRef]
23. Huang, H.; Niu, H.; Dong, J.Y. Synthesis and Crystallization Behavior Study of Syndiotactic Polystyrene-g-Isotactic Polypropylene (sPS-g-iPP) Graft Copolymers. *J. Polym. Sci. Part. A Polym. Chem.* 2011, 49, 2734–2745. [CrossRef]
24. Liu, X.; Niu, H.; Li, Y.; Dong, J.Y. New effort to synthesize star isotactic polypropylene. *Polym. Chem.* 2018, 9, 3347–3354. [CrossRef]

25. Guo, Y.F.; Liu, H.H.; Tang, D.D.; Li, C.X.; Zhao, Y.L. Facile synthesis of silica nanoparticles grafted with quaternized linear, comblike and toothbrushlike copolymers. *Polym. Chem.* 2015, 6, 2647–2658. [CrossRef]

26. Normand, F.; He, X.W.; Widmaier, J.M.; Meyer, G.C.; Herz, J.E. Linear polycondensation of α,ω-dihydroxy polydimethylsiloxane, catalyzed by stannous octoate. *Eur. Polym. J.* 1989, 25, 371–374. [CrossRef]

27. Busico, V.; Corradini, P.; Biasio, R.D.; Landriani, L. $^{13}$C NMR Evidence of the Copresence of $m$-Rich and $r$-Rich Sequences (Stereoblocks) in Polypropylene Molecules. *Macromolecules* 1994, 27, 4521–4524. [CrossRef]

28. Zhulina, E.B.; Adam, M.; LaRue, I.; Sheiko, S.S.; Rubinstein, M. Diblock Copolymer Micelles in a Dilute Solution. *Macromolecules* 2005, 38, 5330–5351. [CrossRef]

29. Fang, B.; Walther, A.; Wolf, A.; Xu, Y.; Yuan, J.; Muller, A.H.E. Undulated Multicompartiment Cylinders by the Controlled and Directed Stacking of Polymer Micelles with a Compartmentalized Corona. *Angew. Chem. Int. Ed.* 2009, 48, 2877–2880. [CrossRef]

30. Wang, X.; Davis, J.L.; Hinestrosa, J.P.; Mays, J.W.; Kilbey, S.M. Control of Self-Assembled Structure through Architecturally and Compositionally Complex Block Copolymer Surfactant Mixtures. *Macromolecules* 2014, 47, 7138–7150. [CrossRef]

31. Reuther, J.F.; Siriwardane, D.A.; Campos, R.; Novak, B.M. Solvent Tunable Self-Assembly of Amphiphilic Rod–Coil Block Copolymers with Chiral, Helical Polycarbodiimide Segments: Polymeric Nanostructures with Variable Shapes and Sizes. *Macromolecules* 2015, 48, 6890–6899. [CrossRef]

© 2019 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/).