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Synthesis of Block Copolymers and Asymmetric Star-Branched Polymers Comprised of Polyacetylene and Polystyrene Segments *via* Ionic Bond Formation

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Summary. Novel ion-bonded AB diblock copolymers and three-arm AB_2 asymmetric star-branched polymers comprised of polyacetylene (A) and polystyrene (B) segments have been synthesized by the stoichiometric reaction of *tert*-amine-chain-end-functionalized poly(phenyl vinyl sulfoxide)s with either chain-end- or in-chain-carboxylated polystyrenes to link the two polymer segments *via* ionic bond, followed by thermal treatment to convert their poly(phenyl vinyl sulfoxide)s to polyacetylene segments. Periodic lamellar morphologies were observed in the cast films of such polymers by TEM measurement. The isolation of the nano-size sheet consisting of polyacetylene lamellar layers was attempted.

Keywords. Anions; Carbanions; End-functionalized polymer; Interactions; Polymerizations.

Introduction

Block copolymers comprised of conducting conjugated polymer segments such as polyacetylenes, polyphenylenes, and poly(phenylenevinylene)s are receiving increasing attention because of their potential applications in the areas of electronic and optical devices [1–3]. These polymers are also expected to exhibit unique physical and mechanical properties in bulk and solution originating from the rigid rod-like structures of the conjugated polymer segments. These block copolymers were generally synthesized by the linking reaction of living anionic polymers with conjugated polymers or well-defined oligomers synthesized by stepwise reactions [4–7]. As an alternative route, several research groups proposed a "soluble precursor" method, in which soluble precursor polymer segments were in advance

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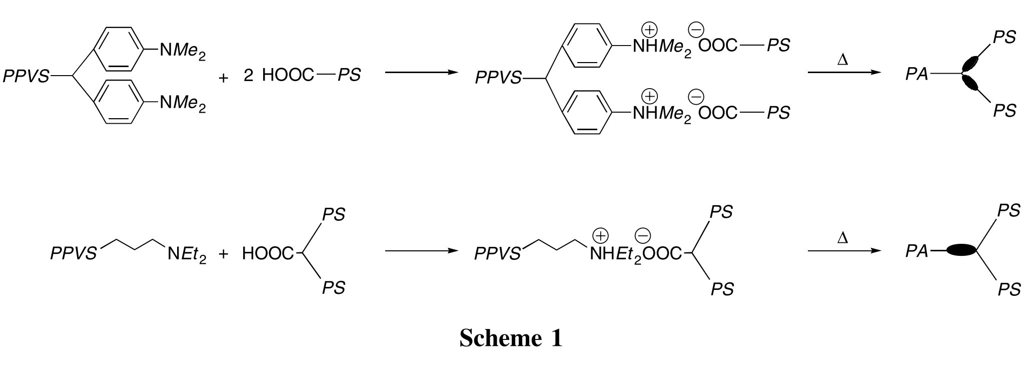
incorporated into the block copolymers obtainable by sequential living polymerization, followed by conversion to the corresponding conjugated polymer segments [8–15]. In practice, polystyrene-*block*-polyphenylene and polystyrene-*block*-polyacetylene were synthesized by this method.

Recently, we have proposed a promising methodology for the synthesis of block copolymers comprised of polyacetylene segments [16]. The methodology involves two synthetic steps: (a) the synthesis of ion-bonded block copolymer by the stoichiometric reaction of chain-end-carboxylated polystyrenes with *tert*-amine-chain-end-functionalized poly(phenyl vinyl sulfoxide)s, and (b) the complete conversion of poly(phenyl vinyl sulfoxide)s to polyacetylene segments by subsequent thermal treatment. Similarly, the synthesis of new asymmetric star-branched polymers comprised of polyacetylene segments has been reported.

Herein, we report on more detailed synthetic studies of block copolymers and asymmetric star-branched polymers by the above-mentioned methodology with use of different chain-functionalized polymers. The morphological study and attempts to isolate the nano-size sheet consisting of polyacetylene lamellar layers are also described.

Results and Discussions

Our synthetic approach herein used for the synthesis of ion-bonded block copolymers and asymmetric star-branched polymers comprised of polyacetylene and polystyrene segments is illustrated in Scheme 1. The synthesis of block copolymers is achieved by stoichiometrically reacting poly(phenyl vinyl sulfoxide) having *tert*-amine terminus with chain-end-carboxylated polystyrene to link the two polymer chains *via* ionic bond, followed by converting the poly(phenyl vinyl sulfoxide) chain to a polyacetylene segment by thermal treatment. The asymmetric star-branched polymers are synthesized by the following two routes: The first synthetic route involves the stoichiometric reaction of chain-end-functionalized poly(phenyl vinyl sulfoxide) with two *tert*-amine functionalities with chain-end-carboxylated polystyrene, followed by thermal treatment. In the second route, the star-branched polymers are synthesized by the reaction of poly(phenyl vinyl sulfoxide) with one



Scheme 1

tert-amine functionality with in-chain-carboxylated polystyrene. In order to realize such ion-bonded polymer syntheses, chain-end- and in-chain-carboxylated polystyrenes as well as poly(phenyl vinyl sulfoxide)s with one and two *tert*-amine functionalities are required as starting chain-functionalized polymers.

Preparation of tert-Amine-Chain-End-Functionalized Poly(phenyl vinyl sulfoxide)s

The anionic polymerization of phenyl vinyl sulfoxide was first reported in 1990 by *Hogen-Esch* and his coworkers [14, 15]. They demonstrated that the polymerization proceeds in a living manner to afford the polymers with controlled molecular weights and relatively narrow molecular weight distributions ($M_w/M_n = 1.2 \sim 1.4$). A series of well-defined block copolymers of phenyl vinyl sulfoxide with styrene was also synthesized. They also successfully demonstrated that the resulting polymer could be quantitatively converted into a polyacetylene segment only by thermal treatment. By this success, the poly(phenyl vinyl sulfoxide)s obtained by the living anionic polymerization become advantageous polyacetylene precursors soluble in organic solvents and well-controlled in chain length. Furthermore, a variety of molecular designs accessible through living polymerization become possible. Subsequently, the synthesis and application of structural similar block copolymers comprised of polyacetylene segments have been reported by several other research groups [17–19].

In general, molecular weight distributions of the polymers obtained by the anionic polymerization have been reported to be relatively but not extremely narrow, the M_w/M_n values being in between 1.2 and 1.4, or higher values [20]. Very recently, we have found that the addition of a 10-fold or more excess of LiCl can be effective to narrow the molecular weight distribution. For example, the M_w/M_n value of the resulting polymer was reduced considerably from 1.45 to 1.12 in the polymerization in *THF* at −78°C with 3-methyl-1,1-diphenylpentyllithium (*sec-Bu*Li/*DPE*) as an initiator. Therefore, the objective *tert*-amine-chain-end-functionalized polymers used in this study were prepared in the presence of a large excess of LiCl. In order to introduce the dimethylaniline moiety of *tert*-aromatic amine functionality at the initiating chain-end, the initiator was prepared from *sec-Bu*Li and 1-(4-*N*,*N*-dimethylaminophenyl)-1-phenylethylene (**1**). A new anionic initiator was also prepared from *sec-Bu*Li and 1-(4-(3-*N*,*N*-diethylaminopropyl)phenyl)-1-phenylethylene (**2**) and used in the polymerization to introduce aliphatic *tert*-amine functionality.

The results are summarized in Table 1. As can be seen, polymers ($M_n < 20$ K) with M_w/M_n values of less than 1.2 are usually obtained by the polymerization carried out in the presence of a large excess of LiCl. The additive effect of LiCl is thus evident. In the case of a high molecular weight polymer ($M_n = 36$ K), the M_w/M_n value was found to be 1.33. However, the addition of LiCl was still effective, since a multimodal distribution was observed in the polymer obtained without LiCl. The resulting polymers all possessed near predictable M_n values based on the ratios of [monomer] to [initiator]. Deviation of the M_n values between observed and predicted was observed when the target molecular weight was 20 K or higher, possibly due to impurities in phenyl vinyl sulfoxide difficult to be removed and/or

Table 1. Anionic polymerization of phenyl vinyl sulfoxide in *THF* at −78°C for 1–15 h[a]

Initiator[b] mmol	LiCl mmol	Monomer mmol	$M_n \times 10^{-3}$		
			Calcd	Obsd[c]	M_w/M_n[d]
*sec-Bu*Li/*DPE*, 0.124	–	5.85	7.40	9.01	1.45
*sec-Bu*Li/*DPE*, 0.0923	2.37	8.19	13.7	18.9	1.12
*sec-Bu*Li/**1**, 0.103	0.523	6.60	10.0	9.46	1.24
*sec-Bu*Li/**1**, 0.0943	2.08	7.45	12.3	18.0	1.10
*sec-Bu*Li/**1**, 0.115	1.75	12.9	17.4	36.0	1.33
*sec-Bu*Li/**2**, 0.148	1.80	12.1	12.8	11.6	1.17
*sec-Bu*Li/**2**, 0.125	1.91	15.9	19.8	20.6	1.29
Cumyl K/**3**, 0.0981	–	6.07	9.83	7.75	1.33

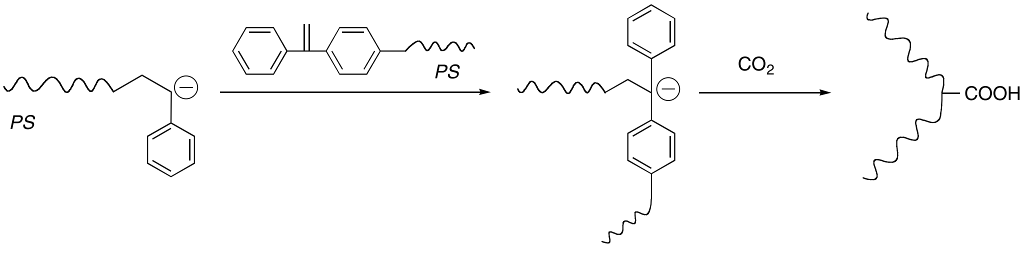
[a] Yields of polymer were quantitative; [b] **1**: 1-(4-*N*,*N*-dimethylaminophenyl)-1-phenylethylene, **2**: 1-(4-(3-*N*,*N*-diethylaminopropyl)phenyl)-1-phenylethylene, **3**: 1,1-bis(4-*N*,*N*-dimethylaminophenyl) ethylene, Cumyl K: cumyl potassium; [c] end-group analysis by ^{1}H NMR (see Experimental); [d] determined by SEC

unavoidable α-proton abstraction of monomer and the polymer. In each sample, dimethylanilino or 3-*N*,*N*-diethylaminopropyl group was quantitatively introduced as confirmed by ^{1}H NMR analysis.

Similarly, two dimethylanilino groups could be introduced at the initiating chain-end by the anionic polymerization with the initiator prepared from *sec-Bu*Li and 1,1-bis(4-*N*,*N*-dimethylaminophenyl)ethylene (**3**) in *THF* at −78°C. The *tert*-amine-chain-end-functionalized poly(phenyl vinyl sulfoxide)s thus synthesized are referred to as *PPVS*–*Ar*N*Me*$_2$, *PPVS*–C_3H_6N*Et*$_2$, and *PPVS*–(*Ar*N*Me*$_2$)$_2$, respectively.

Preparation of Chain-End- and In-Chain-Carboxylated Polystyrenes

Chain-end-carboxylated polystyrenes (*PS*-COOH) were prepared by the reaction of polystyryllithiums (*PS*Li) with CO_2 according to the method reported previously by *Quirk* and his coworkers [21]. The degrees of end-functionalization were determined by TLC-FID to be 91–98%. The synthesis of in-chain-carboxylated polystyrene (*PS*–(COOH)–*PS*) could be achieved by the addition reaction of a 1.1-fold excess of *PS*Li to chain-end-functionalized polystyrene with 1,1-diphenylethylene moiety, followed by treatment with CO_2 as illustrated in Scheme 2.



Scheme 2

Table 2. Chain-end- and in-chain-functionalized polystyrenes[a]

Type[c]	$M_n \times 10^{-3}$			Functionality[b] %
	Calcd	Obsd[d]	M_w/M_n[e]	
PS–COOH	6.75	7.10	1.02	97
PS–COOH	12.4	13.0	1.02	98
PS–COOH	15.4	15.2	1.04	91
PS–COOH	27.7	29.3	1.05	93
PS–(COOH)–*PS*	20.9	20.0	1.04	94
PS–(COOH)–*PS*	20.1	22.6	1.05	93
PS–*Ar*N*Me*$_2$	24.8	24.1	1.04	~100
PS–(*Ar*N*Me*$_2$)$_2$	10.0	10.0	1.04	~100

[a] Yields of polymers were always quantitative; [b] determined by TLC-FID; [c] *PS*–COOH: chain-end-carboxylated polystyrene, *PS*–(COOH)–*PS*: in-chain-carboxylated polystyrene, *PS*–*Ar*N*Me*$_2$: chain-end-functionalized polystyrene with *N*,*N*-dimethylaniline moiety, *PS*–(*Ar*N*Me*$_2$)$_2$: chain-end-functionalized polystyrene with two *N*,*N*-dimethylaniline moieties; [d] end-group analysis by ^{1}H NMR (see Experimental); [e] determined by SEC

SEC profile of the reaction mixture showed two distinct sharp single peaks corresponding to the objective *PS*–(COOH)–*PS* and the deactivated *PS*Li (presumably *PS*–COOH) used in excess in the reaction. The higher molecular weight fraction was isolated in 80% yield by fractional precipitation. The molecular weight measured by SEC agreed with that calculated. The degree of in-chain functionalization was determined to be 94% by TLC-FID analysis. The results are summarized in Table 2.

In order to use in the model reaction, *tert*-amine-chain-end-functionalized polystyrenes were also prepared by end-capping reaction of *PS*Li with either of **1** or **3**. They are referred to as *PS*–*Ar*N*Me*$_2$ and *PS*–(*Ar*N*Me*$_2$)$_2$, respectively. The results are also listed in Table 2.

Synthesis of Block Copolymers and Asymmetric Star-Branched Polymers via Ionic Bonds

Approaches to the synthesis of block copolymers by means of ionic bond formation between the terminal groups of two chain-end-functionalized polymers have been reported by several research groups [22–29]. Furthermore, *Hadjichristidis* and his coworkers have recently demonstrated the possible synthesis of four-arm asymmetric star-branched polymers by the similar ionic interaction of chain-end-functionalized polyisoprene with a SO$_3$H group and polystyrene having three dimethylamino termini [30]. However, they couldn't have the strong evidence of the quantitative ionic bond formation of three functional groups at one chain-end, although the higher-order structure was observed by SAXS and TEM. To the best of our knowledge, no synthetic example of ion-bonded block copolymers and asymmetric stars containing poly(phenyl vinyl sulfoxide) and polyacetylene segments has been reported so far.

Recently, we have reported the synthesis of new AB diblock copolymer and three-arm AB$_2$ asymmetric star-branched polymer comprised of conductive polyacetylene (A) and polystyrene (B) segments linked *via* ionic bond $(\mathrm{NH}(Me)_2{}^{+}\ {}^{-}\mathrm{OCO})$ by the stoichiometric reaction of either *PPVS*–*Ar*N*Me*$_2$ or *PPVS*–(*Ar*N*Me*$_2$)$_2$ with *PS*–COOH [16]. Herein, the synthesis of such polymers is investigated in more detail in order to establish the methodology used for the synthesis as a more general procedure.

As previously reported, it was found that *PPVS*–N*Me*$_2$ was stoichiometrically reacted with *PS*–COOH to link the two polymer chains *via* ionic bond to afford the AB diblock copolymer. The block copolymer formation ($M_w = 13$ K) was evidenced by ^{1}H NMR, FT-IR, and SLS analyses. In this study, the synthesis of a higher molecular weight block copolymer has been carried out by the same reaction of *PPVS*–N*Me*$_2$ ($M_w = 48$ K) with *PS*–COOH ($M_w = 31$ K, COOH content = 93%) under the identical condition. SEC profile of the reaction mixture exhibited only overlapping two peaks corresponding to the starting chain-end-functionalized polymers. No peak for the expected diblock copolymer was observed at all in the same SEC profile. Thus, SEC was not effective for detecting the formation of this kind of ion-bonded block copolymer. This result is consistent with the previous result. On the other hand, the formation of block copolymer was strongly indicated by ^{1}H NMR and IR analyses, respectively. More indicatively, the M_w value of the resulting polymer was determined by SLS to be 69 K, but not 40 K of an average M_w value ((31 K + 48 K)/2). This value is very close to the target value of 70 K assuming that the two chain-end-functionalized polymers were linked to quantitatively form an AB block copolymer. Thus obviously, the higher molecular weight AB block copolymer could be formed *via* ionic bond without any difficulty.

A similar ion-bonded AB block copolymer was obtained by the reaction using *PPVS*–C_3H_6N*Et*$_2$ ($M_w = 14$ K) and *PS*–COOH ($M_w = 31$ K, COOH content = 93%). The M_w value of the resulting polymer determined by SLS was 44 K that agreed well with the expected value of 42 K. Thus, the aliphatic *tert*-amine functionality also works satisfactorily for the synthesis of ion-bonded block copolymer. All results are summarized in Table 3.

Table 3. Block and AB$_2$ star-branched polymers synthesized *via* ionic bond formation

Type	A		B		AB$_n$, $M_w \times 10^{-3}$	
	Polymer	$M_w \times 10^{-3}$	Polymer	$M_w \times 10^{-3}$	Calcd	Obsd[a]
AB	*PPVS*–*Ar*N*Me*$_2$	9.34	*PS*–COOH	7.24	16	13
AB	*PPVS*–*Ar*N*Me*$_2$	47.9	*PS*–COOH	30.8	70	69
AB	*PPVS*–C_3H_6N*Et*$_2$	13.6	*PS*–COOH	30.8	42	44
AB$_2$	*PPVS*–(*Ar*N*Me*$_2$)$_2$	9.34	*PS*–COOH	7.24	23	22
AB$_2$	*PPVS*–(*Ar*N*Me*$_2$)$_2$	7.76	*PS*–COOH	30.8	63	42
A$_3$	*PS*–(*Ar*N*Me*$_2$)$_2$	13.8	*PS*–COOH	15.8	40	24
A$_3$	*PS*–*Ar*N*Me*$_2$	25.1	*PS*–(COOH)–*PS*	20.8	42	43
AB$_2$	*PPVS*–*Ar*N*Me*$_2$	19.8	*PS*–(COOH)–*PS*	20.8	38	28
AB$_2$	*PPVS*–*Ar*N*Me*$_2$	47.9	*PS*–(COOH)–*PS*	20.8	65	49
AB$_2$	*PPVS*–C_3H_6N*Et*$_2$	13.6	*PS*–(COOH)–*PS*	20.8	32	32
AB$_2$	*PPVS*–C_3H_6N*Et*$_2$	26.6	*PS*–(COOH)–*PS*	23.7	47	54

[a] Determined by SLS in *THF*

We also reported that a three-arm AB_2 asymmetric star-branched polymer was synthesized by the reaction of *PPVS*–(*Ar*N*Me*$_2$)$_2$ ($M_w = 9.3$ K) with *PS*–COOH ($M_w = 7.2$ K, COOH content = 97%). Very unfortunately, however, the synthesis of the star-branched polymer could not be reproduced at all, although the reason is not clear at the present. Instead, the AB diblock copolymer ($M_w = 16$ K) was always obtained nearly quantitatively. Higher molecular weight chain-end-carboxylated polystyrene, *PS*–COOH ($M_w = 31$ K, COOH content = 93%), was also reacted with *PPVS*–(*Ar*N*Me*$_2$)$_2$ ($M_w = 7.8$ K) under the same conditions. In this case, the M_w value of the resulting polymer was determined by SLS to be 42 K. Again, this value was far from the molecular weight of the expected three-arm star ($M_w = 63$ K), but nearly equal to that of the AB block copolymer ($M_w = 38$ K) comprised of one poly(phenyl vinyl sulfoxide) segment and one polystyrene segment.

Since the incompatibility of two polymer segments can possibly be influenced in the reaction between polymer chains, a newly synthesized *PS*–(*Ar*N*Me*$_2$)$_2$ ($M_w = 14$ K) was reacted with *PS*–COOH ($M_w = 16$ K, COOH content = 91%) as a model reaction under the same conditions. The resulting polymer was found to have 24 K in M_w value determined by SLS. This is close to the M_w value (28 K) of the polymer formed by linking the two polystyrene segments. Thus, the result of model reaction also indicates the formation of block copolymer, but not the expected three-arm star-branched polymer. One more polymer segment seems to be no longer able to link to the block copolymer once formed. As often mentioned, SEC is not effective to detect the ion-bonded polymer and, therefore, the information on the real product(s) formed in the reaction is not available at the present time. In addition, the isolation of the product(s) by fractional precipitation was not successful. It is of course possible to speculate that the product is a mixture of a three-arm AB_2 star, an AB diblock copolymer, and two starting chain-end-functionalized polymers. However, we consider that the block copolymer may possibly be quantitatively formed in the reaction of *PPVS*–(*Ar*N*Me*$_2$)$_2$ with *PS*–COOH, since the M_w value of the resulting polymer always agreed well with that of the block copolymer in each instance under various conditions.

Since it seems difficult to synthesize the objective three-arm star by the reaction of *PPVS*–(*Ar*N*Me*$_2$)$_2$ with *PS*–COOH, we have designed a new combination of *PPVS*–*Ar*N*Me*$_2$ and in-chain-carboxylated polystyrene (*PS*–(COOH)–*PS*) for the synthesis of the AB_2 asymmetric star-branched polymers as illustrated in the above-mentioned Scheme 1. Prior to the synthesis of star-branched polymer, the model reaction was carried out between *PS*–*Ar*N*Me*$_2$ ($M_w = 25$ K) and *PS*–(COOH)–*PS* ($M_w = 21$ K, COOH content = 94%). Again, a direct evidence for the star-polymer formation was not provided by the SEC analysis of the reaction mixture. On the other hand, the M_w value of the resulting polymer determined by SLS was 43 K which is the same as that ($M_w = 42$ K) of the expected three-arm star-branched polymer formed by completely linking the two polystyrene chains. Accordingly, the synthesis of star was successfully achieved by the above-mentioned reaction.

On the basis of the success of the model reaction, two reactions were carried out between either *PPVS*–*Ar*N*Me*$_2$ ($M_w = 20$ K) or *PPVS*–*Ar*N*Me*$_2$ ($M_w = 48$ K) and *PS*–(COOH)–*PS* ($M_w = 21$ K, COOH content = 94%) under the same conditions. However, the observed M_w values of the resulting polymers obtained by both reactions were 28 and 49 K, respectively. These values were a little bit higher than

21 and 35 K which are the average M_w values of the starting polymers, but considerably smaller than 38 and 65 K which are the M_w values of the expected stars. Estimating from these M_w values, the three-arm AB_2 star-branched polymers were formed only in 43–48% yields. Thus, these results were not consistent with the result obtained by the model reaction and were unsatisfactory in terms of yield of star-branched polymer.

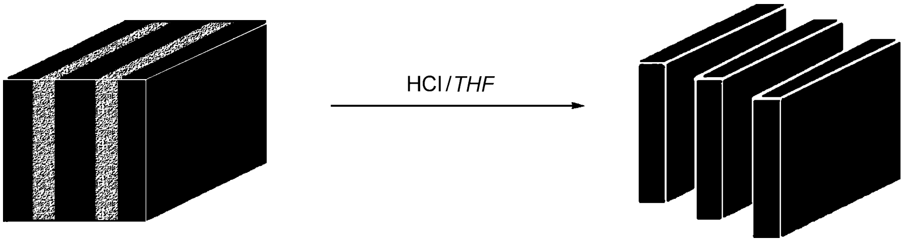
Next, we reacted *PPVS*–$C_3H_6NEt_2$ ($M_w = 14$ K) having a more basic amine terminus with the same in-chain-functionalized polystyrene, *PS*–(COOH)–*PS* ($M_w = 21$ K, COOH content = 94%). In this case, the M_w value of the resulting polymer was determined by SLS to be 32 K and was consistent with 32 K of the expected three-arm star-branched polymer. This may happen because the basicity of the terminal aliphatic *tert*-amine is much higher than that of the terminal dimethylaniline functionality, thus interacting more strongly with carboxylic acid to form a stable ionic bond. The effectiveness of the terminal aliphatic *tert*-amine was also demonstrated by the successful formation of another star-branched polymer with M_w value of 54 K. The star was obtained from *PPVS*–$C_3H_6NEt_2$ ($M_w =$ 27 K) with *PS*–(COOH)–*PS* ($M_w = 24$ K, COOH content = 93%). Thus, we were successful in synthesizing the objective three-arm AB_2 asymmetric star-branched polymer by using *PPVS*–$(CH_2)_3NEt_2$ in place of *PPVS*–*Ar*N*Me*$_2$ in the reaction with *PS*–(COOH)–*PS*.

Synthesis and Morphological Studies of Block Copolymer and AB_2 Asymmetric Star-Branched Polymer Comprised of Polyacetylene and Polystyrene Segments

Both the block copolymer ($M_w = 44$ K) and the three-arm AB_2 star-branched polymer ($M_w = 32$ K) newly synthesized in this study were cast into films, followed by heating at 150°C for 5 h. Their poly(phenyl vinyl sulfoxide) (*PPVS*) chains were converted to the corresponding polyacetylene (*PA*) segments by this thermal treatment as reported previously by several research groups [14, 15]. It was observed that the color of each film gradually changed from pale yellow to black characteristic to *PA*. The films were washed with toluene to remove by-products and characterized by FT-IR and TGA, respectively.

The strong IR absorption band at $1032\,cm^{-1}$ due to the S=O stretching was observed in the starting polymer films and disappeared after thermal treatment, indicating the complete conversion of the *PPVS* chains to *PA* segments. Weight losses by such conversion to *PA* segments could be clearly detected by TGA measurement. As expected, the observed weight losses were in good agreement with those calculated. Thus, new ion-bonded AB diblock copolymer as well as three-arm AB_2 asymmetric star comprised of *PA* and polystyrene segments were obtained.

Their *PA* segments were selectively stained with iodine vapor to clarify the morphological structures by TEM measurement. Similar to our results reported previously, periodic lamellar structures were observed in both films. As illustrated in Scheme 3, we attempted to isolate the nano-size sheet consisting of *PA* lamellar layers from the film by treatment with HCl in *THF*. The film of the block copolymer was similarly cast on mica, followed by thermal treatment. The resulting film on mica was washed several times with *THF* solution containing HCl. By this treatment, the ionic



Scheme 3

bond between *PA* and polystyrene segments may be cleaved from *PA*–$C_3H_6NHEt_2{}^+$ $^-$OCO–*PS* to *PA*–$C_3H_6NHEt_2{}^+Cl^-$ and *PS*–COOH. The polystyrene microdomain was removed from the film by washing with *THF* and, on the other hand, the *PA* layer might remain on mica due to its insolubility in *THF*. Although it was suggested by AFM measurement that the *PA* layer, that is nano-size sheet, shown in Scheme 3 was present in part, clear images could not be obtained by the interference from residual polystyrene segments which remained on the film. Since the methodology for the synthesis of ion-bonded block copolymers and asymmetric star-branched polymers has been established, morphological studies of the resulting polymers, followed by the isolation of their specially shaped nano-objects are now undertaken.

Conclusions

A series of AB diblock copolymers were quantitatively synthesized by the stoichiometric reaction of either *PPVS*–*Ar*NMe_2 (A) or *PPVS*–$C_3H_6NEt_2$ (A) with *PS*–COOH (B) to link the two polymer chains *via* ionic bond. Similarly, the synthesis of three-arm AB_2 asymmetric star-branched polymers was successfully achieved by the reaction of *PPVS*–$C_3H_6NEt_2$ with *PS*–(COOH)–*PS*. The resulting polymers all possessed predictable M_w values of the expected block copolymers and asymmetric stars. Furthermore, novel ion-bonded AB block copolymers and AB_2 asymmetric star-branched polymers comprised of polyacetylene and polystyrene segments have been obtained by thermal treatment of the resulting polymers at 150°C for 5 h to convert their *PPVS* chains to *PA* segments. The lamellar morphologies with *PA* layers were observed in the cast films of such block copolymers and asymmetric star-branched polymers. Unfortunately, the attempt to isolate the nano-size sheet consisting of polyacetylene layers by treatment with HCl in *THF* was not successful, although the formation was suggested by AFM.

The synthesis of ion-bonded asymmetric star-branched polymers having more arms and hyperbranched polymers consisting of polyacetylene segments is now undertaken. Furthermore, their morphological studies and isolation of specially shaped nano-objects derived from morphologies are also under way.

Experimental

Materials

THF was refluxed over sodium wire, distilled over $LiAlH_4$ under a nitrogen atmosphere, and then distilled from its sodium naphthalenide solution on the vacuum line (10^{-6} Torr). *sec*-Butyllithium (*sec-Bu*Li) was used as received. Cumylpotassium was prepared by the reaction of cumyl methyl ether with K–Na alloy in *THF* according to the previous method [31]. Styrene was purified by usual methods. Phenyl vinyl sulfoxide (*PVS*) was synthesized by the oxidation of phenyl vinyl sulfide prepared from benzenethiol and dibromoethane according to the method reported by *Paquette* and *Carr* [32]. It was purified by silica gel column chromatography (hexane/ethyl acetate = 9/1 *v*/*v*), followed by distillation three times over CaH_2. Finally, styrene and *PVS* were distilled on the vacuum line over dibutylmagnesium and CaH_2, respectively. 1,1-Diphenylethylene (*DPE*) was distilled over CaH_2 under reduced pressure and finally distilled from its *Bu*Li solution on the vacuum line. Lithium chloride was dried at 110°C overnight under high vacuum conditions. 1-(4-*N*,*N*-Dimethylaminophenyl)-1-phenylethylene (**1**) and 1,1-bis(4-*N*,*N*-dimethylaminophenyl)ethylene (**3**) were synthesized according to our previous method [16].

Measurements

Both ^1H and ^{13}C NMR spectra were measured on a Bruker DPX300 in $CDCl_3$. Chemical shifts were recorded in ppm downfield relative to $(CH_3)_4Si$ ($\delta = 0$) for ^1H NMR and relative to $CDCl_3$ ($\delta = 77.1$) for ^{13}C NMR as standards. Size exclusion chromatography (SEC) was measured by Tosoh HLC-8020 at 40°C with refractive index detection using *THF* as a carrier solvent at a flow rate of $1.0\,cm^3/min$. Static light scattering (SLS) measurement was performed on a Photal DLS-2000 equipped with a He–Ne laser source (633 nm) at 25°C. The refractive index increment (*dn*/*dc*) was determined on an Otsuka Electronics DRM-1020. Thin-layer chromatography coupled with flame ionization detector (TLC-FID) was performed on an Iatron Iatroscan new MK-5 equipped with Iatrocorder TC-21 using sintered quartz rods (150 mm×2.0 mm) with silica gel. Infrared spectra were recorded on a JASCO FT/IR-460 spectrometer. Transmission electron microscope (TEM) observation was carried out on a JEOL JEM-200CX.

Synthesis of 4-(3-Bromopropyl)benzophenone

To a solution of benzoyl chloride (30.2 g, 214 mmol) and aluminum chloride (21.1 g, 159 mmol) pre-stirred at 60°C for 20 min was added dropwise 3-bromopropylbenzene (25.0 g, 126 mmol) at 60°C for 30 min. The reaction mixture was kept at 60°C with stirring for 4 h. The reaction mixture was poured into 2 *N* HCl aq ($50\,cm^3$) and extracted with dichloromethane ($50\,cm^3$) three times. The organic layer was washed with 5% NaOH aq ($50\,cm^3$, three times) and water ($50\,cm^3$, three times) and dried over $MgSO_4$. After removal of solvent, the crude product was purified by column chromatography (hexane/ethyl acetate = 9/1 *v*/*v*) and dried under vacuum to afford 4-(3-bromopropyl)benzophenone (26.4 g) as yellowish oil in 70% yield [33]. ^1H NMR ($CDCl_3$, 300 MHz): $\delta = 2.24$ (p, 2H, $CH_2C\underline{H}_2CH_2$), 2.88 (t, 2H, $ArCH_2$), 3.39 (t, 2H, CH_2Br), 7.28–7.78 (m, 9H, Ar) ppm.

Synthesis of 1-(4-(3-Bromopropyl)phenyl)-1-phenylethylene

We have reported the synthesis of 1-(4-(3-bromopropyl)phenyl)-1-phenylethylene by a *Grignard* coupling reaction of 1-(4-bromophenyl)-1-phenylethylene with 1-bromo-3-chloropropane followed by a *Finkelstein* halogen exchange reaction [34]. However, the overall yield was not sufficient. Here we report a preferable synthetic route for the title compound in better yield as shown below. To a solution of methyltriphenylphosphonium bromide (26.1 g, 73.1 mmol) and potassium *tert*-butoxide (8.27 g, 73.7 mmol) in *THF* ($100\,cm^3$) was added dropwise 4-(3-bromopropyl)benzophenone (18.0 g, 59.4 mmol) in *THF* ($50\,cm^3$) at 0°C for 20 min under a nitrogen atmosphere. The reaction mixture was kept at 25°C with stirring for 12 h. The reaction mixture was poured into water ($100\,cm^3$) and extracted with ether ($50\,cm^3$) three times. The ethereal layer was washed with aq $NaHCO_3$ solution, with saturated aq NaCl solution, and dried over $MgSO_4$. After filtration, the condensed ethereal layer was poured into hexane to precipitate triphenylphosphine oxide. Flash column chromatography (hexane/ethyl acetate = 100/1 *v*/*v*) gave the title compound in 68% yield (12.2 g) as colorless oil. ^1H NMR ($CDCl_3$, 300 MHz): $\delta = 2.20$ (p, 2H, $CH_2C\underline{H}_2CH_2$), 2.81 (t, 2H, $ArCH_2$), 3.43 (t, 2H, CH_2Br), 5.45 (d, 2H, J = 7.4 Hz, $CH_2{=}$), 7.16–7.37 (m, 9H, Ar) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta = 33.1$

($CH_2\underline{C}H_2CH_2$), 33.7 ($ArCH_2$), 34.1 (CH_2Br), 114.0 (CH_2=), 127.7, 128.0, 128.2, 128.3, 128.4, 139.4, 140.2, 141.6 (Ar), 149.8 (=C) ppm.

Synthesis of 1-(4-(3-N,N-Dimethylaminopropyl)phenyl)-1-phenylethylene (2)

To a solution of 1-(4-(3-bromopropyl)phenyl)-1-phenylethylene (9.20 g, 30.5 mmol) and diethylamine (11.2 g, 153 mmol) in acetonitrile (150 cm^3) was added in portions potassium carbonate (21.1 g, 153 mmol) and the reaction mixture was refluxed for 30 h. After filtering the salt off, the organic layer was washed with brine (50 cm^3). The objective product was quaternarized with 2 *N* HCl aq to dissolve in water. The aqueous layer was washed with hexane to remove unreacted starting materials and neutralized with 10% NaOH aq to neutralize the product. The organic layer was extracted with ethyl acetate (50 cm^3) three times and dried over $MgSO_4$. After filtration and condensation, the crude product was purified by silica gel column chromatography (pre-treated with 3% triethylamine in hexane, hexane/ethyl acetate = 9/1 *v*/*v*) and dried under vacuum to afford 1-(4-(3-*N*,*N*-dimethylaminopropyl)phenyl)-1-phenylethylene (7.15 g, 24.4 mmol) as colorless oil in 80% yield. ^1H NMR ($CDCl_3$, 300 MHz): $\delta = 0.98$ (t, 6H, $J = 10.0$ Hz, CH_3), 1.79 (p, 2H, $J = 7.8$ Hz, $CH_2C\underline{H}_2CH_2$), 2.41–2.56 (m, 6H, NCH_2), 2.62 (t, 2H, $ArCH_2$), 5.42 and 5.68 (2d, 2H, $J = 11.4$ Hz, CH_2=), 6.90–7.56 (m, 9H, Ar) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta = 11.8$ (CH_3), 28.7 ($CH_2\underline{C}H_2CH_2$), 33.6 ($ArCH_2$), 46.9 ($N\underline{C}H_2CH_3$), 52.5 ($CH_2\underline{C}H_2N$), 113.7 (CH_2=), 127.7, 128.1, 128.2, 128.3, 138.9, 141.7, 142.1 (Ar), 149.9 (=C) ppm; IR (KBr): $\bar{\nu} = 1246$ (C–N), 1608 (C=C) cm^{-1}; Anal: calcd for $C_{21}H_{27}N$ C 85.95, H 9.27, N 4.77; found C 85.91, H 9.29, N 4.80.

Anionic Polymerization of Phenyl Vinyl Sulfoxide

The anionic polymerization of *PVS* was carried out under high vacuum conditions (10^{-6} Torr) in the all glass apparatus equipped with break-seals. The functionalized initiators were usually prepared from the reaction of *sec-Bu*Li with a 1.2-fold excess of *DPE* derivatives in *THF* at −78°C for 0.5 h. LiCl was added to this initiator before the polymerization. The polymerization was carried out by adding a *THF* solution of *PVS* into the functionalized initiator system with vigorous shaking and was terminated with degassed methanol. The polymer was precipitated into a large amount of hexane or methanol. The precipitated polymer was collected by filtration, purified by reprecipitation from *THF* solution to methanol, and dried under vacuum. The molecular weight of the polymer was determined by ^1H NMR signal ratio of aromatic protons of main chain (6.9–7.7 ppm) to methyl protons of *sec-Bu* group (0.5–0.8 ppm). Similarly, the molecular weights of functionalized polystyrenes were determined by end-group analysis comparing the signals of aromatic protons (6.3–7.3 ppm) and methyl protons (0.6–0.8 ppm). The functionality of carboxylated polystyrenes was determined by TLC-FID peak area ratio of carboxylated-polystyrene ($R_f = 0$) to polystyrene ($R_f = 0.68$) developed with toluene.

Preparation of Block Copolymers and Star-Branched Polymers via Ionic Bond Formation

The title polymers were prepared by mixing dimethylaniline- or diethylpropylamine-chain-end-functionalized poly(phenyl vinyl sulfoxide)s with chain-end- or in-chain-carboxylated polystyrenes in *THF* at 25°C for 1 h. The amino and carboxyl groups were exactly adjusted at one to one molar ratio. The solution was used for SLS measurement to determine the molecular weight. FT-IR, ^1H NMR, and SEC measurements were carried out with the dried polymer after evaporation and drying under vacuum. The film sample for TEM observation was prepared by casting a *THF* solution of the polymer onto carbon membrane on copper mesh sheet and drying at 25°C overnight under nitrogen atmosphere. The *PPVS* segments in the block copolymer and star-branched polymer films were converted into conducting *PA* segments by heating the films at 150°C for 5 h under high vacuum condition. After washing with toluene, the film was stained with iodine vapor at 25°C for 24 h.

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