行政院國家科學委員會專題研究計畫 成果報告

具有高分子電解質鍊段的團鍊共聚高分子與聚苯胺所組成的混成物與其多尺度自組裝行為研究

研究成果報告(精簡版)

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行政院國家科學委員會補助專題研究計畫 ■成果報告
□期中進度報告

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摘要

本計劃探討團鍊共聚高分子與導電高分子聚苯胺的混成物的特性。混成物的製備是由不同組成的共聚高分子與聚苯胺以不同比例溶解於共同的溶劑再經由溶劑揮發而得。團鍊共聚高分子是經由陰離子聚合及相關的化學反應而得，因此具備了精確的分子量控制。此高分子其中一鍊段為一具有磺酸根的高分子電解質且與聚苯胺之間有強烈的作用力，因此混成物可能形成奈米微相分離結而使其兼具有聚苯胺的導電性與共聚高分子可製備性及機械強度。此研究也探討混成物的巨觀特性、如導電度，與微結構的之間的關連性並學習影響微結構的因素，如共聚高分子的化學組成及混成物的組成等。

關鍵詞：聚苯胺、導電高分子、高分子混成物、高分子電解質、團鍊共聚高分子、奈米微相分離結構、自組裝、陰離子聚合

ABSTRACT

In this study, polymer blends consisting of polyaniline(PANi) and sulfonated block copolymer (BCP) were prepared by solvent casting from the mixtures of PANi solution and sulfonated BCP solution with various compositions. The sulfonated BCPs with accurate control of molecular weight were synthesized through anionic polymerization and sequential analogous chemistry. The sulfonated segment of the BCP showed strong interaction with PANi so that PANi could homogeneously disperse in the blends leading to microphase separated nanostructures. Therefore, the blends were expected to combine the good electrical conductivity of PANi and the mechanical flexibility of the block copolymer. The interplay between the compositions of the blends, the self-assembled nanostructures and the bulk properties of the blends were also investigated.

Key words: PANi, conducting polymer, polyelectrolyte, polymer blend, block copolymer, self-assembly, microphase separation, anionic polymerization.

INTRODUCTION

Polyaniline is one of the most extensively investigated conducting polymer because of its promising electronic conductivity and environmental stability for various applications (in what area?). However, the major drawbacks of polyaniline are the brittleness, poor solubility in common solvents, and the difficulty in processing. To solve the above issues of PANi, one of the popular approaches is the incorporation of PANi into an electrical insulating conventional polymer matrix for the possibility to combine the good processability and mechanical performance of the conventional polymers with the electrical and optical properties of PANi. These blends are usually obtained by in situ polymerization of aniline in the presence of the insulating polymer or by blending PANi with polymers in solution or in melts.[1] The use of PVC[2], thermoplastic[3], polystyrene[4] and rubbers in blends with PANi were studied.[5,6] It has been suggested that the compatibility between the polymer matrix and PANi as well as the functional protonic acid for doping have strong influences on the dispersion of PANi, the morphology of the blends, and the bulk properties.

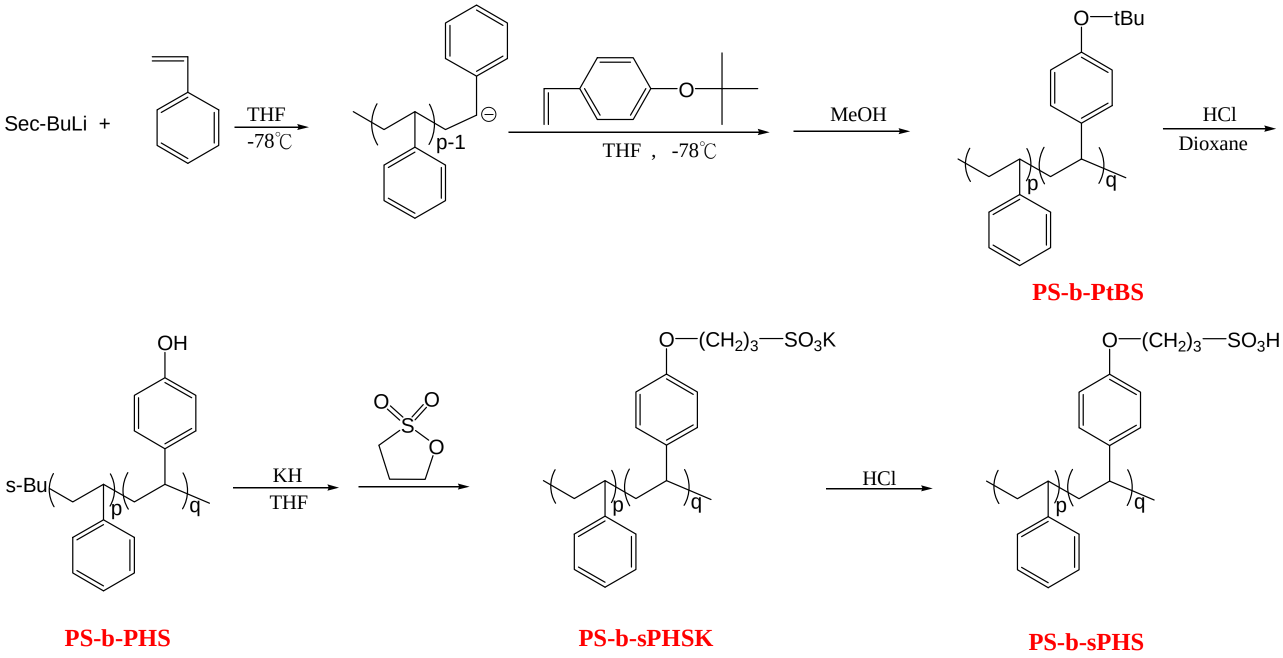
Among various methods in fabricating PANi blends, solution blending was reported to be a more efficient approach to prepare homogeneous blends when both polymers are soluble in the same solvent. Nevertheless, the two components, PANi and conventional non-conducting polymer, are basically immiscible leading to phase separation in micrometer scale in the blends. As the miscibility of these blends was enhanced, the homogemeity, the electrical conductivity, and the mechanical properties could be substantially improved. The most used method to increase the miscibility was the introduction of compatibilizers such as surfactants and ionic polymers (polyelectrolytes)[7], e.g. sulfonated polycarbonates and polystyrene sulfonic acid (PSSA)[8], owing to their dual functionalities to serve as the doping reagents to induce electrostatic interaction simultaneously.

In this study, we tried to combine the self-assembly behavior of the block copolymer and the electrostatic interaction between the polyelectrolytes and PANi to prepare homogeneous blend with microphase separated nanostructures. Ionic BCPs with various compositions were synthesized through anionic polymerization and the following chemistry. The ionic segment contains pendant sulfonic acids to dope and entangle with PANi while the non-ionic segment is responsible for the mechanical strength and flexibility. Variables affecting the morphologies of the blends including the MW of each block of ionic BCP, the MW of PANi, and the ratio between PANi and ionic BCP and the preparation condition were investigated. The interplay of the above variables, morphology and bulk properties were also studied.

EXPERIMENTAL

Synthesis of poly(styrene-*block*-sulfonated hydroxystyrene) (PS-b-sPHS). Poly(styrene-*block*-4-*tert*-butoxystyrene), PS-PtBS, was synthesized through anionic polymerization with sequential monomer addition under nitrogen atmosphere in THF at -78℃. The molecular weight of the PS block is determined by GPC using THF as eluting solvent and the molecular weight of the PtBS block is calculated from the molar ratio between the PtBS block and the PS block as suggested by NMR spectrum. The PtBS block was then converted to poly(hydroxystyrene), PHS, by reacting PtBS with hydrochloric acids. The conversion percentage was identified by the NMR spectrum. The reaction of cyclic sultone and PS-b-PHS gives the potassium salt of sulfonic acids attached to the PHS via propylene spacers, which could be further transformed into the acid form, denoted as PS-b-sPHS by acid treatment. The synthesis route is illustrated in **Sheme.1**.

Synthesis of polyaniline. Polyaniline (Emeraldine base, EB) was synthesized by adapting a procedure described in literatures.[9,10] Calculated amount of aniline and DBSA was dispersed in DI water, and then desired amount of $(NH_4)_2S_2O_8$ (APS) dissolved in DI water was added to the reactor. The emulsion polymerization was carried out at 0℃ for 24hrs and was terminated by methanol. The product in reactor was greenish emeraldine salt and 4wt% $NH_4OH_{(aq)}$ was then added to de-dope the polyaniline to obtain the blue emeraldine base.



Scheme.1 Synthesis route for sulfonated block copolymer, PS-b-sPHS

Preparation of blends consisting of PS-b-sPHS and PANi. Desired amount of PANi (emeraldine base) was dissolved in NMP. PS-b-sPHS was also dissolved in another bottle of NMP at 80℃. The two solutions were then mixed at 80℃. The blends can be obtained by solvent casting through slowly removal of NMP at 80℃.

Conductivity measurement. The electric conductivity of PANi and the blends were measured by four-probe conductivity measurement. Powder PANi was pressed to became ingot and the blends was in the form of thin film for the resistance measurement

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RESULT and DISCUSSION

Synthesis of PS-b-sPHS block copolymer. Three PS-b-PtBS block copolymers with different molecular weights and molecular weight ratios between the two blocks were synthesized. The three different compositions were designed to study the molecular weight effect on the morphology and the conductivity of the corresponding blends. The M_n of each block and the polydispersity, determined from GPC, are listed in **Table.1**. **Figure.1(a)** shows the GPC traces of the PS-b-PtBS-1 copolymer having a M_n of 27,900 g/mole for PS block and a total M_n of 40,140 g/mole with a narrow molecular weight distribution around 1.11. The accurate MW of the PtBS block was obtained from the molar ratio of PtBS/PS calculated from the NMR spectrum as shown in **Figure.1(b)** The conversion of PtBS to PHS was successfully carried out indicated by the disappearance of the peak at $\delta = 1.25$ppm in the NMR spectrum shown in **Figure.2(a)**. After the attachment of sulfonic acids to PHS, the block copolymer became insoluble in any d-solvent. In order to identify the attachment ratio of the sulfonic acid groups, the $-SO_3H$ groups were converted to $–SO_2Cl$ through the reaction with thionyl chloride to enhance the solubility of the block copolymer in common organic solvents. From the **Figure.2(b)**, the NMR spectrum of PS-b-sPHSCl suggested the attachment ratio (or say degree of sulfonation) was more than 85%.

Table.1 Composition, molecular weight and PDI of PS-b-PtBS BCPs synthesized

Polymer	M_n of PS from GPC	PDI of PS	Total M_n from GPC	PDI of BCP	M_n of PtBS from NMR	Total M_n from NMR
PS-b-PtBS-1	27900	1.13	40141	1.12	18500	46400
PS-b-PtBS-2	8133	1.24	31760	1.09	26025	34158
PS-b-PtBS-3	19735	1.53	42016	1.11	23682	43417

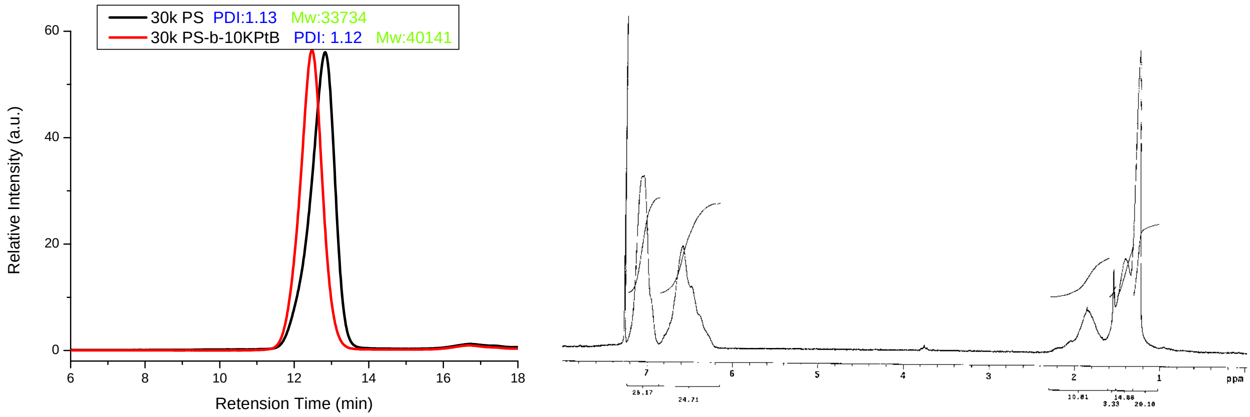

Figure.1 (a) left: GPC traces of PS-b-PtBS1 and the PS block; and **(b)** right: NMR spectrum

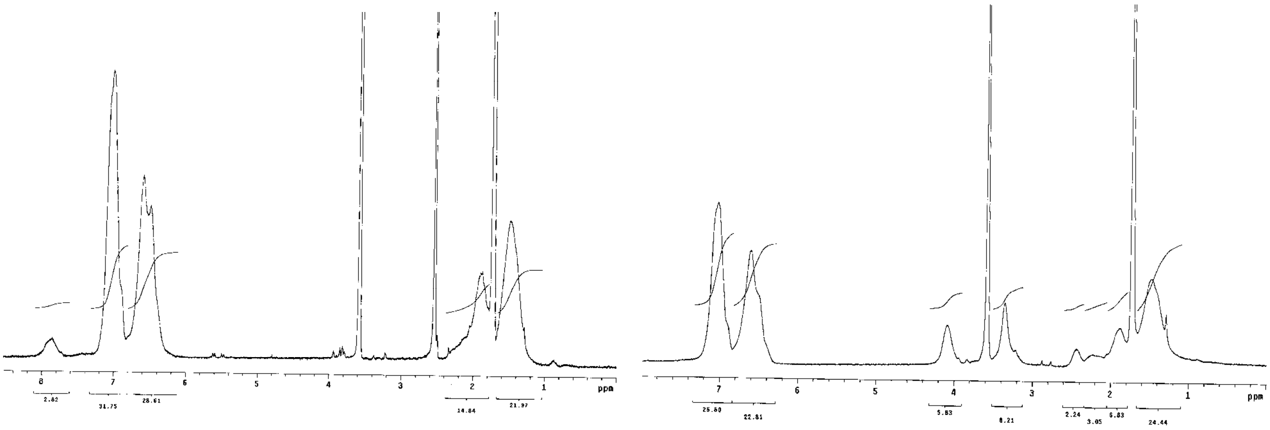

Figure.2 (a) left: NMR spectrum of PS-b-PHS1; and **(b)** right: NMR spectrum of PS-b-sPHSCl-1

Synthesis and properties of PANi. Three different batches of PANi were prepared by varying the ratio of aniline to DBSA. DBSA acts as surfactant and doping reagent simultaneously in the emulsion polymerization of aniline. Changing aniline/DBSA ratio was expected to alter the size of the PANi obtained and the conductivity as well. The feed ratios and the conductivities of the PANi synthesized are listed in **Table.2**. It's found that the electric conductivity of PANi increase with the amount of DBSA added, which could be attributed to the higher doping level. However, the MW of PANi obtained were not available due to its insolubility in the common solvents used in GPC.

Table.2 PANi prepared from different feed ratios and their conductivities.

Sample	Aniline/DBSA molar ratio	R (resistence) (Ω)	Conductivity (S/cm)
PANi-1	1:1	1	0.637
PANi-2	2:1	2	0.445
PANi-3	3:1	4.3	0.177

Blends of PANi and PS-b-sPHS. Since PS is hydrophobic while sPHS is hydrophilic, the block copolymer could form micelles in most of common solvents at room temperature. High temperature therefore is preferred to dissolve the sulfonated BCP. NMP is the only solvent we found which could dissolve both PANi and PS-b-sPHS. The mixtures of the sulfonated BCP solution and the PANi solution were greenish which suggested that the sulfonic acid groups of the block copolymer could interact with PANi strongly to dope PANi. The thin film, for example, obtained from the mixture of 4wt% PS-b-sPHS1 in NMP and 4wt% PANi-3 in NMP with 1: 1 volume ratio, exhibited a rough surface and cracked easily. The poor mechanical properties of the thin film might be attributed to the high T_g of PS as well as the macroscopic phase separation between PANi and PS-b-sPHS. As the solvent evaporated, the block copolymer chains which didn’t interact with the PANi and the undoped PANi might precipitate first. In addition, the high MW fractions of PANi might not entangle completely with sPHS segments, leading to heterogeneous dispersion of PANi. Therefore, the optimization of the parameters of the blends, including the composition of PS-b-sPHS, the MW of PANi, the ratio between BCP and PANi and the concentration of the solution, is needed for further study to obtain homogeneous blends with ordered microphase separated nanostructures. Unfortunately, conductivity and mechanical properties are not available so far due to the brittleness of the samples.

CONCLUSION

Sulfonated block copolymers, PS-b-sPHS, with various molecular weights and compositions were synthesized successfully. All the polymers possess narrow molecular weight distribution. PANi were also prepared with different conditions for the variation of conductivity and molecular weight. It has been shown that these BCPs can interact strongly with PANi. Thin films of the blends of the BCPs and PANi were obtained from solvent casting and which exhibited certain degree of macrophase separation. Further research is needed to optimize the blends to achieve homogeneous distribution of PANi in the polymer matrix for good conductivity and mechanical property.

REFERENCE

1. Anand, J.; Palaniappan, S.; Sathyanarayana, D. N. *Prog. Polym. Sci.* **1998**, *23*, 993.
2. Shacklette, L. W.; Han, C. C.; Luly, M.H. *Synth. Met.***1993**, *55-57*, 3532.
3. Davies, S. J.; Ryan, T. G..; Wilde, C. J.; Beyer, G. *Synth. Met* **1995**, *69*, 209.
4. Zilberman, M.; Titelman, G. I.; Siegman, A.; Haba, Y.; Narkis, M.; Alperstein, D. J. *Appl. Polym. Sci.* **1997**, *66*, 243.
5. Shiratori,S. S.; Rubner,M.F. *Macromolecules* **2000**, *33*, 4213.
6. Yoo, D.; Shiratori, S. S.; Rubner, M. F. *Macromolecules* **1998**, *31*, 4309.
7. Lin, D. S.;Yang, S. M. *J. Appl. Polym. Sci.* **2005**, *98*, 1198.
8. Sun, L. ; Liu, H. ; Clark, R. ; Yang, S. C. *Synth. Met.***1997**, *84*, 67.
9. Ikkala, O. T. ; Laakso, J.; Vakipartb, K.; Virtanen, E.; Ruohonen, H.; Jarvinen, H.; Taka, T.; Passiniemi, P.; Osterholm, J.-E. *Synth. Met.***1995**, *69*, 97-100.
10. Bae, W. J. ; Kim, K. H. ; Park , Y. M. ; Jo, W. H. *Chem. Commun.* **2003**, 2768.