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# 2017 IEEE International Conference on Applied System Innovation (IEEE ICASI 2017)

服務機關：國立中正大學

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## 摘要

此次前往於日本札幌所舉行之 2017 IEEE International Conference on Applied System Innovation, IEEE ICASI 2017(2017國際創新應用系統國際研討會），在會議中見到許多跨領域統合的合作。在與會過程見識到關於無機混摻以提升導電度及可圖案化之多工高分子等相關材料的演說，雖然其研究目的與我們有著相當大的差異，然而、其引用之技術及研發之觀念與我們在深耕計畫中之題目，〝矽碳材料於橡膠分散技術之開發〞大致相同，即增加高分子材料與無機材料之交互作用則可大幅提高複合材料之物性。

此行吾等發表題目為「以陰離子聚合法製備具有不等嵌段長度之苯乙烯嵌段共聚物 SBSIS 與性質研究」，討論 SIB-橡膠之物理性質與熱性質，並介紹相關運用與發展性。在與參與會者之討論後，也擴展我們未來應用之範圍：改質烷化矽填加劑以增加矽碳材料在橡膠中之分散性。

# 目次

## 目的

此行目的為參與日本札幌所舉行之2017 IEEE International Conference on Applied System Innovation, IEEE ICASI 2017(2017國際創新應用系統國際研討會）。職在高分子領域之涉獵並不深(過去或有接觸，然真正進行高分子合成及加工則是在三年前深耕計畫開始執行時），因此，此行之目的之一乃在於了解我們所合成之材料，除了應用於橡膠產業，有無其他應用範圍。而第二個目的則在於參訪酒廠，以了解製酒程序中之各化工單元與品質之相關性。

## 過程

此次會議為期共6天，從106年5月13日 至 5月17日 結束。其過程簡述如下:

5月12日

1. 起程，參觀北海道大學。

5月13日

1. 到達會場，了解週遭交通路線，及會議室。

5月14日

1. 報到
2. 領取會議相關資料，瞭解此次會議議程時間及參與重要演講。
   主要演講者專題:
   a. Relevant length scales, size effect, and nanomechanics of metallic glasses
   b. Fabrication and Applications of Nano-particle Doped Nano-Micro- Patternable Multi-Functional Polymers
   c. Understanding Big Data Through Visualization

5月15日

1. 與蔣教授討論連續式SSBR合成之結果。
2. 與高應大教授討論本次學術會議行程安排，及題目範圍之優缺點(此結果可為爾後參與或承辦國際研討會之參考。

5月16日

1. 學生楊士軒報告陰離子合成SBSIS（styrene butadiene styrene isoprene styrene）嵌段彈性高分子之合成、物性、及其應用之研究〝Preparation of block copolymer SBSIS having various polystyrene block lengths via anionic polymerization and the properties research〞。
2. 與學生討論會議中聽眾提出之問題。
3. 參訪威士忌製造工廠，了解乾燥，發酵，熟成，蒸餾，及調配等化工程序對造酒、及其品質之影響。

5月17日

1. 參觀運河城。
2. 參觀千歲機場outlet百貨公司。

5月18日

1. 回程

## 心得與建議

此次行程之目的為(1)參加 IEEE 之會議及(2)了解製酒程序與成品酒品質之關聯性，藉此以提供國內酒廠技術性之建議。大致上此行已達到當初之目的。然而在參加會議方面，由於會議之設計與當初自己想法有些出入；我原以為會議之論文偏於應用面，且得以和不同領域之學者討論SIS或SBS材料除了橡膠及黏著材料有無其他例如導電、導磁或感應器材料之應用。然在會場上卻發現自己在這方面之受益較為有限。反而與蔣教授談起最近之研究結果，有著更豐碩之建議，其理由仍在於會議之內容過於廣泛，而參與之學者又鮮有陰離子聚合之經驗。然而在參訪酒廠方面，卻有著不同過去自己思維之啟發性想法，以下就這兩點提出個人之一些看法:

(1) IEEE 之會議主演講者 Khosia 提出奈米顆粒摻雜於多功能可圖案化高分子(patternable mutli-functional polymers)。這方面之研究可應用之領域包括太陽能電池、高強度輕質材料、藥物、及感測器。其發表之演講與我們相關研究之著墨並不多。然較為有趣的是將金屬或金屬氧化物摻雜於含有機矽氧化合物之高分子以應用於微電子元件。Khosia教授之演講啟發我們應用陰離子聚合之特性，以製備不同末端官能基之高分子，而藉由橡膠方法連接不同性質之金屬或金屬氧化物，以改質材料本身之光學行為，藉此，以提昇其應用性。例如:塑橡膠之填加劑，以增加過濾不同波長之光源，這些產品除可應用於光電產業，亦可應用於溫室以調節或控制植物生長。

(2) 討論SIB-橡膠之物理性質與熱性質，並介紹相關運用與發展性，該會議主席為臺灣 科技大學-陳建光教授，會議上陳教授也熱情詢問關於SBSIS之工業運用前景，及結構上如何影響高分子之Tg (Glass Transition Temperature) 點、及Td (Thermal Degradation Temperature) 點。此外，SBSIS與同類型之SBSBS、SISIS之間之差異為何亦為會議討論之重點。

(3) 我對製酒之興趣，主要來自於金門某私人酒廠之發酵及蒸餾設備一直是他們技術之瓶頸。

由於，我並非這方面專家，故也無法提供他們解決之方法，然在參觀酒廠後，我發現日本生產高級酒之方式與我的想法有著相當大之出入，包括：

i. 高級酒之蒸餾採多次批式蒸餾，而由人工控制蒸餾器之溫度、壓力，而非由自動控制調整控制參數。

ii. 劣酒才採用現代連續式蒸餾設備，而高級酒乃採用前一世紀之銅造蒸餾器。
發酵前，原料之乾燥極為重要，其原因可能與後面發現成品中酯類之結構有關，然我至今尚不知其中之奧妙。

iii 酒桶之製作之工藝直接影響到酒之風味，可惜受限於自己之專業，仍不知其中火烤及在空隙加入不知名香草，對酒品質之影響

附錄(1)：　演講全文

# Preparation of block copolymer SBSIS having various polystyrene block lengths via anionic polymerization and the properties research.

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## Abstract

Two types of linear pentablock copolymers SBSIS, namely, ends-big and middle-big type were prepared by anionic polymerization of styrene (St), isoprene (Ip) and 1,3-butadiene (Bd) in a nonpolar solvent. Various samples having a number average molecular weight (Mn) of 60,000 g/mole were synthesized and characterized. The correlation between molecular structure and characteristic properties allows us to understand the effect on physical properties of important parameters such as styrene content, linking method, monomer proportions, and magnitude of end segment.

**Key words:** anionic polymerization, block copolymer, styrene, isoprene and butadiene

## Introduction

Anionic polymerization dates back to early twenties century. Mattews and Strange [1] in 1910 and Harries [2] in 1911 used organometallic species to polymerize polyisoprene, afterwards Ziegler and his co-worker [3-6] made headway with polymerizing diene-series. Combine anion and other methods varies the anionic polymerization and makes it more complete.

Thermoplastic elastomers (TPE) have unique properties that behave as vulcanized rubber at room temperature but as thermoplastics after heating. The properties combine advantages of rubber and thermoplastics so that TPEs are known as general plastics. By tuning molecular weights and alignments of monomers, we can induce the TPEs to perform a dramatic physical and chemical differences . The molecules we synthesized in this paper—styrenic copolymers (SBCs)—are a kind of TPEs. SBCs mainly contain styrene, butadiene and isoprene. In the polymer, styrene is the hard segment and plays the a role as a bridging which fasten the shape of polymer un room temperature; butadiene and isoprene have flexible characteristics that can improve the elasticity of macromolecule relatively. While heating, styrene will fuse and make polymer melt, we can process, shape, reform polymer under this situation. TPEs integrate the elasticity of rubber and the plasticity of plastics, those broaden the utilizations containing shoes industries, biomedical materials, commodities etc [7, 8].

Mori, Y. et al. [9] and Alhad Phatak and Stephen F. Hahn et al. [10] who compare triblock with pentablock, and figure out that pentablock may optimize physical properties with their structure. Mingyi Liao et al. [11] also point that styrene–isoprene–butadiene terpolymers have improved characteristics. Therefore, we synthesize pentablock copolymer, and change the ratio of monomers under nonpolar solvent tofurther investigate the physical properties.

## Experimental

### *Materials*

Styrene were obtained from Sigma-Aldrich Co., Ltd. Cyclohexane were purchased from Duksan Pure Chemicals Co., Ltd. 1,3-butadiene was gained from Taida Chemical Co., Ltd. Sec-BuLi and isoprene were acquired from Acros Co., Ltd. Monomers and solvent were purified on activated alumina columns to remove stabilizing agents and polar moieties.

*Polymerization*

Cyclohexane and sec-BuLi were induced into glass reactor, then injected amount of styrene with syringe. Add orderly Bd, St, Ip, St after styrene reacted completed. Merge methanol into the reactor to quench the polymerization. All above steps should be operated under N2 condition. The Mn of copolymers measuring by SEC had been described in Table I.

*Characterization*

The molecular weights was determined by GPC witch including Waters 2489 UV/Visible detector and Waters 2414 refractive index detector. Analyses of the molecular microstructure were performed by Bruker Avance III 400 MHz. $T_d$ and $T_g$ points were detected by Dopunt TA Instrument Co. TGA2050. The morphologies of polymer were obtain form DSR Dopunt TA Instrument Co. Discovery HR-1. FTIR figures were determined by Shimadzu Co. IRPrestige-21.

## Results and Discussion

### *Syntheses and Characterizations*

From SEC, as fig. 1 displayed that the molecule weights had raised as we expected. All polymers we synthesized had the same tendencies and PDI<1.10 as figure 1. The cause of we synthesized the copolymers in nonpolar solvent was to reduce 1, 2- and 3, 4-addition of polyisoprene and polybudadiene that might induce copolymers aging, color change etc. We could confirm the microstructures of polymers by 400MHz 1H-NMR. As fig. 2 revealed that is successful to have expected copolymer under this environment even there were few of peaks indicating 1, 2- and 3, 4-addition. FTIR spectrum showed specific peaks of functional groups in the copolymers for affirmation as fig. 3 indicated.

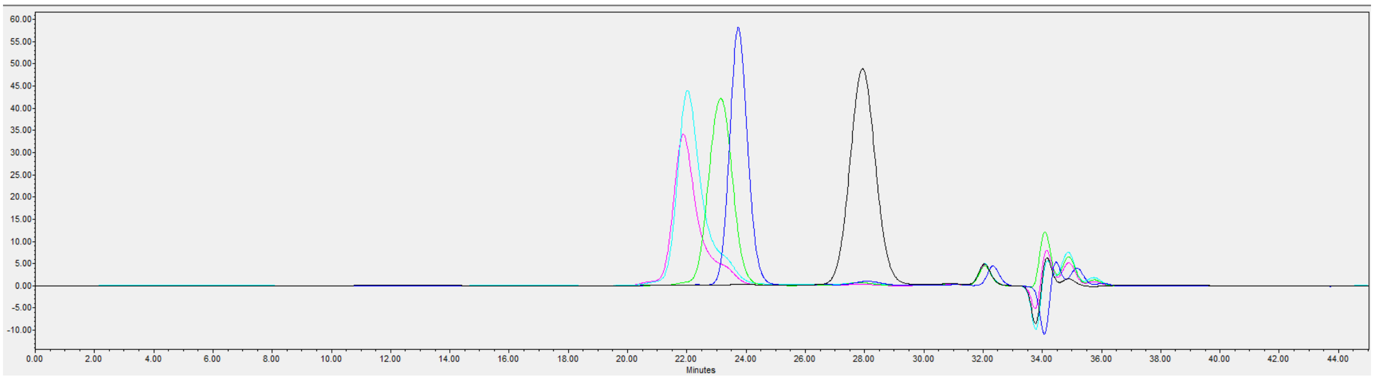

Fig. 1. SEC figure of SBSIS which contains 30% styrene. As retention time decreases, the molecular weight rises. This figure is a representation of all copolymers.

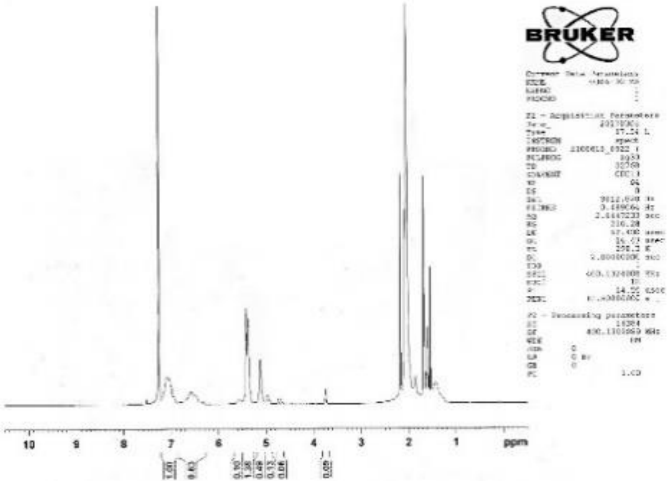

Fig. 2. $^1$H-NMR spectrum of middle-big SBSIS with 60% styrene-content. This figure is a representation of all copolymers.

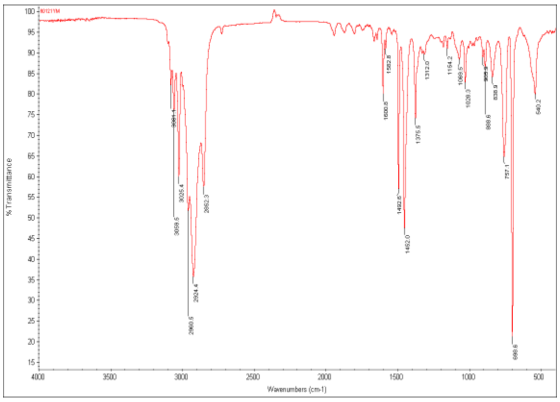

Fig. 3. FTIR spectrum of middle-big SISIS with 60% styrene-content. This figure is a representation of all copolymers.

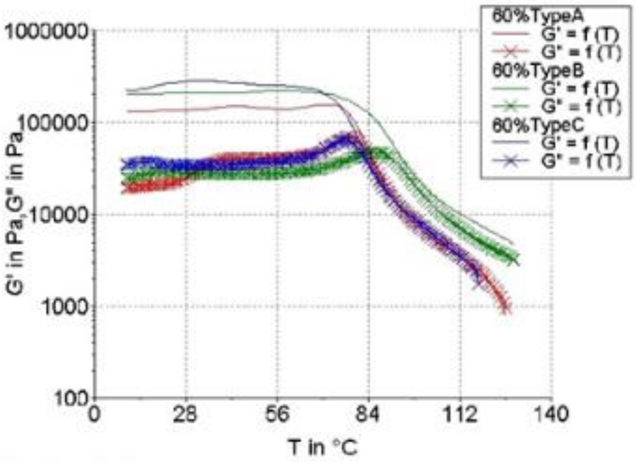

Fig. 4. DMA measurement of G' (storage modulus) and G" (loss modulus) with different block lengths in 60% PS-content SBSBS: (a) Type A stood for equal block length of copolymer. This type was synthesized for extra purposes. (b) Type B stood for ends-big type. (c) Type C stood for middle-big type. This figure is a representation of all copolymers.

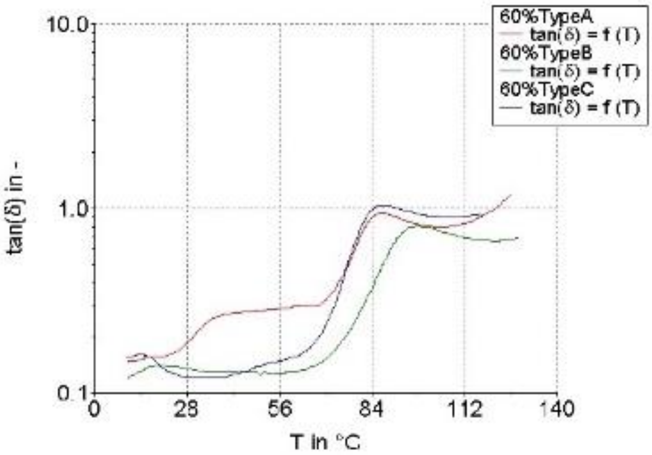

Fig. 5. DMA measurement of tanδ with different block lengths in 60% PS-content SBSBS: (a) Type A stood for equal block length of copolymer for extra investigations. (b) Type B stood for ends-big type. (c) Type C stood for middle-big type. This figure is a representation of all copolymers.

TABLE I

Molecular characteristics of copolymers.

| Polymer A[a] | St-content (%) | Mn[c] (kg/mol) | PDI[d] | $T_d$[e] | $T_g$1[f] | $T_g$2[g] |
|---|---|---|---|---|---|---|
| SISIS[a] | 30 | 64.4 | 1.08 | 358.39 | -60.05 | — |
| SISIS[a] | 60 | 56.6 | 1.06 | 364.02 | -58.72 | 71.19 |
| SISIS[a] | 90 | 53.6 | 1.10 | 384.08 | — | 74.08 |
| SBSBS[a] | 30 | 65.0 | 1.09 | 405.6 | -98.98 | — |
| SBSBS[a] | 60 | 58.8 | 1.09 | 397.72 | -103.30 | 61.85 |
| SBSBS[a] | 85 | 63.4 | 1.10 | 394.11 | -105.67 | 78.83 |
| SBSIS[a] | 30 | 55.0 | 1.09 | 379.66 | -77.21 | — |
| SBSIS[a] | 85 | 56.5 | 1.03 | 372.78 | — | 77.42 |
| SISIS[b] | 30 | 63.0 | 1.08 | 357.97 | -59.79 | — |
| SISIS[b] | 60 | 57.8 | 1.08 | 364.48 | -57.53 | 74.35 |
| SISIS[b] | 90 | 61.8 | 1.10 | 384.68 | — | 78.28 |
| SBSBS[b] | 30 | 59.6 | 1.09 | 409.4 | -102.28 | — |
| SBSBS[b] | 60 | 55.2 | 1.09 | 401.35 | -96.08 | 72.17 |
| SBSBS[b] | 85 | 53.6 | 1.10 | 393.77 | -103.52 | 82.77 |

[a] Middle-big type copolymers.
[b] Ends-big type copolymers.
[c, d] SEC with polystyrene standards in THF for calibration.
[e, f] TGA with heating rate: 10℃/min.
[eg] DSC with heating rate: 10℃/min.

### *Thermal properties*

TGA measurements displayed the copolymers' $T_d$s, and revealed the thermal stabilities of products. According to the results, the $T_d$ of SBSIS appeared among SISIS's and SBSBS's with same type. Instead of containing isoprene, the copolymer which contained butadiene had a higher $T_d$ especially 30% styrene-content SBSBS. Due to alignments of main chain is more orderly and regular in the SBSBS than SISIS. SBSBS could array in a tight crystal which had a strong effect between each chain and raised $T_d$, this reason made molecules to composite with more energies. In the case of dissimilar styrene-content, the big-types and middle-types both showed that $T_d$ increased as the amount of styrene. Thermal stabilities would decrease if there were methylene groups existed in the main chain, those might decrease regularities and $T_d$ s.

Most of lock copolymers have phase separation. The circumstances lead copolymers to reveal their Tgs with different segments. The $T_g$ of St is about 100℃, Bd is about -105℃, and Ip is around -80℃. In the 60% styrene-content of SISIS and SBSBS, the $T_g$ of St decreased, and the points of Bd and Ip inversely. When copolymerized with two kinds of monomer, the main chain bonding had impact on each, and drew their $T_g$s close at the interface. Above phenomena could be confirmed from the data of Table I.

### *Morphologies of copolymers*

DMA tests could allow us to know how elasticity transformed while temperature change. For instance, it was apparently fig. 4 to observe that middle-big type SBSBS with 60% styrene-content changed from glassy region to transition region. The $T_g$ point located at 84℃ where G' and G'' intersected. How the content of blocks had impacts on $T_g$ point could realize by fig. 5. The $T_g$ point of ends-big type is more higher than the others' owing to the end lengths of copolymers had more influences in $T_g$ point. Above appearances could be confirmed from the data of Table I.

## Conclusion

With SEC, $^1$H-NMR and FTIR, we successfully synthesize the copolymers we mentioned in abstract. It is obviously to realize pentablock copolymers have better physical properties as mentioned in discussions. Due to orderly arrangements and strong chain effects between main chains, SBSBS copolymers had upper $T_d$ points than SBSIS and SISIS, so that they could be used in industries with higher temperature. $T_g1$ and $T_g2$ points seemed to be drew closer as we copolymerized different monomers. SBSBS had the larger difference in $T_g$ points than SBSIS and SISIS which illustrated this kind of copolymers had much stronger chain effect to bind the structure. DMA showed morphologies of the copolymers transformed with temperature gradient. From glassy region to transition region, elasticity changed accompanying with intersection of storage modulus to loss modulus. The point was also an index of $T_g$ point though it was not as accurate as data from TGA, it still offered a comparison to consult.

## Acknowledgements

We are grateful for financial supports, guides and assistances from Taiwan USI Corporation.

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## 附錄(2)：活動相片

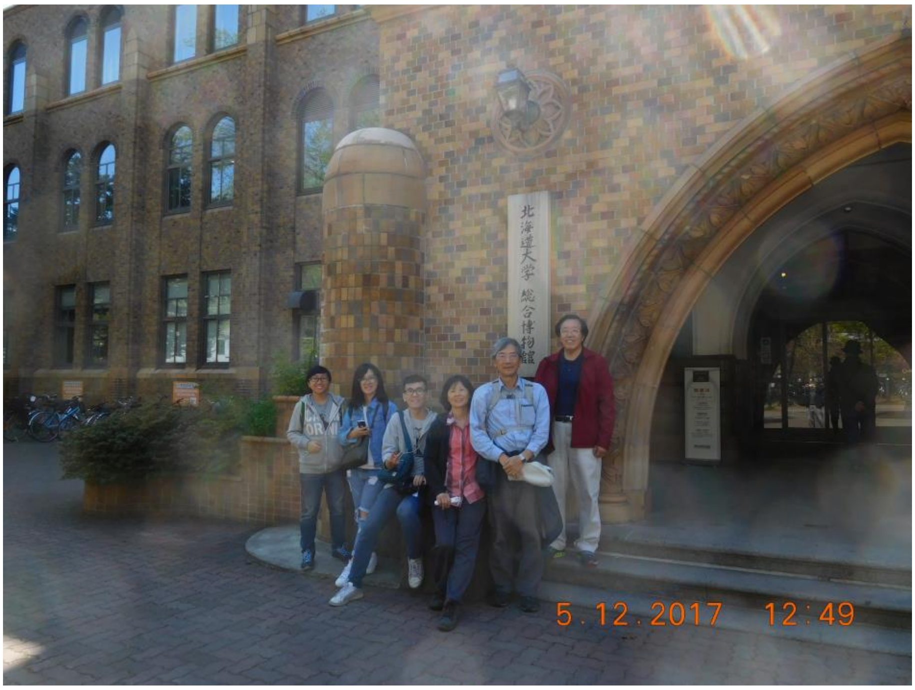

Fig. 1

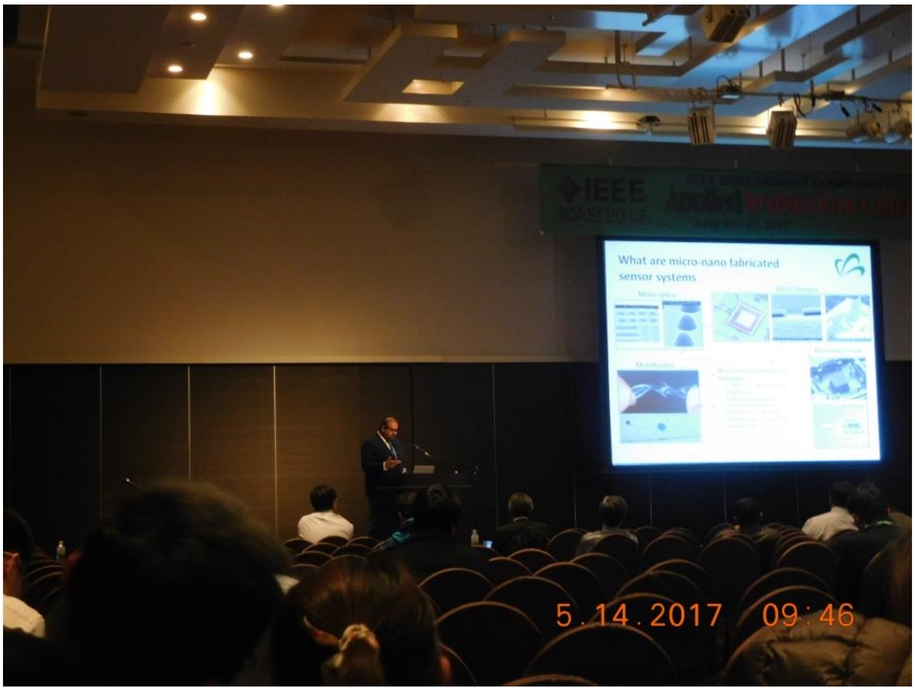

Fig. 2

Fig. 3

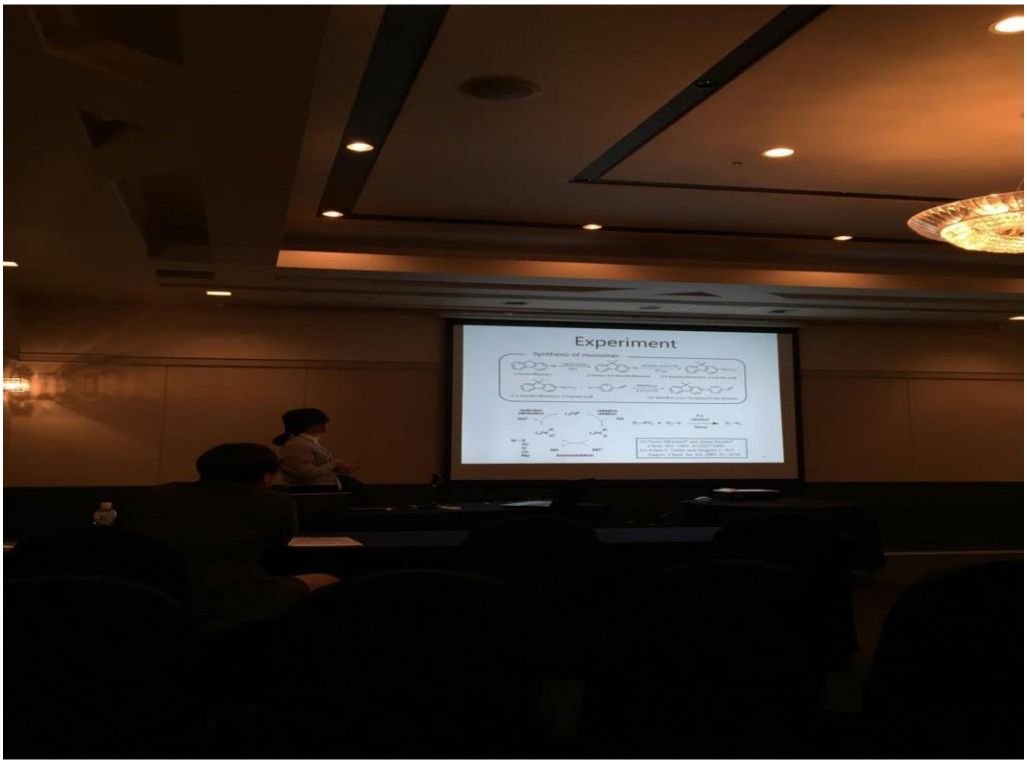

Fig. 4