

# **Synthesis of High Ionic Conductivity Polymer Solid Electrolyte for Lithium-ion Battery**

Name: Catherine Laurent

Student ID No.: B10835008

Major: IATP Chemical Engineering field

Advisor: 邱昱誠 Yu-Cheng Chiu

2022 06 13

# Synthesis of High Ionic Conductivity Polymer Solid Electrolyte for Lithium-ion Battery

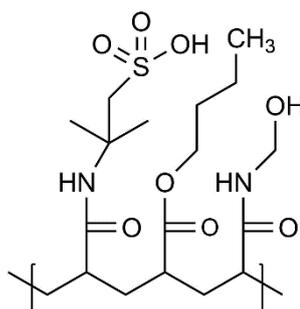
## Abstract

Polymer with high ion conductivity is known for its widespread application, it is still a challenge to improve the self-healing properties while still maintaining its high ion conductivity. Herein, a p(AMPS-*co*-BA-*co*-NMA), self-healing copolymer with high ion conductivity, is created by copolymerization of 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPS), n-Butyl acrylate (BA), and N-(hydroxymethyl)acrylamide (NMA) in methanol. Followed by membrane dialysis and evaporation of the solvent. Synthesis of p(AMPS) and p(BA) are also done in the similar manner. The result shows that a p(AMPS-*co*-BA-*co*-NMA), p(AMPS), and p(BA) are polymerized successfully. To know further about p(AMPS-*co*-BA-*co*-NMA), p(AMPS), and p(BA) properties and structure, Nuclear Magnetic Resonance Spectroscopy (NMR), Gel Permeation Chromatography (GPC), and tensile test are conducted.

## Introduction

Self-healing polymers with high ion conductivity are gaining massive attention in recent years due to their wide potential in electronic devices. As the electrolyte is one of the key components in electronic devices, such as in a lithium-ion battery, it is bound to go through deformations that will eventually affect the effectiveness of the device. By adding self-healing property, it would matter immensely on its endurance.

As shown in figure 1, p(AMPS-*co*-BA-*co*-NMA) is prepared by free radical polymerization between AMPS, BA, and NMA with azobisisobutyronitrile (AIBN) as the initiator (Figure 2). AMPS is highly ionic conductive and has remarkable self-healing ability (Diao et al., 2020), BA is flexible and has a great chain mobility (Wen et al., 2017), while NMA is a thermal-triggered self-cross-linker and also has remarkable self-healing ability (Laysandra et al., 2020).



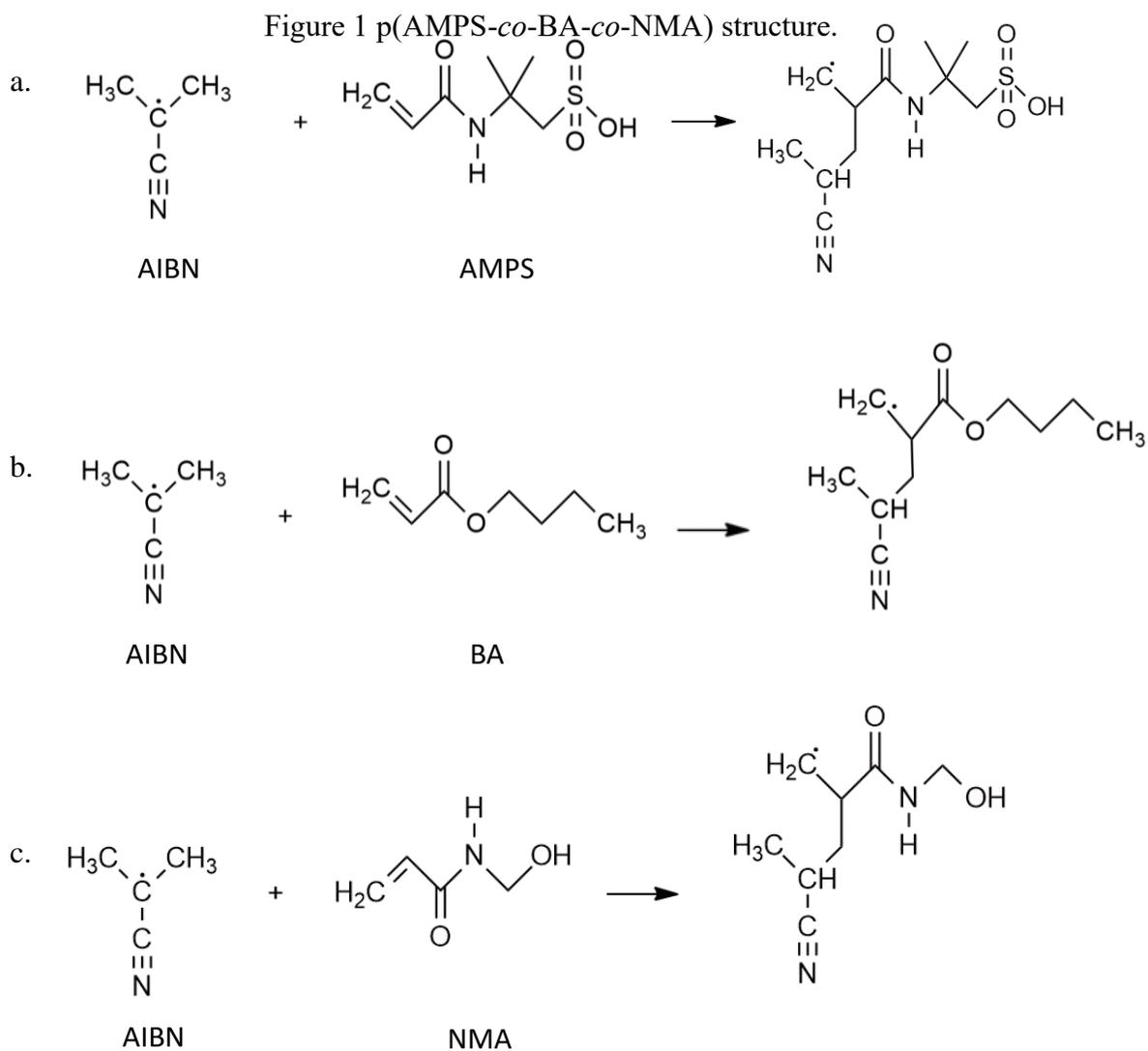


Figure 2(a) Free radical polymerization of AMPS and AIBN. (b) Free radical polymerization of BA and AIBN. (c) Free radical polymerization of NMA and AIBN.

Due to the hydrogen bonding between AMPS (Figure 3), p(AMPS-co-BA) will have a self-healing ability. Aside from that, AMPS has strong sulfonic and amide groups which are conducive to the dissociation of lithium salts and can absorb large volumes of anions through hydrogen bonding (Yang et al., 2020). This will affect greatly the conductivity of the polymer.

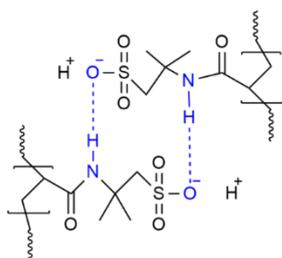


Figure 3 Hydrogen bonding between AMPS.

Aside from AMPS, NMA also has hydrogen bonding due its structure having N, O, and H. This structure lets NMA to have a self-healing ability.

### **Motivation**

To successfully synthesis and know the properties of self-healing polymer with high ion conductivity p(AMPS-*co*-BA-*co*-NMA), p(AMPS), and p(BA).

### **Description of Research Work**

#### **A. Free Radical Polymerization**

a. Free Radical Polymerization of p(AMPS-*co*-BA-*co*-NMA) are done by these steps:

1. Weigh AMPS, BA, and NMA with the ratio of 3:6:1
2. Pour BA and methanol (solvent) into round bottomed flask. Then input argon gas and heat the liquid component.
3. Put AMPS, NMA, and AIBN (initiator) into Schlenk flask. Then in input argon gas and vacuum solid components alternatingly for 45 minutes.
4. Mix together solid and liquid components then heat to 65°C and stir for 24 hours.
5. Purify in membrane (membrane dialysis) for 3 days. Change the solvent every 12 to 24 hours.
6. Evaporate to remove most of the solvent and store polymer.

b. Free Radical Polymerization of p(AMPS) are done by these steps:

1. Weigh AMPS with desired weight.
2. Pour methanol (solvent) into round bottomed flask. Then input argon gas and heat the liquid component.
3. Put AMPS and AIBN (initiator) into Schlenk flask. Then in input argon gas and vacuum solid components alternatingly for 45 minutes.
4. Mix together solid and liquid components then heat to 65°C and stir for 24 hours.
5. Purify in membrane (membrane dialysis) for 3 days. Change the solvent every 12 to 24 hours.

6. Evaporate to remove most of the solvent and store polymer.
- c. Free Radical Polymerization of p(BA) are done by these steps:
1. Weigh BA with desired weight.
  2. Pour BA and THF (solvent) into round bottomed flask. Then input argon gas and heat the liquid component.
  3. Put AIBN (initiator) into Schlenk flask. Then in input argon gas and vacuum solid components alternatingly for 45 minutes.
  4. Mix together solid and liquid components then heat to 65°C and stir for 24 hours.
  5. Purify in membrane (membrane dialysis) for 3 days. Change the solvent every 12 to 24 hours.
  6. Purify with precipitation method and use THF as the solvent.
  7. Store polymer.

## B. Nuclear Magnetic Resonance Spectroscopy (NMR)

### a. p(AMPS-co-BA-co-NMA)

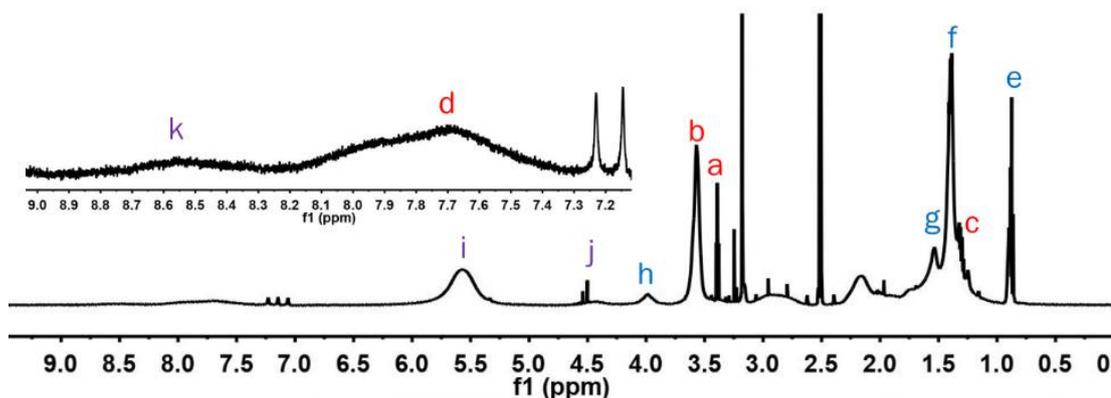


Figure 4 NMR test result of p(AMPS-co-BA-co-NMA)

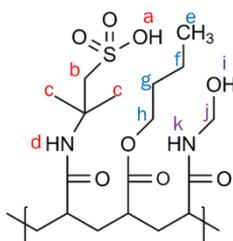


Figure 5 Structure of p(AMPS-co-BA-co-NMA)

As seen on figure 4, peaks a, b, c, and d are part of AMPS, peaks e, f, g, h are part of BA, and peaks i and j are part of NMA.

Free radical polymerization of p(AMPS-co-BA-co-NMA) is done with the ratio of 3:6:1

sequentially using Dimethyl sulfoxide (DMSO) as the solvent. Based on the NMR data, this copolymer has the AMPS:BA:NMA ratio of 0.31:0.63:0.06.

b. p(AMPS)

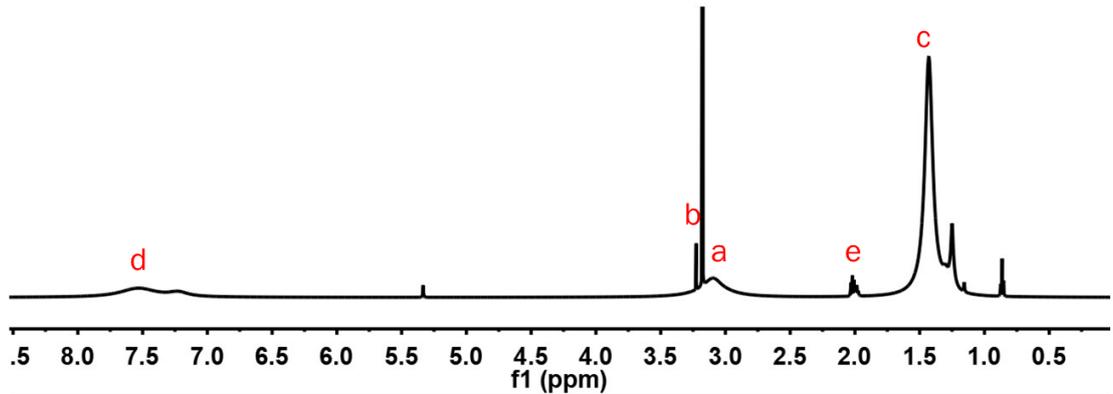


Figure 6 NMR test result of p(AMPS)

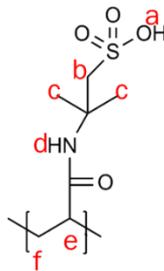


Figure 7 Structure of p(AMPS)

Figure 6 shows the result of NMR after removing what is detected as solvent and impurities. The NMR test is done using DMSO as the solvent. Peaks a, b, c, d, and e shown are parts of p(AMPS) structure shown in figure 7.

c. p(BA)

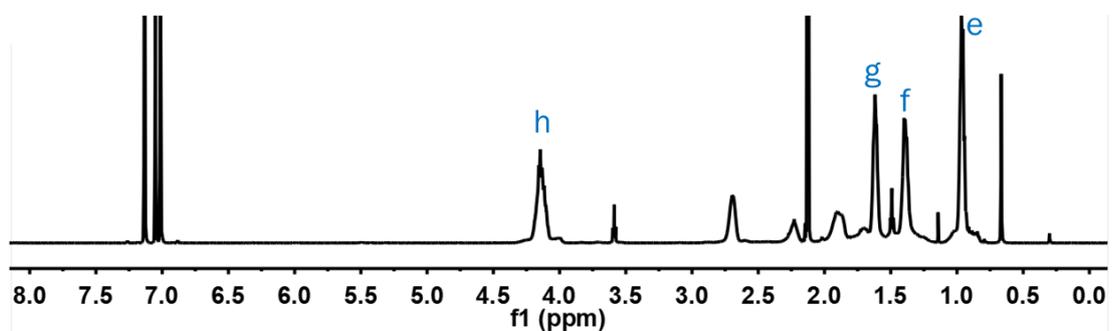


Figure 8 NMR test result of p(BA)

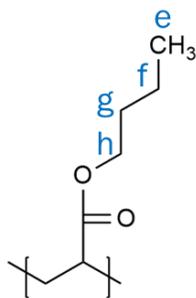
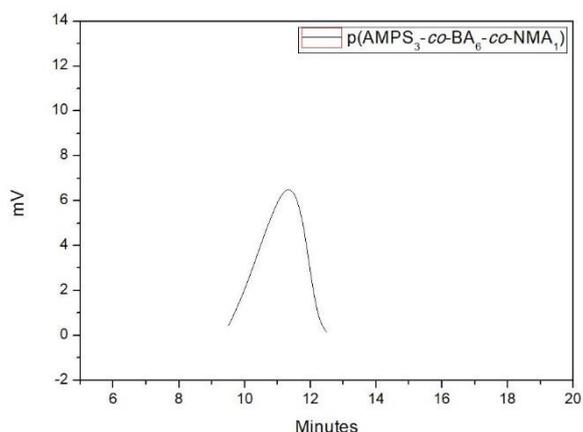


Figure 9 Structure of p(BA)

Figure 8 shows NMR test using toluene as the solvent. The high peaks at 7 ppm and 2 ppm are suspected to be toluene. Peaks e, f, g, h shown are part of p(BA) structure shown in figure 9 even though there might be slight shifting.

### C. Gel Permeation Chromatography (GPC)

#### a. p(AMPS-co-BA-co-NMA)



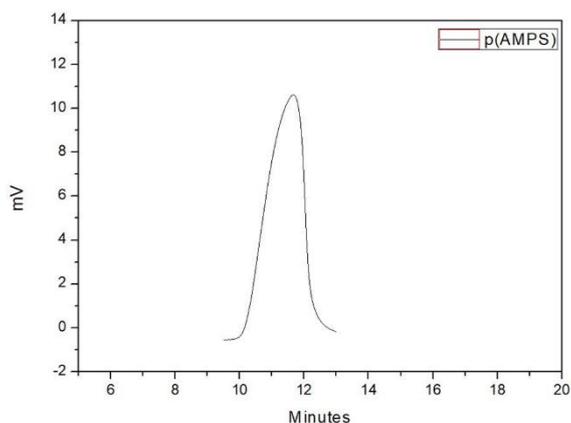
Mw= 2859286

Mn= 2334194

PDI = Mw/Mn = 1.22496

Figure 10 GPC test result of p(AMPS-co-BA-co-NMA)

#### b. p(AMPS)



Mw= 2229726

Mn= 1933271

PDI = Mw/Mn = 1.15334

Figure 11 GPC test result of p(AMPS)

#### D. Tensile test

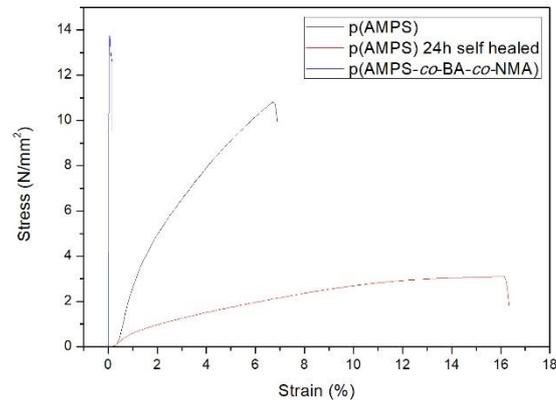


Figure 12 Tensile test result of p(AMPS), p(AMPS) 24 h self-healed, and p(AMPS-co-BA-co-NMA)

As shown in figure 12, the black line represents pristine p(AMPS), red line represents p(AMPS) that has undergone 24 hours of self-healing, and blue line represents p(AMPS-co-BA-co-NMA). Based on the figure, p(AMPS-co-BA-co-NMA) is hard and brittle because AMPS and NMA cross-links, p(AMPS) is slightly softer than p(AMPS-co-BA-co-NMA), while p(AMPS) 24 h self-healed is soft and tough. These 3 samples are 24 hours exposed to air, which makes them to absorb water due to the presence of OH in AMPS and NMA structure. p(AMPS) absorbs more water and became softer than p(AMPS-co-BA-co-NMA). This happens because p(AMPS) is 100% AMPS and has more OH compared to p(AMPS-co-BA-co-NMA) which is 30% AMPS and 10% NMA.

## Conclusion

Synthesis of p(AMPS-*co*-BA) and p(AMPS) can be done in the same solvents, initiator, and other conditions. While p(BA) cannot be polymerized under the same conditions with p(AMPS-*co*-BA) and p(AMPS) since it will form two immiscible layers due its hydrophobic properties even though the polymers are formed successfully. Changing the solvent to THF and further purification with precipitation method is need to produce miscible p(BA).

By conducting NMR test, each polymer structures can be obtained and checked if the synthesis is done successfully. NMR test also shows the ratio of copolymer. There might be some unusually high peaks which are normally the solvents and shifting of the peaks might happen. Based on the NMR test results, p(AMPS-*co*-BA) has a ratio of 0.31:0.63:0.06. While p(AMPS) and p(BA) show that they have the right structure even though there are solvent peaks visible and slight shifting.

GPC test provides information about the polymer's weight average molecular weight (Mw), number average molecular weight (Mn), and polydispersity index (PDI). The tests show that p(AMPS-*co*-BA) has Mw= 2859286, Mn= 2334194, and PDI = Mw/Mn = 1.22496. Meanwhile, p(AMPS) has Mw= 2229726, Mn= 1933271, PDI = Mw/Mn = 1.15334.

Tensile test provides information about mechanical properties of polymers such as tensile strength, modulus of elasticity, hardness, elongation, and fatigue limit. The figure shows that p(AMPS-*co*-BA-*co*-NMA) is hard and brittle, p(AMPS) is slightly softer than p(AMPS-*co*-BA-*co*-NMA), while p(AMPS) 24 h self-healed is soft and tough.

These properties of polymers and copolymers are important for future studies regarding solid electrolyte in battery application. By conducting various tests, the perfect mixture of copolymers can be chosen according the required criteria.

## References

- Diao, W., Wu, L., Ma, X., Wang, L., Bu, X., Ni, W., Yang, X., & Fang, Y. (2020). Reversibly highly stretchable and self-healable zwitterion-containing polyelectrolyte hydrogel with high ionic conductivity for high-performance flexible and cold-resistant supercapacitor. *Journal of Applied Polymer Science*, *137*(34), 48995. <https://doi.org/10.1002/app.48995>
- Hu, Y.-H., Chen, C.-Y., & Wang, C.-C. (2004). Thermal degradation kinetics of poly(n-butyl acrylate) initiated by lactams and Thiols. *Polymer Degradation and Stability*, *84*(3), 505–514. <https://doi.org/10.1016/j.polymdegradstab.2004.01.009>
- Laysandra, L., Chuang, C.-H., Kobayashi, S., Au-Duong, A.-N., Cheng, Y.-H., Li, Y.-T., Mburu, M. M., Isono, T., Satoh, T., & Chiu, Y.-C. (2020). Design of Self-Cross-Linkable Poly(n-butyl acrylate)-co-poly[N-(hydroxymethyl)acrylamide] Amphiphilic Copolymers toward Elastic and Self-Healing Properties. *ACS Applied Polymer Materials*, *2*(12), 5432–5443. <https://doi.org/10.1021/acsapm.0c00760>
- Sinirlioglu, D., Muftuoglu, A. E., & Bozkurt, A. (2014). Preparation of thin films from New Azolic copolymers and investigation of their membrane properties. *Journal of Macromolecular Science, Part A*, *51*(5), 420–434. <https://doi.org/10.1080/10601325.2014.893134>
- Wen, H.-F., Wu, H.-C., Aimi, J., Hung, C.-C., Chiang, Y.-C., Kuo, C.-C., & Chen, W.-C. (2017). Soft poly(butyl acrylate) side chains toward intrinsically stretchable polymeric semiconductors for field-effect transistor applications. *Macromolecules*, *50*(13), 4982–4992. <https://doi.org/10.1021/acs.macromol.7b00860>
- Yang, G., Cai, H., Li, X., Wu, M., Yin, X., Zhang, H., & Tang, H. (2020). Enhancement of the electrochemical performance of lithium-ion batteries by sio2@poly(2-acrylamido-2-methylpropanesulfonic acid) nanosphere addition into a polypropylene membrane. *RSC Advances*, *10*(9), 5077–5087. <https://doi.org/10.1039/c9ra08273e>
- Zheng, Y., Xu, D., Tian, S., Li, M., Wang, W., & Liu, K. (2021). Polar Poly(N-butyl acrylate)-g-polyacrylonitrile elastomer with high temperature elasticity and healability as flexible electronic substrate. *Fashion and Textiles*, *8*(1). <https://doi.org/10.1186/s40691-020-00235-4>