Front. Chem. China 2008, 3(1): 10–13
DOI 10.1007/s11458-008-0002-7

RESEARCH ARTICLE

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Preparation of a bipolar membrane by photografting polymerization

Abstract A single-sheet bipolar membrane was synthesized via photografting polymerization of an acrylic acid cation exchange layer onto the surface of a commercial homogeneous anion exchange membrane with benzophenone (BP) as the main initiator, diphenyl (2,4,6-trimethylbenzoyl)-phosphine oxide (TPO) and 2-hydroxy-2-methyl-1-phenyl-1-propanone (1173) as co-initiators and divinylbenzene (DVB) or neopentylene glycol diacrylate (NPGDA) as crosslinking agent. It was found that when benzophenone was used as single initiator and the crosslink agent is absent, the grafting degree (D_g) increases with the prolongation of irradiation time. The grafting degree reaches a maximum at 60 seconds reaction time when the crosslinking agent is added, and the grafting degree is higher when using NPGDA instead of DVB as crosslinking agent. The grafting degree increases as the composite initiator system is used. When polymerization was initiated by BP and TPO, and the dosage of NPGDA was 2.5% mol concentration of monomer, the grafting degree reaches 30.1%.

Keywords bipolar membrane, photografting polymerization, ion exchange membrane

1 Introduction

A bipolar membrane is composed of the cation- and anion-exchange layers located on different sides of the membrane and the interface layer between the ion-exchange layers. In the last few decades, bipolar membrane technologies have rapidly progressed. When this membrane is used in conjunction with a monopolar membrane, the combined system can be applied in many fields such as the chemical industry, environmental protection and biochemistry.

Reports on bipolar membrane first appeared in the 1950s. Since the 1980s, the effective investigations on the mechanism, membrane structure, materials and preparation process result in significant improvement on the [1–9].

The preparation methods of bipolar membranes are divided into two major kinds. One is the two layer lamination which involves different techniques such as hot pressing, gluing and casting. Due to the existence of the physical interface or adhesive between the layers, the membranes have low ion transfer capability, high membrane electric resistance and low operation current density. Therefore, it is difficult to prepare the desired thin ion-exchange layer using this technique method.

The other technique is the mono-sheet or single-sheet method. In this technique the negative ions and positive ions were introduced respectively on the different sides of the matrix film. The traditional method adopts polyethylene soaked with the solution of styrene, divinylbenzene and benzoyl peroxide. After polymerization, sulfonation and quaternarization to produce the cation- and anion-exchange layers, the cation-and anion-exchange layers are obtained by quaternarization and sulfonation respectively. The grafting methods, induced chemistry, radiation and plasma, were also reported [10–19].

Till now, a few bipolar membranes are commercially available. Bipolar membrane fabrication technology has been monopolized by a few companies such as Asahi Glass Company (Japan), Tokuyama Soda Co. Ltd (Japan), WSI Technologies Inc. (USA), and FuMA-Tech (Germany).

In China, the research of bipolar membrane was not carried out until the 1990's. Some articles introducing bipolar membrane technology appeared and investigations on its application were developed. There is still a large gap in performance between self-prepared membranes and commercial membranes. Furthermore, the domestic studies mainly focus on the application rather than membrane fabrication, so only a few studies on preparation were reported [12,16–19].The preparation

Translated from *Journal of Beijing Technology and Business University*, 2007, 25(1): 15–18 [译自: 北京工商大学学报]

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of an adequately functional bipolar membrane requires the optimization of its different components. The choice of a suitable preparation route for the desired materials should be part of this optimization.

Photografting polymerization has the advantages of low cost, quick reaction and continuous operation. The ultraviolet ray has a limited penetration depth; it is suitable for preparing the materials which have different properties on different sides.

In this study, photografting polymerization was introduced to prepare bipolar membranes. The single-sheet membranes were synthesized by joining the photografted cation-exchange layer and commercial homogeneous anion-exchange membrane via a covalent bond.

2 Experimental

2.1 Materials

Homogeneous anion exchange membrane (model JAM-I-10) was purchased from Beijing Huanyu Lida Co., Ltd. Acrylic acid (AA, Beijing Yili Fine Chemicals Company) was distilled under vacuum. Divinylbenzene (Chengdu Kelong Chemical Reagent Factory), Neopentyl glycol diacrylate (NPGDA, Tianjin Tianjiao Chemical Industry Co., Ltd.), Benzophenone (BP, Tianjin Yuanhang Chemicals Company), and acetone (Atoz Fine Chemicals Co., Ltd.) were used as received. Diphenyl(2,4,6-trimethyl-benzoyl)-phosphine oxide (TPO) and 2-hydroxy-2-methyl-1-phenyl-1-propanone (1173) were donated by Insight High Technology Co., Ltd.

2.2 Photografting procedures

The photografting polymerization device was made with a high pressure mercury lamp (1 kW, Beijing Institute of Electric Light Source). The commercial anion exchange membrane pieces of 2 cm × 2 cm were washed with deionized water, then dried and weighed. The reaction solution using AA as monomer, DVB and NPGDA as crosslink agents, BP as main initiator, and TPO and 1173 as co-initiators was bubbled with nitrogen. The solution was placed between the commercial anion exchange membrane and a bi-oriented polypropylene (BOPP) film. This set was irradiated for a given time, and then the membranes were extracted with deionized water for 12 hours.

2.3 Characterization

The grafting effect was evaluated by the grafting degree (D_g). $D_g = (W - W_0)/W_0 \times 100\%$, where the W and W_0 represent the weight of grafted and original membranes, respectively.

3 Results and discussion

A bipolar membrane was realized by photografting the cation exchange layer of AA onto the surface of the commercial anion exchange membrane. The D_g was influenced by the irradiation time, crosslink agent and initiator. In the following discussion, the dosage of crosslinking agent indicates the mole ratio of the crosslinking agent to the monomer, and the content of the co-initiator (TPO or 1173) is the ratio of co-initiator concentration to that of the BP.

3.1 Irradiation time

With a constant concentration of BP (0.10 mol/L) and different crosslinking agents, the effect of irradiation time on the grafting degree was investigated. The results in Fig. 1 indicate that the D_g is low and increases with the prolongation of irradiation time when the crosslinking agent was absent. The longer reaction time is beneficial to the increase of D_g, which reaches 1.09% at 120 s irradiation.

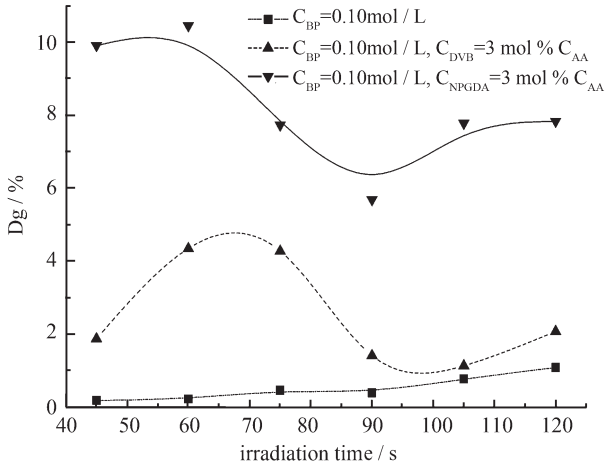

Fig. 1 The effect of irradiation time on grafting degree

The D_g has an obvious increase when the crosslinking agents were added, and the effect of NPGDA is more remarkable than that of DVB. Using NPGDA as crosslinking agent, the D_g comes down when it rises to a maximum of 10.45% at 60 s, and rises slowly after exceeding 90 s. Similar to the NPGDA, during 60 to 70 s, the grafting degree of DVB has a maximum of 4.35%. When using NPGDA as crosslinking agent, the resulting bipolar membranes have higher flexibility even with a higher grafting degree. On the contrary, membranes using DVB as crosslinking agent are rigid due to the existence of benzene ring.

3.2 Composite initiator system

From Fig. 1, it was concluded that when BP is used alone the grafting degree is low even though it is a typical photografting initiator. The topmost grafting degree is just about 10.45% even if the crosslinking agent is added. The composite initiator system that consist of the grafting initiator BP and homopolymerization initiators, TPO or 1173, and the presence of a crosslinking agent increase the grafting degree and a uniform AA grafting layer is obtained.

Figure 2 gives the result of photografting initiated by a composite system with some constant reaction conditions, i.e., BP concentration is 0.10 mol/L, the concentration of NPGDA is 3 mol% of BP concentration, and the irradiation time is 60 s.

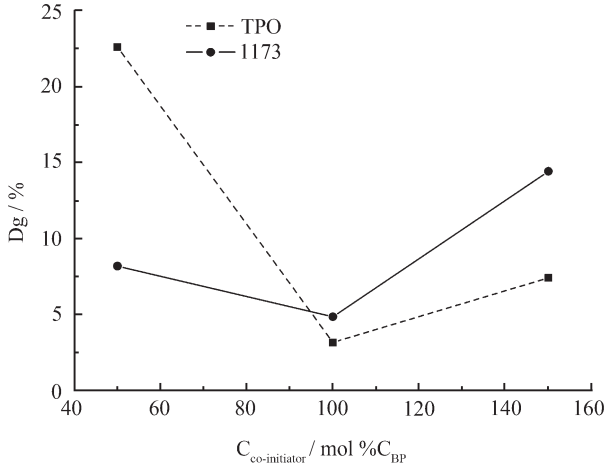

Fig. 2 The relationship of co-initiator and grafting degree

The plots in Fig. 2 indicate that the composite initiator systems have minimum D_g when the ratio of BP to co-initiator is 1:1. This is probably understood by the competition of grafting and homopolymerization. In the system of BP and TPO, the grafting degree has a maximum of 22.61% at the low ratio of TPO (50%). On the other hand, the system of BP and 1173 has a low D_g at the ratio of 50% and a higher D_g (14.42%) at the ratio of 150%. Therefore at low ratio (less than 1) TPO is better and high ratio (more than 1) 1173 is appropriated.

3.3 Crosslinking agent

Figure 3 shows the variation in D_g with the increase of NPGDA ratio from 0.5% to 3.0% when the concentration of BP is 0.05 mol/L, the co-initiator TPO is 50 mol% of BP, and irradiation time is 60 s.

With the increase of crosslinking agent concentration, the D_g firstly increases to a maximum of 30.10% at an NPGDA ratio of 2.5%, and then decreases rapidly. This phenomenon suggests that the crosslink formed in a thicker polymer layer and thus the D_g was improved. Whereas the excessive cross linker (exceeded 2.5%) restrained the grafting and thus the Dg decreased.

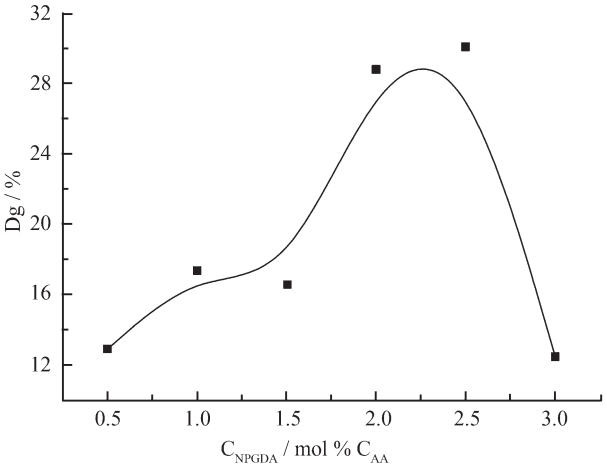

Fig. 3 The effect of crosslinking agent on grafting degree

4 Conclusions

The bipolar membrane was fabricated by photografting a cation exchange layer of poly (acrylic acid) onto the surface of the commercial homogenous anion exchange membrane. Without the crosslinking agent, the grafting degree increases at a low level with the prolongation of irradiation time. The addition of a crosslinking agent makes the Dg increase evidently, the D_g is higher using NPGDA as the crosslink agent instead of DVB and the maximum appears at a reaction time of 60 s. A composite initiator system, BP blend with the co-initiator, improves the D_g. Using TPO as co-initiator, an NPGDA content of 2.5 mol% of monomer as crosslinking agent, the D_g has a peak value of 30.1%.

Acknowledgements This work was supported by the Scientific Research Common Program of Beijing Municipal Commission of Education (KM200410011004).

References

1. Kemperman A J B. Handbook on Bipolar Membrane Technology. Twente University Press, 2000
2. Gao Congjie, Li Dong, Lu Xueren, Zhang Jianfei. A brief introduction to bipolar membrane and electrodialytic hydrolysis. Technology of Water Treatment, 1994, 20(3): 133–139 (in Chinese)
3. Xu T W. Electrodialysis process with bipolar membranes (EDBM) in environmental protection-a review. Resources Conservation and Recycling, 2002, 37: 1–22
4. Xu Tonwen, Sun Shusheng, Liu Zhaoming, Yang Weihua, Li Sanqing, Li Xudi, He Binglin. The functions and

constructions of a bipolar type ion exchange membrane electrolytic cell. Membrane Science and Technology, 2000, 20(1): 53–59 (in Chinese)
5. Chen Cuixian, Yu Lixin and Dai Youyuan. Review on and further development of some new membranes and membrane processes. Technology of Water Treatment. 1996, 22(6): 307–313 (in Chinese)
6. Xu T W. Development of bipolar membrane-based processes. Desalination, 2001, 140: 247–258
7. Franken T. Bipolar membrane technology and its application. Membrane Technology, 2000, 125: 8–11
8. Liao S Z, Mo J X. The development of bipolar membrane and its application. Technology of Water Treatment, 1995, 21(6): 311–318 (in Chinese)
9. Yasuda Naoto, Irihama Hideki. Method for regeneration of ion exchange resin. JP: 2005219011 A2, 2005-08-18
10. Chlanda, Frederick Paul, Lan Mingjye. Bipolar membranes and methods of making same. CN: 87104069A, 1987-12-16 (in Chinese)
11. Hsueh C L, Peng Y J, Wang C C, Chen C Y. Bipolar membrane prepared by grafting and plasma polymerization. J Membr Sci, 2003, 219: 1–13
12. Fu Rongqiang, Xu Tongwen, Yang Weihua, Pan Zhongxiao. preparation of a mono-sheet bipolar membrane by simultaneous irradiation grafting polymerization of acrylic acid and chloromethylstyrene. Journal of Applied Polymer Science, 2003, 90: 572–576
13. Strathmann H, Rapp H J, Bauer B. Theoretical and practical aspects of preparing bipolar membrane. Desalinations, 1993, 90: 303–323
14. Yokoyama Y, Tanioka A, Miyasaka K. Preparation of a single bipolar membranes by plasma induced graft polymerization. J Membr Sci, 1989, 43: 165
15. Akihiko Tanioka, Yutaka Yokoyama, Mitsuru Higa, Keizo Miyasaka. Membrane potential of bipolar membranes prepared by plasma induced grafted polymerization on porous polyolefin. Colloids and Surfaces B: Biointerfaces, 1997, (9): 1–7
16. Hao Jihua, Chen Cuixian, Li Lin, Yu Lixin, Jiang Weijun. Preparation of bipolar membranes (I). Journal of Applied Polymer Science, 2001, 80: 1658–1663
17. Liao S Z, Mo J X. Technology of Water Treatment, 1997, 23(3): 146–150 (in Chinese)
18. Fu Rongqiang, Xu Tongwen, Yang Weihua. Bipolar and its preparation method. CN: 1704151A, 2005-12-07 (in Chinese)
19. Fu Rongqiang, Xu Tong wen, Yang Weihua. A bipolar membrane with low hydrolysis voltage and its preparation method. CN: 1727058, 2006-02-01 (in Chinese)