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Optimization of reaction for synthesis of polyisobutylene amine between amination agent and epoxy polyisobutylene

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Abstract: An optimization study on the amination reaction of epoxy polyisobutylene for synthesis of polyisobutylene amine is presented. The experimental results indicate that *n*-butanol and ethylenediamine are the suitable solvent and amination agents for the reaction, respectively. The reaction yield of the amination reaction is notably increased with the enhanced molar ratio of either *n*-butanol against epoxy polyisobutylene or ethylenediamine against epoxy polyisobutylene. Also, the yield is enhanced with increasing temperature and time during the experimental range. Strikingly, the yield reaches as high as 91.30% under optimal conditions; with the molar ratio of ethylenediamine, *n*-butanol and PIBO of 10∶6∶1, the reaction temperature of 150 ℃ and the reaction time of 6 h. In addition, the yield of the reaction is slightly decreased with the enhanced water content of the system. Accordingly, the mass concentration of water should be controlled within 1.7% during the reaction.

Key words: polyisobutylene amine; synthesis; optimization; amination reaction; epoxy polyisobutylene

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Carbon deposits can be formed at various locations of the engine, such as the combustion chamber, injection nozzle and inlet valve during the running process of the engine. It has been recognized that carbon deposits can obviously affect engine efficiency and emissions[1-7]. To address this issue, gasoline additives have been proved to be an efficient agent to be used widely for cleaning up the carbon deposit and protecting the engine. Among them, polyisobutylene amine (PIBA) is a type of surfactant with the function of removing deposits and coke from the nozzle, intake valve and combustion chamber. As a commonly used gasoline additive, it can also prolong the life of the engine and reduce its fuel consumption with the addition of necessary amount of PIBA into the used gasoline [8].

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Due to its practical applications, emerging efforts have been made to develop the synthetic route of PIBA[9-11]. However, disadvantages are still present in these routes. For example, some routes present the trace residual of halogen in PIBA and induce serious environmental pollution when the product burns with gasoline in the engine[9]. The routes without halogen introduction are played under high pressure (up to several million Pascal) and lead to the expensive equipment investments and a high risk process[10-11].

To the best of our knowledge, epoxy groups can efficiently react with amines[12-15]. Recently, our group has developed a new route for the synthesis of PIBA. Briefly, epoxy polyisobutylene (PIBO) is synthesized through the epoxidation reaction of polyisobutylene (PIB) using hydrogen peroxide. Then, PIBO is aminated to produce PIBA. The whole process takes place under moderate conditions and no halogen is introduced into the product. It is necessary to optimize the reaction parameters during the development of the synthetic route[16-19]. In our route of PIBA preparation, the epoxidation reaction of PIB was studied in the previous paper of our group[20]. Here, we mainly focus on exploring the optimal conditions of the amination reaction process. Specifically, the suitable solvent and amination agent of the reaction as well as their feeding ratio are determined. The optimal conditions including temperature and time are discussed. Furthermore, the effect of the water concentration on the amination reaction is also carried out in this manuscript.

1 Experimental

1.1 Materials

PIBO is prepared by PIB using hydrogen peroxide as the oxidizer according to our previously reported strategy[20]. The average molecular weight of the PIBO is about 1 000 and its content of epoxy group is 68%. The other reagents are commercially available and purchased with A.R. grade. They are used without further purification.

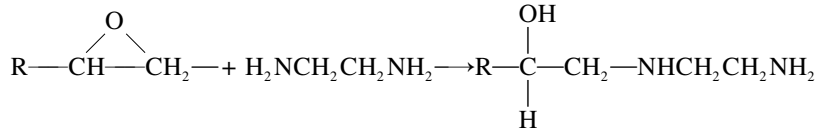
1.2 Reaction mechanism

PIBO can react with amination agents and then form PIBA. The reaction is carried out without catalyst. However, the obtained PIBA may react with PIBO, which is an

unnecessary side reaction to reduce the amine value of the product and damage the application performance of PIBA. The scheme of the amination process is shown in Fig. 1.

The amination reaction is evaluated using the parameter, the yield of amination reaction, which is defined as the measured amine value dividing the theoretical maximum amine value of the reaction. The average molecular weight of the PIBA product is about 1 040 g/mol.

Main reaction



Side reactions

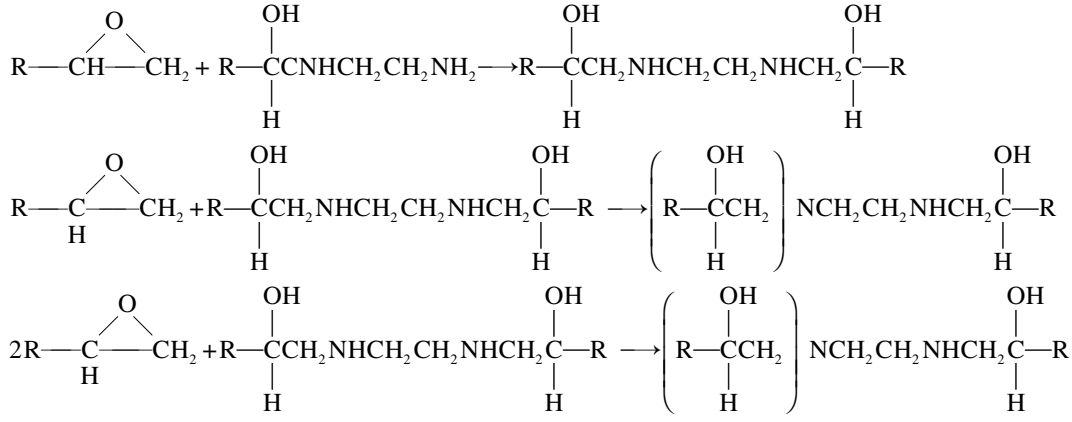


Fig. 1 Mechanism of the reaction of epoxy polyisobutylene

1.3 Amination procedure

The amination reaction is carried out in a sealed tank, equipped with a thermometer, manometer and stirrer. The temperature of the tank is controlled automatically with ± 1 ℃. A certain amount of solvent, amination agent and PIBO are added together to the tank at room temperature. After sealing, the air in the tank is removed using the vacuum pump. After closing the exhaust pipe, the solution is vigorously stirred and raised to the reaction temperature. The reaction is continued for several hours and the crude product is poured out after it has cooled to room temperature. The pale yellow liquid, PIBA, is obtained after removing the volatile components in the crude product by using a rotary evaporator under the conditions of 5 kPa and 100 ℃ until no mass loss is observed.

1.4 Determination of amine value

The amine value is used to calculate the yield of amination reaction. It is determined in accordance with the Chinese petrochemical industry standard SH/T0251—1993.

2 Results and Discussion

2.1 Selection of the suitable reaction solvent

Since PIBO and the amination agent are immiscible, the suitable solvent of this reaction is necessary. Benefiting from a long chain, *n*-butanol is miscible with PIBO. At the same time, the polarity of *n*-butanol causes it to become miscible with the amination agent. So, the addition of *n*-butanol as solvent results in the reaction system being partially miscible. It encourages the rate of the main reaction and reduces the occurrence of the side reaction. In addition, due to its low boiling point, *n*-butanol is easily separated from the reaction system by evaporation. Therefore, *n*-butanol is considered as a suitable solvent of the reaction.

2.2 Selection of the suitable amination agent for the reaction

In order to reduce the formation of combustion chamber deposits (CCD), the amination agent with small molecular weight is considered to be the suitable reaction candidate. Therefore, some of the common amines which include diethylamine, ethylenediamine, ethanolamine and diethylene triamine are selected as the potential amination agents of this reaction. The molar ratio of the feeding PIBO, *n*-butanol and amination agent is 1∶30∶30 in order to make the system miscible. The reaction is carried out under the temperature of 150 ℃ and continues for 8 h before the amine value of the product is determined.

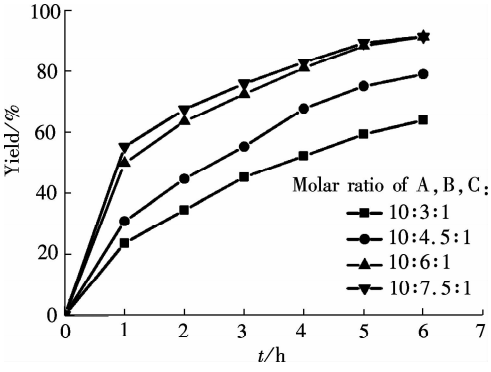
The yield of reaction is 62.85%, 97.42%, 91.02% and 98.04% using diethylamine, ethylenediamine, ethanolamine and diethylene triamine, respectively. It illustrates that the primary amine can be considered as the potential amination agent used in the reaction. Due to the hydroxy group, a pull electronic group, the amination reaction using ethanolamine obtains the lowest degree among the three amination agents. However, the yield of diethylamine is much lower than the primary amines. The

reason is believed to be the steric effect of two ethyl groups in its molecular structure. Furthermore, comparing the price of these candidates, ethylenediamine is selected to be the preferred amination agent.

2.3 Determination of the optimization of reaction feeding ratio

2.3.1 Optimization of *n*-butanol feeding ratio

It has been mentioned that *n*-butanol is considered to be the reaction solvent for the amination reaction. Fig. 2 shows the effect of the added amount of *n*-butanol on the yield of amination reactions. It indicates that the yield enhances with the increased amount of *n*-butanol until the molar ratio of *n*-butanol and PIBO reaches 6∶1. The reason may be that when the added *n*-butanol reaches a certain amount, the dissolved hylenediamine in the system is sufficient to make the chemical reaction rate become the rate-determining step of the process. At that time, high *n*-butanol feeding will affect the amination reaction little. However, excessive feeding will increase the cost of the subsequent separation operation. Herein, the suitable molar ratio of *n*-butanol and PIBO is determined as 6∶1.



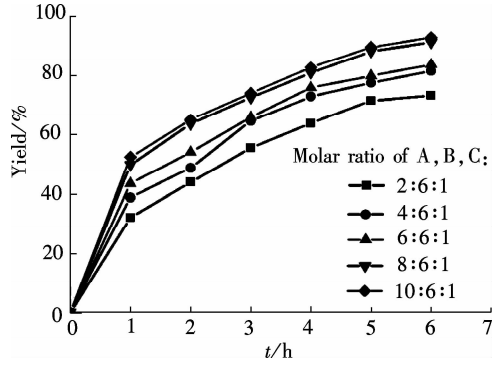
A—ethylenediamine; B—*n*-butanol; C—PIBO

Fig. 2 Influence of added *n*-butanol on the yield of reaction

2.3.2 Optimization of ethylenediamine feeding ratio

The mechanism of the amination reaction indicates that the main reaction and side reactions are the competitive reaction. The increased amount of ethylenediamine effectively inhibits the side reactions. In order to optimize the feeding ratio of ethylenediamine and PIBO, the yield of reaction with different molar ratios of ethylenediamine and PIBO is measured, as shown in Fig. 3. This indicates that the yield of reaction increases with the enhanced molar ratio of ethylenediamine and PIBO. It also illustrates that the yield only slightly increases with more ethylenediamine when the molar ratio is higher than 10∶1. At that time, the yield of amination reaction can reach more than 90%. The obtained product can meet all of the indicators in its practical applications. Due to the increasing separation cost of excessive ethylenediamine, the suitable molar ratio of ethylenediamine and PIBO is believed to be 10∶1.

In short, the optimum molar ratio of ethylenediamine, *n*-butanol and PIBO is determined as 10∶6∶1.



A—ethylenediamine; B—*n*-butanol; C—PIBO

Fig. 3 Influence of added ethylenediamine on the yield of reaction

2.4 Determination of the optimum parameters of reaction conditions

The temperature and time of the reaction are the key parameters for the synthesis process. Furthermore, the selectivity of the main reaction and the side ones sometimes depends on the reaction temperature. In order to select the suitable temperature and time of the reaction, experiments exploring the relationship between temperature and the yield of reaction are carried out. The results are illustrated in Fig. 4. It indicates that a higher temperature encourages the reaction rate during the experimental stage. Also, the selectivity of the reaction is satisfied at a high temperature. When the reaction time reaches 6 h, the yield reaches 91.30%, 96.76% and 97.17% at the temperature of 150, 160 and 180 ℃, respectively. It is speculated from Fig. 4 that the yield of the experiment at 150 ℃ can be further improved if the reaction time is longer than 6 h. Although the higher temperature encourages the reaction rate, the energy consumption is also increased. It is more serious that the cost of equipment investment is increased because the operation pressure of the reaction system enhances with the increasing temperature. It has been proved that the product can meet the indicators of practical applications when the yield of amination reactions is higher than 90%. Therefore, the optimum parameters of the reaction are determined as a temperature of 150 ℃ and the reaction time of 6 h.

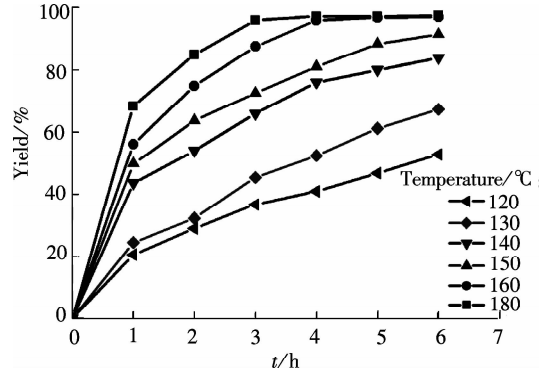


Fig. 4 Influence of temperature on the yield of reaction

The verification experiments are carried out under optimal conditions. The experimental results prove that the PIBA products can successfully meet the indicators of practical applications.

2.5 Determination of the effect of water content on the reaction

PIBO is obtained through the reaction between PIB and hydrogen peroxide. It inevitably contains little water. Since the excessive *n*-butanol and ethylenediamine are collected through evaporation and recycled, the water from PIBO can be enriched in the system. Therefore, the effect of water content on the amination reaction is discussed. The result shown in Fig. 5 indicates that the yield is linearly decreased with the increasing water content during the experimental range. When the mass content of water is increased to about 1.7%, the yield is reduced to about 90%. If the water content is further enhanced, the product of amination reaction will not meet the indicators of practical application any more. Therefore, it is necessary to remove the water when the water mass concentration of the system reaches about 1.7%.

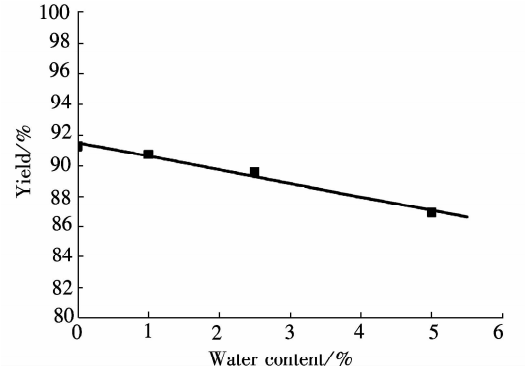


Fig. 5 Influence of water content on the yield of reaction

3 Conclusion

The amination reaction of epoxy polyisobutylene for polyisobutylene amine preparation is studied. The suitable solvent and amination agent for the reaction is demonstrated to be *n*-butanol and ethylenediamine, respectively. Detailed experimental analysis is carried out to determine the optimum conditions for the reaction. Specifically, it is demonstrated that the yield of the amination reaction reaches 91.30% with the molar ratio of ethylenediamine, *n*-butanol and PIBO of 10:6:1, the reaction temperature of 150 ℃ and the reaction time of 6 h. Furthermore, the mass concentration of water can affect the yield of the reaction and it should be limited to less than 1.7%.

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胺解剂与环氧聚异丁烯反应制备聚异丁烯胺工艺优化

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摘要:对以环氧聚异丁烯为原料胺解制备聚异丁烯胺反应的工艺优化进行了研究. 实验结果表明,正丁醇和乙二胺是适用于该反应的溶剂和胺解剂. 胺解反应的收率随着加入的正丁醇以及乙二胺与聚异丁烯摩尔比的增加而显著提高. 同时,在实验研究范围内反应收率随着反应温度和反应时间的增加而提高. 在乙二胺:正丁醇:环氧聚异丁烯的摩尔比为 10:6:1,反应温度为 150℃,反应时间为 6 h 的最优工艺条件下,反应收率可达 91.30%. 此外,胺解反应的收率随着体系中水含量的增加而略微降低. 因此,反应过程中,体系所含水的质量分数应控制在 1.7% 以下.

关键词:聚异丁烯胺;合成;优化;胺解反应;环氧聚异丁烯
中图分类号:TQ031