Study on Synthesizing Polycarbonate with Triphosgene

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Abstract—Polycarbonate is a widely used thermoplastic engineering plastic with excellent properties. Using triphosgene and Bisphenol A as raw materials, polycarbonate is synthesized by interfacial polycondensation. The effects of catalyst dosage, molar ratio of raw material, reaction temperature and reaction time on the molecular weight of the product are investigated, and the optimal reaction conditions are obtained. The structure of the product is verified by infrared absorption spectroscopy. The rotary viscometer measures the intrinsic viscosity of the sample and calculates the viscosity average molecular weight of the sample to be 50000. The glass transition temperature of the product is detected to be 148.5°C by dilatometer. The polycarbonate synthesized by the new method meets the quality requirements.

1. Introduction

Polycarbonate(PC), mainly bisphenol A(BPA) type polycarbonate, is a kind of excellent thermoplastic engineering plastics containing carbonate group in the molecular chain, with outstanding impact resistance and creep resistance, and good heat resistance and cold resistance [1]. It is widely used in automobile, electrical and electronic, building materials, communication equipment, optical disc and daily necessities and other fields[2].

There are two main reports on the synthesis methods of polycarbonate. One is the phosgene interface method, which uses phosgene and Bisphenol A as raw materials to prepare polycarbonate through interfacial polycondensation; the other is the melt transesterification method, which uses diphenyl carbonate and bisphenol A as raw materials to prepare polycarbonate through melt polycondensation. The phosgene interface method uses highly toxic phosgene, which brings risks to the experiment or production process. The melt transesterification method needs to be carried out under high temperature and high vacuum conditions, especially the absolute pressure of the latter stage of the reaction is required to be less than 1mmHg [3]. The operating conditions are extremely harsh, and high temperature easily affects the color of the product. Triphosgene (BTC), also called solid phosgene, is a stable solid compound. Because it is relatively safe in transportation and storage, it has been used more and more widely instead of phosgene in industrial production. Using the triphosgene to synthesize polycarbonate, which not only avoids the highly toxic phosgene, but also enables the reaction to proceed at near normal temperature and pressure. It is a good new method for polycarbonate production. In this paper, we choose triphosgene instead of phosgene and bisphenol A to synthesize polycarbonate by interfacial polycondensation, and its structure and thermal properties are characterized, which provides technical basis for industrial production.
2. Experiment

2.1. Reagents and instruments
Triphosgene (99%), bisphenol A (99%), triethylamine (AR), dichloromethane (AR), sodium hydroxide (AR). The experimental instruments include WQF-510A FTIR infrared spectrometer, DHJ-8s rotary viscometer, and 30cm dilatometer.

2.2. Synthesis of polycarbonate
A condensing tube, a dropping funnel and a stirrer are installed on the 250ml three-necked flask. Put the flask in the water bath. Add 10.27g bisphenol A and sodium hydroxide solution into the flask, heat up to 40°C, stir until bisphenol A is completely dissolved, then add 0.6g triethylamine, and slowly add the pre-prepared triphosgene dichloromethane solution(5.64g triphosgene is dissolved in 100mL dichloromethane), and then continue the reaction for 60min, then separate the dichloromethane solution of the lower layer, wash with deionized water to neutrality, recover the solvent dichloromethane in the rotary evaporator. The remaining white fibrous solid is washed with hot acetone to obtain the product.

The polymerization equation is shown in Figure 1.

![Polymerization equation of polycarbonate]

2.3. Testing and characterization
The structure of the product is characterized by the infrared spectrometer, the potassium bromide tablet is pressed, and the scanning range is set to 400~4400 cm⁻¹. The dilatometer is used to detect the glass transition temperature of the product. The rotary viscometer is used to measure the intrinsic viscosity of the sample at 20°C, and then the viscosity average molecular weight of the sample is calculated by the Mark-Houwink formula [4].

Mark-Houwink formula:

\[ [\eta] = kM^\alpha \Rightarrow M = (\eta/[k])^{1/\alpha} \]

Where, \([\eta]\) is the intrinsic viscosity, \(M\) is the viscosity average molecular weight, \(k\) is the proportional constant, \(k = 1.11 \times 10^{-2}\), \(\alpha\) is the expansion factor, \(\alpha = 0.82\) [5].

3. Results and Discussions

3.1. The effect of catalyst dosage on product molecular weight
The molecular weight reflects the degree of polymerization of the polymer and has a direct impact on its performance. Therefore, this experiment uses the molecular weight of the product as the basis for selecting the best reaction conditions.

In this experiment, triethylamine is selected as the reaction catalyst [6]. Take bisphenol A 10.27g (45mmol) and triphosgene 5.64g. Keep the reaction temperature at 40°C and the reaction time for 60 minutes. Investigate the effect of the amount of catalyst triethylamine on the molecular weight of the product.
Fig. 2 The effect of catalyst dosage on product molecular weight

It can be shown from Figure 2, when the amount of triethylamine is low, the molecular weight of the product increases with the increase of the amount of triethylamine. When the amount of triethylamine is 0.6g, the catalytic effect is basically achieved, and it is meaningless to continue to increase the amount of catalyst. From the perspective of saving, the optimal amount of catalyst is 0.6g, that is, 0.0584g/g (BPA). At this time, the maximum viscosity average molecular weight of the product polycarbonate is 50000.

3.2. The effect of raw material molar ratio on product molecular weight

Take bisphenol A 10.27g (45mmol) and catalyst 0.6g. Keep the reaction temperature at 40°C and the reaction time for 60 minutes. Investigate the effect of raw material molar ratio on the molecular weight of the product.

According to the polymerization equation, the theoretical mole ratio of raw material bisphenol A and triphosgene is 3:1. Due to the hydrolysis reaction of triphosgene in the alkaline solution of sodium hydroxide, a part of triphosgene is wasted, so triphosgene should be appropriately excessive. When bisphenol A is 45mmol, triphosgene should be greater than 15mmol. It can be seen from Figure 3 that the molecular weight of the product gradually increases with the increase of the amount of triphosgene, but when the amount of triphosgene is too much, the excess triphosgene will act as a blocking agent, which restricts the polymerization reaction and reduces the molecular weight. According to Figure 3, when the amount of triphosgene is 19mmol (5.64g), the product has the largest molecular weight. At this time, the molar ratio of bisphenol A to triphosgene is 3:1.27.
3.3. The effect of the reaction temperature on product molecular weight
Take bisphenol A 10.27g, catalyst 0.6g and triphosgene 5.64g. Keep the reaction time for 60 minutes. Since the boiling point of dichloromethane is 40°C, when investigating the reaction temperature of 45°C and 50°C, we replace the solvent with chloroform, which has similar properties to dichloromethane. Investigate the effect of the reaction temperature on product molecular weight.

![Fig.4 The effect of the reaction temperature on product molecular weight](image)

It can be seen from Figure 4 that the molecular weight of the product first increases and then decreases with the reaction temperature increases. When the reaction temperature is low, the reaction rate is slow and the reaction system is viscous, which is not conducive to the progress of the reaction. With the reaction temperature increases, the reaction rate, the degree of polymerization and molecular weight all increase. When the reaction temperature reaches 40°C (the boiling point of dichloromethane), the molecular weight of the product is the largest. Because it is a reflux reaction, the reaction temperature at this time is also very well controlled. We replace the solvent with chloroform and continue to increase the reaction temperature, the side reactions such as hydrolysis and oxidation intensify, and the molecular weight decreases. Therefore, the optimal reaction temperature in this experiment is 40°C.

3.4. The effect of reaction time on product molecular weight
Take bisphenol A 10.27g, catalyst 0.6g and triphosgene 5.64g. Keep the reaction temperature at 40°C. Investigate the effect of reaction time on product molecular weight.

![Fig.5 The effect of reaction time on product molecular weight](image)
It can be seen from Figure 5 that the degree of reaction polymerization and molecular weight gradually increases with the reaction time increases. When the reaction time reaches 60min, the molecular weight of the polycondensation reaction is the highest. When the reaction time is prolonged, the side reaction increase and the molecular weight of the product decrease slightly. The optimal reaction time is 60min.

3.5. Product characterization

3.5.1 Product structure analysis

Figure 6 shows the infrared absorption spectrum of the product. In the figure, 1774cm⁻¹ is the characteristic absorption peak of C=O stretching vibration, indicating that there is C=O in the sample; the absorption peak at 1502cm⁻¹ is caused by the stretching vibration of the benzene ring skeleton, indicating that the sample contains benzene ring; 1230cm⁻¹, 1191cm⁻¹ and 1160cm⁻¹ are caused by the stretching vibration of C-O, indicating that there is C-O in the sample; 1016cm⁻¹ and 825cm⁻¹ correspond to the fingerprint peaks of the para aromatic ring; 2969 cm⁻¹ is saturated with C-H stretching vibration peak, indicating that there is -CH₃ in the sample. It can be seen from the infrared absorption spectrum that the product is polycarbonate.

3.5.2 Product glass transition temperature determination

Figure 7 is the relationship graph of capillary liquid column height and temperature.
The temperature corresponding to the turning point of the slope of the two straight lines in the figure is the glass transition temperature of the product, which is 148.5°C, which is consistent with the polycarbonate prepared by the phosgene interface method and the melt transesterification method.

4. Conclusion

Based on the results and discussions presented above, the conclusions are obtained as below:

1. Using bisphenol A and triphosgene as raw materials, triethylamine as catalyst, polycarbonate is synthesized by interface polycondensation method. The optimal reaction conditions are: the molar ratio of raw materials n (BPA): n (BTC) is 3: 1.27, catalyst dosage is 0.0584g/g (BPA), the reaction temperature is 40°C, and the reaction time is 60min.

2. The product is proved to be bisphenol A type polycarbonate by infrared absorption spectroscopy. The maximum viscosity average molecular weight is calculated to be 50000. The glass transition temperature of the product is 148.5°C. The polycarbonate produced by the new method is consistent in quality with the existing polycarbonate.

3. The new method not only avoids the highly toxic phosgene, but also enables the reaction to proceed at near normal temperature and pressure, which provides important guiding significance for industrial production. Further optimization of reaction conditions to improve the molecular weight of products will be the direction of future research.

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