

Condensation polymers: synthesis, properties, and applications

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Abstract. With the widening of the application fields of polycondensation polymers, many types of modifiers have been used to modify the molecular structure of polycondensation polymers. In recent years, more and more researchers have focused on the study of the molecular structure modification of polycondensation polymers and gradually ignored the research on the synthesis methods and properties of polycondensation polymers. This review covers the synthesis strategies of four common polycondensation polymers in the market, including polyamide (PA), polycarbonate (PC), polyester (PET), and phenolic resin. Two general synthesis routes of PET starting from dimethyl terephthalate and terephthalic acid were suggested; the synthesis strategies of PA-66 and PA-6 were discussed; the synthesis methods of aromatic PC from bisphenol A polycarbonate by phosgene or transesterification were summarized; the general synthesis methods of thermoplastic phenolic resin and thermosetting phenolic resin were discussed. In addition, some new synthesis methods and modification methods of these polycondensation polymers were reviewed. Besides, the properties, application, and market value of these polycondensation polymers were summarized. It is hoped that it will be helpful for the new synthesis of polycondensation polymers.

1 Introduction

Condensation polymers are one of the largest polymer classes. They play an important role in the production of packaging, fibers, electronic materials, and insulating materials. While, it is still challenging to produce these kinds of polymers through the economic friendly method in a large scale. Therefore, it is essential to have a good understanding of the fundamental theory of these polymers, especially the synthetic mechanism, as more efforts should be devoted to developing the fabrication strategies for the industrial scale. Polyethylene terephthalate (PET), polyamide (PA), phenolic resin, and polycarbonate (PC) are the four representative polymers that have been widely studied in the past decades. Thus, it is necessary to look back to go through the developing history of the polymers and evaluate the recent progress. In this review, firstly, the preparation of raw materials, esterification/transesterification, condensation, and polycondensation process were elaborated. Secondly, some other advanced synthetic techniques developed recently would also be introduced in this review. Besides that, the properties of each condensation polymers and its practical applications were presented. Finally, current market volume and future prospects were talked.

2 Polyethylene Terephthalate (PET)

Polyester, one of the most important polymer categories in chemistry, plays an important role in our daily lives. One of the representatives in polyester is polyethylene terephthalate, which could be abbreviated PET. It could be formed by polymerizing the repeated monomer units of ethylene terephthalate. It is also worth noting that PET is of great commercial significance nowadays because of its wide range of outstanding features, such as high strength and light weight. That is why it is commonly used in the production of beverage bottles, fabrics and electronic devices. The production of PET has reached around 360 million tones and covered nearly 16 % of European consumption, and it was predicted to continue growing in the next few years [1,2].

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2.1 Synthetic routes of PET

2.1.1 Production of PET from Dimethyl Terephthalate

2.1.1.1 Preparation of the raw materials

The first way to produce PET relies on the application of dimethyl terephthalate (DMT). One is by the direct esterification of terephthalic acid, which is followed by further distillation. It is also worth mentioning that methanol can esterify the terephthalic acid instantaneously even without a catalyst. The second way to prepare DMT is through a multistep process between p-xylene (PX) and methanol. At first, PX and methyl toluate could be oxidized at 120-140°C with catalyst. Then the oxidized mixture would react with methanol, and the raw ester formed could be processed further by fractional distillation to extract DMT [3]. For the preparation of ethylene glycol (EG), EO needed to be prepared at first from the catalytic oxidation of ethylene with the function of silver. The hydrolysis of EO in the presence of water would directly lead to EG production [4].

2.1.1.2 Transesterification

DMT is pretreated with inert gas at first, and the treated mixture could react with EG at 150-200°C and 100 kPa [5]. The methanol produced during this process is continuously removed from the system. The reaction mechanism has been shown in Figure 1.

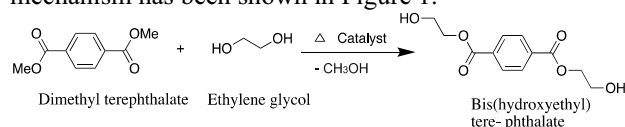


Fig. 1. A schematic illustration of the transesterification process. Ester linkage is formed, and methanol is eliminated at the end.

2.1.1.3 Pre-condensation and Polycondensation

In the pre-condensation process, the reaction conditions are at 250-280 °C and 2-3 kPa. At the polycondensation stage, the temperature would reach 290°C and 100 Pa [6]. The polycondensation must be accelerated by specific catalyst, such as antimony and germanium. The reason for that is the active catalyst would weaken the thermal stability of the final polymer, dampening the properties of PET [7]. When the defined melt viscosity is reached, the polycondensation would be terminated.

2.1.2 Production of PET from Terephthalic Acid

2.1.2.1 Preparation of the raw materials

The second way to synthesize PET relies on the use of EG and terephthalic acid (TA). TA is produced through the oxidation of para-xylene with cobalt-manganese-bromine catalyst in acetic acid. Compressed air and the mixture of p-xylene, acetic acid is constantly adding to the operator

in order to maximize the high conversion rate. This process for exploiting terephthalic acid is widely used nowadays in the industrial scale because of the high yield (>95mol %) [8].

2.1.2.2 Esterification

Diacid terephthalic acid and the diol EG made from the esterification process are mixed under 3-6 bar and 250 Celsius [9]. One of the intriguing features of this reaction is the absence of need of catalyst, and the diacid functionalities are capable to self-catalyze the diol through esterification. See Figure 2.

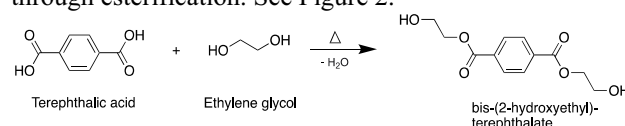


Fig. 2. Schematic illustration of the esterification mechanism. Ester linkage is formed, and water as the one of the products at the end esterification process.

2.1.2.3 Polycondensation

The polycondensation process is performed at a high temperature (~300°C) with the presence of antimony oxide (Sb₂O₃) [4]. In order to ensure the polymer growing linearly, it is vital to carefully control the stoichiometric ratio of the reactants. Simply adjusting the amounts of limiting reagents added to the system could effectively manipulate the molecular weight of the final polymer. However, the polycondensation process still faces some challenges by bringing about several side reactions when the formed DEG through the dimerization of EG reacted with the diacid functionalities of terephthalic acid [8], therefore leading to the difficulty of processing the final polymer.

Besides these two well-known processes to make PET, other advanced methods have been introduced nowadays. Gan et al. introduced the approach to produce nano-sized PET powder by using polyester fiber, and this new technology largely increased the crystallinity and reduced the need for milling [9]. Through the glycolysis method and electrospinning technique, the recycled PET (RPET) could be made from the wasted PET bottles [10]. RPET manufactured in this way showed high mechanical strength and low elastic modulus, which provided a promising future for applications in textile industries and filters.

Compared to DMT used for the production of PET, TA showed a faster reaction rate because of its self-catalysis nature in direct esterification process. From the economic angle, the smaller molecular weight of TA (about 30 g/mol lower than DMF) could bring about less storage cost. That is why TA process is the most common technique employed for the manufacture of PET.

2.2 Properties of PET

PET is unreactive and inert towards many reactants and solvents, such as water. But it is soluble in trifluoroacetic acid and hexafluoroisopropanol [11]. PET possesses high

mechanical strength and greater Young's Modulus (~3 GPa) [4]. Good-gas-barrier and thermal properties are present in PET as well. PET could form an excellent physical barrier with oxygen and carbon dioxide, which is the most important feature to preserve the taste for food. The large relative molecular mass and the stabilization of aromatic rings can retain the polymer's general stiffness, remaining unchanged at high temperatures.

2.3 Applications of PET

PET is widely used nowadays, especially in packaging, such as bottles. The good physical barrier formed between the liquid and gases, and inert nature made it capable of maintaining the flavor of the beverage. In addition, the light weight and transparency also play a role on the popularity of the manufacture of PET bottles. PET fabrics could be made through its monofilaments. The strong, flexible and low friction properties lead to the popularity of the production and consumption of curtains, bed sheets, and clothing. Because of the high dimensional stability and good electrical insulating features, PET is commonly employed in electrical fields, especially in the manufacture of instrument case, solar junction boxes and solenoids.

2.4 Market analysis and prospects

The demand for PET increased at an approximate rate (~ 1 million metric tons each year) in the past ten years. With that average annual growth, the global capacity would reach 42 million metric tons [12], and that huge consumption exerts more pressure on the recycling for PET. Nowadays, several advanced recycling techniques, such as the synthesis of PET based on the glycolysis of waste PET fiber, were introduced. Most of them showed a satisfactory result and could be utilized on an industrial scale. In the past few years, the average rate of recycling for PET in Europe had already been reached 26%, and it is aiming to achieve 60% for plastics by the end of 2030 [13]. The demand for recycled post-consumer products is the main driving force for that. Overall, the market of PET showed a promising future from the progress made on recycling technologies and growing environmental awareness from the citizens.

3 Polyamide(PA)

3.1 Polyamide-6(PA-6)

PA-6 is one of the most manufactured polyamide products in the world. Due to its high strength, good fatigue resistance, good water absorption, and chemical stability, PA-6 is now widely used in textiles and engineering plastics. The preparation of PA-6 was first described in 1937, which is by the polymerization of ϵ - caprolactam (CL), and first used as the material by DuPont in 1937 [14].

3.1.1 Synthesis route of PA-6

3.1.1.1 Production of linear PA-6 from CL

3.1.1.1.1 Synthesis of CL

The first generation of preparing CL was invented by Dutch company DSM and Germany company BASF, using benzene to make cyclohexanone oxime, then get CL through rearrangement reaction. The technology was not so ripe, atom utilization is low and pollution issue was severe. The main reaction is listed in Figure 3 [16].

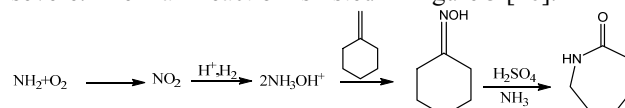


Fig. 3. Synthesis of caprolactam.

Second generation focused on improvement of oximation reaction. Using the molecular sieve to catalyze the reaction of cyclohexanone, ammonia and hydrogen peroxide, the second generation successfully improve the production rate and partly reduce pollution. The improved reaction can be checked in Figure 4 [17,18].

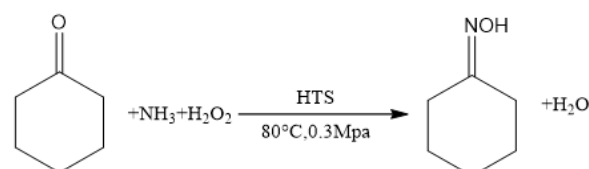


Fig. 4. Improvement of secondary generation technology.

Third generation, which is also the newest technology for now, is attempting to solve pollution and cost problems. By improving the way of forming Beckmann Rearrangement, it is possible to get CL in a green and environmentally friendly way. The technology was first invented by the Japanese company Sumitomo Chemical, and it was the only company that completely master this technology [18].

3.1.1.1.2 Hydrolysis and Polycondensation

The main reaction of making PA-6 via CL is shown in Figure 5.

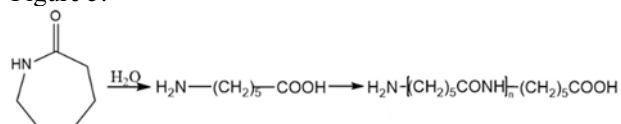


Fig. 5. Polymerization of PA-6.

The technology route was first used to manufacture PA-6 by Germany company called I.G. Farbon in 1943. There are several ways to prepare PA-6 by this technology route, and more common ones use VK tubes to form hydrolysis polymerization in atmospheric pressure. However, for better application, a product needs to have relative viscosity of 2.8-3.5, which the normal polymerization method cannot achieve. To meet different demands for product, different technologies were invented.

First technology is solid state polycondensation. It has two steps to form. First, polycondensation conventionally to get nylon chips in low viscosity, then put pure nitrogen

to vacuum dryer. The nylon chip experience drying and crystallization, the chain structure will reform, after which viscosity of chip will raise. It is the most convenient method to increase viscosity of nylon-6 chip.

Other technology including two order polymerization. The first order is to mix the melted monomer and water in the first container, and raise the pressure to polymerization. viscosity can reach 1.7 in this step. Then contents flow to second container to polymerize in atmospheric pressure, for monomers will evaporate along with water, the polymerization degree will raise swiftly, finally output nylon-6 chips with high viscosity [19].

In spare of the industrial method to make nylon-6. Some laboratory described other possible ways to get nylon-6 with anion and cation as catalysts. Using amino hexanoyl and phosphoric acid will shorten the polymerization time, and metal ion like SnCl₂, CuCl₂ have the same effect to raise the reaction rate. Cation catalyzing polymerization is getting more and more common these days, for its outstanding ability to increase reaction speed and economize power.

3.1.2 Production of modified Polyamide 6

There are plenty of works to research different modified PA-6. Some representative works will be introduced briefly.

Nanocomposite PA-6. Polyamides are widely used as matrix material for composite. The first polyamide used as nanocomposite was PA-6, produced by Toyota company in 1987 [20]. It contains 4 wt% of nanoclay. Nowadays, various nanomaterials are able to be added to PA-6. By adding 2wt% of multi-walled carbon nanotube into PA-6, the modulus, strength, and hardness of PA6 was remarkably improve. This research led to invent electrically conducting nonwoven PA6 membranes. Another example is graphene-PA6 composites prepared by in situ ring opening polymerization, which has an excellent improvement in mechanical property for only 0.1wt% of graphene. Different properties of different nanocomposite PA-6 are listed in Table.1 [21].

Table.1 Different properties of various nanocomposites

Materials	Tensile strength (MPa)	Thermal conductivity (W/mk)	Electrical conductivity (S/m)
Graphene	130±10 GPa	(4.84±0.44)E3 to (4.50±0.48)E3	7200
CNT	60-150 GPa	3.500E3	3000-4000
Nanosized steel	1769	5-6	1.35×E6
Plastic (HDPE)	18-20	0.46-0.52	Insulator
Rubber	20-30	0.13-0.142	Insulator
Fiber (Levlar)	3620	0.04	Insulator

Branched PA-6. Since 1978, Tomalia reported a method to make polyamidoamine (PAMAM). He used methyl acrylate to ammonia to give the triester. After

starbranched, the product was called “starburst”. The same method was used to polymerization of PA-6 and PAMAM, to make branched PA-6. It has higher gel point, and extra thermal stability, could be used in various areas [22].

3.1.3 Properties and Applications of PA-6

PA-6 has high strength, good fatigue resistance, good water absorbed ability and great and chemical stability. Thus, it is widely used as engineering thermoplastics. However, another application of Nylon-6 may be more usual to make synthetic fiber. The strength of nylon fiber is 1-2 times than cotton and 4-5 times than wool, which makes nylon a great material for textile. All these special properties have contributed to the importance of nylon-6 in plastic business ever since it was created.

3.2 PA-66

Nylon-66 is the earliest polyamide product to be manufactured in history. Since synthesis in laboratory in 1935 for the first time, PA-66 held the leadership of world polyamide market as materials of synthesis fabric and engineering plastics. PA-66 has various advantages, including high strength, high mechanical strength, easy to modified, etc. PA-66 and further product is now applied in various areas such as vehicle part, electronic appliances, packaging materials, playing an important role in everyday life.

3.2.1 Synthesis route of PA-66

3.2.1.1 Production of PA-66 via condensation

The production of PA-66 is not a direct polycondensation process, industrially, this research first synthesizes PA-66 salt, which is considered the monomer of PA-66, then polyamide-66 salt condensation to get PA-66 polymer.

3.2.1.1.1 Synthesis of Polyamide-66 salt

Polyamide-66 salt is actually hexamethylene diamine adipate. This route is mainly order to avoid blocking effect, making polymerization degree high enough. Main reaction of synthesize polyamide-66 salt is shown in Figure. 6 [23].

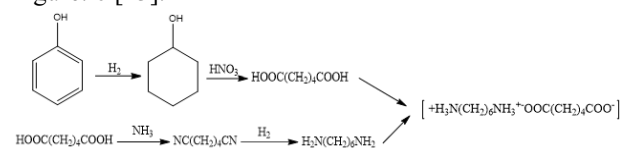


Fig. 6. Synthesis of PA-66 salt.

Using different solvent will leads to different PA-66 salt producing technology. Water solvent technology. Using water as the solvent to reaction, first solve hexanediamine into soft water, then add adipic acid slowly with stirring. Under nitrogen protection and process polymerization, after dehydration and concentration, product is finally made. Dupont Company,

Monsanto Company and some other uses this technology. It doesn't need organic solvent such as ethanol, so its advantages are convenience and safety. However, it has high demand for quality of intermediate, and is not easy for transport.

Solvent crystallization technology. Using methanol or ethanol as solvent, solve hexanediamine in organic solvent and slowly add adipic acid. Stir till the crystal comes out. This technology has significant requirement for the purity of monomers, and mainly used by British company ICI and BASF. The bright side of this technology is that it is easy to delivery and product quality is guaranteed. Short cone include sensitive to light, heat, oxygen, and humidity [24].

3.2.1.1.2 Polymerization of Polyamide 66

Polymerization of polyamide-66 is to polymerize polyamide-66 salt, using different polymerization method. This paper will briefly discuss them.

Continuous condensation technology. The polyamide-66 salt will be solved in water and react with slight heat, nitrogen, compressing to 1-2 times atmospheric pressure. Then polymerize for another two times or more to increase degree of polymerization, excepting steam, molding in some way to complete synthesis.

Melt batch polymerization technology. It is limited in one reactor; monomers are heat and polymerization in molten state. The technology is easy, but it has many weak points such as long technological process, require enough space, need heat resistance reactor. Other technology, take solid polymerization for example, pass the synthesis of PA-66 salt, process reaction directly with two monomers adipic acid and hexanediamine with low temperature and pressure. It is a simple and environment friendly way to manufacture nylon-66, so it raises many eyes of expectation. Recent study is focusing on metal catalysis, and industrial process is remaining unclear [25].

3.2.2 Production of modified Polyamide 66

PA-66 nanocomposites. Nanocomposites of polyamides are widely researched these years. Since work of Toyota laboratory came out, more and more group began to pay attention to this modification. PA-66 nanocomposites have significantly higher stiffness and strength than normal polyamide materials, and have extra stability, ionic conductivity, tunable biodegradability. What's more, depending on exact contents it contains, the nanocomposites have different useful properties, and can be applied in different areas. PA-66 nanocomposites with organoclay, with carbon nanotube, with cellulose, etc, are widely and deeply studied by research group around the world [26-28].

3.2.3 Properties and Application of Polyamide 66 products

Nylon-66 has better heat resistance, rigidity, water absorption than nylon-6, and has high crystal point, its strength is even higher than steel. Nowadays, nylon-66

industry has been a mature Industrial chain, nylon product is widely used for manufacturing film, filament, Staple fiber and mostly, engineering plastic. In 2007, nylon-66 yield has reached 2-2.4 million tons per year, makes nylon -66 one of the most important condensation polymer in the world.

4 Polycarbonate (PC)

4.1 Introduction

Polycarbonate (PC) is a typical kinds of condensation polymer containing carbonate ester group in the molecular chain. According to the structure of ester group, it can be divided into aliphatic group, aromatic group, aliphatic group - aromatic group and other types. The low mechanical properties of aliphatic and aliphatic-aromatic polycarbonate limit their application in engineering plastics. Only aromatic polycarbonate has been industrially produced.

Aromatic polycarbonate is a kind of carbonate polymer with aryl group in the molecular chain, and bisphenol A polycarbonate is the main type. It has good mechanical properties, dimensional stability, chemical stability and thermal stability, which means it has the practical value of polycarbonate. Among them, bisphenol A polycarbonate has become one of the important varieties of thermoplastic engineering plastics with excellent properties which are produced in large scale. It is prepared by the reaction of aromatic dihydroxy compounds with diphenyl carbonate or photo gasification. It can be used in machinery, electronics, instrument, instrument and military industry. Since it has particularities in structure, polycarbonate has become a common plastic used in industry. In this part of report, it would mainly focus on bisphenol A polycarbonate [29,30].

4.2 Synthetic mechanism of Bisphenol A Polycarbonate

Basically, there are two methods to produce bisphenol A polycarbonate: phosgene method and transesterification method.

4.2.1 Phosgene Method to produce Bisphenol A Polycarbonate

The phosgene method is also called the solvent method, which can be divided into the solution phosgene method and the interface phosgene method. The reaction is usually carried out in an organic solvent. The general reaction can be listed in Figure 7 [31].

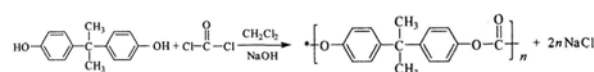


Fig. 7. The reaction to produce bisphenol A polycarbonate by phosgene method.

In the solution phosgene method, first add bisphenol A to dichloromethane to dissolve, and then pass phosgene into the dichloromethane solution of bisphenol A for

absorption. At the same time, the hydrogen chloride gas produced by the reaction is neutralized with sodium hydroxide solution to achieve the purpose of treating harmful gases. Another method is called interface phosgene method, which is a method of interface condensation and the whole process can be divided into two stages. First, bisphenol A (BPA) forms a salt with an alkaline aqueous solution, and then reacts with phosgene to produce a low-molecular-weight polymer. After that, the low molecular weight polymer and phosgene undergo secondary polycondensation under the action of the catalyst.

4.2.2 Transesterification Method to produce Bisphenol A Polycarbonate

Currently, the most common use of transesterification method is the melt transesterification method. This reaction is also divided into two steps. First, under the catalysis of the quaternary ammonium salt, bisphenol A (BPA) and diphenyl carbonate (DPC) react to form methoxy carbonylated bisphenol A (MPC). Then, the disproportionation reaction further produces polycarbonate. The general reaction is shown in Figure 8.

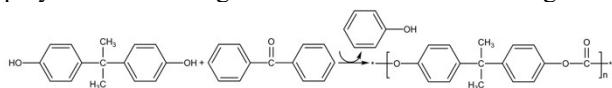


Fig. 8. Reaction to produce bisphenol A polycarbonate by transesterification method.

4.2.3 The Industrial Production

The main industrial production methods of bisphenol A type polycarbonate are transesterification and interfacial polycondensation. Due to the high purity, easy processing and relatively high molecular weight of the products produced by interfacial polycondensation, the interfacial polycondensation process is the main production process of polycarbonate in the world at present, so far about 90% of the polycarbonate production by interfacial polycondensation method [32].

4.3 Application and Prospects

Good mechanical properties (high impact resistance and creep resistance) over a wide range (15~130°C), high transparency, good dimensional stabilities, and electrical insulation. As engineering plastics, it is widely used in transparent materials, electrical parts, medical instruments and mechanical housings [33]. It can also be used for cooling water circulation and oil field water injection as scale inhibitor and dispersant [33].

Global polycarbonate supply is in an oligopolistic competition pattern. As of the end of 2019, there were approximately 38 major PC devices in the world, with a total production capacity of approximately 6.4 million tons. In terms of the regional distribution of production capacity, China continues to rank first in the world with a total production capacity of 1.66 million tons, accounting for 26% of the total global production capacity. The United States and South Korea rank second and third

respectively, accounting for 14% and 13% of the world's total capacity respectively [6]. At present, the global PC production giants are still Covestro, Saudi SABIC and Japan's Mitsubishi. Their total production capacity accounts for 56.3% of the global production capacity, showing an oligopolistic competition pattern [29-30, 33].

5 Phenolic resin

5.1 Introduction

All phenolic compounds and aldehydes by condensation reaction resin is collectively referred to phenolic resin. Among them, the most commonly used phenolic resin is the condensation product of phenol and formaldehyde. This kind of phenolic resin is the first thermosetting resin to realize industrialization, which is also the phenolic resin mainly mentioned in this article. Phenolic resin is widely used in industry because of its easy availability of raw materials, convenient synthesis and its properties after curing. Two kinds of phenolic resins with different properties can be synthesized by controlling the molar ratio of phenol to formaldehyde and the pH value of the reaction system: thermoplastic phenolic resin without hydroxymethyl reaction functional group and self-curing phenolic resin with hydroxymethyl structure. In the following chapter or part, it is going to talk about general synthetic methods of thermoplastic phenolic resin and thermosetting phenolic resin, and two new synthetic methods of modified phenolic resin. Finally, the properties and market value of phenolic resin are analyzed briefly.

5.2 Synthesis of phenolic resin

5.2.1 Synthesis of thermoplastic phenolic resin

Thermoplastic phenolic resin is a kind of thermoplastic linear resin synthesized under the condition of $\text{pH} < 7$ and the molar ratio of formaldehyde to phenol is less than 1. This kind of resin does not contain hydroxymethyl groups in the molecule, As shown in Figure 9, the addition reaction between phenol and formaldehyde mainly generates ortho and para hydroxymethyl phenol. Hydroxymethyl phenol is unstable and will continue to react with phenol to form various isomers of bi-phenolic. The reaction rate of bi-phenolic with formaldehyde is approximately the same as that of phenol with formaldehyde [34]. Therefore, the isomer of bi-phenolic can continue to react with formaldehyde to further increase the molecular chain of the polycondensation product, and finally get linear phenolic resin through the para or ortho connection of the phenol ring. According to the different pH value, two kinds of phenolic resins can be obtained: normal phenolic resin and high-ortho phenolic resin, the possible idealized molecular structure is shown in Figure 10. Generally, under the condition of $\text{pH} < 3$, the polycondensation reaction is mainly realized by the para position of phenolic hydroxyl group, and the content of 2,4'-linked products is 50-75%, which is

normal phenolic resin. Under the condition of pH = 4-7 and under the action of special divalent metal catalysts (such as compounds containing manganese, cobalt, zinc, etc.), the condensation reaction position is mainly in the ortho position of phenolic hydroxyl group, and the final 2,2-linked products content can reach 75-100%, which is high-ortho phenolic resin [35].

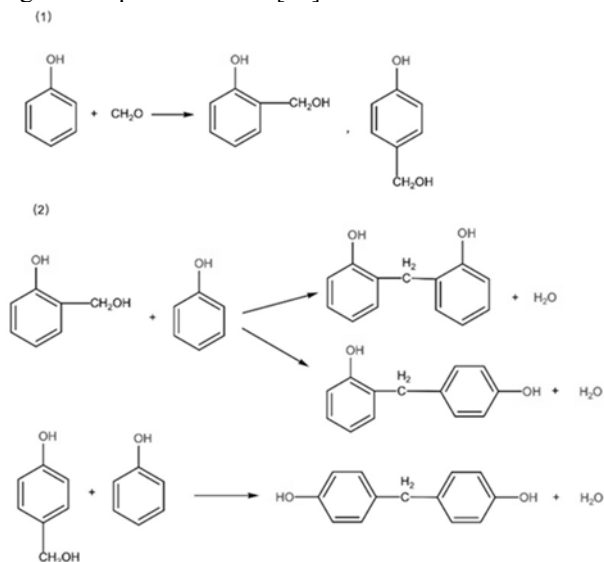


Fig. 9. Formation process of bi-phenolic methane: (1) Synthesis of ortho and para hydroxymethyl phenol (2) Synthesis of bi-phenolic methane.

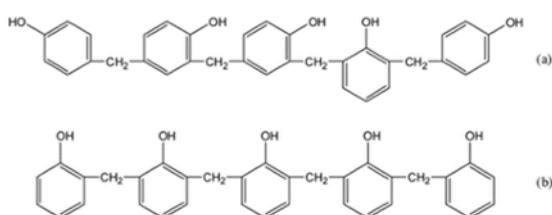


Fig. 10. Possible molecular structure of (a) normal phenolic resin and (b) high-ortho phenolic resin.

5.2.2 Synthesis of thermosetting phenolic resin

Thermosetting phenolic resin was synthesized by condensation of phenol and excess formaldehyde (molar ratio 1.1-1.5) with alkaline catalyst (pH = 8-11). The reaction process is shown in Figure 11. Firstly, a variety of hydroxymethyl phenols are generated by the addition reaction of phenol and formaldehyde. Then, the molecular weight of hydroxymethyl phenol was increased by further polycondensation. Usually when the reaction temperature is below 60°C, the polycondensation reaction rarely occurs, and the addition reaction is about 5 times the polycondensation reactions. When the temperature is higher than 60°C, the polycondensation reaction began to increase. The degree of reaction can be controlled by temperature and time [36]. Different degree of reaction will form different thermosetting phenolic resin. As the polycondensation proceeds, a linear resin is formed. The second-order phenolic resin with branched chain and partial cross-linking was obtained by further polycondensation. Because the second-order phenolic resin still has reactive hydroxymethyl group, the

molecular chain will crosslink to form a three-dimensional network structure and form the third-order phenolic resin [37]. Thermosetting phenolic resin is a resin containing hydroxymethyl reactive groups, which can be cross-linked and cured under heat or acidic conditions. Its possible ideal molecular structure is shown in Figure 12.

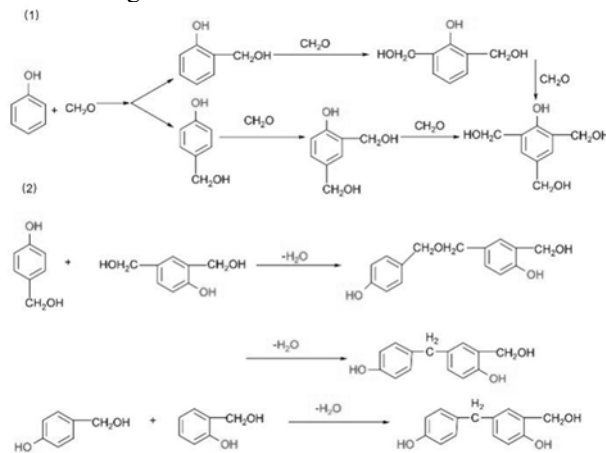


Fig. 11. Formation process of hydroxymethyl-phenol and polyhydric phenol alcohols: (1) Synthesis of hydroxymethyl-phenol (2) Synthesis of polyhydric phenol alcohols.

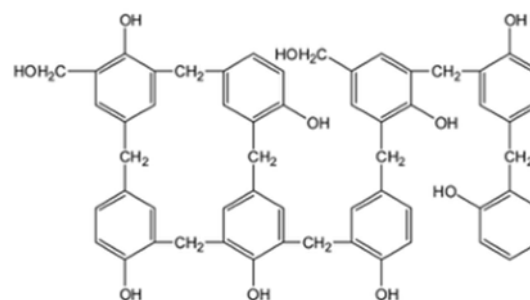


Fig. 12. Possible molecular structure of thermosetting phenolic resin.

5.2.3 Synthetic process of modified phenolic resin

In order to improve the poor heat resistance and flame resistance of phenolic resin, green production problems, researchers have selected a variety of modifiers to modify the molecular structure of phenolic resins. In this article, some modified synthesis methods of phenolic resin were reviewed, including the synthesis of nickel modified thermoplastic phenolic resin and the production of renewable phenolic resin with lignin-derived monomers instead of formaldehyde.

Thermoplastic phenolic resin is widely used in molding compounds, its heat resistance and properties at high temperature cannot meet the needs of some manufacturers. The heat resistance of phenolic resin can be improved by synthesizing Ni-modified thermoplastic phenolic resin. The main method is: under the acidic catalyst, formaldehyde and phenol are used as raw materials to produce thermoplastic phenolic resin at high temperature, then the temperature is lowered, and the Ni-modified thermoplastic phenolic resin is synthesized by adding modified nickel sulfate at low temperature. The Ni modified thermoplastic phenolic resin can also produce

carbon nanotubes under the catalysis of Ni and carbonization at high temperature [38]. This is a new method to prepare carbon nanotubes from modified thermoplastic phenolic resin.

Most phenolic resins are synthesized from petroleum-based phenol and formaldehyde, which have adverse effects on the environment and human health. By using lignin-derived monomers to synthesize renewable phenolic resin, formaldehyde can be replaced. The main method is (Figure 13): hydroxymethyl is introduced into the aromatic benzene ring by reducing the ester and aldehyde groups in the para position of lignin-derived monomers. Then, vanillyl and syringic alcohols were directly polymerized into corresponding polymers without formaldehyde using oxalic acid as catalyst. This method of synthesizing phenolic resin is not only green and sustainable, but also has the potential to supplement or replace petroleum-based polymer materials [6].

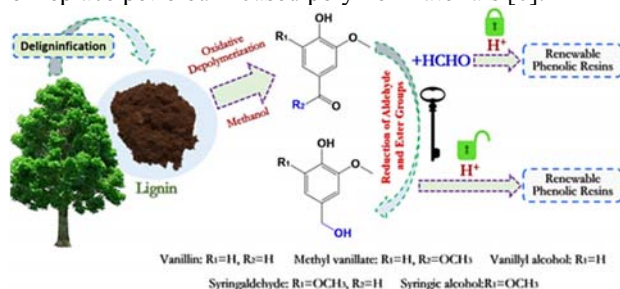


Fig. 13. Schematic illustration of the renewable phenolic resin synthesis based on lignin-derived monomers [39].

5.3 Properties and applications of phenolic resin

Because of its high strength and elastic modulus, corrosion resistance, electrical insulation, low curing temperature and good processability, phenolic resin is widely used in the manufacture of various plastics, coatings, adhesives, and synthetic fibers. By controlling the reaction degree, resin products suitable for different uses can be obtained. For example, if the reaction degree is low, the water-soluble phenolic resin with low average molecular weight can be obtained, which can be used as wood binder; When the controlling reaction is that the product dehydrates into semi-solid resin, this kind of product is called resol resin, which is soluble in alcohol solvent and suitable for coating and matrix material of composite materials; If the reaction is controlled to dehydrate into a solid resin, it can be used as phenolic molding compound or a binder for special purpose.

5.4 Market analysis and prospects of phenolic resin

As of 2016, there are about 200 phenolic resin manufacturers in China, with a production capacity of about 1.3 million t/a and a production of about 1.02 million tons. The main consumption fields of phenolic resin are phenolic molding plastics, wood processing, laminate, grinding, friction materials, fire resistance, insulation materials. Table 1 shows the specific consumption of phenolic resin in recent years in China [40].

Table 2. Consumption of phenolic resin in China in recent years.

Application area	2007	2008	2009	2010	2014
Phenolic molding compound/t	12.4	12.1	11.9	12.3	13.5
Wood processing, laminate/t	11.6	10.7	10.8	11.3	12.3
Grinding and friction materials/t	11	10	10	10.6	12
Fire resistant and insulating materials/t	10.6	8.8	9	9.8	11.3
Foundry materials/t	4.9	4.4	4.5	5	6
Coating/t	2.3	1.9	1.8	2	2.3
Other types/t	2.2	1.7	1.8	2	2.7
Total/t	55	49.6	49.8	53	60.1

With the application of phenolic resin wider, more and more researchers focus on modifying phenolic resin to obtain better performance of phenolic resin, which has a good promotion for the research and development of phenolic resin.

6 Conclusion

In summary, four important condensation polymers, including polyethylene terephthalate (PET), polyamide (PA), polycarbonate (PC), phenolic resin were described from synthetic process to application as representative examples in this review. Both synthetic laboratory strategies and industrial routes were discussed, respectively, with these four polymers. Two general synthesis routes of PET, starting from dimethyl terephthalate and terephthalic acid were suggested. TA synthesis path has priorities with higher molecule weight and faster reaction rate than DMT process. In the case of PA, the synthetic strategies for PA-66 and PA-6 were mainly discussed. It is foreseeable that cation catalyzed polymerization for PA-6 and PA-66 are of great industrialization interest. Some modified PA product like nanocomposites showed a greater improvement in strength and rigidity to go further to the edge. PC is also one of the most utilized condensation polymers and is majorly used in medical instruments and mechanical housings because of their high transparency and stable nature. Bisphenol, a polycarbonate, was chosen as a representative example of aromatic PC, which could be made either through phosgene or transesterification methods. In the case of phenolic resin, the general synthesis methods of thermoplastic phenolic resin and thermosetting phenolic resin were discussed. Besides that, properties (chemical, physical, and mechanical) and practical application of each condensation polymer were briefly introduced to facilitate the fundamental understanding of the polymers. Condensation polymers contribute to the consumption fields of packaging, insulation materials, and textile industries enormously.

Thus, it needs researchers to put more effort into the invention of new and greener synthetic processes for these four polymers. More importantly, making laboratory production be widely employed on an industrial scale.

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