# Reactive extrusion process and thermodynamic characterization of low molecular weight polyphenylene ether

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**Abstract:** This paper investigates how to regulate the molecular weight of polyphenylene ether (PPO) through reactive extrusion technology. When the dosage of the initiator dicumyl peroxide (DCP) is fixed at 1.25% (mass fraction), bisphenol A (BPA), as an efficient chain transfer agent, significantly reduces the number average molecular weight ($M_n$) of PPO by increasing its dosage from 0.67 wt% to 4.17% (mass fraction), with $M_n$ decreasing systematically from 12,406 g·mol$^{-1}$ in pure PPO to one-third of that (e.g., $F_3$: 4556 g·mol$^{-1}$). When the BPA dosage is fixed at 4.17% (mass fraction), the effect of DCP on Mn is non-monotonic: at 1.125 wt% ($S_2$), $M_n$ reaches its lowest value of 2828 g·mol$^{-1}$, but excessive DCP (1.25%, $S_3$) inhibits the chain transfer efficiency due to a sharp increase in radical concentration, causing $M_n$ to rebound to 4556 g·mol$^{-1}$. Thermogravimetric analysis (TGA) further verifies the effect of molecular weight regulation: the initial decomposition temperature ($T_5$%) of modified PPO decreases with the reduction of $M_n$ (pure PPO: 480℃ ), as the increase in low molecular weight chain ends accelerates thermal decomposition; $S_2$ (with the lowest $M_n$) has the lowest $T_5$% (393 ℃ ). In summary, BPA can linearly regulate $M_n$, while DCP has an optimal threshold of 1.125% (mass fraction). Both factors, through the mechanisms of chain transfer and termination, jointly determine the molecular weight and thermal stability of PPO.

**Key words:** copper-clad laminate; low molecular weight polyphenylene ether; reactive extrusion; chain transfer agent; initiator

**Classification number:** TQ326.53 **Article number:** 1009-797X(2026)08-0017-05

**Document code: B** **DOI:**10.13520/j.cnki.rpte.2026.08.007

Polyphenylene ether (PPO), as a special engineering plastic introduced in the 1960s, has become an ideal material for electronic packaging materials in the new era due to its unique comprehensive performance advantages. It not only possesses excellent thermal stability and extremely low water absorption, but also exhibits stable dielectric properties within a wide frequency range (permittivity of 2.7~3.0, dissipation factor of 0.002~0.005), perfectly meeting the stringent requirements of high-frequency circuits for signal integrity. Furthermore, its excellent mechanical strength and creep resistance, coupled with good processing and molding characteristics, make it irreplaceable in the field of precision electronic packaging.

However, conventional high molecular weight polyphenylene oxide (PPO) exhibits inherent defects such as high melt viscosity, poor rheological properties, lack of thermosetting properties, and insufficient interfacial compatibility, which lead to processing difficulties and severely restrict its processing applicability in the field of electronic packaging materials. To address this technical bottleneck, low molecular weight polyphenylene ether modified materials demonstrate unique advantages: while retaining the excellent properties of the base material, they significantly improve

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processing fluidity through molecular weight regulation (melt index increased by 3 to 5 orders of magnitude), and simultaneously introduce crosslinkable functional groups to achieve thermosetting properties. This breakthrough has garnered widespread attention in the field of advanced packaging.

There are generally two traditional methods for preparing low molecular weight PPO: direct monomer polymerization and solution redistribution reaction. Among them, direct monomer polymerization has limitations such as the need to use highly active oxidative coupling catalysts, difficulty in completely removing residual metal catalysts, which affects the purity of electronic packaging materials; wide molecular weight distribution, making it difficult to precisely control the target molecular weight; low reaction efficiency, multiple side reactions, and complex post-treatment of products. On the other hand, the solution redistribution reaction requires a large amount of toxic solvents such as toluene as the reaction medium, followed by energy-intensive solvent recovery processes, and residual solvents lead to excessive volatile organic compounds in the materials. In addition, its reaction cycle is long, the reaction rate in the solution phase is slow, making continuous production difficult. Finally, product separation is challenging, requiring steps such as precipitation and filtration, which introduce the risk of impurities (such as solvent residues and encapsulation of by-products). Therefore, there is an urgent need to develop new preparation methods that are efficient, low-cost, and environmentally friendly.

The reactive extrusion technology employed in this experiment not only facilitates solvent-free continuous production but also achieves material melting, mixing, reaction, and extrusion in a single step through a twin-screw extruder, completely eliminating the use of solvents and aligning with the trend of green manufacturing. Furthermore, the molecular weight is precisely controllable, enabling the use of DCP/BPA synergistic regulation and redistribution reaction. DCP serves as a radical initiator, triggering the breakage of the PPO backbone; BPA, as a chain transfer agent, captures free radicals through its phenolic hydroxyl group, terminating chain growth and regulating the degree of chain scission. Compared to the aforementioned two traditional preparation methods, this approach significantly enhances production efficiency and shortens the reaction time to minutes (compared to hours in the solution method).

## 1 Experimental part

### 1.1 Experimental materials

Polyphenylene Oxide (PPO): Mitsubishi Engineering Plastics Co., Ltd., Japan; Bisphenol A (BPA): Analytical Reagent, Shanghai Aladdin Biochemical Technology Co., Ltd.; Dicumyl Peroxide (DCP): Analytical Reagent, Chengdu Kelong Chemicals Co., Ltd.

### 1.2 Experimental equipment and instruments

Torque rheometer, RM200C, Harbin Hapu Electrical Technology Co., Ltd.; movable parallel twin-screw extrusion platform, SJSP-20×25, Harbin Hapu Electrical Technology Co., Ltd.; low-speed mixer; differential scanning calorimeter (DSC): Q-20, TA Instruments, USA; thermogravimetric analyzer (TGA): Q-50, TA Instruments, USA; electronic balance counter, LQ-6, Ruian Ante Weighing Equipment Co., Ltd.

### 1.3 Sample preparation

First, the amount of initiator was fixed. About 120g of PPO was weighed using an electronic balance. Then, according to the preset ratio (with PPO as 100 parts, the initiator was added in 1.25 parts, and the chain transfer agents were added in 0.67, 1.25, and 4.17 parts, respectively, named F1, F2, and F3), the corresponding masses of initiator DCP and chain transfer agent BPA were weighed. The three sets of samples were then mixed using a low-speed mixer for 60 minutes to ensure uniform dispersion. Subsequently, the pre-mixture was reacted and extruded through a parallel co-rotating twin-screw extruder, with the process parameters set as follows: screw speed of 50 r/min, and temperatures from the feeding section to the head at each zone being 100℃, 165℃, 225℃, 300℃, 315℃, 315℃, and 310℃, respectively. High-purity nitrogen was continuously introduced through the feeding port to form an inert atmosphere. Finally, the extrudate was solidified by water cooling and pelletized. After obtaining the optimal amount of chain transfer agent, the amount of initiator was fixed, and the above steps were repeated (the initiator was added in 1, 1.125, and 1.25 parts, respectively, named S1, S2, and S3).

### 1.4 Analysis and testing

(1) Differential scanning calorimetry (DSC)

The melting behavior and crystallization characteristics of the blend were characterized using a differential scanning calorimeter (TA Instruments, DSC Q20, USA). Accurate samples (3~5 mg) were weighed and placed in a standard aluminum crucible. The testing procedure was as follows: First, heat the sample from 30℃ to 250℃ at a rate of 10℃/min to eliminate thermal history; then cool it down to 30℃ at the same rate, recording the first cooling curve; finally, heat it up again to 250℃ at a rate of 10℃/min, obtaining the second heating curve.

(2) Thermogravimetric analysis (TGA)

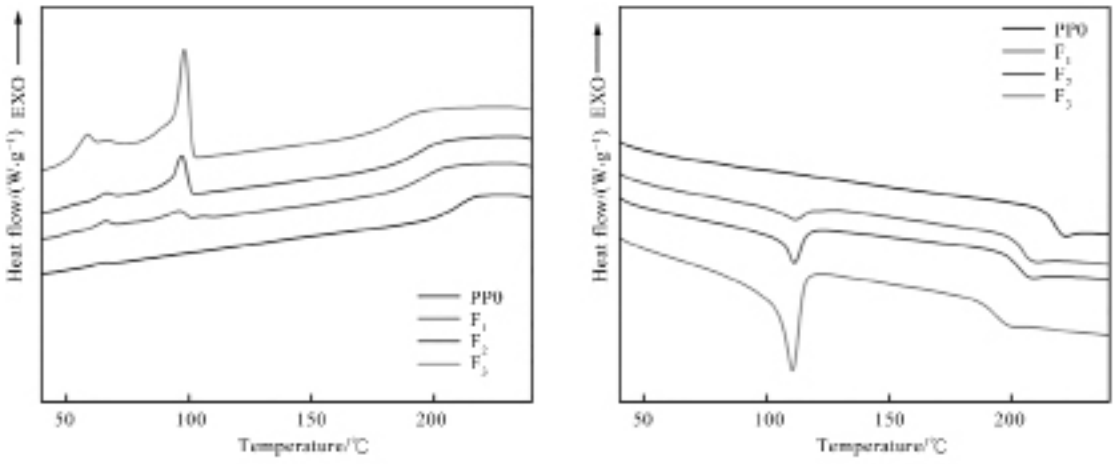
The thermal stability changes of PGA samples were evaluated using a thermogravimetric analyzer (TA Instruments, TGA Q50, USA). Accurate samples (3-5 mg) were weighed and heated from room temperature (approximately 30℃) to 600℃ at a constant rate of 10℃/min under a nitrogen atmosphere (flow rate of 60 mL/min). The changes in sample mass with temperature were continuously monitored and recorded to obtain the thermogravimetric (TG) and differential thermogravimetric (DTG) curves.

## 2 Results and Discussion

### 2.1 Differential scanning calorimetry analysis

Figure 1 shows the DSC cooling and secondary heating curves of PPO modified by reactive extrusion with different amounts of BPA added. As a key thermodynamic parameter of polymer materials, the relationship between the glass transition temperature ($T_g$) and the molecular weight of the polymer can be expressed by several formulas. Among them, the Fox-Loshaek formula is the most commonly used to describe the relationship between Tg and Mn for polymers with very low molecular weight, as shown in Equation (1).

$$\frac{1}{T_g} = \frac{1}{T_{g,\infty}} + \frac{1}{T_{g,\infty}^2}\frac{1}{M_n} \quad (1)$$




(a)Cooling curve (b) Heating curve

**Figure 1 DSC curves of PPO modified by reactive extrusion with different amounts of BPA added**

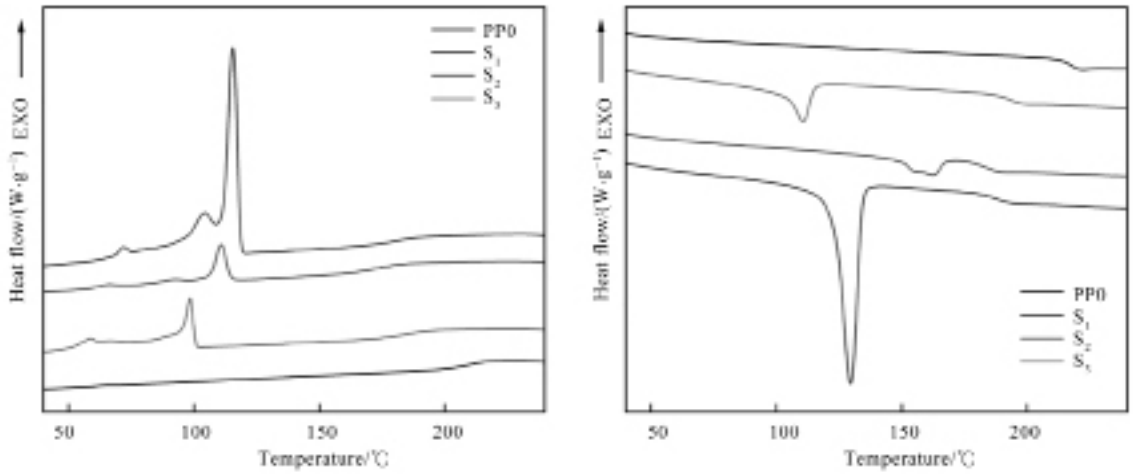
Where Tg represents the glass transition temperature of the polymer material, Tg,∞ denotes the glass transition temperature of the polymer material when the molecular weight is infinitely large, K is a characteristic constant, and Mn is the number average molecular weight of the polymer. Specifically, K=149274g·K·mol-1 and Tg,∞=500.90K. Substituting Tg into formula (1), the results are presented in Table 1.

**Table 1 Tg and Mn of PPO modified by reactive extrusion with different amounts of BPA added**

| Sample name | $T_g$/℃ | $M_n$/(g·mol$^{-1}$) |
|---|---|---|
| Pure PPO | 216 | 12406 |
| F1 | 205 | 6263 |
| F2 | 199 | 4894 |
| F3 | 197 | 4556 |

The results indicate that BPA exhibits extremely high chain transfer efficiency in this system, significantly regulating the molecular weight of PPO, particularly the number average molecular weight (Mn). As the amount of BPA in the system gradually increases from 0.67 wt% to 4.17% (mass fraction),

the frequency of the chain transfer reaction shows a clear positive correlation with the concentration of BPA. This enhanced chain transfer effect directly leads to a systematic decrease in the Mn of PPO. Detailed data analysis reveals that even a trace addition of BPA (0.67%) is sufficient to significantly reduce the Mn of the product by approximately 50% compared to the pure PPO system without BPA, which is extremely effective. When the amount of BPA is further increased, the decrease in molecular weight becomes even more pronounced, and Mn can be effectively regulated to approximately one-third of the molecular weight of pure PPO. The mechanism of action is primarily attributed to the phenolic hydroxyl groups in the molecular structure of BPA, which can efficiently capture the growing macromolecular active radical chain (PPO·). This capture behavior is not a simple termination, but rather triggers a chain transfer reaction: BPA donates a hydrogen atom to the active chain end, converting itself into a phenoxy radical, while simultaneously terminating the growth of the original polymer chain prematurely (forming a saturated end group). The newly generated phenoxy radical then has the ability to initiate new chain growth, becoming the starting point for a new polymerization reaction. The results indicate an inverse relationship between the concentration of the chain transfer agent and the final polymer molecular weight.




(a) Cooling curve　　(b) Heating curve

**Figure 2 DSC curves of PPO modified by reactive extrusion with different amounts of DCP added**

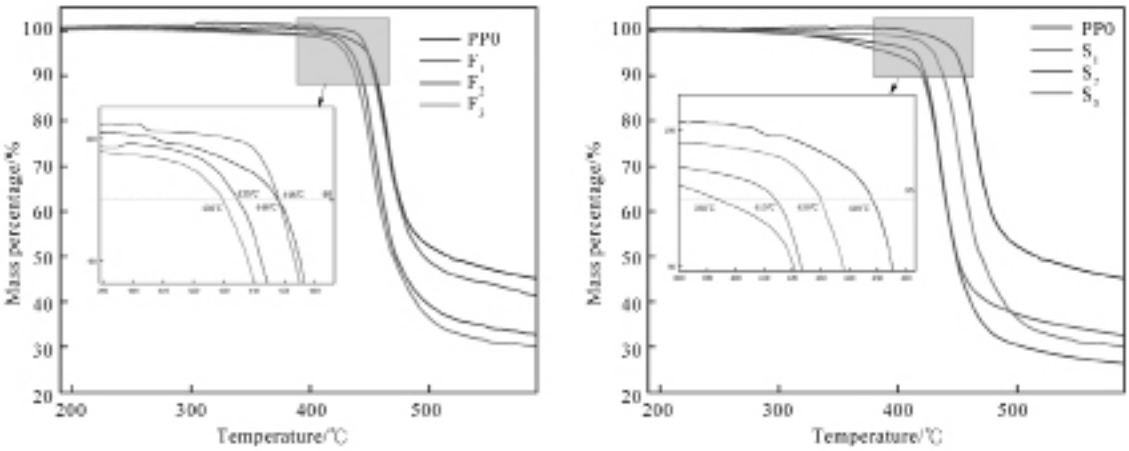
Similarly, Figure 2 shows the DSC cooling and secondary heating curves of reactive extrusion modified PPO with different amounts of DCP added. By substituting the measured Tg into formula (1), the results are presented in Table 2. Under the condition of a fixed BPA addition of 4.17% (mass fraction), the DCP dosage exhibits non-monotonic regulation on the molecular weight Mn of PPO: as the DCP dosage increases from 1% to 1.125%, Mn continuously decreases (at this time, the concentration of active chains initiated by DCP increases, promoting the chain transfer effect of BPA phenolic hydroxyl groups). However, when DCP is increased to 1.25% (sample S3), Mn is higher than that of the 1.125% (mass fraction) DCP sample (S2). This phenomenon stems from the sharp increase in the concentration of free radicals initiated by excessive DCP, leading to a significant increase in ineffective termination side reactions (growth chain coupling to form long chains), which inhibits the chain transfer efficiency of BPA and causes a rebound in molecular weight. This reveals that there is an optimal addition threshold for DCP (1.125%), where too low a dosage leads to insufficient chain transfer, while too high a dosage results in ineffective termination of free radicals, which adversely affects the chain transfer process and disrupts the molecular weight regulation effect.

**Table 2 Tg and Mn of PPO modified by reactive extrusion with different added amounts of DCP**

| Sample name | $T_g$/℃ | $M_n$/(g·mol$^{-1}$) |
|---|---|---|
| Pure PPO | 216 | 12 406 |
| S1 | 186 | 3 277 |
| S2 | 180 | 2 828 |
| S3 | 197 | 4 556 |

## 2.2 Thermogravimetric analysis

As shown in Figure 3, unmodified PPO exhibits excellent thermal stability, with an initial decomposition temperature (characterized by the temperature corresponding to a 5% weight loss, T5%) as high as 480℃. In contrast, the T5% values of low molecular weight PPO samples modified by reactive extrusion with BPA/DCP showed varying degrees of decrease, and this trend was highly consistent with the evolution of Mn. Specific data reveals that when the DCP addition amount is 1.125% (mass fraction) (corresponding to sample S2), the system reaches the lowest Mn value (2828 g·mol$^{-1}$), and its T5% also drops to a minimum of 393℃, significantly lower than that of unmodified PPO. However, when the DCP dosage is increased to 1.25 wt% (sample S3), due to the excessive initiator leading to an increase in ineffective chain termination reactions, the molecular weight undergoes an unexpected rebound (Mn increases to 4556 g·mol-1), and its T5% also rises to 415℃. The correlation mechanism between thermal stability and molecular weight lies in the fact that a significant decrease in molecular weight leads to a sharp increase in the concentration of chain ends per unit mass of PPO. Compared to the internal structure of the polymer chain, chain ends are more sensitive to heat and are more likely to fracture first when heated, thus becoming the preferential starting point for thermal decomposition. Therefore, the decrease in Mn directly weakens the overall thermal stability of the material.




(a) PPO modified with varying amounts of BPA (b) PPO modified with varying amounts of DCP

**Figure 3 TGA curve of reactive extrusion modified PPO**

## 3 Conclusion

This study utilized twin-screw extrusion technology to prepare low molecular weight PPO through reactive extrusion modification of PPO using DCP and BPA. The thermal properties and molecular weight evolution of the depolymerized products were systematically characterized. The results showed that BPA, as an efficient chain transfer agent, could linearly reduce the molecular weight (Mn) of PPO, with a small addition reducing Mn by approximately 50%. DCP had an optimal threshold (1.125%): excessive DCP would inhibit chain transfer efficiency due to ineffective chain coupling termination, leading to a rebound in Mn. Thermogravimetric analysis further verified the effect of molecular weight regulation. In summary, BPA can achieve linear regulation of PPO molecular weight, while DCP requires precise control to balance chain transfer and termination competition, providing a theoretical basis for the targeted preparation of low molecular weight PPO. When the addition of BPA was 1.125% (mass fraction) and the addition of DCP was 4.67% (mass fraction), the modification effect was optimal - the molecular weight reached its lowest.