

退火处理丁基羟基茴香醚多晶型

## Polymorphic Modifications by Annealing, Butylated Hydroxyanisole

试样	丁基羟基茴香醚
Sample	Butylated hydroxyanisole
应用	活性成分(口服抗糖尿病药)
Application	Active ingredient (oral antidiabetic)
条件	测试仪器: DSC
Conditions	Measuring cell: DSC 坩埚: 40 $\mu$ l铝坩埚, 密封。 Pan: Al 40 $\mu$ l, hermetically sealed. 试样制备: 原样品或先经退火。 Sample preparation: As received or annealed beforehand. 测试: A)以2.5K/min由30 $^{\circ}$ C升温至70 $^{\circ}$ C B)由35 $^{\circ}$ C升温至60 $^{\circ}$ C, 在60 $^{\circ}$ C恒温10min, 然后降温至30 $^{\circ}$ C。 第二次升温以2.5K/min由30 $^{\circ}$ C至70 $^{\circ}$ C。 Measurement: A) Heating from 30 $^{\circ}$ C to 70 $^{\circ}$ C at 2.5 K/min B) Heating from 35 $^{\circ}$ C to 60 $^{\circ}$ C, held isothermally for 10 min at 60 $^{\circ}$ C, then cooling to 30 $^{\circ}$ C Second heating run from 30 $^{\circ}$ C to 70 $^{\circ}$ C at 2.5 K/min. 气氛: 氮气, 50 ml /min Atmosphere: Nitrogen, 50 ml /min

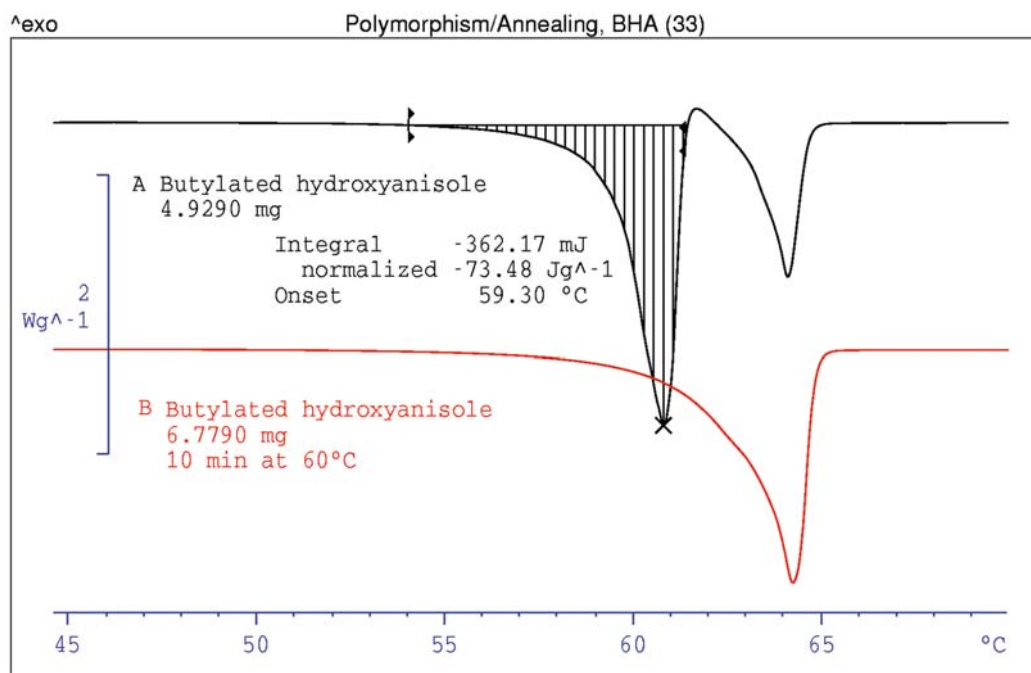


图 3.32 未经(A)和经退火(B)的丁基羟基茴香醚的 DSC 曲线

Figure 3.32 DSC curves of Butylated hydroxyanisoles unannealed (A) and annealed (B)

## 解释

### Interpretation

如图 3.32 曲线 A 所示，未处理的试样呈现带有一个结晶峰的两个熔融峰。经退火处理的试样仅呈现一个熔融峰(曲线 B)。可在略高于第一个晶型的熔程起始点的温度退火，迫使试样结晶为另一种晶型。由“3.3 升温速率对丁基羟基茴香醚多晶型检测的影响”已知，第一种晶型的熔融热 $\Delta H$ 约为 100J/g，而第二种晶型的熔融热(由本例)仅为 84.5J/g。单向转变体系第一个峰的熔融热 $\Delta H$ 是小于第二个峰的。因而，本例中可能是双向互变体系。要搞清情况，可用热台显微镜在约 60°C 进行测试。双向互变体系在两个吸热相之间是没有液相生成的。如果出现液相，则是单向转变体系，物质(曲线 B)不是 100%结晶的。

The untreated sample shows two melting peaks with a recrystallization step, as shown by curve A in figure 3.32. The annealed sample exhibits just one melting peak (curve B). Annealing at a temperature slightly above the onset of the melting range of the first modification forces the sample to crystallize to the other form. As known from “3.3 Influence of Heating Rate on the Detection of Polymorphism, Butylated Hydroxyanisole”, the heat of fusion  $\Delta H$  of the first modification is about 100 J/g and that of the second form (from this example) only 84.5 J/g. With monotropic systems, the heat of fusion  $\Delta H$  of the first peak is smaller than that of the second peak. Consequently in this case it could be an enantiotropic system. In order to clarify the situation, a measurement at about 60 °C with the hot stage microscope should be performed. In an enantiomeric system no liquid phase is formed between the two endotherms. If a liquid phase appears, then this is a monotropic system and the substance (curve B) was not 100% crystalline.

## 计算

### Evaluation

测定起始温度和焓变。括弧中表示因熔融与再结晶过程重叠而导致测定不确定的值。对试样B只表示第二次升温。

The onset temperatures and the enthalpy changes are determined. The values that can not be determined with certainty because of the overlap of the melting and recrystallization processes are shown in brackets. In the case of sample B only the second heating run is shown.

试样 Sample	起始点 Onset °C	$\Delta H$ J/g	起始点 Onset °C	$\Delta H$ J/g
A(未处理) A (untreated)	59.3	(73.5)	63.0	(27.0)
B(在 60°C 10 min) B (10 min at 60 °C)	—	—	62.7	84.5

## 结论

### Conclusion

物质的贮存条件或工艺条件不适当，可造成晶型改变，尤其是当转变温度接近贮存或加工温度时。

Unfavorable storage or processing conditions of a substance can lead to crystal modification changes, especially when the transition temperature lies close to the storage or processing temperature.