Heraeus

Epurio

ELECTRONIC CHEMICALS

ABOUT HERAEUS

Heraeus, the technology group headquartered in Hanau, Germany, is a leading international family-owned portfolio company.

The company's roots go back to a family pharmacy startedin 1660. Today, the **Heraeus** group includes businesses in the environmental, electronics, health and industrial applications sectors. Customers benefit from innovative technologies and solutions based on broad materials expertise and technological leadership.

In the 2020 financial year, the FORTUNE Global 500 listed group generated revenues of € 31.5 billion with approximately 14,800 employees in 40 countries. **Heraeus** is one of the top 10 family-owned companies in Germany and holds a leading position in its global markets.

About Heraeus Epurio LLC

Heraeus Epurio LLC is an award-winning specialty chemicals producer that develops Photo-Acid Generators (PAGs), Polymers, Monomers, and Crosslinkers for the **semiconductor, display, electronic and aerospace industries.**

We are experts in producing materials with **low trace metals**, while also having extensive experience in synthesizing a wide variety of organic compounds.

We provide **quality customized service** and are known in our industry as the reliable partner in development, from molecule to multi-tonne scale, to after-sales and technical support.

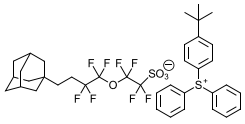
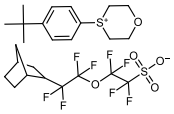
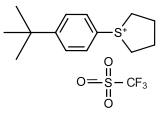
PHOTO ACID GENERATORS

Heraeus Deep UV PAG

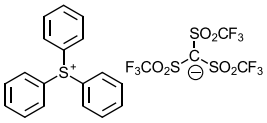
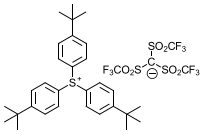
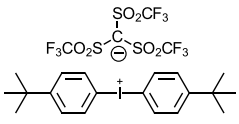
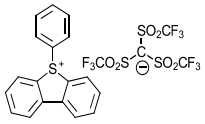
Based on 30 years of experience in producing electronic-grade photoactive materials as Daychem Laboratories in Dayton (OH), **Heraeus** has put together selected chromophores together with vintage acids to create different classes of advanced technology products for critical layer resists in high resolution.

Most of these products are available in ultra-pure (UP) quality with purity above 99.5% and content of all 26 metals below 10 ppb. This makes even conventional chemistry available for new frontiers in resist resolution.

Heraeus Ionic PAG Strong acid

Product Name	Chemical Structure	Properties	Features
PA-253		Strong acid generation m.p. 128–129°C	ArF
PA-313		Strong acid generation m.p. 129–130°C	ArF
PA-320		Strong acid generation m.p. 142–143°C	ArF

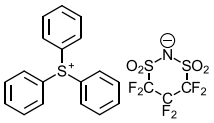
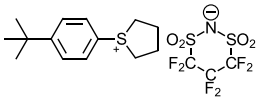
Heraeus Ionic PAG C1 acid

Product Name	Chemical Structure	Properties	Features
TPS-C1		Strong acid(C1) generation m.p. 76–78°C	Deep UV
TTBPS-C1		Strong acid(C1) generation m.p. 164–165°C	Deep UV
DTBPIO-C1		Strong acid(C1) generation m.p. 104–105°C	Deep UV
PA-304		Strong acid(C1) generation m.p. 130–131°C	Deep UV

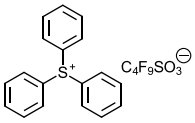
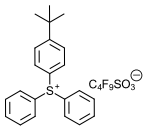
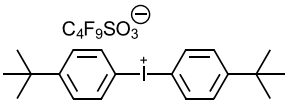
Commercialized product

Ionic PAG

Heraeus Ionic PAG – N3 acid

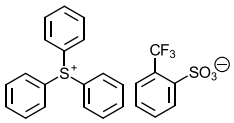
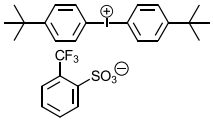
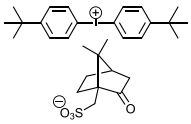
Product Name	Chemical Structure	Properties	Features
TPS-N3		Strong acid(N3) generation m.p. 104–105°C	Deep UV
TBPTMS-N3		Strong acid(N3) generation m.p. 177–178°C	Deep UV

Heraeus Ionic PAG – Nf acid

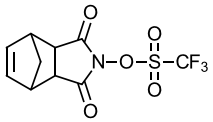
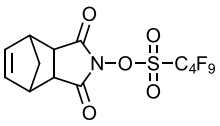
Product Name	Chemical Structure	Properties	Features
TPS-Nf		Low diffusion strong acid(nonaflic acid) generation m.p. 84–88°C	Deep UV
TBPDPS-Nf		Low diffusion strong acid(nonaflic acid) generation m.p. 131–137°C	Deep UV
DTBPIO-Nf		Low diffusion strong acid(nonaflic acid) generation m.p. 175–177°C	Deep UV

Commercialized product

Heraeus Ionic PAG – other acids

Product Name	Chemical Structure	Properties	Features
TPS-TFMBS		Weak acid (o-trifluoromethylbenzenesulfonic acid) generation m.p. 156–157°C	Deep UV
DTBPIO-TFMBS		Weak acid (o-trifluoromethylbenzenesulfonic acid) generation m.p. 162–164°C	Deep UV
DTBPIO-CS		Weak acid (camphorsulfonic acid) generation m.p. 215–217°C	Deep UV

Heraeus Non-ionic DUV PAG

Product Name	Chemical Structure	Properties	Features
⊛ MDT		White powder Strong acid (triflic acid) generation m.p. 88–89°C	Deep UV
PA-229		White powder Low diffusion strong acid (nonaflic acid) generation m.p. 54–56°C	Deep UV

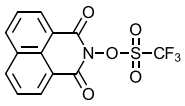
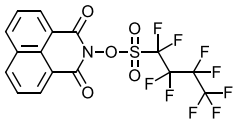
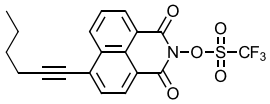
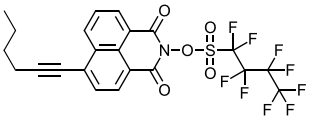
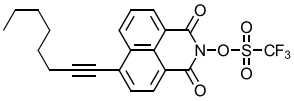
⊛ **Commercialized product**

HERAEUS I-LINE AND BROADBAND PAG

Following the growing market demand for highly sensitive, high solubility i-line PAG for various chemical amplified resist applications, **Heraeus** developed a set of I, h and g-line with the addition of broadband products.

Purity is according to the proven electronic grade quality of **Heraeus**, and most of the PAG's are scaled up cost-effectively in production to deliver up to ton quantities per year, making them also attractive for semiconductor Packaging and Display resists.

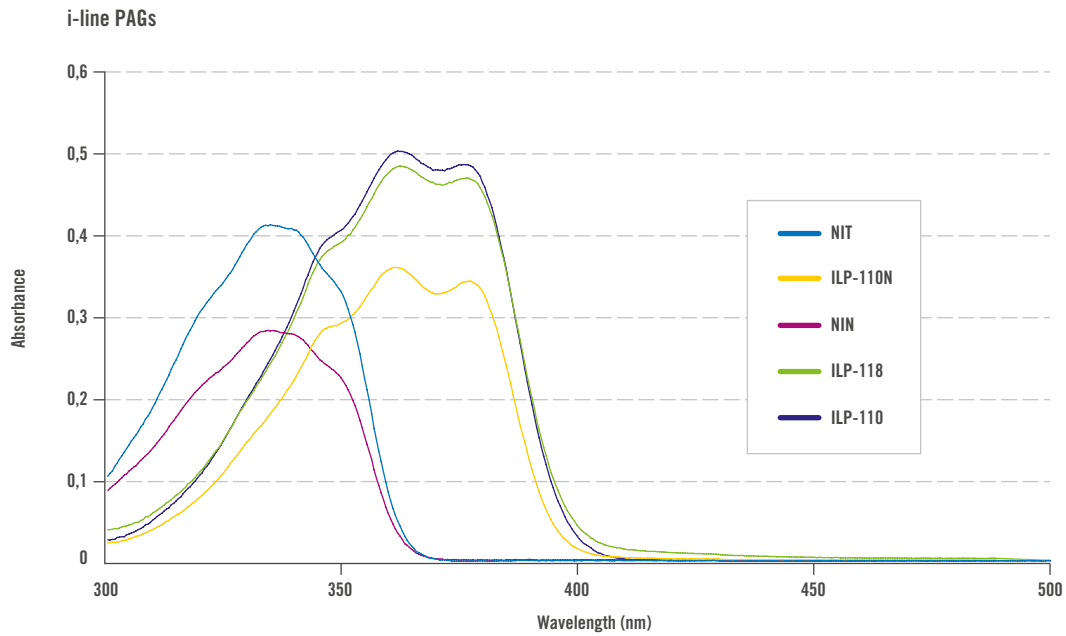
Heraeus Standard i-line strong acid PAGs

Product Name	Chemical Structure	Properties	Features
✻ NIT		White powder Strong acid(triflic acid) generation m.p. 210–214°C	i-line
✻ NIN		White crystalline powder. Low diffusion Strong acid(nonaflic acid) generation m.p. 148.5–149.5°C	i-line
ILP-110		Light-yellow powder Strong acid(triflic acid) generation m.p. 113–114°C	i-line
✻ ILP-110N		Low diffusion strong acid (nonaflic acid) generation m.p. 122–124°C	i-line
ILP-118		Light-yellow powder Strong acid(triflic acid) generation m.p. 66–68°C	i-line

✻ **Commercialized product**

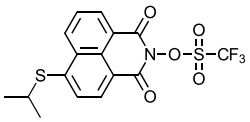
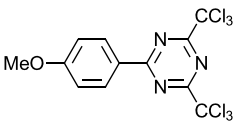
NON-ionic PAG

UV spectrum of i-line strong acid PAGs



* Sample concentration: 0.001% in MeCN

Heraeus i, h-line strong acid PAGs

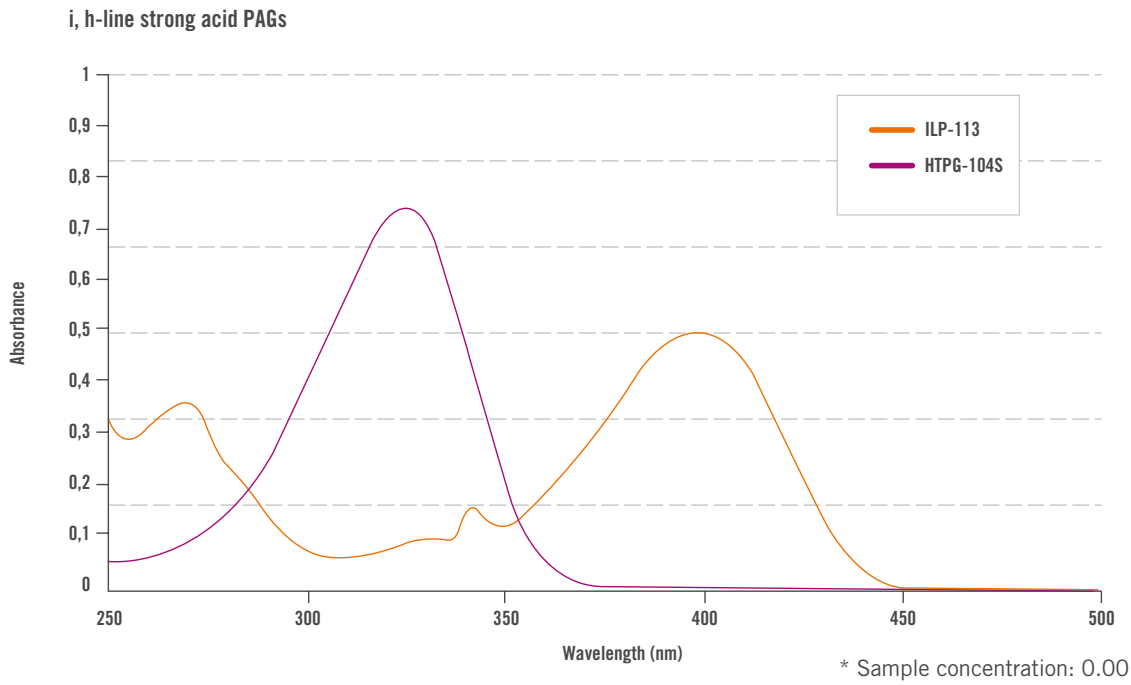
Product Name	Chemical Structure	Properties	Features
ILP-113		Yellow powder Strong acid (triflic acid) generation m.p. 125–126°C	i, h-line broadband
HTPG-104S		White powder Strong acid (HCl) generation m.p. 143–145°C	i-line

Commercialized product

i-line PAG

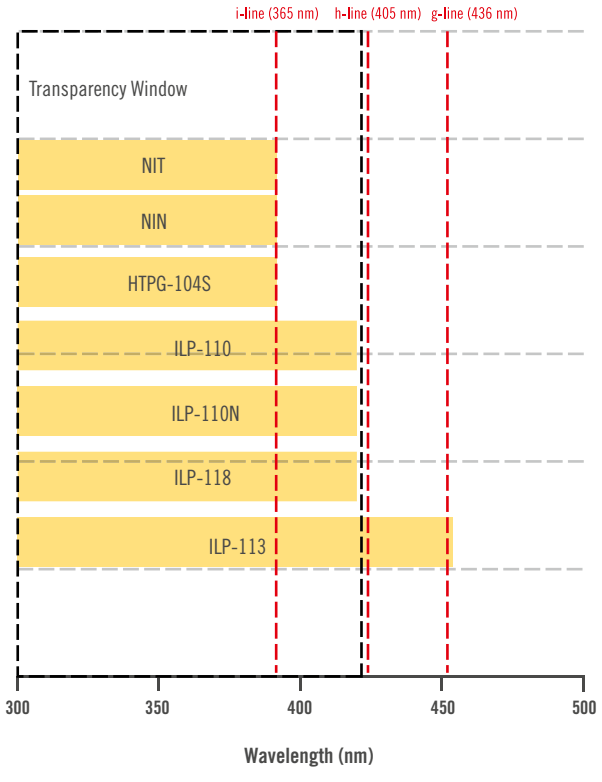
PAG

UV spectrum for i, h-line strong acid PAGs

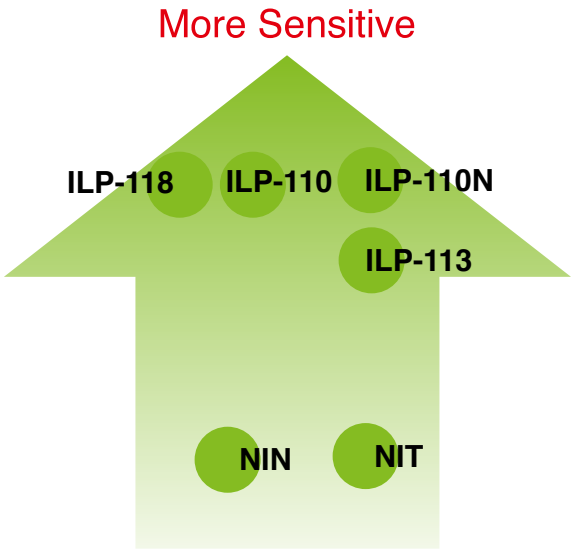


* Sample concentration: 0.001% in MeCN

UV absorption range of PAGs



Formulation and relative i-Line sensitivity

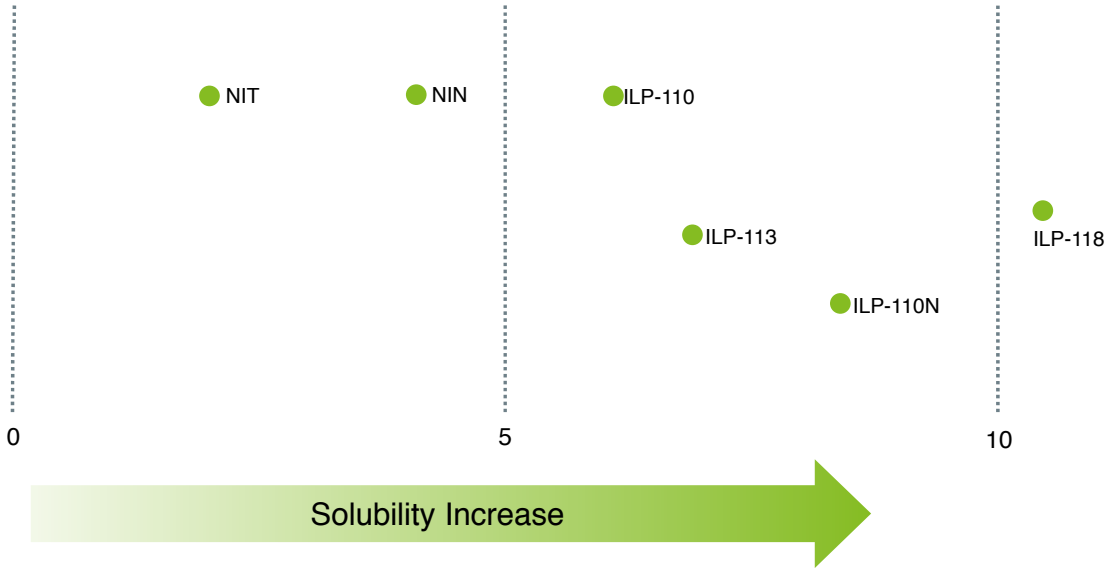


Each resist has the same molar equivalent of PAG

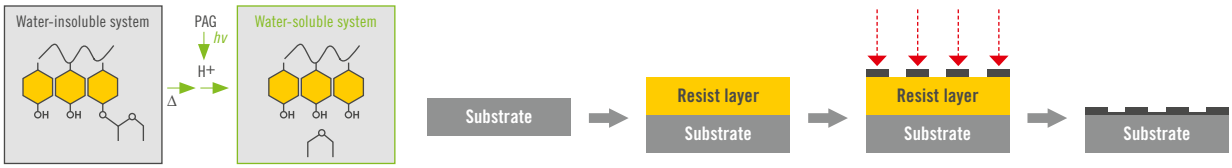
Resist consists of 30%-protected PHS, PAG, and TEA as quencher in PGMEA

UV

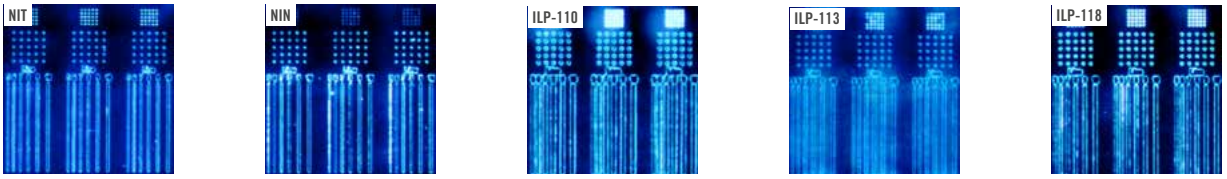
Solubility in PGMEA, %(w/w, RT)



Patterning test: Positive tone chemical amplified resist



Patterning test results



Coating Thickness

–1um by spin coating /
SOB condition: 110˚C, 60sec

Exposure

10sec (1sec + about 7.0 mJ) /
Light source: **LED i-line** / No PEB

Development

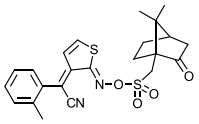
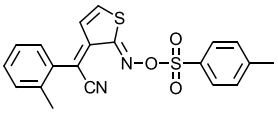
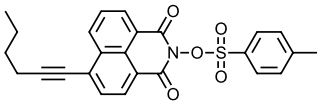
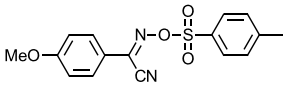
2.38% TMAH, 23˚C, 60sec

Heraeus i, h, g-line weak acid PAG

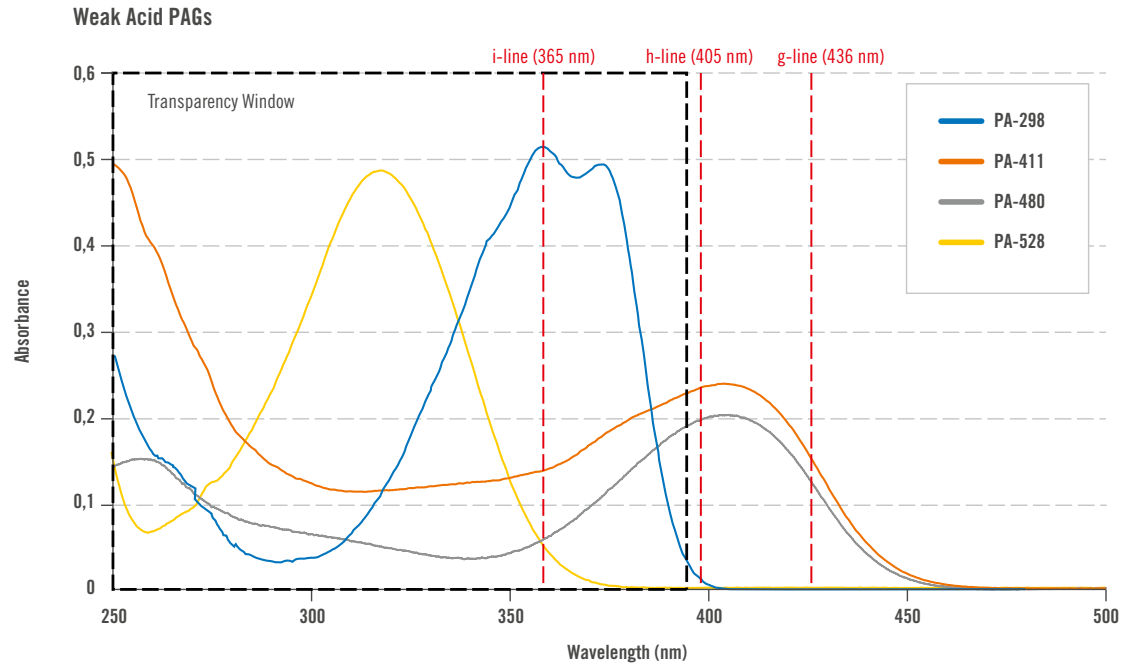
According to the market demand for weak acids for sensitive resin systems, **Heraeus** offers proven sensitive chromophore-weak acid combinations as cost-effective alternatives to existing systems.

Purity and quality consistency are a given for this product range.

Heraeus i, h, g-line weak acid PAGs

Product Name	Chemical Structure	Properties	Features
PA-480		Yellow powder Weak acid(sulfonic acid) generation m.p. 143–145°C	i, h, g-line
PA-411		Yellow powder Weak acid(tosylic acid) generation m.p. 136–139°C	i, h, g-line
PA-298		Yellow powder Weak acid(tosylic acid) generation m.p. 130–131°C	i-line
PA-528		White powder Weak acid(tosylic acid) generation m.p. 134°C	i-line

UV spectrum for i, h, g-line weak acid PAGs



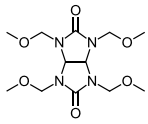
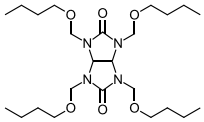
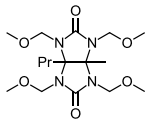
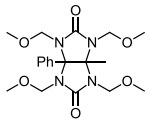
*Sample concentration: 0.001% in MeCN

HERAEUS CROSSLINKERS

Heraeus has a long tradition of manufacturing glycoluril-based crosslinkers in high purity for semiconductor resists. This is why processes have been developed and scaled up to reduce or remove contamination with formaldehyde and methylene chloride.

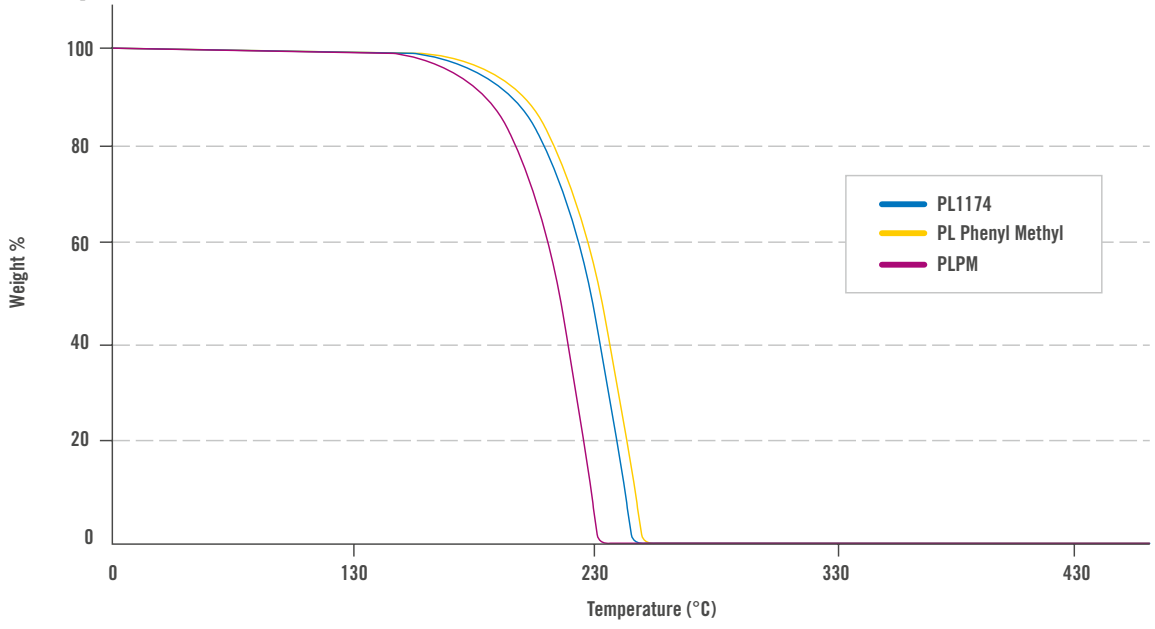
Today the low-metal contamination and the methylene chloride-free (MCF) products from **Heraeus** define the new standard in the semiconductor industry. Various chemical modifications have significantly lowered the sublimation tendency.

Furthermore, **Heraeus** developed certified MCF versions of crosslinkers to comply with international regulations against hazardous, halogenated materials, and to provide safe and environmentally-friendly products.

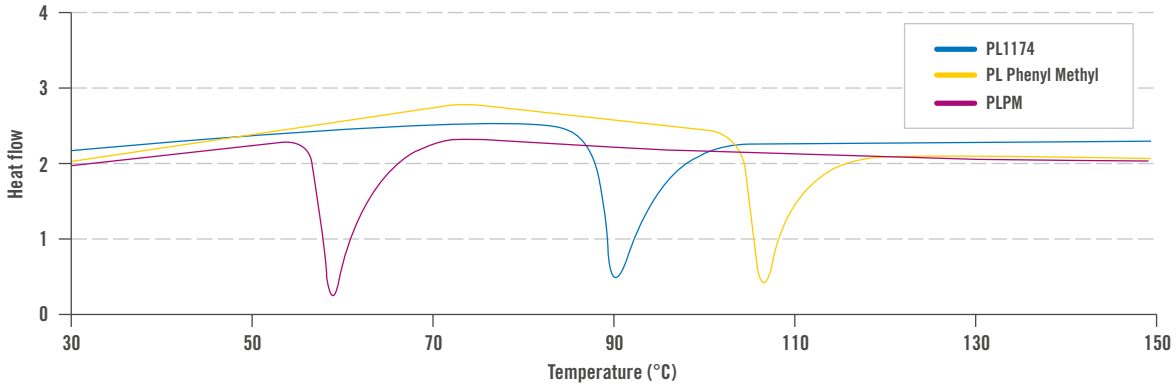
Product Name	Chemical Structure	Properties	Features
✻ PL-1174		White crystalline powder m.p. 107–113°C Available methylene chloride-free (MCF) and UP	
✻ TBGU		Colorless liquid Available methylene chloride-free (MCF) and UP	
✻ PLPM		White powder m.p. 87–89°C Available methylene chloride-free (MCF) and UP	
PL Phenyl Methyl		White powder m.p. 136–138°C Available methylene chloride-free (MCF) and UP	

✻ **Commercialized product**

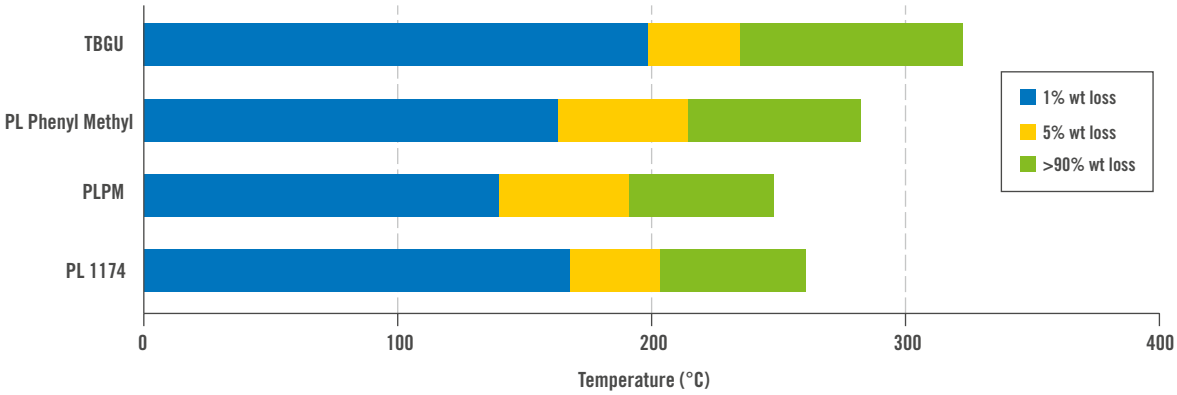
Comparison of TGA



Comparison of DSC



Decomposition temperatures



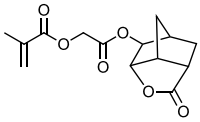
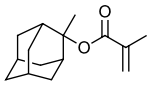
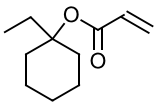
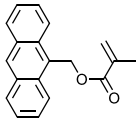
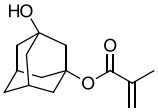
Solubility for crosslinkers

Solubility into 100 mL of	PLPM (-MCF)	PL Phenyl Methyl	PL1174	TBGU a
Water	7.7 g	<0.3 g	11.8 g	–6 g
Methanol	46 g	3.4 g	22.6 g	miscible
IPA	10 g	<2 g	<2 g	miscible
EL	25 g	<2 g	6 g	miscible
PGMEA	10 g	<2 g	<2 g	miscible
PGME	10 g	<2 g	<2 g	miscible

HERAEUS MONOMERS: ACRYLATE

With long experience in critical layer polyacrylate-based resists, **Heraeus** developed and scaled up a number of monomers with sterically hindered groups.

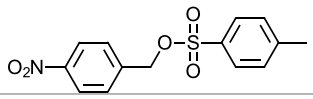
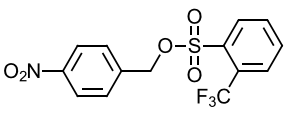
From UP-grade for new critical layer developments, to high-end memory and logic chips-related photo materials such as PR, BARC, and hardmask applications, where cost and volume availability are important factors, we offer the entire product range.

Product Name	Chemical Structure	Properties	Features
✻ MNLMA		White powder m.p. 74~77°C	Multi-layer photo-litho-graphic application
MAdMA		Colourless liquid	Multi-layer photo-litho-graphic application
ECHA		Colourless liquid	Multi-layer photo-litho-graphic application
9-AMM		Yellow powder m.p. 86–88°C	Multi-layer photo-litho-graphic application
HAdMA		White powder m.p. 89–91°C	Multi-layer photo-litho-graphic application

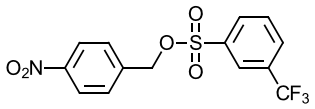
HERAEUS THERMAL ACID GENERATORS

With thicker film resist demands, more and more formulations contain thermal acid generators to enable final curing during post-baking.

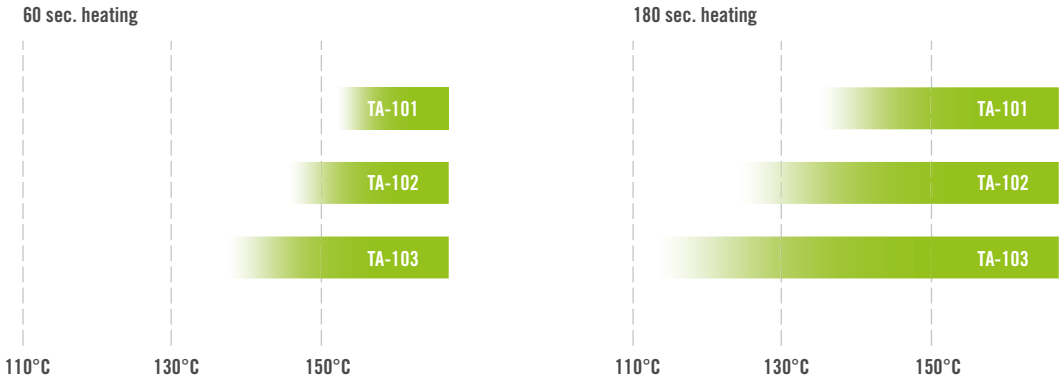
An IP-free set of products with different acid-releasing temperatures is available from **Heraeus**. Semiconductor-grade purity and effective costs are mandatory in the final application.

Product Name	Chemical Structure	Properties	Features
✻ TA-101		White powder 4.5% (w/w) in PGMEA m.p. 101–102°C	
TA-102		White powder 2.5% (w/w) in PGMEA m.p. 126–127°C	

✻ **Commercialized product**

Product Name	Chemical Structure	Properties	Features
TA-103		White powder 5% (w/w) in PGMEA m.p. 101–102°C	

Acid generation – temperature by heating



Formulation

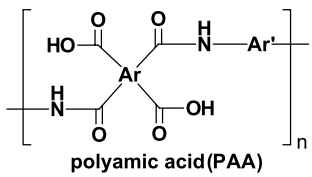
TAG + Fluorescein (Acid indicator)
PHS-EVE (resin)
PGMEA (solvent)

Test

Coating on glass
→ baking on hot plate
→ Measuring transmittance

HERAEUS POLYIMIDE PRECURSORS

Heraeus can toll manufacture polyamic acids and other PI precursors to suit customers' needs. Production capacity stands at 2 tons of output per day, and can safely handle all major solvents, diamines, and dianhydrides.

Product Name	Chemical Structure	Properties	Features
Polyamic acids (PAA) for Polyimides	 polyamic acid(PAA)	High dielectric stability at high temperatures, chemically resistant and can be made colorless	Used as coatings in flex circuits, display, battery applications, photovoltaic and anywhere PI films are needed
PMR (Polymerizable Monomeric Reactants) Resins	Various diamine dianhydride mixtures	Used in temperatures over 350°C	Used in composites for high-temperature aerospace applications

Commercialized product

Custom synthesis service

Heraeus provides all kinds of chemical compounds based on the customer's requirements, using our high-level synthesis technology and long experience in electronic materials. Rapid and smooth transition from g-scale to kg-scale is provided. Please get in touch with our sales team.

Purification technology

High-end photoresist applications in semiconductors require super-low chemical impurity and metal ions content. Heraeus has begun producing ultra-purification-grade products for advanced semiconductor photoresists. Our new production facility, equipped with full clean room environment, has been fully operational since 2021.

EN/09.2022/www.datagraphis.de

- **Headquarters:** Hanau, Germany
- **Production:** Dayton, Ohio, USA
- **Sales offices:**
  Heraeus Materials Technology Taiwan Ltd., Taipei, Greater China
  Heraeus Electronic Chemicals (Shanghai) Co., Ltd., Shanghai, Greater China
  Heraeus Korea, Suwon, South Korea
  Heraeus K.K., Tokyo, Japan
  Heraeus Epurio LLC, Dayton, Ohio, USA

hepn_customerservice@heraeus.com

heraeus-epurio.com