

## **BASF Acrylates and Methacrylates**

## **Tert.-Butyl Acrylate (TBA)** Product Information Brochure

#### **Product Information**

*Tert.*-Butyl Acrylate (TBA) is a mono-functional monomer with a characteristic high reactivity of acrylates and a bulky, hydrophobic moiety. TBA can be easily polymerized and copolymerized in solution, in emulsion and in bulk.

Copolymers of TBA can be synthesized with a large variety of monomers, e.g. acrylates, methacrylates, acrylic acid, methacrylic acid, acrylamides, acrylonitrile, vinyl acetate or styrene etc..

TBA is especially used to impart the following characteristics and benefits to polymers:

- Tert.-Butyl moiety leads to high hydrophobicity
- Comparatively high glass transition temperature (T<sub>a</sub> 50 °C) imparts hardness to polymers
- Branching of the *tert*.-butyl moiety promotes interlocking between different polymer chains
- Bulkiness of the *tert.*-butyl moiety reduces polymer chain entanglements (within one polymer chain)
- Selective heat and chemical resistance allows polymer modification in processing or final application

### Benefits for your Application

- Low water uptake
- Improved alkaline hydrolytic stability
- Excellent weatherability
- Reduced viscosity at high solid content (in solution)
- Enhanced opacity in coatings
- Improved cohesion
- Good interaction with associative thickeners

### Tert.-Butyl Acrylate (TBA)



## **Specification & Physicochemical Properties**

Specification <sup>1</sup>	Unit	Value
Assay (GC)	%	≥ 99.00
Acid Value (as Acrylic Acid; ASTM D 1613)	%	≤ 0.1000
Water content (ASTM E 203)	%	≤ 0.040
Standard Stabilization MEHQ (ASTM D 3125)	ppm	15 ± 5
Color on dispatch (ASTM D 1209)	APHA	≤ 10

Monomer related data	Unit	Value
Appearance		Clear, colorless
Physical Form		liquid
Density @ 25°C	g/cm <sup>3</sup>	0.883
Boiling Point	°C	120
Freezing Point	°C	-70
Viscosity @ 20 °C	mPa s	0.9
Vapor Pressure @ 23,4 °C	mbar	20
Hansen Solubility Parameters δD, δP, δH (calc.)		15.1, 3.4, 5.6

Unit				
	TBA	MMA	BA	Styrene
L/mol s	26,260	650	28,250	260
kJ/mol	17.5	22.4	17.8	28
L/mol s	1.9*10 <sup>7</sup>	2.7*10 <sup>6</sup>	2.1*10 <sup>7</sup>	-
	Unit L/mol s kJ/mol L/mol s	Unit TBA   L/mol s 26,260   kJ/mol 17.5   L/mol s 1.9*10 <sup>7</sup>	Unit TBA MMA   L/mol s 26,260 650   kJ/mol 17.5 22.4   L/mol s 1.9*10 <sup>7</sup> 2.7*10 <sup>6</sup>	Unit TBA MMA BA   L/mol s 26,260 650 28,250   kJ/mol 17.5 22.4 17.8   L/mol s 1.9*10 <sup>7</sup> 2.7*10 <sup>6</sup> 2.1*10 <sup>7</sup>

Polymer related data	Unit				
		TBA	MMA	BA	Styrene
Glass Transition Temperature (T <sub>g</sub> )	°C	50	105	-48	100
Brittle Temperature (T <sub>b</sub> )	°C	44-45	26-31	no data	90
Decomposition Temperature (onset)	°C	230	No data	345	300

Regulatory <sup>2</sup>			
Germany (REACH)	YES		
Switzerland (CHEMINV)	YES		
US (TSCA)	YES		
Canada (DSL)	YES		
Japan (ENCS)	YES		
South Korea (ECL)	YES		
Australia (AICS)	YES		
Philippines (PICCS)	YES		
China (IECSC)	YES		
New Zealand (NZIOC)	YES		

1: Status 2020: Please refer to the Technical Information Sheet (TI)

2: Status 2020. Please refer to Product Information Sheet (PIS)

## Water Uptake

Protection of the substrate and durability of the polymer film are main requirements of polymeric binders for various applications (e.g. decorative coatings). A low water uptake can have a significant impact to achieve the following benefits:

- Resistance to efflorescence from substrates
- Better adhesion and cohesion of a paint film
- Lower leaching of paint components
- Better dimensional stability and reduced swelling
- Lower tendency to degradation
- Higher resistance to microorganism growth
- Lower tendency to formation of stains and snail trails

#### Water uptake measurements of different polymer compositions



Water uptake measurements of polymer films with similar Tg. Dried polymer dispersion films (thickness 1-2 mm, 1 week drying time at room temperature) with known weight ( $w_0$ ) were immersed in deionized water. After 24, 48 and 72 h, respectively, the films were taken out and weighed again (w). Water uptake (%) = (w-w\_0)\*100/w\_0

#### Hydrolysis Degree of TBA and MMA



A 0.5 M monomer solution in 0.5 M aqueous NaOH was stirred for 1 h at 60 °C. The aqueous phase was separated, and the amount of hydrolysis product (Na acrylate/ Na methacrylate) determined titrimetrically.

### **Hydrolytic Stability**

The bulky ester group protects TBA from alkaline hydrolysis .

Alkaline hydrolytic stability of the polymeric binder is essential for many substrates to which coatings are applied (plaster, concrete etc.). Additionally, several alkaline formulation additives require an alkaline resistant polymeric binder.



## **Hydrophobicity**

The water contact angle measurement is an easy way to assess the polarity of a polymer film surface. Hydrophobic groups (like the *tert*.-butyl group) can modify the acrylic backbone by reducing the polarity. Measurements of the contact angle show that the water contact angle increases with TBA content of the copolymer due to increased hydrophobicity.



## Viscosity

TBA containing polymer solutions show a low viscosity at high solid content: Bulkiness of the *tert*.-butyl moiety increases space requirements and reduces polymer chain entanglements in solutions.

That way less solvent (VOC) is needed and brings additional benefit from an environmental point of view.

Zero viscosity (at 25 °C) of a 30 wt% polymer solution in toluene with comparable M<sub>w</sub>.



## Cohesion

The cohesive energy density is a parameter for interaction of polymer chains in a dried polymer film. An increased cohesive energy can improve the protection of the substrate and the durability of the polymer film.

Substitution of MMA by TBA leads to improved cohesion. Branching of the *tert*-butyl moiety promotes interlocking of the TBA ester groups. The polymer chains encounter a higher resistance when sliding past one another under applied force. This positively influences the mechanical stability and cohesive strength of the film. Relative cohesive energy density (CED) of dried polymer dispersion films with similar T<sub>g</sub>: (CED = storage modulus (G<sup>'</sup>) x strain (%) (linear viscoelastic region))



## Adhesion

Formulated paints with TBA containing binder show improved adhesion on steel and alkyd substrates. The risk of delamination and flaking of the applied coating is largely reduced.

#### Adhesion on Steel

Pictures of formulated architectural paints (semi-gloss, low PVC) from different polymer binders on steel after adhesion test (tested by UNIFAB according to NF EN ISO 2409).



Standard coating with TBA/BA polymeric binder



Standard coating with MMA/BA polymeric binder

Adhesion of formulated architectural paints (semi-gloss, low PVC) from different polymer binders on steel (tested by UNIFAB according to NF EN ISO 2409) and on alkyd (tested by ATI according to ASTM D3359).

Steel		Alkyd
Polymer binder <sup>1</sup>	Rank	Polymer binde
MMA/BA	4-5	BA/MMA
BA/TBA	1-2	

Rank: 0 -5 (0 best , 5 worst)

 $^1 \, \text{Binder}$  formulation also contains ~1% Acrylic Acid and

~1% Acrylic Amid (please refer to the Guiding Recipe)

Polymer binder <sup>1</sup>	Rank	
BA/MMA	1-2	dry adhesion
	4	wet adhesion
BA/TBA	0	dry adhesion
	0	wet adhesion

## Opacity

Opacity measurements of dried formulated architectural paints (semi-gloss, low PVC) from polymer binders on draw-down test cards, 150  $\mu$ m wet film thickness (tested by UNIFAB).

Polymer binder	Opacity [%]
Commercial, styrene acrylic	98.2
Commercial, pure acrylic	98.4
BA/MMA	97.9
BA/TBA	99.1

Opacity (hiding power) is the ability of a paint to obscure the surface to which it is applied. Paint formulations with TBA containing binder can improve the opacity of the final coating.

TBA polymer binders allow an effective use of titanium pigments in paint formulations. TBA polymer binders will either enhance opacity at equal formulation cost or reduce formulation cost and potentially  $CO_2$  footprint (reduction of titanium pigment) while keeping up the performance level of the coating.

## Opacity

X-Section of dried architectural paint films with and without TBA.



TBA containing paint formulations boost the interaction between thickener and binder and lead to a more homogeneous distribution of the pigments in the dried paint.

Analytical ultracentrifugation of archit	ectural
paints with TBA/MMA and BA/MMA	binder
normed fraction of free binder [%].	



Polymer binder	Low shear viscosity [Krebs units]	High shear viscosity [Poise]
BA/MMA	90	1.8
BA/TBA	95	2.3

Viscosities of architectural paints (semi-gloss, low PVC) with Rheovis PU 1340 and Rheovis PU 1191 as HEUR associative thickeners.

Low shear viscosity: Measured according to ASTM D562 using a Stormer type viscometer.

High shear viscosity: Measured according to ASTM D4287 using an ICI cone plate viscometer with 10.000 s<sup>-1</sup>

### **Contact Information**

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### **Thickener Response**

TBA containing polymers allow an effective use of viscosity modifiers. The hydrophobic *tert*.-butyl group promotes interactions with the hydrophobic moieties of associative thickeners used in paint formulations.

TBA containing binders show a superior thickening response: Increased low-shear and high-shear viscosities of paint formulations with associative thickeners (e.g. HEUR or HASE thickeners).

## Appendix: Guiding Recipe TBA in All Acrylic Dispersions

### Further Guiding Recipes can be provided after request.

Target application:	Binder for Architectural Paints

**Target Tg:** 10-20 °C

#### Applied monomers

Tert-butyl acrylate (66.1 wt%), Butyl acrylate (31.1 wt%), Acrylamide (1.5 wt%), Acrylic acid (1.3 wt%)

Initiator Solution	n (1)	Pre-Emulsion (2)		Reactor Charge (3)	
Sodium persulfate	1.3 g <sup>1)</sup>	Demineralized water	267.1 g	Demineralized water	234.7 g
Demineralized water	17.6 g	Dowfax 2A1	3.6 g <sup>1)</sup>	Disponil LDBS 20	0.9 g <sup>1)</sup>
		Lutensol AT 18	2.4 g <sup>1)</sup>		
		Acrylic acid 7.8 g			
		Acrylamide 9.0 g <sup>1)</sup>			
		Tert-butyl acrylate	396.6 g		
		Butyl acrylate	186.6 g		

1) = 100% active matter

#### Reaction

The reactor (a 2-litre glass reactor equipped with anchor stirrer (220 rpm), thermocouple, reflux condenser and feed vessels) is charged with components (3), 30.3 g of the pre-emulsion (2) and heated up to 90 °C. The temperature is kept at 90 °C and 3.4 g of the initiator solution (1) are added in one shot. After 5 minutes, the remaining initiator solution (1) and pre-emulsion (2) are fed to the reactor in parallel within 180 min. After completion of the addition, the reaction mixture is stirred for 15 min at 90 °C.

#### **Post Reaction**

13.0 g aqueous sodium hydroxide solution (6.5 wt%) are added in one shot at 90°C. Then, 9.0 g aqueous tert-butyl hydroperoxide solution (4 wt%) and 13.2 g aqueous acetone bisulfite solution (4.6 wt%) are added within 60 min. Thereafter, 35.0 g water are added in one shot. The reaction mixture is cooled down to ambient temperature, neutralized with aqueous sodium hydroxide solution (5 wt%) and filtered over a 125 µm filter.

#### Analytics

Residual monomer:	< 1000 ppm
T <sub>g</sub> :	14 °C
Particle diameter::	~ 190 nm
Solid content:	48 wt%