ACRYESTER® TB

Tertiary-Butyl Methacrylate

Product Guide & Literature

MITSUBISHI RAYON COMPANY, LTD.

Tokyo Japan

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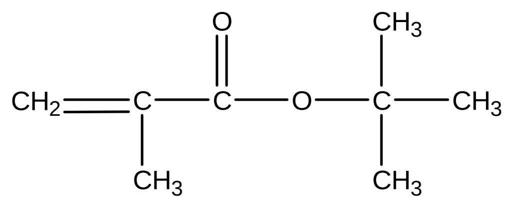
General Chemical Information

Chemical name	*tertiary*-Butyl methacrylate
Product code	TBMA
Chemical structure	
Molecular formula	$C_8H_{14}O_2$
Molecular weight	142.20
Appearance	Clear liquid with ester odor

Specification Information

Specification Item	Specification Value	Typical Value
Color (APHA)	20 (max.)	5 (max.)
Purity	98.0% (min.)	99.9%
Water content (when shipped)	0.1% (max.)	0.01%
Specific gravity (20 °C/4 °C)	0.874 - 0.880	0.878
Free acid (as MAA)	0.05% (max.)	0.01%
Inhibitor (MEHQ)	180 - 220 ppm	200 ppm
Packing	▪ 18 MT or 42,000 lb. bulk isotank ▪ 170 kg (375 lb.) net weight steel drums ▪ 15 kg (33 lb.) polyethylene pails	

Introduction

Mitsubishi Rayon Company, Ltd. (MRC or the Company) is pleased to introduce and offer to prospective users the unique properties and advantages of *tertiary*-butyl methacrylate (TBMA). This compound is a highly versatile monomer with applications across many areas. The following five sections discuss the advantages and properties of polymers produced using TBMA:

1. High homopolymer T_g
2. Superior solubility properties
3. Increased hydrolysis and water resistance
4. Enhanced long term UV weatherability
5. Ability to form specialty acid functional resins
6. Ability to be used in anionic polymerizations

MRC has substantially increased its TBMA capacity owing to the chemical's increasing use worldwide. The Company's capacity increases have allowed MRC to achieve beneficial economies of scale through which MRC has been able to significantly lower TBMA's cost. These cost reductions have resulted in the monomer's growing use in conventional, high-volume industrial coatings beyond TBMA's previous uses that were generally limited to specialty applications.

1. High Homopolymer T_g

TBMA's high T_g value of 107 °C for its homopolymer is substantially higher than its n-butyl methacrylate (n-BMA) (20 °C) and isobutyl methacrylate (IBMA) (48 °C) analogs. The compound's high T_g value enables chemists to significantly increase the T_g of acrylic copolymers while still retaining the favorable solubility profile and other polymer properties commonly associated with the butyl group. TBMA's T_g is slightly higher than the homopolymer of methyl methacrylate (MMA) (105 °C) which allows one for one replacement of MMA with TBMA without any change in T_g of the resulting polymer.

	TBMA Homopolymer	MMA Homopolymer	n-BMA Homopolymer	IBMA Homopolymer	CHMA[1] Homopolymer
T_g	107 °C	105 °C	20 °C	48 °C	83 °C

[1] Cyclohexyl methacrylate.

2. Superior Solubility Properties

TBMA's low solubility parameter affords chemists a number of advantages in formulating coatings. The most important advantage is that TBMA can be used to replace MMA in copolymers in order to obtain resins that are easily dissolvable in lean or oxygenated solvents. This advantage becomes particularly important when using VOC exempt solvents such as acetone, methyl acetate, or *tertiary*-butyl acetate, as well as the proposed VOC exempt solvent, dimethyl carbonate. See example 1.

Another important solubility advantage associated with this compound is its beneficial use in making higher solids formulations. TBMA based resins have substantially less viscosity in most common solvents when compared to MMA analogs. This feature allows less solvent to be used to attain desired viscosity (while still maintaining the high Tg properties normally achieved using MMA). See data at Figure 1 for toluene. MRC also has comparable data using ethyl acetate and MEK.

In addition, the ability to use lean solvents is especially advantageous in formulating products for the coating of plastics. Molded plastic surfaces can be harmed by strong solvents and create cracking and pitting in the plastic. Formulators using TBMA based resins, combined with lean solvents, can expect superior finishes and properties when coating plastic articles.

	TBMA Homopolymer	MMA Homopolymer	CHMA Homopolymer
Solubility parameter	8.0 - 8.5	9.3 - 9.45	7.9

Example 1: *Solubility in lean solvents*

Formulation: TBMA/2-EHA/MAA

Monomer ratios: 70%/30%/1%

Polymerization method: Suspension polymerization

Typical Properties

Appearance	White, non-dusting beads
Non-volatiles	98.0% (min.)
Molecular weight	80,000
Calculated Tg	45 °C
Calculated solid acid value	3.3 mg KOH/g

Solubility Transparency

Solvent	Transparency
Isopar H (Exxon)	Good / Clear
Exxsol D40 (Exxon)	Good / Clear
LAWS (Shell)	Excellent / Clear
Methyl cyclohexane	Excellent / Clear
n-Hexane	Excellent / Clear

Viscosity of the Polymer

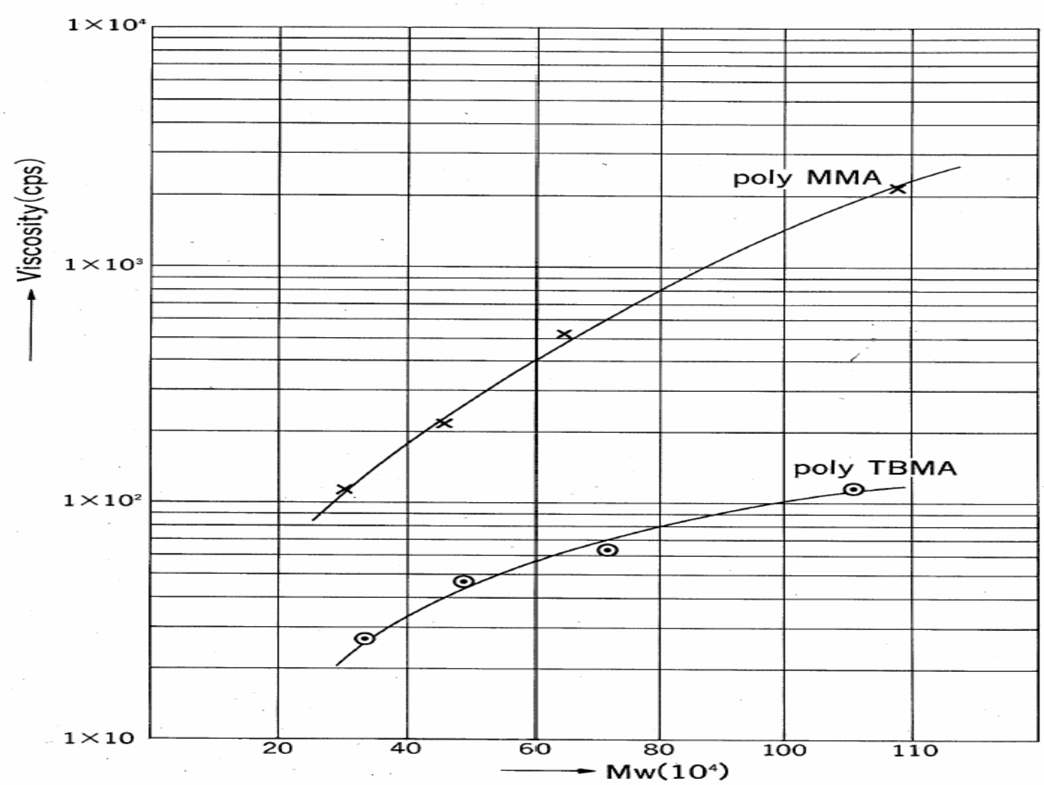


Fig.1 Viscosity vs Mw

Polymerization: Suspension at 75°C
Mw = Weight average molecular weight: G.P.C. method
Solution: 30% toluene soln.
Viscosity: rotary viscometer method (cps at 25°C)

3. Increased Hydrolysis and Water Resistance

TBMA's water solubility is very low compared to MMA and comparable to cyclohexyl methacrylate (CHMA), which has been described as a very effective monomer for resistance to attack by water. Most water resistant or hydrophobic alkyl monomers (e.g., 2-EHA, LMA, SMA) have very low Tg values where water resistance comes with the disadvantage of having softer coatings, In addition, TBMA is very resistant to hydrolysis because the *tertiary*-butyl group's steric hindrance protects the ester linkage from hydrolytic attack. Optimal water resistance properties are generally achieved when TBMA is used in the range of 15% to 30%.

	TBMA Homopolymer	MMA Homopolymer	CHMA Homopolymer
Water solubility	0.05%	1.72%	< 0.01%

4. Enhanced Long Term UV Weatherability

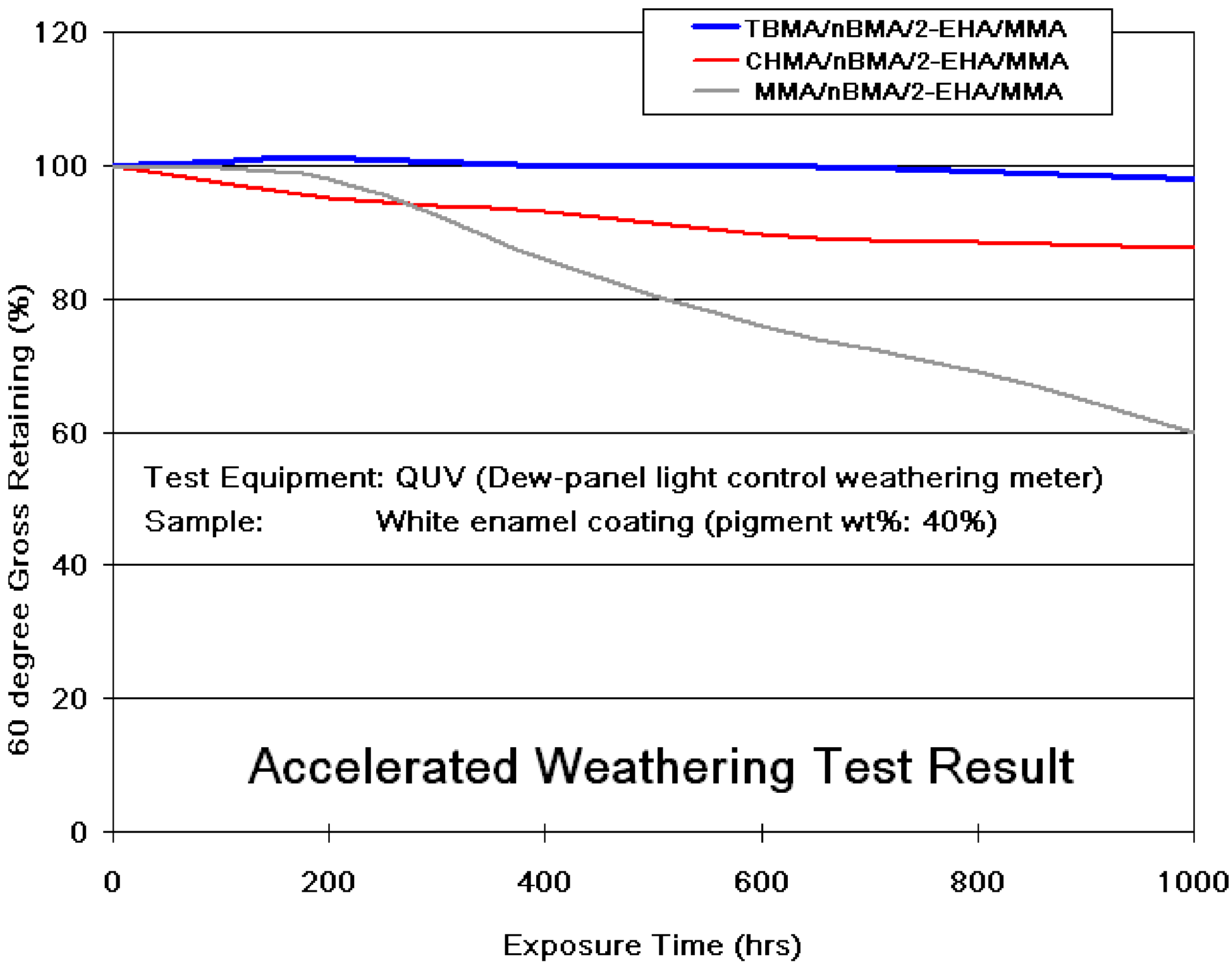
TBMA's most attractive property is its ability to impart significant weatherability to high gloss polymer films compared with those produced from other acrylate or methacrylate monomers. Accelerated weathering tests of multi-component polymers have shown that polymers produced with TBMA, in the range of 15% to 30%, exhibit minimal loss in gloss when compared to analogous polymers made with MMA or CHMA. For example, multi-component polymers, containing TBMA, have shown almost no loss in gloss after 1,000 hours of UV exposure. By comparison, the same percentage of CHMA in an equivalent multi-component polymer had over 10% loss in gloss and the MMA analog had over a 40% loss in gloss.

Example 2: *Wood coating weatherability*

Formulation: TBMA/n-BMA/2-EHA/MMA

Copolymer information: The figure below compares the weatherability of three different copolymers. The first monomer (i.e., TBMA, CHMA, or MMA) identified in each of the three copolymers is used at 30%. The ratios of the three remaining monomers in each copolymer have been varied in order to obtain a copolymer having a calculated Tg value of 25 °C

Polymerization method: Emulsion polymerization



5. Ability to Form Specialty Acid Functional Resins

TBMA also has the unique characteristic of forming ionomer or acid/acid anhydride functionalities in acrylic resins. Although acrylic acid and methacrylic acid can easily be used to create polymers with acid functionalities, the use of these two compounds tends to form block copolymers where numerous acid groups bunch closely together in various sections of the polymer. TBMA, owing to it similarities in both polarity and reactivity to MMA and other common monomers, will polymerize randomly and evenly across the polymer backbone. Once the TBMA has been polymerized on the chain, heating the resin above 150 °C drives off the tert-butyl or isobutylene group from the polymer to create the *dispersed* acid/acid anhydride functionality.

6. Ability to be Used in Anionic Polymerizations

TBMA's steric hindrance of the carbonyl group not only enhances water resistance, but also allows its use in anionic polymerization reactions. Most acrylates and methacrylates cannot be used in anionic polymerizations due to the prevalence of side reactions that occur at the ester linkage causing the polymerization reaction to terminate. TBMA can be used even under room temperature conditions in anionic polymerizations since the ester linkage is protected from attack by the protective *tertiary*-butyl group.

The use of anionic polymerization affords polymer chemists the versatility of making specialized *block* copolymers, *star* or *dendritic* polymers, and narrow molecular weight polymers. The finished polymer properties of enhanced solubility, weatherability, and water resistance are still retained when TBMA is used. Acid functionalized resins can now be made anionically as discussed in Section 5, *Ability to Form Specialty Acid Functional Resins*.

TBMA's high purity and low residual alcohol and acidity levels enable the monomer to be used without further purification in anionic polymerizations.[2]

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[2] *Tertiary*-butanol is typically present at 0.003%.

General Properties

Chemical name	*tertiary*-Butyl methacrylate
Specific gravity (20 °C/4 °C)	0.878
Refractive index (n_{D20})	1.4196
Viscosity (20 °C)	0.93 mPa · s
Freezing point	< -60 °C
Specific heat	0.48 cal/g · °C 2.01 J/g · °C
Boiling point	67 °C (93 hPa)
Solubility (20 °C)	Water in: 0.3% In water: 0.05%
Flash point	29.5 °C / 85.1 °F [closed cup]

Toxicology Data

Skin irritation	PII = 2.1, moderate irritant (Draize Test in rabbits)
Eye irritation	Irritating when tested in rabbits
Oral mouse LD_{50}	8,549 mg/kg
Dermal rat LD_{50}	> 2,000 mg/kg
Inhalation rat LC_{50}	10.17 mg/liter [4-hour]
Skin sensitization	Negative (Guinea Pig Maximization Test) Negative (Freund's Complete Adjuvant Test)
Ames gene mutation test	Negative
Chromosomal aberration test	Positive

International Chemical Inventory Status

Japan (ENCS)	2-1039
U.S. (TSCA Inventory)	CAS RN 585-07-9
Europe (EINECS)	209-548-7

Reactivity Information – Q and e Values

	TBMA	MMA
Heat of polymerization	54.4 KJ/mole	54.4 KJ/mole
Q-value	0.71	0.74
e-value	0.32	0.40

Reactivity Information – Reactivity Ratios

M_1 = TBMA	r_1	r_2
M_2 = Styrene	0.49 ± 0.03	0.58 ± 0.03