

# Synthetic Rubber

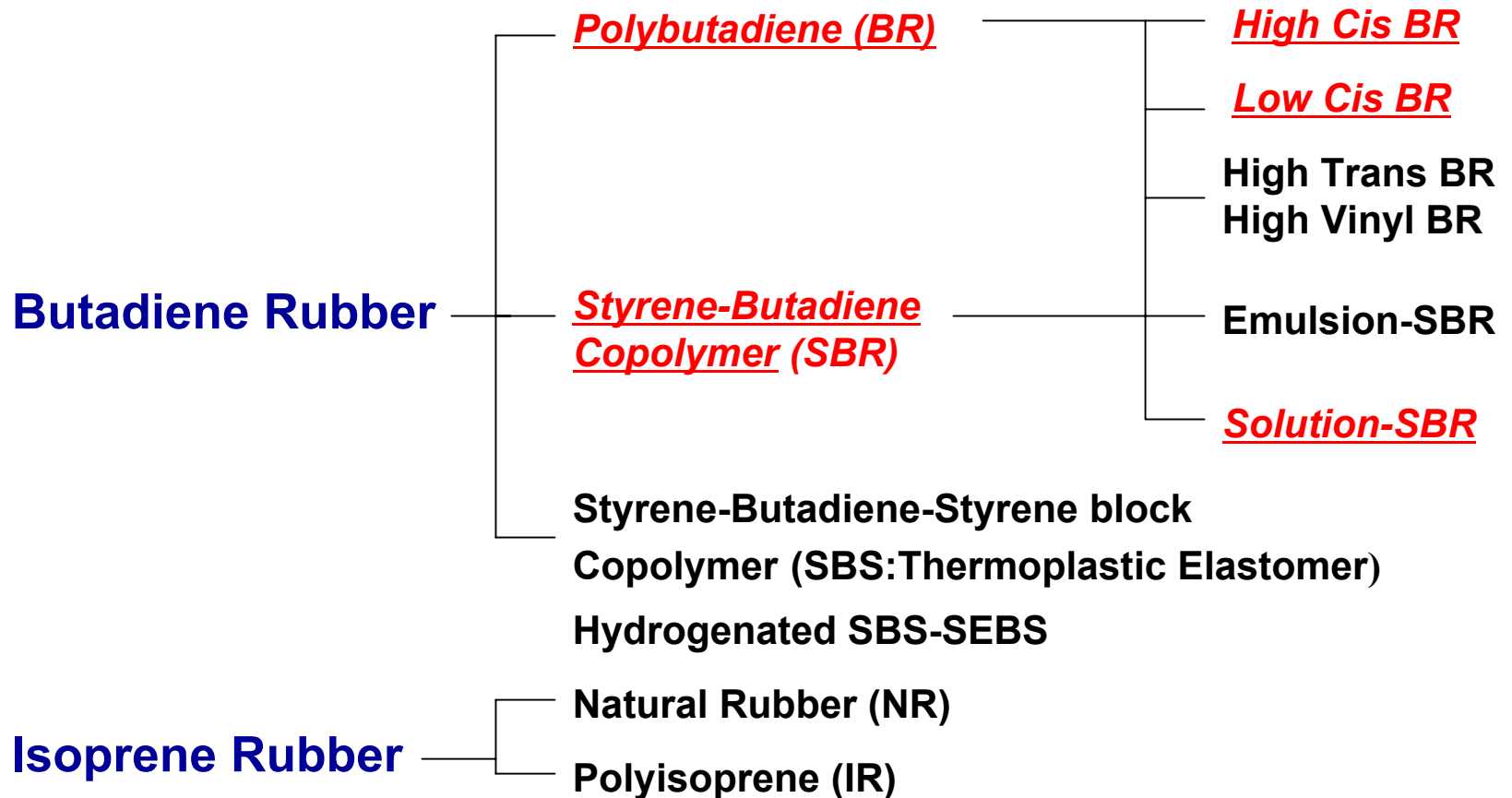
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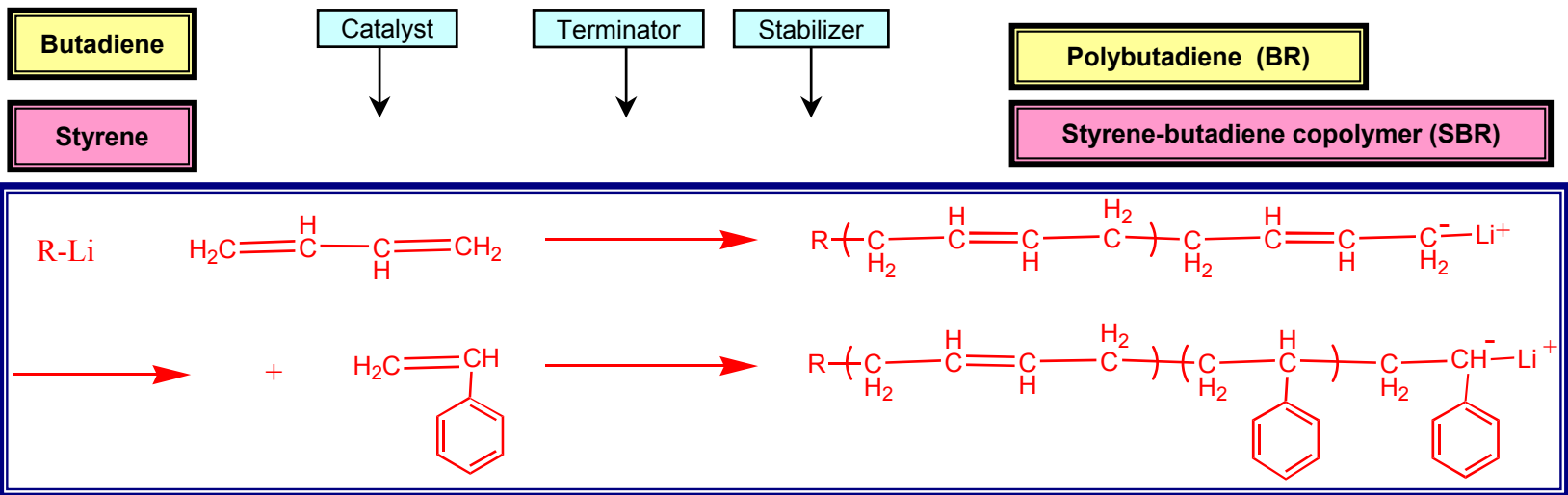
For HIPS, MBS and Mass-ABS

Mitsubishi International  
Corporation

# Classification of Diene Rubber



# Characteristics of Solution Polymerization Technique



Control of Macro-structure

Molecular Weight	Controllable by ratio between Feed Monomer/Catalyst because of living anionic polymerization
MWD (Mw/Mn)	Narrow due to living anionic polymerization. Changeable according to polymerization conditions and reactions
Branch	Little during polymerization. Easily controlled by adding coupling agent

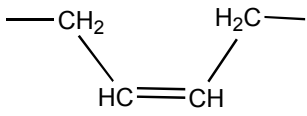
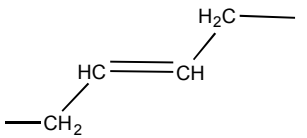
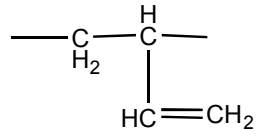
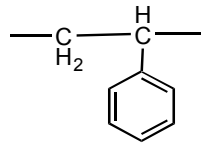
Control of Microstructure

Microstructure (polybutadiene parts)	1,4-Cis; 1,4-Trans; 1,2-Vinyl
Bound Styrene Content	Vinyl content easily controlled by adding modifier (polar compounds)
Block Styrene Content	Easily controlled by butadiene/styrene feed ratio
Hydrogenated (Bd)	Random, block, tapered      Controlled by polymerizations conditions
	1,2-Vinyl....Butylene      1,4-Cis Trans....Ethylene

# Relationship between Low Cis, High Cis Rubber

	Polymerization	Polymer Structure
Low Cis Rubber	<b>Anionic polymerization</b> (Solution) RLi catalyst	<ul style="list-style-type: none"> <li>■ MWD narrow, Little branching</li> <li>■ Microstructure: Cis 35%, Trans 52%, Vinyl 13%</li> <li>■ Tg: -98 degree C Tm: nil</li> <li>■ Control of polymer structure Large variation               <ul style="list-style-type: none"> <li>-- Vinyl content</li> <li>-- Block SBR, Random SBR</li> <li>-- Coupling reaction, Terminal modification, etc.</li> </ul> </li> </ul>
	<b>Radical polymerization</b> (Emulsion) Potassium peroxodisulfate	<ul style="list-style-type: none"> <li>■ Broad MWD, Much branching</li> <li>■ Microstructure: Cis 12%, Trans 70%, Vinyl 18%</li> <li>■ Control of polymer structure Little variation               <ul style="list-style-type: none"> <li>-- Styrene content</li> <li>-- Molecular weight</li> </ul> </li> </ul>
High Cis Rubber	<b>Coordinate polymerization</b> (Solution) Ni catalyst Co-Al catalyst	<ul style="list-style-type: none"> <li>■ Broad MWD (Mw/Mn 3), Much branching</li> <li>■ Microstructure: Cis 96%, Vinyl 4%</li> <li>■ Tg: -105 degrees C Tm: 10 degrees C</li> <li>■ No copolymerization of styrene</li> </ul>

# Microstructure of Polybutadiene

Polymer structure		Homopolymer Tg , Tm	
		Tg (Elasticity)	Tm (Crystallization)
<b>Cis Bond</b>		<b>-110 ° C</b>	<b>-10 ~ 0 ° C (YES)</b>
<b>Trans Bond</b>		<b>-100 ° C</b>	<b>50~ 100° (YES)</b>
<b>Vinyl Bond</b>		<b>-7 ° C •</b>	<b>Nil (NIL)</b>
<b>Styrene</b>		<b>100 ° C •</b>	<b>Nil (NIL)</b>

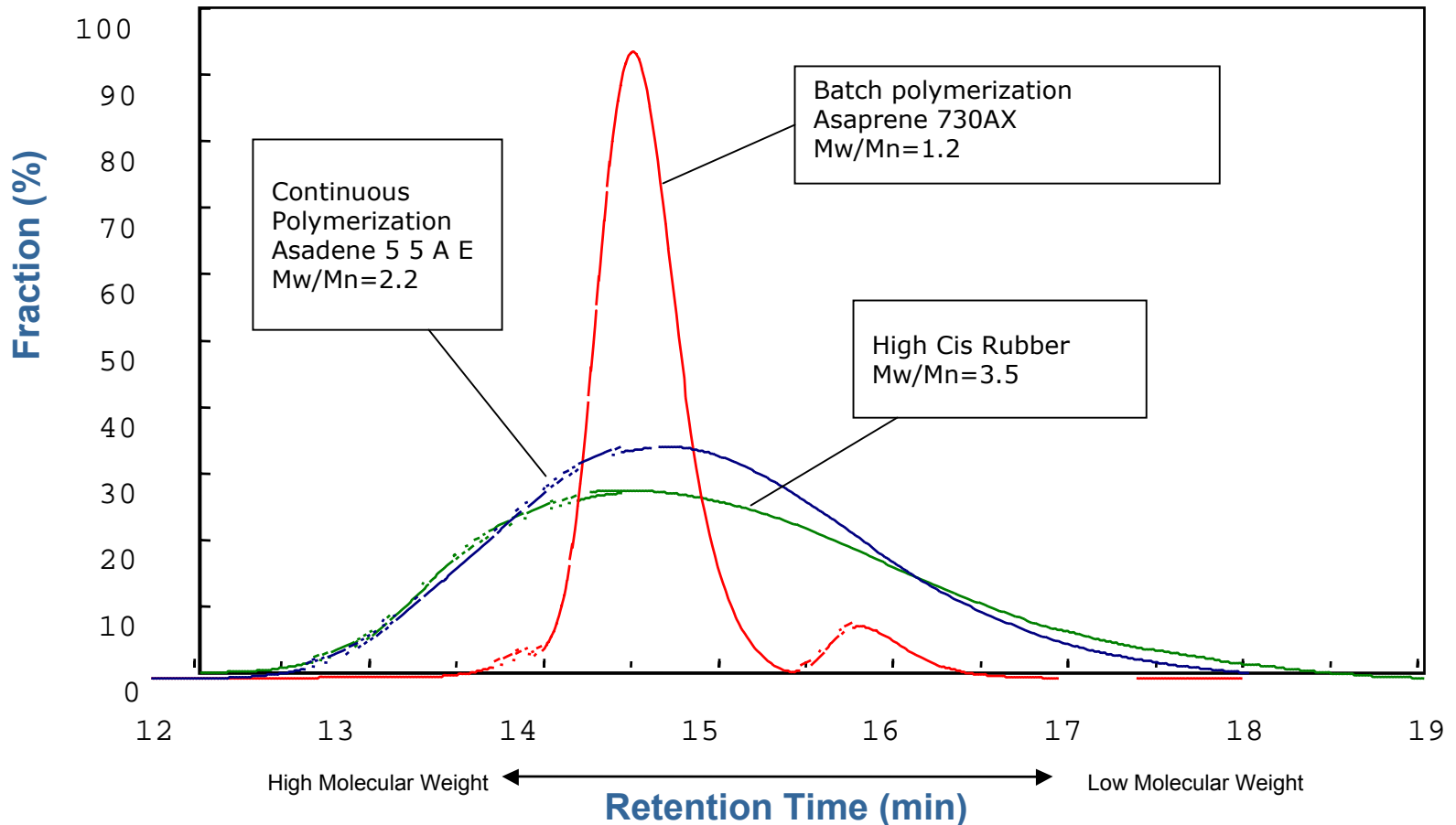
# Microstructure of Polybutadiene (2)

Catalyst	Microstructure (%)			Styrene Copolymerizable
	Cis	Trans	Vinyl	
<u>RLi</u>	35	52	13	○
<u>RLi / Polar solvent</u>	~30	~ 50	~ 70	○
<u>Ni</u> • Ni(Naphtanate) • $AlR_3$ • $BF_3 \cdot (C_2H_5)_2$	96 ~ 98	1 ~ 2	1 ~ 2	×
<u>Co</u> • Co(Octanate) <sub>2</sub> • $AlR_2Cl$ • $H_2O$	96 ~ 98	1 ~ 2	1 ~ 2	×
<u>Radical</u> • $K_2S_2O_8$	10 ~ 20	60 ~ 80	15 ~ 20	○

○ = Copolymerizable with styrene

× = Not copolymerizable with styrene

# Comparison of Batch Polymerized Rubber with Continuous Polymerized Rubber: Molecular weight Distribution



# Synthetic Rubber for HIPS Use

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- Acquired Characteristics
  - Ability to crosslink/Graft during HIPS polymerization
  - Styrene insolubles (gel) → Extremely low
  - Impurity → Extremely low
  - Colorless
  - Handling → Improved cold flow



# Synthetic Rubber for HIPS Use

- Commercial Rubber for HIPS Use
  - Polybutadiene rubber: Low Cis BR, High Cis BR
    - Comparison of Low Cis BR with High Cis BR as rubber for HIPS:

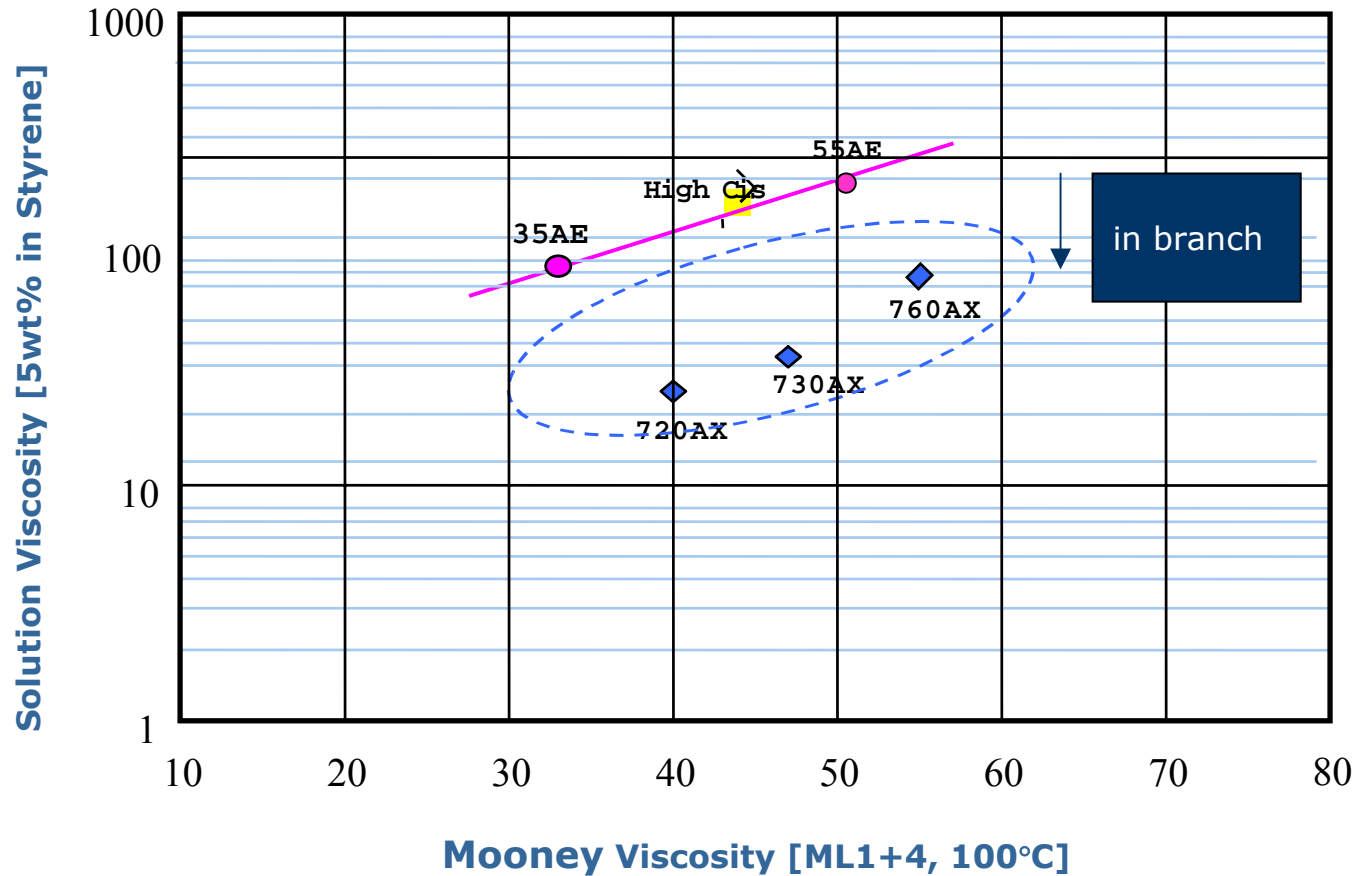
	Graft	Crosslinking
Low Cis BR	High reactivity	High reactivity
High Cis Br	Low reactivity	Low reactivity

- Styrene-butadiene copolymer
  - Random SBR
    - Block SBR
      - Special grade: Super high gloss HIPS, Transparent HIPS, etc.

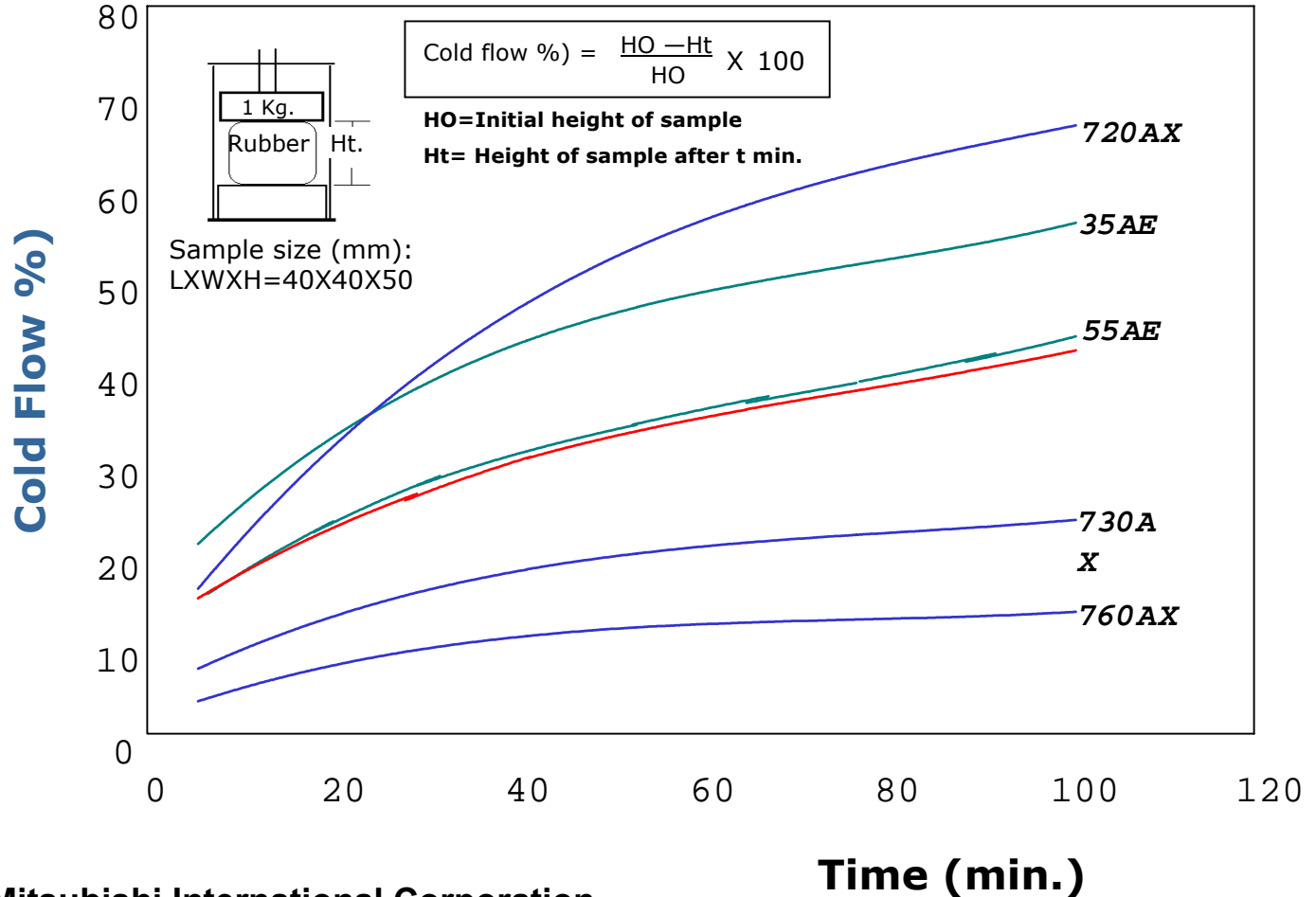
# Synthetic Rubber for HIPS (Mass-ABS)

	Grade	Styrene (%)	ML	SV (CPS)	Microstructure (%)			
					CIS	TRANS S	VINYLL	
General	Asadene 55AE	0	50	170	35	52	13	General purpose
	Asadene 35AE	0	33	85	35	52	13	
Low SV	Asaprene 720AX	0	40	25	33	49	18	High Gloss
	Asaprene 730AX	0	47	35	33	49	18	
Low Modulus	Asaprene 760AX	0	55	77	33	49	18	High Impact
PH-BR	H300A	0		75	Partially hydrogenated BR			Thermal Stability
SBR	Asaprene 610A	15	-	10	35	51	14	High Gloss Mass-ABS
	Asaprene 625A	35	-	20	35	51	14	Transparent
	Asaprene 670A	39	-	34	35	51	14	Super High Gloss

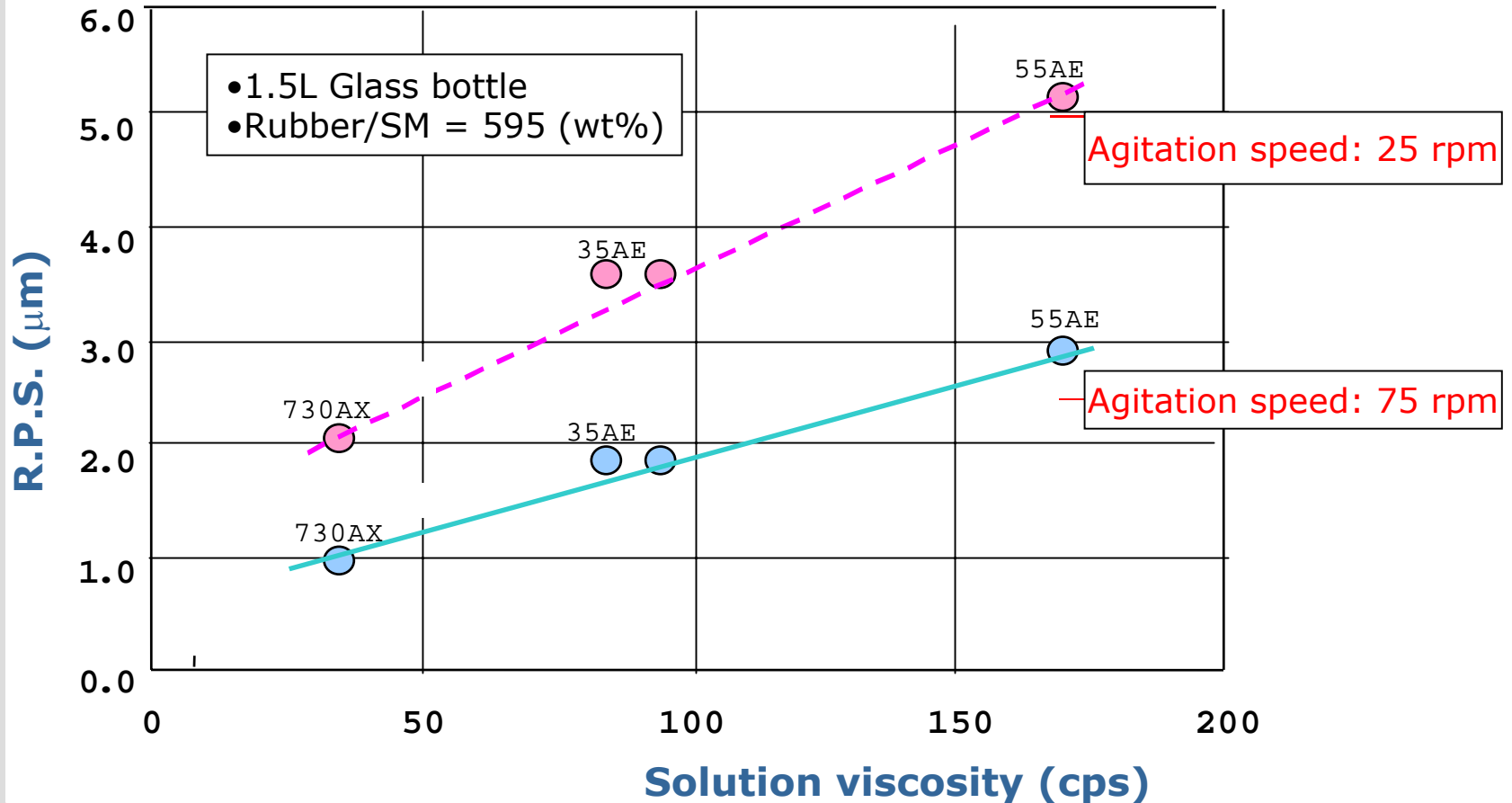
# Relationship between Mooney and Solution Viscosities



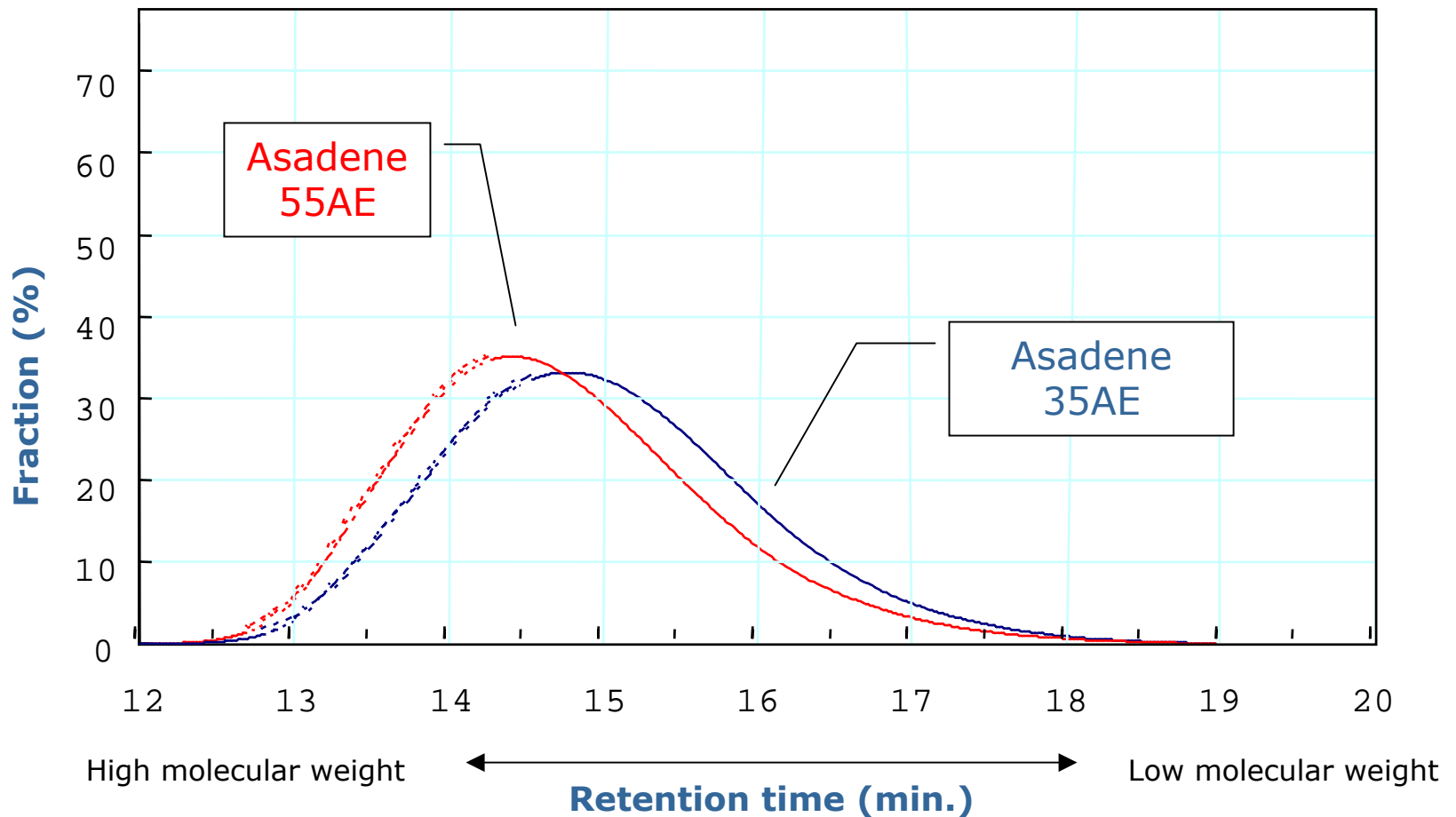
# Cold Flow of Asaprene, Asadene, Other Rubbers



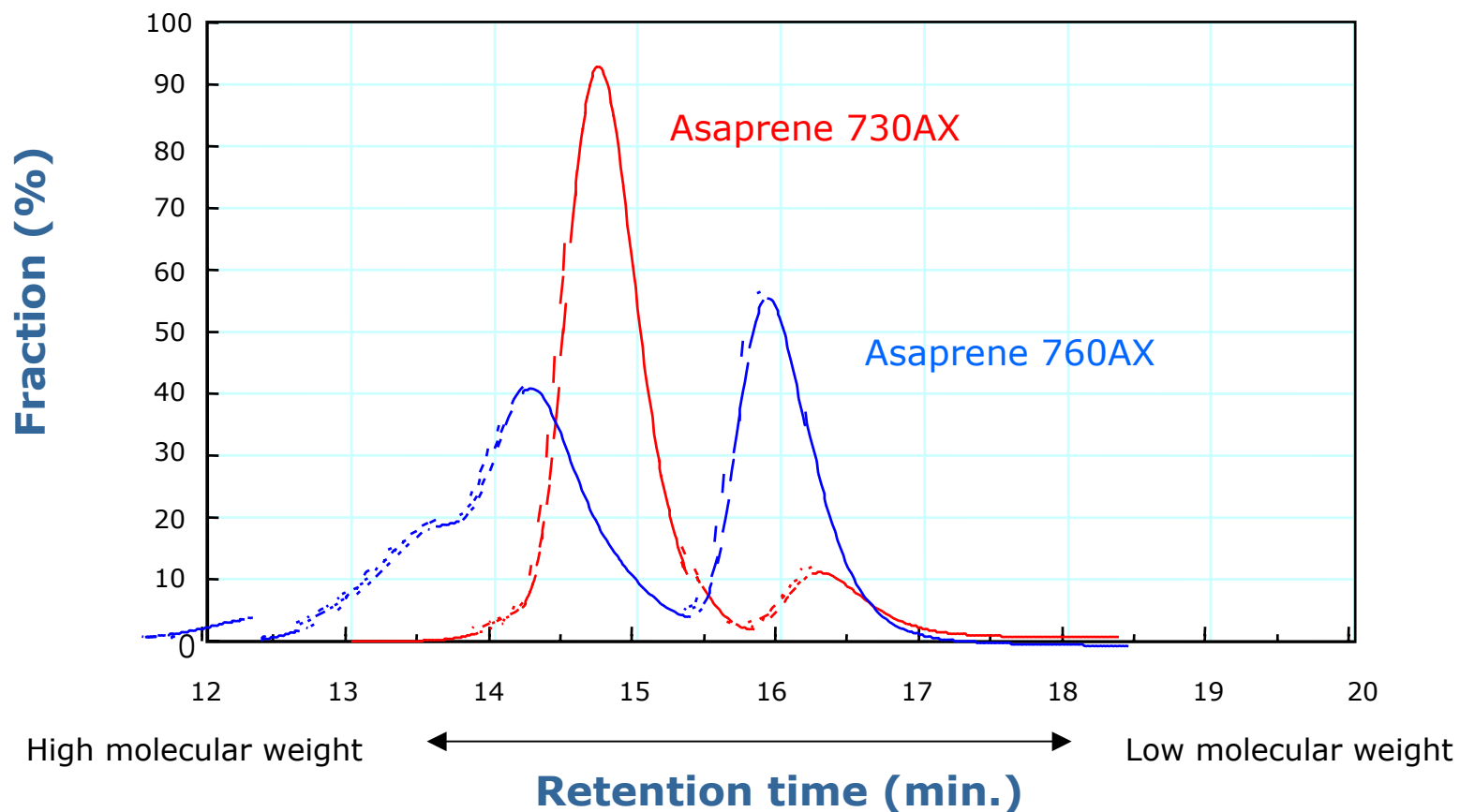
# Relationship between Solution Viscosity and Rubber Particle Size (Using Polybutadiene rubber)



# Molecular Distribution of Weight for Asadene 55AE/35AE

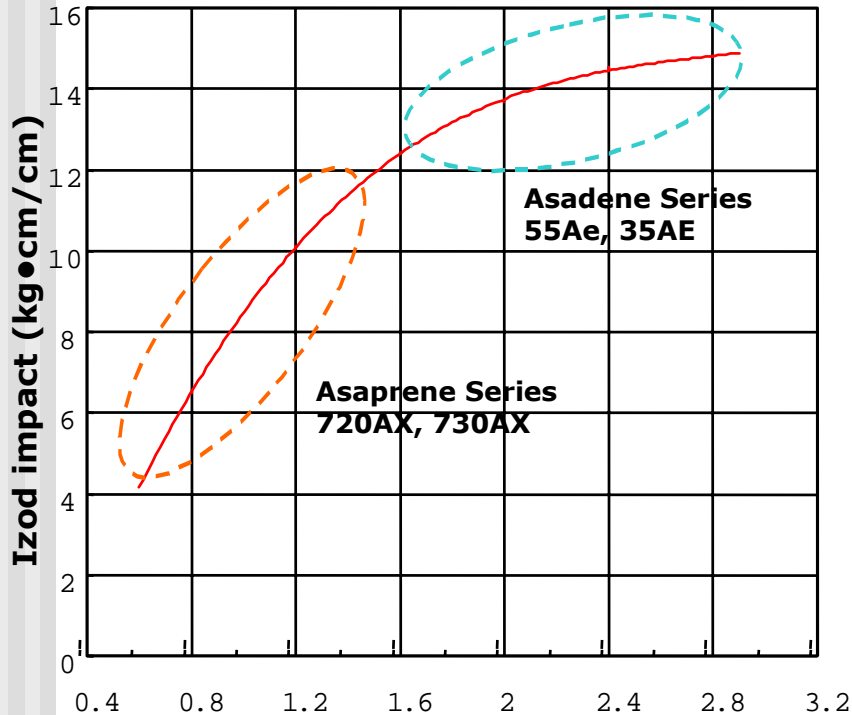


# Distribution of Molecular Weight in Asaprene Series

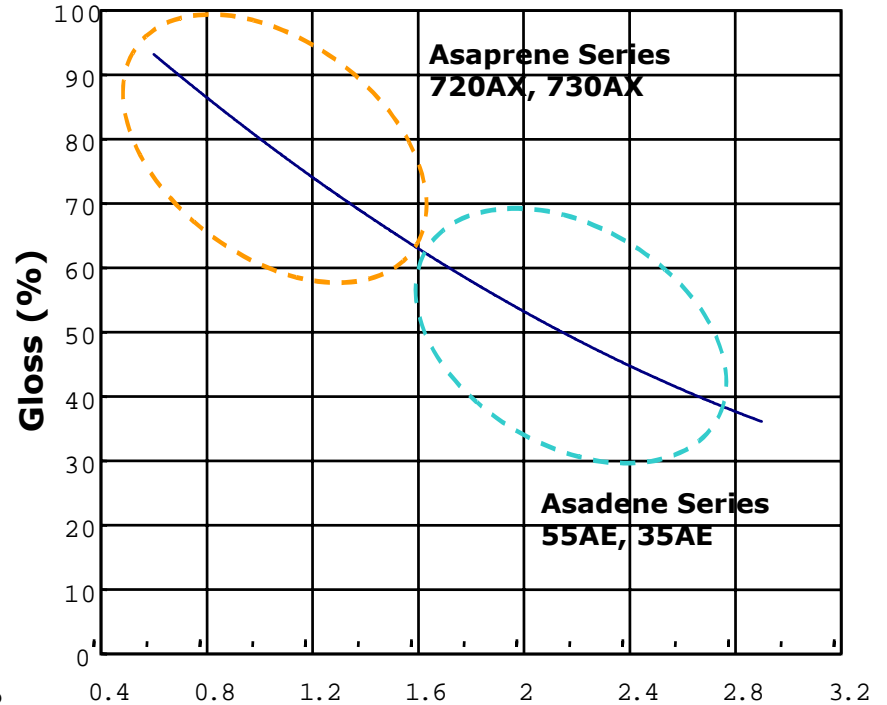


# Relationship between Rubber Particle Size and Izod, Gloss (Using polybutadiene rubber)

(Using polybutadiene rubber)



Rubber particle size (μm)



Rubber particle size (μm)



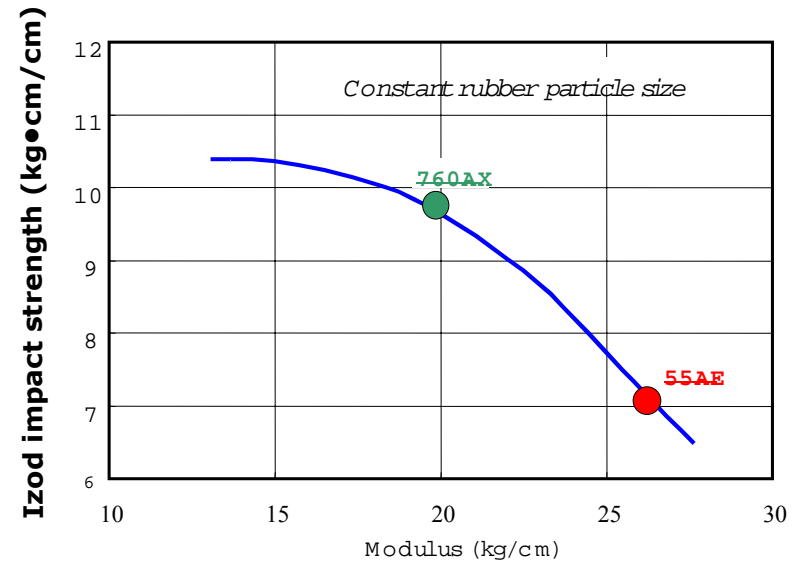
# Asaprene 760AX

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- Rubber for super high-impact PS
- Molecular structure
  - Polybutadiene rubber
  - Branched structure
  - Vinyl/cis/trans: 18/33/49
  - Solution viscosity: 77cps

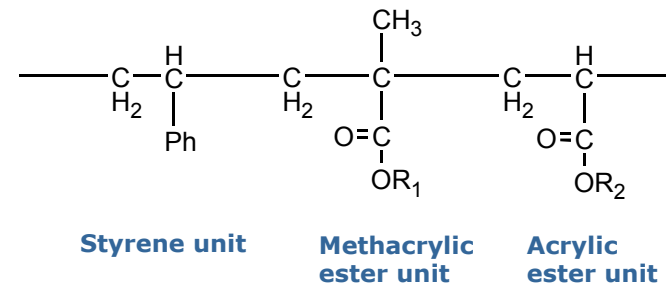
# Asaprene 760AX

- Characteristics
  - By using low-modulus Asaprene rubber, impact energy can be absorbed easily



# Asaprene 670A (1)

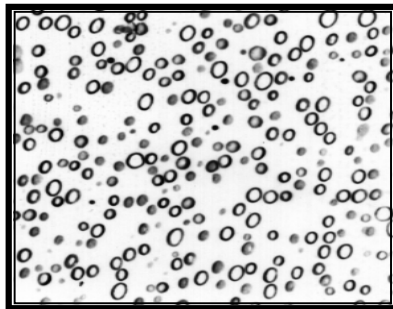
- Rubber for
  - Super high-gloss HIPS
  - Transparent HIPS
- Molecular structure
  - Styrene-butadiene rubber (39% styrene)
  - Vinyl/cis/trans: 14/36/50
  - Solution viscosity: 34 cps



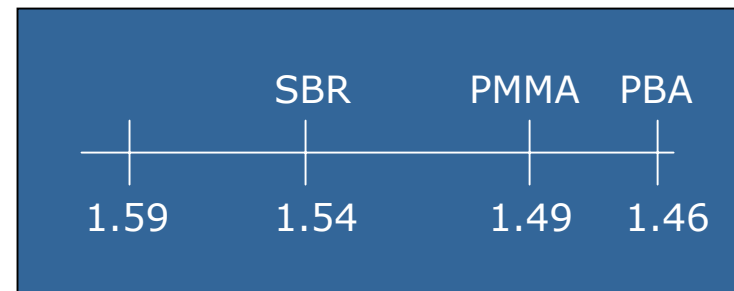
# Asaprene 670A (2)

- Characteristics
- Allows for easy formation of core-shell rubber particles
- Makes it easy to obtain transparent HIPS
- Corresponds to refractive Index of Styrene/Methacrylic copolymer and rubber phase

Core-shell particles  
(thermal polymerization)



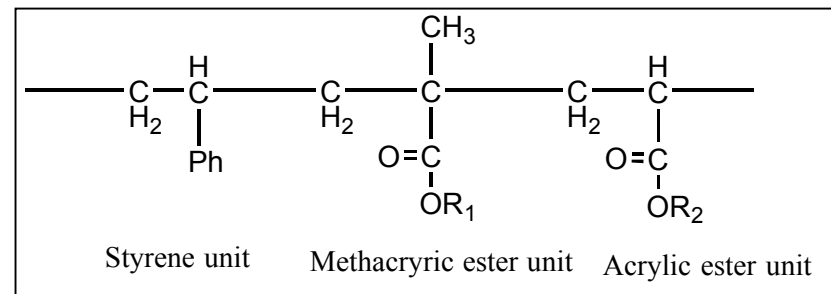
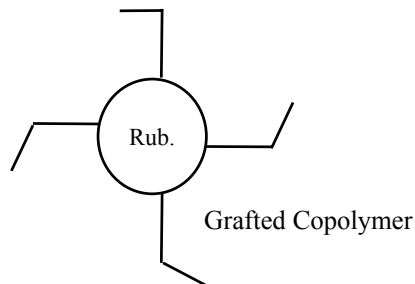
## Refractive Index



# Asaprene 625A (1)

- Rubber for transparent HIPS
- Molecular structure
  - Styrene-butadiene rubber (35% styrene)
  - Vinyl/cis/trans: 14/36/50
  - Solution viscosity: 20 cps

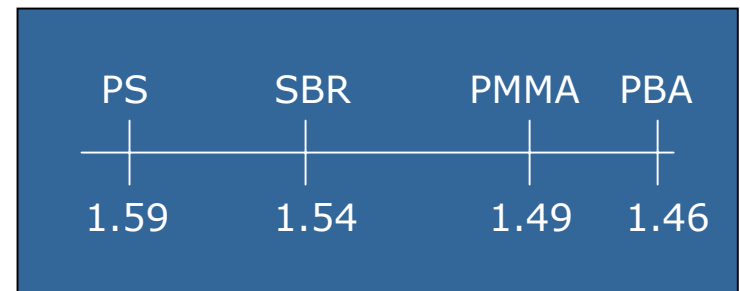
Matrix Resin



# Asaprene 625A (2)

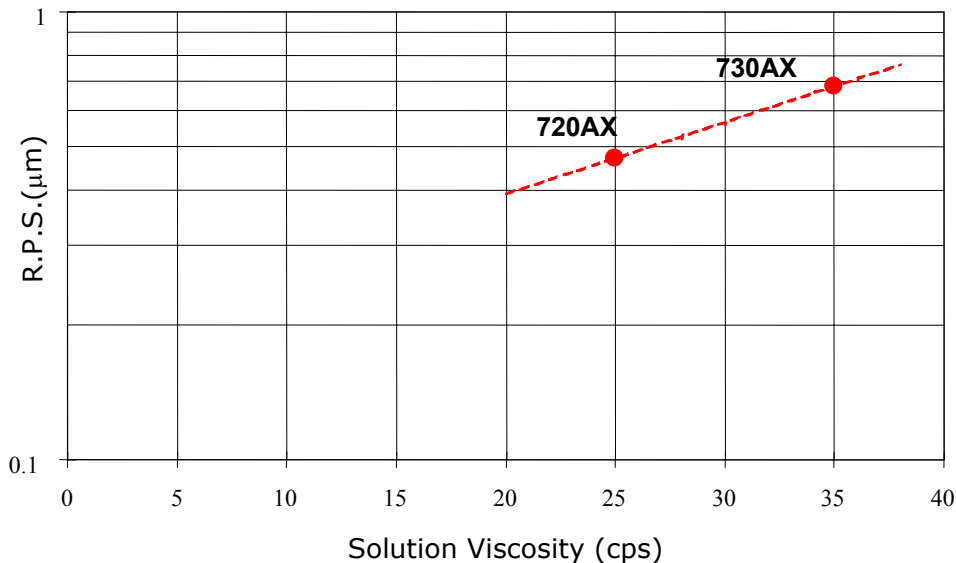
- Characteristics
  - Transparency HIPS are easily obtained compared with other styrene-butadiene block copolymers
  - Easier to handle:
    - Bale is
      - Easier to cut
      - Less likely to crack
      - Bites into cutter more easily

## Refractive Index

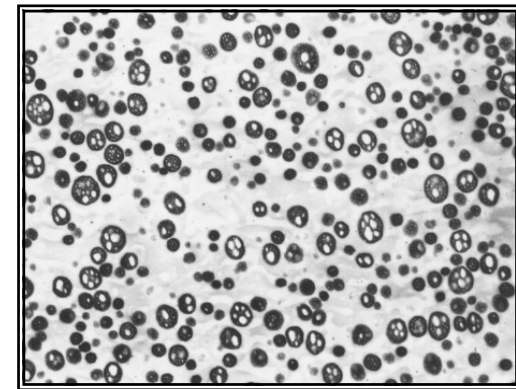


# Asaprene 720AX

- Rubber for high-gloss mass ABS
- Characteristics:
  - Easier to obtain small rubber particles
- Molecular structure:
  - Polybutadiene rubber
  - Vinyl/cis/trans: 18/33/49
  - Solution Viscosity: 25 cps



Relationship between Solution viscosity and R.P.S.

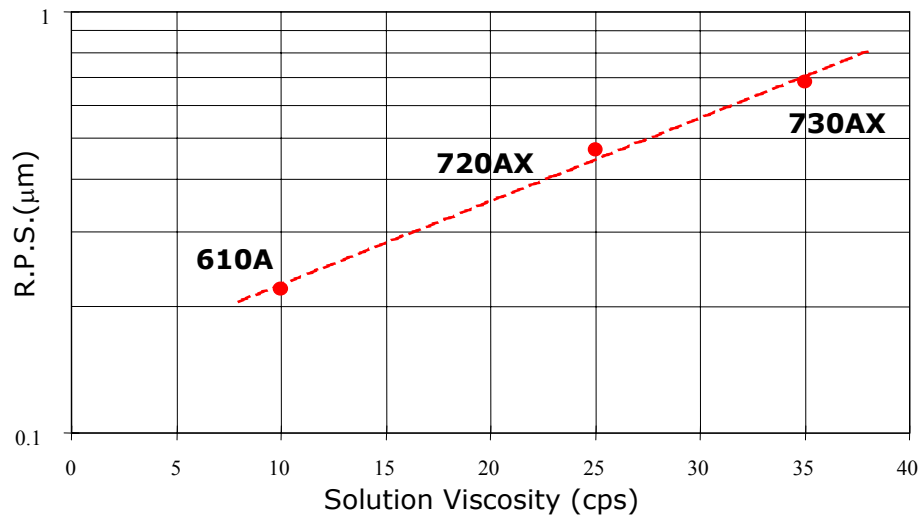


Mass ABS with Asaprene 720AX

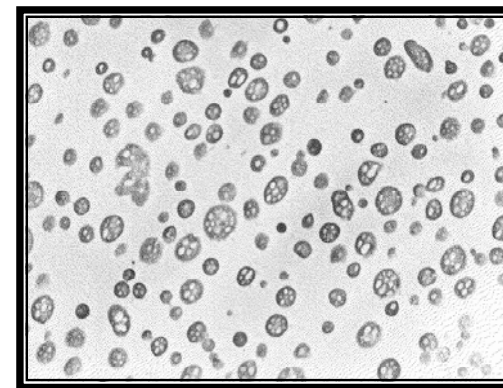
# Asaprene 610A

- Rubber for high-gloss mass ABS
- Characteristics:
  - Easier to obtain small rubber particles

- Molecular structure
  - Styrene-butadiene rubber (15% styrene)
  - Vinyl/cis/trans: 14/36/50
  - Solution viscosity: 10 cps



**Relationship between Solution viscosity and R.P.S.**

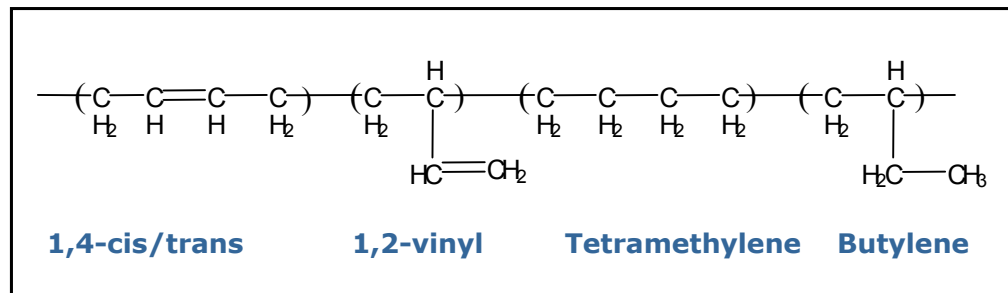


**Mass ABS with Asaprene 610A**



# H300A (1)

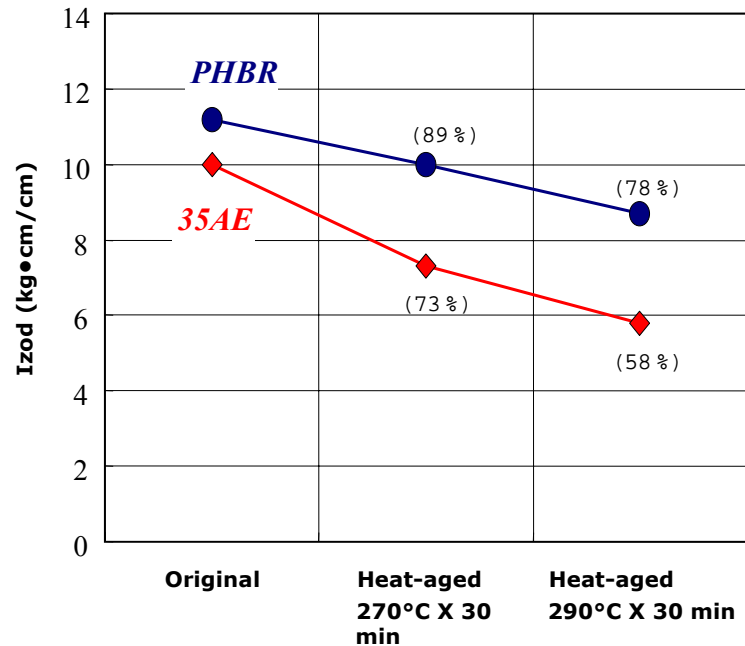
- Rubber for HIPS with excellent thermal stability
- Molecular structure:
  - 1,4-cis/trans: 63%
  - 1,2-vinyl: 1%
  - Tetramethylene: 26%
  - Butylene: 10%
  - Solution viscosity: 75 cps



# H300A (2)

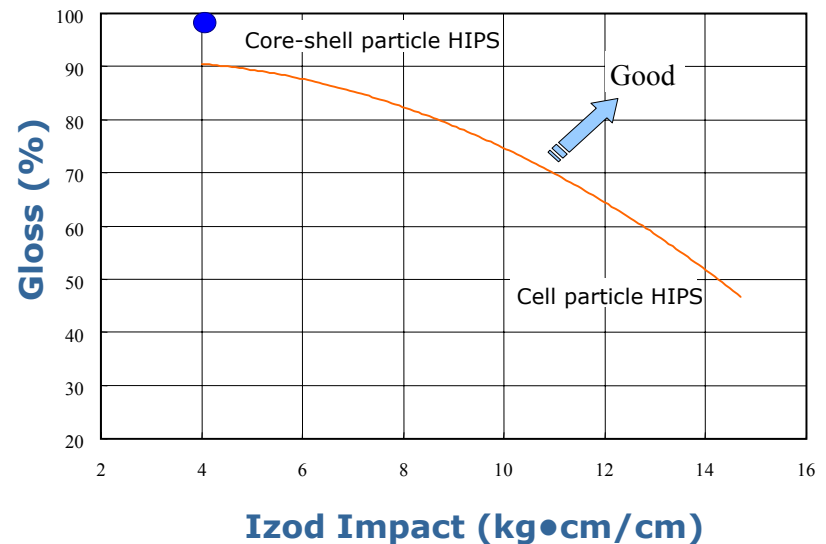
## ■ Characteristics

- HIPS and styrenic copolymer (e.g. mass-polymerized ABS) with PHBR have excellent thermal stability.
- As a result, the decline in impact strength is very small when molding at high temperatures
- Outstanding capabilities for recycling applications



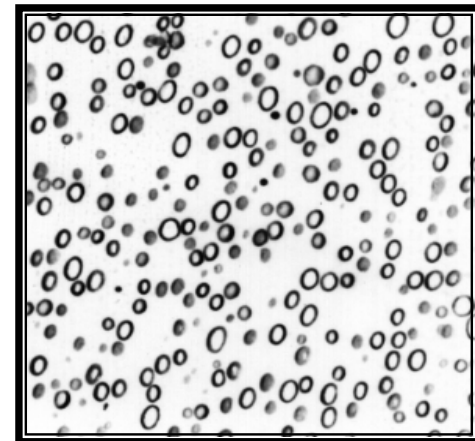
# Asaprene 630A (1)

- Rubber for translucent (high-gloss) HIPS
- Molecular structure
  - Styrene-butadiene rubber (22% styrene)
  - Vinyl/cis/trans: 14/36/50
  - Solution viscosity: 33cps



# Asaprene 630A (2)

- Characteristics
  - Core-shell rubber particles can be obtained easily
- Comparison with other styrene-butadiene block copolymers:
  - Less rubber content
  - Easier to handle: Bale is
    - Easier to cut
    - Less likely to crack
    - Bites into cutter more easily
  - Dissolving time is shorter



**Core-shell particles**

# Asaprene 610A, 720AX (1)

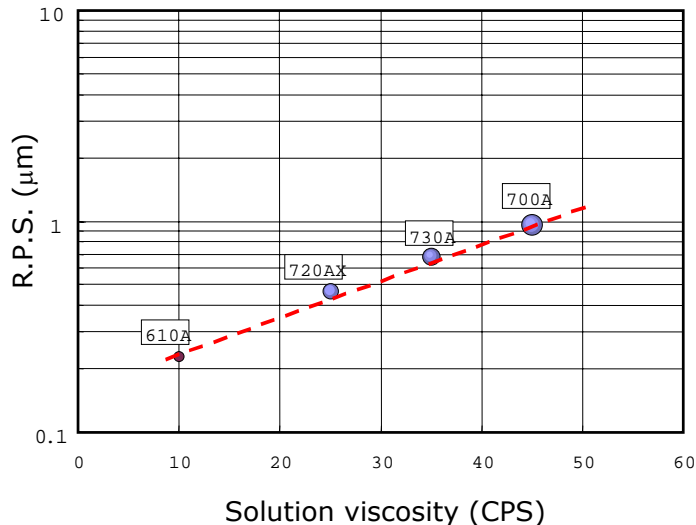
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- Rubber used for mass ABS
- Molecular structure
  - 610A
    - Styrene-butadiene rubber (15% styrene)
    - Vinyl/cis/trans: 14/36/50
    - Solution viscosity: 10cps
  - 720AX
    - Polybutadiene rubber
    - Vinyl/cis/trans: 18/33/49
    - Solution viscosity: 25cps

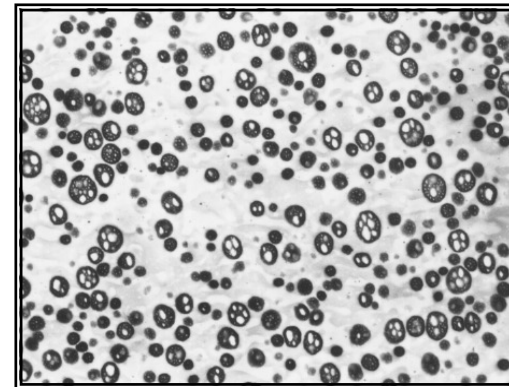
# Asaprene 610A, 720AX (2)

## ■ Characteristics

- Small rubber particles the size of ABS are easily obtained, making it possible to obtain a high-gloss ABS



**Relationship between Solution Viscosity and R.P.S.**



### Polymerization Condition

- Apparatus : 1.5L glass bottle
- Composition : SM/AN/Rub.=65/25/10 (wt%)
- Initiator: 150ppm
- Chain Transfer: 1200ppm

# Next Steps

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- Mitsubishi International offers a variety of outstanding synthetic rubbers for HIPS and Mass-ABS applications
- To learn more about how MIC can meet your product needs, please contact us at (212) 605-2440, or email [rafi.khan@mitsubishicorp.com](mailto:rafi.khan@mitsubishicorp.com)

**Thank you.**