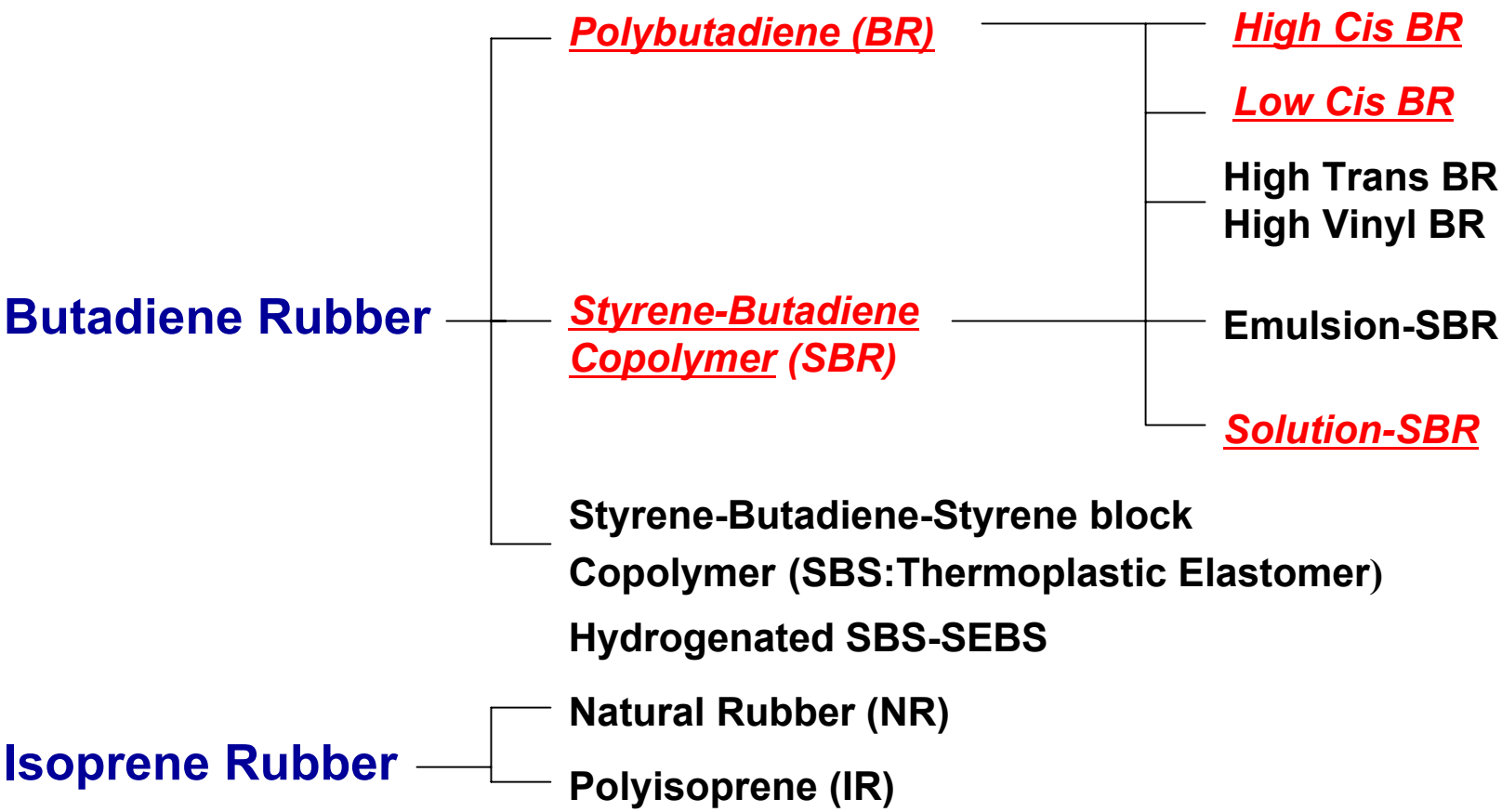
# Synthetic Rubber

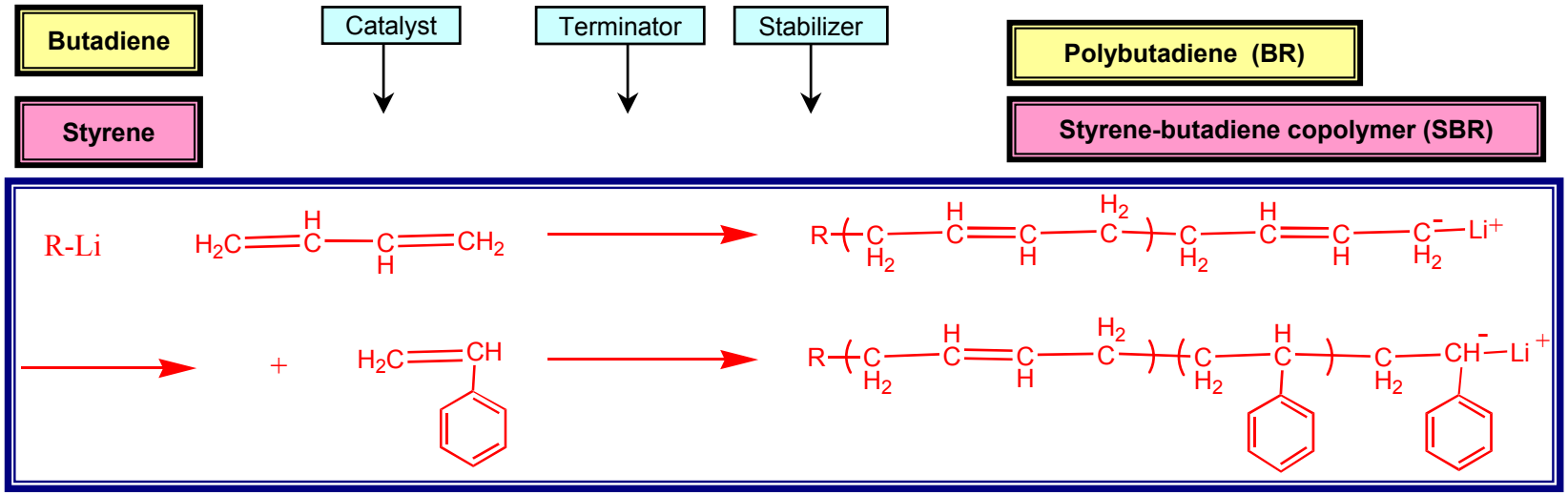
For HIPS, MBS and Mass-ABS

Mitsubishi International Corporation

# Classification of Diene Rubber



# Characteristics of Solution Polymerization Technique




Control of Macro-structure

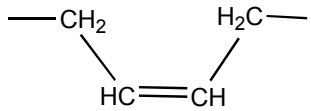
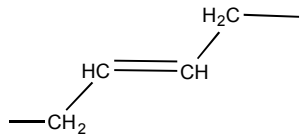
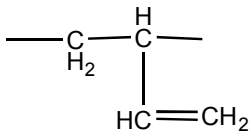
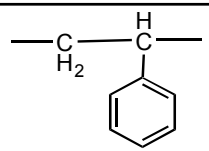
| | |
|---|---|
| Molecular Weight | Controllable by ratio between Feed Monomer/Catalyst because of living anionic polymerization |
| MWD (Mw/Mn) | Narrow due to living anionic polymerization. Changeable according to polymerization |
| | conditions and reactions |
| Branch | Little during polymerization.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

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

# Relationship between Low Cis, High Cis Rubber

| | Polymerization | Polymer Structure |
|---|---|---|
| Low Cis Rubber | **Anionic polymerization**<br>(Solution)<br>Rli catalyst | ■ MWD narrow, Little branching<br>■ Microstructure: Cis 35%, Trans 52%, Vinyl 13%<br>■ Tg: -98 degree C Tm: nil<br>■ Control of polymer structure Large variation<br>-- Vinyl content<br>-- Block SBR, Random SBR<br>-- Coupling reaction, Terminal modification, etc. |
| | **Radical polymerization**<br>(Emulsion)<br>Potassium peroxodisulfate | ■ Broad MWD, Much branching<br>■ Microstructure: Cis 12%, Trans 70%, Vinyl 18%<br>■ Control of polymer structure Little variation<br>-- Styrene content<br>-- Molecular weight |
| High Cis Rubber | **Coordinate polymerization**<br>(Solution)<br>Ni catalyst<br>Co-Al catalyst | ■ Broad MWD (Mw/Mn 3), Much branching<br>■ Microstructure: Cis 96%, Vinyl 4%<br>■ Tg: -105 degrees C Tm: 10 degrees C<br>■ No copolymerization of styrene |

# Microstructure of Polybutadiene

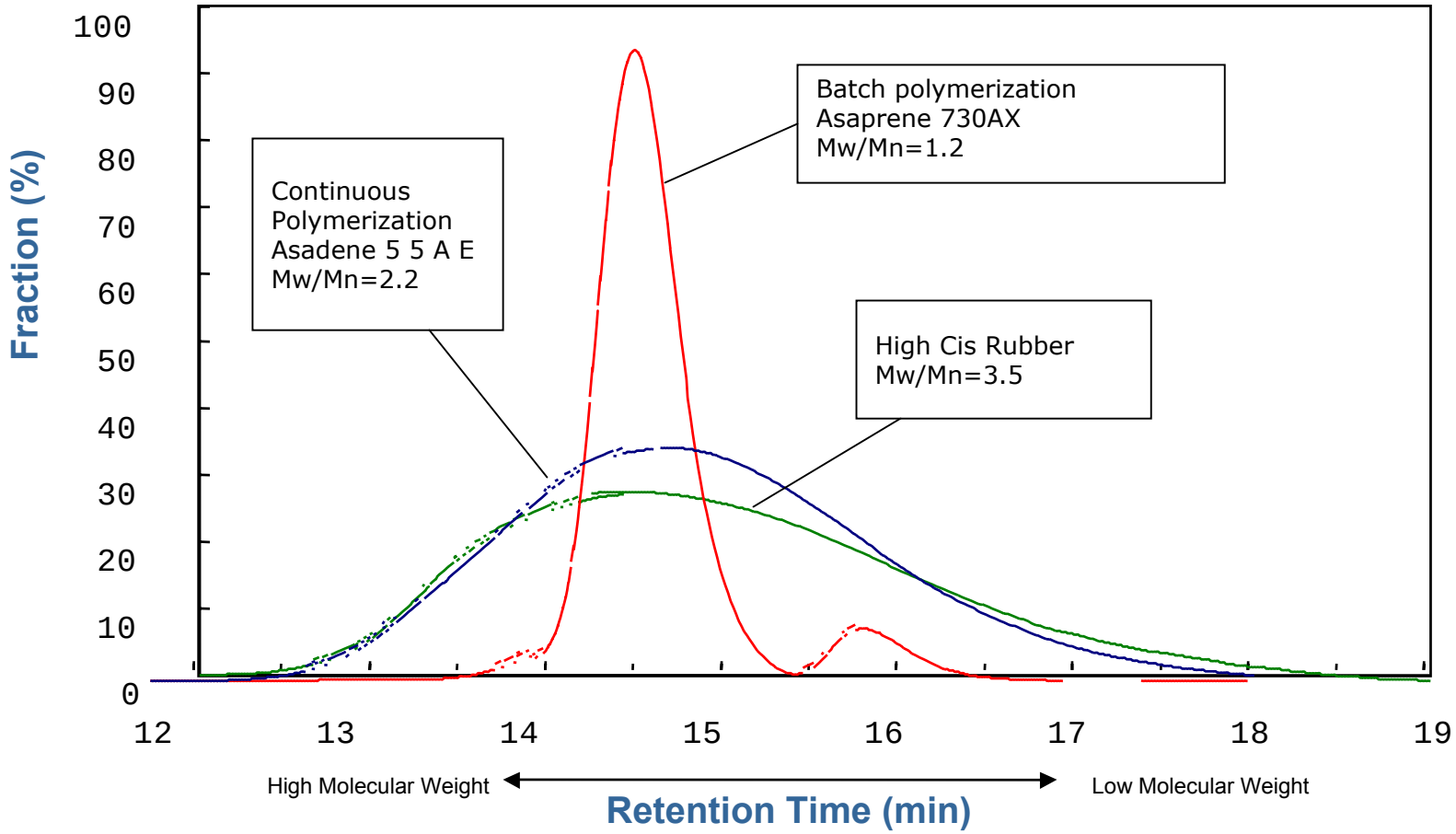
| Polymer structure | | Homopolymer Tg , Tm | |
|---|---|---|---|
| | | Tg (Elasticity) | Tm (Crystallization) |
| Cis Bond |  | -110 ° C | -10 ~ 0 ° C (YES) |
| Trans Bond |  | -100 ° C | 50~ 100° (YES) |
| Vinyl Bond |  | -7 ° C • | Nil (NIL) |
| Styrene |  | 100 ° C • | Nil (NIL) |

# Microstructure of Polybutadiene (2)

| Catalyst | Microstructure (%) | | | Styrene Copolymerizable |
|---|---|---|---|---|
| | Cis | Trans | Vinyl | |
| **RLi** | 35 | 52 | 13 | ○ |
| **RLi / Polar solvent** | ~30 | ~ 50 | ~ 70 | ○ |
| **Ni**<br>• Ni(Naphtanate)<br>• $AlR_3$<br>• $BF_3 \cdot (C2H5)_2$ | 96 ~ 98 | 1 ~ 2 | 1 ~ 2 | × |
| **Co**<br>• $Co(Octanate)_2$<br>• $AlR_2Cl$<br>• $H_2O$ | 96 ~ 98 | 1 ~ 2 | 1 ~ 2 | × |
| **Radical**<br>• $K_2S_2O_4$ | 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

- 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:

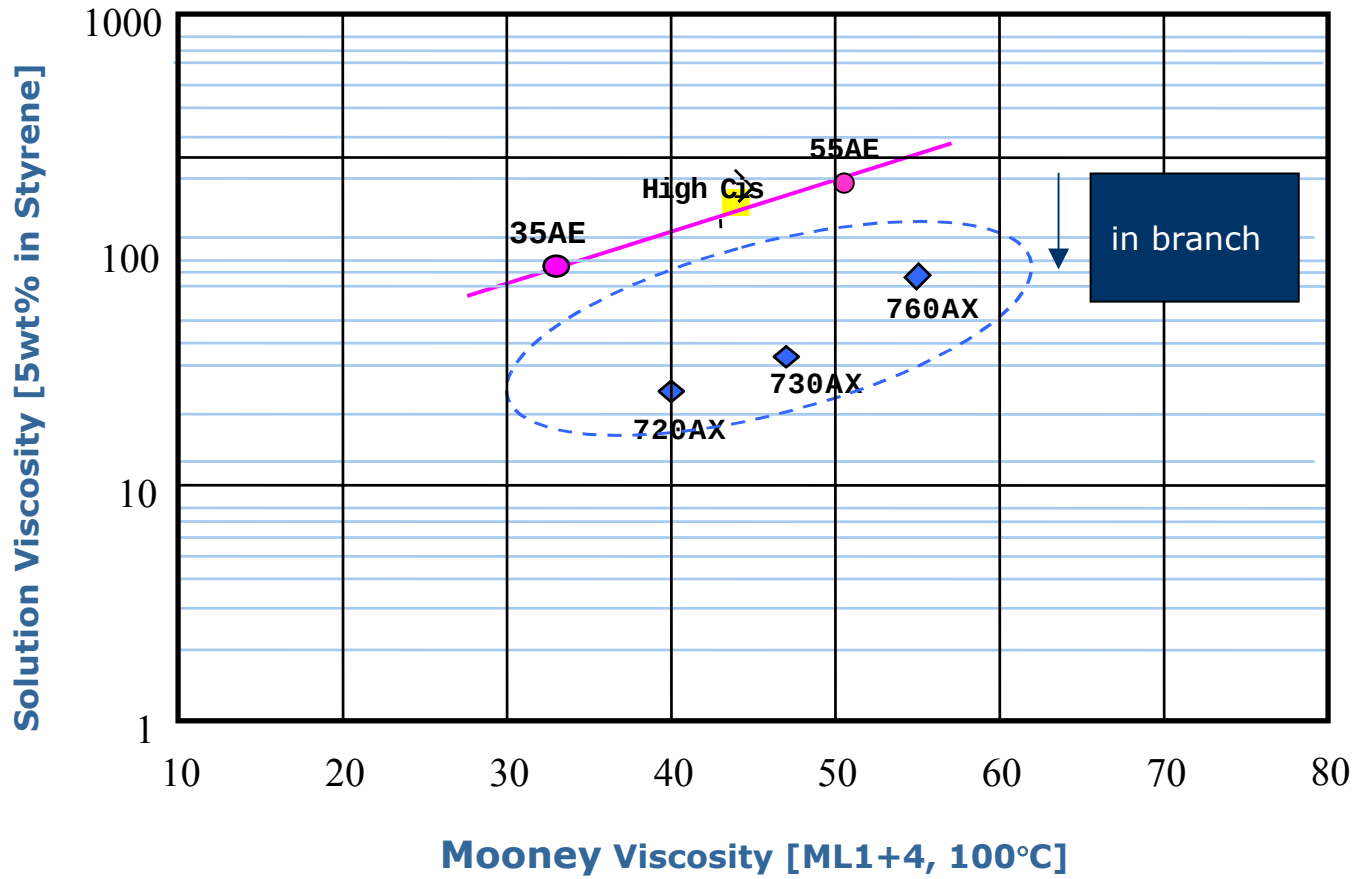
| | Graft | Crosslinking |
|---|---|---|
| Low Cis BR | High reactivity | High reactivity |
| High Cis Br | Low reactivity | Low reactivity |

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

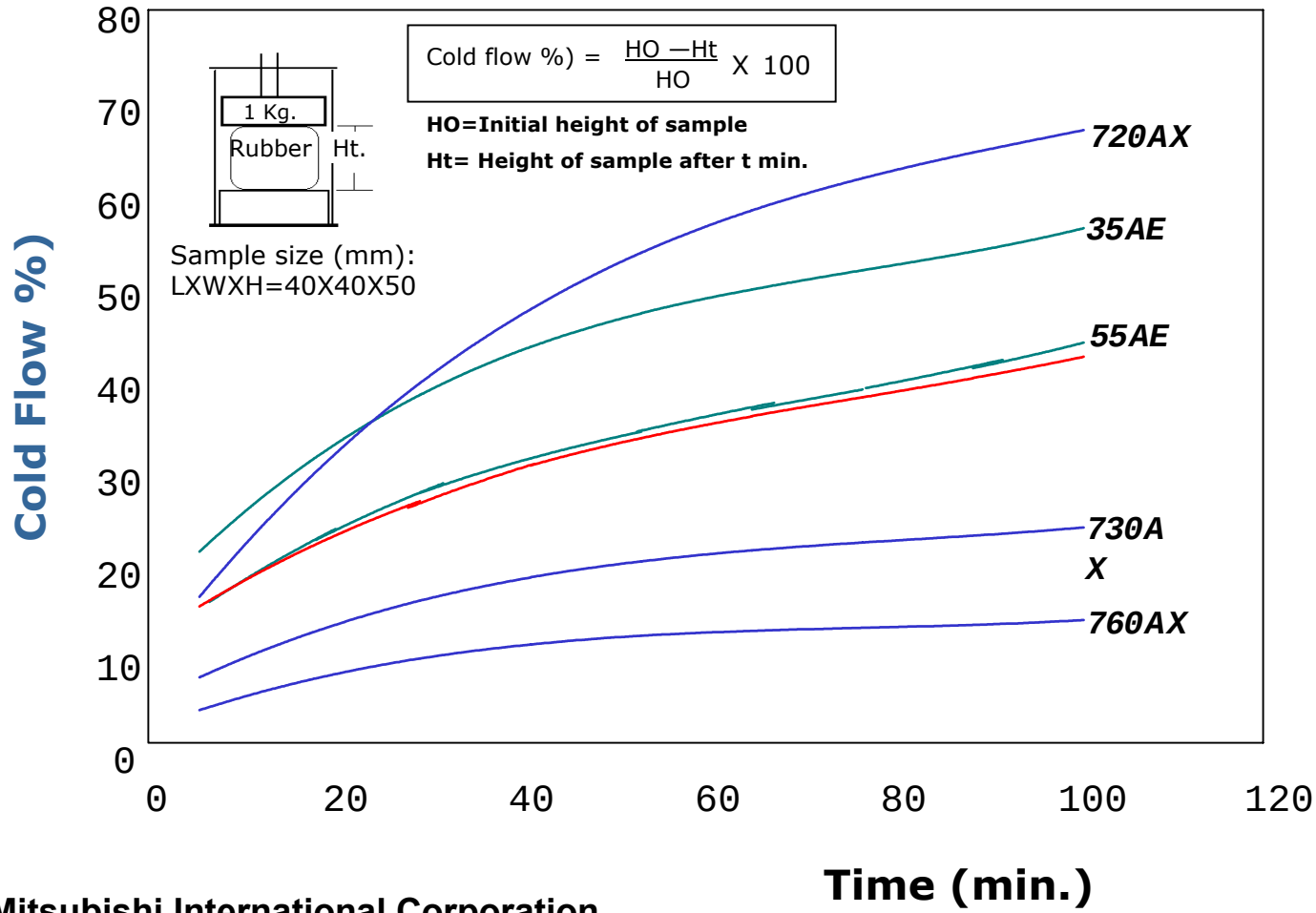
# Synthetic Rubber for HIPS (Mass-ABS)

| | Grade | Styrene (%) | ML | SV (CPS) | Microstructure (%) | | | |
|---|---|---|---|---|---|---|---|---|
| | | | | | CIS | TRANS S | VINYL L | |
| 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 |

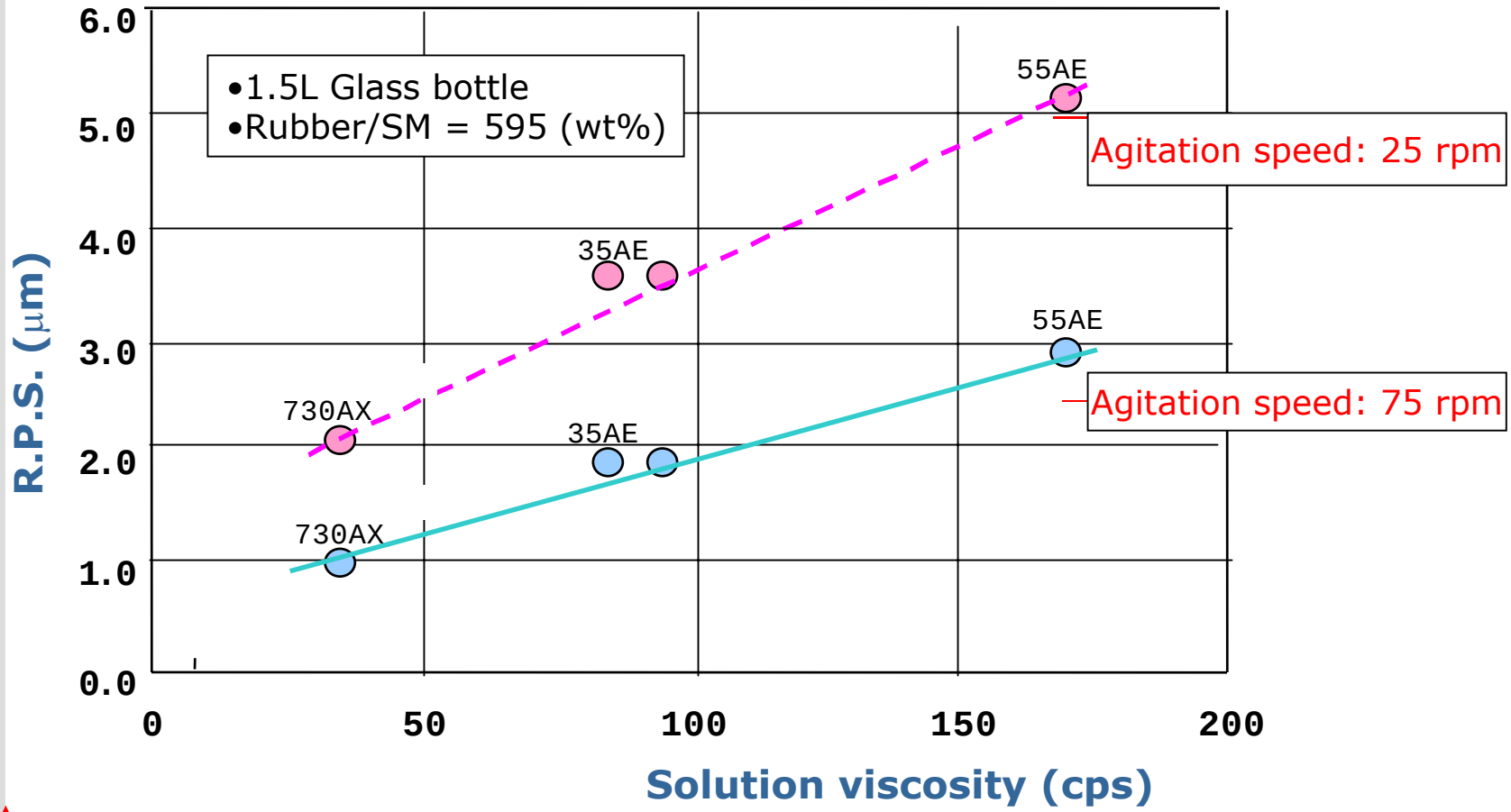
# Relationship between Mooney and Solution Viscosities



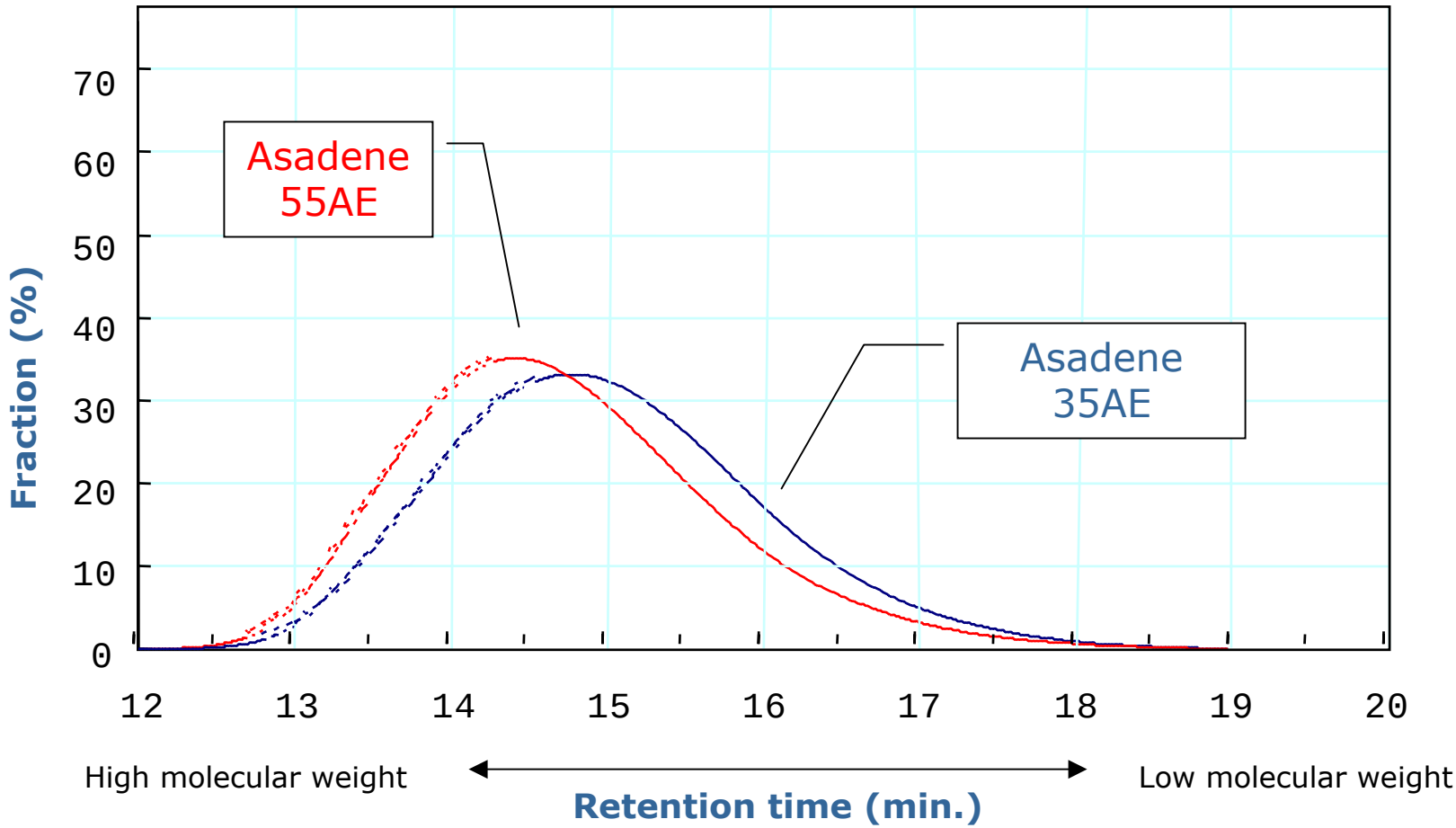
# Cold Flow of Asaprene, Asadene, Other Rubbers



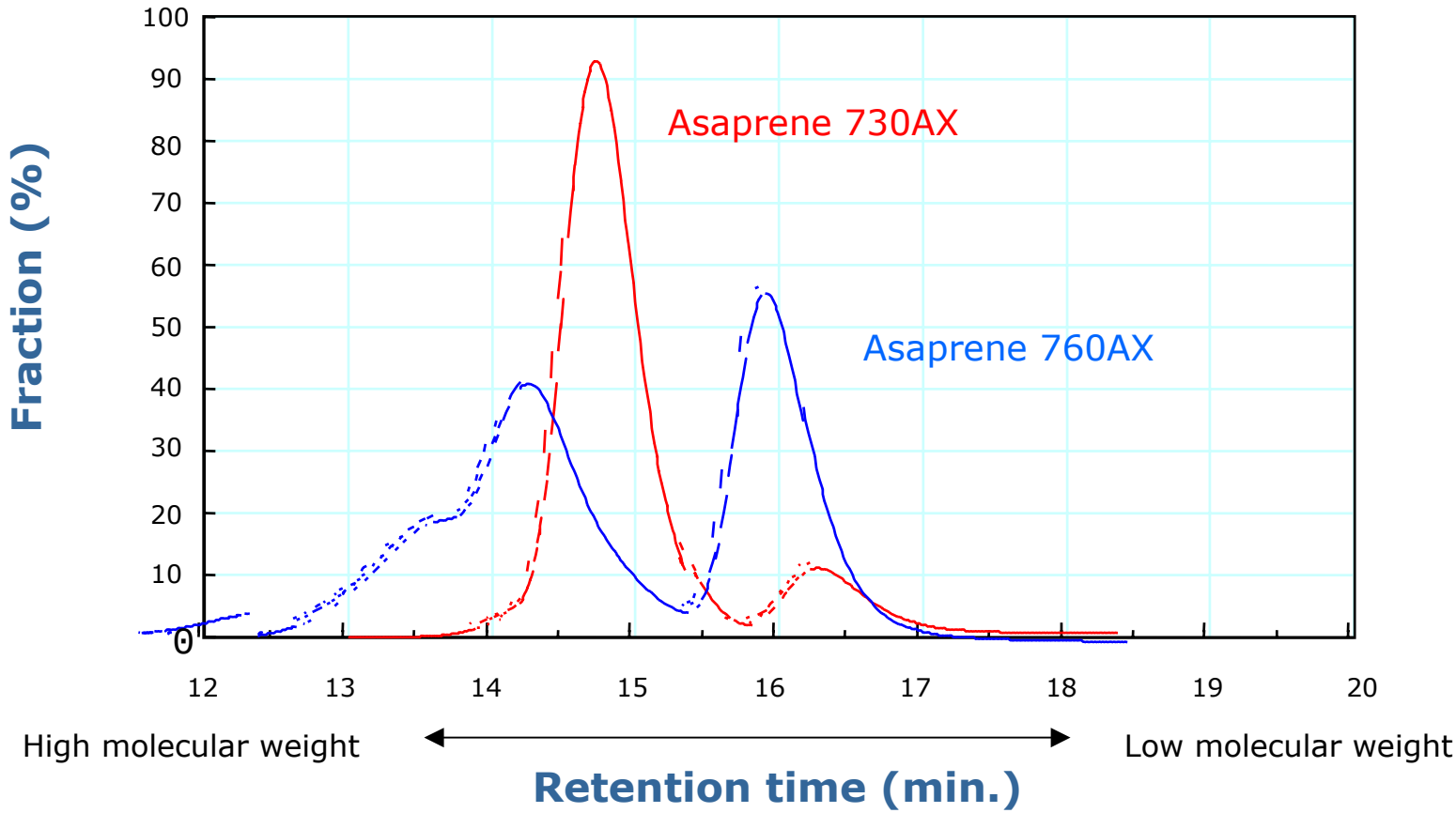
# Relationship between Solution Viscosity and Rubber Particle Size (Using Polybutadiene rubber)



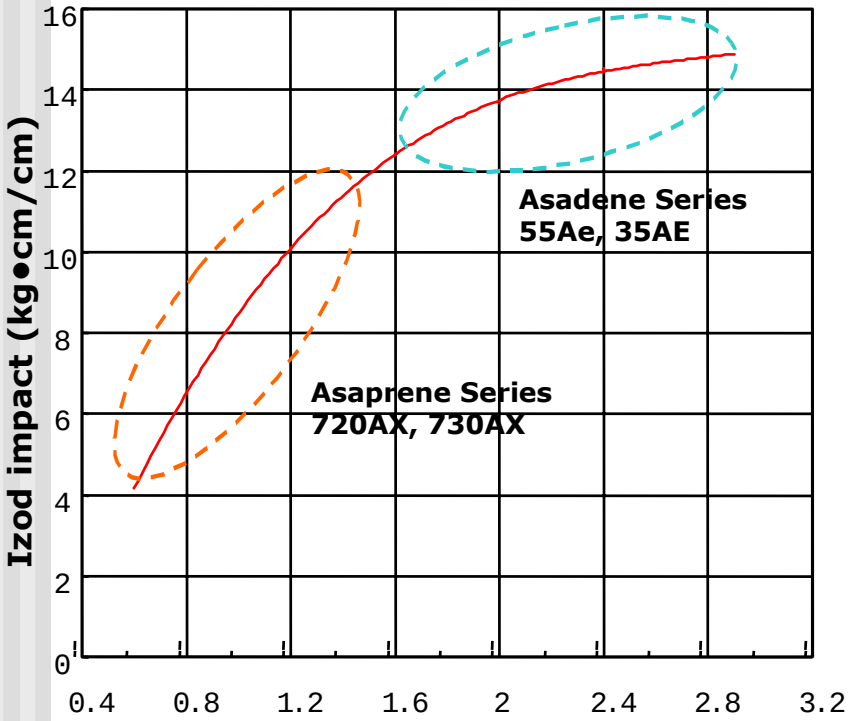
# Molecular Distribution of Weight for Asadene 55AE/35AE



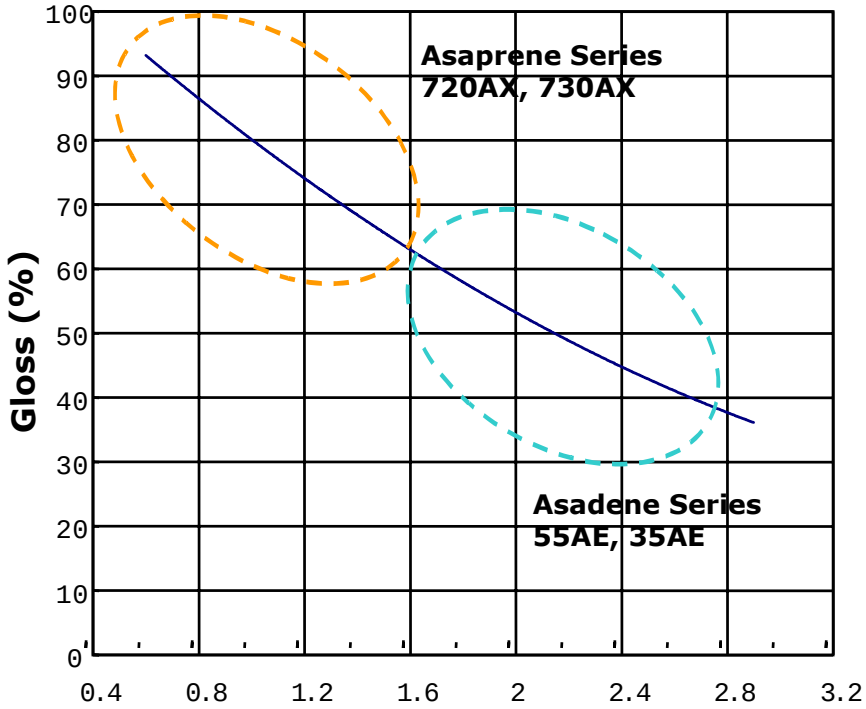
# Distribution of Molecular Weight in Asaprene Series



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




Rubber particle size (μm)



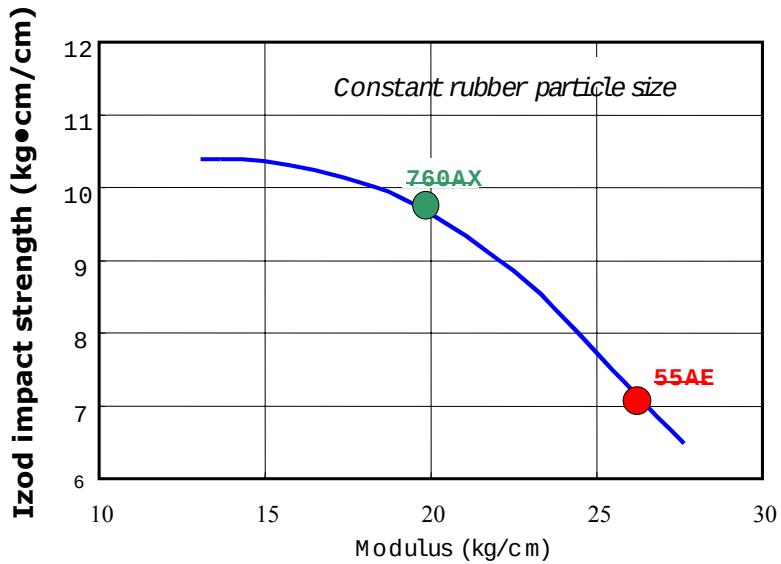

Rubber particle size (μm)

# Asaprene 760AX

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

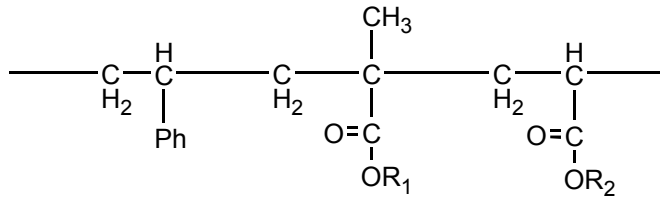
# Asaprene 760AX

- 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

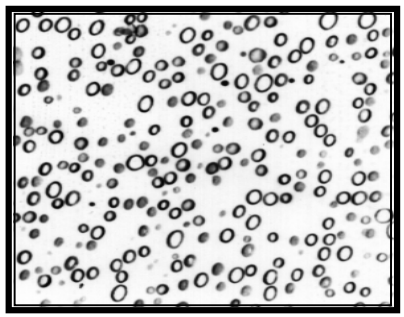



Styrene unit | Methacrylic ester unit | Acrylic ester unit

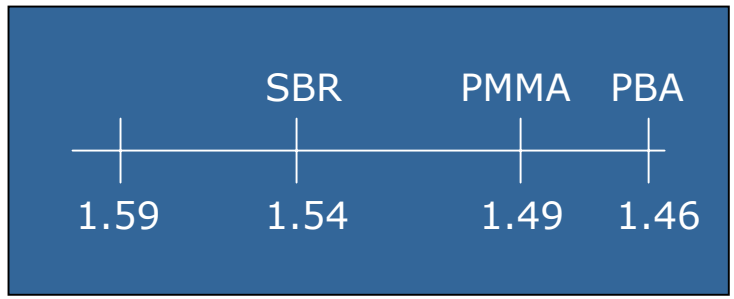
# Asaprene 670A (2)

- 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 polymeri-zation)

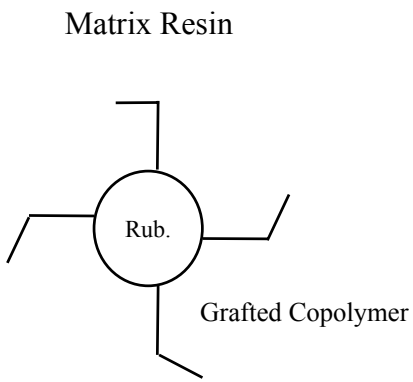


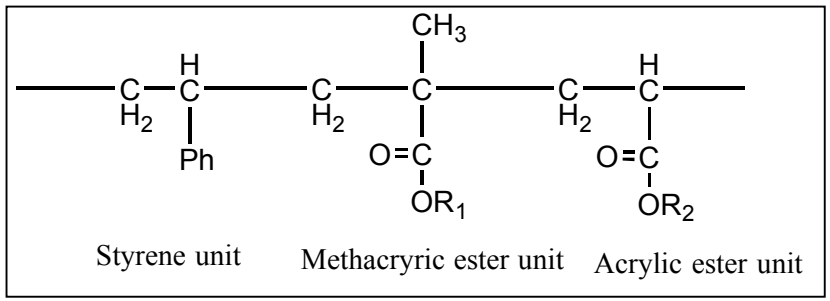
Refractive Index



# Asaprene 625A (1)

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

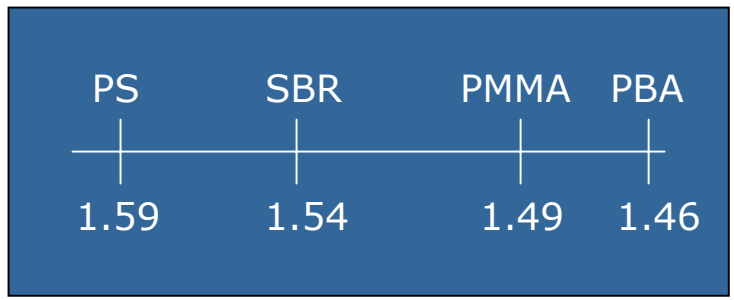


# Asaprene 625A (2)

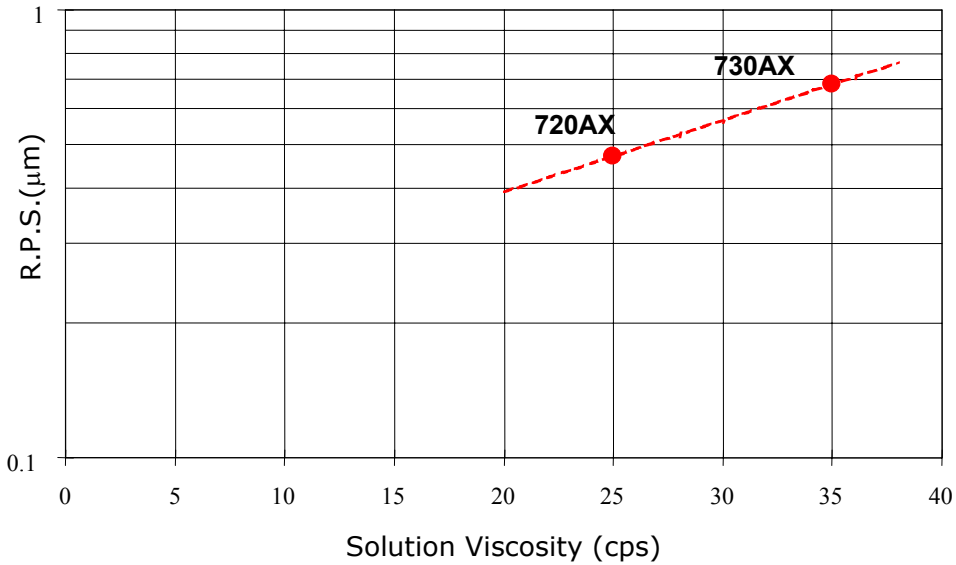
- Characteristics
  - Transparency HIPS are easily obtained compared with other styrene-butadiene block copolymers
  - Easier to handle:
    - Bale is
      - Easier to cut
      - Less likely to crack
      - Bites into cutter more easily

Refractive Index

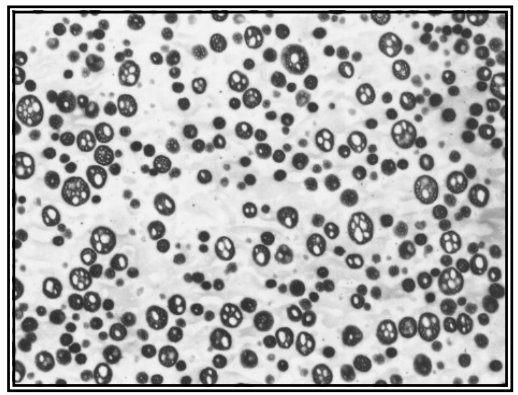


# Asaprene 720AX

- 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.**

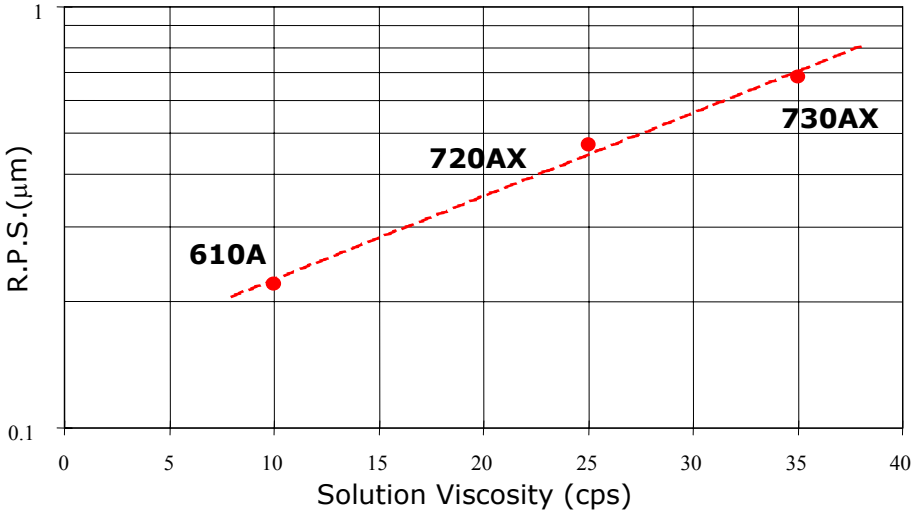


**Mass ABS with Asaprene720AX**

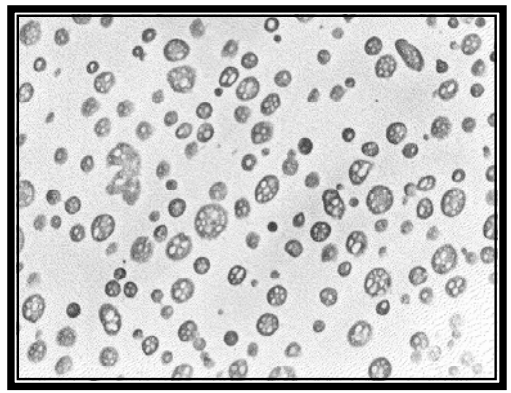
# Asaprene 610A

- 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



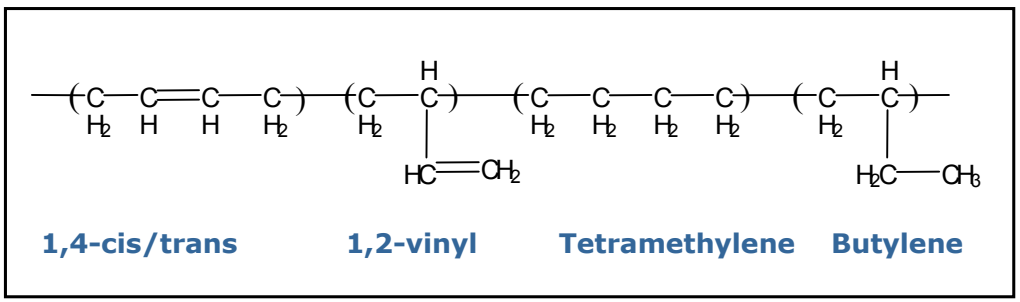

**Relationship between Solution viscosity and R.P.S.**



**Mass ABS with Asaprene 610A**

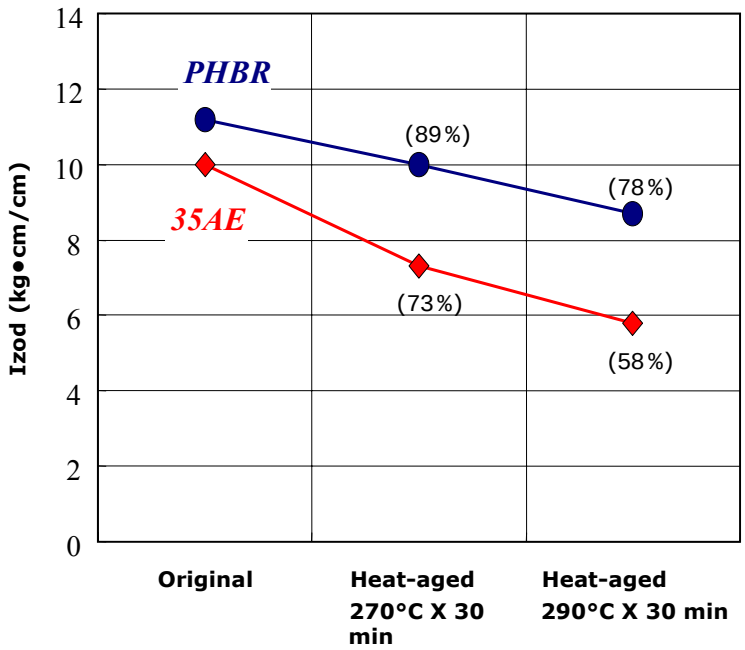
# H300A (1)

- 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



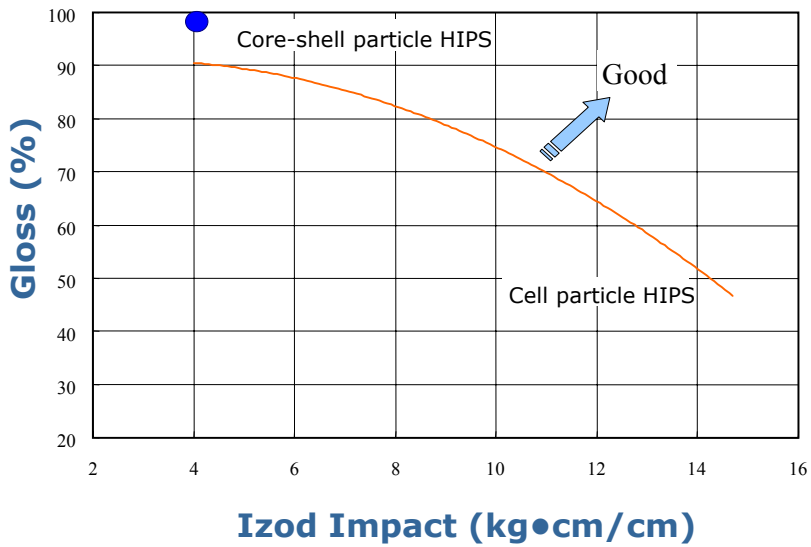
# H300A (2)

- 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



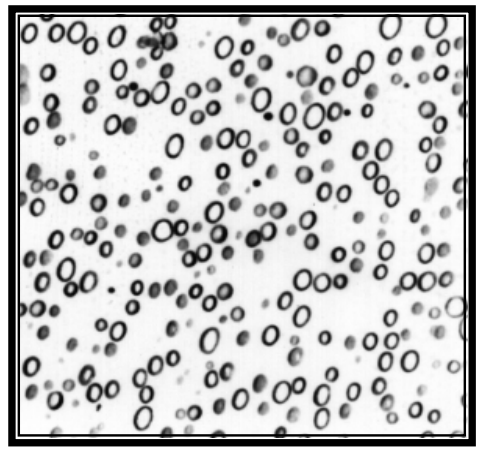
# Asaprene 630A (1)

- 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



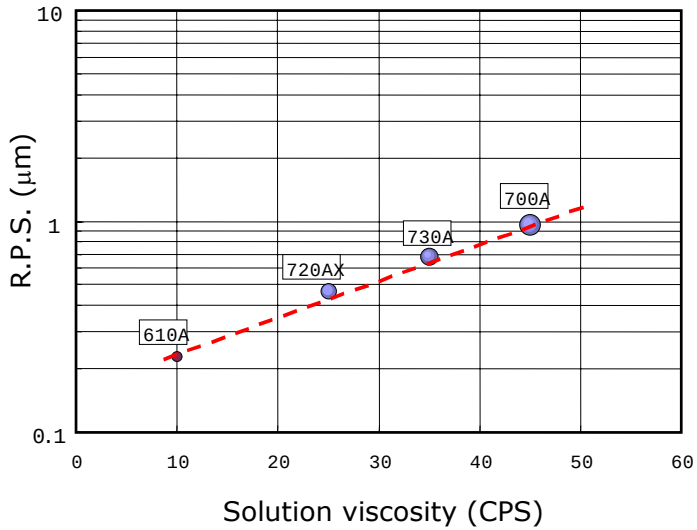
Core-shell particles

# Asaprene 610A, 720AX (1)

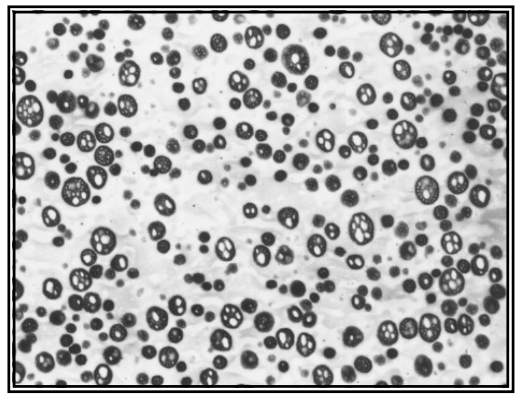
- Rubber used for mass ABS
- Molecular structure
  - 610A
    - Styrene-butadiene rubber (15% styrene)
    - Vinyl/cis/trans: 14/36/50
    - Solution viscosity: 10cps
  - 720AX
    - Polybutadiene rubber
    - Vinyl/cis/trans: 18/33/49
    - Solution viscosity: 25cps

# 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

- 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

**Thank you.**