

There will be a quiz on Friday

January 24, 2025



* From the Hitchhikers Guide to the Galaxy – Douglas Adams

EMAC 276 - Homework Assignment #1

Due: Friday January 24, 2024

Prof. Olah

We have spent some time on the Hierarchical Structure concept within several disciplines; i.e., biology, polymer science, mechanical engineering, management, etc.

Other than the examples we have provided in class, your assignment is to identify one additional example of the hierarchical structure concept.

In your description you must:

1. Identify the example and the discipline it involves.
2. Explain the number of hierarchical levels and the scale of each level.
3. Identify the relationship in your example of the three concepts of hierarchical structures:
 - a. Scale
 - b. Interaction
 - c. Architecture
4. Please keep your answer to one page.

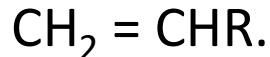
EMAC 276

Lesson 3: Polystyrene and Styrofoam

Andy Olah, Ph.D.
January 22, 2024

What is a “Vinyl” Type Polymer?

Vinyl polymers are the most common type of polymers derived from “vinyl-type” monomers having the general structure:



Where,

polystyrene – R = C₆H₅

polyvinyl chloride – R = Cl

polyvinyl acetate – R = O₂CCH₃

polyacrylonitrile - R = CN

Not to be confused with poly(vinyl chloride) (PVC) materials which have traditionally been identified as “vinyls”; i.e., vinyl siding, vinyl records, etc.

Olefin polymers are a subgroup of vinyl monomers produced from alkenes having a C_nH_{2n} monomer structure:

polyethylene – R = H => CH₂ = CH₂; (n = 2) => C₂H₄

polypropylene – R = CH₃ => CH₂ = CH-CH₃; (n = 3) => C₃H₆

polybutylene – R = CH₂-CH₃ => CH₂ = CH-CH₂-CH₃; (n=4) => C₄H₈

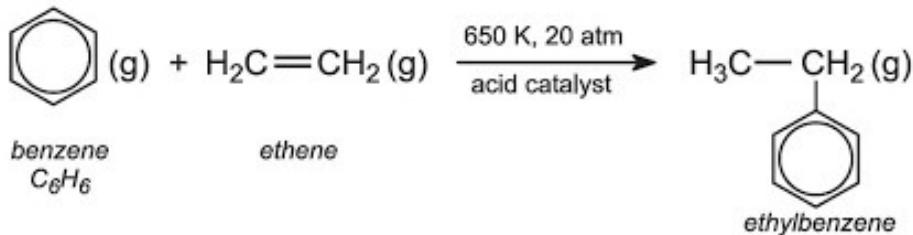
History of Polystyrene

- 1839 - Eduard Simon (Germany) – isolated styrene monomer (called Styrol) which developed into a thickened mass after several days.
- 1866 – Marcellin Berthelot (France) – recognized the formation of styrol to form a colloid-like material.
 - “One knows that styrene heated in a sealed vessel at 200°C, for several hours, it is changed into a resinous colloid (*polystyrene* ?), and that this colloid, [when] distilled abruptly, reproduces styrene.”
- 1926 – Hermann Staudinger (Germany) – identified a specific type of colloid as true macromolecules – i.e., polymers and in turn this materials was identified as polystyrene.
- 1931 – I.G. Farben/BASF (Germany) began manufacturing polystyrene.
- 1944 – Dow Chemical develops and patents a process to produce Styrofoam.
- 1952 – BASF produces and exhibits a process for expanded polystyrene beads.
- 1954 – Koppers Company and Dart Container develops a process for producing styrofoam cups.

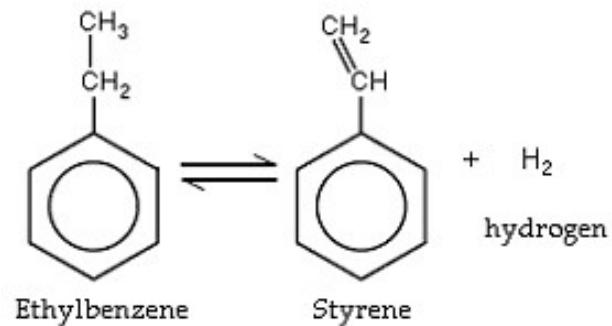
Synthesis of Styrene Monomer

Synthesis of Ethylbenzene with Aluminum Chloride

Reacts at ~380°C



Dehydrogenation to form Styrene



In current industrial practice **ethylbenzene dehydrogenation** is typically performed in a fixed-bed reactor in the **temperature** range 540–650 °C and uses potassium-promoted iron(III) oxide mixed with additional promoters to stabilize the morphology of the catalyst or avoid sintering.

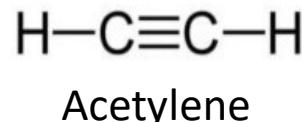
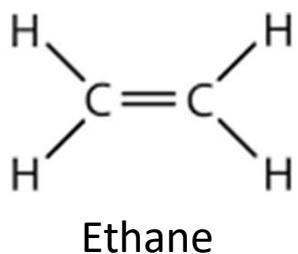
Does there exist a similar but alternative route without dehydrogenation?

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF
ROCHESTER.]

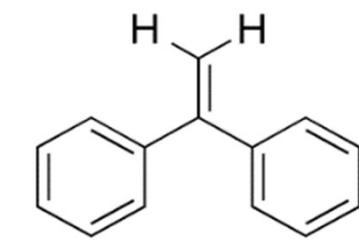
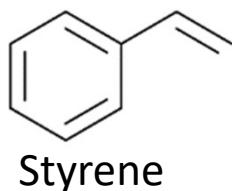
THE CONDENSATION OF ACETYLENE WITH BENZENE AND
ITS DERIVATIVES IN THE PRESENCE OF
ALUMINUM CHLORIDE.

By OTTO W. COOK AND VICTOR J. CHAMBERS.

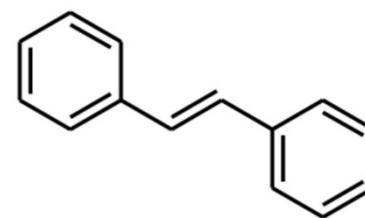
Received August 23, 1920.



The first and most important work on this condensation was that of Varet and Vienne.¹ They passed acetylene through a mixture of benzene and aluminum chloride, and reported the formation of a product containing 80% phenyl ethylene (styrene), 15% *unsym.* diphenylethane and 5% *sym.* diphenylethane (dibenzyl). Neither the actual amounts obtained, referred to the reacting materials, nor the conditions under which the runs were made, were stated.



1, 1 Diphenylethane



1, 2 Diphenylethane

¹ Varet and Vienne, *Compt. Rend.*, **164**, 1375 (1886)

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF
ROCHESTER.]

THE CONDENSATION OF ACETYLENE WITH BENZENE AND
ITS DERIVATIVES IN THE PRESENCE OF
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Received August 23, 1920.

I. Condensation with Benzene.

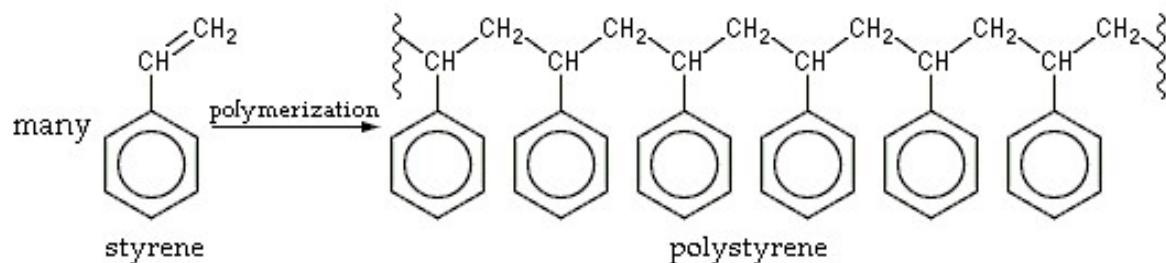
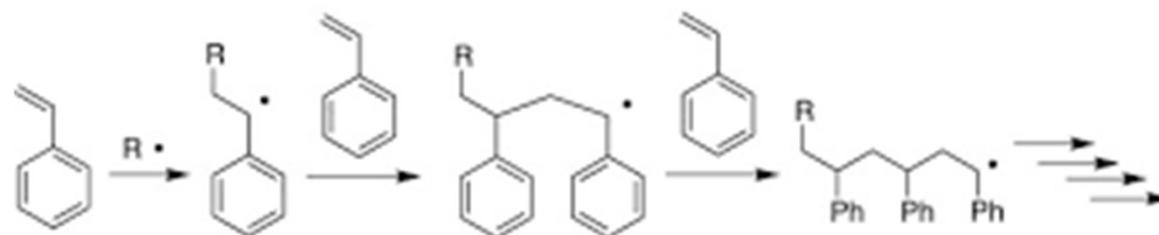
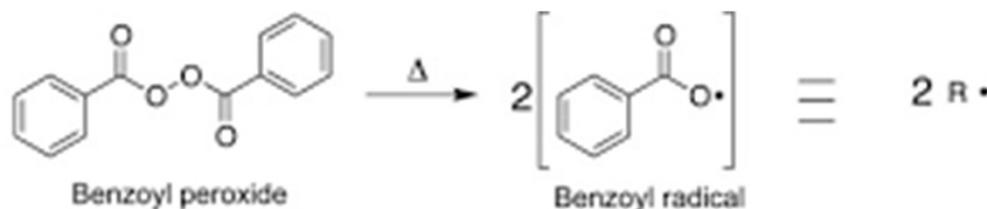
In the majority of these runs, the temperature was held within a few degrees' variation of a given point. When the mixture was left undisturbed, the temperature gradually rose to about 70° to 80° as the reaction proceeded, and, after about 3 hours, started to diminish. The condensation product consisted of a dirty yellow oil. When this oil was hydrolyzed and distilled with steam, it gave 2 volatile fractions and a black tarry residue.

The first fraction was unchanged benzene, together with some toluene and xylene, formed by the action of the aluminum chloride on benzene itself. A small portion of a material, b. p. 140–145°, was also obtained. This gave evidence of the presence of styrene, which, however, was not present in sufficient quantity to be isolated.

The second fraction, which came over very slowly (in from 4 to 6 hours), when dried, boiled at 280° to 290° and was identified as *unsym.* diphenylethane, b. p. 286°, by oxidation to benzophenone and the formation of benzophenone oxime, m. p. 140°.

The residue, dried and distilled, gave 2 principal fractions. One consisted of some diphenyl-ethane which had not come over with steam. The other fraction, which distilled above 360°, solidified, and, after several recrystallizations from alcohol, yielded long brown needles, m. p. 181°. On oxidation, it gave anthraquinone. It is therefore identified as the 9,10-dimethyl-anthracene hydride of Anschutz.¹ No dibenzyl could be found.

Free Radical Polymerization of Polystyrene



A **free radical** can be defined as any molecular species capable of independent existence that **contains an unpaired electron in an atomic orbital**. The presence of an unpaired electron results in certain common properties that are shared by most radicals. Many radicals are unstable and highly reactive. They can either donate an electron to or accept an electron from other molecules, therefore behaving as oxidants or reductants.

Peroxide Initiators for Free Radical Polymerization

| Initiator | Radical Generated |
|--|-------------------|
| Benzoyl peroxide (BPO) | |
| Di- <i>tert</i> -butyl peroxide (DTBP) | |
| Azobisisobutyronitrile (AIBN) | |

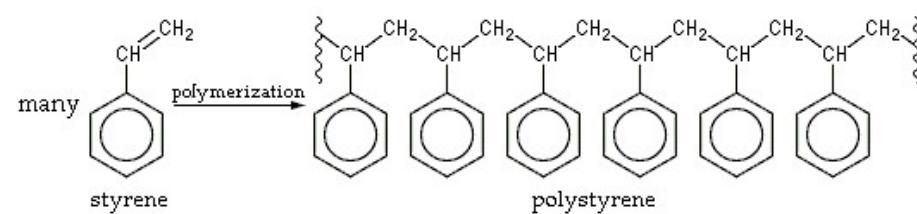


TABLE 3-12 Thermal Decomposition of Initiators^{a,b,c}

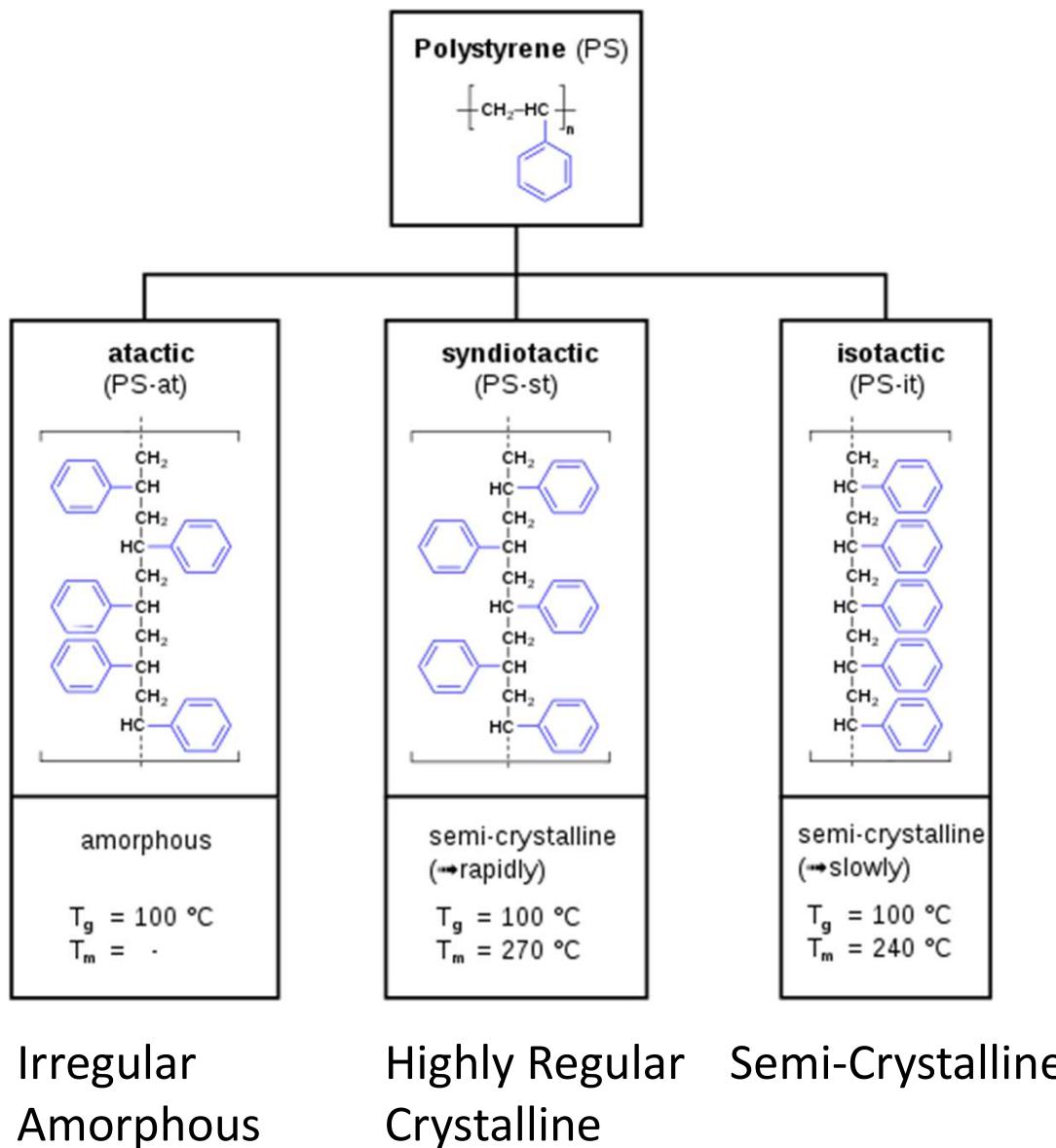
| Initiator | $k_d \times 10^5$ | T (°C) | E_d |
|-------------------------------|-------------------|--------|-------|
| 2,2'-Azobisisobutyronitrile | 0.845 | 60 | 123.4 |
| Acetyl peroxide | 2.39 | 70 | 136.0 |
| Benzoyl peroxide | 5.50 | 85 | 124.3 |
| Cumyl peroxide | 1.56 | 115 | 170.3 |
| <i>t</i> -Butyl peroxide | 3.00 | 130 | 146.9 |
| <i>t</i> -Butyl hydroperoxide | 0.429 | 155 | 170.7 |

^aAll data are for decompositions in benzene solution.

^bData from Brandrup and Immergut [1989].

^cThe units of k_d are sec⁻¹; the units of E_d are kJ/mole.

Atactic, Syndiotactic and Isotactic Polystyrene



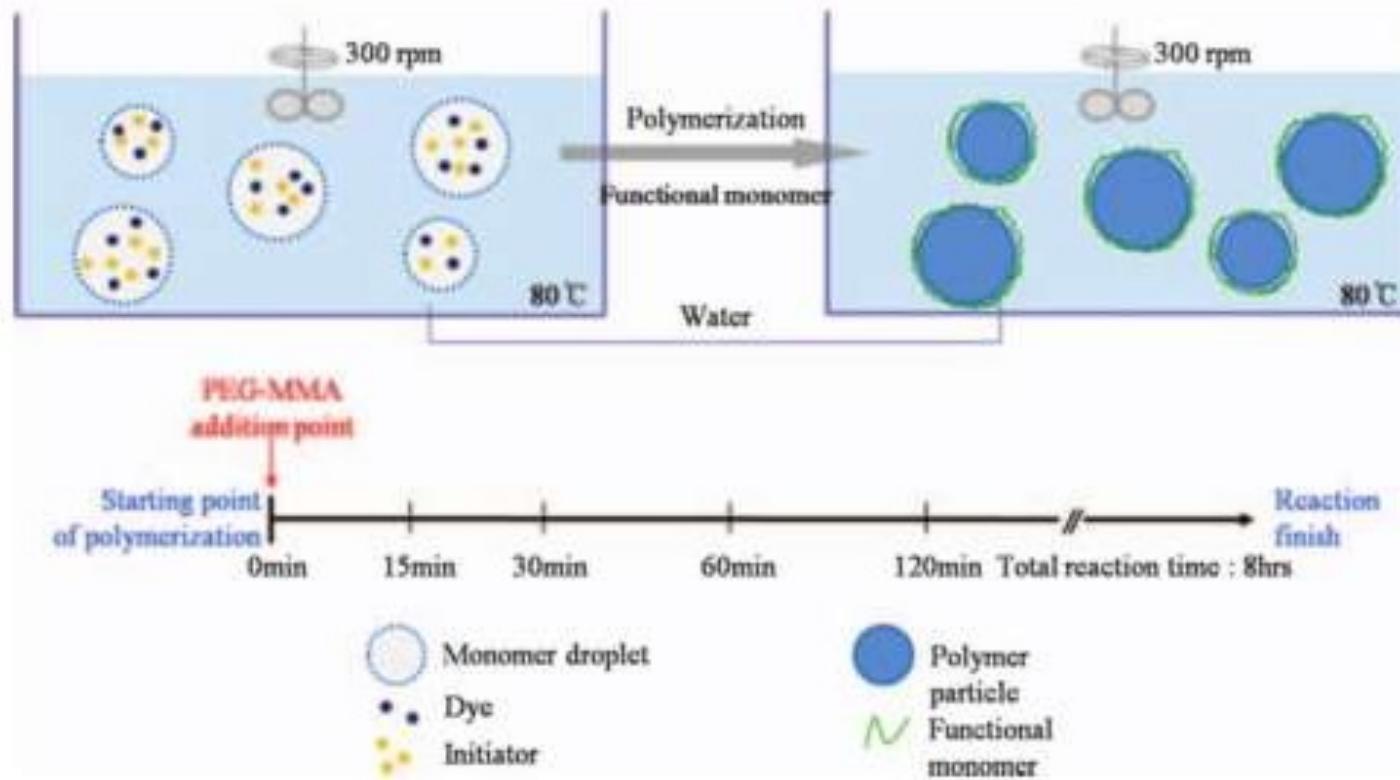


Figure 1. Schematic diagram of suspension polymerization of polystyrene and PEG-MA.

Polystyrene Suspension Polymerization

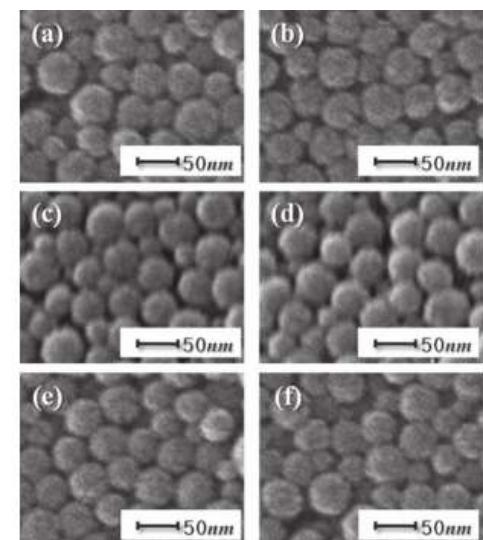
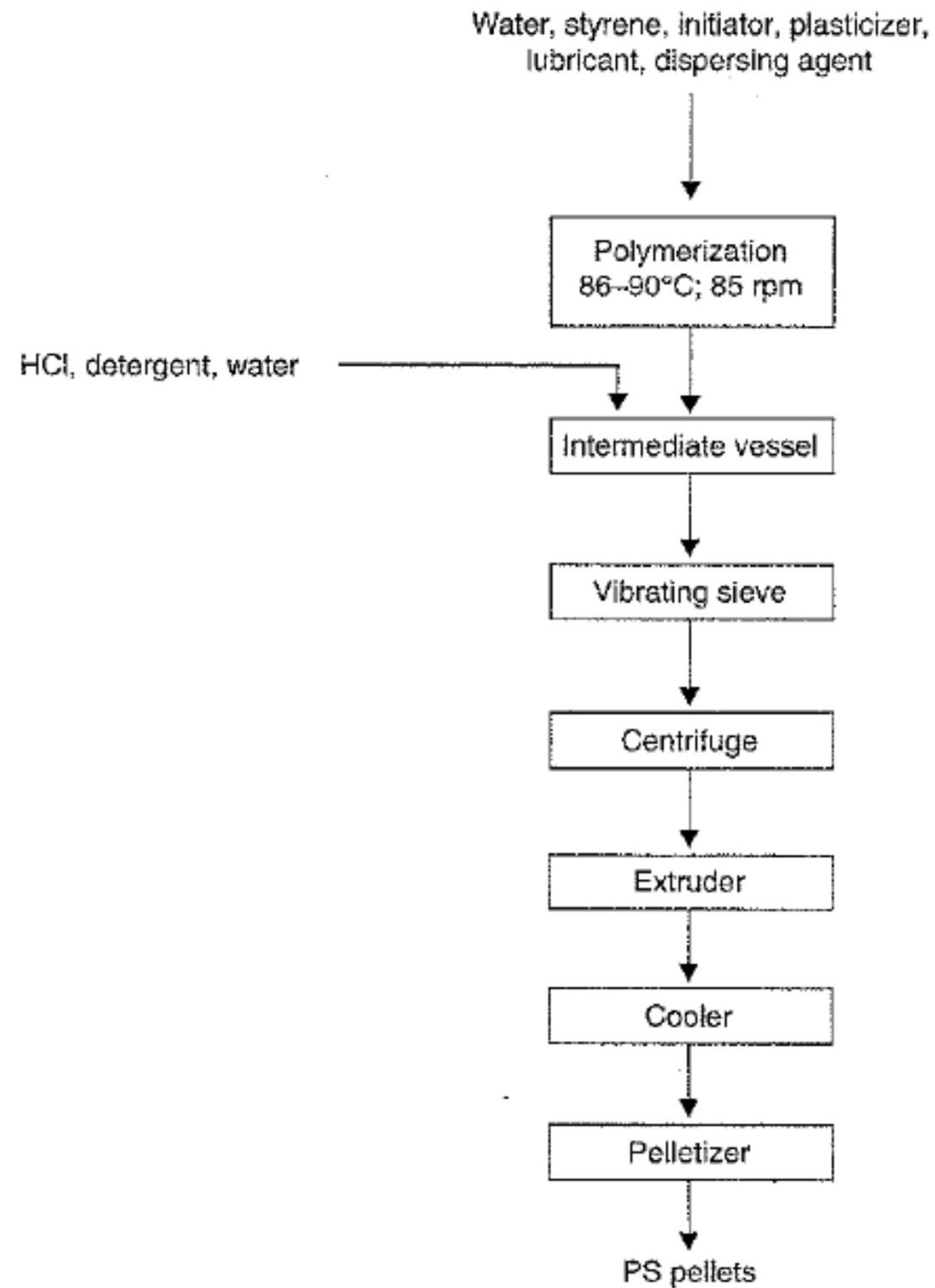


Figure 2. SEM images of (a) PS, (b) PM 300-1, (c) PM 300-5, (d) PM 300-9, (e) PM 475, (f) PM 950.

Flow Diagram for the Suspension Polymerization of Polystyrene



Polystyrene – Suspension Polymerization



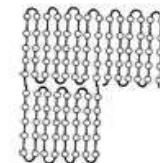
Raw polystyrene beads
from reactor/pelletizer.



Polystyrene is an Amorphous Polymer

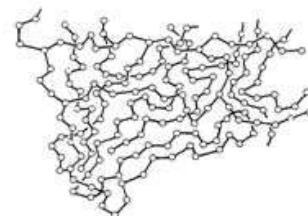
- ***Crystalline:***

- Periodic 3-D, repeating array of molecules



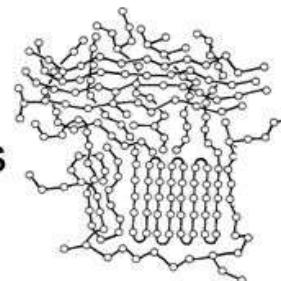
- ***Amorphous:***

- Literally “without structure”
 - No repeating array



- ***Semi-crystalline:***

- Structure containing regions of both crystalline and amorphous molecular arrangements



MOLECULAR MOTION IN POLYSTYRENE

Molecular Transitions In Atactic Polystyrene

(b)

$$T < T_g$$



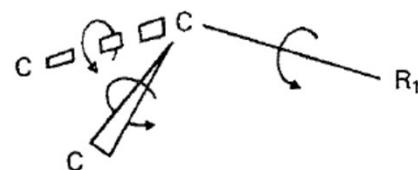
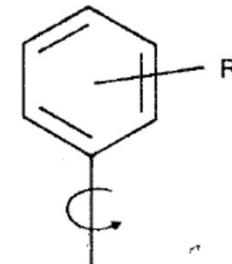
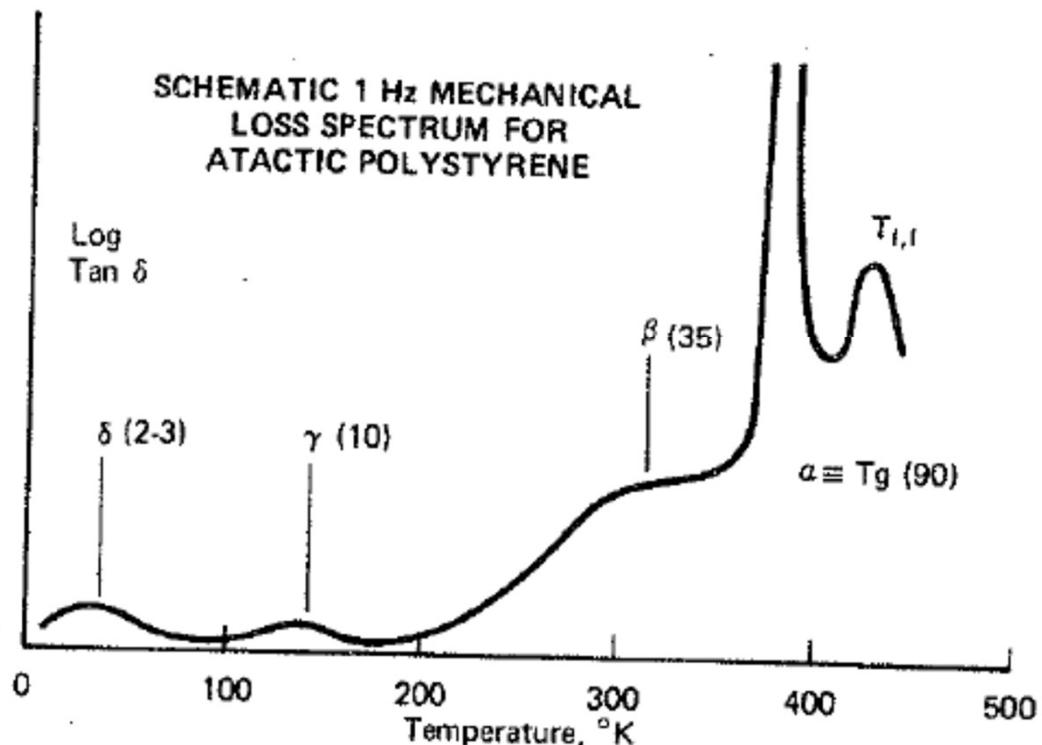
$$T > T_g$$



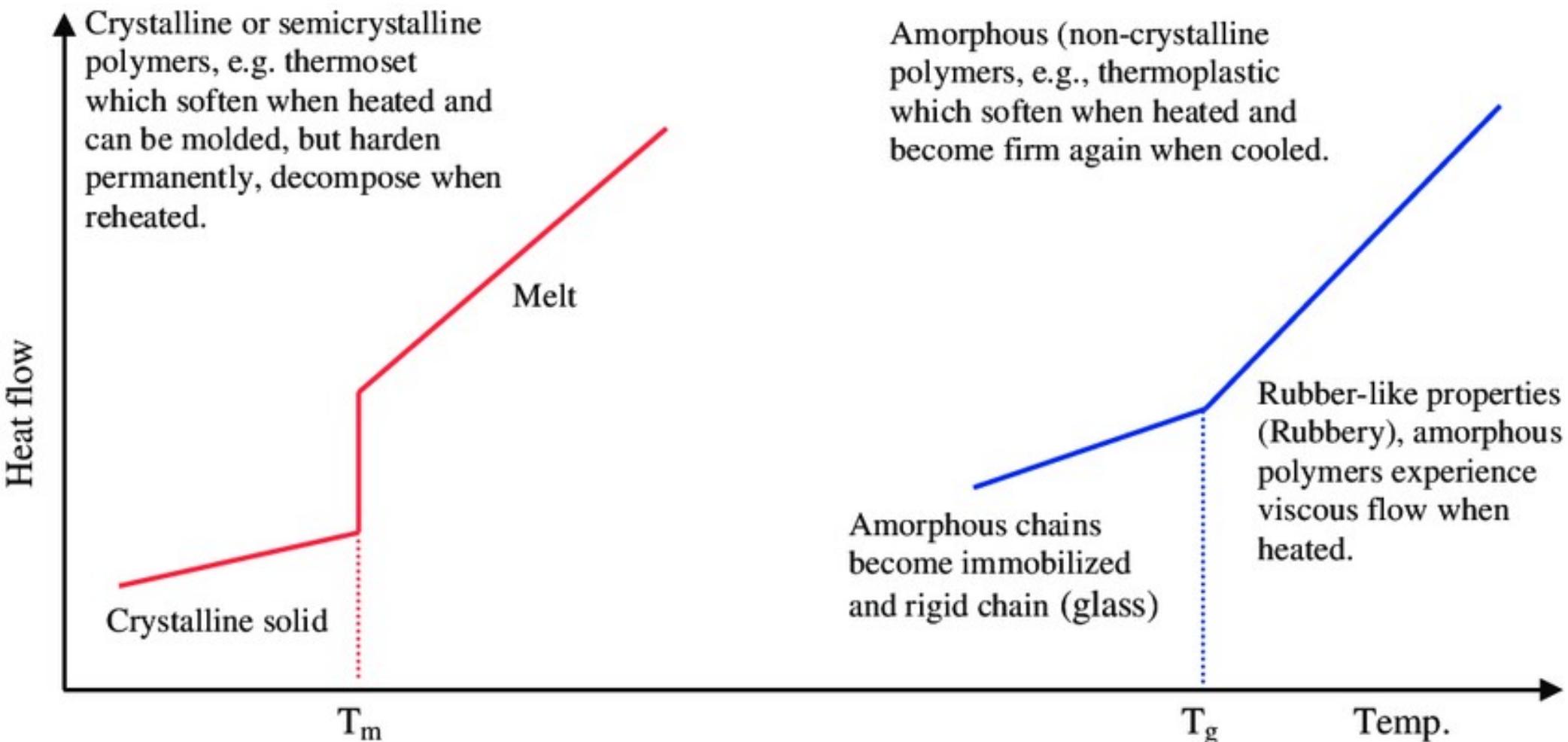
"frozen" backbone

crankshaft-like
chain motion

Tg the
Glass Transition Temperature



Heat Flow for Amorphous and Semi-Crystalline Polymers



T_g as a Function of Molecular Weight

The glass transition temperature of polystyrene is identified as ~100 C.

Table 1 The Molecular Weights and Molecular Weight Distributions of the PS Samples

| Sample | Mw | Mn | Mw/Mn |
|--------|--------|--------|-------|
| PS 1 | 1940 | 1690 | 1.15 |
| PS 2 | 4380 | 3570 | 1.23 |
| PS 3 | 5480 | 5200 | 1.04 |
| PS 4 | 12600 | 12000 | 1.05 |
| PS 5 | 35100 | 30500 | 1.15 |
| PS 6 | 65000 | 63700 | 1.02 |
| PS 7 | 275000 | 258000 | 1.07 |
| PS 8 | 950000 | 925000 | 1.03 |

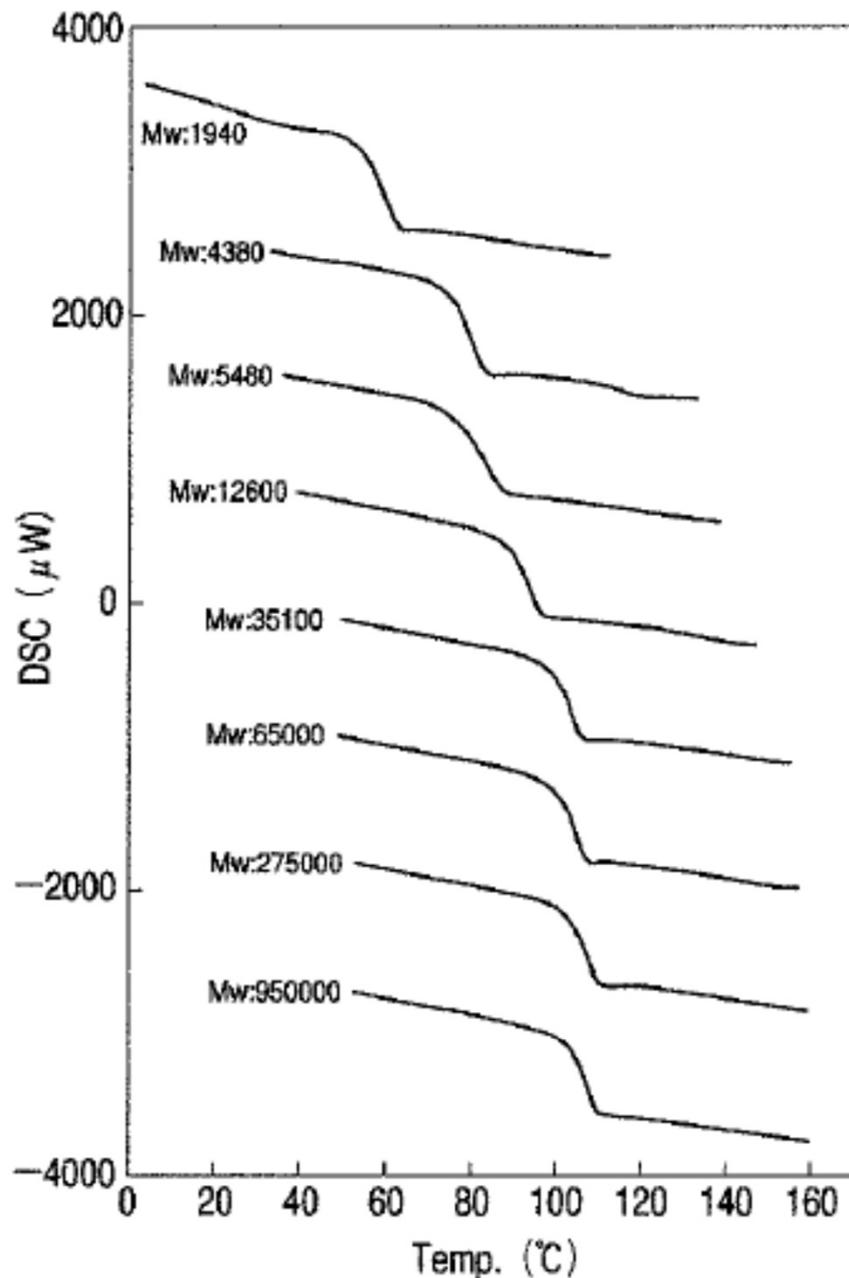


Figure 2 DSC Measurement Results for the PS Samples

Tg as a Function of Molecular Weight

Table 1 The Glass Transition Temperature (Tg) Measurement Results for the PS Samples

| Sample | Mw | Tg (°C) | | |
|--------|--------|-------------------|-------------------|-------------------|
| | | Tig ^{*1} | Tmg ^{*2} | Teg ^{*3} |
| PS 1 | 1940 | 56.8 | 60.4 | 64.2 |
| PS 2 | 4380 | 76.2 | 79.9 | 83.7 |
| PS 3 | 5480 | 77.0 | 82.4 | 87.8 |
| PS 4 | 12600 | 89.6 | 93.4 | 96.7 |
| PS 5 | 35100 | 100.2 | 103.1 | 105.9 |
| PS 6 | 65000 | 100.6 | 104.0 | 107.3 |
| PS 7 | 275000 | 103.5 | 106.4 | 109.4 |
| PS 8 | 950000 | 103.9 | 106.7 | 109.7 |

*1 Onset temperature of Tg

*2 Mid-point temperature of Tg

*3 End temperature of Tg

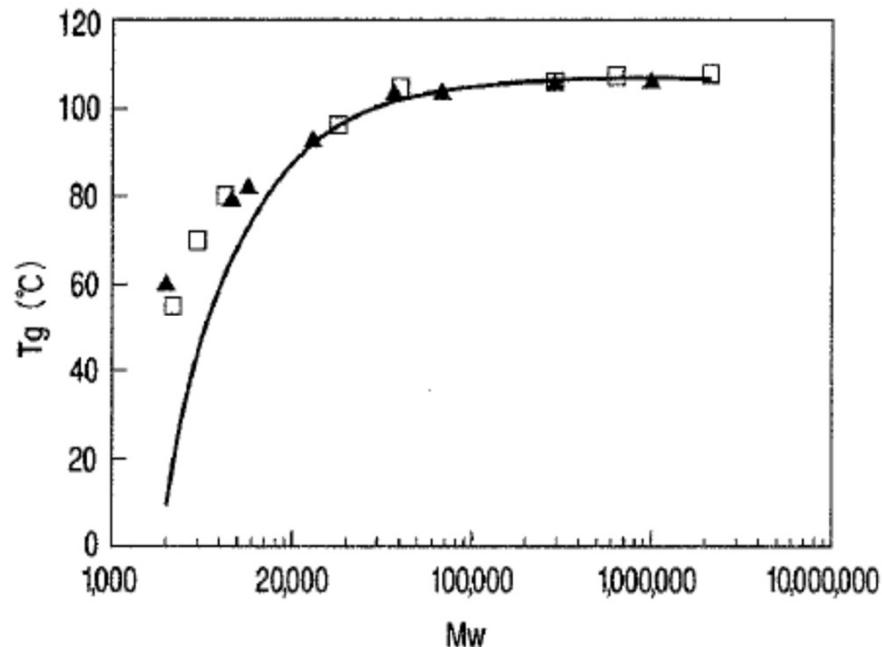
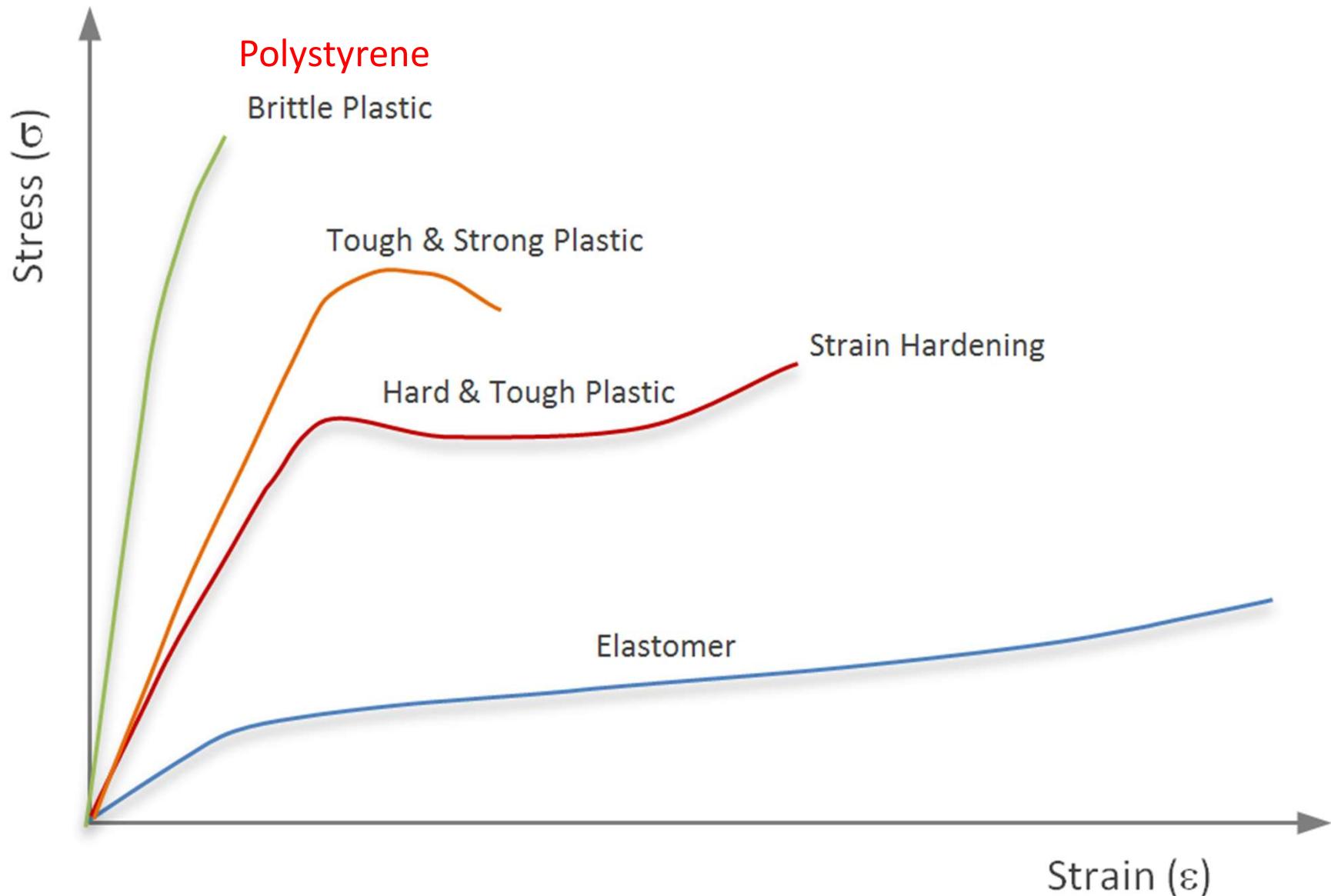


Figure 3 Dependence of Glass Transition Temperature on Molecular Weight
▲ Measurement results from this experiment (Figure 2 and Table 2)
□ Measurement results of P.Claudy et al.
— Results calculated from the theoretical formula of T.G.Fox et al.

Unmodified Polystyrene is a Very Brittle Material



Patented Oct. 5, 1948

US 2,450,436

UNITED STATES PATENT OFFICE

MANUFACTURE OF CELLULAR THERMOPLASTIC PRODUCTS

Otis Ray McIntire, Midland, Mich

assignor to

The Dow Chemical Company, Midland,
a corporation of Delaware

Application July 28, 1947, Serial No. 763,989

12 Claims. (Cl 18-48).

This invention concerns an improved method for the manufacture of cellular thermoplastic products. It pertains especially to the production of such products in the form of substantially uniform cellular masses of considerable size, e.g., of 2 inches, or greater, thickness or diameter, from the resinous benzene-soluble polymers and copolymers of nonovinyl aromatic compounds having the vinyl group attached directly to a carbon atom of the aromatic nucleus, particularly styrene.



Overcoming the Brittle Deficiency of PS

- **Ray McIntire: Styrofoam Inventor**
- Dow Chemical Company scientist **Ray McIntire** invented foamed polystyrene aka Styrofoam. McIntire said his invention of foamed polystyrene was purely accidental. His invention came about as he was trying to find a flexible electrical insulator around the time of World War II.
- Polystyrene, which already had been invented, was a good insulator but too brittle. McIntire tried to make a new rubber-like polymer by combining styrene with a volatile liquid called isobutylene under pressure. The result was a foam polystyrene with bubbles and was 30 times lighter than regular polystyrene. The Dow Chemical Company introduced Styrofoam products to the United States in 1954.

UNITED STATES PATENT OFFICE

MANUFACTURE OF CELLULAR THERMOPLASTIC PRODUCTS

Otis Ray McIntire, Midland, Mich

1. In a method for the production of a substantially uniform solid cellular thermoplastic article which is composed of individual closed cells having thin walls of a solid thermoplastic polymer, the smallest linear dimension of which article is at least 2 inches, the steps which consist in charging a vessel with a solid thermoplastic polymer, also introducing into the vessel a normally gaseous agent capable of being dissolved by the polymer so that the polymer and the normally gaseous agent are in contact with one another, subjecting the mixture to supers-atmospheric pressure while at a temperature within the range of from room temperature to below the critical temperature of said agent for a time sufficient to form a gel of the polymer, which gel is capable of flowing, the normally gaseous agent having been introduced and dissolved in the polymer gel in amount such as to be vaporized substantially completely upon release of the pressure with resultant swelling and cooling, due principally to the heat of vaporization of said agent, of the polymer to form a cellular mass which, when formed, is at a temperature within the range of between -30° C. and ten degrees above the heat distortion temperature of the polymer, and opening an outlet, having an aperture of minimum cross sectional area corresponding to that of a circle of at least three fourths inch diameter, near the bottom of the vessel so as to cause the gel to flow from the vessel and form the cellular product.
10. The method, as described in claim 7, where in the polymer is one selected from the class consisting of the thermoplastic polymers of mono vinyl-aromatic compounds and thermoplastic copolymers of monovinyl-aromatic compounds, and the normally gaseous agent is composed for the most part of at least one olefin having from three to four carbon atoms in the molecule.
11. The method described in claim 7 wherein the polymer is polystyrene.

Extruded Polystyrene Foam - XPS

Styrofoam is a trademarked brand owned and manufactured by The Dow Chemical Company comprising closed cell extruded polystyrene foam (XPS), commonly called *Blue Board*. This material is used as foam building insulation board used in walls, roofs, and foundations for thermal insulation and water barrier.



Patented June 15, 1954

US 2,681,321

UNITED STATES PATENT OFFICE

PRODUCTION OF POROUS MATERIALS FROM FILM-FORMING ORGANIC THERMOPLASTIC MASSES

Fritz Stastny, Weinheim (Bergstrasse), and
Rudolf Gaeth, Ludwigshafen (Rhine), Germany,
assignors to Badische Arilin- & Soda
RFhaibnrei,k GAekrtmeanngeysellschaft, Ludwigshafen
No Drawing. Application February 24, 1951,
Serial No. 212,66
Claims priority, application Germany
February 27, 1950
12 Claims. (C. 260-2.5)

12. A process for the production of porous polystyrene which comprises homogeneously dispersing in monostyrene a non-reactive volatile organic liquid in which polystyrene is insoluble, polymerizing this mixture at temperatures below the boiling point of the liquid under the conditions employed, and heating the resulting mass to a temperature above the boiling point of the liquid and above the Softening point but not more than about a few degrees above the softening point of the resulting polystyrene by contacting said mass with hot water, the relative proportions of mono-styrene and said liquid employed being such that the polymerization product is a solid body containing the liquid dispersed throughout.

Patented August 23, 1960

US 2,950,261

UNITED STATES PATENT OFFICE

PROCESS OF MAKING EXPANSIBLE PARTICULATE STYRENE POLYMER BY DIFFUSION OF A VOLATILE LIQUID HYDROCARBON INTO SAID POLYMER PARTICLES

Kari Buchholz, Ludwigshafen (Rhine), Fritz Siaastny, Weinheim, Bergstrasse,
and Rudolf Gaeth, Ludwigshafen (Rhine), Germany,
assignors to Badische Anilin & Soda-Fabrik Aktiengesellschaft, Ludwigshafen (Rhine), Germany
No Drawing. Filed Sept. 8, 1954, Ser. No. 454,848

Claims priority, application Germany Sept. 25, 1953

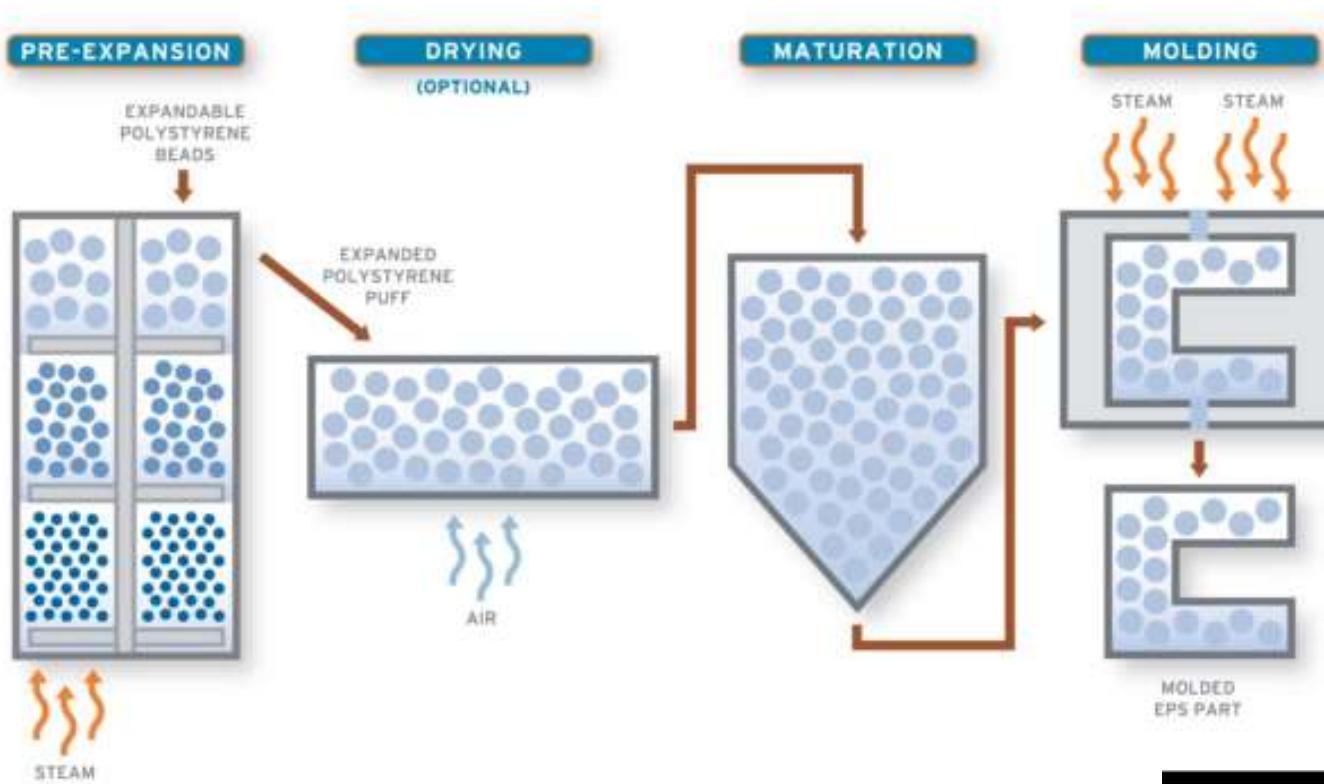
7 Claims. (C. 260-2.5)

1. In a process for the production of an **expansible particulate styrene polymer by diffusing a volatile liquid hydrocarbon into fine particles of a styrene polymer**, wherein said hydrocarbon is selected from the class consisting of aliphatic and cycloaliphatic hydrocarbons in which said polymer is insoluble and boiling below the softening point of said polymer, the improvement which comprises contacting said polymer particles in a closed vessel with a diffusion mixture in which said polymer is insoluble and consisting essentially of a major proportion of water and a minor proportion of said hydrocarbon, and maintaining said particles and said mixture in contact at a temperature above 40° C. and below the softening point of said polymer to diffuse said hydrocarbon into said particles.

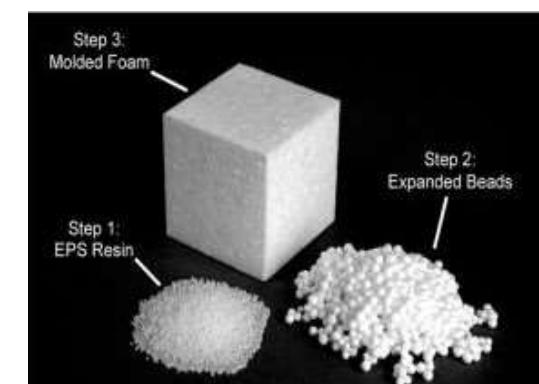
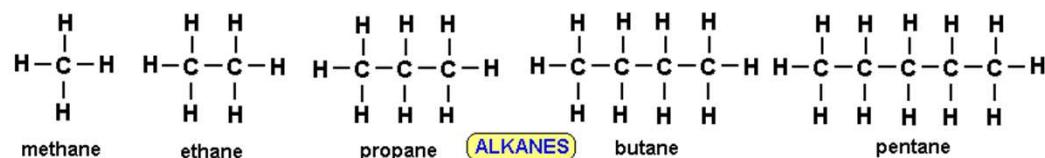
Expanded Polystyrene - EPS

Manufacturing

Expanded Polystyrene (EPS) - Manufacturing Process



Blowing Agents for Expanded Polystyrene (EPS)



Difference Between Extrudable Polystyrene Foam (XPS) and Expandable Polystyrene Foam (EPS)



XPS



EPS

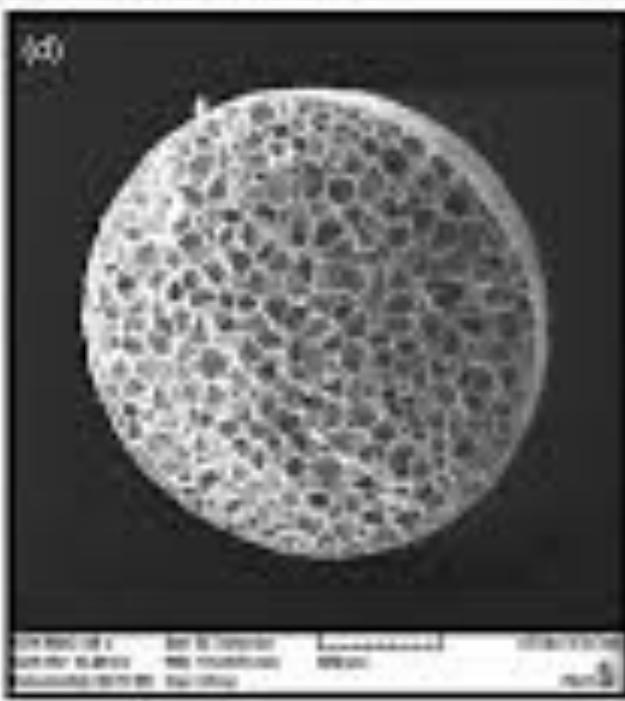
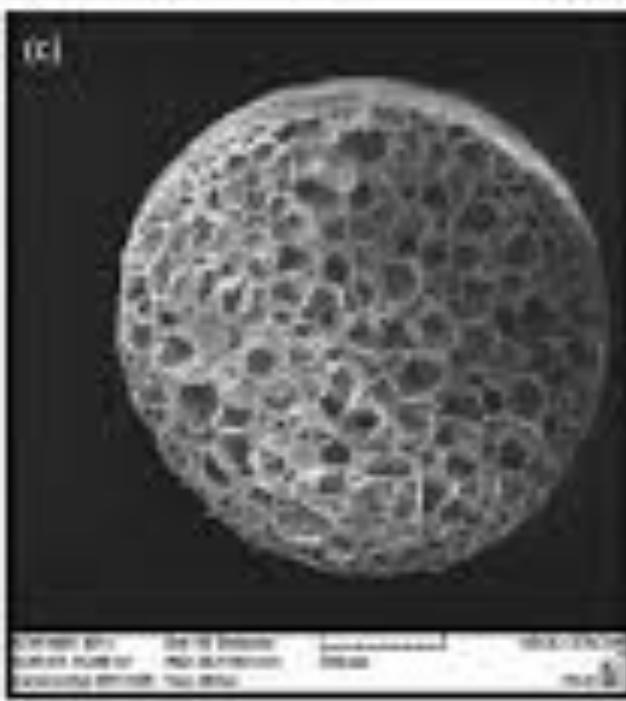
Expanded Polystyrene Foam - EPS

In the United States and Canada, the colloquial use of the word *styrofoam* refers to another material that is usually white in color and **expanded (not extruded)** polystyrene foam (EPS). It is commonly used in food containers, coffee cups, and as cushioning material in packaging.

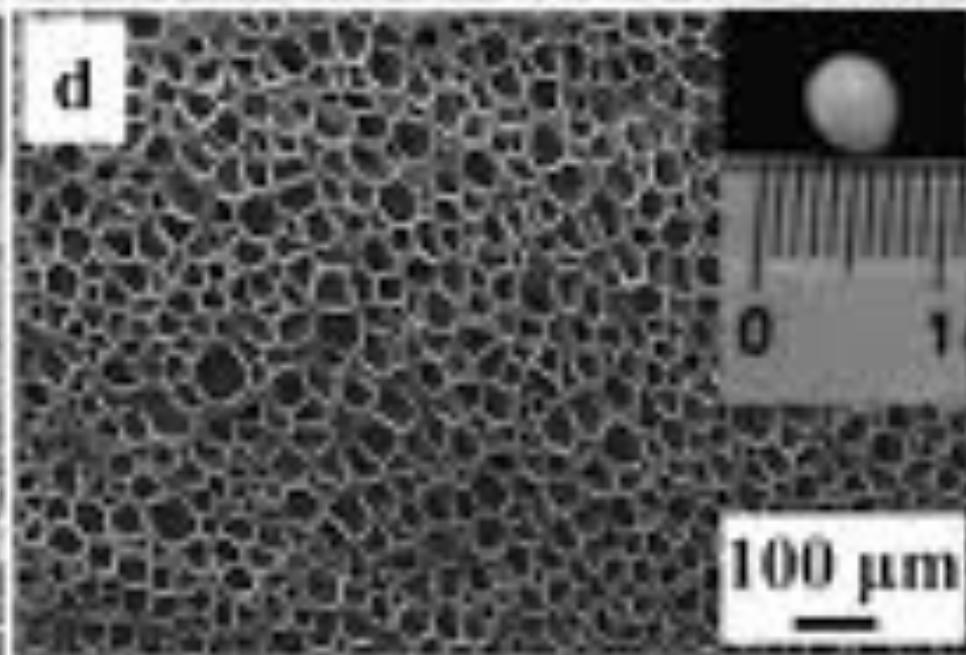
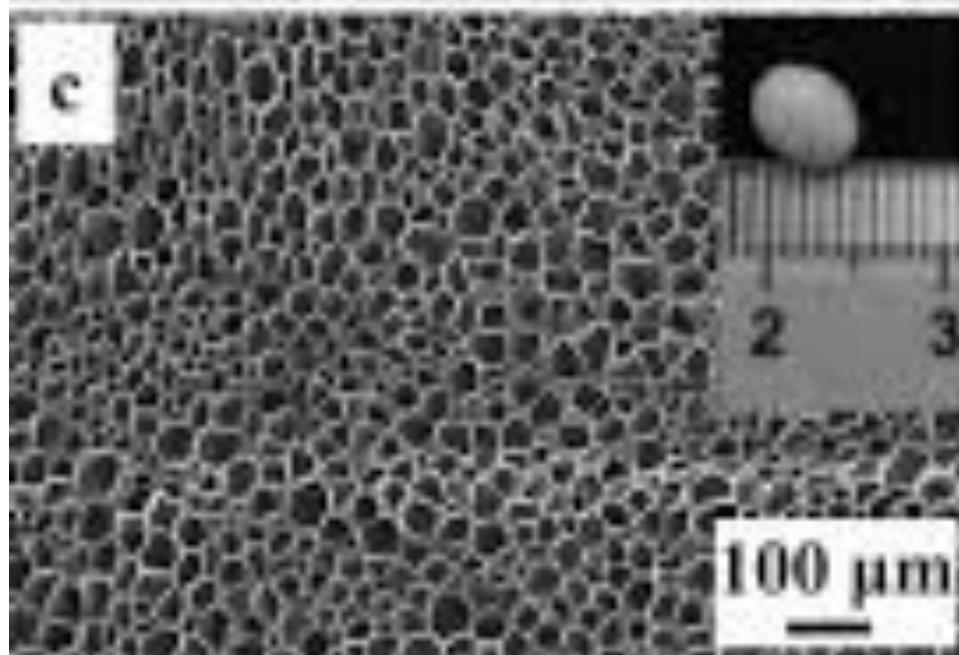
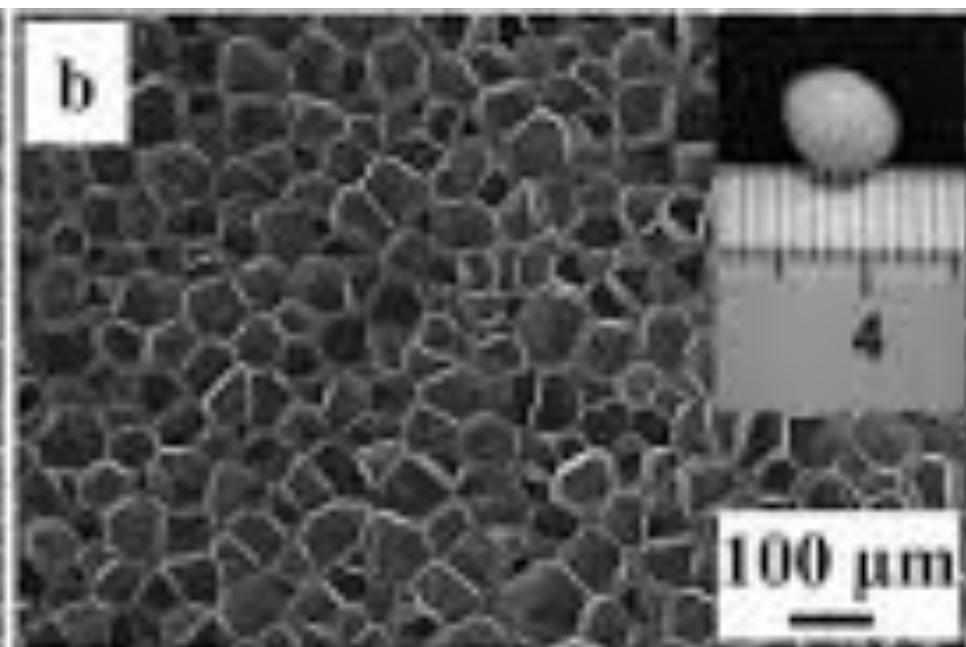
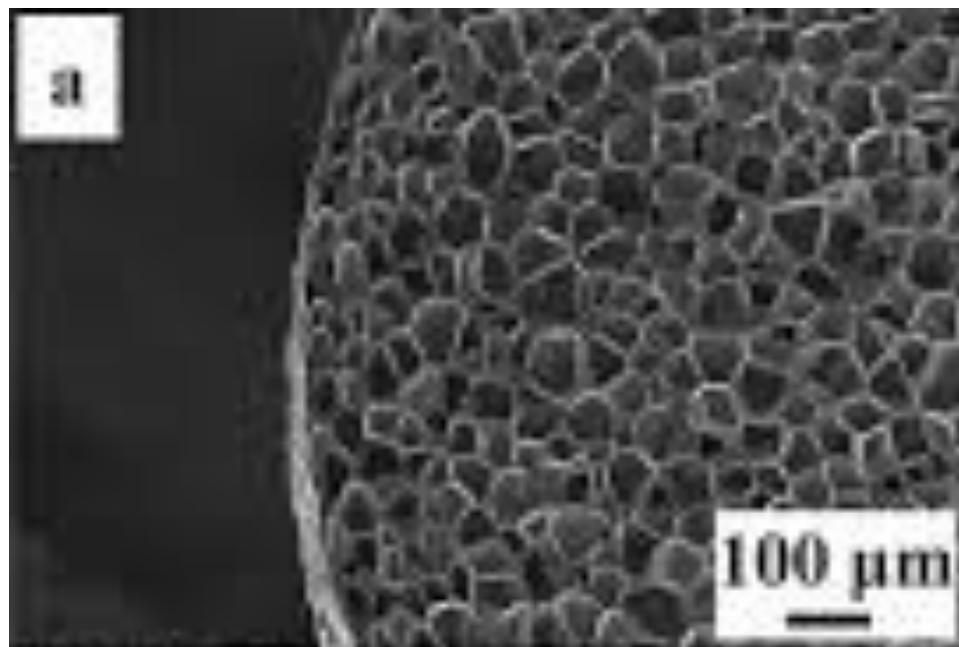
Therefore, the trademarked term **Styrofoam** is different from the generic term *styrofoam*.



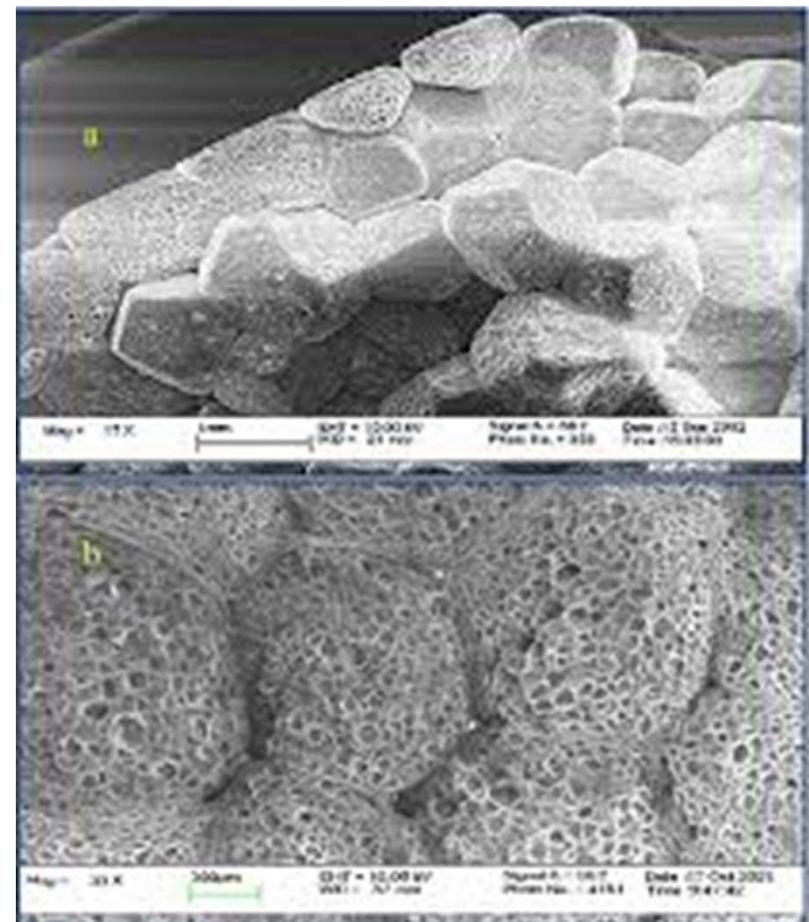
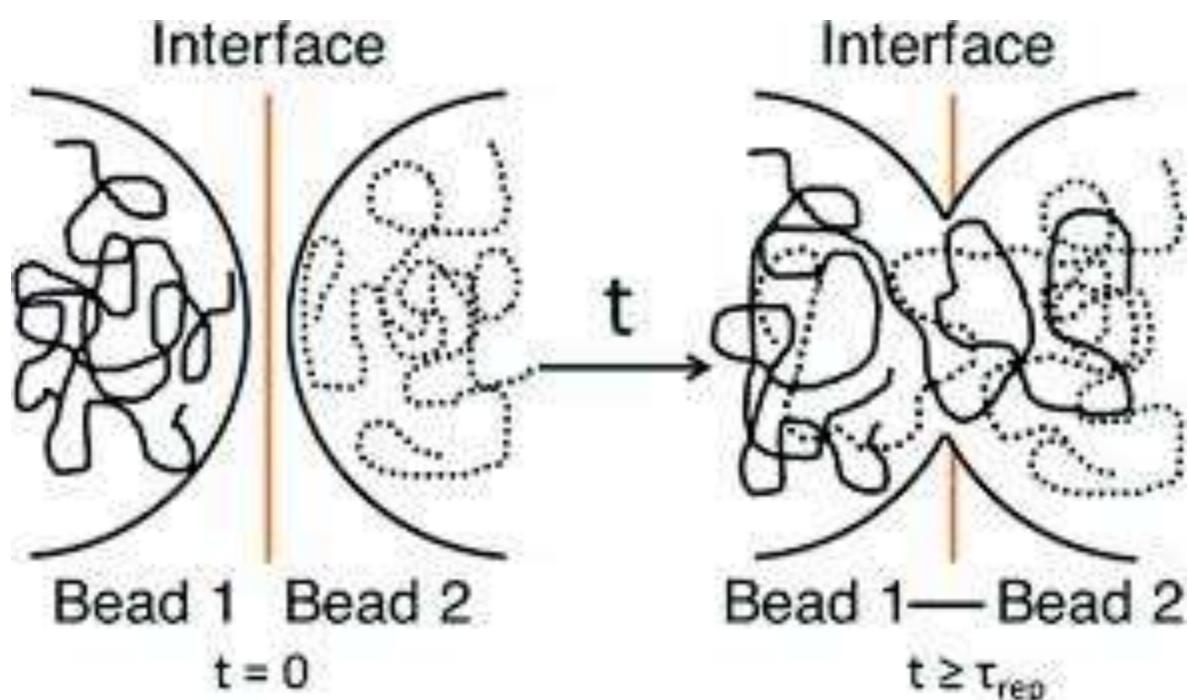
EPS Morphology before Molding



Cell Morphology of EPS



Molding of EPS



Morphology of EPS after Molding

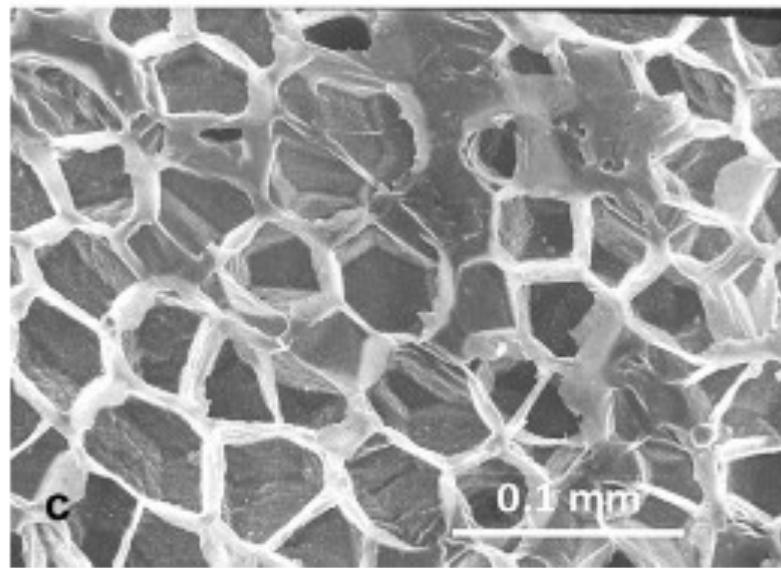
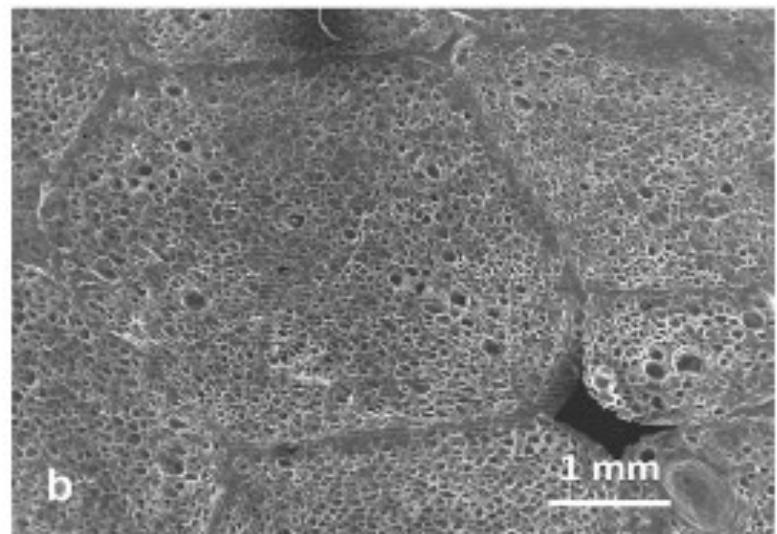
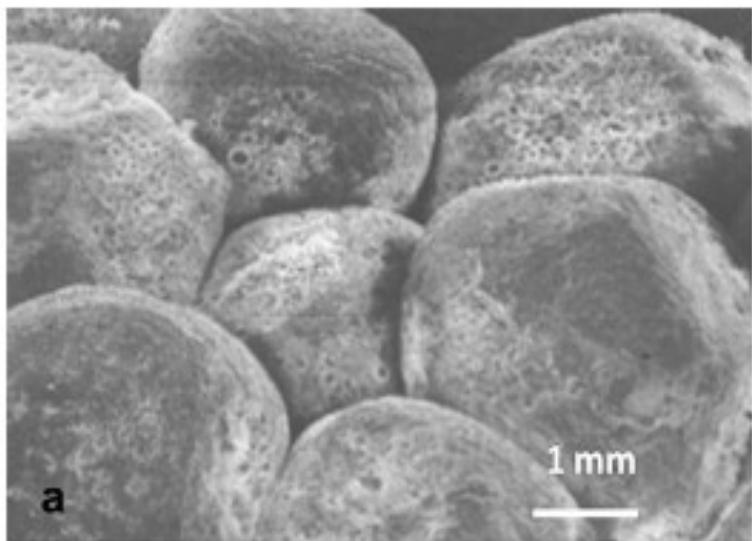
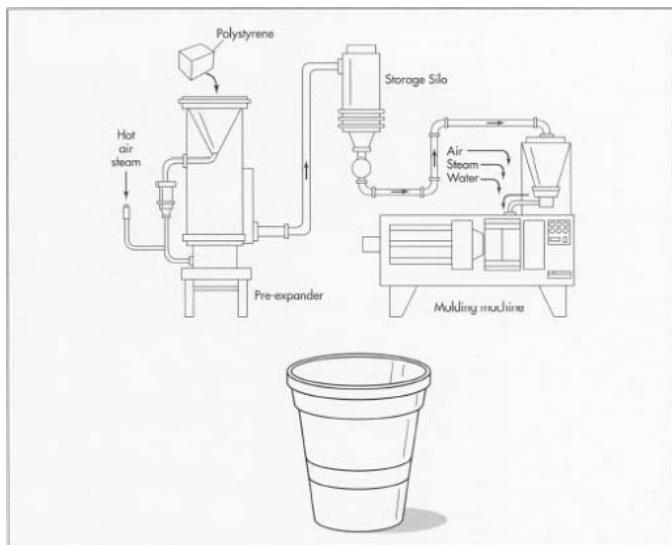


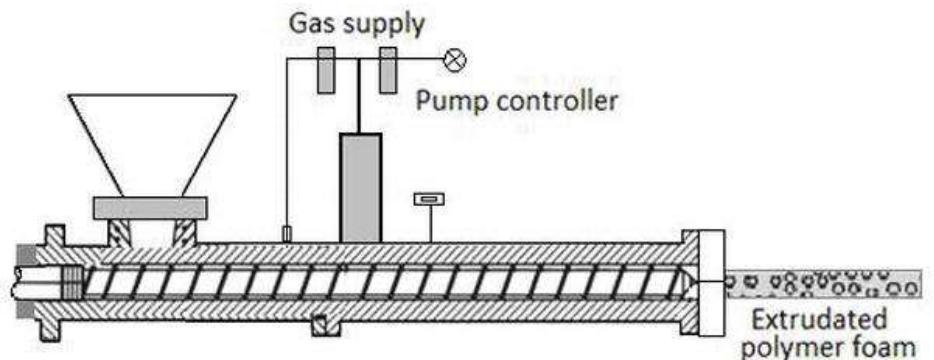
Fig. 1. Internal structure of expanded polystyrene. a) beads, b) beads and closed cells, c) closed cells.

EPS vs XPS

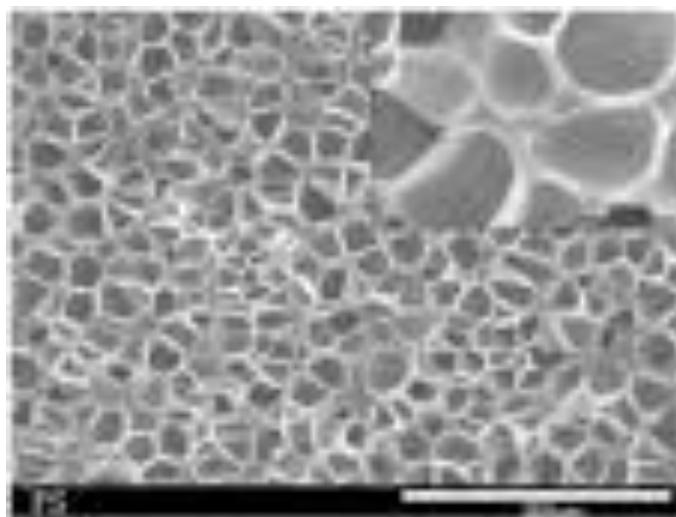
EPS – Expanded Polystyrene



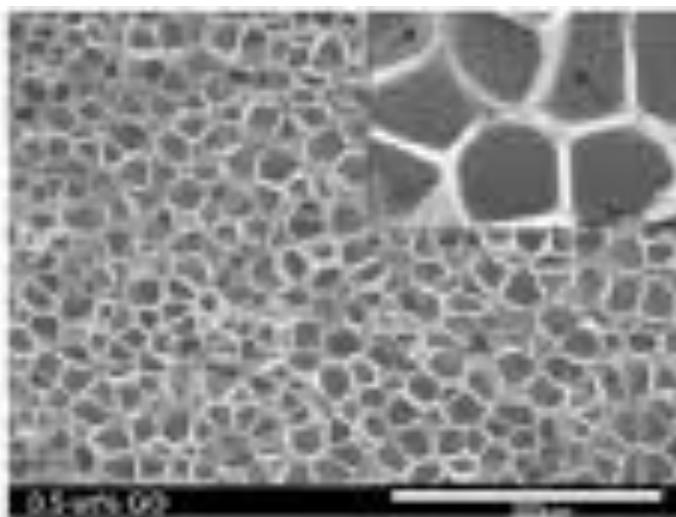
XPS – Extruded Polystyrene



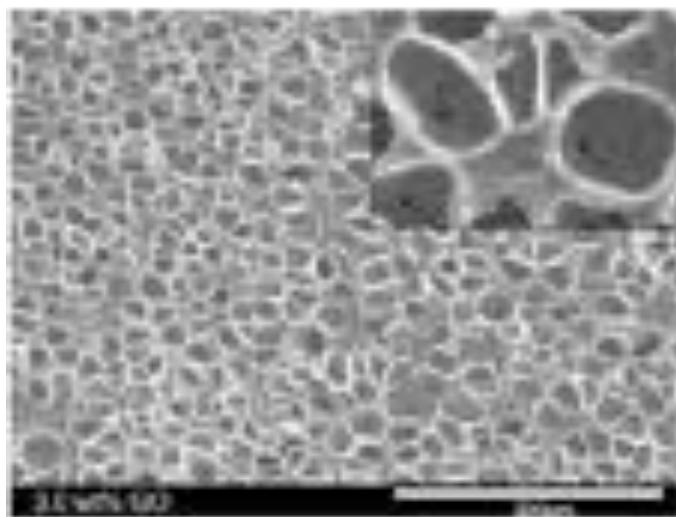
Morphology of XPS



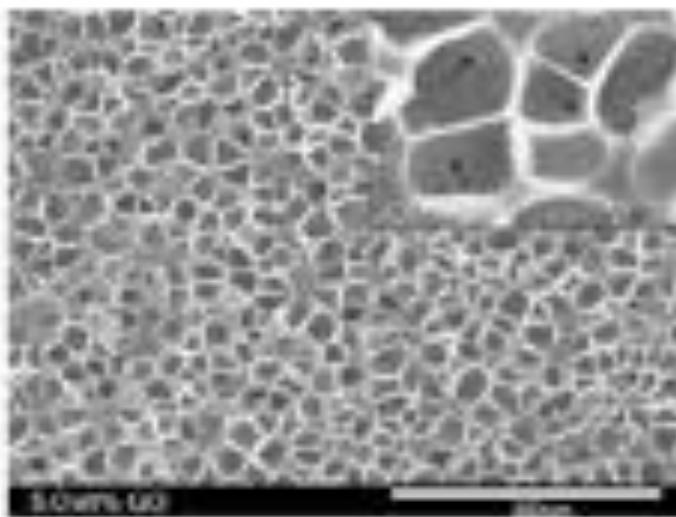
Average cell size: 19.2 μm
Cell density: $1.1 \times 10^6 \text{ cells/cm}^3$



Average cell size: 18.5 μm
Cell density: $1.4 \times 10^6 \text{ cells/cm}^3$



Average cell size: 16.0 μm
Cell density: $1.6 \times 10^6 \text{ cells/cm}^3$



Average cell size: 15.0 μm
Cell density: $2.0 \times 10^6 \text{ cells/cm}^3$

EPS is Used in Movie Set Design



EPS vs XPS

Expanded vs Extruded Polystyrene

More Information Online

WWW.DIFFERENCEBETWEEN.COM

DEFINITION

Expanded Polystyrene

Expanded polystyrene or EPS is a thermoplastic foam material that we produce from solid beads of polystyrene.

Extruded Polystyrene

Extruded polystyrene or XPS is a foam material that we produce from solid polystyrene crystals.

RAW MATERIAL

We produce expanded polystyrene from solid beads of polystyrene.

We produce extruded polystyrene using solid polystyrene crystals.

PRODUCTION PROCESS

Produced via the expansion of gas that is trapped inside the polystyrene beads by heating.

Produced via extruding a hot, thick fluid of polystyrene crystals.

EFFECT ON ENVIRONMENT

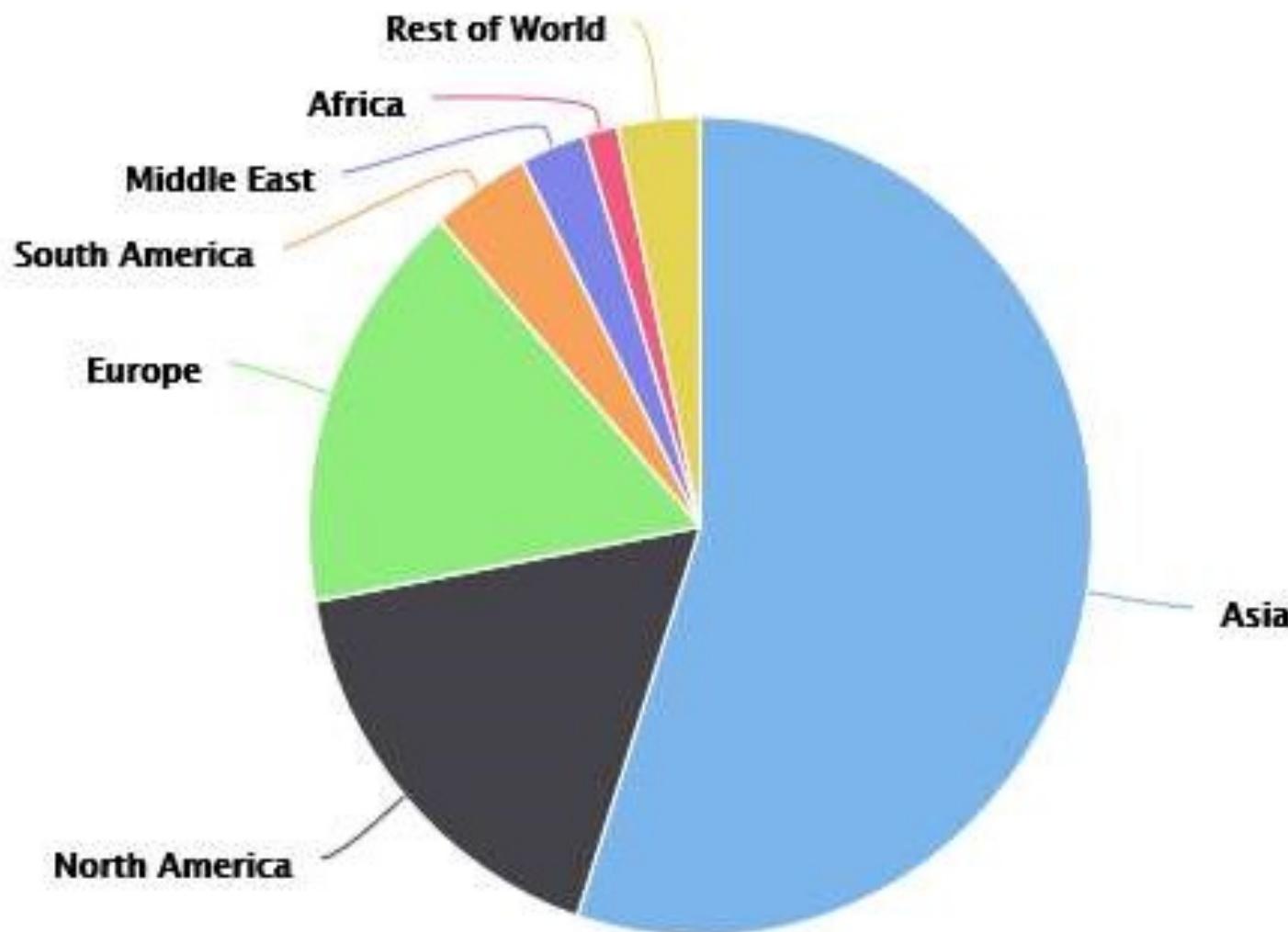
The production of expanded polystyrene has a minimum harmful effect on the environment.

The production of extruded polystyrene has considerable harm to the environment.

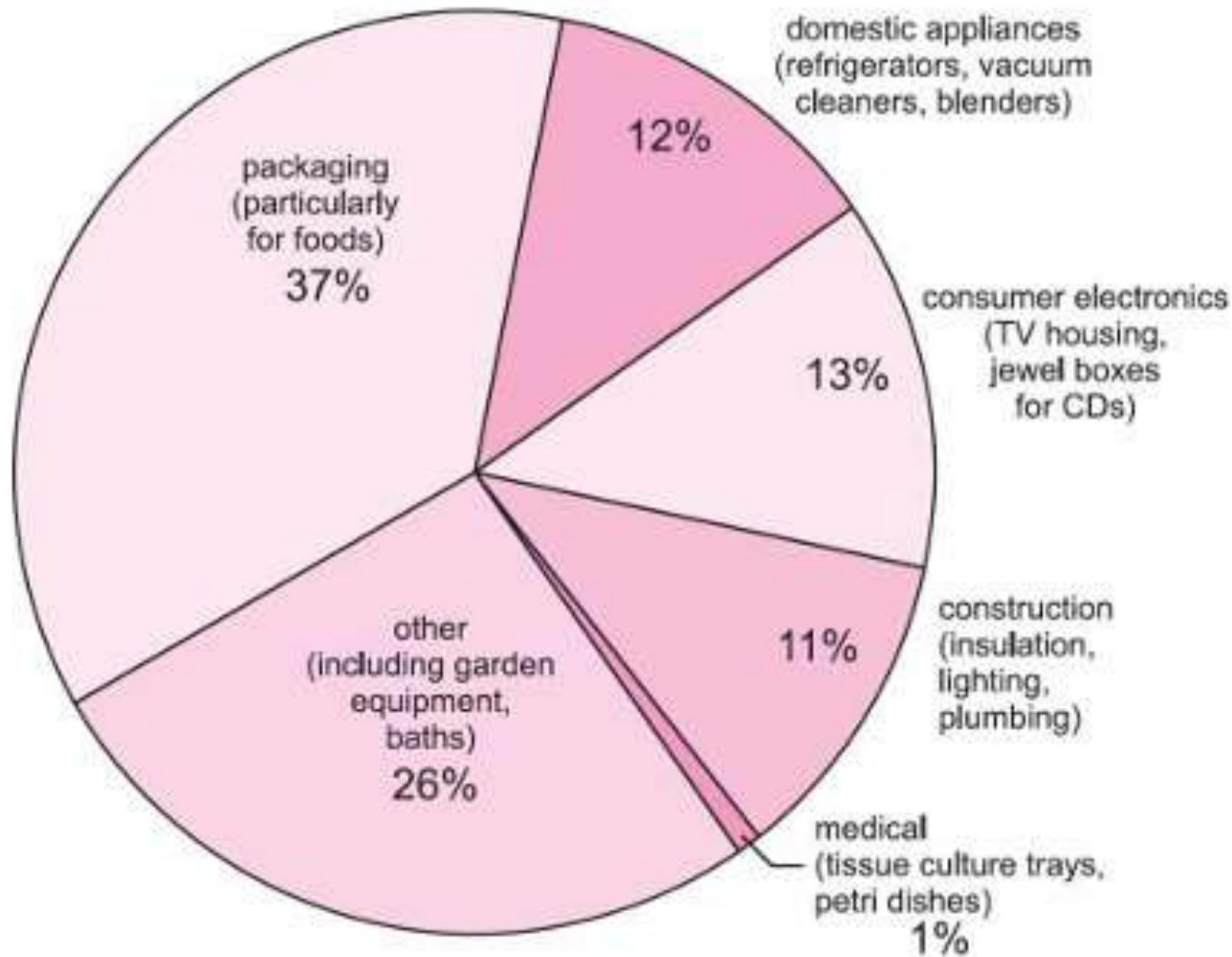
Where is it made? - Geographically

Global Polystyrene Production Capacity – 2016 (In %)

Production Capacity – 14.7 million tons

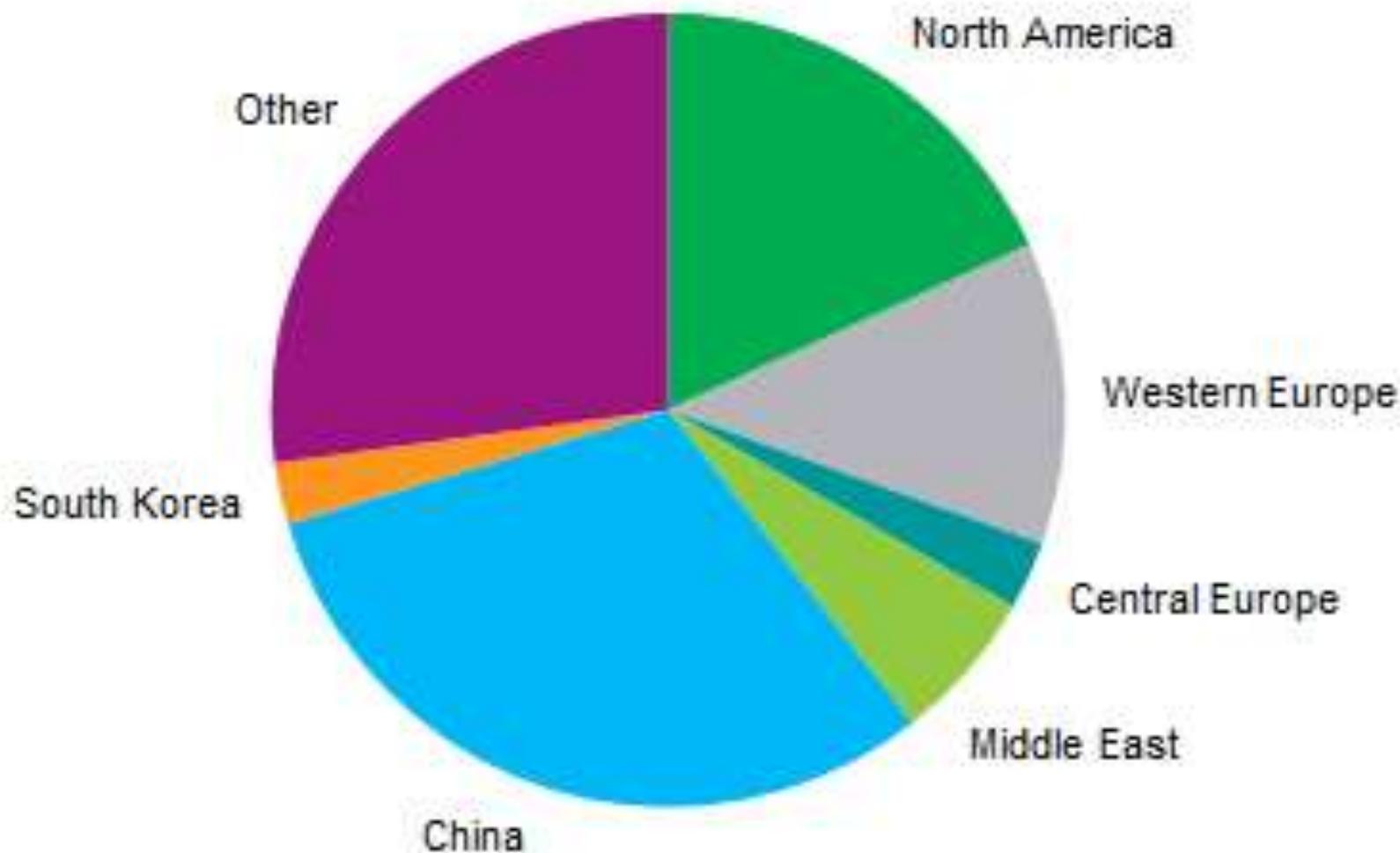


Where does it go? – Applications



Where does it go – Geographically?

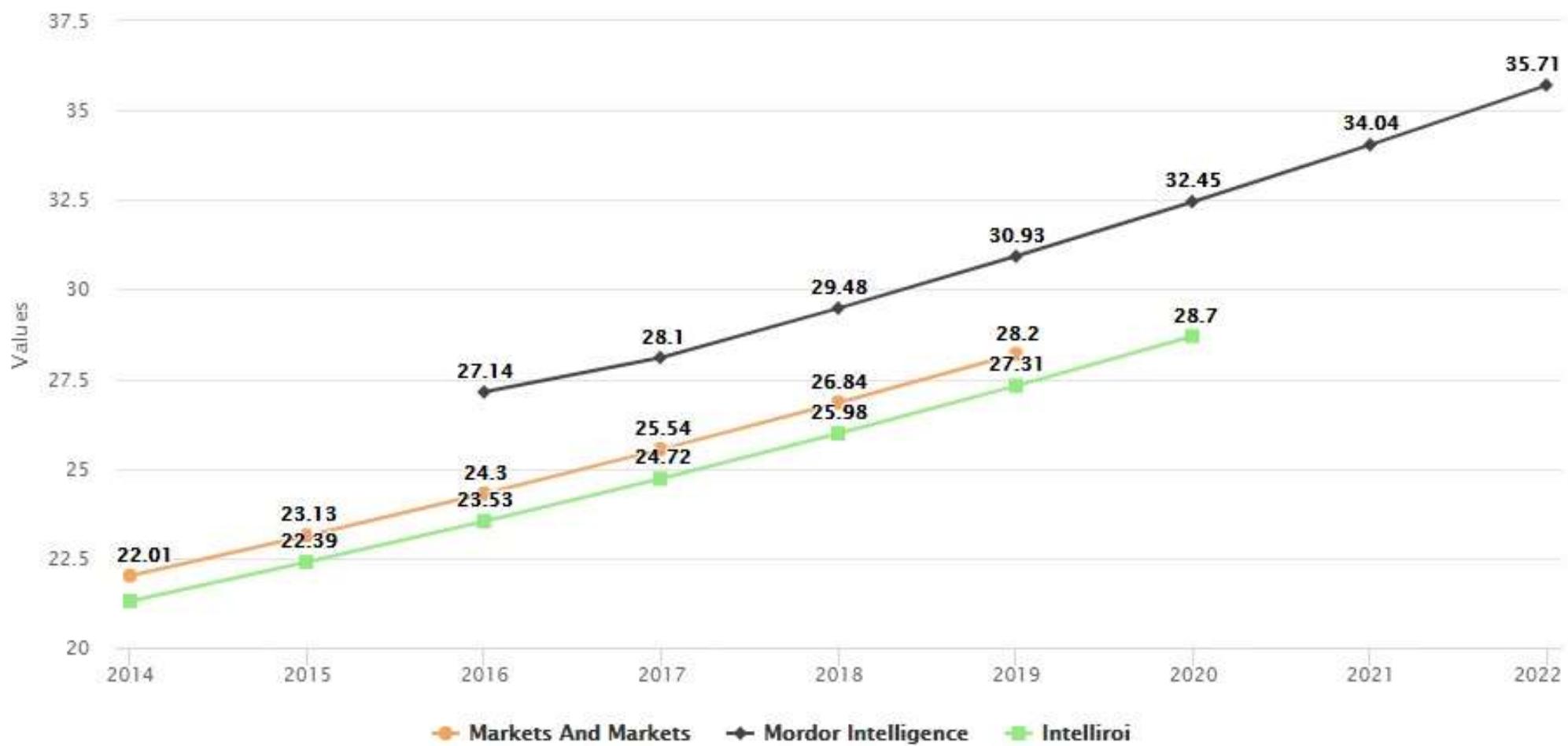
World consumption of polystyrene—2019



Market Size

World Polystyrene Market

(In US\$ bn)



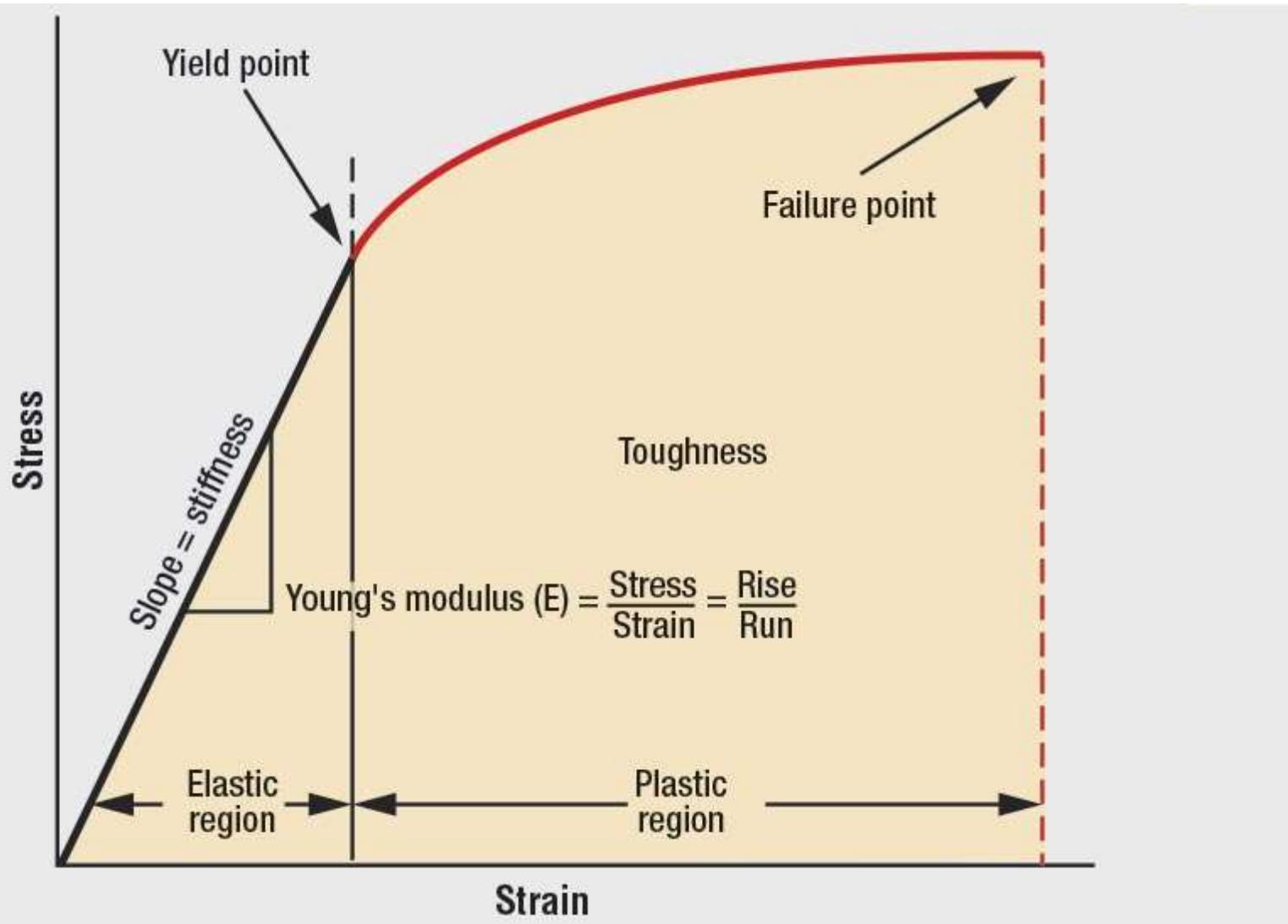
Comparative Pricing

Market Prices Effective Mid-December 2018

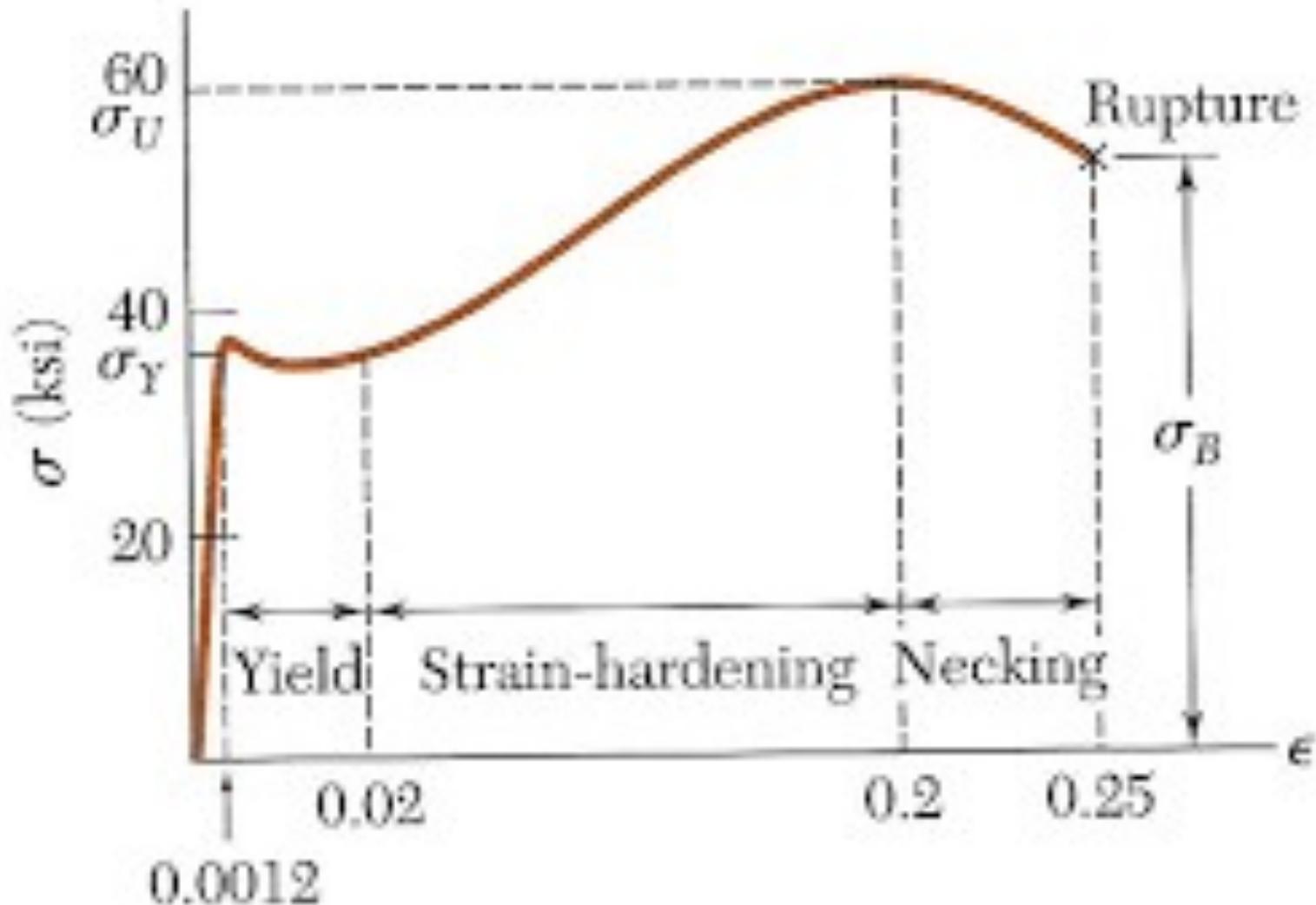
| Resin Grade | ¢/lb |
|----------------------------------|---------|
| POLYETHYLENE (railcar) | |
| LDPE, LINER | 98-100 |
| LLDPE BUTENE, FILM | 81-83 |
| NYMEX 'FINANCIAL' FUTURES | 43 |
| JANUARY | 43 |
| HDPE, G-P INJECTION..... | 103-105 |
| HDPE, BLOW MOLDING..... | 93-95 |
| NYMEX 'FINANCIAL' FUTURES | 48 |
| JANUARY | 48 |
| HDPE, HMW FILM | 110-112 |
| POLYPROPYLENE (railcar) | |
| G-P HOMOPOLYMER, INJECTION | 82-84 |
| NYMEX 'FINANCIAL' FUTURES | 72 |
| JANUARY | 72 |
| IMPACT COPOLYMER..... | 84-86 |
| POLYSTYRENE (railcar) | |
| G-P CRYSTAL..... | 108-110 |
| HIPS..... | 114-116 |
| PVC RESIN (railcar) | |
| G-P HOMOPOLYMER..... | 83-85 |
| PIPE GRADE..... | 82-84 |
| PET (truckload) | |
| U.S. BOTTLE GRADE | 73-75 |



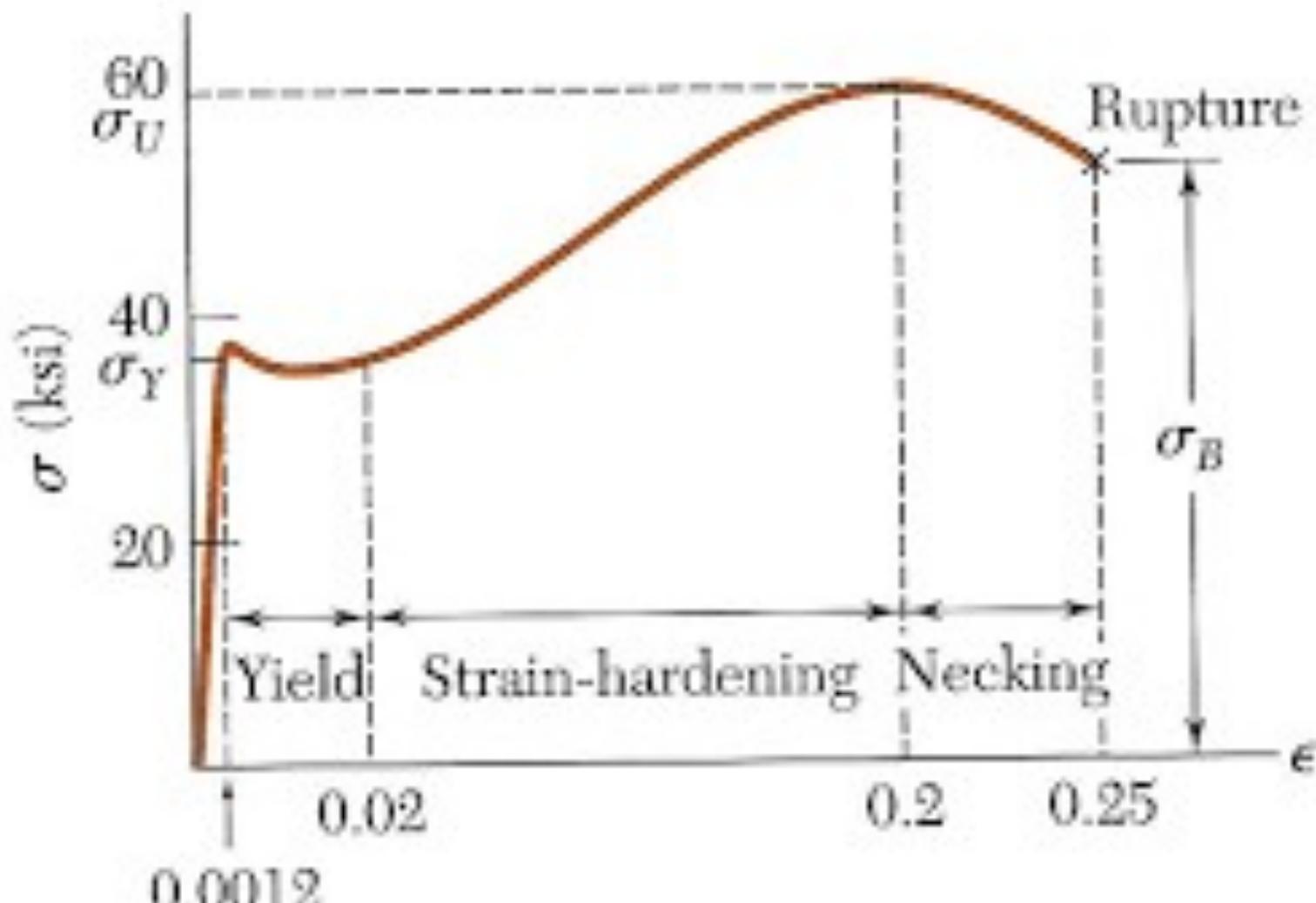
Next Time – Variations on the Theme Polystyrene



Next Time – Variations on the Theme Polystyrene

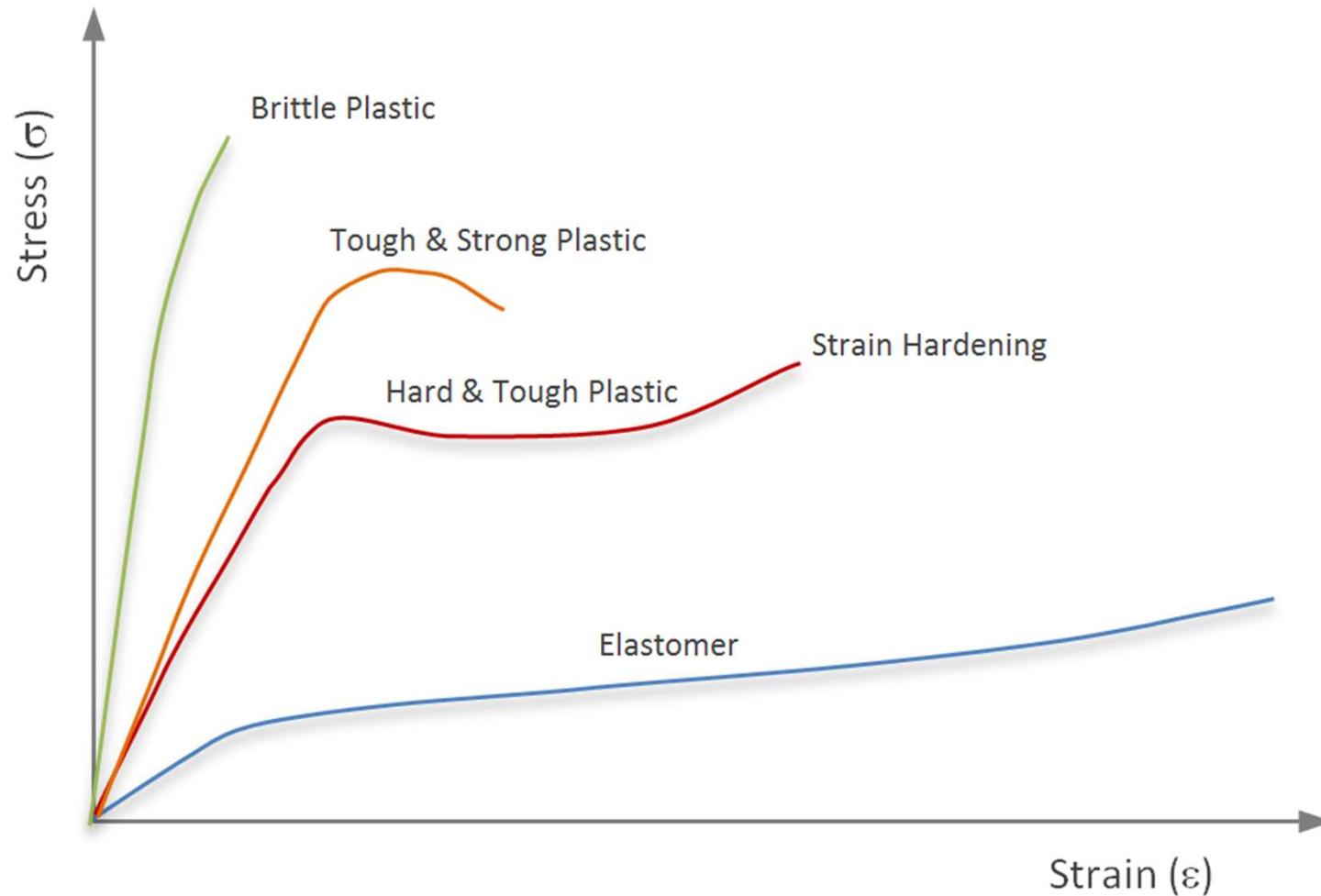


Next Time – Variations on the Theme

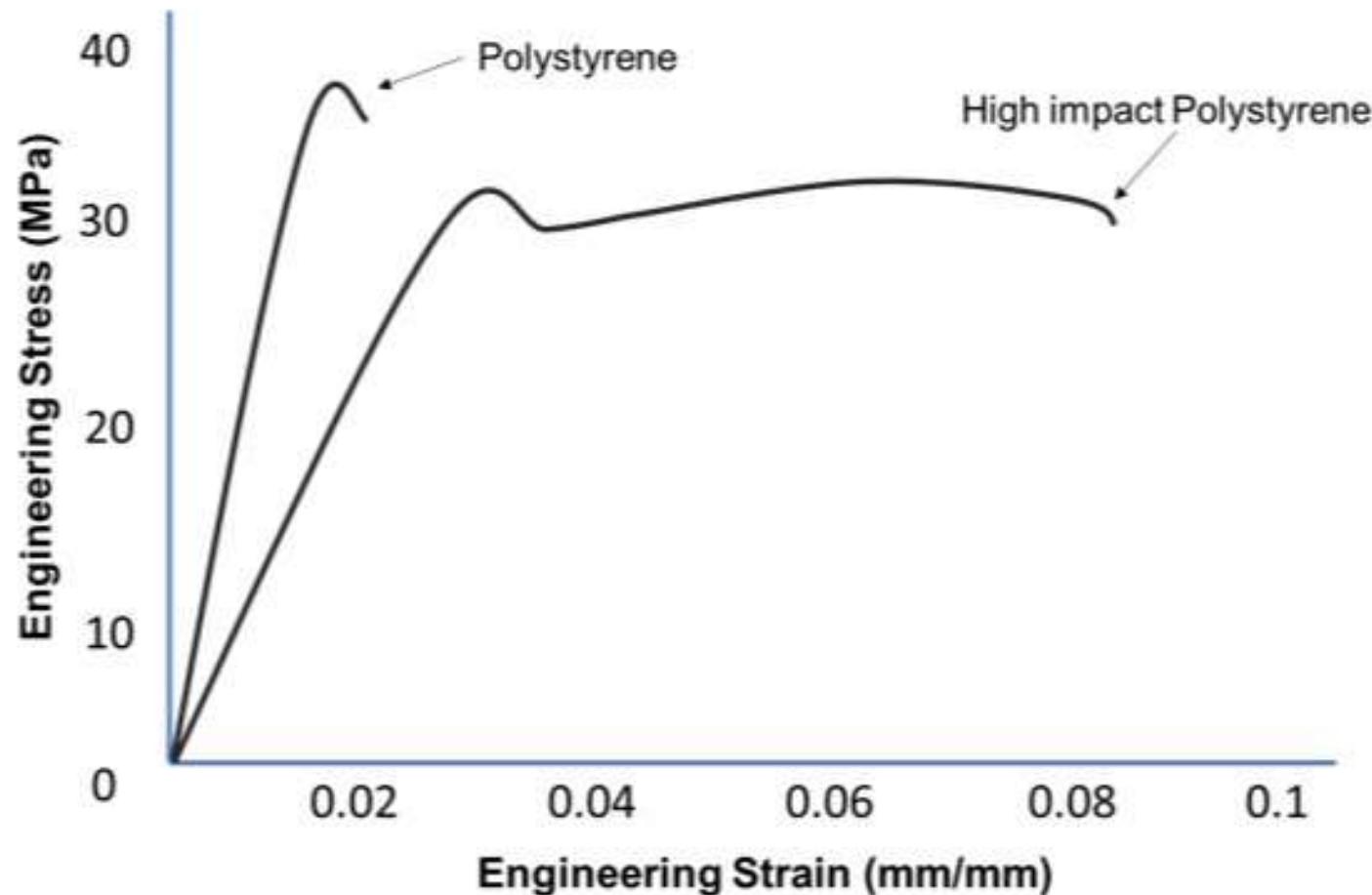


(a) Low-carbon steel

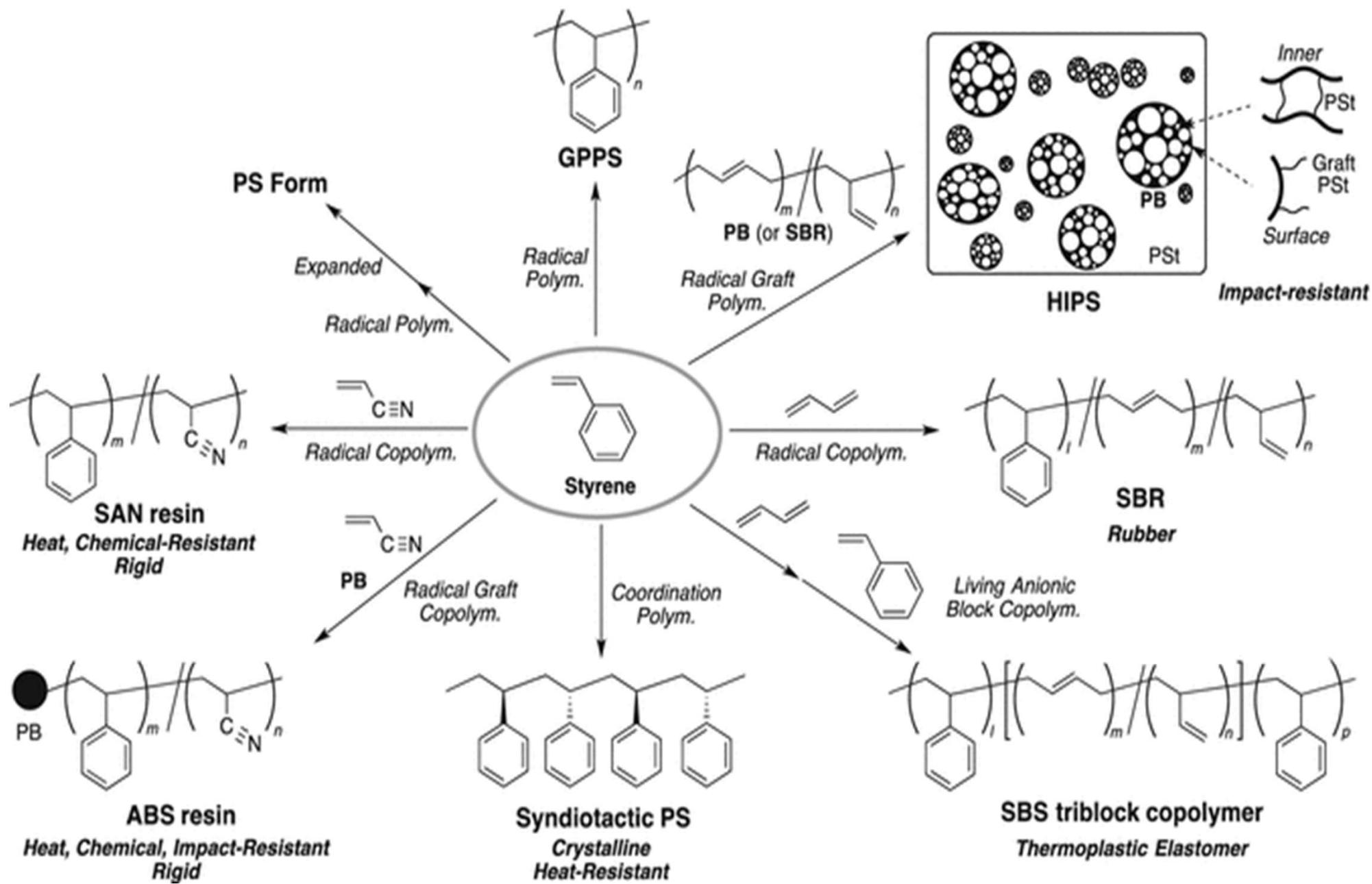
Next Time – Variations on the Theme Polystyrene



Next Time – Variations on the Theme Polystyrene



Numerous Styrenic Forms



Lesson 2: Polystyrene and Styrofoam

Questions?



There was a very cautious man
Who never laughed or played
He never risked, he never tried,
He never sang or prayed.
And when he one day passed away,
His insurance was denied,
For since he never really lived,
They claimed he never really died.

Unknown

Dr. Andy Olah, amo5@case.edu, C: 216-272-0505

“I’m at that age where my mind still thinks I’m 29, my humor suggests I’m 12, while my body mostly keeps asking if I’m sure I’m not dead yet.”