

EMAC 276

Lecture 6: The Vinyl Chloride Family

Poly(Vinyl Chloride) - PVC

Polyvinylidene Chloride - PVDC

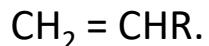
Chlorinated Poly(Vinyl Chloride) - CPVC

Andy Olah, Ph.D.

January 29, 2025

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 Poly(Vinyl Chloride)

- 1838 Henri Victor Regnault (Fr): Photo-initiated polymerization of vinyl chloride monomer (VCM) when exposed to sunlight.
- 1872 Eugen Baumann (Gr): Photo-initiated polymerization of vinyl chloride monomer (VCM) when exposed to sunlight.
- 1913 Friedrich Heinrich August Klatte (Gr): First patent on the photo-initiated polymerization of VCM with sunlight.
- The US Patent was filed by Klatte on July 3, 1914 and issued on October 2, 1917; US 1,241,738
- With the publication of the patent the first industrial interest in PVC began:

UNITED STATES PATENT OFFICE.

FRITZ KLATTE AND ADOLF ROLLETT, OF SCHWANHEIM-ON-THE-MAIN, GERMANY,
ASSIGNEES TO THE FIRM OF CHEMISCHE FABRIK GREISHEIM-ELEKTRON, OF
FRANKFORT-ON-THE-MAIN, GERMANY, A CORPORATION OF GERMANY.

PLASTIC COMPOSITION AND PROCESS OF PRODUCING IT.

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PLASTIC COMPOSITION AND PROCESS OF PRODUCING IT.

1,241,738.

Specification of Letters Patent.

Patented Oct. 2, 1917.

No Drawing.

Application filed July 2, 1914. Serial No. 348,689.

"If instead of organic vinyl esters, vinyl halids, for instance vinyl chlorid, or vinyl bromid be ***polymerized masses are obtained which are not industrially utilizable***, they being opaque, porous, and chalk-like, and readily crumbling to a white powder."

"In accordance with this invention it is however possible to obtain from ***these valueless masses*** valuable products if the said masses be dissolved in the hereinbefore described manner and then be converted again to the solid state. By this treatment from the aforesaid masses products are obtained which are suitable for all purposes for which cellulose esters or celluloid have hitherto been used, namely a substitutes for horn, amber, or artificial resins or lacquers or for impregnating purposes and also for the production of films artificial threads and the like."

When PVC was Invented Polymer Science was in Transition

Science had a problem with plastics because it was the credo of chemistry that very large molecules cannot be stable. Until 1920 it was generally accepted that molecules can join together in large clusters and form colloids, but that they cannot really be big themselves. The basic concepts of today's viewpoint were expressed by a few visionaries between 1860 and 1920, but these remained individual opinions.



Polymers became Recognized as Macromolecules



Hermann Staudinger, 1917, in his laboratory in Zurich.

At the ETH in Zurich, Hermann Staudinger developed and taught a different vision: his work with polystyrene, polyoxymethylene and caoutchouc led him to believe the size of molecules was nearly limitless and they would form long chains. He published this concept for the first time in 1920 and coined the term «macromolecule» in 1926. The existence of such giant molecules met with a great deal of skepticism and only gradually began to find acceptance. Staudinger's experimental results were later explained by others in line with the laws of physics: notably Kurt H. Meyer and Hermann F. Mark, who in Ludwigshafen in 1928 shed light on the structure of cellulose, silk, chitin and caoutchouc via X-ray analysis, and Werner Kuhn, who in 1934 was the first to conclusively expound the viscosity of polymeric solutions and in Karlsruhe, then Kiel and then in Basel established the theoretical basis for rubber elasticity and the deformation of macromolecules.

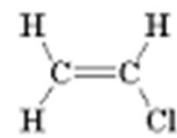
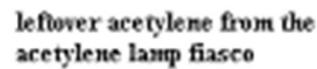
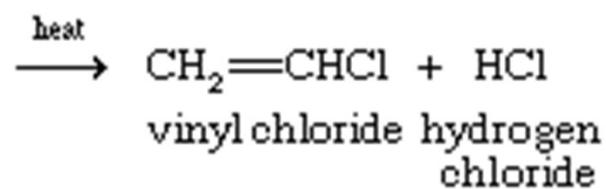
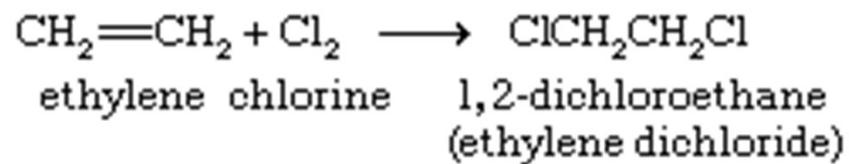
What is caotchouc?

caou-tchouc/noun

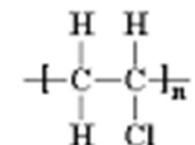
'kou,CHōok,-,CHōo(k)/noun:
unvulcanized natural rubber.



There are Two Pathways for Vinyl Chloride Monomer (VCM) Synthesis



vinyl chloride



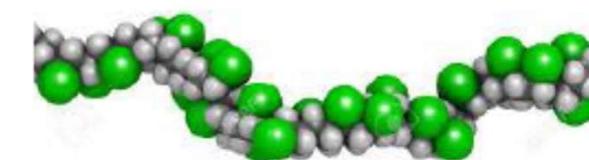
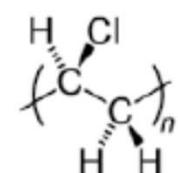
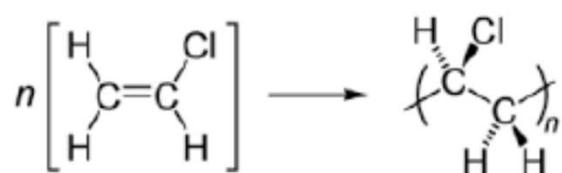
poly(vinyl chloride)

Health Effects of Vinyl Chloride Monomer

Chronic **effects** VCM is a known human carcinogen. Occupational overexposure has produced a specific cancer (angiosarcoma of the liver) and is associated with hepatocellular and cholangiocellular cancer.

In the 1960s, polyvinyl chloride (PVC) was shown to be associated with Raynaud's phenomenon and later with malignancies, including hemangiosarcoma of the liver. The **carcinogenicity** of PVC was established as a result of the review of all evidence in 1974 by the US Office of Technology Assessment and OSHA

The Structure of Poly(Vinyl Chloride)



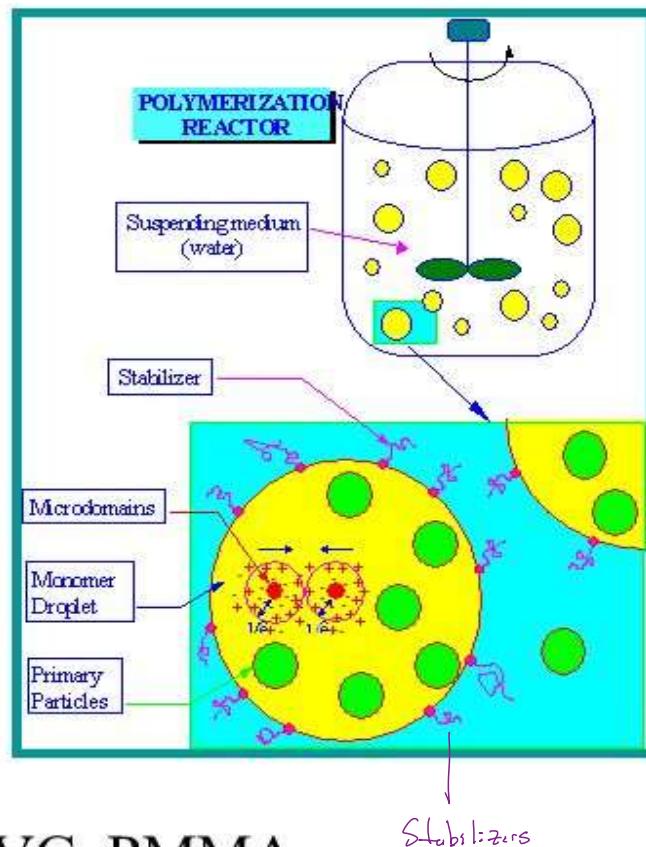
Nearly 57% of the mass of poly(vinyl chloride)
is chlorine.

Suspension polymerization

- Disperse monomer droplets in a noncompatible liquid (e.g. H₂O)
- Polymerize the monomer by an initiator (soluble in the monomer)
- Stabilize the dispersion with a stabilizer (e.g. poly(vinyl alcohol) or methyl cellulose)
- Isolate granular bead products by filtration or spray drying
- Heat transfer is efficient and reaction is easily controlled
- Similar to bulk polymerization in kinetics and mechanism

Commercial uses

For making **granular polymers**, e.g. PS, PVC, PMMA



The Hierarchical Structure of Poly(Vinyl Chloride) when Suspension Polymerized

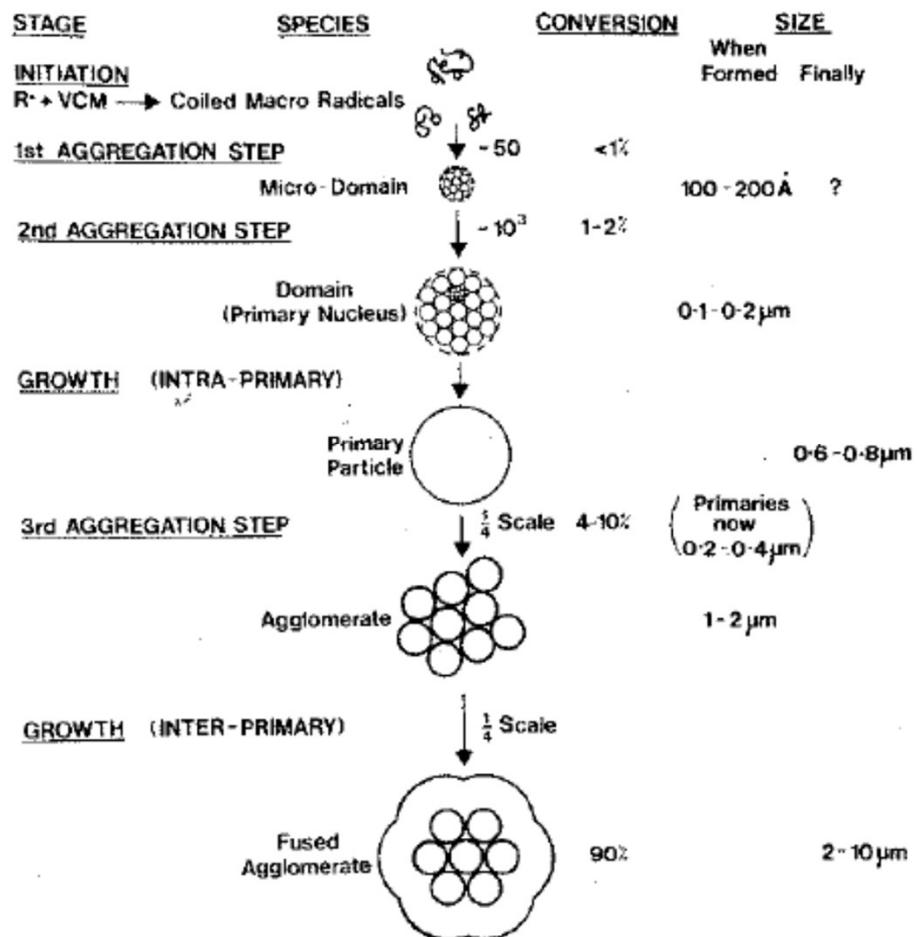


FIG. 7.27. Schematic representation of the mechanism of VCM polymerisation.

MORPHOLOGY OF PVC

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<u>STAGE</u>	<u>SPECIES</u>	<u>CONVERSION</u>	<u>SIZE</u>
<u>INITIATION</u>	$R \cdot + VCM \rightarrow$ Coiled Macro Radicals		When Formed
<u>1st AGGREGATION STEP</u>	Micro-Domain	$\downarrow -50$ \downarrow	Finally $100-200\text{\AA}$?
<u>2nd AGGREGATION STEP</u>	Domain (Primary Nucleus)	$\downarrow -10^3$ \downarrow	$0.1-0.2\mu\text{m}$
<u>GROWTH (INTRA-PRIMARY)</u>	Primary Particle	\downarrow	$0.6-0.8\mu\text{m}$
<u>3rd AGGREGATION STEP</u>		$\downarrow \frac{1}{4} \text{ Scale}$ \downarrow	$(\text{Primaries now } 0.2-0.4\mu\text{m})$

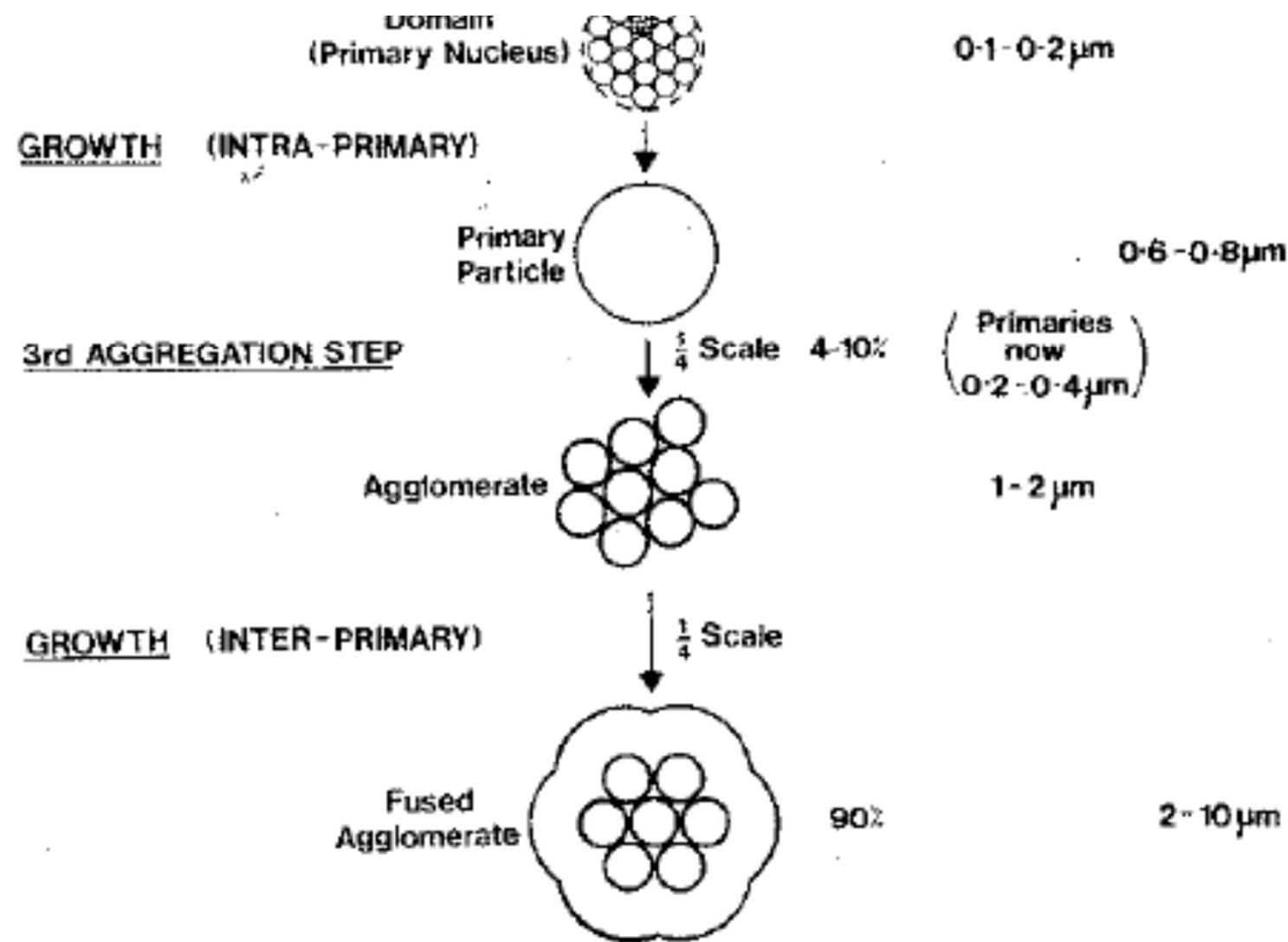


FIG. 7.27. Schematic representation of the mechanism of VCM polymerisation.

The Hierarchical Structure of Poly(Vinyl Chloride) when Suspension Polymerized

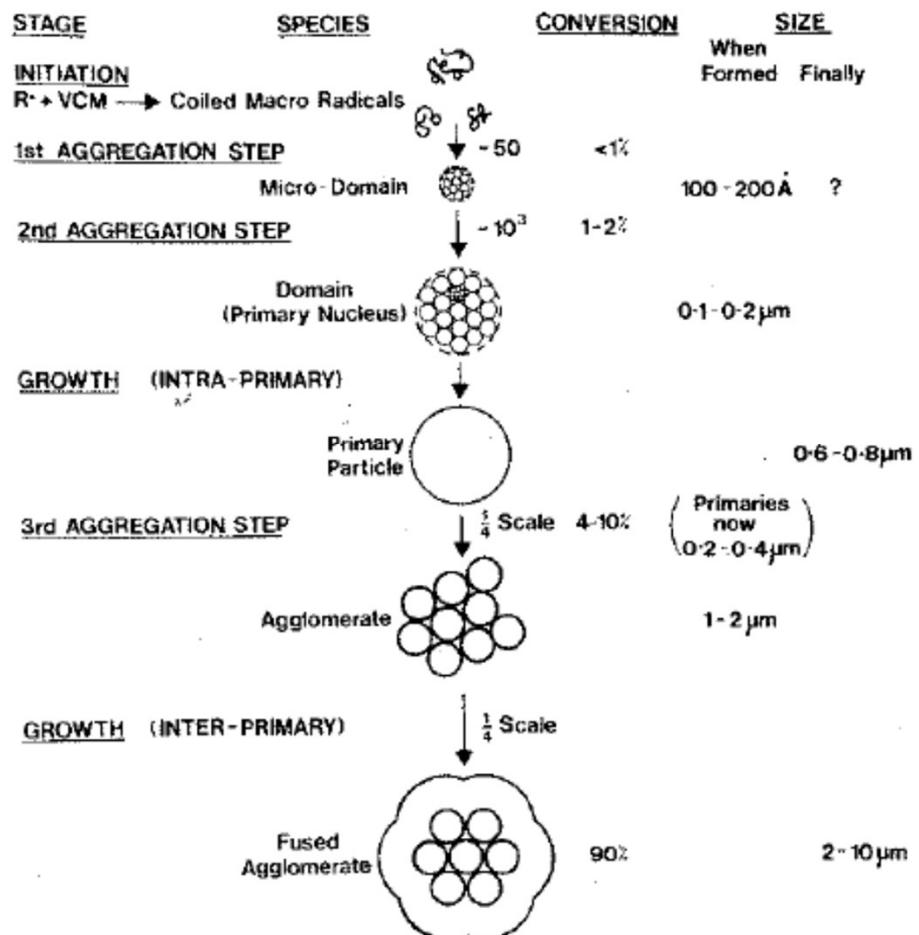


FIG. 7.27. Schematic representation of the mechanism of VCM polymerisation.

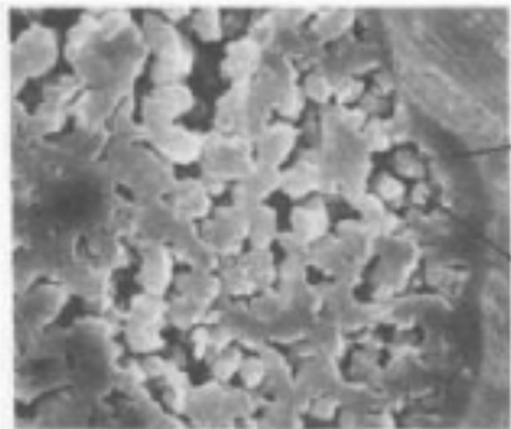
Downat Temp of PVC is T_g
 → Classified as amorphous like PS

Micrographs and Schematic of the Grain Structure of PVC

Summers, James W., J. Vinyl & Add. Tech., Vol 3(2) 130-139, 1997



Grain: 150 um dia.



Skin: 2 – 5 um thick

Primary Particles: 1 um dia.

Can see Hierarchical
Structure here

Fig . 5 A PVC suspension grain showing the formation from monomer droplets an da cross section showing the skin and primary particles.

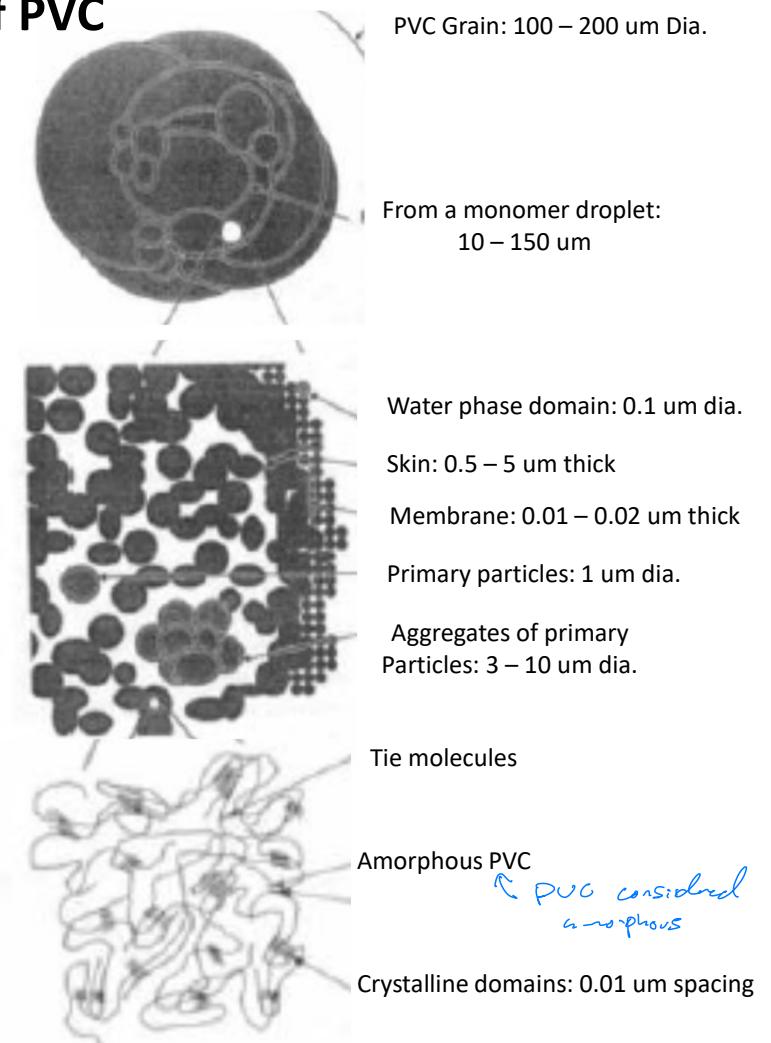
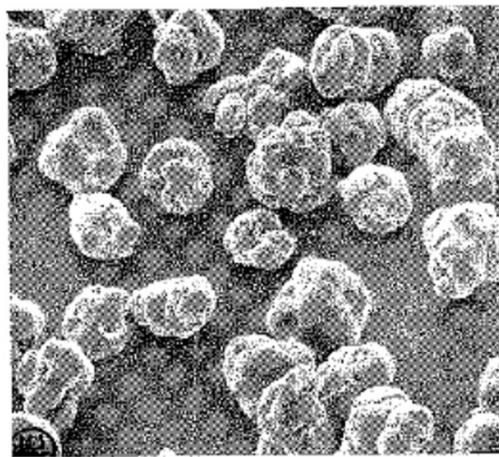


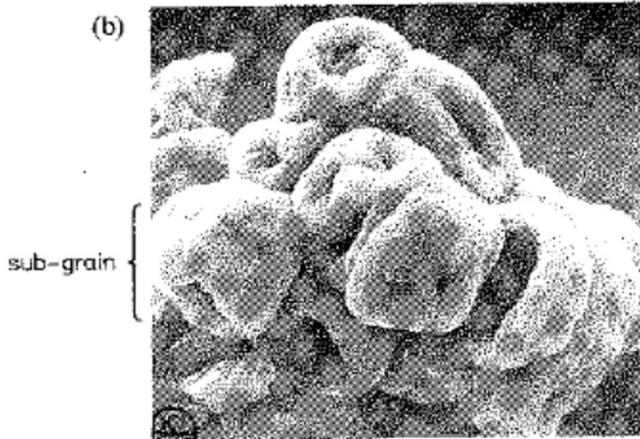
Fig. 6 The hierarchical structure of PVC

(a)



100 μm

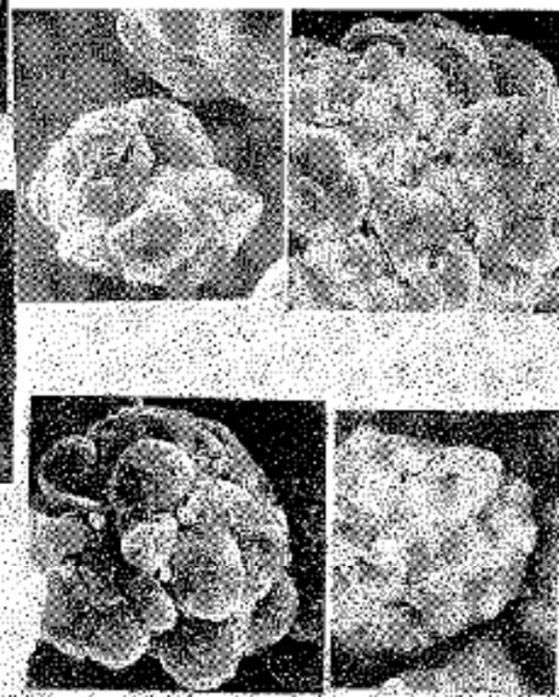
(b)



20 μm

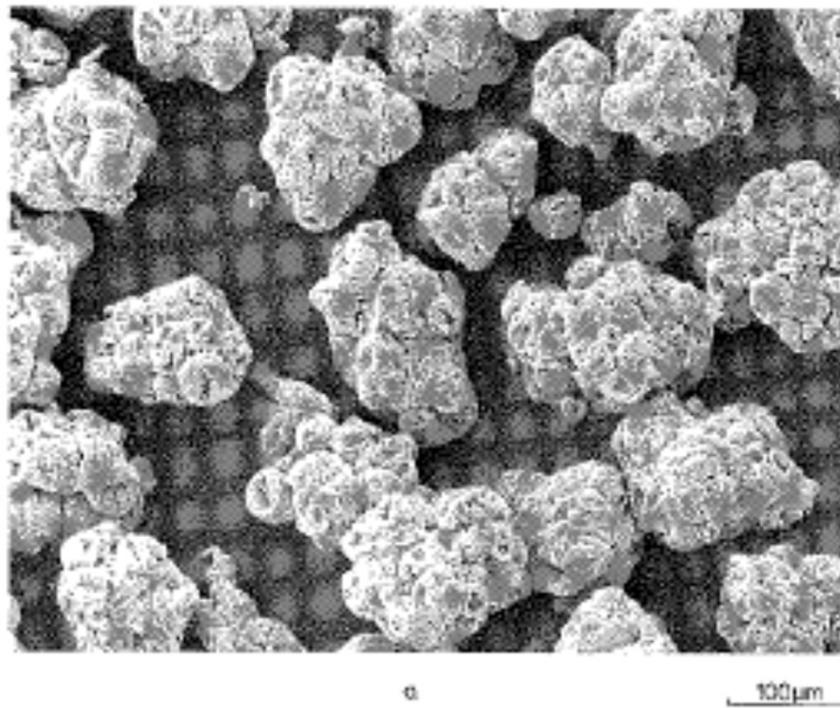


20 μm



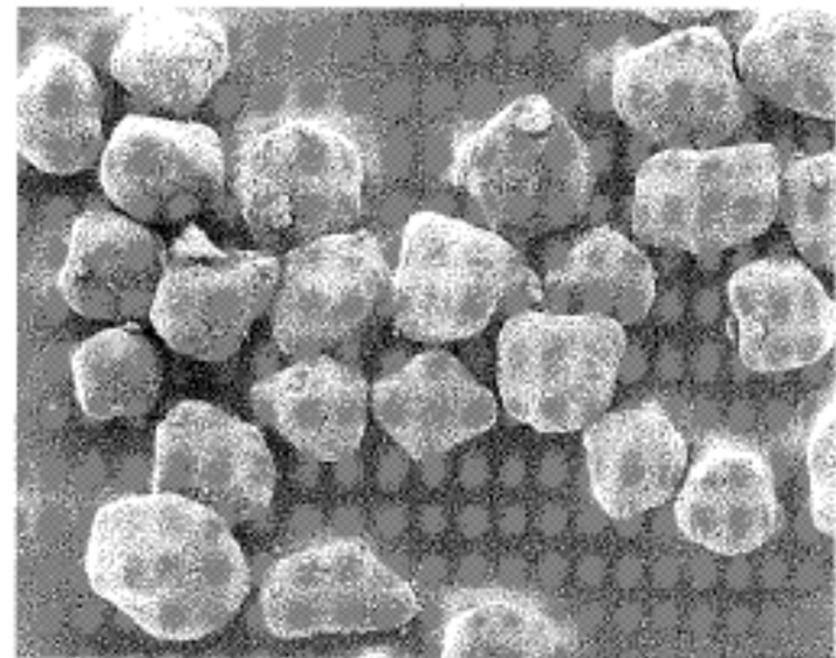
20 μm

Comparison of Suspension and Bulk Polymerized PVC



Suspension Polymerized

Aggregates of primary particles
as they grow



→ Not used today
Bulk Polymerized

Tries to prevent aggregation

Table 4. Quick Reference for Commercial PVC Molecular Weights.

Inherent Viscosity ASTM D1234	K Value 1% in Cyclohexanone	Number Average Molecular Weight $M_n (\times 10^{-3})$	Weight Average Molecular Weight $M_w (\times 10^{-3})$
0.42	45	15.0	30.0
0.47	48	18.0	36.0
0.52	50	20.0	40.0
0.57	53	22.5	45.0
0.62	55	25.0	50.0
0.67	57	27.5	55.0
0.73	59	30.5	61.0
0.78	61	33.0	67.0
0.83	63	36.0	72.0
0.88	65	38.5	78.0
0.92	67	41.0	82.5
0.98	69	44.0	89.5
1.03	70	47.0	95.0
1.08	72	50.0	101.0
1.13	74	52.5	107.5
1.21	76	57.0	117.0
1.30	79	62.5	128.5
1.40	82	68.5	141.0
1.60	87	81.0	166.0
1.80	92	93.5	195.0

Different Nomenclature Exists
for Describing the Molecular Weight
of Poly(Vinyl Chloride)

IV

K -Value

M_n

M_w

M_z } over 2
 M_{z+1} } distribution

PDI
 $M_w \approx 2 M_n$
 for all
 due to
 specific
 conditions

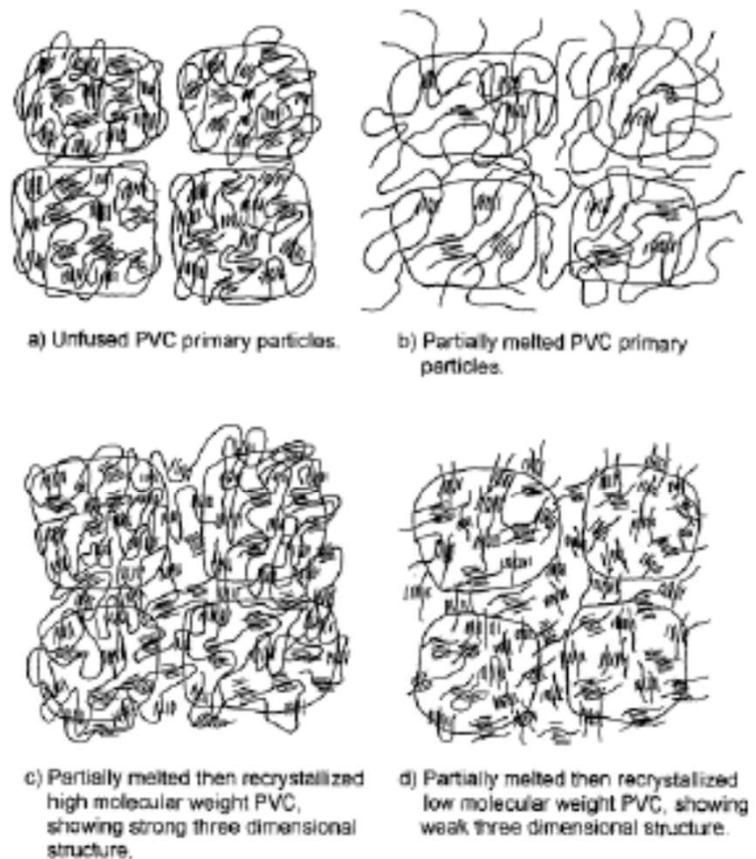
Basis for the Difficulty in Processing PVC

Must overcome primary particle memory by heat and melt mixing during processing.

Fig. 12. Model for PVC fusion, accounting for molecular weight effects and processing temperature effects.

Initially PVC had Little or No End-Use Application

Poor contact
→ drop
in impact



Summers, James. W., J. Vinyl & Add. Tech.,
Volume 3(2), 130 – 139 (1997).

Patented Oct. 10, 1933

1,929,453

UNITED STATES PATENT OFFICE

1,929,453

SYNTHETIC RUBBER-LIKE COMPOSITION AND METHOD OF MAKING SAME

**Waldo L. Semon, Silver Lake Village, Ohio, as-
signor to The B. F. Goodrich Company, New
York, N. Y., a corporation of New York**

I claim:

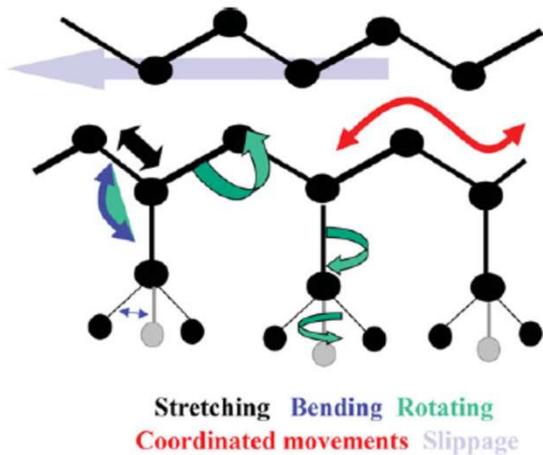
1. The method of manufacturing a resilient rubber-like composition, which comprises dissolving an insoluble polymerized vinyl halide at an elevated temperature in a composition which will dissolve the polymerized vinyl halide only at temperatures considerably above room temperature, in such proportions as to form a stiff, resilient position to gel by cooling it.

Waldo Semon Plasticized PVC

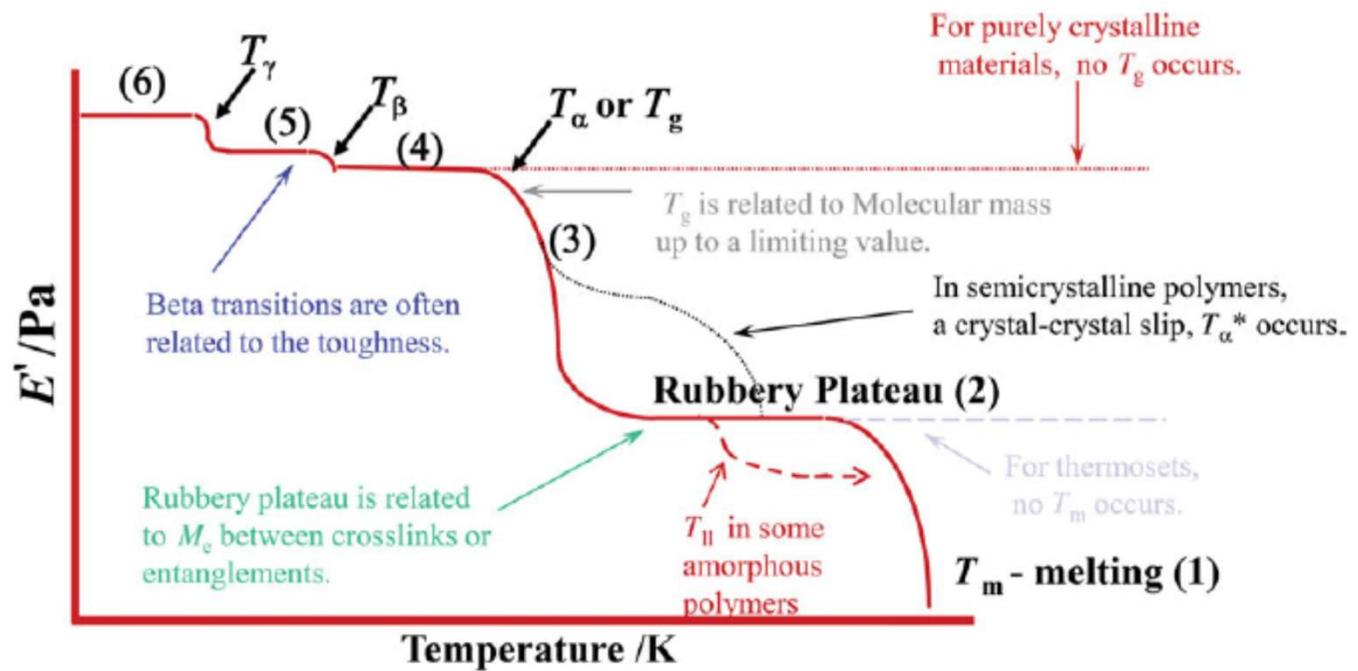


Assigned at Goodrich to develop methods for prolonging the integrity of rubber, Semon's curiosity led him to conduct experiments with vinyl polymers, then considered a waste product in the industrial production of rubber. He discovered that by mixing PVC powder in a solvent and heating it, he could produce a malleable gel that would retain its shape when cooled. With capital in short supply after the stock market crash of 1929, there was little enthusiasm for investing in Semon's PVC compound at the company, whose principal product was tires. Semon nonetheless persisted in exploring the compound, perfecting practical applications suited to its qualities. Waterproof, fire-resistant, and nonconductive, "vinyl," as it eventually became known to the public, proved an inexpensive, functional fabric for umbrellas, raincoats, shoe heels, shower curtains, automobile seats, and dozens of other commonly used objects. Semon patented the process in 1933--it is one of 116 U.S. patents.

Thermal Transitions in Amorphous Polymers



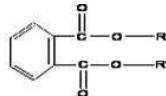
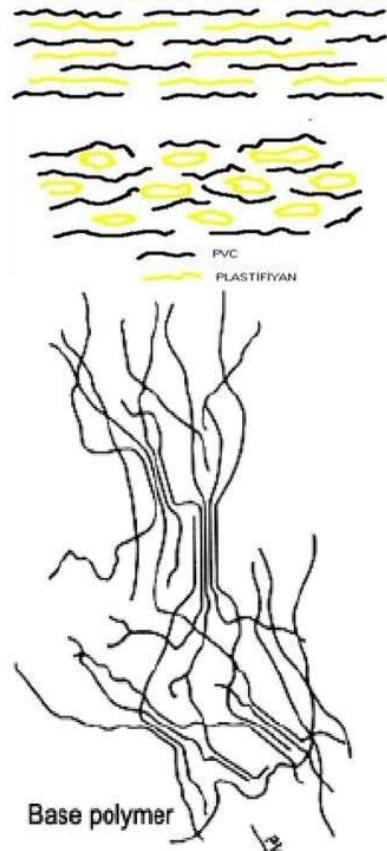
The Crankshaft Model of
Polymer Molecular Motions



(6)	(5)	(4)	(3)	(2)	(1)
Local motions	Bend and stretch	Side groups	Gradual main chain	Large-scale chain	Chain slippage

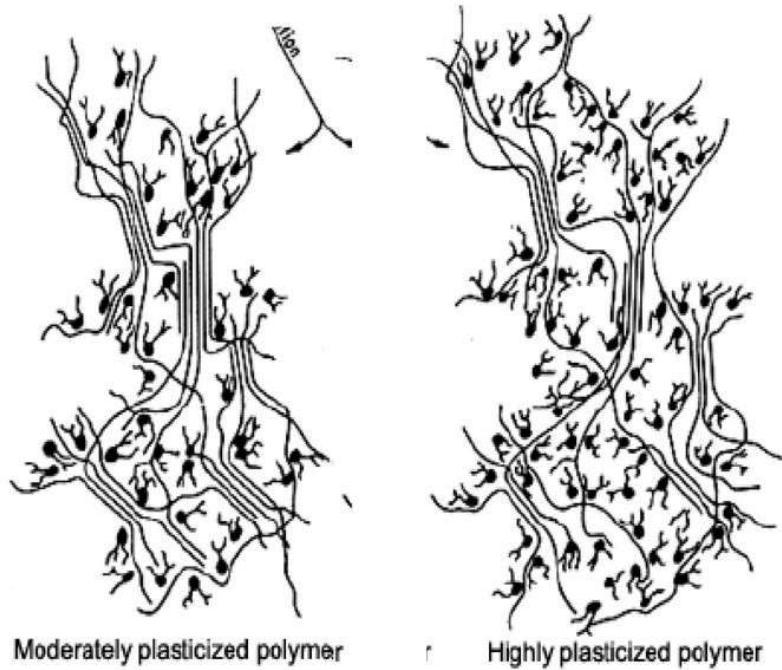
Fundamental Function of a Plasticizer

PVC and Plasticizers



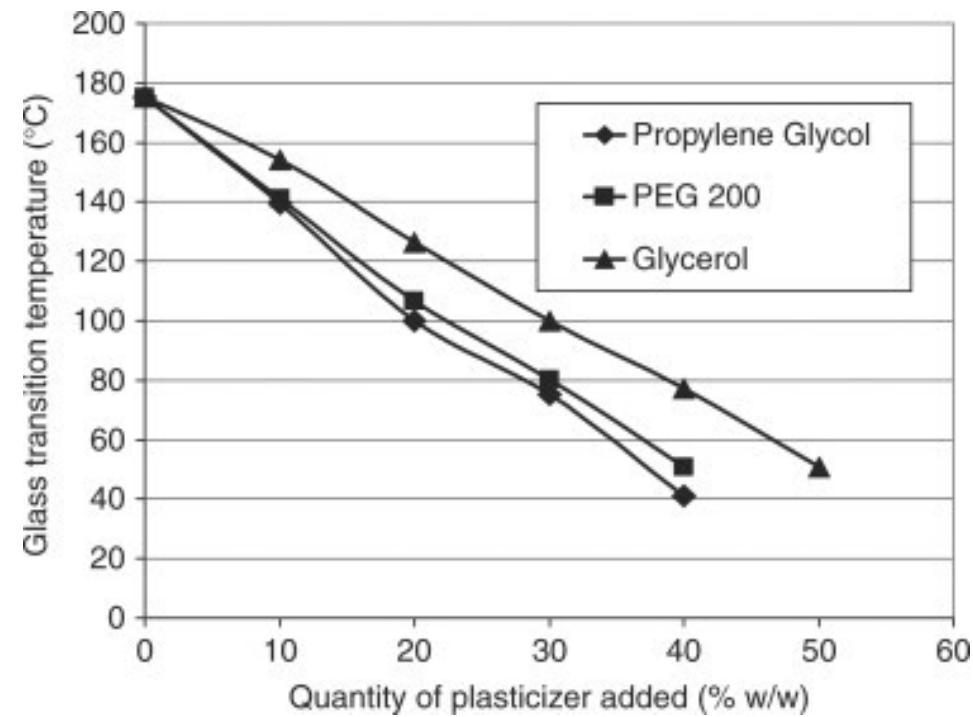
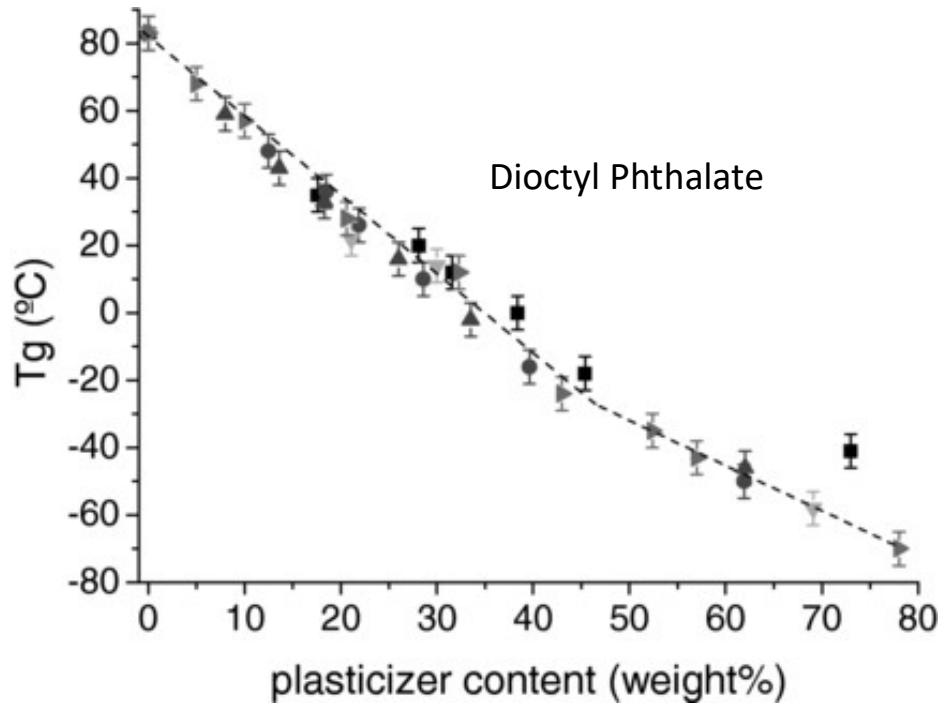
Chemical Formula of DOTP, DIDP, DINP, and DOP.

Orthophthalates: R'=alcohol; for DOP R'=2-ethyl hexanol; for DIDP R'=isodecyl alcohol; for DINP R'=isononyl alcohol

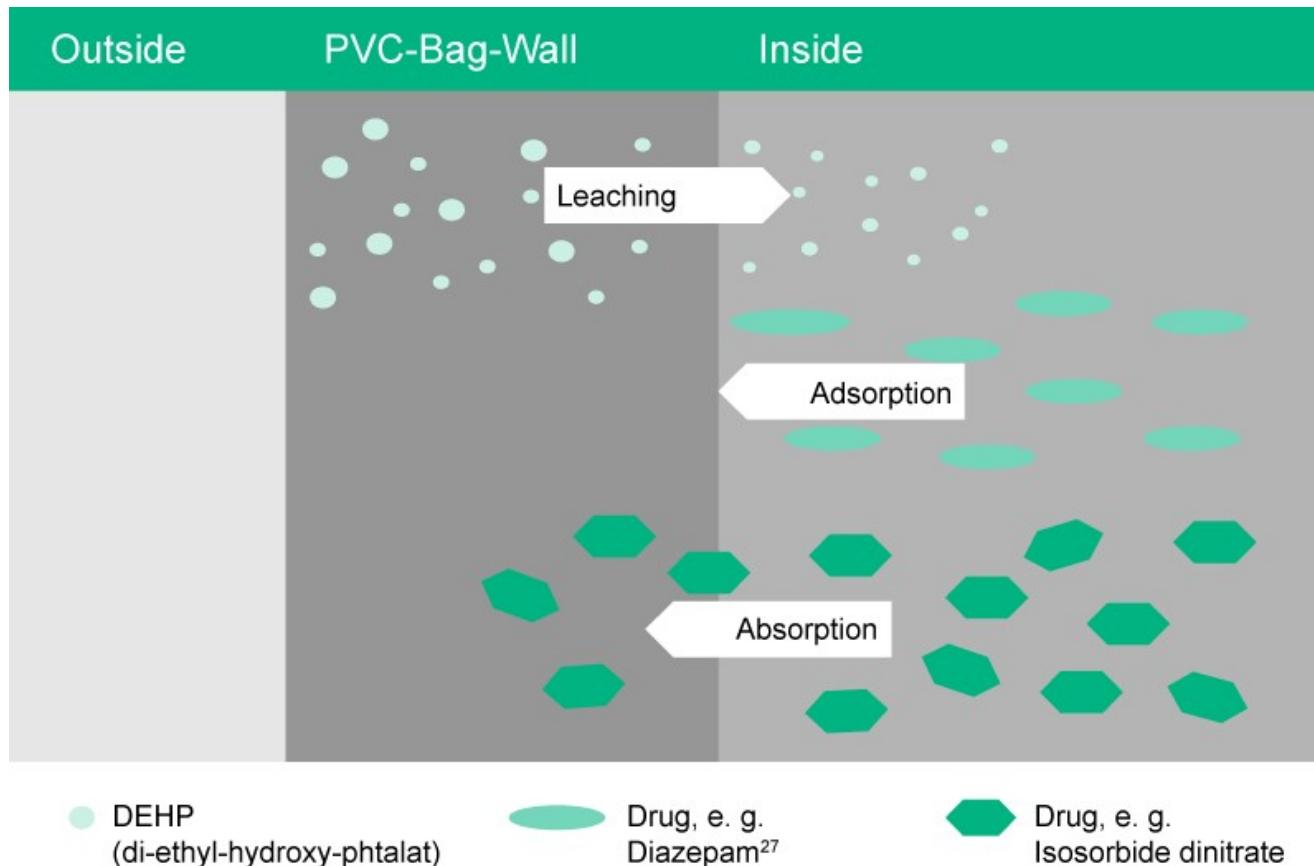


Plasticizers usually possess long alkyl chains which have the effect of screening the long polymer chains from each other, thereby, preventing them from reforming the chain-chain interactions which gives the unplasticized polymer its rigidity.

Influence of the Plasticizer Concentration on T_g



Be Aware of the Mechanism of Plasticizer Leaching



Certain Phthalates are Known to have Health Effects

Plastic dolls from Disney's smash hit *Frozen* franchise are being recalled over safety fears.

The Elsa and Anna dolls are said to contain potentially toxic materials which could harm children's reproductive systems and livers.

"The plastic material of the dolls contains an excessive amount of bis(2-ethylhexyl) phthalate (DEHP), di-'isononyl' phthalate (DINP) and dibutyl phthalate (DBP) (measured values up to 1% by weight, 1% by weight and 0.15% by weight respectively).

It said the products were made in outside the US and were most commonly sold online.

- Carcinogen
- Mutagen
- Teratogen
- Endocrine Disruptor



Health Effects Influence

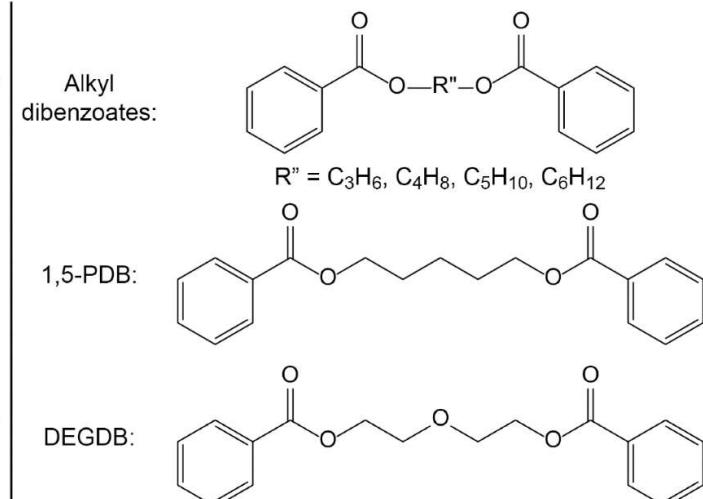
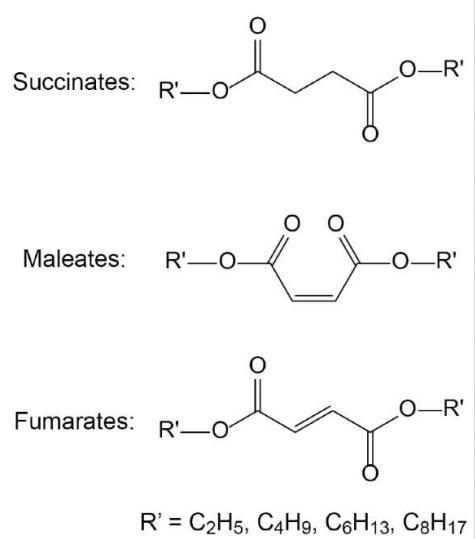
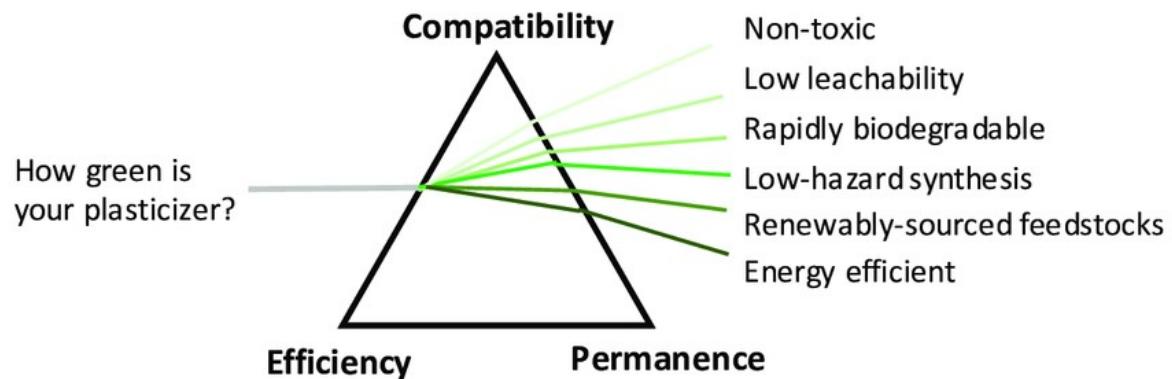
A **carcinogen** is any substance, radionuclide, or radiation that promotes carcinogenesis, the formation of cancer. This may be due to the ability to damage the genome or to the disruption of cellular metabolic processes.

Teratogen: Any agent that can disturb the development of an embryo or fetus. *Teratogens* may cause a birth defect in the child. Or a *teratogen* may halt the pregnancy outright. The classes of *teratogens* include radiation, maternal infections, chemicals, and drugs.

In genetics, a **mutagen** is a physical or chemical agent that changes the genetic material, usually DNA, of an organism and thus increases the frequency of mutations above the natural background level.

Endocrine disruptors are chemicals that can interfere with **endocrine** (or hormonal) systems at certain doses. These disruptions can cause cancerous tumors, birth defects, and other developmental disorders. Any system in the body controlled by hormones can be derailed by hormone **disruptors**.

A New Generation of Plasticizers for Poly(Vinyl Chloride)



Since Certain Plasticizers May Migrate, Be Careful when Using these Materials in Analytical Testing

This **plastic tubing** is made of **Tygon** formulation E-3603 polyvinyl chloride (**PVC**) and is for use with peristaltic and vacuum pumps in lab applications. ... This **plastic tubing** is rated as very flexible as it bends more easily than flexible or rigid **tubing**.



Certain Products Relative to Plasticizer Level

DINP = Di-isobutyl Phthalate

Table 5.3 Typical Properties of General Purpose Vinyl Plastic Products

	Rigid	Semirigid	Flexible	Very flexible	Extremely flexible
DINP, phr	0	34	50	80	600
Wt% of composition	0	25	33	44	86
<i>Typical properties</i>					
Specific gravity, 20/20 °C	1.40	1.26	1.22	1.17	1.02
Hardness Durometer A, 15 s	—	94	84	66	< 10
Flexural stiffness ^a at 23 °C					
MPa	> 900	69	12	3.4	—
psi	> 130,000	10,000	1,700	500	—
Tensile strength ^b					
MPa	> 41	31	21	14	—
psi	> 6,000	4,500	3,100	2,000	—
Elongation (%) ^b	< 15	225	295	400	—
Brittleness ^c					
°C	> 23	-16	-32	-47	—
°F	> 73	+3	-26	-53	—
<i>Examples</i>					
	Bottles, pipe, siding, records	Shades, shoe heels, thin films, produce wrap	Wall-cover- ing, book- binders, produce upholstery, garden hose	Boots, gloves, water beds	Fishing lures

Do not drink out of garden hose - plasticizers

Examples of Plasticized PVC Products



Plasticization was first
tried to make use of PVC
but came at health costs

Other than Plasticizing Poly(Vinyl Chloride) was Still an Unusable Material

Frazier Groff – Charleston, West Virginia - 1933

"By experimentation I have discovered that a preferred type of vinyl resins are those resulting from the conjoint polymerization (by which is meant polymerization of two or more compounds while in mutual contact of a vinyl halide, such as vinyl chloride, and an oxygen-containing vinyl compound, by which is meant particularly the vinyl esters of aliphatic acids, of which ester vinyl acetate is typical. The proportion of these substances in the original monomeric mixture is a controlling factor upon the resin produced. I prefer to use more than about 70% by weight of the vinyl halide and 30% or less by weight of the vinyl ester of an aliphatic acid."

"The resin must further possess a high fusion point, low solubility, and it must be tough and uniform in regard to all of these properties."

Example I

100 parts of vinyl resin
60 parts of ground barytes*
40 parts of rottenstone**
1 part of carnauba wax
1 part of calcium stearate
1 part of lime

* barite – predominantly barite sulfate

** rottenstone – weathered siliceous limestone used as a powder

Reactivity Ratios for Free Radical Polymerization (Vinyl Chloride and Vinyl Acetate)

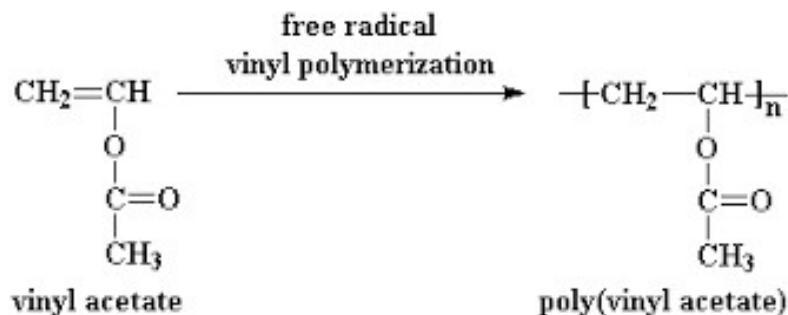
Products of Monomer Reactivity Ratios in Copolymerization

Copolymer Composition (r ₁ , r ₂)								
Monomer	r ₁	r ₂	Copolymer	r ₁	r ₂	Copolymer	r ₁	r ₂
Butadiene								
1.0			Styrene					
0.71	0.55		Vinyl Acetate					
0.30	0.34	0.39	Vinyl Chloride					
0.19	0.24	0.30	1.0	Methyl Methacrylate				
0.10	0.16	0.12	0.96	0.61	Vinylidene Chloride			
0.04	0.14	0.90	0.75	0.96	0.80	Methyl Acrylate		
0.02	0.02	0.25	0.13	0.24	0.34	0.84	Acrylonitrile	

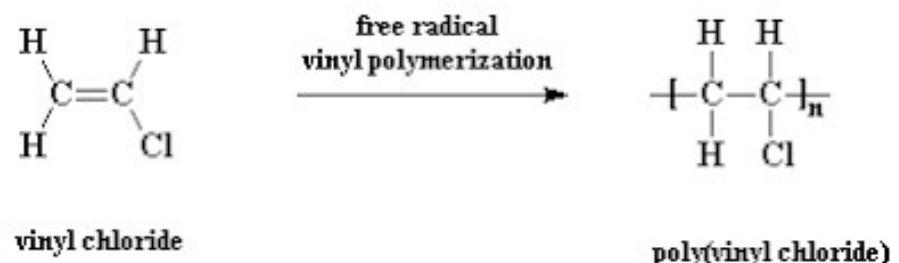
$$r_1 * r_2 = 0.39 < 1 \Rightarrow \text{Alternating Copolymer}$$

Copolymerization of Vinyl Chloride and Vinyl Acetate

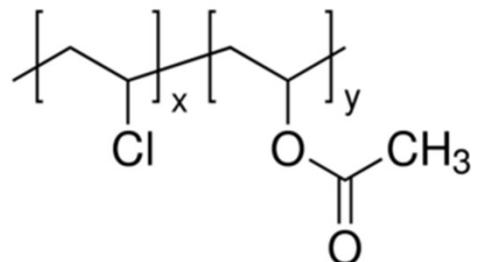
Vinyl Acetate Monomer and Homopolymer



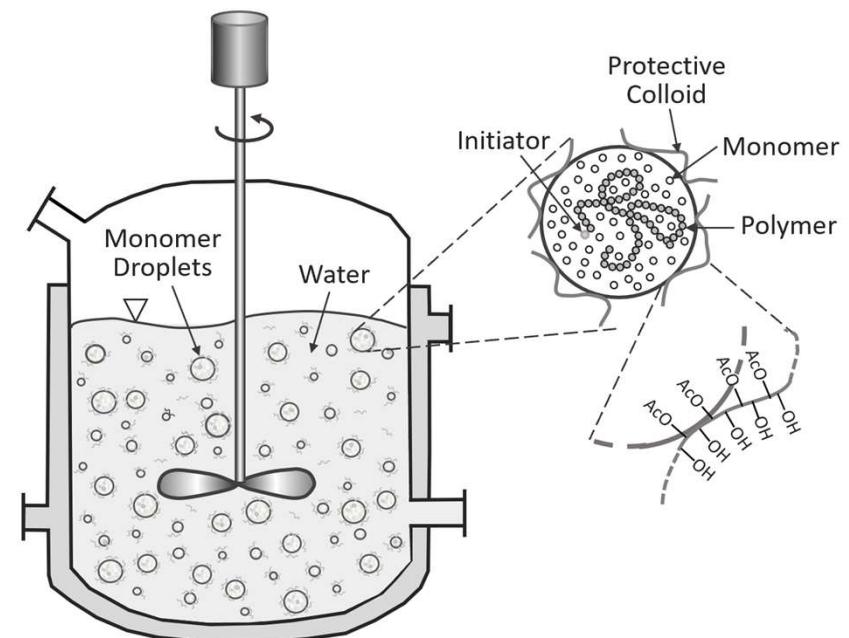
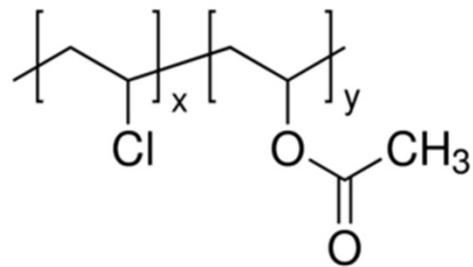
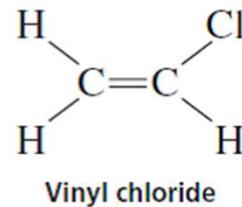
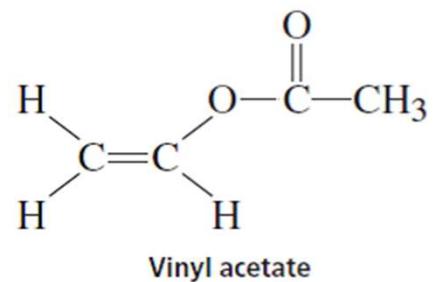
Vinyl Chloride Monomer and Homopolymer



Poly (Vinyl Chloride-co-Vinyl Acetate) Copolymer



Suspension Polymerization is the Common Process for Producing Poly(Vinyl Chloride-co-Vinyl Acetate)



Patented: October 31, 1933

US 1,932,889

United States Patent Office

US 1,932,889

RECORD

**Frazier Groff, Charleston, W. Va., assignor to
Carbide and Carbon Chemicals Corporation, a
Corporation of New York**

**Do Drawing. Application August 10, 1931
Serial No. 556,299**

I claim: -

1. A record having a reproducing surface formed from a composition containing a vinyl resin identical with that resulting from the conjoint polymerization of a vinyl halide and a vinyl ester of an aliphatic acid in the proportions of at least 70% of the vinyl halide and which is less than about 30% soluble in toluene at 20 deg to 30 deg C, said record being characterized by a low surface noise level, resistance to needle wear, slight wear on the needle, toughness, and water resistance.

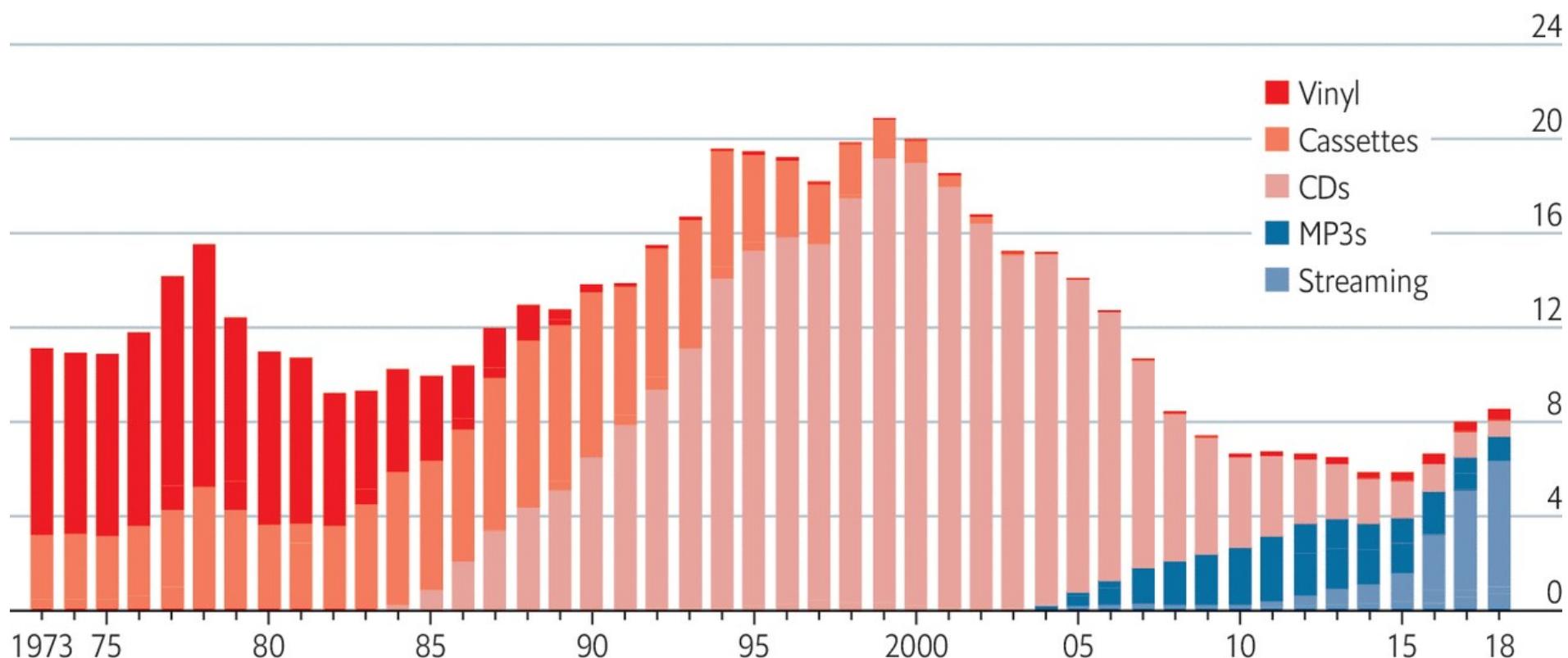


History of Voice Reproduction

- 1878 – Edison's First Recorder Patent
- 1887 – Berliner's First Patent
- 1895 – Berliner's Record Patent
- 1925 – Last Edison Cylinder Record Produced
- 1933 – First PVC (vinyl) Record Patent
- 1978 – Peak of Vinyl Record Production
- 1982 – End of 8-Track Era
- 2002 – End of Cassette Era
- 2018 – Best Buy Stopped Selling CD's
- 2020 – Vinyl Records Expected to Outsell CD's

Track records

United States, recorded-music revenues by format, 2018 \$bn



Source: Recording Industry Association of America

The Economist

Vinyl Records Outsell CDs for First Time Since 1987

Music lovers in the United States bought 41 million vinyl albums
and 33 million CDs in 2022

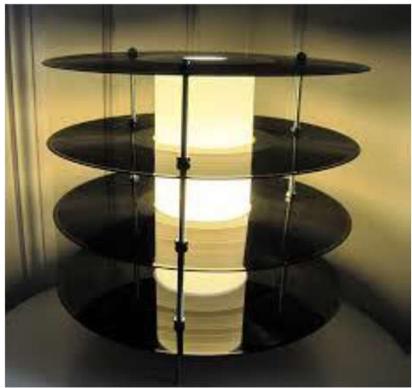
by Sarah Kuta, Smithsonian Magazine, March 16, 2023

In 2022, listeners purchased 41 million vinyl records, compared to just 33 million CDs.

Vinyl sales grew by 17 percent last year, bringing in \$1.2 billion in revenue. CDs made \$483 million, a drop of 18 percent.

Even so, both records and CDs made up only a small fraction of the music industry's revenue in 2022. **The majority—roughly 84 percent—came from streaming services, per the RIAA.**

There are Nontraditional Uses for Vinyl Records



Poly(Vinyl Chloride) is Highly Sensitive to Thermal Degradation

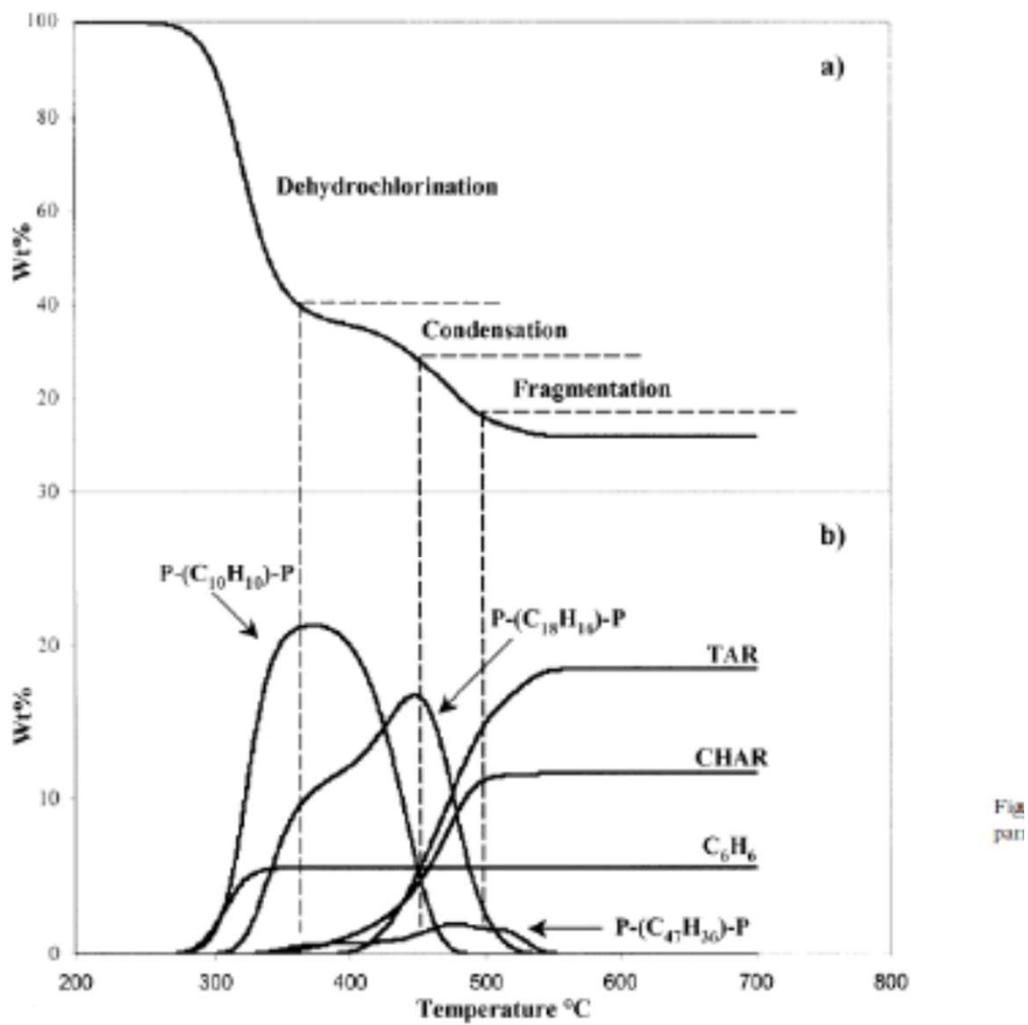


Fig. 1. Predicted dynamic TGA with a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$; panel (a) residue (wt.%) behavior and identification of the main thermal decomposition phases panel (b) benzene, PAH and char formation profiles. The TAR fraction represents the total amount of volatile aromatics.

Lesson 6: The Vinyl Chloride Family

Questions?



Dr. Andy Olah, amo5@case.edu, O: 216-368-0606, C: 216-272-0505

We all get heavier as we get older . . . because there's a lot more information in our heads.

That's my story and I'm sticking to it.