

EMAC 276

Lesson 7: The Vinyl Chloride Family; PVC, Part 2

Poly(Vinyl Chloride) - PVC

Polyvinyldine Chloride - PVDC

Chlorinated Poly(Vinyl Chloride) – CPVC

Poly (1,2 Dichloroethylene)

Andy Olah, Ph.D.

January 31, 2025

There will be a quiz on Monday, February 10th



* From the Hitchhikers Guide to the Galaxy – Douglas Adams

EMAC 276 - Homework Assignment #2

Due: Friday, February 14, 2025

Dr. Olah

During our classes we identified several common polymers that when initially discovered were described as “value-less”, “impossible to process”, “a useless mass”, etc. We also identified several methods (“tricks”) that were subsequently utilized to develop these polymers into successful products; many which are still with us today.

Your exercise is to select one polymer (either from our in-class discussion or from outside our class discussion) and describe 1) the polymer and the initial performance deficiency, 2) the action taken to overcome this deficiency, and, 3) the ensuing product(s) developed from this modification.

If you choose to use an “in class” example your maximum score will be 10.

If you choose to use an “outside the class” example your maximum score will be 12. (i.e., final score +2)

Your answer shall be short comprising between one-half to one page.

Your answer is shall be structured accordingly:

Paragraph #1: Identify and describe the polymer and it's initial deficiency **(3 Points)**

Paragraph #2: Identify the modification or “trick” which was utilized to overcome this deficiency. **(5 Points)**

Paragraph #3: Identify the commercial product or products resulting from this modification. **(2 Points)**

Poly(Vinyl Chloride) is Highly Sensitive to Thermal Degradation

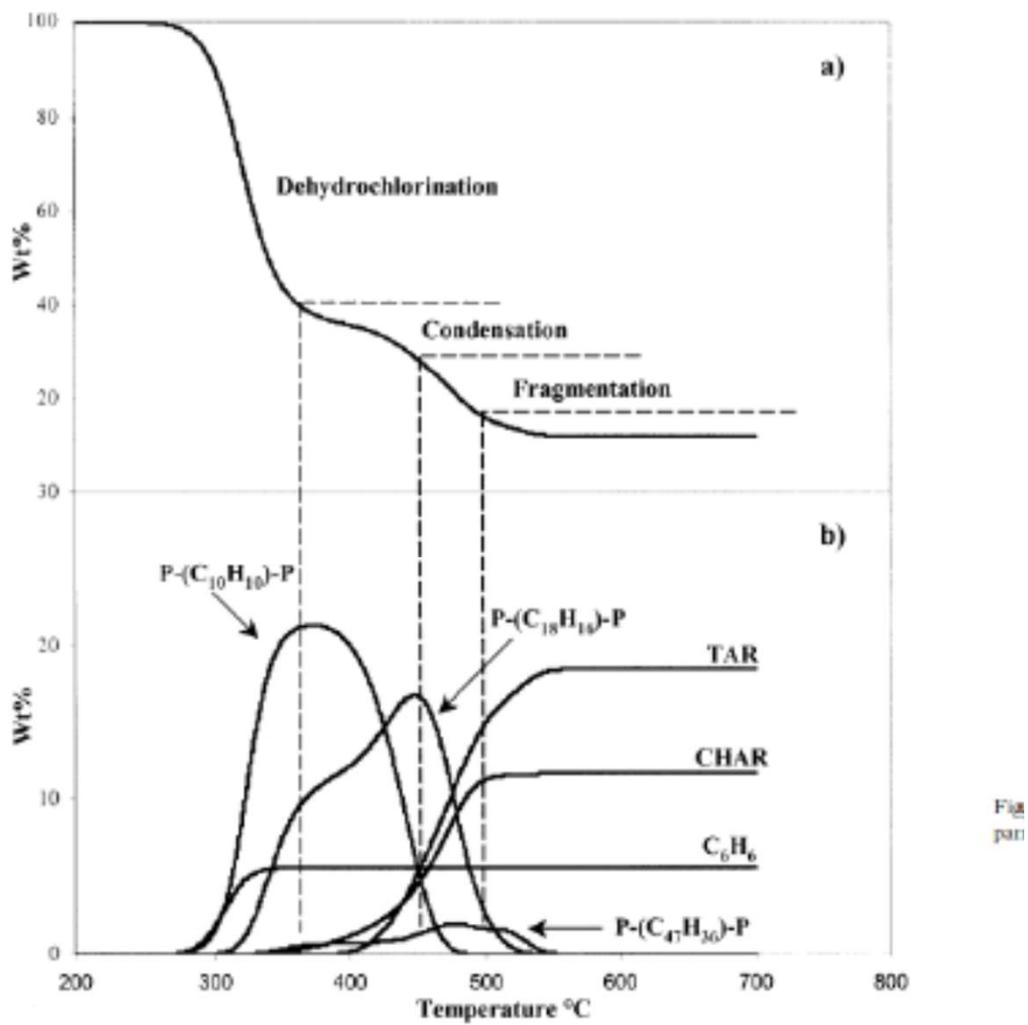
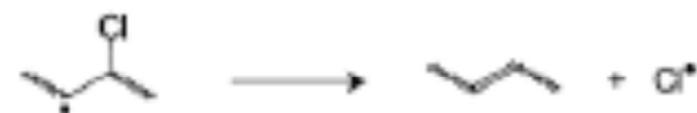


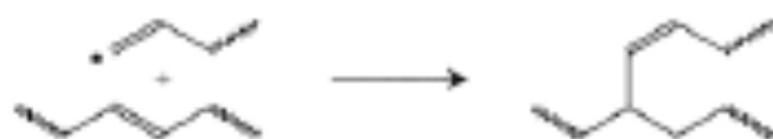
Fig. 1. Predicted dynamic TGA with a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$; panel (a) residue (wt.%) behavior and identification of the main thermal decomposition phases panel (b) benzene, PAH and char formation profiles. The TAR fraction represents the total amount of volatile aromatics.

a) Dehydrochlorination



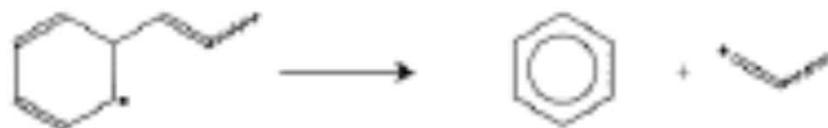
Dehydrochlorination

b) Condensation



Condensation

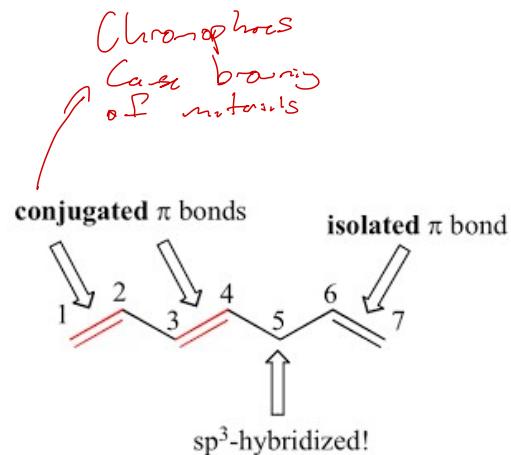
c) De-alkylation



De-alkylation

Fig. 2. Sketched mechanisms of the main radical chain propagation steps: panel (a) dehydrochlorination; panel (b) condensation; panel (c) de-alkylation.

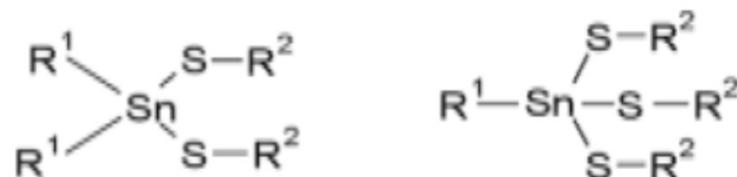
Discoloration Arising from an Increase in Conjugated Double Bonds



No.	Different PVC formulations ^c		Degradation time at 180 °C (min)									
	Ca/Na/Zn-AMMA	CaSt ₂ /ZnSt ₂	0	5	15	25	35	45	55	65	75	120
No.13	0 g	0 g										
No.14	3 g	0 g										
No.15	2 g	0 g										
No.16	1 g	0 g										
No.17	0 g	3 g										
No.18	0 g	2 g										
No.19	0 g	1 g										

^cVarious quantities Ca/Na/Zn-AMMA were added to 100 g PVC/50 g DOTP. The mass ratio of Ca-AMMA : Na-AMMA : Zn-AMMA is 45 : 3 : 2(g : g : g). The mass ratio of CaSt₂ : ZnSt₂ is 4:1(g : g).

The Most Common Stabilizers for Poly(Vinyl Chloride) are Organo-Tin Based

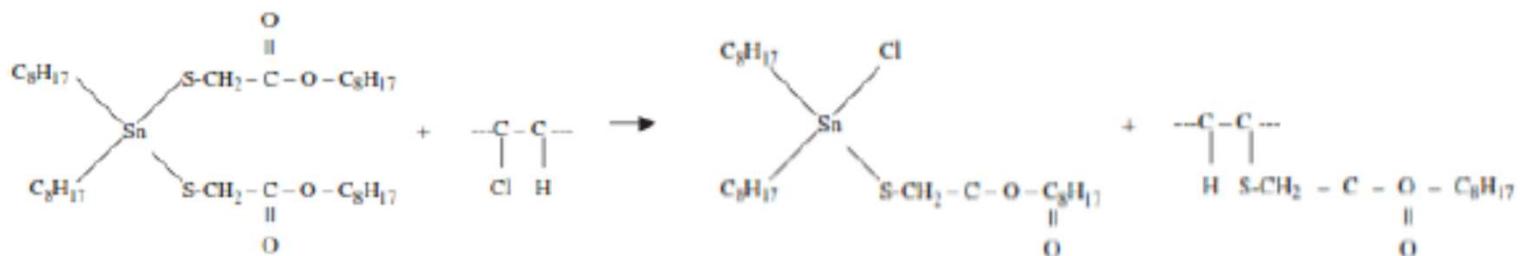


Sn- R¹ S- R²

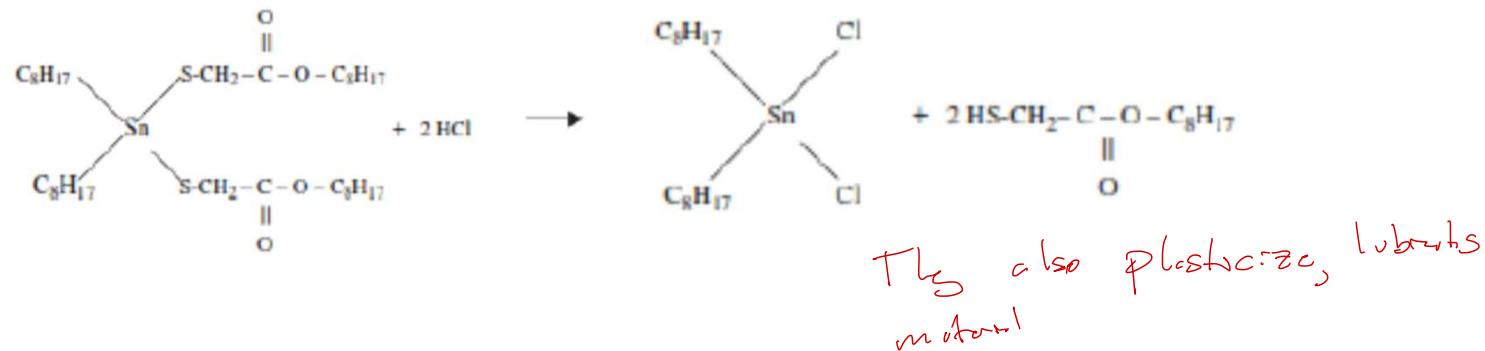
CH ₃ -/	Methyltin -S-CH ₂ -CO-O-alkyl	thioglycolates (alkyl is mostly ethylhexyl or iso-octyl)
n-C ₄ H ₉ -	Butyltin -S-CH ₂ -CH ₂ -CO-O-alkyl	mercaptopropionates
n-C ₈ H ₁₇ -	Octyltin -S-CH ₂ -CH ₂ -O- CO alkyl -S-alkyl -S-	mercaptoethanol esters (so-called reverse esters) alkylmercaptides sulfides

Tin Stabilizers are Unique Since they Perform Multiple Functions

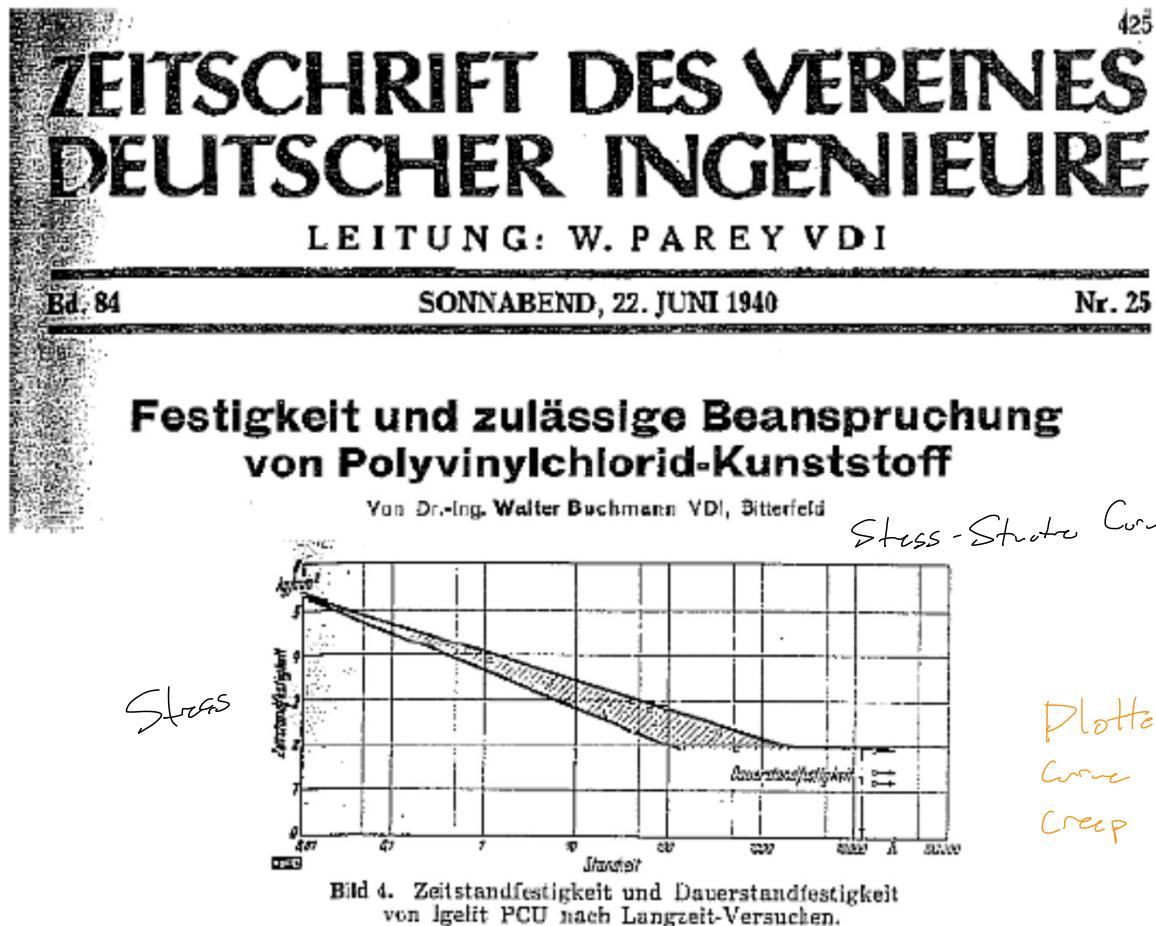
1. Labile chlorine atoms are substituted by S atoms and conjugated double bond formation is prevented:



2. HCl which is evolved as a result of PVC degradation and speeds up the conjugated double bond formation, enters into the reaction by scavenging.



Development of Rigid PVC Pipe and Fitting Compounds



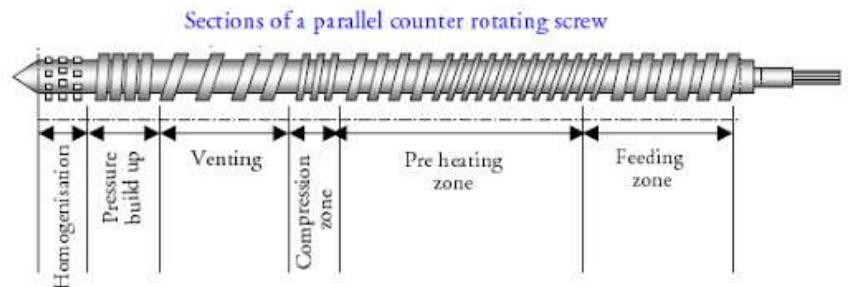
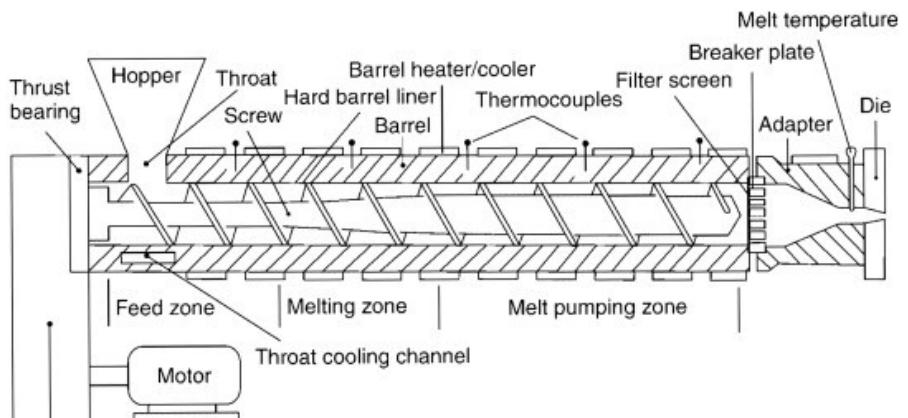
PVC pipe was first produced in Germany Between 1936 and 1939.

Plotted on log
curve today due to
Creep

T_{inc}

Compound Development and Extrusion Engineering and Design Allowed for Rigid PVC Processing

Material	PHR (Parts by weight per hundred parts of resin)
PVC resin ($k = 60$)	100.0
Stabilizer (butyl tin)	1.5
Acrylic processing aids/impact modifier	6.0 <i>\leftarrow Much higher not needed for PS</i>
Internal lubricant (calcium stearate., etc)	1.0
External lubricant (ester group)	1.2
Filler (CaCO_3)	3.0
Color pigments (metal oxides)	3.0
Chemical foaming agents (azodicarbonamide)	0.5
Recycled PVC	0.0

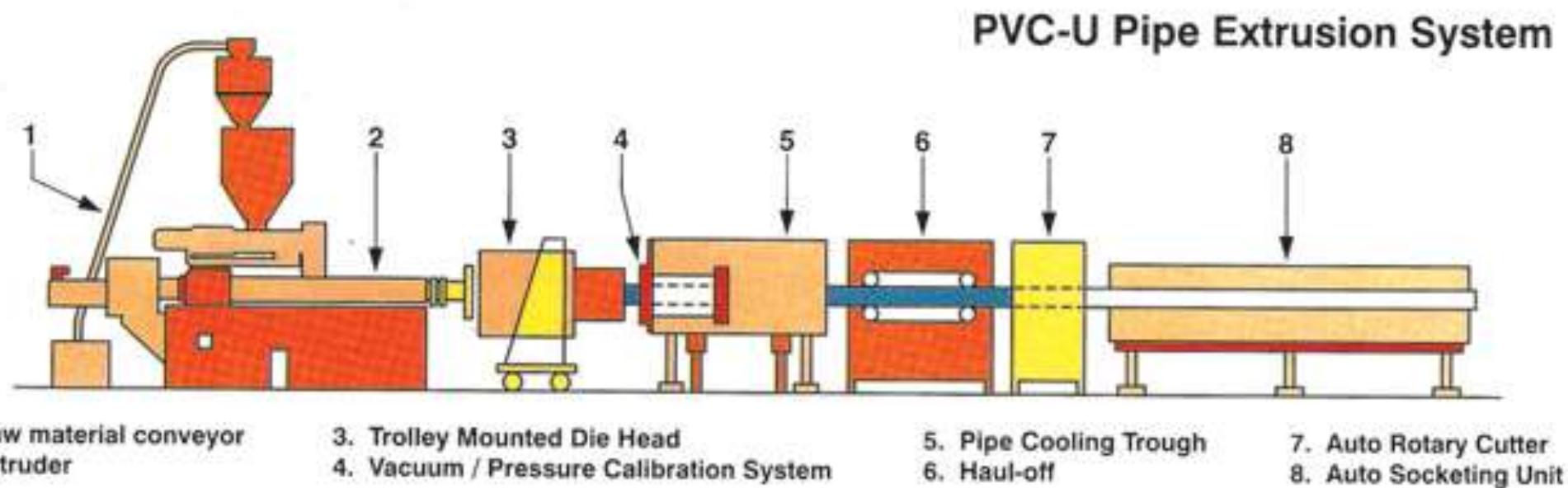


Standardization of PVC Rigid Compound - 1985

TABLE I
PPI PVC RANGE COMPOSITION FOR LISTING AT 73°F (23°C)

<u>Ingredient</u>	<u>Qualification Requirements</u>	<u>Allowable Content Range (in parts per hundred parts of resin)</u>
PVC Resin	Compliance to B.1 and Listing by PPI	100
Heat Stabilizer	Compliance to B.2 and Listing by PPI	0.3 - 1.0
Calcium Stearate	Compliance to A.2	0.4 - 1.5
Paraffin Wax	Compliance to A.3	0.6 - 1.5
Polyethylene Wax	Compliance to A.4	0.0 - 0.3
Titanium Dioxide	Compliance to A.5	0.5 - 3.0
Calcium Carbonate	Compliance to A.6	0.0 - 5.0
Process Aid	Compliance to B.2 and Listing by PPI	0.0 - 2.0
Colorant	Compliance to B.2 and Listing by PPI, or compliance to TR-3 Part D.1 Listing By PPI	See Table 9
Combination and Functional Equivalent		

Extrusion Process for PVC Pipe Manufacturing



Die Tooling Design for Plastic Pipe Manufacturing

Design Parameters

CTS Copper tube size

IPS iron pipe size

Pipe Die

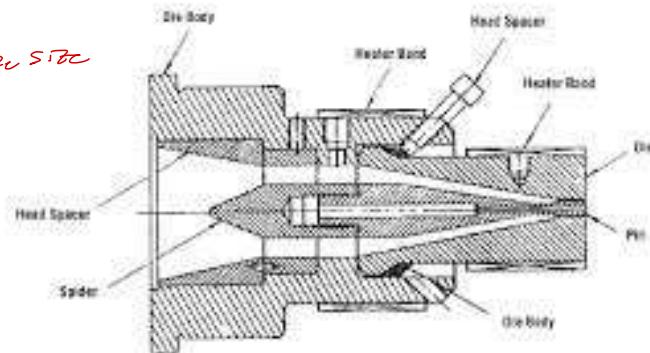
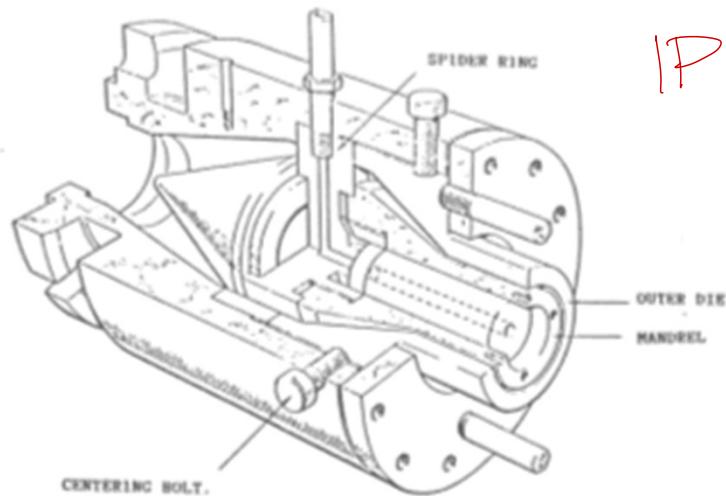
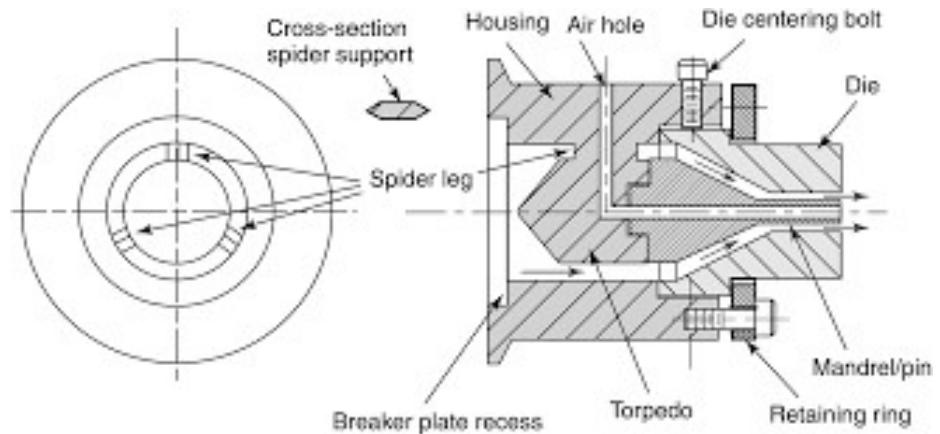
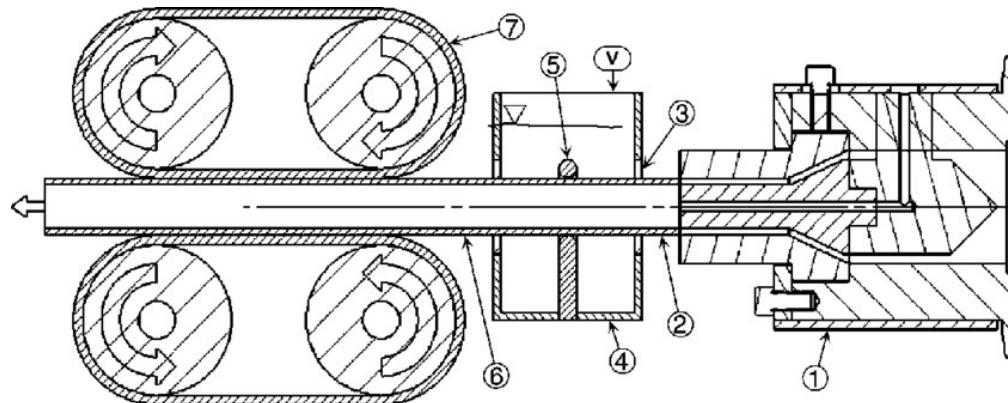


Figure 30. Pipe Die



How to Accurately Size the Pipe (OD & Wall)



Calibrators or Sizing Sleeves to accurately Specify the OD of the pipe.

Wall thickness is sized by increasing or decreasing the rate of the puller.

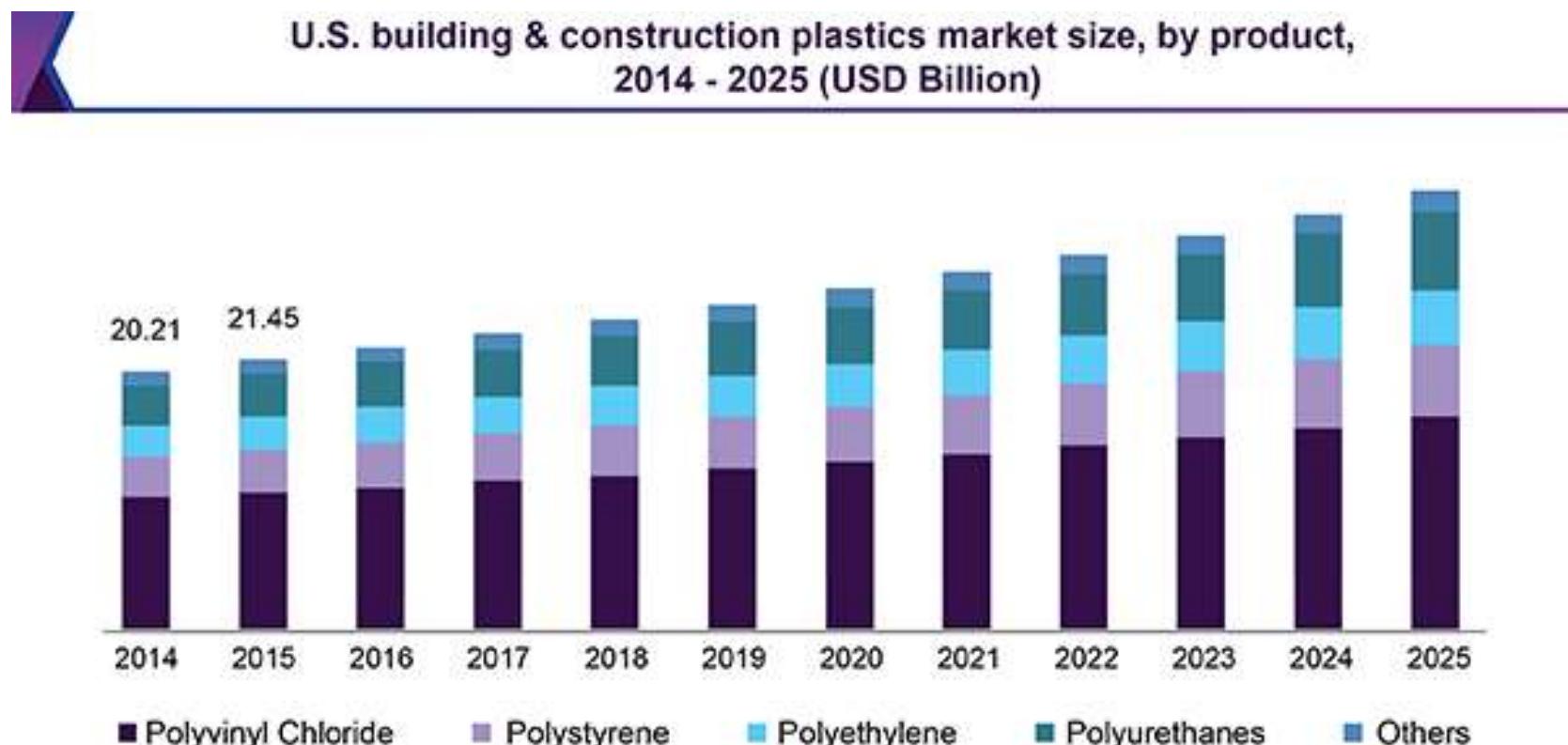
PVC Pipes are Produced in Various Sizes



The Future of PVC Pipe

The PVC pipe market is expected to reach an estimated \$51.5 billion by 2024 with a CAGR of 5.8% from 2019 to 2024. The major drivers for this **market** are growth in residential and non-residential construction activities and replacement of aging pipelines.

PVC Position in the Building and Construction Market Segment



Source: www.grandviewresearch.com

Further Development of PVC Rigid Compounds Resulted in Vinyl Siding

Patented: February 21, 1967

US 3,304,676

United States Patent Office

US 3,304,676

SIDING CONSTRUCTION

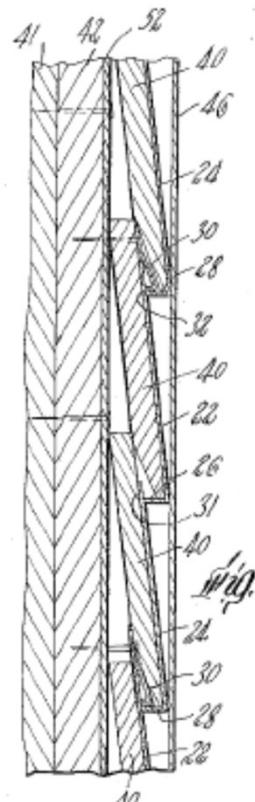
Stanley H. Sallie, Mansfield, and Norman D. Olson

Sherborn, Mass., assignors to Bird & Son, inc., East

Walpole, Mass., a corporation of Massachusetts

Filed Jan. 29, 1964, Serial No. 340,917

"To accomplish some of its objects, the invention provides a multiple paneled plastic siding unit of organic plastic material of a uniform color throughout its cross-section and its surfaces. Each siding unit is adapted to interlock with adjacent units above and below it as well."



Why was PVC Siding Originally Produced Only in Pastel Colors?



SUZANNE DECHILLO/THE NEW YORK TIMES/SHUTTERSTOCK



Double 4"



Double 5"



Double 4" Dutch Lap



Beaded



Insulated

The Problem was that Heat Distortion Occurred with Darker Colors – Both Temporary and Permanent



New Technology was Developed to Produce Dark Colors What Changed?



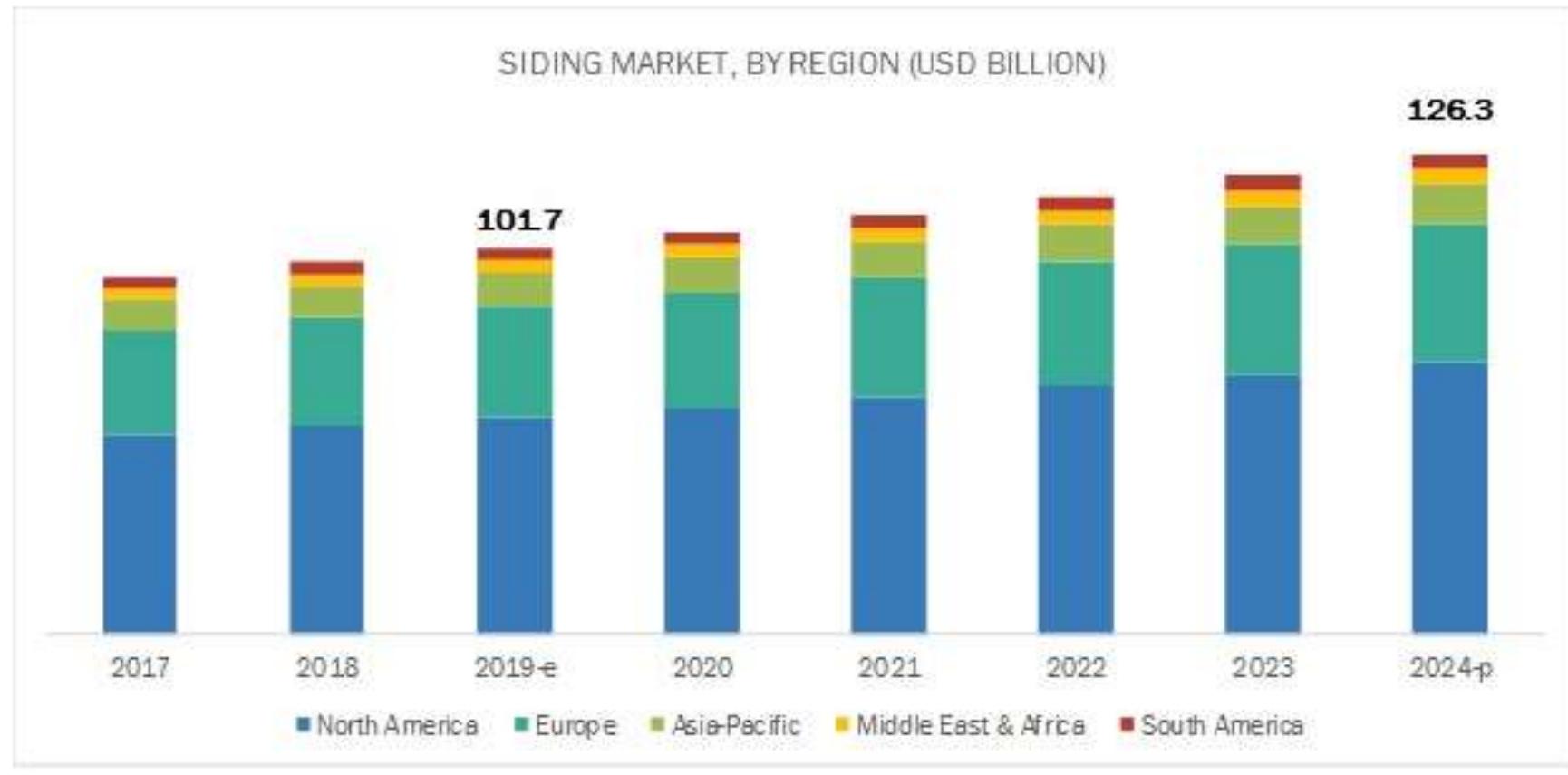
What Changed?

Several New Technologies have been Introduced:

- Profile Foam Backed Siding
 - Reinforce
 - Insulate
- Reflective Surfaces/Paint
 - Dissipation of Heat
- Use of Multilayer Profile
 - CPVC Substrate with PVC & Acrylic



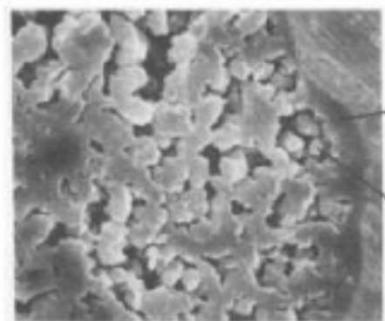
The Vinyl Siding Market Continues to Grow



Micrographs and Schematic of the Grain Structure of Poly(Vinyl Chloride)



Grain
~150 μm dia.



Skin
~2 - 5 μm thick

Primary particles
~1 μm dia.

primary particles.

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

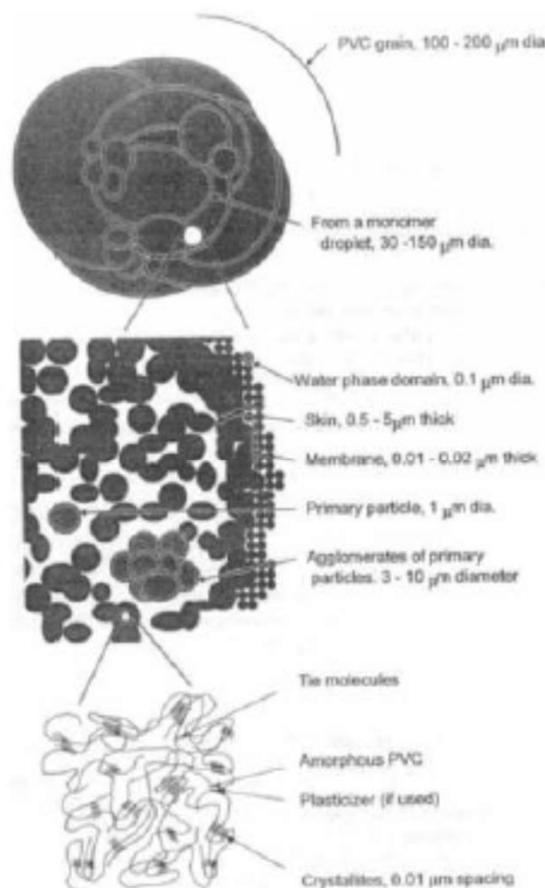


Fig. 1. The microstructure of PVC.

First Patent for Chlorinated Poly(Vinyl Chloride) CPVC

December 4, 1934

US 1,982,765

United States Patent Office

US 1,982,765

ARTIFICIAL MASS

Curt Schonburg, Bittenfeld, Germany assignor to

I. G. Farbenindustrie Aktiengesellschaft,
Frankfurt-on-the-Main, Germany

1. The process which comprises treating polymerized vinyl chloride in the presence of an organic solvent or swelling agent with chlorine.
2. The process which comprises treating polymerized vinyl chloride in the presence of a chlorinated aliphatic hydrocarbon with chlorine.
3. The process which comprises treating polymerized vinyl chlorine in the presence of an organic solvent or swelling agent with chlorine until the dried polymerization product contains 64 to 66 percent of chlorine.

Patented: November 1, 1980

US 4,412,898

United States Patent Office

US 4,412,898

**PROCESS FOR CHLORINATION OF PVC IN
WATER WITHOUT USE OF SWELLING AGENTS**

**Alan J. Olsen, Westlake, Robert G. Vielhaber, Doylestown, both of Ohio
assignor to The B.F. Goodrich Company, Akron, Ohio**

United States Patent Office

US 4,412,898

PROCESS FOR CHLORINATION OF PVC IN
WATER WITHOUT USE OF SWELLING AGENTS

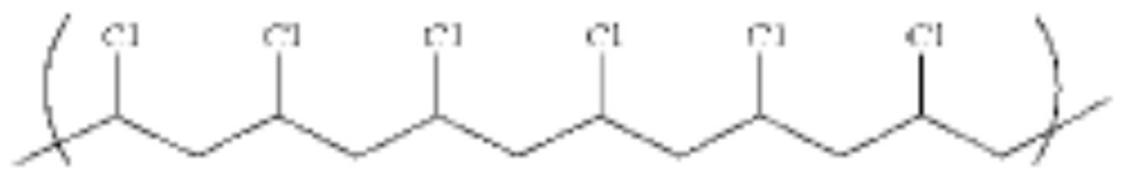
Alan J. Olsen, Westlake, Robert G. Vielhaber, Doylestown, both of Ohio
assignor to The B.F. Goodrich Company, Akron, Ohio

1. A process for producing chlorinated poly(vinyl chloride) resin having a density within the range from about 1.50 to 1.65 g/cc at 25° C., comprising:

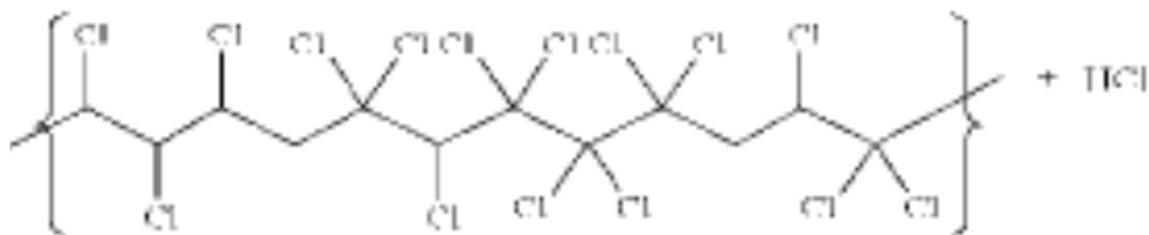
- (a) introducing an aqueous suspension of poly(vinyl chloride) containing from about 15 to about 35% by wt poly(vinyl chloride) into a reactor operable under elevated pressure;
- (b) removing essentially all oxygen from said suspension and reactor;
- (c) introducing chlorine into the reactor until the pressure therewithin is in the range from about 10 psig to about 100 psig;
- (d) soaking the poly(vinyl chloride) under said pressure for a period of from about 1 minute to about 45 minutes at a "soak" temperature in the range from about 60° C. to about 85° C.;
- (e) irradiating the poly(vinyl chloride) with ultraviolet light at a relatively high and constant intensity in the range from about 2 watts to about 50 watts per gallon of said aqueous suspension;
- (f) increasing the temperature of said suspension by at least 5° C.

- (f) increasing the temperature of said suspension by at least 5° C. autogenously from said soak temperature to a finishing temperature in the range from about 80° C. to about 120° C.;
- (g) maintaining a finishing temperature in the range from about 80° C. to about 120° C. during chlorination;
- (h) continuing to introduce chlorine into the reactor as the reaction proceeds, so that the pressure in the reactor is maintained substantially constant within said range of pressure;
- (i) stopping flow of chlorine into the reactor when sufficient chlorine has been added to produce a suspension of chlorinated poly(vinyl chloride) having said density upon completion of the reaction; and,
- (j) separating solid macrogranular chlorinated poly(vinyl chloride) from said suspension of chlorinated poly(vinyl chloride) product characterized by having a heat distortion temperature measured by ASTM Test Method D648 which is in the range from about 100° C. to about 135° C.

The Production of CPVC from PVC



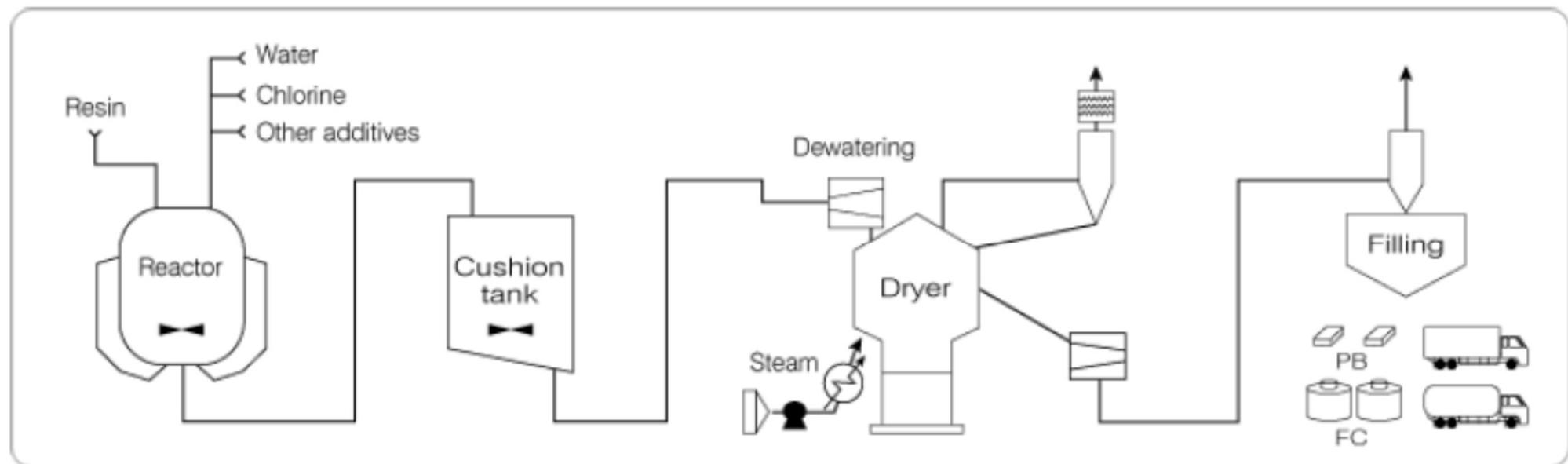
PVC Powder in a Water Slurry
Vacuum + Liquid Chlorine
Ultraviolet Light



Neutralize the HCl and Dry

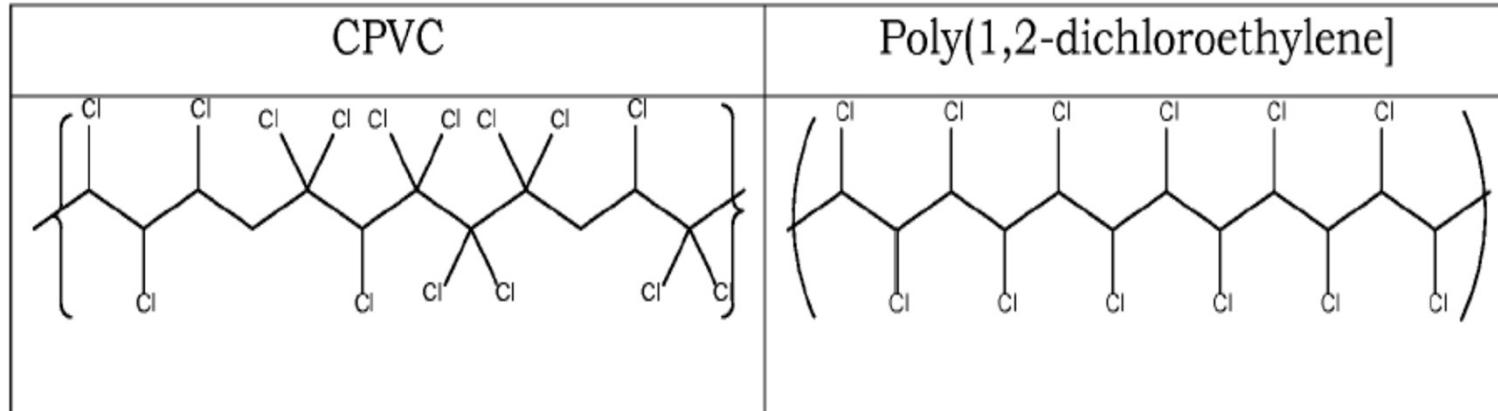
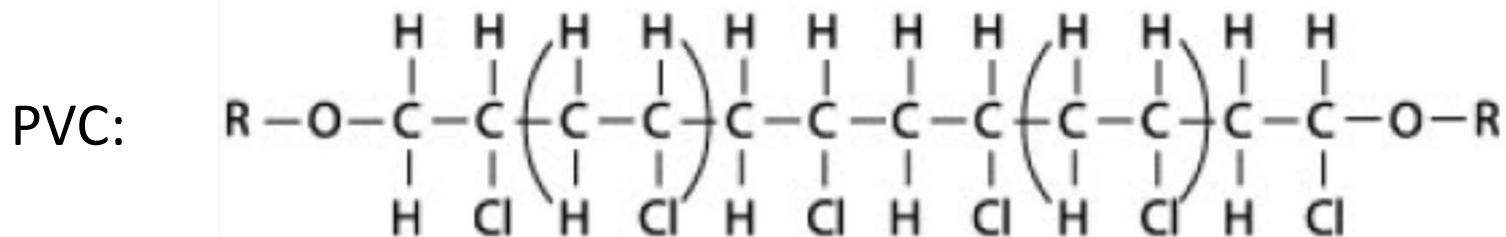
Compound

Production Scheme for Chlorinating Poly(Vinyl Chloride)



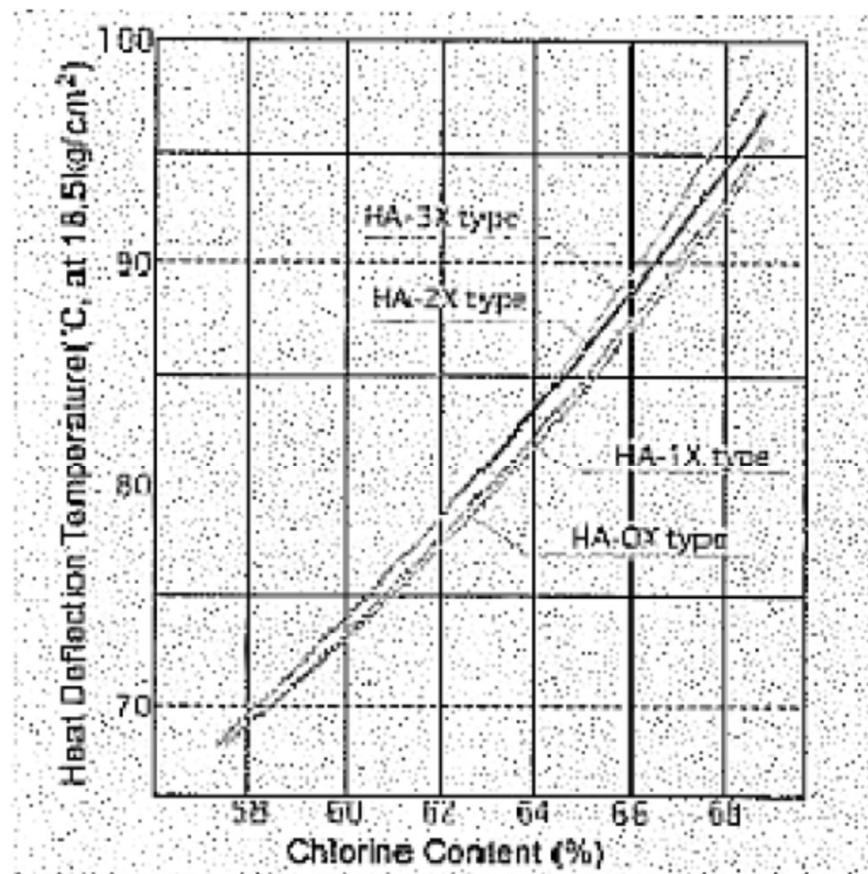
Due to the high acid level (HCl) during chlorination all reactors were titanium.

Understanding the Structure of CPVC



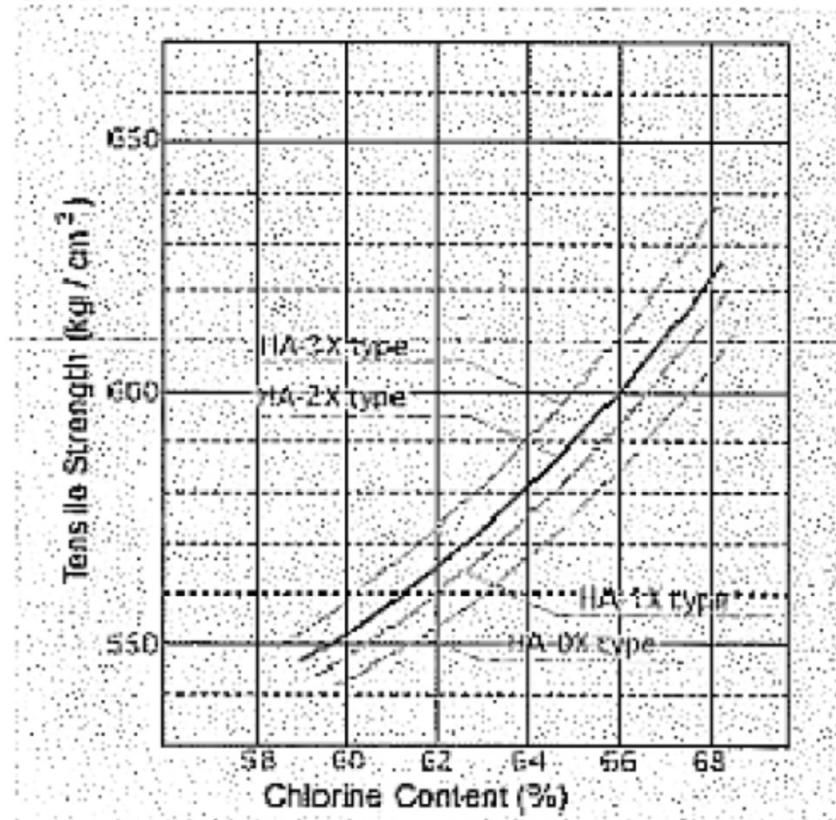
Chlorination of PVC was based on the need to approach the structure of Poly(1,2-dichloroethylene)

Influence of Chlorine Content upon the Heat Deflection Temperature of CPVC



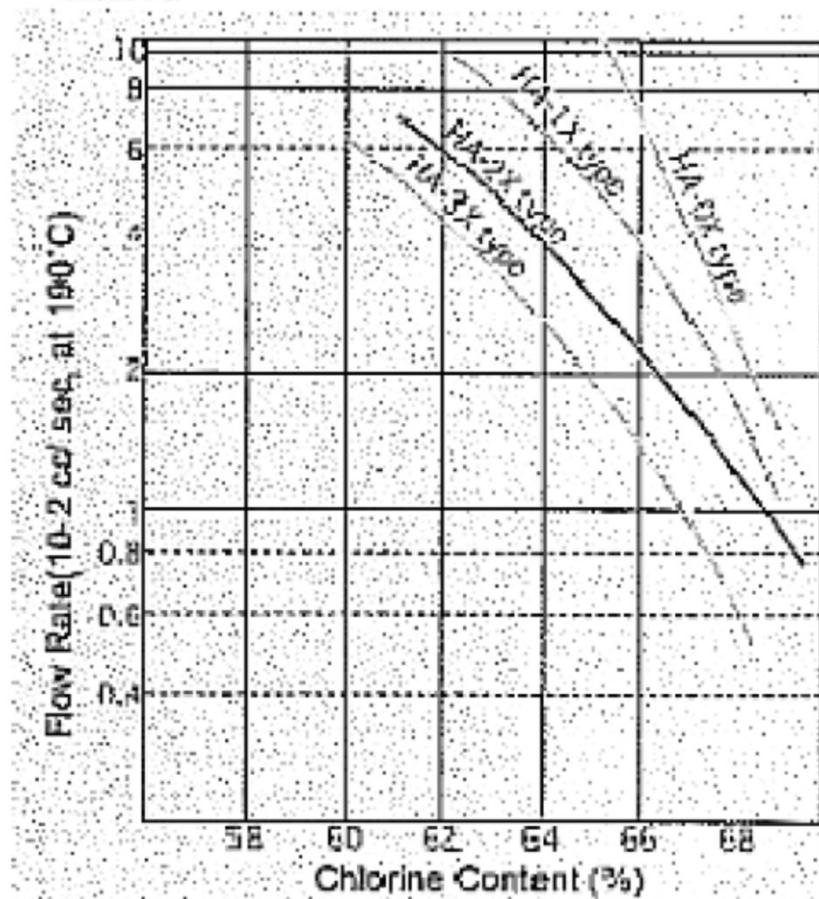
Influence of Chlorine Content upon the Tensile Strength of CPVC

Chart 3



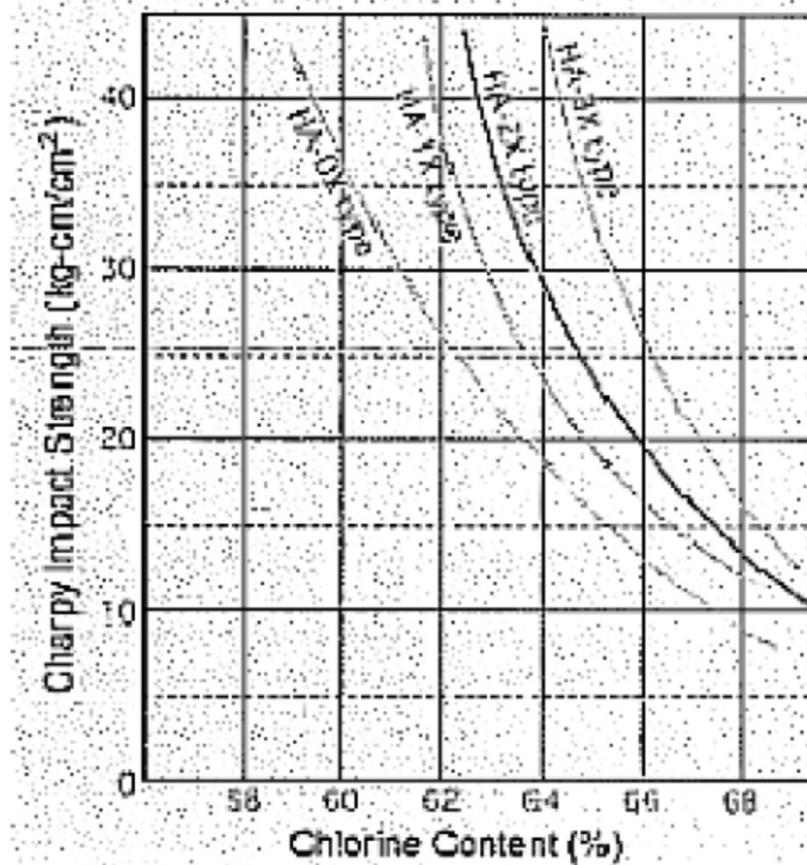
Influence of Chlorine Content upon the Flow Rate of CPVC

Chart 2



Influence of Chlorine Content upon the Charpy Impact Strength of CPVC

Chart 4



CPVC Applications are Primarily in Fluid Handling



CPVC Applications do Extend Into Higher Arenas



Why?

Discovery of Polyvinylidene Chloride Product

Ralph Wiley accidentally discovered polyvinylidene chloride in 1933. He, then, was a college student who worked part-time at Dow Chemical lab as a dishwasher. While cleaning laboratory glassware, he came across a vial he could not scrub clean. Dow made this material into a greasy, dark green film, first called "Eonite" and then "Saran".

Ralph Wiley went on to become one of Dow Chemical's research scientists and invent and develop many plastics, chemicals and production machines.

June 6, 1939

2,160,931

United States Patent Office

US 2,160,931

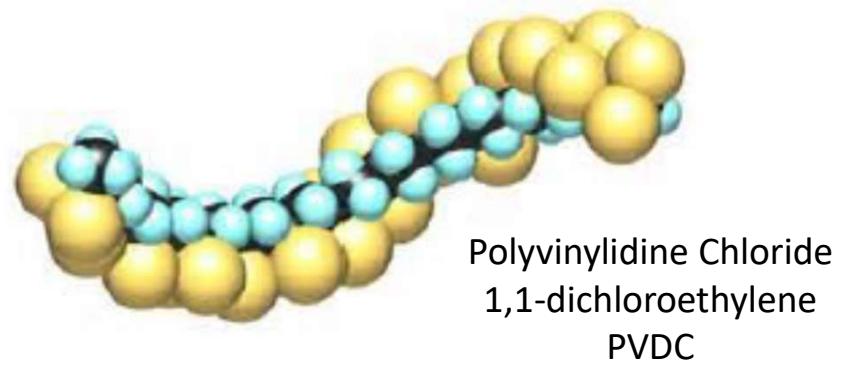
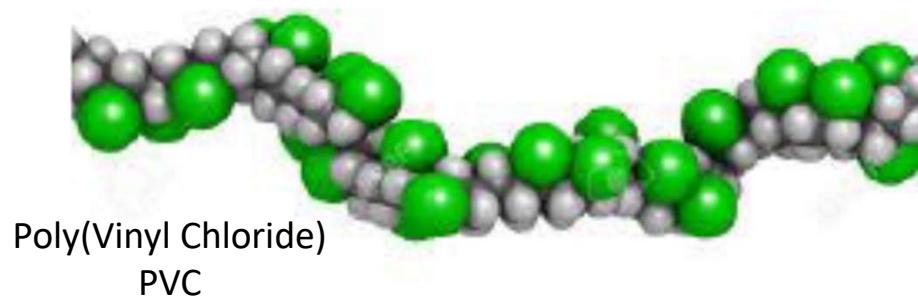
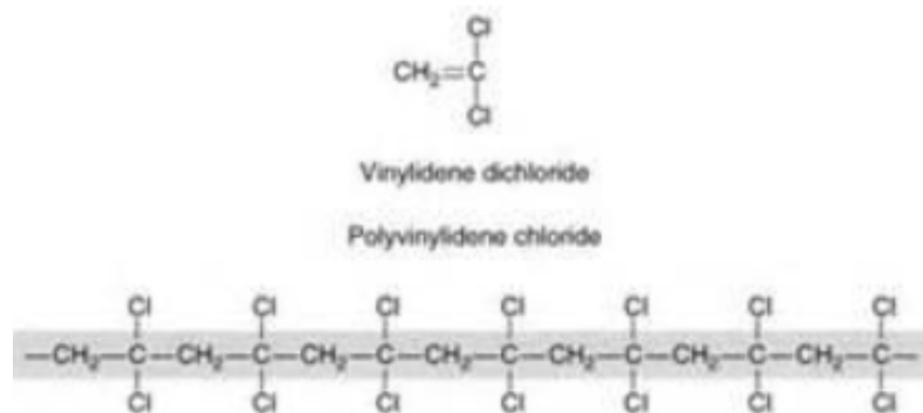
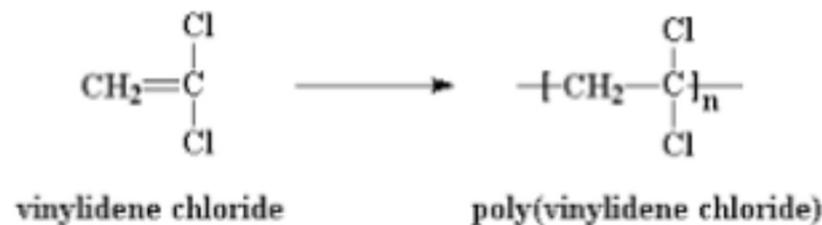
CO-POLYMERIZATION PRODUCTS

**Ralph M. Wiley, Midland, Mich., assignor to
The Dow Chemical Company, Midland, Mich.,**

Application July 1, 1934

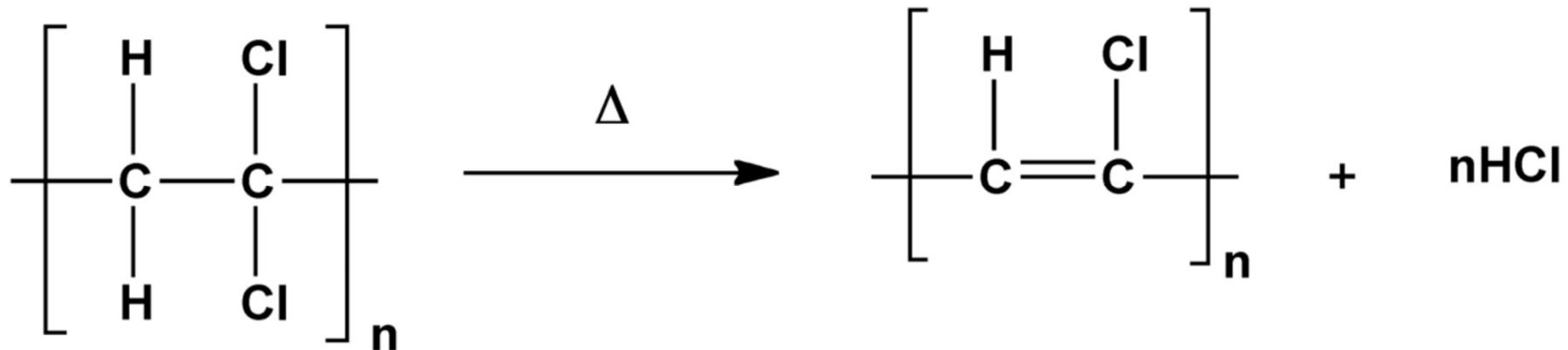
In a process for preparing a plastic, the step which consists in reacting 1,1-dichloroethylene with not more than an equal amount of vinyl chloride to produce polymeric bodies containing between about 5 and about 30 percent by weight of the vinyl chloride co-polymerized with said 1,1 dichloroethylene.

Polyvinylidene Chloride, 1,1-Dichloroethylene (PVDC)



Polyvinylidene Chloride is an Unstable Polymer

- Vinylidene chloride polymers undergo thermal decomposition in two distinct stages. The first occurs at very modest temperature ($120\text{-}160\text{ }^{\circ}\text{C}$) and corresponds to the elimination of hydrogen chloride. This initial degradation corresponds to the loss of hydrogen chloride uncomplicated by other processes.
- The dehydrogenation is a radical chain process with distinct initiation, propagation, and termination steps. Both initiation and propagation reflect first-order loss of hydrogen chloride. It is this initial degradation step that is of concern for the processing of these polymers.

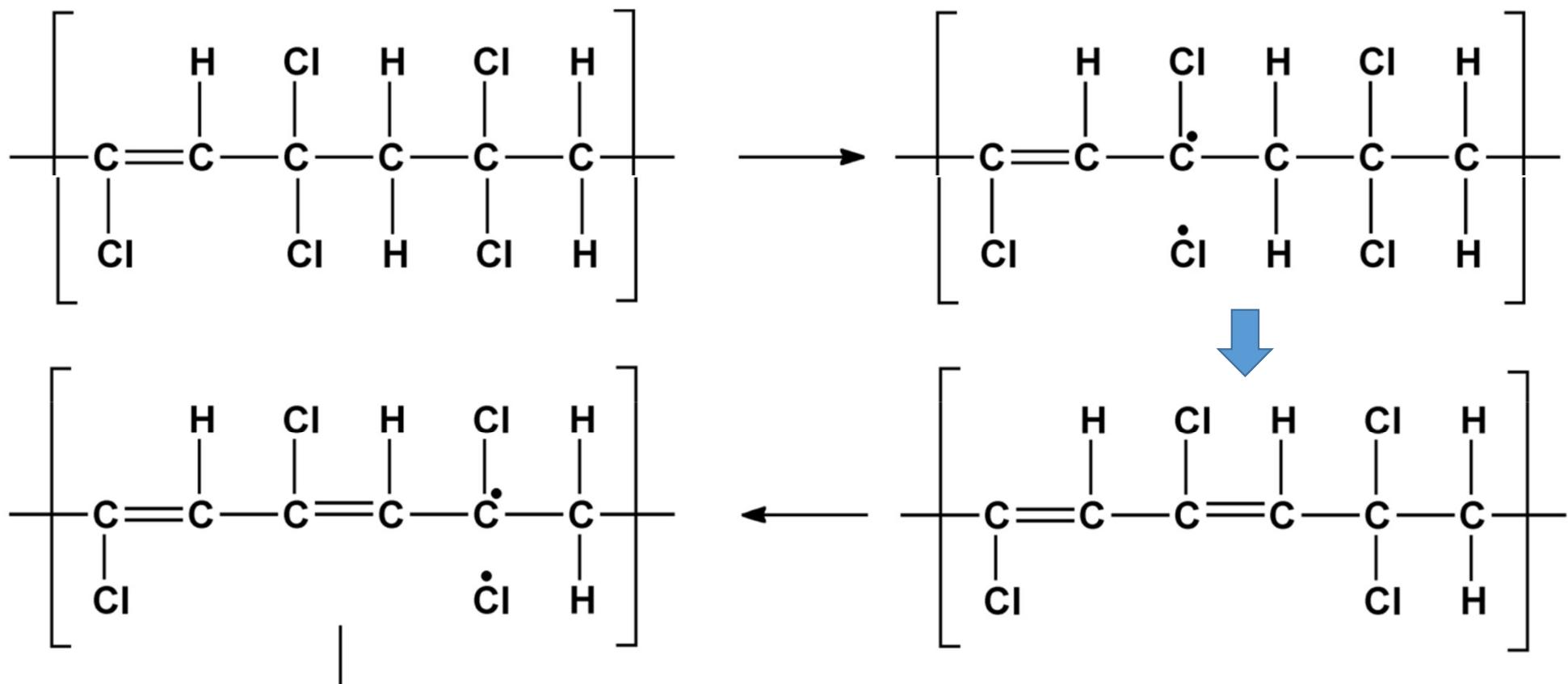


Polyvinylidene Chloride is an Unstable Polymer

- When exposed to ultraviolet light, poly(vinylidene chloride) copolymers undergo a similar release of hydrogen chloride resulting in the formation of polyene sequences in the polymer backbone. Crosslinking between polymer chains may also occur when these double bonds undergo Diels-Alder condensations. PVDC properties are therefore strongly affected by UV-treatment: it will indeed lead to coloration and an increase of the permeability and the polymer gel content. Moreover, as already mentioned previously, double bonds created by pre-treatment of PVDC by UV radiation play the role of activating sites for the polymer thermal degradation.

Polyvinylidene Chloride is an Unstable Polymer

- At higher temperatures, the unsaturated materials generated by initial degradation undergo extensive cross-linking via cycloaddition reactions to form aromatic structures and ultimately a highly porous, strongly absorptive carbon.



Reactivity Ratios for Free Radical Polymerization (1,1-Dichloroethylene and Vinyl Chloride)

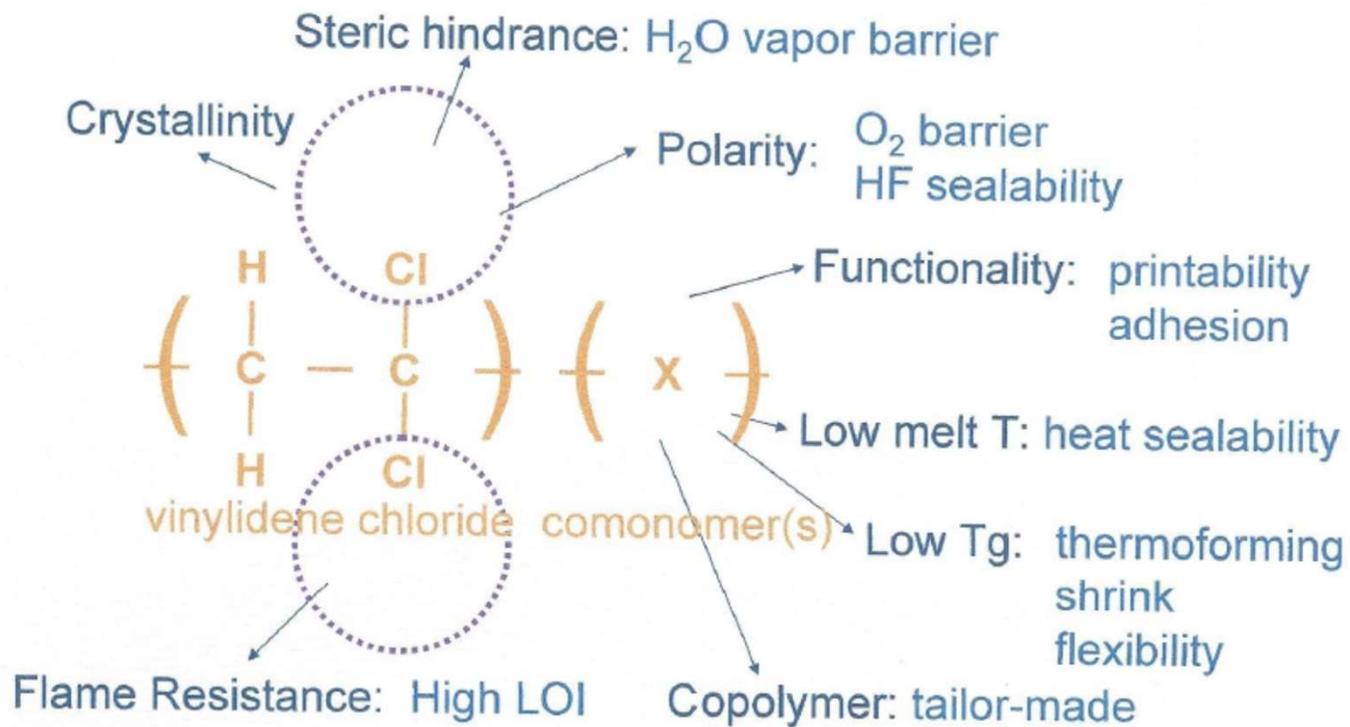
Products of Monomer Reactivity Ratios in Copolymerization

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

$r_1 * r_2 \sim 1 \Rightarrow$ Random Copolymer – A A B B B A A A B A B A A A

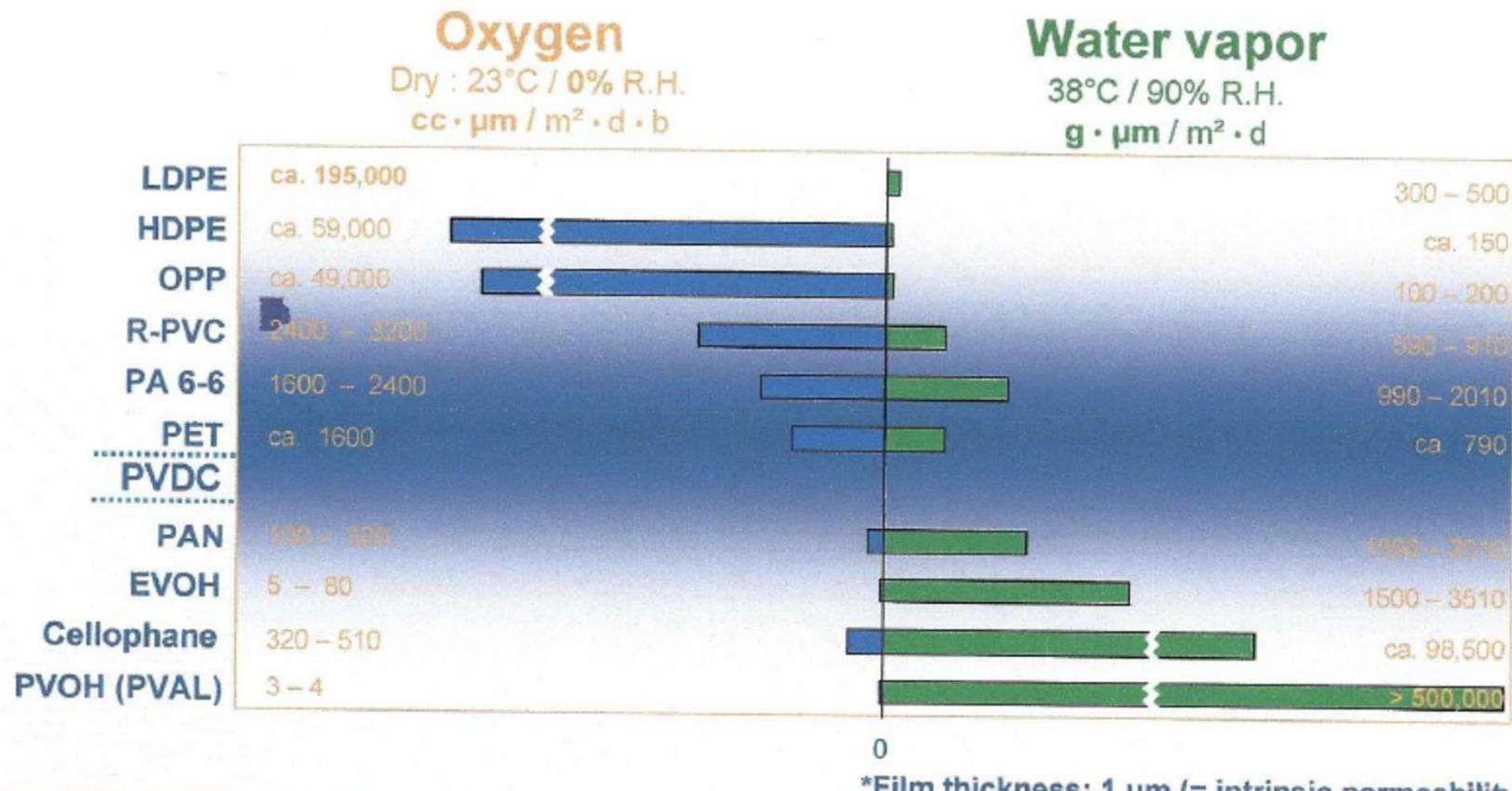
Commercial Benefits of Polyvinylidene Chloride in Packaging

What is PVDC?



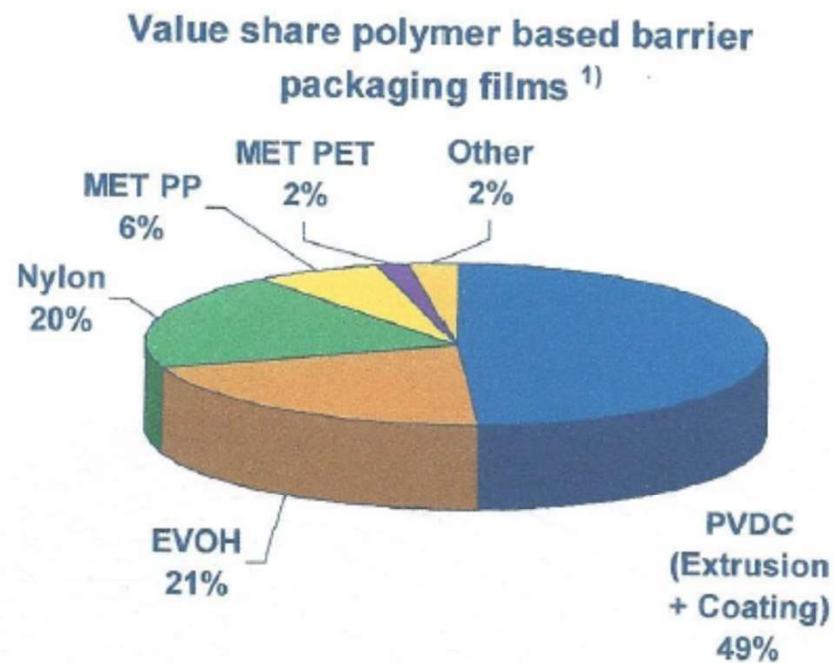
Commercial Benefits of Polyvinylidene Chloride in Packaging

Permeability of various polymers*



Commercial Benefits of Polyvinylidene Chloride in Packaging

- PVDC remains the leading barrier polymer in high performance packaging films



¹⁾ Source: [2] Kline & Company, High-Performance Barrier Packaging Films USA 2005

Commercial Benefits of Polyvinylidene Chloride in Packaging

- PVDC prevents :
 - Moisture loss or gain
 - Oxidation of ingredients
 - Aroma and odor transfer
 - Oil and fat permeation
- PVDC provides:
 - Seal integrity (heat, HF, ultrasonic)
 - Consumer appeal
 - Transparency and gloss
 - Antimist
 - Printability
 - Scratch resistance
- Regulatory compliance for direct pharmaceutical and food contact



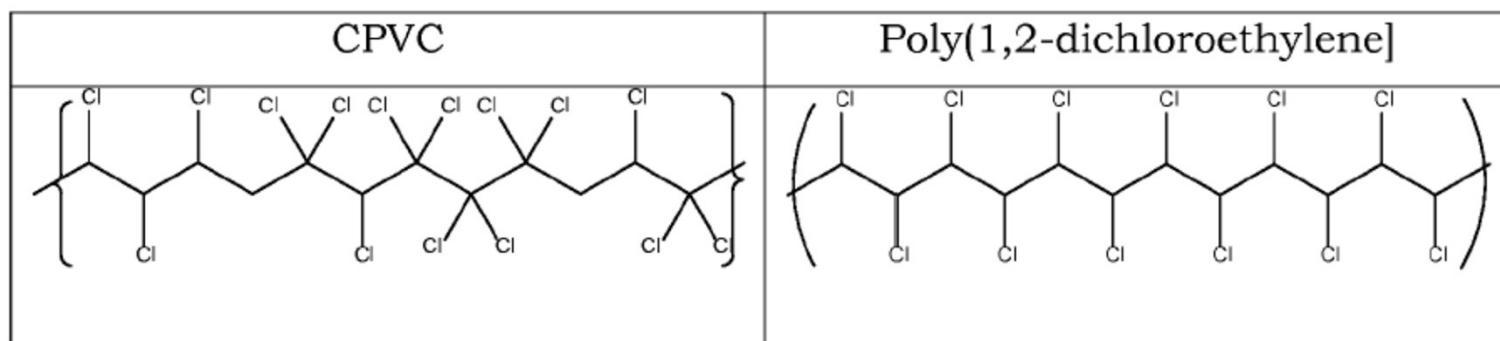
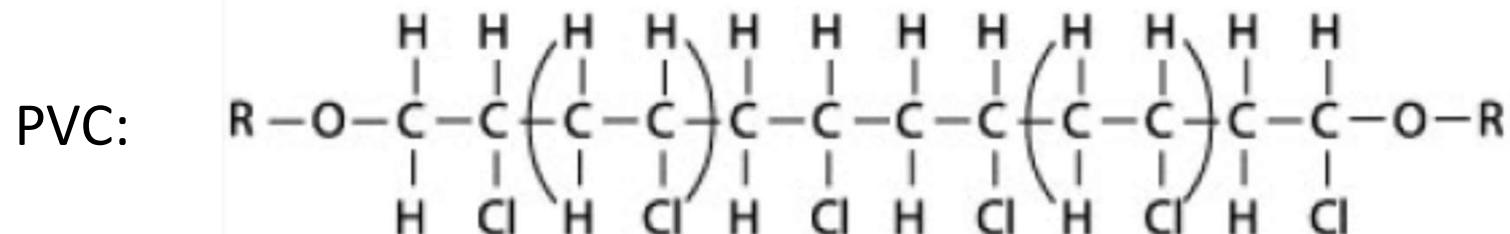
The Introduction of the Product Saran

In 1943, John Reilly (Ralph Wiley's boss) and Ralph Wiley of The Dow Chemical Co. completed the final work needed for introduction of PVDC, which had been invented in 1939.

The word "Saran" was coined by a combination of John Reilly's wife's and daughter's names, Sarah and Ann Reilly. In 1949, Dow introduced **Saran Wrap**, a thin, clingy **plastic wrap** that was sold in rolls and used primarily for **wrapping** food. It quickly became popular for preserving food items stored in the refrigerator.

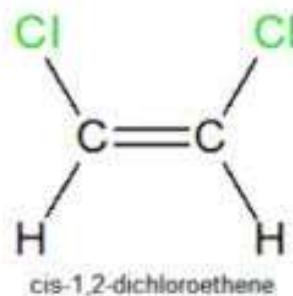
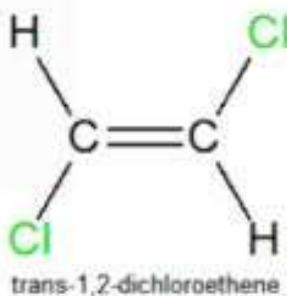


The Pursuit of Poly(1,2-dichloroethylene) Continued

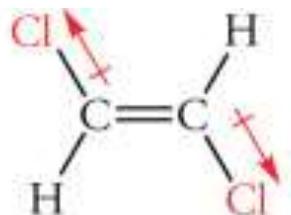


Chlorination of PVC was based on the need to obtain the structure close to Poly(1,2-dichloroethylene)

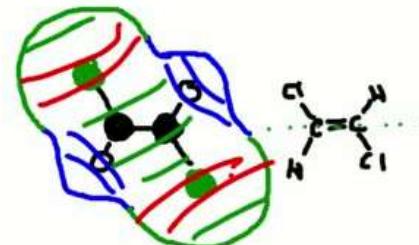
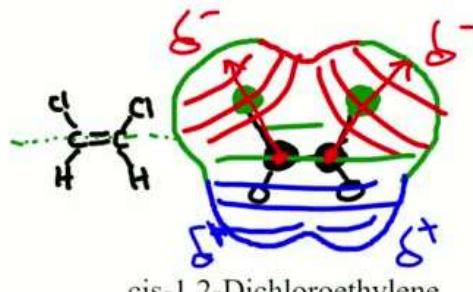
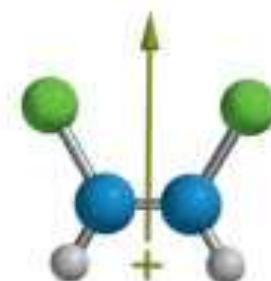
The Problem



cis-1,2-dichloroethene



trans-1,2-dichloroethene



The Four Approaches to Produce Poly(1,2-dichloroethylene) B.F. Goodrich - 1992

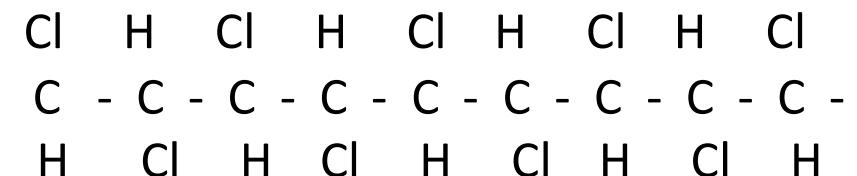
- Replicate the Dow Chemical Company Patent
US 3,367,925: 2-6-1968, Gordon Liu & **Coleman Bryan**
- High Pressure Free Radical Polymerization
Lou Cohen: BFG – Avon Lake, OH
- Metallocene Polymerization Methods – New Catalysts
Dr. Bryan Goodall: BFG – Brecksville, OH
- Novel Chlorination Method
BFG: Private Lab: Avon Lake '92–'93 & Brecksville '93 -'18

Projects to Produce Poly(1,2-dichloroethylene)

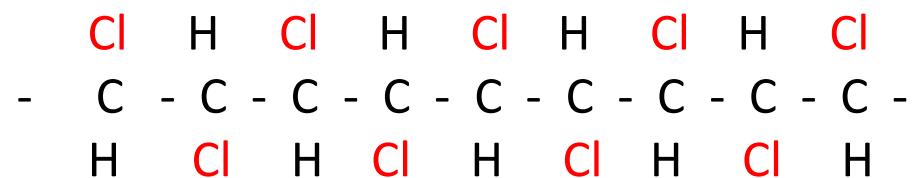
1. Replicate the Dow Chemical Company Patent
Failed to Produce Polymer
2. High Pressure Free Radical Polymerization
Failed to Produce Polymer
3. Metallocene Polymerization Methods – New Catalysts
Failed to Produce Polymer
4. Novel Chlorination Method
???????????

Novel Chlorination Method Basis

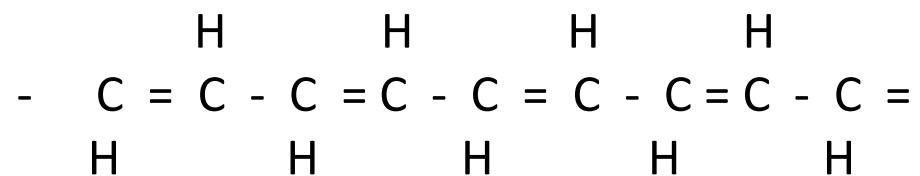
1st Draw Structure of Poly(1,2-dichloroethylene)



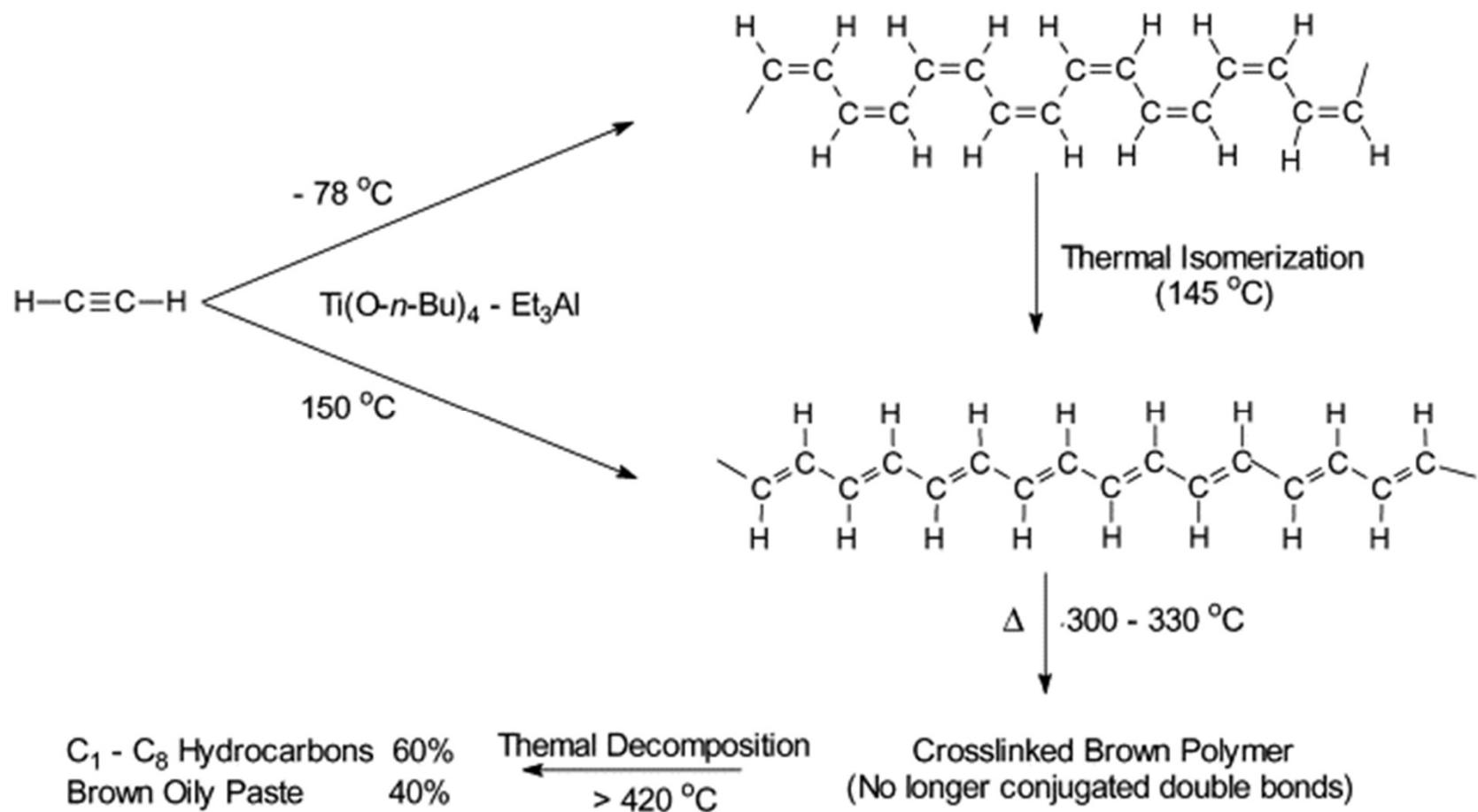
2nd Identify and Remove all Chlorines



3rd Identify Resulting Structure



Polyacetylene



Development Time-Line

- First done in 1997-98: Slurry polymerization and chlorination in an aromatic solvent.
 - Polyacetylene in slurry is a very dark (cobalt blue) slurry
 - Upon chlorination in solution changes to a white powder then clear solution.
 - Precipitates to a white powder; identified as 95% poly(1,2 DCE) w/ Tg > 200 C
 - Downside, carryover of chlorinated organic solvents.
 - Project stalled Needed to transition to gas phase.
- BFG became Noveon, Inc. (2001) – Privately held.
 - Sold project to CEO (2003)
 - Needed to develop gas phase technology
- Noveon became Lubrizol (2004)
 - Project stalled due to acquisition.
 - Resold to new CEO as a corporate funded project 2007.
 - Added new members Fields, Burrington.

(12) **United States Patent**
Fields et al.

(10) **Patent No.:** US 9,279,026 B2
(45) **Date of Patent:** Mar. 8, 2016

**POLYACETYLENE AND CHLORINATED
POLYACETYLENE AND PRODUCTION
PROCESSES THEREOF**

Applicant: **Lubrizol Advanced Materials, Inc.,**
Cleveland, OH (US)

Inventors: **Garry L. Fields**, Richfield, OH (US);
James D. Burrington, Gates Mills, OH
(US); **Andrew M. Olah**, Spencer, OH
(US)

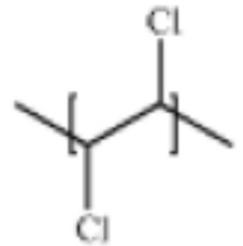
Assignee: **Lubrizol Advanced Materials, Inc.,**
Cleveland, OH (US)

Provisional application No. 61/549,370, filed on Oct.
20, 2011.

Indirect Pathway to Poly(1,2-dichloroethylene)

What is Claimed is:

1. A polymer composition comprising polyacetylene of formula $(C_2H_2)_n$ wherein n is greater than 10, and wherein the polymer composition is in the form of a granular solid.
12. Chlorinated polyacetylene (CPA) comprised primarily of repeat units equivalent to 1,2-dichloroethylene and repeat units equivalent to acetylene, wherein the CPA is in the form of a granular solid.
2. The polymer composition of claim 19 wherein the chlorinated polyacetylene exhibits an Mw as measured by GPC of at least 30,000.



Indirect Pathway to Poly(1,2-dichloroethylene)



Te□	Ex. 3	Ex. 4	Ex. 5	Ex. 6	Ex. 7	Ex. 8	Ex. 9
Wt % Cl (NMR) (CHCl/HC=CH)	70.0 11.6	68.0 7.0	68.1 7.1	69.3 9.6	68.0 7.0	67.4 6.2	66.7 5.5
Mol % CHCl	92.06	87.50%	87.65%	90.57	87.50%	86.11%	84.62%
DSC (Tg)	203.7	174.9	187.0	188.7	141.0	188.2	191.8
Rx (Al/Ti)	0.27	0.30	0.22	0.244	0.244	0.325	0.27
(Rx Temp (F.))	(90-110)	(85-105)	(78-90)	(77-120)	(77-120)	(78-83)	
Max Temp	113 F.	119 F.	93 F.	126 F.	126 F.	100 F.	
GPC							
Mw	39718	30446	67566	33791	4065	33996	69155
Mn	9661	7183	9157	7243	1911	6208	11774
M _p	9837	9093	8016	8325	2200	7003	10643
Mw/Mn	4.11	4.24	7.38	4.67	2.13	5.48	5.87

Lesson 7: PVC, CPVC, PVDC, 1,2 DCE

Questions?



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

"Just remember, once you're over the hill you begin to pick up speed."