Chem 466 Letre #17 03/25/2014

· Timplications of monomer reactivity on formation of block copolymors: eg. PMMA-6-PS-6-PMMA cannot use: Lit + = fo b/c of attack at carbonyl (a) ]  $y^{e} i^{e} = \begin{cases} \phi & \phi'' = f_{o} \\ \phi & \phi'' = f_$ (6) re Li€ Pn-1 b/c MMA carbanion reactivity is too low to instate styrene polym.

Na/naphthalene in polar solvent, p.s. 7415 (c) can use Nat > Nat + e 27 **e**ø Na⊕ 0 green fransfer (showing all e<sup>e's</sup> to leap trach of them) 0 @Nat - CH2-CH Nat : CI+- CH2 N& O. bifunctional/ 0 bidirectional dimenzation via vadical mitiator combination mitiation + propagation of styrene M-2 10 Nato Nat m-4 0 D 0 to reduce telechelic polystyrene - capable of equil. chain end hunchonalization of triblock copolymer formation Minitation + propagation of MMA 2n= =0 CH30-H termination PmmA-6-PS-6-PMMA colorless Ut-CH2 H Jn H -cH, CH Ø D paren central unit space bidrectional PMMA PMMA

How to prepare PS-6-PMMA-6-PS? 5 cannot use approach for PMMA-6-PS-6-PMMA (bidirectional growth from center of structure) Cannot polym sequentially styrene, MMA, styrene o/c Rome ( cannot pour segue ) 20 insufficient reactivity to initiate styrese polyer. . Il for both ends o consider growth from 60th ends inward + coupling to core PS-6- PMMA-core-PMMA-6-PS start nouth cougle growth start here @ bele @ here @ @ @ eg. n jer m Ko Jour let jer botta fin fe 1/2 Br~ 5N2 The for the fit tail-to-head heat to-tail remember, fire nech can see that growth begins from ends, proceeds inward + terminate, w/ compling to core anistic stops: 1) withation 2) propagation 3) terminator in enismic polym, ideally fermination occurs only when a terminator is added intentionally (reversible vs. Trevenible

Kraton Polymers - Giving Innovators Their Edge Some of the most montant anionically-polymerized wateriog are Skraton Headquarters in Howton, TX Kraton Polymers - Giving Innovators Their Edge Page 1 of 2 Ca 💻 NEWS & EVENTS OUR COMPANY PRODUCTS & SOLUTIONS INVESTOR RELATIONS INNOVATION **Driving Innovation with Pioneering** SBS Asphalt Modification P Performance. Leader. Recyclable. ExamI from 2011 Chem466





#### Techtextil North America

#### March 19-21, 2013

Dr. John Flood, Senior Scientist, at Kraton Polymers will host a technical presentation entitled, "New Durable Elastic Nonwoven Fabrics Using Styrenic Block Copolymers. " Kraton's SBC technology enables the elastic nonwoven industry to manufacture durable and semi-durable elastic nonwoven materials that mimic textiles and also provides fabrics with flexibility, softness, drape, and durability. The presentation is scheduled during the morning session, between 8:30 am - 11:15 am. The paper was written in collaboration with Seong-Ho Shin of Baiksan Lintex CO., LTD, a leading fabric manufacturer based in Korea. For more information, please contact Stephanie Earley at

stephanie.earley@ Kraton.com.





#### Brazil Road Expo Booth #132

#### March 19-21, 2013

To learn more about Highly Modified Asphalt (HiMA), a new SBS polymer technology developed by Kraton Performance Polymers for asphalt paving, please visit us at booth # 132. We are also, hosting a private technical seminar on "Next Generation in Asphalt Pavement Design" on March 20,2013 at the Transamerica Expo Center, São Paulo. For information about this event, please contact Marta Afonso at marta.afonso@kraton.com. TRADESHOW



#### IDEA 2013 Hall B Booth #1353

#### April 22-25, 2013

Through our advanced polymer technology, we enable you to successfully deliver customized solutions for adhesion, nonwovens, and performance fabrics.

Consider Kraton your global partner for innovation providing you the proven resources to grow your business. Let's work together to create breakthrough opportunities. To learn more about our products, please visit booth 1353.

#### NEWS

KRATON PERFORMANCE POLYMERS TO DISCUSS PERFORMANCE OF NEXAR™ POLYMERS IN WATER TREATMENT APPLICATIONS

 Polystyrene-b-polybutadiene-b-polystyrene triblock copolymers (abbreviated SBS, developed by Shell Oil Company and manufactured by Kraton Polymers) are high performance elastomers. They obtain their properties by phase separation of the polystyrene and polybutadiene components into nanoscopic domains, whereby the glassy polystyrene acts as physical crosslinks for the rubbery polybutadiene.

Name: ANSWER KEY

[printed]

(a) Polystyrene-b-polybutadiene-b-polystyrene can be synthesized either by sequential anionic polymerizations of styrene, butadiene and styrene followed by termination, or by sequential polymerizations of styrene and butadiene followed by coupling onto a bi-functional core. Draw the final structures that would result from each of those two techniques, represented by the following sequences of reactions (be certain to include all regiochemistries and stereochemistries for the butadiene repeat units, include brackets for the different block segments, parantheses for the copolymer segment, degrees of polymerization and chain ends): [30 points (15 pts/each)]

#### Sequential polymerization method



Kraton Performance Polymers, Inc. (NYSE: "KRA"), a leading global producer of styrenic block copolymers and other engineered polymers is pleased to announce its sponsorship and participation in the "Advances in Materials and Processes for Polymeric Membrane Mediated Water Purification," workshop sponsored by the American Chemical Society (ACS). The event will be held at the Asilomar Conference Grounds in Pacific Grove, California from February 24-27, 2013.

Read More>>

#### KRATON PERFORMANCE POLYMERS TO SHOWCASE CARIFLEX™ POLYISOPRENE PRODUCTS, THE ULTIMATE NATURAL RUBBER ALTERNATIVE, AND KRATON™ ERS POLYMERS AS PROVEN ALTERNATIVES TO PVC IN MEDICAL APPLICATIONS, MD&M WEST, ANAHEIM CONVENTION CENTER, ANAHEIM, CA FEBRUARY 12-14, 2013

Kraton product experts will be available to discuss how Cariflex polyisoprene products are the ideal alternative to natural rubber for applications that demand extreme purity, exceptional protection, comfort, and consistently high quality. Cariflex products effectively serve medical market applications including surgical gloves, catheters, tube connectors, needle shields, medical stoppers, probe covers, and cohesive bandages. They offer a pure and versatile option for manufacturing applications that require the high tensile strength and tear resistance of natural rubber without the impurities that cause discoloration, odor, and allergic reactions.

Read More>>

#### KRATON PERFORMANCE POLYMERS PUBLICIZES LATEST ADVANCEMENTS IN NEW HSBC TECHNOLOGY FOR ADHESIVES AND SEALANTS

HOUSTON, Oct. 8, 2012 /PRNewswire/ -- Kraton Performance Polymers, Inc. (NYSE: "KRA"), a leading global producer of styrenic block copolymers or "SBCs," announces plans to showcase its latest advancements in adhesives and sealants at the 2012 ASC Adhesive & Sealant Council Fall Conference & Expo from October 21-23, 2012. The company is also scheduled to present a paper on new HSBC technology on Oct. 22, 2012 from 11:15 a.m. - noon.

Read More>>

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OUR COMPANY NEWS & EVENTS

ENTS PRODUCTS & SOLUTIONS

INVESTOR RELATIONS INNOVATION



# OUR HISTORY

## Ground Breaking Innovation is What We Do Best

Innovation

History of Innovation

Achievements

## WORLDWIDE

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## FIRST DISCOVERY

Starting with the first discovery of the unique properties of anionically polymerized block copolymers in 1961 (Holden & Milkovich), Kraton Performance Polymers has supplied a continual stream of innovation, leadership, research and development and capital investment to the SBC industry for over 40 years. As the world-market leader, Kraton contributes its expertise and technology to enhance the processing and performance of hundreds of applications for everyday living, from packaging tape, to elastic components for diapers, to improved roads and roofing.

## 1960'S INVENTION AND THE FIRST MAJOR KRATON APPLICATION: FOOTWEAR

- In an attempt to increase the green strength of anionically polymerized polyisoprene in 1961, Kraton scientists discover that styrene block copolymers have unique thermoplastic and strength properties.
- In 1964, Kraton® D polymer (supplied from the pilot plant in Torrance, California) is formulated into leisure shoes which are lighter and which have improving traction compared to PVC. This launches the first major market for SBCs.
- In 1965 the first patent on unsaturated thermoplastic triblock copolymers is issued
- Kraton patents and develops the technology for hydrogenated Kraton rubber (Kraton G polymer), which increases the compatibility with polyolefins and oil for compounds while extending the UV and thermal stability of styrenic block copolymers

1970'S NEW PLANTS AND REVOLUTIONIZING PRESSURE SENSITIVE ADHESIVES

- In 1971 Kraton commercializes several Kraton D polymer grades from the new K-1 plant in Belpre, OH
- Hydrogenated diblock copolymers are commercialized as a Viscosity Index improver in motor oil and justify the construction of the first large scale Kraton G plant in Belpre, OH (1974)
- justify the construction of the first large scale kraton G plant in Belpre, OH (1974)
- Kraton launches a new hot melt pressure sensitive adhesive technology featuring SIS Kraton D polymers.
  Kraton is instrumental in forming the Tappi Hot Melt Adhesives Conference to create a forum for the industry to share hot melt adhesive technology.

## 1980'S BRINGING INNOVATION TO ROADS AND ROOFING WORLDWIDE

- Kraton D polymer is accepted globally as the preferred modifier for bitumen used in roofing products
- Kraton D polymer is added to bitumen used in roads, increasing durability and improving rutting and low temperature cracking resistance. Kraton works closely with government agencies, industry forums, and customers to develop performance specifications for modified asphalts in roads
- Functionalized block copolymers are patented and introduced in 1987 for impact modification of engineering thermoplastics
- Kraton G compounds are used in elastic components of disposable diapers to provide comfort, stretch and fit

## 1990'S SOFT TOUCH TECHNOLOGY GAINS APPEAL

- "Soft touch" compounds based on Kraton rubber catch on for all types of end-use products including grips for sporting goods, power tools and personal care items
- Kraton commercializes a series of high styrene SBS (75% styrene) for clear rigid packaging and PS-b-PB-b-PS
  polystyrene modification
- Kraton introduces a latex version of anionically polymerized polyisoprene for glove and medical applications

aqueous dispersion/emulsion

2000'S NEW INNOVATIONS, NEW GLOBAL STANDARD

- Kraton S polymer (S-I/B-S), a new product that extends the SIS polymer supply and provides unique adhesive properties, is introduced
- A new family of SEBS polymers with an enhanced rubber midblock for improved compatibility and clarity with polypropylene is commercialized. These polymers are also very unique because of low hardness and low viscosity
- Kraton offers more than 100 grades of elastomers and compounds made in 6 different plants around the world.

KRATON'S CORE VALUES

. Results

"Making it Happen... Safely!"



OUR COMPANY NEWS & EVENTS

PRODUCTS & SOLUTIONS

INVESTOR RELATIONS INNOVATION

## MEDICAL APPLICATIONS



Products & Solutions

Products by Category

Products by Market

Safety Data Sheets

#### WORLDWIDE CONTACTS

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India and SE Asia E: Joydeep.Mukerjea@kraton.com

Japan P: +81-3-5461-7430 E: info.jp@kraton.com Kraton Performance Polymers is the world's leading producer of styrenic block copolymers, or SBCs. SBCs are highly-engineered synthetic elastomers, which are used in a wide variety of products to impart clarity, flexibility, resilience, strength, durability and processability. SBCs are a fast growing subset of the broader elastomers industry. We pioneered these products over 35 years ago and offer a broad line of SBCs to customers worldwide. In addition to medical applications, our products are used in a wide variety of pplications including automotive applications, numerous consumer products (diapers, tool handles, razors), tapes, labels, packaging systems, road and roofing materials, and footwear products. We offer our customers a broad portfolio of products that includes more than 100 core commercial grades of SBCs.

Our polymers offer the following:

- USP Class VI Toxicology Requirements
- FDA Clearance
- Easy Processability
- Superior Toughness
- Clarity (pure and in blends)
- No Plasticizers

EO, EB and gamma sterilization are possible with the neat polymers. Steam sterilization is possible when the polymers are used in combination with other polymers, or in coextrusions. Grades are offered with high resilience, low compression set, good puncture and reseal properties and with no plasticizers needed.

#### COMPARATIVE PROPERTIES

Property	Kraton Polymers	PVC	
Specific Gravity g./cc	.90-1.05	1.05-1.45	
Shore A	50-80	55-75	

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C

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South America Sales and Market Development P: +55-19-3874-7270 E: imprensa@kraton.com

	Flex Modulus kpsi	0.9-4.5	0.6-1.4
	Tensile psi	850-2800	1200-2000
	Elongation %	550-850	400-500

#### **KRATON® G POLYMERS**

Kraton G polymers are SBCs with a hydrogenated midblock. They are elastic and flexible with the additional benefits of enhanced oxidation and weather resistance, higher service temperatures, and increased processing stability. They provide formulation flexibility, ease of processing in commonly used thermoplastic technology, clarity in polyolefin blends, and offer such performance benefits as softtouch, improved grip, and UV stability. SEBS, SEPS, and SEP grades are also used for sealants and high performance adhesives.

Kraton polymer grade	General use	
G1650, G1651, G1657 and G2705	Formulations Blends Compunds	
1403P, MD6459*, D2109, D2122, G2832 and MD6932 (new)*	Cast Film Molding Extrusion	
New Grades Coming Soon	Blown Film	

\*MD grades will be listed in Drug Master File upon commercialization.

#### PRODUCTS

Kraton polymers are used as alternatives to PVC in the following applications:

- Bags Sterile and Non Sterile
- Bedding Products
- Compression Devices
- Diagnostic Equipment
- Gloves
- Intravenous Products
- Medical Film
- Patient ID Bracelets
- Plastic Wrap
- Respiratory Therapy Products
- Shower Curtains
- Tubing

KRATON'S CORE VALUES



"Making it Happen... Safely!"

most significant 1,4-cis 1,2-Many possible regio-+stereo-chemistries 1, 4-trans] 5 indistinguishable least sterically trindered attack + stabilized allylic amon intermediates 4,1-015 41-trans for isoprere polym M 2 3 P Ν OT XSCH30H Joli® 01 2 lassy rubberg m 9 6-PI-6-PS glassy es. Fraton isophene styrene cat. (hydrogenation H bloche copolymens (SBCS) "un saturated the unoplastic tribbode copolymers" (eg. Kraton & products SBCs My drogenated midblock · increases compatibility of polyolefins (polyethylene, polypiopylere, etc.) + oil · andends UV + thermal stability (by removal of reactive allere groups

# Cari*flex*<sup>™</sup> Polyisoprene Products

## Pure. Strong. Soft.

The perfect balance of comfort, purity and strength in a natural rubber alternative.



- → Cariflex<sup>™</sup> polyisoprene products are the ideal alternative to natural rubber for applications that demand extreme purity, exceptional protection and consistently high quality.
- Cariflex products offer a pure and versatile option for manufacturing applications that require the high tensile strength and tear resistance of natural rubber without the impurities that cause discoloration, odor and allergic reactions.
- Available in solid rubber or latex form, Cariflex products are a clean, high-performance alternative for medical supplies, consumer products and a myriad of other industrial applications.
- When you need extreme purity, protection and performance, consider Cariflex products.

## **Products and Grades**

## Solid Rubber

- Manufactured in Belpre, Ohio
- Shipped in 25-kg bales (55 pounds)
- Available in two grades: IR0307 and IR0310

With different molecular weight distributions, each grade performs differently during processing. Your Cariflex IR sales manager can assist you in selecting the grade that is best suited to your equipment and manufacturing processes.

## **Polyisoprene Latex**

- Produced in Brazil and Japan
- Shipped in 200-liter (55 gallon)
  steel drums or 1,050-liter (275 gallon)
  IBC tote containers
- Available in two interchangeable grades: IR0401 BU (Brazil) and IR0401 SU (Japan)

## **Simply Better**

Cariflex derives its inherent purity from our simple and highly efficient polymerization process. We are the only company in the world using an anionic solution polymerization process to produce this type of synthetic rubber. To further enhance quality and ensure its stability, the latex is pasteurized before shipment.

## Compare Your Options, and Choose Cariflex<sup>™</sup> Products

Cariflex products are superior, in many respects, to both natural rubber and synthetics produced using titanium/aluminum catalysts. Commonly known as Ziegler-Natta, catalysts of this type leave higher levels of metal residue in the rubber, resulting in a yellowish color and reduced stability that must be addressed by adding substantial levels of antioxidants. Ziegler-Natta catalysts also produce a significant amount of "gel" particles that can have an adverse effect on product quality.

#### Comparison between Cariflex IR, polyisoprene produced in "Ziegler-type" process, and Natural Rubber (NR)

	Cariflex IR	Ziegler IR	NR
1,4-cis content (%w)	91	>96	>98
1,4-trans content (%w)	1.5	0.5	1.0
3,4-vinyl content (%w)	6.5	3.5	(2
Macrostructure	linear	branched	branched
Mw distribution	narrow	broad	very broad
Green strength	de low/medium	medium	high
Gel content	zero	medium	high
Ash	low 0 2	medium	high
Trace metals (ppm)	(1º70)	400-3,000 (incl. Al)	~1,000
LVN (dl/g)	6-10	2.5-4.5	6–7
Mw (kg/mol)	2,000	1,000	2,000
Mooney visc. (MU)	40-80	60-90	<120
Flow (of compound)	excellent	good	medium/good
Color	white/clear	yellow/amber	dark
Smell	very tow/tow	low/medium	variable

## Applications

## Medical

- Surgical gloves
- Catheters

when have

- Tube connectors
- Needle shields
- IV bag and medical bottle stoppers
- Cohesive bandages

## **Consumer and Industrial**

- Electronics
- Condoms
- Footwear
- Food packaging adhesives
- Paint additives
- Resins



## **Company Profile**

Cariflex<sup>™</sup> products are manufactured by Kraton Polymers, a leading global producer of engineered polymers used to enhance the performance of products that touch virtually every aspect of our lives. The original inventor of styrenic block copolymer (SBC) chemistry in the 1960s, Kraton has a history of innovation dating back almost 50 years. Used in a myriad of applications, Kraton adds utility, value and customer appeal to products ranging from adhesives and coatings, paving and roofing to personal care items, medical supplies, electronic and automotive components. Kraton offers approximately 800 products to more than 700 customers in over 60 countries worldwide. Dedicated to "Giving Innovators Their Edge," we also collaborate with manufacturers on custom solutions to specific needs.

## **Supply and Distribution**

In response to strong and growing demand for Cariflex products, we have expanded both our U.S. plant in Ohio where Cariflex polyisoprene rubber is manufactured, and our Cariflex polyisoprene latex production facility in Brazil. With significantly increased capacity and an unmatched global service network, you can be assured of secure supplies and prompt shipment anywhere in the world.

## **Global Distribution**

- Global Headquarters
- Innovation Center
- Manufacturing Facility
- Technical Service
- Customer Service



#### U.S.A. Headquarters

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For more information, please visit our website at www.kraton.com or email info@kraton.com.

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