CNSL-derived novel, property-modifying difunctional (co)monomers for commercial polymers

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Organization: CSIR-NCL, Pune
TechEx.in Case Manager: Devanshi Patel (devanshi@venturecenter.co.in)
The Opportunity

◆ Novel difunctional co-monomers from cashew nut shell liquid (CNSL) for modifying important properties of commercial engineering/specialty polymers/plastics: Global engineering plastics market ~ 90-100 b$; Volumes ~ 20-25 million tons

◆ As an example of a monomer, the global Bisphenol market is valued roughly 20 b$.

Difunctional (step-growth) monomers:
- Bisphenols
- Diacids
- Diisocyanates
- Diamines
- Diacyl hydrazides
- Dialdehydes
- Dihalides

Engineering/specialty polymers for modification:
- Aromatic polycarbonates
- Polyarylates
- Polyethersulfones
- Polyetheretherketones
- Polyetherimides
- Epoxy resins
- Polybenzoxazines
- Cyanate esters
- Bismaleimides

Properties that can be modified:
- Bound flexibilizing C-15 alkyl chain serving as an internal plasticizer (tuning of Tg)
- Solubility improvement
- Wider processing window
- Shear thinning behavior
- Mold-releasing properties
- Moisture resistance

◆ CNSL is an abundantly available and cheap raw material which is a by-product of cashew processing industry.

◆ Cost ranges between - Rs 25-35 / kg; Global availability of CNSL exceeds 4000 ktons/ annum.
Who should be interested and why?

<table>
<thead>
<tr>
<th>Who?</th>
<th>Why?</th>
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<tbody>
<tr>
<td>Manufacturers of high performance/specialty polymers</td>
<td>• Novel co-monomers offering new / improved properties</td>
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<td></td>
<td>• Increased renewable content</td>
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<td>Manufacturers of specialty chemicals from CNSL</td>
<td>• New addition to product portfolio</td>
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<td>• Higher value products</td>
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<td>Consumers of conventional petro-based RMs for products like polymers,</td>
<td>• CNSL is cheap and abundantly available renewable resource material</td>
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<td>varnishes, resins, etc and wish to explore bio-based options</td>
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<td>Already using CNSL derivatives for producing end products in various</td>
<td>• Expertise of the research group will help address this well</td>
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<td>applications, looking for improved product properties</td>
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</table>
About the Technology: Toolbox of Value Added Chemicals and Difunctional Monomers

Process technology features:

◆ A range of difunctional monomers (bisphenols, diacids, diisocyanates, diamines, diacyl hydrazides, dialdehydes, dihalides, etc.) and polymer additives are produced utilizing 3-pentadecyl phenol derived from cashew nut shell liquid (CNSL) using NCL’s technology.

◆ **Novel cost effective bisphenols:** used as difunctional monomers to synthesize various high performance polymers such as polycarbonates, polyarylates, polyethersulfones, polyetheretherketones, polyetherimides, epoxy resins, polybenzoxazines, ... etc.

◆ **Novel brominated phenoxy compounds:** precursors of monomers, high performance polymers, ...and many more

*Polym. Chem., 2014, 5, 3142-3162*
Selected Monomers

Diamine and Bisphenols

Bisphenols with ether linkage

Dialdehyde and Diacylhydrazide

Diacid

Dialdehyde
### Examples of property modifications

<table>
<thead>
<tr>
<th>Monomer</th>
<th>Polymer</th>
<th>Property for modification</th>
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<tbody>
<tr>
<td>Bisphenol</td>
<td>Aromatic polycarbonates</td>
<td>- Shear thinning behavior</td>
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<td></td>
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<td>- Mold releasing properties</td>
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<td></td>
<td></td>
<td>- Tuning of Tg</td>
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<tr>
<td></td>
<td></td>
<td>- Optical grade</td>
</tr>
<tr>
<td></td>
<td></td>
<td>- BPA replacement</td>
</tr>
<tr>
<td>Bisphenol</td>
<td>Polyarylates</td>
<td>- Processability improvement</td>
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<td></td>
<td></td>
<td>- BPA replacement</td>
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<tr>
<td>Bisphenol</td>
<td>Poly(arylene ether ether ketone)s</td>
<td>- Solubility improvement</td>
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<td></td>
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<td>- Tuning of Tg</td>
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<tr>
<td></td>
<td></td>
<td>- Applications of solution-cast films in industries such as packaging, microelectronics,</td>
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<tr>
<td></td>
<td></td>
<td>photolithography and gas separation membranes</td>
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<tr>
<td></td>
<td></td>
<td>- BPA replacement</td>
</tr>
<tr>
<td>Bisphenol</td>
<td>Epoxy resins</td>
<td>- Ease of workability due to liquid state</td>
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<tr>
<td></td>
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<td>- Improvement in ductility and impact resistance</td>
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<tr>
<td></td>
<td></td>
<td>- BPA replacement</td>
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<tr>
<td>Bisphenol</td>
<td>Polybenzoxazines</td>
<td>- Next generation thermosetting resins as replacement for epoxies</td>
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<td>Diamine</td>
<td>Polyimides</td>
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Match Maker/ Renewable Chemicals & Materials/ 9 Apr 2021/ PPW_Monomers
### Current status

#### Technology status:
- Demonstrated at lab scale (50 g-1 Kg)
- Patent protected

#### Patents:
- Priority date: as below
- Coverage: IN, US, EP
- Approved: US, EP

#### Publications:
- 18 publications (in following slide)

<table>
<thead>
<tr>
<th>Sr. No</th>
<th>Patent Title</th>
<th>Priority Date</th>
<th>Granted No</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.</td>
<td>Hydrophobically modified poly(acrylic acid) [PAA] and process of preparation thereof</td>
<td>11 Aug 2009</td>
<td>US7,572,863</td>
</tr>
<tr>
<td>5.</td>
<td>1,1-Bis(4-hydroxyphenyl)-3-alkylcyclohexanes, method for their preparation and polycarbonates prepared therefrom</td>
<td>03 July 2001</td>
<td>US6255439</td>
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*Match Maker/ Renewable Chemicals & Materials/ 9 Apr 2021/ PPW_Monomers*


Team & Organization

Lead Scientist: Dr Prakash P. Wadgaonkar
Emeritus Scientist, Polymers and Advanced Materials Laboratory, Polymer Science and Engineering Division, CSIR-NCL

Expertise:
Sustainable and Green Chemistry (Monomers and Polymers)
Controlled Polymerization Methods
New Macromolecular Architectures and Structure-Property Co-relationships
High Performance Polymers, Thermosets,
Self-Healing Polymers,
Specialty Polymer Applications

Awards/Honors:
Prof. M Santappa Award (2006);
Prof. Sukumar Maiti Award (2004);
CSIR Technology Award (2003);
Dunlop Award (1984).

PhDs Guided: 23;
RA/Post-doc's Trained: >50
Publications: 215 (h-Index: 35)
International Patents: 24

NCL is a constituent lab of the CSIR, India
Attractive models of engagement and flexible terms for IP
Publicly funded non-profit R&D lab & DSIR recognized SIRO
=> R&D project sponsors can claim tax benefits; Eligible for CSR support

Key assets and strengths
- Team strength: Strong expertise in small organic molecule (monomers) and polymer synthesis
- Well equipped wet chemistry labs and facilities for polymer synthesis (polycondensation chemistries, melt reactors, SSP reactors, anionic polymerization)
- State-of-the-art analytical facilities for characterization of polymers
- Process engineering lab, flow synthesis facilities
- Pilot plant facility: Proof-of-concept (gm scale) to Kg scale synthesis
- Track record of technology transfer and working with both Indian and multinational companies:
Next Steps

- Process optimization as per industry needs (to meet product specifications, number of process steps, etc)
- Scale-up

Seeking Industrial partners interested in:

- Licensing technology knowhow with patents
- Sponsoring further technology advancement and scale-up
- Utilizing the chemistry skills for other projects
- Collaborative development
- Licensing of patents
For more information, contact:

Devanshi Patel
devanshi@venturecenter.co.in
+91-74100-45655
5. https://www.sridevigroup.com/CNSLApplications.html#:~:text=CNSL%20is%20extensively%20used%20in,chemical%20industry%2C%20Automobile%2C%20pesticides