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Tech Transfer Hub

Council of Scientific and Industrial Research
National Chemical Laboratory

Match Maker/ Renewable Chemicals & Materials/ 9 Apr 2021

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

Lead Inventor: Dr Prakash Wadgaonkar

Organization: CSIR-NCL, Pune

TechEx.in Case Manager: Devanshi Patel (devanshi@venturecenter.co.in)

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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.

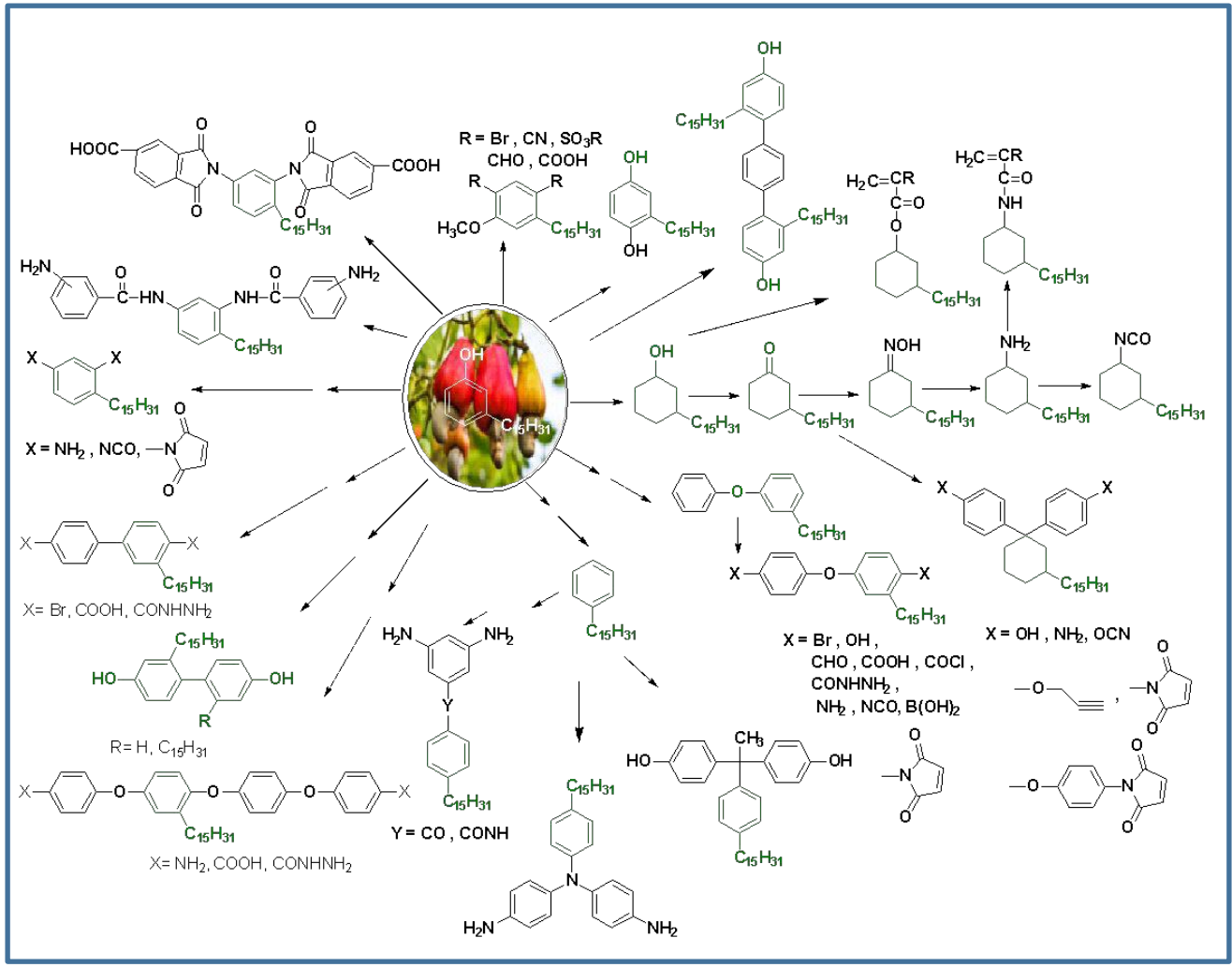
Who should be interested and why?

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

About the Technology: Toolbox of Value Added Chemicals and Difunctional Monomers

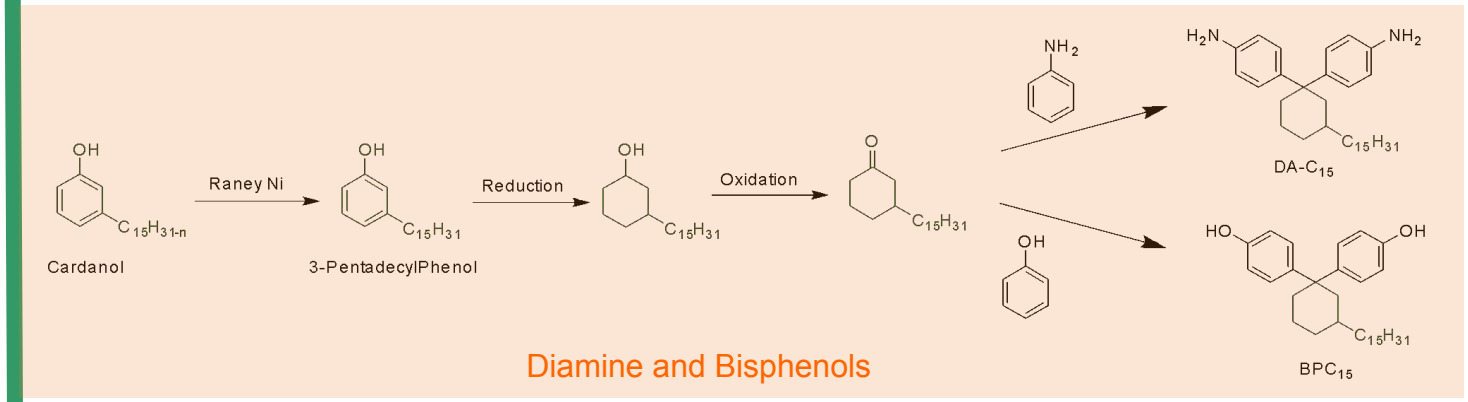
Process technology features:

- 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

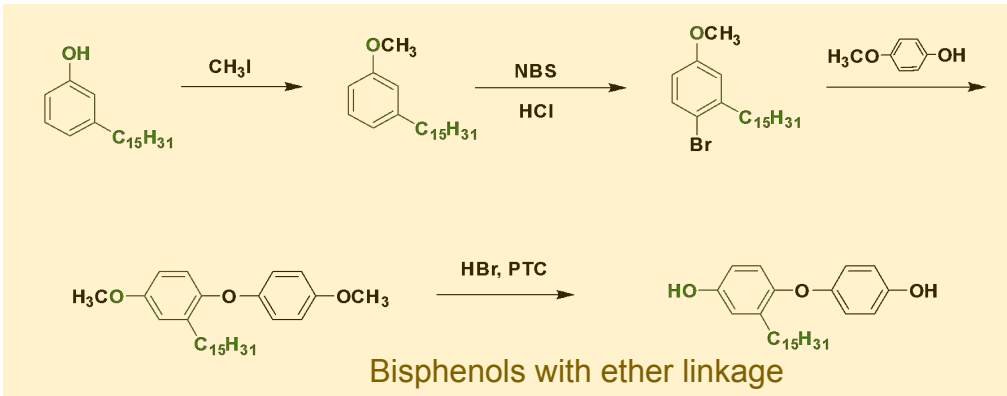


Polym. Chem., 2014, 5, 3142-3162

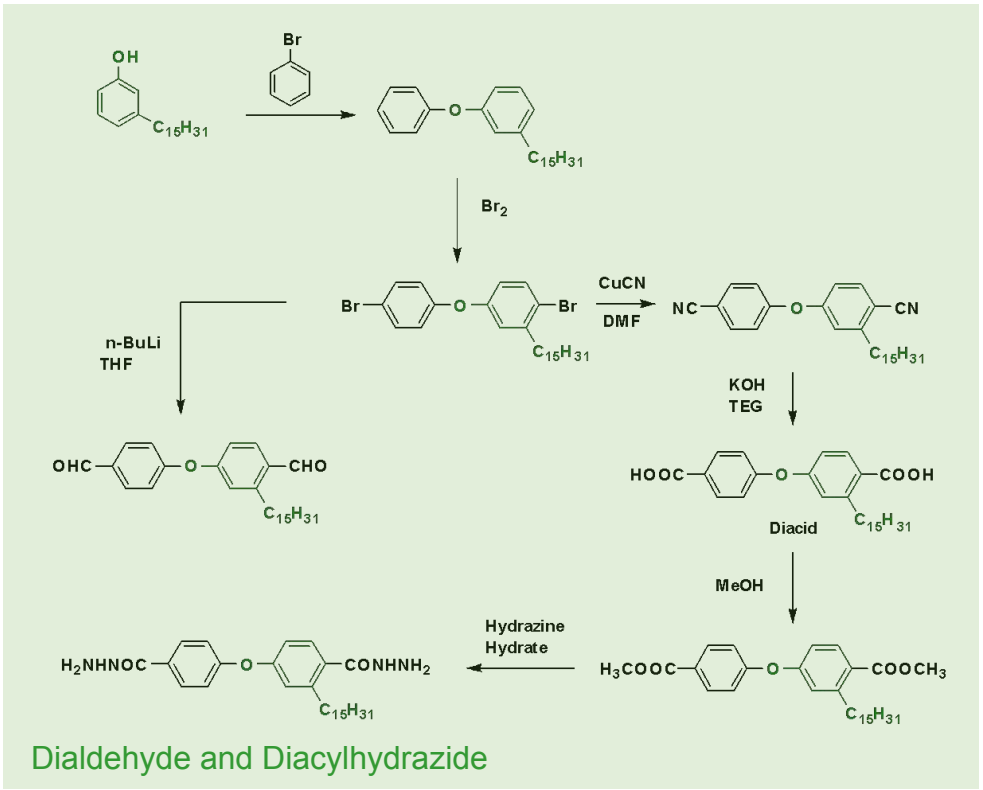
Selected Monomers



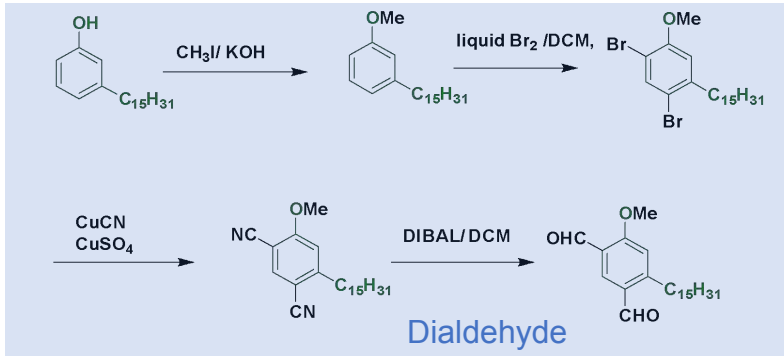
Diamine and Bisphenols



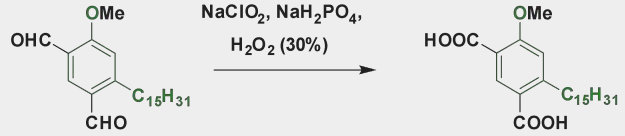
Bisphenols with ether linkage



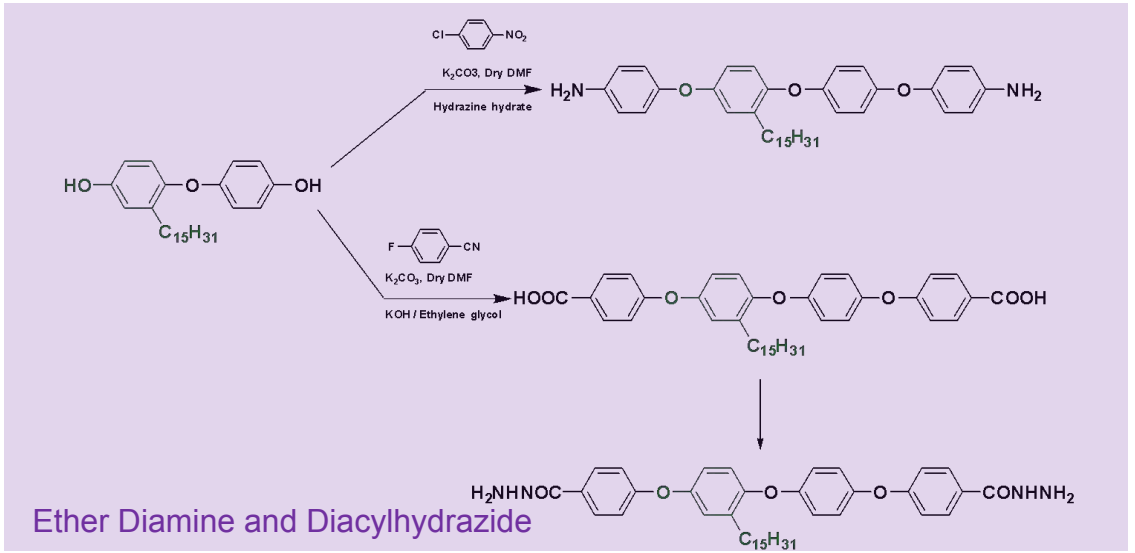
Dialdehyde and Diacylhydrazide



Dialdehyde



Diacid



Ether Diamine and Diacylhydrazide

Examples of property modifications

Monomer	Polymer	Property for modification
Bisphenol	Aromatic polycarbonates	• Shear thinning behavior • Mold releasing properties • Tuning of Tg • Optical grade • BPA replacement
Bisphenol	Polyarylates	• Processability improvement • BPA replacement
Bisphenol	Poly(arylene ether ether ketone)s	• Solubility improvement • Tuning of Tg • Applications of solution-cast films in industries such as packaging, microelectronics, photolithography and gas separation membranes • BPA replacement
Bisphenol	Epoxy resins	• Ease of workability due to liquid state • Improvement in ductility and impact resistance • BPA replacement
Bisphenol	Polybenzoxazines	• Next generation thermosetting resins as replacement for epoxies • BPA replacement
Diamine	Polyimides	• Solubility improvement • Tuning of Tg • Applications of solution-cast films in industries such as packaging, microelectronics, LC display devices, photolithography and gas separation membranes

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)

Sr .No	Patent Title	Priority Date	Granted No
1.	Synthesis of disuphonic acids starting from cashew nut shell liquid (CNSL): crosslinking catalysts for silane functionalized polyolefins	05 Dec 2011	IN313504 , WO2013084248 A1, US9133089, EP2788319
2.	Hydrophobically modified poly(acrylic acid) [PAA] and process of preparation thereof	11 Aug 2009	US7,572,863
3.	Bisphenol compound and process for preparation thereof	04 Nov 2008	US7,446,234
4.	1-Bromo-4-(4'-bromophenoxy)-2-pentadecyl benzene and preparation thereof	20 Nov 2007	US7,297,822
5.	1,1-Bis(4-hydroxyphenyl)-3-alkylcyclohexanes, method for their preparation and polycarbonates prepared therefrom	03 July 2001	US6255439
6.	Antistatic and antidust agents, compositions thereof, and methods of manufacture	11 Jan 2005	US6841598

Publications

1. More AS, Patil AS, Wadgaonkar PP (2010) **Poly(amideimide)s containing pendant pentadecyl chains: synthesis and characterization**. Polym Degrad Stab 95:837–844. Link
2. More AS, Sane PS, Patil AS, Wadgaonkar PP (2010) **Synthesis and characterization of aromatic polyazomethines bearing pendant pentadecyl chains**. Polym Degrad Stab 95:1727–1735. Link
3. More AS, Menon SK, Wadgaonkar PP (2012) **New poly(1,3,4-oxadiazole)s bearing pen-tadecyl side chains: synthesis and characterization**. J Appl Polym Sci 124:1281–1289. Link
4. More AS, Naik PV, Kumbhar KP, Wadgaonkar PP (2010) **Synthesis and characterization of polyesters based on 1,1,1-[bis(4-hydroxyphenyl)-4′-pentadecylphenyl]ethane.** Polym Int, 59:1408–1414. Link
5. More AS, Pasale SK, Wadgaonkar PP (2010) **Synthesis and characterization of poly-amides containing pendant pentadecyl chains.** Eur Polym J 46:557–567. Link
6. More AS, Pasale SK, Honkhambe PN, Wadgaonkar PP (2011) **Synthesis and characterization of organo-soluble poly(ether ether ketone)s and poly(ether ether ketone ketone)s containing pendant pentadecyl chains**. J Appl Polym Sci 121:3689–3695. Link
7. Sadavarte NV, Halhalli MR, Avadhani CV, Wadgaonkar PP (2009) **Synthesis and characterization of new polyimides containing pendent pentadecyl chains**. Eur Polym J 45:582–589. Link
8. Sadavarte NV, Avadhani CV, Naik PV, Wadgaonkar PP (2010) **Regularly alternating poly(amideimide)s containing pendent pentadecyl chains: synthesis and characterization**. Eur Polym J 46:1307–1315. Link
9. Sadavarte NV, Avadhani CV, Wadgaonkar PP (2011) **Synthesis and characterization of new organosoluble aromatic polyamides and polyazomethines containing pendent pentadecyl chains.** High Perform Polym 23:494–505. Link
10. Sadavarte NV, Patil SS, Avadhani CV, Wadgaonkar PP (2013) **New organosoluble aromatic poly(esterimide)s containing pendent pentadecyl chains: synthesis and characterization.** High Perform Polym 25:735–743. Link
11. Voirin C, Caillol S, Sadavarte NV, Tawade BV, Boutevin B, Wadgaonkar PP (2014) **Functionalization of cardanol: towards biobased polymers and additives.** Polym Chem 5:3142–3162. Link
12. Tawade BV, Salunke JK, Sane PS, Wadgaonkar PP (2014) **Processable aromatic polyesters based on bisphenol derived from cashew nut shell liquid: synthesis and characterization**. J Polym Res 21:617. Link
13. Tawade BV, Shaligram SV, Valsange NG, Kharul UK, Wadgaonkar PP (2016) **Synthesis and properties of poly(arylene ether)s based on 3-pentadecyl 4,4'-biphenol**. Polym Int 65:567 Link
14. More AS, Naik PV, Kumbhar KP, Wadgaonkar PP (2010) **Synthesis and characterization of polyesters based on 1,1,1-[bis(4-hydroxyphenyl)-4′-pentadecylphenyl]ethane**. Polym Int 59:1408. Link
15. Tawade BV, Kulkarni AD, Wadgaonkar PP (2015) **Synthesis and characterization of polyetherimides containing multiple ether linkages and pendent pentadecyl chains**. Polym Int 64:1770. Link
16. Chatterjee D, Sadavarte NV, Shingte RD, More AS, Tawade BV, Kulkarni AD, Ichake AB, Avadhani CV, Wadgaonkar PP (2017) **Step-Growth Polymers from Cashew Nut Shell Liquid (CNSL)-Based Aromatic Difunctional Monomers**, Cashew Nut Shell Liquid, Springer, Cham, 163-214 Link
17. Matmour R, More AS , Wadgaonkar PP, and Gnanou Y (2006) **High Performance Poly(styrene-b-diene-b-styrene) Triblock Copolymers from a Hydrocarbon-Soluble and Additive-Free Dicarbanionic Initiator** *J. Am. Chem. Soc.* 25: 8158–8159. Link
18. Shingte RD, Tawade BV Wadgaonkar PP, (2017), **Partially bio-based processable polyimides based on aromatic diamine derived from cardanol Green Materials**, 5: 74-82, Link

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

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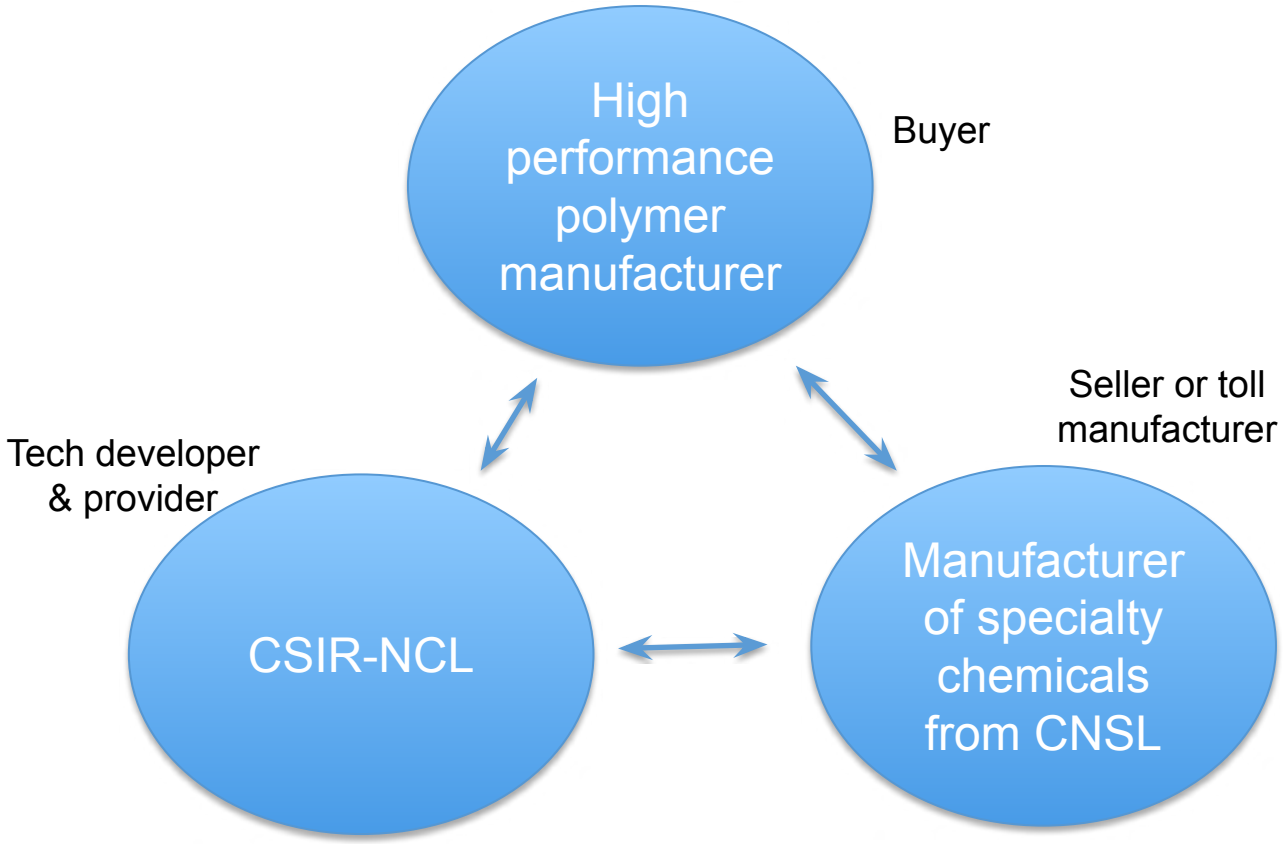
- NCL is a constituent lab of the CSIR, India
- Attractive models of engagement and flexible terms for IP
- Publicly funded non-profit R&D lab & DSIR recognized SIRO => R&D project sponsors can claim tax benefits; Eligible for CSR support
- Key assets and strengths
  - Team strength: Strong expertise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

EXCEL, SOLVAY, Procter&Gamble, DOW, GE, sabic, BASF We create chemistry

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

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For more information, contact:

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References> Market and Industry data

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   https://www.marketsandmarkets.com/Market-Reports/engineering-plastics-market-687.html
2. https://www.ceresana.com/en/market-studies/plastics/engineering-plastics/market-study-engineering-plastics-abs-san-pa-pc-pom-pmma-pbt-ptfe.html
3. http://cashewindia.org/statistics
4. Comparative Study of Cashew Nut Shell Liquid and a Commercial Demulsifier for Treating Crude Oil Emulsions C. O. Victor-Oji, U. J. Chukwu and O. Akaranta, CSIJ (2019), 28(4): 1-17.
5. https://www.sridevigroup.com/CNSLApplications.html#:~:text=CNSL%20is%20extensively%20used%20in,chemical%20industry%2C%20Automobile%2C%20pesticides
6. https://www.reportsanddata.com/report-detail/cashew-nut-shell-liquid-cnsl-market