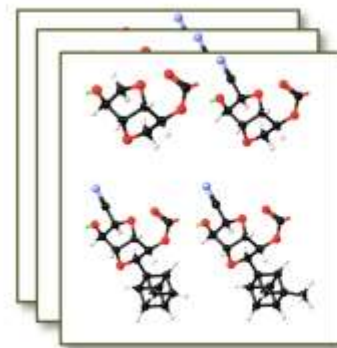


# *De Novo* Polymer Design Breakthrough

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January 2024



A screenshot of a software interface, likely a materials design tool, showing a table of data. The table has columns for 'Name', 'Molecular Weight', 'Density', 'Melting Point', and 'Glass Transition Temperature'. The data is organized into a grid with various parameters and values.

Name	Molecular Weight	Density	Melting Point	Glass Transition Temperature
1	1000	1.2	150	200
2	2000	1.3	160	210
3	3000	1.4	170	220
4	4000	1.5	180	230
5	5000	1.6	190	240
6	6000	1.7	200	250
7	7000	1.8	210	260
8	8000	1.9	220	270
9	9000	2.0	230	280
10	10000	2.1	240	290

# Materials Design Webinar Series

- Each webinar session runs several times to accommodate schedules
  - Share the webinar series with your colleagues!
  - Registration details <http://www.materialsdesign.com/webinars>
- We will be recording this webinar
  - Watch any of our earlier webinars anytime
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- Vote for the next webinar topic!
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  - Log out and log back in again
  - Check your audio output
  - Google Chrome (most recent 2 versions) Mozilla Firefox (most recent 2 versions) Apple Safari (most recent 2 versions) Microsoft Edge (most recent 2 versions)

# Please Ask Questions!

The screenshot shows the 'GoToWebinar Control Panel' window. It has a sidebar on the left with icons for full screen, mute, and raise hand. The main area is divided into 'Audio' and 'Questions' sections. The 'Audio' section shows 'Computer audio' selected, a 'MUTED' status, and volume controls. The 'Questions' section shows a list of questions and answers, and a text input field with a 'Send' button.

**full screen** →

**during discussion:  
raise hand  
to speak** →

**Use the raise hand icon to bring  
attention to your question**

**any time during webinar:  
type your question here  
and then press Send** →



# Webinar Speakers

***Katherine Hollingsworth***

*khollingsworth@materialsdesign.com*

***Jozef Bicerano***

*bicerano@polymerexpert.biz*

***David Rigby***

*drigby@materialsdesign.com*

***Clive Freeman***

*cfreeman@materialsdesign.com*



**BICERANO & ASSOCIATES**



# Jozef Bicerano, PhD

*Bicerano & Associates Consulting, LLC*



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# *De Novo* Polymer Design Breakthrough

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January 2024



A screenshot of a software interface showing a table of data. The table has columns for 'Name', 'Molecular Weight', 'Density', and 'Volume'. The data is organized into a grid with various numerical values.

Name	Molecular Weight	Density	Volume
1	1000	1.0	1000
2	2000	2.0	2000
3	3000	3.0	3000
4	4000	4.0	4000
5	5000	5.0	5000
6	6000	6.0	6000
7	7000	7.0	7000
8	8000	8.0	8000
9	9000	9.0	9000
10	10000	10.0	10000

# **“POLYMER EXPERT”:**

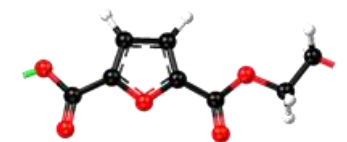
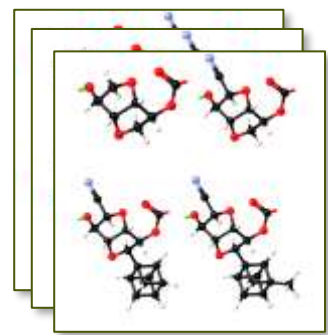
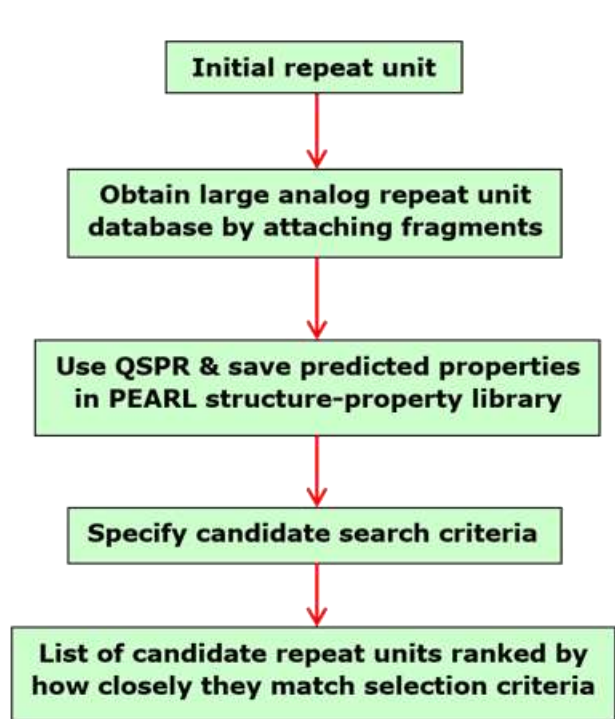
**A SOFTWARE TOOL FOR  
*DE NOVO* POLYMER DESIGN**



# Overview

- Polymer Expert is a new “expert system” software tool for use in high-throughput materials R&D, consisting of:
  - A database including:
    - More than 1.1 M repeat units.
    - Properties of each repeat unit as predicted by using quantitative structure-property relationships (QSPR).
  - *MedeA* tools to search through this database for promising candidates either interactively or in batch mode.
- Strength:
  - **For the first time ever, Polymer Expert makes powerful polymer informatics techniques for *de novo* polymer design readily accessible for researchers to use on their personal computers.**

# Polymer Expert At-A-Glance



A screenshot of the PEARL software interface, showing a table of candidate repeat units ranked by how closely they match selection criteria. The table has columns for 'Candidate', 'QSPR', and 'PEARL'. The 'PEARL' column contains numerical values representing the ranking of each candidate.

Candidate	QSPR	PEARL
1	0.95	10000
2	0.92	10000
3	0.90	10000
4	0.88	10000
5	0.85	10000
6	0.82	10000
7	0.80	10000
8	0.78	10000
9	0.75	10000
10	0.72	10000
11	0.70	10000
12	0.68	10000
13	0.65	10000
14	0.62	10000
15	0.60	10000
16	0.58	10000
17	0.55	10000
18	0.52	10000
19	0.50	10000
20	0.48	10000
21	0.45	10000
22	0.42	10000
23	0.40	10000
24	0.38	10000
25	0.35	10000
26	0.32	10000
27	0.30	10000
28	0.28	10000
29	0.25	10000
30	0.22	10000
31	0.20	10000
32	0.18	10000
33	0.15	10000
34	0.12	10000
35	0.10	10000
36	0.08	10000
37	0.05	10000
38	0.02	10000
39	0.00	10000
40	0.00	10000

# Key Benefits

- Rapid generation of candidates for *de novo* polymer design.
- Easily used by researchers on their personal computers.
- Based on a robust QSPR method that has been used in polymer R&D for more than three decades, thus avoiding the limitations of alternative approaches based on ML/DL.
- Implements algorithms crafted to only propose candidates synthesizable from chemically realistic monomers.
- Seamless integration into *MedeA* enables candidates of interest to be easily studied further by using simulations.

# Four Implementation Steps

## 1. Construct initial database of repeat units.

- Captures full chemical diversity of the polymer design space.
- Repeat units that can be derived at least partially from biobased fragments are labeled.

## 2. Implement algorithm to build database of 1,100,503 repeat units.

- Substitute fragments from a large fragment library for hydrogens.
- All repeat units in database can be obtained after no more than two fragment substitutions on a repeat unit in the initial database, to limit synthetic complexity.

## 3. Use QSPR to create library of repeat units and predicted properties.

## 4. Implement two search options for identifying candidates in library:

- Identification of analogues of a user-specified polymer.
- Identification of polymers with properties near user-specified targets.

# Polymer Expert in Action

- Exploring PET analogs
  - Similarity based analogs
  - Property based analogs
- Interactive illustrations...

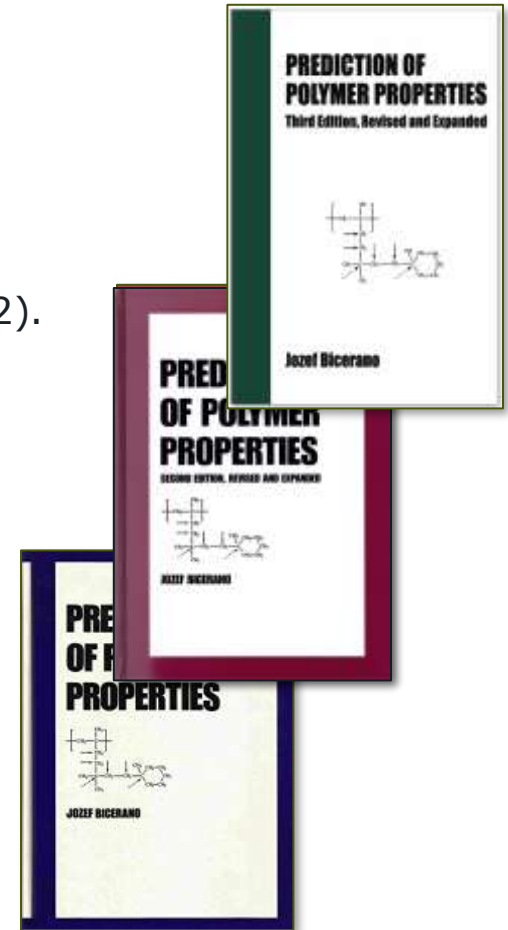
**P3C:**

**COMPUTATIONAL ENGINE  
OF "POLYMER EXPERT"**



# Overview

- 1) P3C is an implementation of the quantitative structure-property relationships (QSPR) developed by J. Bicerano, *Prediction of Polymer Properties* (3rd edition), Marcel Dekker, New York (2002).
- 2) QSPR based on topological connectivity indices.
- 3) Strength:
  - **No “group contributions” => predictions for polymers composed of groups not yet encountered will generally be reliable.**
- 4) Applicability: Repeat units built from C, N, O, H, F, Si, S, Cl, and Br, thus covering typical commercial polymers.
- 5) Allows creation of “designer correlations” by user.



# P3C At-A-Glance

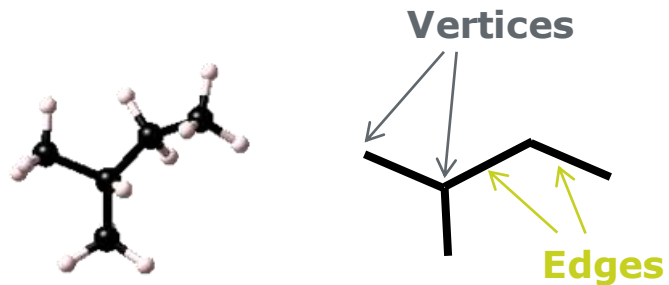
1. *MedeA* P3C computes a wide range of properties using empirical correlations for any desired thermoplastic polymer system.
2. *MedeA* provides an extensive library of repeat units and *MedeA* P3C can use any sketched or standard repeat unit as input.
3. *MedeA* P3C determines properties for polymer and copolymer systems using correlative methods.
4. Additionally, the descriptors that *MedeA* P3C employs can be used to create 'designer correlations' for specific polymer types, to maximize accuracy with a restricted correlation scope.

# Key Benefits

1. Rapid evaluation of polymer and copolymer properties.
2. Establish the underlying molecular basis for key properties.
3. Validated correlations based on topological indices.
4. Designer correlations for targeted system analysis.

# Connectivity Indices (I)

Uses hydrogen-suppressed graph of the molecules:



# Connectivity Indices (II)

1. Atomic indices are defined as:

1. **Simple connectivity index  $\delta$** : Number of non-hydrogen atoms to which the non-hydrogen atom is bonded
2. **Valence connectivity index  $\delta^v$** : information of the electronic configuration of the non-hydrogen atom (incorporates the number of valence electrons, number of hydrogens bonded to it, and the atomic number):

$$\delta^v \equiv \frac{Z^v - N^H}{Z - Z^v - 1}$$

2. Bond indices are defined as products of the atomic indices of the atoms involved in the bond:

1. **Simple bond index**  $\beta_{ij} = \delta_i \cdot \delta_j$
2. **Valence bond index**  $\beta_{ij}^v = \delta_i^v \cdot \delta_j^v$

# Connectivity Indices (III)

## 1. Zeroth-order connectivity indices defined as:

$${}^0\chi \equiv \sum_{\text{vertices}} \frac{1}{\sqrt{\delta}}$$

level of heavy atom branching (higher heavy branching » lower  ${}^0\chi$  index)

$${}^0\chi^v \equiv \sum_{\text{vertices}} \frac{1}{\sqrt{\delta^v}}$$

information related to the bonding content (neighboring valence electrons)

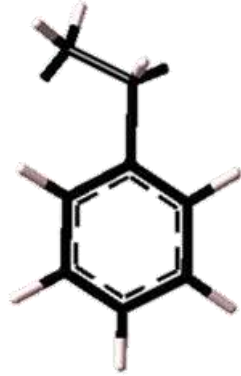
## 2. First-order connectivity indices defined as:

$${}^1\chi \equiv \sum_{\text{edges}} \frac{1}{\sqrt{\beta}}$$

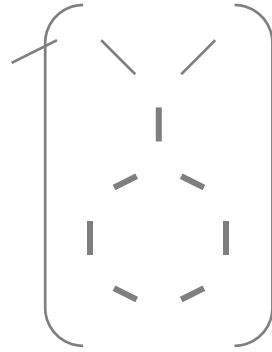
$${}^1\chi^v \equiv \sum_{\text{edges}} \frac{1}{\sqrt{\beta^v}}$$

## 3. High-order connectivity indices incorporate larger-scale structural features (paths, branches, clusters and rings)

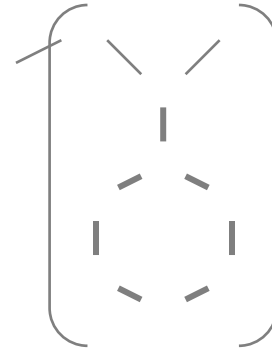
# Connectivity indices for PS



**Polystyrene  
monomer**



**Simple atomic  
indices  $\delta$**



**Valence atomic  
indices  $\delta^v$**

$$\delta^v \equiv \frac{Z^v - N^H}{Z - Z^v - 1}$$

$$\delta^v \equiv \frac{4 - N^H}{6 - 4 - 1}$$

# Correlations

## 1. A **property** is calculated from a **correlation**:

1. based on **connectivity indices**
2. augmented with **correction terms** relating to key features contained within constituent repeat units (atomic and group correction terms dependent upon the number of certain types of atoms or groups that may be present)

## 2. **Designer correlations** are improved correlations highly **tuned to specific systems**

1. not widely applicable
2. once such correlations have been established, they may be employed to generate property data for novel repeat units

# List of Predicted Properties

## Thermophysical

- Glass transition temperature,  $T_g$
- Temperature of half decomposition
- Change in molar heat capacity at  $T_g$
- Coefficient of volumetric thermal expansion
- Cohesive energy
- $C_p$  of liquid
- $C_p$  of solid
- Density
- Molar volume
- Solubility parameter
- Surface tension
- van der Waals volume
- Thermal conductivity

## Electronic and Optical

- Diamagnetic susceptibility
- Dielectric constant
- Molar refraction
- Refractive index
- Volume resistivity

## Mechanical

- Brittle fracture stress
- Bulk modulus
- Poisson's ratio
- Shear modulus
- Shear yield stress
- Young's modulus

## Entanglement

- Entanglement molecular weight
- Entanglement length
- Critical molecular weight
- Steric hindrance parameter
- Characteristic ratio
- Molar stiffness function
- Additive portion of molar viscosity-temperature function
- Activation energy for viscous flow at zero flow rate
- Zero-shear viscosity

## Transport

- Permeability to  $\text{CO}_2$ ,  $\text{N}_2$ , and  $\text{O}_2$
- Zero shear viscosity
- Diffusion coefficients for  $\text{N}_2$  and  $\text{O}_2$

# Continuing Enhancements

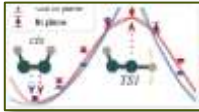
1. P3C was developed internally by Materials Design from the cited book without any input from its author.
2. The author started to collaborate with Materials Design two years ago, mainly focusing on the development of the new “Polymer Expert” module.
3. Many enhancements of P3C have also resulted from this collaboration, as documented in the product literature.

# P3C in Action

- Interactive illustration...

# Polymer Simulation Webinars

- Interview with Dr. Jozef Bicerano, a world-expert in polymer modeling
- Use of Polymer Theoretical Concepts in Atomistic Polymer Simulation Software, Dave Rigby
- A Conversation with Bruce Eichinger – the background of atomistic Polymer simulation
- Using *MedeA* to Study Formation and Properties of Polymer Networks, Dave Rigby
- An Introduction to the *MedeA* User Interface, Clive Freeman
- Predicting Elastic Properties Using Ab Initio And Forcefield Based Simulations, Dave Rigby and Walter Wolf
- *MedeA* Training: Multiscale Modeling of Polymers Using the *MedeA* Environment, Marianna Yiannourakou and Jörg-Rüdiger Hill



# Related *MedeA* Tutorials

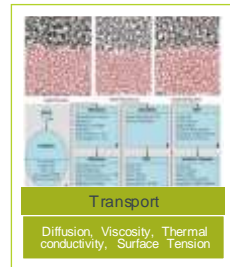
## An Introduction to *MedeA* VASP:

Learn how to set up and run *VASP* calculations with *MedeA*



## Predicting Polymer Properties Using *MedeA* P3C:

Learn how to quickly predict polymer properties with *MedeA* P3C



## Identify Biobased Polyethylene Terephthalate Alternatives:

Identify how to identify and design polymer materials with desired properties

## Permeability of O<sub>2</sub> in Polystyrene:

Learn how to set up GIBBS Monte Carlo simulations to calculate solubility, LAMMPS molecular dynamics simulation to calculate diffusivity and combine this to estimate permeability.



See related application notes too!

Available here: <https://www.materialsdesign.com/application-notes>

# Prediction of Polymer Properties Using Correlation in the Patent Literature

Some recent patent application citing *Prediction of Polymer Properties*

(Of the [481](#) examples listed by [patents.google.com](https://patents.google.com) in January, 2024)



Viscosity Improvement

Impact Resistance

Resists

Resists



Anti-Vibration

Resists

RAFT

Resists

# Summary & Conclusions

- Polymer informatics:
  - Term used in referring to implementations of cheminformatics for polymers.
  - A powerful new approach for the rapid and systematic exploration of immense polymer design spaces to identify synthesis candidates that hold the greatest promise of meeting desired performance, processing, and cost targets.
  - Will greatly accelerate exploration of polymer design spaces.
- Polymer Expert:
  - Makes powerful polymer informatics techniques for *de novo* polymer design readily accessible for researchers to use on their personal computers for the first time ever.
  - Based on robust QSPR method, avoids limitations of alternative approaches that use ML/DL.
  - Integrated seamlessly into *MedeA* environment.
- Further details:
  - See program documentation on website of Materials Design, Inc.
  - J. Bicerano, D. Rigby, C. Freeman, B. LeBlanc, and J. Aubry, ["Polymer Expert – A Software Tool for de novo Polymer Design"](#), Computational Materials Science, accepted for publication.

# Question and Answer Session



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***Clive Freeman***

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# Questions about Materials Design Webinars

***Katherine Hollingsworth***

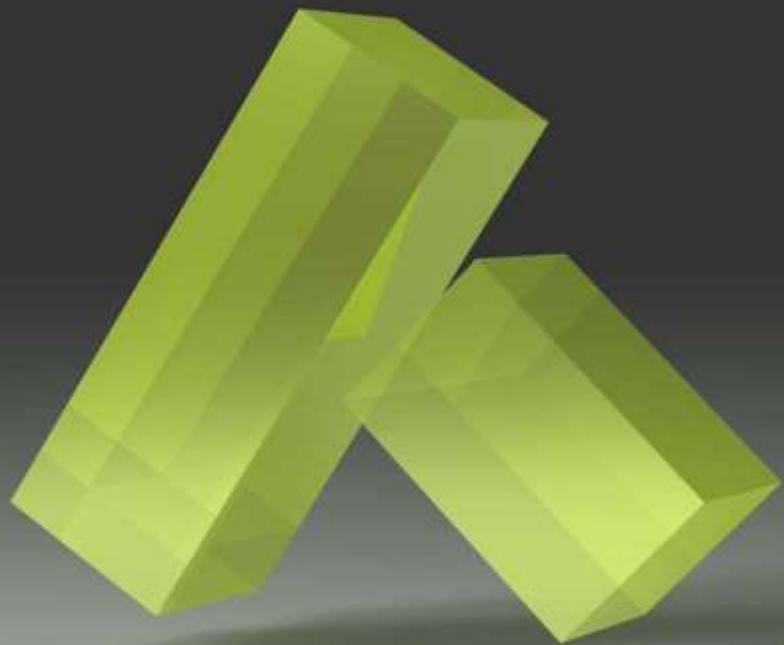
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# MedeA

*Innovation by Simulation*