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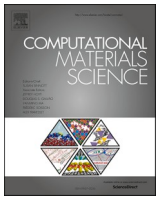

Full Length Article

Polymer expert – A software tool for *de novo* polymer design

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ABSTRACT

A versatile and user-friendly "expert system" for *de novo* polymer design, named Polymer Expert, has been developed and implemented. Polymer Expert can be used to rapidly generate novel candidate polymer repeat units to meet desired performance targets. It is anticipated to accelerate innovation through materials science in industries that use polymers and polymer matrix composites. It was implemented by (1) generating an initial repeat unit database, (2) expanding this initial database into a large analog repeat unit database, (3) performing calculations for all repeat units in the large analog database by using quantitative structure–property relationships (QSPR) of broad applicability, and (4) integrating the resulting searchable library of repeat units and their predicted properties (PEARL, acronym for Polymer Expert Analog Repeat-unit Library) as a new module in a materials modeling and simulation software suite. Its use is illustrated by identifying biobased alternatives for poly(ethylene terephthalate) (PET) and bisphenol-A polycarbonate (BPAPC), alternatives for highly crystalline polypropylene homopolymer (PPHP) and 10% glass fiber containing polypropylene (PP10GF), and polymers that may provide unusually high dielectric constants. Many promising candidates were unobvious and unlikely to have been identified without using a polymer informatics approach. Future work will focus on improving the quality of candidate repeat units by refining the QSPR method, enhancing the diversity of candidate repeat units by expanding PEARL, providing additional interactive search options, and converting Polymer Expert into a versatile R&D platform that users can customize for their own needs.

1. Introduction

Modern polymer science emerged as a scientific discipline almost two centuries ago, focusing on understanding, modifying, and finding applications for naturally occurring biobased polymers. Beginning in the first half of the 20th century, the rapid growth of the petrochemical industry stimulated the development of a great variety of synthetic polymers, used nowadays in every area of technology, by starting with precursors obtained from fossil fuel feedstocks. During the last quarter of the 20th century, concerns related to sustainability led to the revival and rapid growth of interest in biobased polymers, with special focus on biobased precursors and the polymers that can be synthesized at least partially from biobased precursors.

Despite this immense amount of work, only a very small portion of the full design space of all synthesizable polymers has been explored thus far. Vast numbers of additional polymers can potentially be synthesized and evaluated.

Materials informatics [1–15] is a powerful new approach for the rapid and systematic exploration of immense material design spaces to identify candidates that hold the greatest promise of meeting desired performance, processing, and cost targets. Polymer informatics, defined as materials informatics focusing on polymers, will greatly accelerate the exploration of polymer design spaces as its capabilities are enhanced and its use becomes widespread.

Polymer informatics software tools implement a wide variety of methods. Machine Learning / Deep Learning (ML/DL) methods, using "data mining" tools such as artificial neural networks, Bayesian inference, or genetic function algorithms, are popular. Methods can also be based on Quantitative Structure-Property Relationships (QSPR). It is often helpful to combine different methods synergistically in the same software tool, for example by using QSPR for predicting some properties and ML/DL methods to provide additional predictions for properties for which a QSPR of acceptable quality is unavailable. In seeking candidates manifesting properties controlled mainly by the electronic structure rather than the larger-scale features of the material, the most promising approaches combine quantum mechanical (QM) calculations, most often

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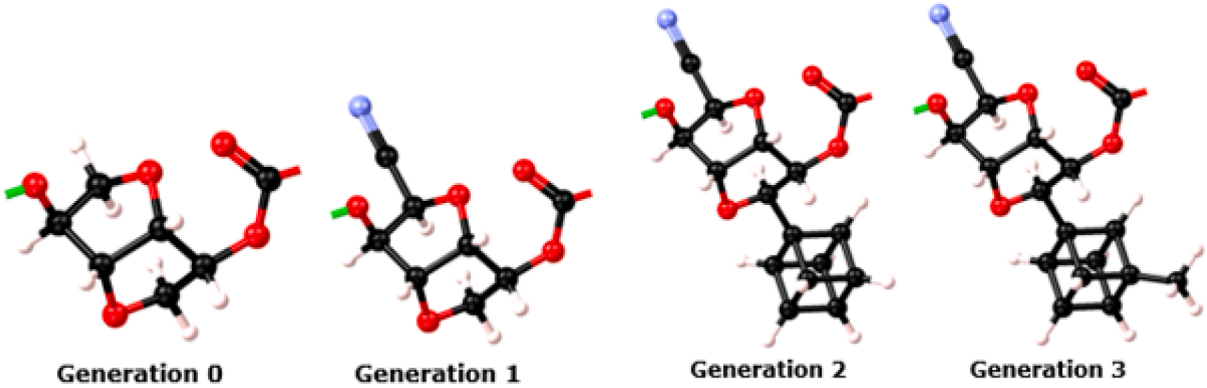

Fig. 1. Example illustrating the construction of new generations of repeat units by starting from a "seed" repeat unit and replacing a randomly selected hydrogen with a fragment from the fragment library in successive steps. The repeat unit of PIC is from Generation 0 because it was in the initial database. A repeat unit generated after 1, 2, or 3 iterative steps starting from the repeat unit of PIC as the seed is labeled as a Generation 1, 2, or 3 derivative of PIC. Only Generation 0, 1, and 2 repeat units were included in the final database.

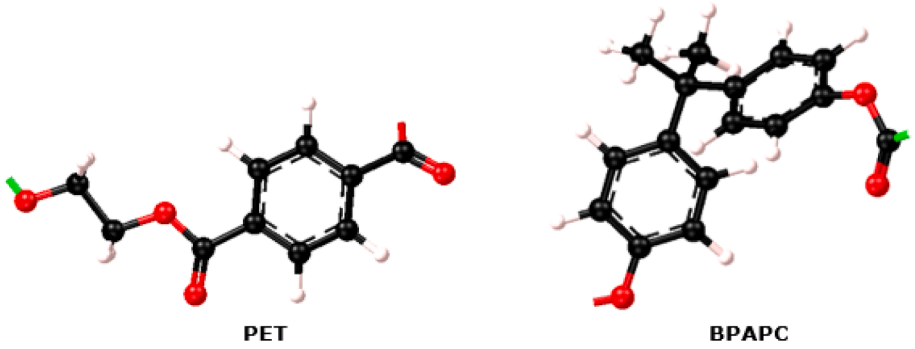

Fig. 2. Repeat units of polymers for which biobased analogues were searched in PEARL.

Table 1
Properties calculated by QSPR for PET and BPAPC and used in searching PEARL for biobased alternatives to them.

Property	Weight	PET	BPAPC
Density (g/cm^3)	0.5	1.32	1.17
Glass transition temperature (K)	1.0	369.53	416.36
Refractive index	0.5	1.56	1.59
Dielectric constant	0.5	3.28	2.90
Young's modulus (MPa)	1.0	2054.21	2268.77
Brittle fracture stress (MPa)	1.0	170.09	117.29

Table 2
Property targets used in searching PEARL for PPHP and PP10GF alternatives.

Property	Weight	PPHP	PP10GF
Glass transition temperature (K)	0.5	327	402
Young's modulus (MPa)	1.0	1724	2965
Brittle fracture stress (MPa)	1.0	32	39
Density (g/cm^3)	None (pass-fail criterion)	≤1.0	≤1.1
Dielectric constant	None (pass-fail criterion)	≤2.4	≤2.9

using density functional theory (DFT), with ML/DL methods.

The technical challenges involved in the development of new polymer informatics software tools can be summarized as follows:

- Experimental datasets tend to be sparse because measured values for most properties are not reported for most polymers that are synthesized. Research papers and patents commonly list only a few measured properties for polymers that were synthesized. Comprehensive technical datasheets listing values for every important property are typically only available for commercial polymers sold in significant volumes.
- It is difficult to capture and curate immense amounts of data. For example:
  - o Many properties (such as the glass transition temperature) can be measured by using different methods that produce different values.
  - o Samples of what is nominally the same polymer used in different measurements may differ in attributes such as quality, purity, additive content, reinforcing agent content, direction(s) and extent of orientation that may be present, and percent crystallinity.
- It is essential to ensure synthetic realism of proposed structures during *de novo* design. The software tool needs to have safeguards to ensure that the candidates it proposes can (at least in principle) be synthesized. This is one of the biggest challenges in drug design via cheminformatics, where a starting "seed" molecule can be grown in all three principal directions by attaching fragments. It is, fortunately, less of a challenge in thermoplastic polymer design via polymer informatics, where one can ensure synthetic realism by starting with a "seed" repeat unit and growing from that repeat unit only by attaching fragments at substitution points along it rather than growing from it in all three directions.
- A quantitative criterion is needed to rank candidates in terms of the proximity of their predicted properties to targeted properties. A common approach is to allow the user to provide the targeted properties and calculate the mean square distance of the normalized predicted properties from the targeted ones. Normalization of the values of the properties ensures that the figure of merit is independent of the choice of units. A smaller mean square distance means a higher rank.

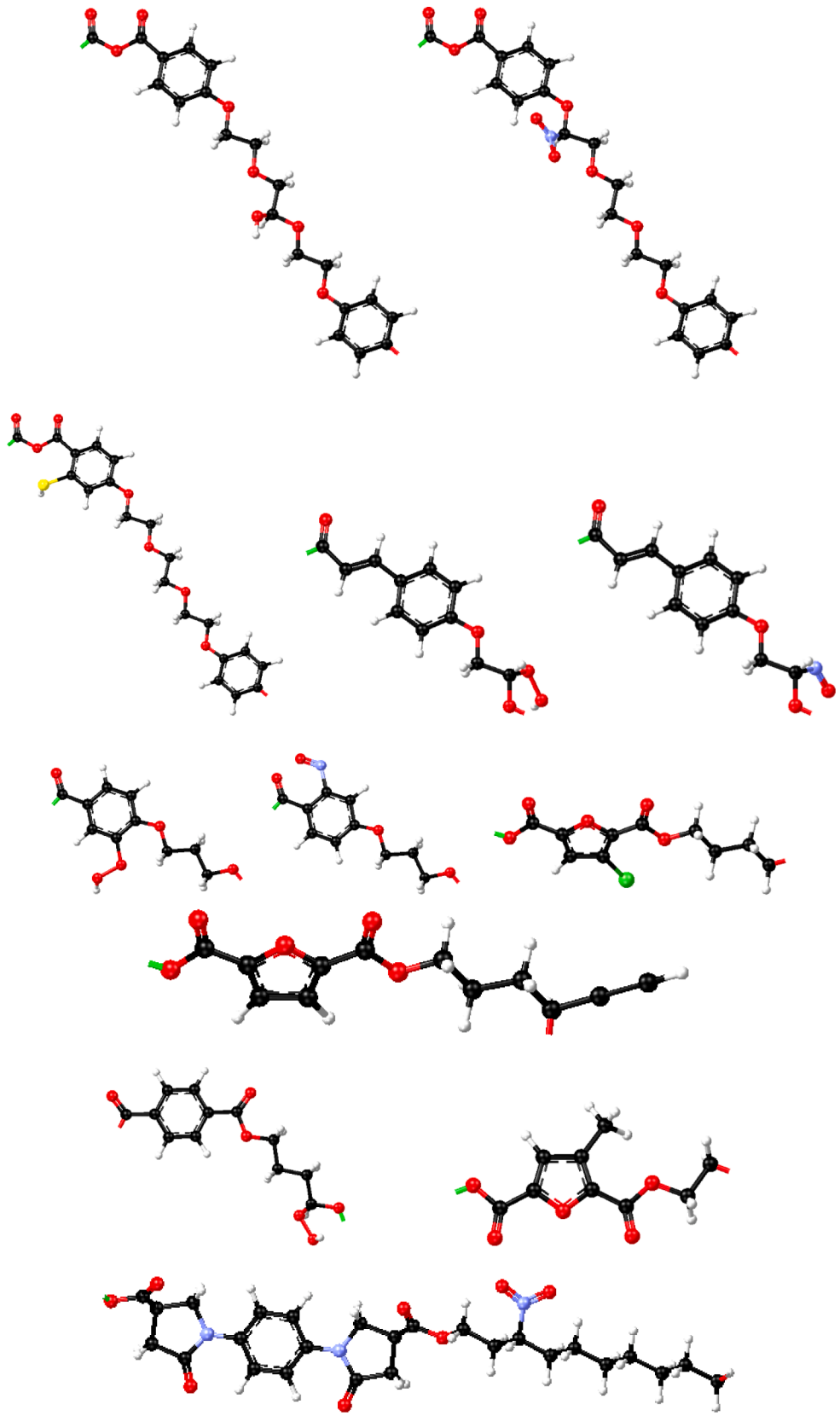

Fig. 3. The 20 repeat units in PEARL that can be synthesized at least partially from biobased precursors and that provide the closest matches to PET in terms of the search criteria provided in Table 1 are shown. The repeat units identified by the chosen search criteria show polymers with multiple oxygen (red atoms) and aromatic moieties, and the search results also show many repeat units derived from furanoate (furan-2,5-dicarboxylate) fragments, as might be expected. [Poly(ethylene furanoate) (PEF) is, of course, an established biobased alternative to PET. It provides the 99th closest fit using the present search criteria. It provides the 37th closest fit in another search not specifying any properties so that all calculated properties are included and the closest fits are more likely to be similar in size to the repeat unit of PET.].

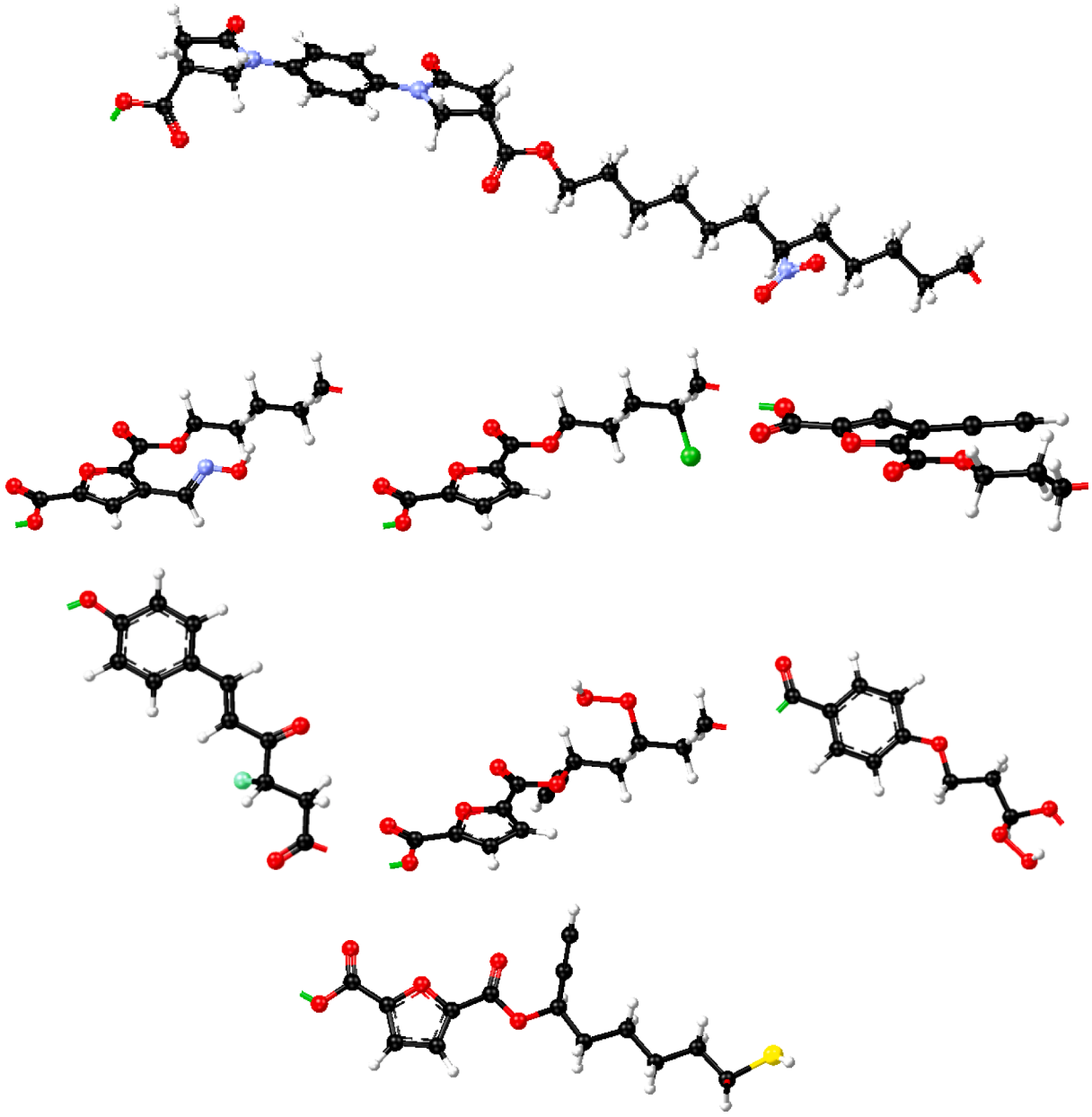

Fig. 3. (*continued*).

- It is important for the software tool to provide a rough estimate of the relative ease of synthesis of the synthetically realistic candidates that it proposes. The relative ease of synthesis can vary greatly among proposed candidates. A reasonable estimate of the relative ease of synthesis can help a researcher make decisions such as whether to focus synthetic work on a candidate predicted to provide a slightly inferior fit to the ideal performance target but to be far easier to synthesize.

This paper describes a versatile and user-friendly new "expert system" named Polymer Expert for *de novo* polymer design. Polymer Expert can be used to rapidly generate novel candidate polymer repeat units to meet desired performance targets. It is anticipated to accelerate innovation through materials science in industries that use polymers and polymer matrix composites. It is integrated seamlessly as a new module into the MedeA materials modeling and simulation software suite of Materials Design, Inc., to facilitate simulations for candidates it generates that a user wants to investigate in greater depth. For example, incorporating the statistical nature of polymer chains (e.g., chain length/molar mass distribution), topological structures (e.g., branches, monomer sequences), and morphological aspects (e.g., crystallinity in the case of semicrystalline polymers) into the design criteria is also desirable, but extremely challenging to implement within an exclusively polymer informatics based computational framework. The integration of Polymer Expert into a comprehensive materials modeling and simulation software suite allows its use as an exclusively polymer informatics based computational framework to identify short preliminary lists of promising candidate polymers which can then be investigated by using other modules in the software suite for further comparison in terms of such additional characteristics.

Polymer Expert was implemented by (1) generating an initial repeat unit database, (2) expanding this initial database into a large analog repeat unit database, (3) performing calculations for all repeat units in the large analog database by using quantitative structure–property relationships (QSPR) of broad applicability [16], and (4) integrating the resulting searchable library of repeat units and their predicted

Table 3
Comparison of property targets with value for candidate providing closest match and range over 20 candidates providing closest matches in search for PET alternatives that can be synthesized at least partially from biobased precursors.

Property	Weight	Target	Closest Match	Minimum of Range	Maximum of Range
Density (g/cm^3)	0.5	1.32	1.32	1.26	1.37
Glass transition temperature (K)	1.0	369.53	369.42	344.82	386.16
Refractive index	0.5	1.56	1.56	1.54	1.57
Dielectric constant	0.5	3.28	3.29	3.15	3.37
Young's modulus (MPa)	1.0	2054.21	2057.09	1880.77	2363.52
Brittle fracture stress (MPa)	1.0	170.09	169.39	154.81	169.39

properties (PEARL, acronym for Polymer Expert Analog Repeat-unit Library) as a new module in a materials modeling and simulation software suite, as described in Section 2. Standard capabilities of the user interface, which are available to users of the new module as a result of this integration, will not be reviewed in this section which will focus on the new capabilities provided by the new module itself.

The QSPR method used in the implementation of Polymer Expert has the advantage of incorporating a built-in solution to the well-known challenge of how to represent the repetitive nature of a polymer chain. For a given polymer, the repeating units may not be unique, and the structural factors and their numbers may vary. As pointed out by other researchers, one solution that captures the repetitive or periodic nature of a polymer is the periodic graph representation where the two terminal ends of the polymer chain are connected, forming a ring [17,18]. By using such polymer structure representation, the accuracy of model can be improved as well for polymer properties predictions [19,20] and polymer design [21]. The built-in solution to this challenge, used in the QSPR method performing as the computational engine of Polymer Expert, is detailed in Chapter 2, Section 2.B of Reference [16], titled "Extension of Connectivity Index Calculations to Polymers". It is based on a periodic graph presentation, but it utilizes a small molecular unit, and takes chain continuation into account consistently and unambiguously without introducing any truncation errors.

The use of Polymer Expert is illustrated in Section 3 by identifying biobased alternatives for poly(ethylene terephthalate) (PET) and bisphenol-A polycarbonate (BPAPC), alternatives for highly crystalline polypropylene homopolymer (PPHP) and 10 % glass fiber containing polypropylene (PP10GF), and polymers that may provide unusually high dielectric constants.

Future work will focus on improving the quality of candidate repeat units by refining the QSPR method, enhancing the diversity of candidate repeat units by expanding PEARL, providing additional interactive search options, and converting Polymer Expert into a versatile R&D platform that users can customize for their own needs, as described in Section 4.

The conclusions are presented in Section 5.

2. Method

The method used in Polymer Expert was implemented in four steps which are listed in this paragraph and discussed below in detail.

1. An initial database of repeat units was constructed. This initial database captures the full chemical diversity of the polymer design space by including the vast variety of structural types of repeat units that have already been reported.
2. An algorithm was developed and implemented to build a large analog database of repeat units by starting from this initial database. The algorithm involved the substitution of fragments from a large fragment library for hydrogens.
3. The QSPR method introduced in [16] was used to create PEARL, a library consisting of the full analog database of 1,100,503 repeat units and their predicted properties.
4. Two different options were implemented for users to identify candidates for synthesis by searching through PEARL:
   a. Identification of analogues of a user-specified polymer.
   b. Identification of polymers with properties near user-specified targets.

2.1. Preparation of initial database

The construction of PEARL required capturing the full chemical diversity of the polymer design space by preparing an initial database that included the vast variety of structural types of repeat units that have already been reported. Since the additional repeat units in PEARL were all going to be prepared by making substitutions (as described below) on repeat units beginning from this initial database, any significant type of chain backbone chemical diversity missing from the initial database would remain missing in the much larger database.

An initial database of 1,384 polymer repeat units was prepared by surveying the literature, to obtain comprehensive coverage of the polymer design space explored thus far. The repeat units listed in [16] and in many other reference books, scientific papers, and patents were included, to be as comprehensive as possible in covering the previously explored portion of the polymer design space where the properties predicted by QSPR can be used to rank candidates in terms of promise for targeted applications.

While this initial database contains a few polymers with extended conjugation along the chain backbone, it was decided not to cover this "intrinsically conducting polymer" portion of the polymer design space in a comprehensive manner because the suitability of such polymers for major applications is determined by properties related to the electronic structure, and thus requiring QM calculations rather than QSPR. This is the only portion of the full polymer design space that was not given comprehensive coverage.

Research on polymers that can be synthesized at least partially from biobased precursors [22] is accelerating. We attempted to capture the full chemical diversity of such polymers that have been reported thus far. The repeat units in the initial database that are derivable with at least some biobased content are labeled. To increase awareness of opportunities for progress, the "biobased" label is attached to any polymer for which a viable biobased synthetic pathway has been published, even if the polymer is only manufactured on a commercial scale by starting from fossil fuel feedstocks at this time. The label remains in any repeat unit in PEARL built by substitutions on a labeled repeat unit in the initial database. Such labeling provides users the choice of either focusing on the biobased portion of the polymer design space or looking at the full design space. For readers interested in learning more about biobased polymers, references [23–37], which constitute only a small portion of the relevant literature that we studied, list some especially interesting and informative recent papers.

The length of the fully extended conformation of the repeat unit, l_m, is used as a QSPR input parameter in predicting some properties. It was, therefore, important to ensure that each repeat unit in the initial database was in its fully extended conformation and that a reliable and consistent procedure was used to calculate l_m for all repeat units. The following approach was used for this purpose:

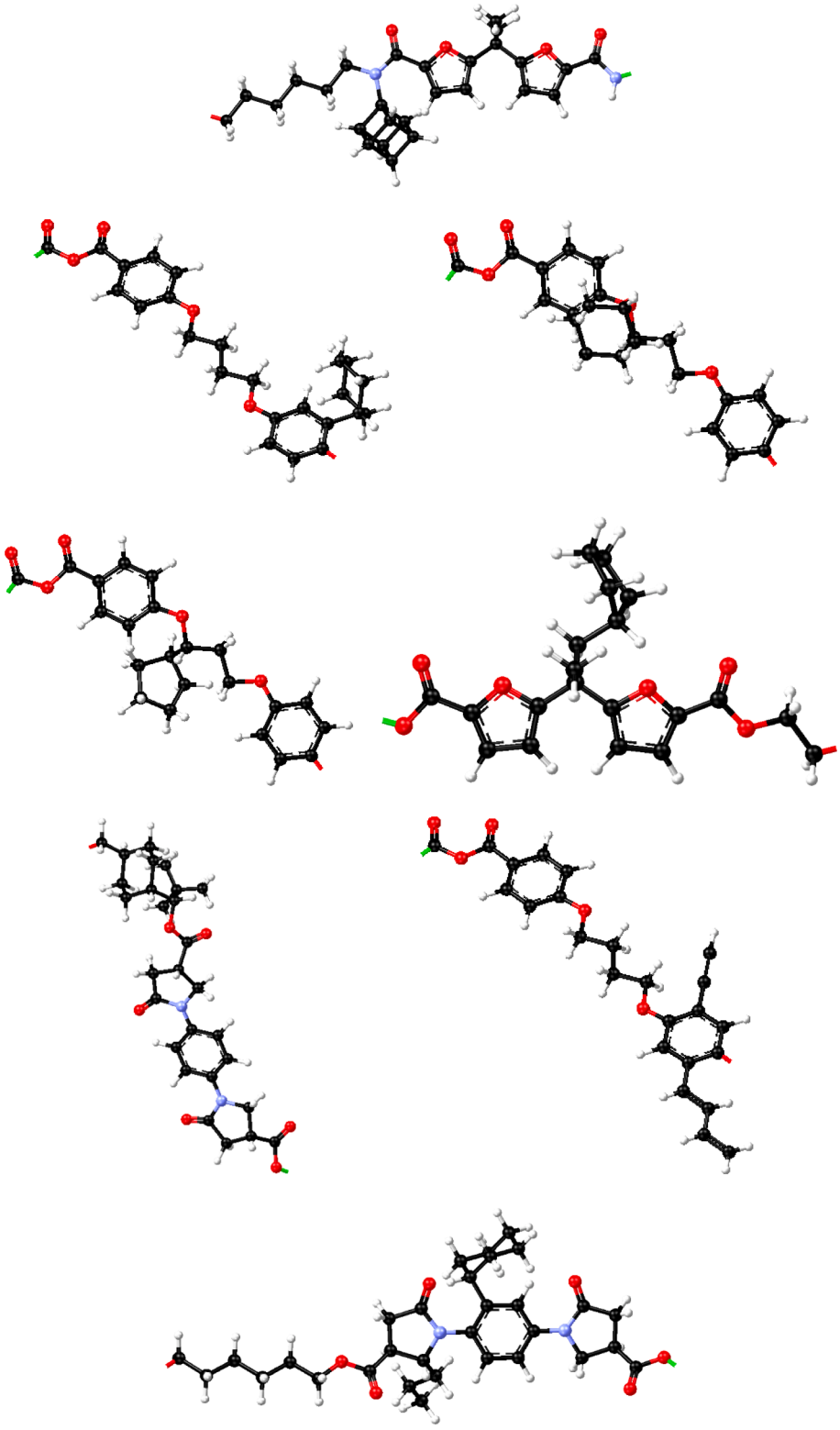

Fig. 4. The 20 repeat units in PEARL that can be synthesized at least partially from biobased precursors and that provide the closest matches to BPAPC in terms of the search criteria provided in Table 1 are shown. The BPAPC alternatives comprise repeat units containing more (and some of them bulky) side groups and less planarity than the PET alternatives.

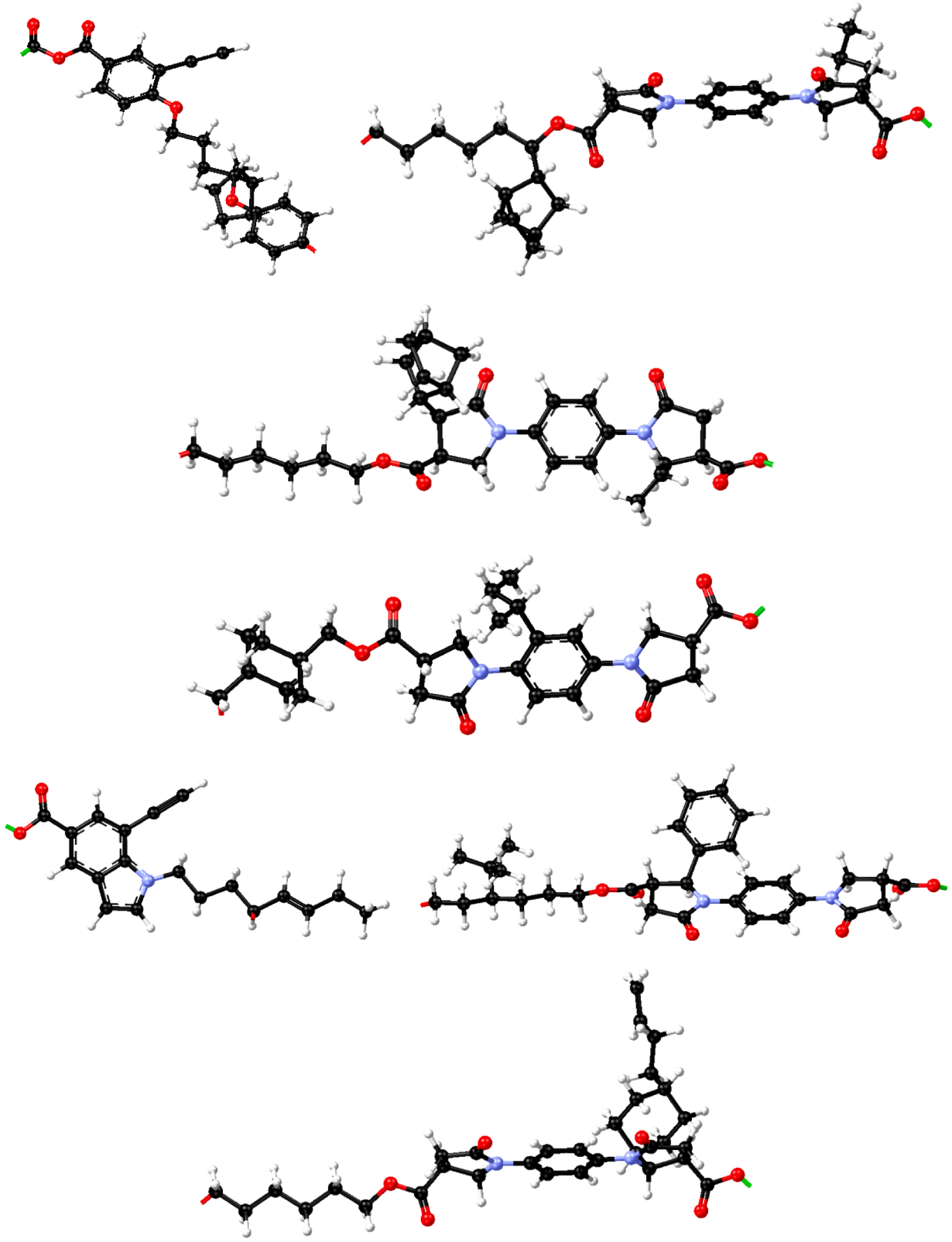

Fig. 4. (*continued*).

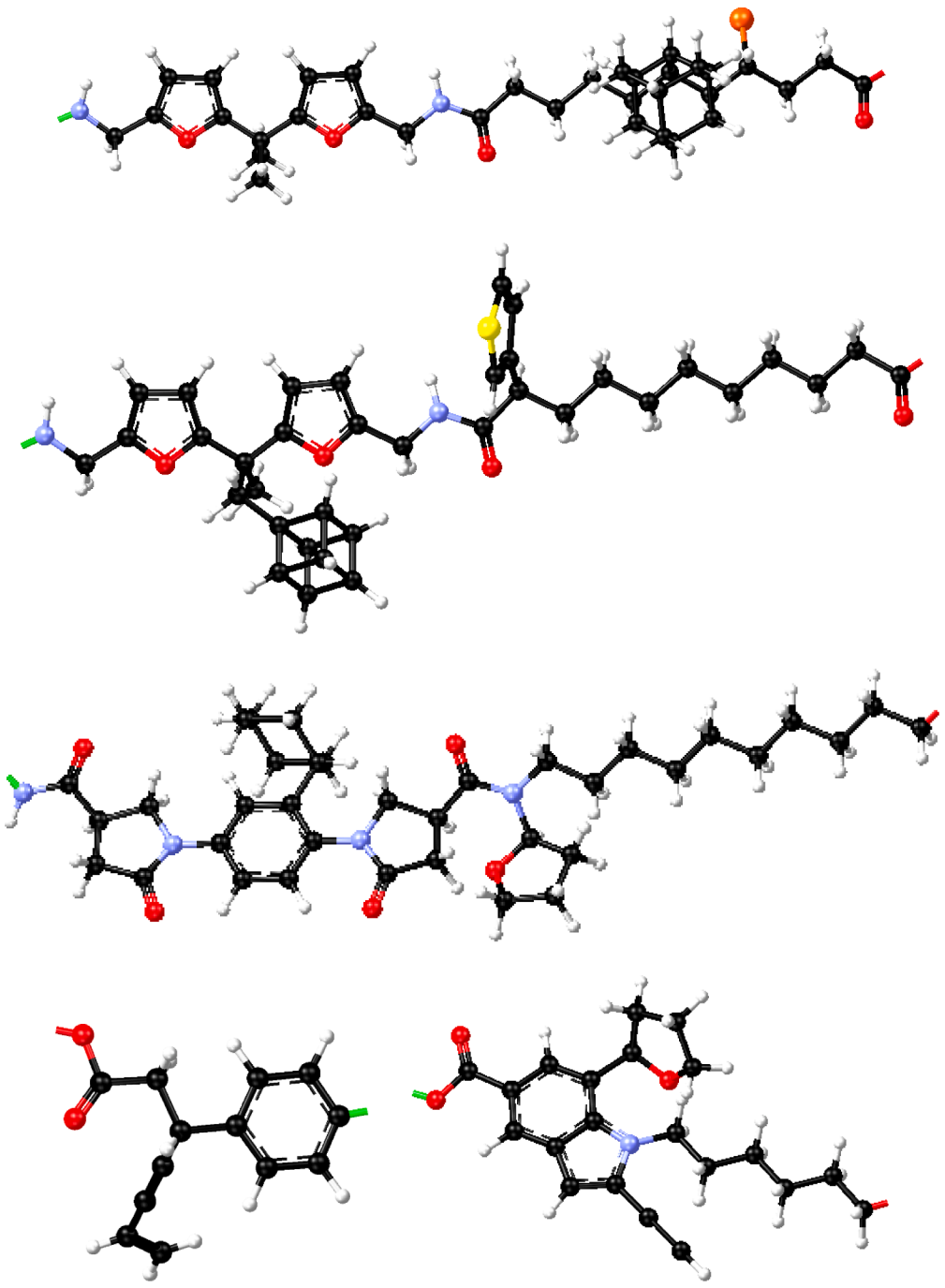

Fig. 4. (*continued*).

1. Use the molecular builder tools provided by the user interface to construct repeat units.
2. Use these molecular builder tools (and especially the dihedral angle variation options) to extend each repeat unit into its most extended conformation as judged visually.
3. Create a trimer of each repeat unit, with dihedral angles between successive repeat units selected such that the trimer is also in its most extended conformation as judged visually.
4. Optimize the geometry of each trimer by using a semiempirical quantum mechanical method (the PM7 option in the MOPAC module of the software suite).
5. Save the geometry of the central repeat unit of each fully extended trimer after geometry optimization in the database.

2.2. Preparation of large analog database

An algorithm was developed and implemented to substitute fragments from a large fragment library for hydrogens to build a large analog database of repeat units. The algorithm utilized a combinatorial growth stage, followed by a stochastic growth stage, and a culling stage to eliminate duplicates. Fragments containing elements other than C, N, O, H, F, Si, S, Cl, and Br were excluded since the applicability of the QSPR method used to predict properties is limited to polymers constructed from these elements.

The following process was used by the algorithm:

1. Combinatorial growth steps (exhaustive):

Table 4
Comparison of property targets with value for candidate providing closest match and range over 20 candidates providing closest matches in search for BPAPC alternatives that can be synthesized at least partially from biobased precursors.

Property	Weight	Target	Closest Match	Minimum of Range	Maximum of Range
Density (g/cm^3)	0.5	1.17	1.17	1.15	1.20
Glass transition temperature (K)	1.0	416.36	413.78	397.86	421.99
Refractive index	0.5	1.59	1.59	1.57	1.61
Dielectric constant	0.5	2.90	2.90	2.82	2.99
Young's modulus (MPa)	1.0	2268.77	2282.07	2282.07	2704.49
Brittle fracture stress (MPa)	1.0	117.29	117.72	111.32	121.63

- o For each of the "Generation 0" repeat units in the initial database:
  - Determine if it has at least one hydrogen that can be replaced by an organic substituent, thus excluding repeat units such as -CF_2CF_2- (polytetrafluoroethylene) which does not have any hydrogens from the list of candidates for growth.
  - Select the hydrogen if there is one (as in -$CHFCF_2$-, polytrifluoroethylene) or select a hydrogen randomly if there are ≥ 2 [as in -CH_2CHF-, poly(vinyl fluoride)].
  - Replace the selected hydrogen with a substituent selected from a library of 80 common organic fragments. The names and molecular structures of the fragments are provided in the Supplementary Materials.
  - Repeat the selection of a hydrogen and the replacement of the selected hydrogen with a fragment for each fragment in the library.
    - o Each initial repeat unit that contains at least one hydrogen has been combined once with each fragment during the construction of Generation 1 repeat units in the database after the completion of these combinatorial steps.

2. Stochastic growth steps (iterative):
   - o Make random selections:
     - Randomly select one repeat unit in Generation 0 or Generation 1 with one or more substitution site from among the repeat units added thus far to the library.
     - Randomly select one modifying fragment from the fragment library.
     - If there is more than one possible substitution site on the repeat unit, then also randomly select one of the substitution sites.
       - o Replace the hydrogen at the selected substitution site of the selected repeat unit with the selected fragment.
     - If the repeat unit selected randomly for growth is in Generation 0, the newly added repeat unit is in Generation 1.
     - If the repeat unit selected randomly for growth is in Generation 1, the newly built repeat unit is in Generation 2, and is excluded from consideration during further growth steps to avoid the addition of repeat units of great synthetic complexity.
       - o Repeat these steps, adding each newly created repeat unit to the set of repeat units whose attached hydrogens may serve as substitution sites.
       - o Stop this process when the database contains a large number of repeat units.
3. Eliminate duplicates in a culling step, and finally eliminate outliers in a quality control step discussed in Section 2.3 after the completion of QSPR calculations on the algorithmically generated repeat units, resulting in 1,100,503 unique repeat units.
   - o Here is a simple example of why the culling step is needed. The repeat unit –CH_2CH_2- of polyethylene is in the initial database. When –CH_2CH_2- is selected as the seed, and chloride (-Cl) is selected as the fragment that will replace a hydrogen atom, the repeat unit -CH_2CHCl- of poly(vinyl chloride), which is also in the initial database, is obtained.
   - o After the quality control step, the final database contains 1,293 (0.1 %) Generation 0, 101,347 (9.2 %) Generation 1, and 997,863 (90.7 %) Generation 2 repeat units.
     - In another run, where stochastic growth was allowed to proceed beyond Generation 2, 64.5 % of the repeat units were found to be of Generations ≥ 3 and would thus have required ≥ 3 substitution steps derive from a Generation 0 repeat unit.
     - Stopping growth at Generation 2 was, therefore, important for balancing optimally between maximizing chemical diversity and minimizing synthetic complexity.
       - o Many synthetically realistic repeat units with potentially attractive predicted properties that have never been reported can be discovered by searching this database.
       - o Repeat units in the full database obtained through random substitutions on those labeled as biobased in the initial database retain the biobased label.

The construction of new repeat units by using this algorithm is illustrated with an example in Fig. 1. Each repeat unit in the full database is labeled by identifying the repeat unit in the initial database which served as its "seed" and which substitution(s) was (were) made to construct it from its seed. For example, the biobased repeat unit of poly (isosorbyl carbonate) (PIC) is in Generation 0 because it was in the initial database. A repeat unit generated after 1, 2, or 3 substitution steps starting from the repeat unit of PIC as the seed is labeled as a Generation 1, 2, or 3 derivative of PIC. After visual examination of some Generation 3 repeat units, it was decided to exclude repeat units in Generation 2 from further growth steps to avoid the addition of repeat units of great synthetic complexity.

2.3. QSPR calculations to produce library of repeat units and their predicted properties

The P3C module implements the QSPR method introduced in [16] for predicting the properties of isotropic (unoriented) amorphous uncross-linked polymers. This method is also applicable to the amorphous phases of semicrystalline polymers, and to properties not very sensitive to percent crystallinity for highly crystalline polymers. Minor refinements that were made to the method since publication are noted in the software documentation.

The consistent use of predicted properties obtained by using a robust and time-tested QSPR method circumvents the challenges caused by dataset sparseness that arise if only experimental data are used, the challenges involved in curating vast amounts of sometimes contradictory data, and the inconsistencies that would arise if sparse experimental data for the initial polymers were to be mixed with predicted properties in the same library.

QSPR calculations were performed on all repeat units in the algorithmically generated database. A quality control step was then applied by creating Ashby diagrams [38] for pairs of properties as well as histograms of the values of properties. Outliers (repeat units whose homopolymers are predicted to have density > 2.2 g/cm^3, Young's modulus $> 9{,}000$ MPa, and/or Poisson's ratio < 0.2 at room temperature) that may fall outside the applicability limits of the QSPR method were thus identified and removed.

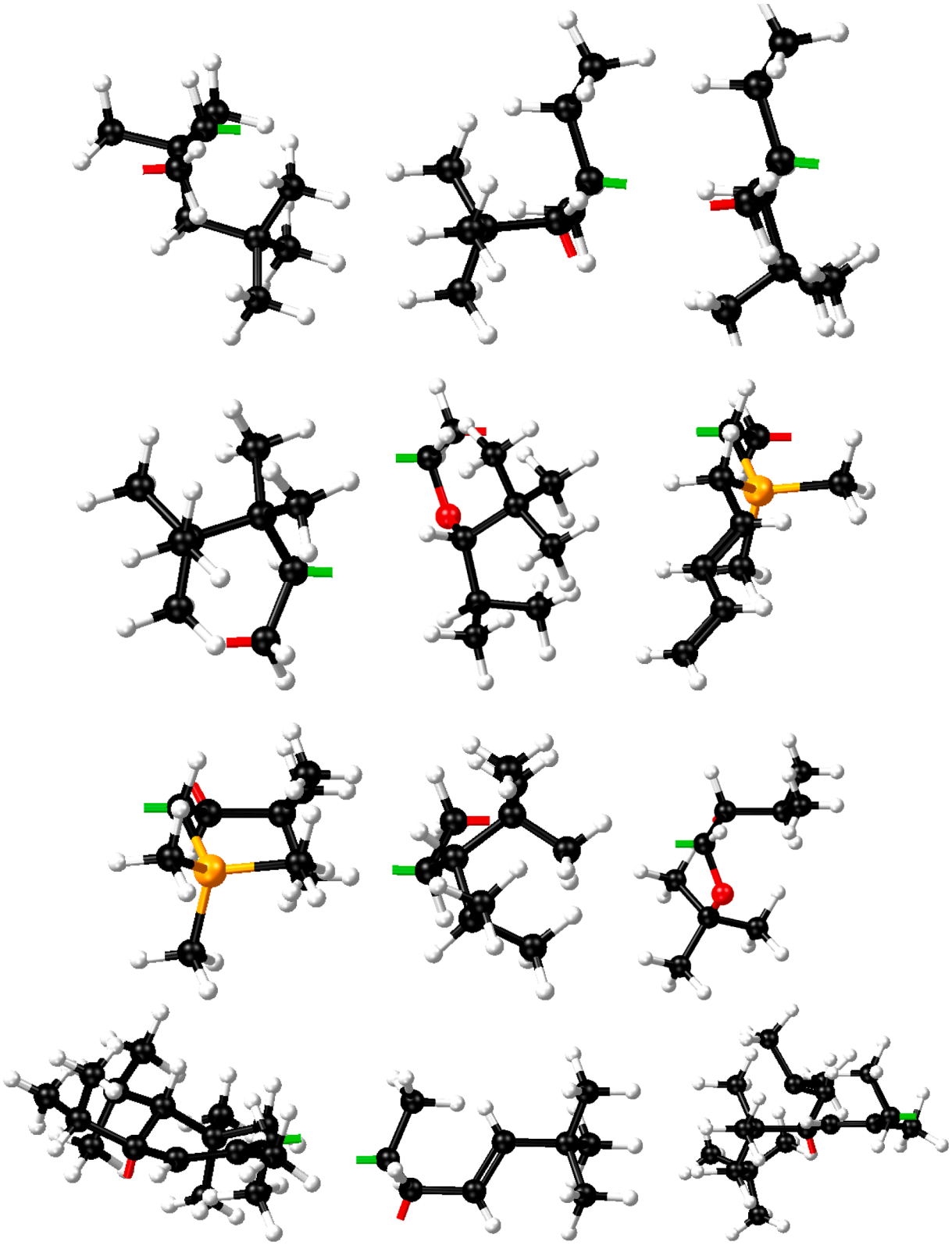

Fig. 5. The 20 repeat units in PEARL that provide the closest matches to PPHP in terms of the search criteria provided in Table 2 are shown. The PPHP alternatives tend to have large (and some of them branched) side groups, and include some silanes (the gold atoms are silicon) and some unsaturated groups.

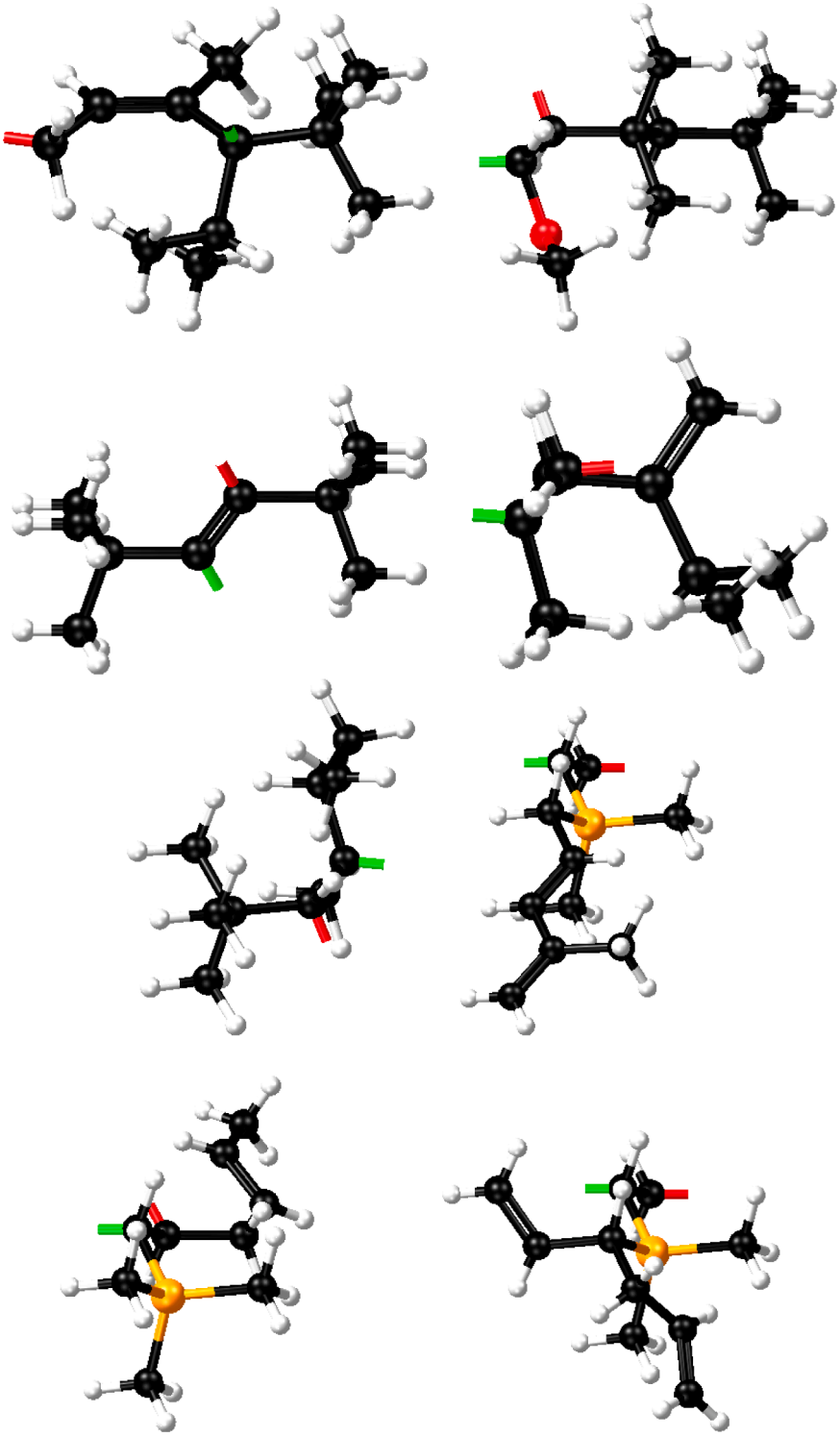

Fig. 5. (*continued*).

The resulting final virtual library (named PEARL) of repeat units and predicted properties is rapidly searchable to identify candidates for *de novo* design.

2.4. Two options for identifying candidates from synthesis by searching PEARL

2.4.1. Identification of analogues of a user-specified polymer

One search option involves placing the repeat unit of a polymer on the active screen of the user interface and searching for analogues in PEARL. It is not necessary for the repeat unit placed on the active screen in a search for analogues to be in PEARL itself. It only needs to be a repeat unit for which the QSPR method can be used to predict properties.

The search for analogues can be performed either by clicking on a box asking Polymer Expert to identify polymers that will manifest similar properties or by specifying the properties to be considered. The computational procedure described below will be used in either case. All

Table 5
Comparison of property targets (excluding properties for which only a pass-fail criterion is imposed) with value for candidate providing closest match and range over 20 candidates providing closest matches in search for PPHP alternatives.

Property	Weight	Target	Closest Match	Minimum of Range	Maximum of Range
Glass transition temperature (K)	0.5	327	321.73	298.40	321.73
Young's modulus (MPa)	1.0	1724	1675.48	1675.48	2129.60
Brittle fracture stress (MPa)	1.0	32	32.22	29.84	40.51

properties calculated by the QSPR method will be considered and weighted equally if the user clicks on the box asking Polymer Expert to identify polymers that will manifest similar properties. Only properties selected by the user will be considered, and they will be assigned the weights specified by the user, if the user selects the properties to be considered.

The QSPR method calculates both "extensive" (molar) properties (such as molar volume, cohesive energy per mole, and heat capacity per mole) which depend on the size of the repeat unit and "intensive" properties (such as density, solubility parameter, and glass transition temperature) which do not. Asking Polymer Expert to identify polymers that will manifest similar properties without specifying any properties hence leads to search results where the candidate repeat units are likely to be similar in "size" to the targeted repeat unit. By contrast, the user can identify repeat units of any size that are likely to provide the best match in terms of important intensive properties by selecting the properties to be considered.

The default option is to conduct the search over all repeat units included in PEARL. The user is also given the option to limit the search to repeat units in PEARL carrying the label indicating that they can be prepared at least partially from biobased precursors.

If the selected properties are not considered to be of equal importance, the user can assign different weights w to them ($0 < w \leq 1$) based on their relative importance. The default value is $w = 1$ for each property if the user does not assign weights.

For example, the repeat units of PET and of BPAPC (Fig. 2) were placed on the active screen in two separate runs, and Polymer Expert was asked in each run to search for biobased analogues based on proximity in terms of density ($w = 0.5$), glass transition temperature ($w = 1.0$), refractive index ($w = 0.5$), dielectric constant ($w = 0.5$), Young's modulus ($w = 1.0$), and brittle fracture stress ($w = 1.0$). The use of these weights produces candidates expected to provide excellent matches to PET and BPAPC in their thermal and mechanical properties while not being very different from them in the lower-weighted but also considered properties.

It is important to understand why brittle fracture stress σ_b (rather than shear yield stress σ_y) was chosen as the target criterion for strength. Shear yield stress is proportional to Young's modulus (E) according to the QSPR used in the calculations: $\sigma_y \approx 0.028 \cdot E$. The use of σ_y in addition to E as a criterion would, hence, be redundant. On the other hand, a polymer which has $\sigma_b < \sigma_y$ will fail by brittle fracture when the value of σ_b is reached so that it will not manifest yielding behavior; and in general, the larger the σ_b/σ_y ratio, qualitatively the more ductile the polymer will be. The use of criteria based on E and σ_b thus ensures that the candidate polymers will be similar to PET or to BPAPC in terms of their stiffness (E), shear yield stress (σ_y) which is simply proportional to E, and ductility (σ_b/σ_y ratio).

For each property P, the mean μ and standard deviation σ were computed over all repeat units in PEARL. All values of property P were then shifted so that they each became mean-centered and they each had unit variance. This transformation was applied to the desired property values in searching PEARL for each property. Hence, the search and library variables were all transformed so that the "distances" in property space were of similar magnitude even if they involved multiple properties.

Polymer Expert rapidly computed the normalized weighted squared deviation, R^2, between those six properties calculated by QSPR (Table 1) for the targeted polymer (PET in one run, BPAPC in the other run) and all polymers in PEARL, and listed candidates in the order of increasing R^2 (declining quality of match) beginning with candidates most similar to the target candidate (those with smallest R^2).

R^2 is defined by Equation (1) when using this search option. N is the number of specified properties; and w_i, P_{ic}, and P_{it} denote, respectively, the weight and the values of the i'th property ($i = 1, 2, \ldots, N$) predicted by QSPR for library polymers and for the target polymer.

$$R^2 = \sum_{i=1}^{N} w_i (P_{ic} - P_{it})^2 \tag{1}$$

2.4.2. Identification of polymers with properties near user-specified targets

The other search option involves listing targets for properties of interest and looking for polymers in PEARL for which the properties predicted by using QSPR are all near those targets.

The default option is to conduct the search over all repeat units included in PEARL. The user is also given the option to limit the search to repeat units in PEARL carrying the label indicating that they can be prepared at least partially from biobased precursors.

If the selected properties are not considered to be of equal importance, the user can assign different weights w' to them ($0 < w' \leq 1$) based on their relative importance. The default value is $w' = 1$ for each property if the user does not assign weights.

The QSPR method used in the preparation of PEARL only predicts the properties of isotropic amorphous thermoplastics. For example, the properties listed for PET in Table 1 are only for its amorphous phase. The properties of articles manufactured by using PET vary significantly depending on percent crystallinity and extent of orientation introduced by the fabrication process. Furthermore, product grades optimal for use in different fabrication processes also differ somewhat from each other. A user interested in identifying PET alternatives optimal for different uses would be able to do so by using the second search option and explicitly listing property targets instead of identifying PET as the generic target.

Polypropylene, which is highly crystallizable, and which is often modified by the addition of ingredients such as reinforcing fibers or impact modifiers, provides a helpful example of the utility of this option. The QSPR method only calculates the properties of the amorphous phase of polypropylene. Many properties crucial in applications of polypropylene depend strongly on its percent crystallinity. If reinforcing fibers or impact modifiers are added, many properties crucial in applications of such modified products also depend on the type(s) and percentage(s) of the additional ingredient(s). Using the first search option (specifying polypropylene as the target polymer) would not identify any viable alternatives for either PPHP or PP10GF whose mechanical properties differ greatly from the mechanical properties of the amorphous phase of polypropylene calculated by using the QSPR method.

There is considerable variation between several important properties of different PPHP product grades and different PP10GF product grades, but these properties fall into different ranges for PPHP and for PP10GF. The specification of targeted properties typical for PPHP and PP10GF (Table 2) led to the identification of viable candidates for alternatives. The mechanical property (Young's modulus and tensile strength) values used in defining the targets were taken from the technical datasheets of two commercial products sold by the RTP Company at the date of completion of this paper; namely, RTP 100 and RTP 101 HB, respectively. The reasoning behind the choice of the brittle fracture stress

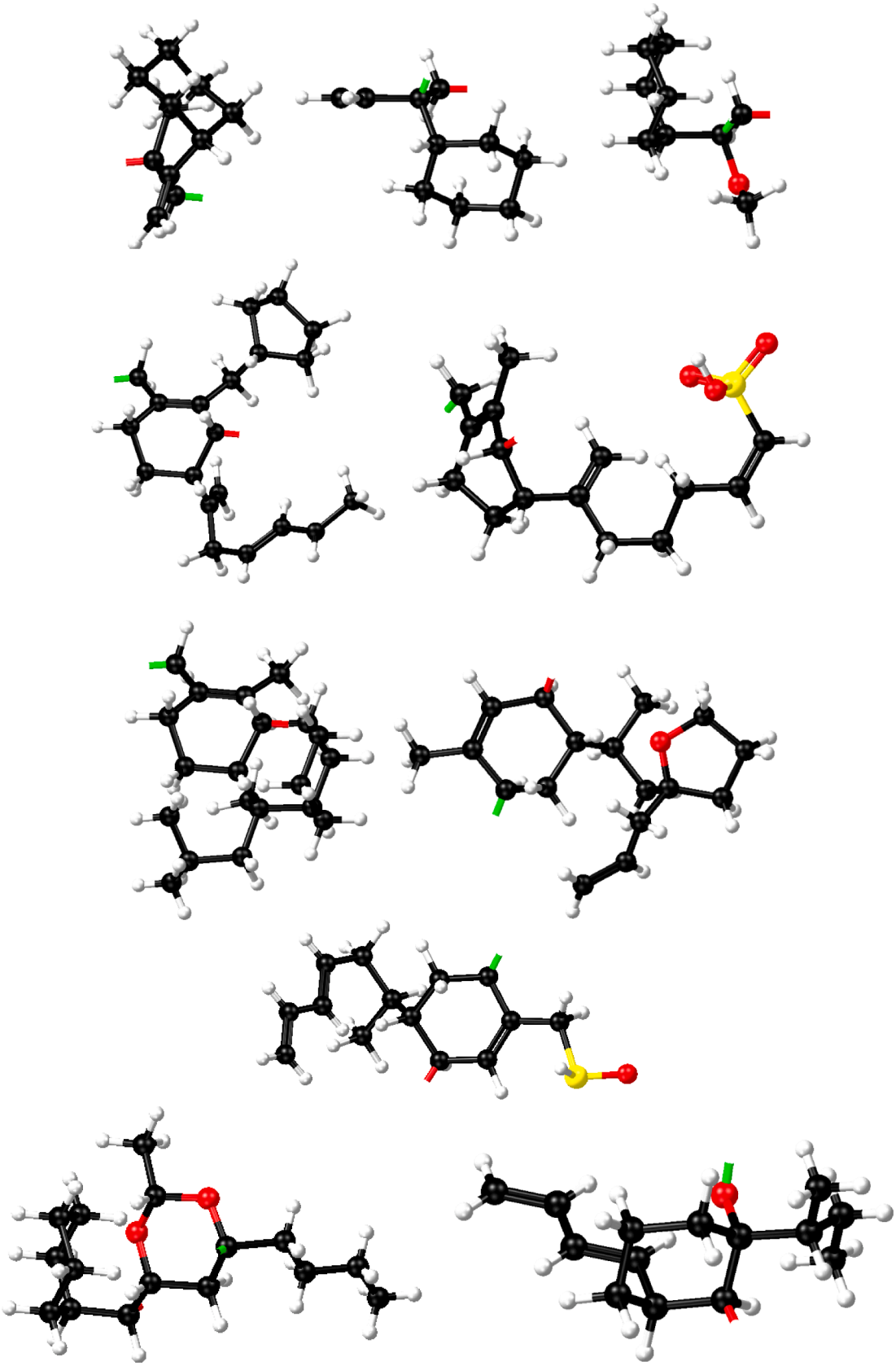

Fig. 6. The 20 repeat units in PEARL that provide the closest matches to PP10GF in terms of the search criteria provided in Table 2 are shown. The PP10GF alternatives include some repeat units containing one or more structural features such as saturated rings, sulfur-containing fragments, and/or halogens.

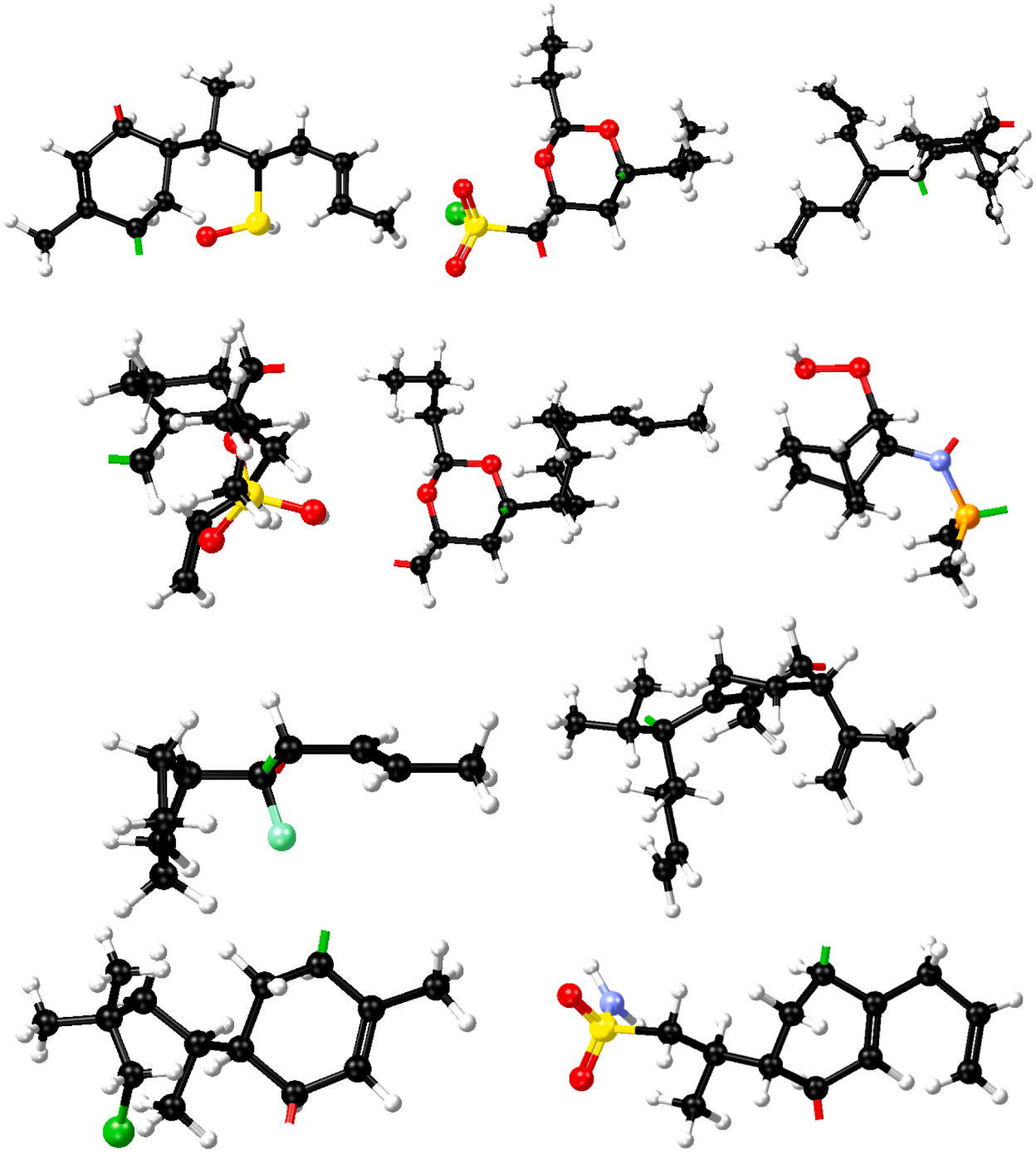

Fig. 6. (*continued*).

instead of the shear yield stress as the tensile strength criterion is the same as for PET and BPAPC.

The first three criteria differentiate PPHP from PP10GF in terms of the mechanical and thermal properties that differ greatly between them and that determine if PPHP or PP10GF is more suitable for a given application. PPHP is more flexible, while PP10GF is stronger and also exhibits greater dimensional stability with increasing temperature. When an inexpensive lightweight polymer of low polarity is needed, PPHP is preferred if the article to be fabricated needs to have greater flexibility, while PP10GF is preferred if the article needs to have greater strength and dimensional stability. The mechanical properties are assigned w'=1.0. The glass transition temperature (used instead of the heat distortion temperature under a load of 1.82 MPa which cannot be calculated by the QSPR method) is assigned w'=0.5, assuming (for purposes of illustration) that mechanical properties at room temperature are more important than dimensional stability at high temperatures to a particular user.

The density differs very little between PPHP (0.91 g/cm^3 for RTP 100) and PP10GF (0.97 g/cm^3 for RTP 101 HB). Such small differences are not crucial in choosing between them for any application. The density was, therefore, included with upper limits in the searches to ensure that all candidates were lightweight, just like PPHP and PP10GF.

Polymers that lack polar bonds tend to have a low dielectric constant, and hence the dielectric constant can be used for qualitative estimation of chemical resistance to different classes of solvents and environmental agents. PPHP has a dielectric constant of 2.2. The addition of 10 % by

Table 6
Comparison of property targets (excluding properties for which only a pass-fail criterion is imposed) with value for candidate providing closest match and range over 20 candidates providing closest matches in search for PP10GF alternatives.

Property	Weight	Target	Closest Match	Minimum of Range	Maximum of Range
Glass transition temperature (K)	0.5	402	401.92	391.63	409.34
Young's modulus (MPa)	1.0	2965	2957.72	2823.22	3181.35
Brittle fracture stress (MPa)	1.0	39	39.30	37.58	43.72

Table 7
Numbers and percentages of repeat units in PEARL that provide polymers with predicted dielectric constants in different ranges.

Range	Number	%	Range	Number	%
1.9880 to 1.99	3	0.0003	4.50 to 4.99	3942	0.3582
2.00 to 2.49	36,710	3.3357	5.00 to 5.49	781	0.0710
2.50 to 2.99	489,693	44.4973	5.50 to 5.99	143	0.01300
3.00 to 3.49	438,013	39.8011	6.00 to 6.49	30	0.00272
3.50 to 3.99	109,486	9.9487	6.50 to 7.0428	4	0.00045
4.00 to 4.49	21,698	1.9716			

weight of glass fibers increases the dielectric constant (to 2.7 for RTP 101 HB). The dielectric constant was, therefore, included with upper limits in the searches to ensure that candidates would not far exceed their targeted polymers in polarity.

Only properties with a specific target value were used in calculating the normalized weighted mean square deviation R'^2. R'^2 was calculated relative to the target values for those three properties, after shifting all values of each property in the same manner as was described earlier so that they each became mean-centered and they each had unit variance.

R'^2 is defined by Equation (2) when using this search option. N' is the number of specified properties; and w'_j, P'_{jc} and P'_{jt} denote, respectively, the value of the j'th property ($j = 1, 2, \ldots, N'$) predicted by using QSPR for library polymers and for the target polymer.

$$R'^2 = \sum_{j=1}^{N'} w'_j \left(P'_{jc} - P'_{jt}\right)^2 \tag{2}$$

The examples above used the properties of two existing products (PPHP and PP10GF) as targets to illustrate this search option. It should be noted, however, that this search option is very flexible. It can, for example, also be used to search for polymers that may provide unique user-defined property combinations not matching those of any existing polymer.

3. Applications

Five examples of applications will be provided below. It will be seen that many promising candidates in each application are unobvious and unlikely to have been identified without using a polymer informatics approach.

3.1. Identification of biobased alternatives for PET

Alternatives that can be prepared with a significant percentage (but ideally 100 %) of biobased content were sought for PET. The search criteria (see Section 2.4.1) targeted the identification of candidates expected to provide an excellent match for the thermal and mechanical properties while not being extremely different for some additional properties.

The 20 repeat units in PEARL that can be synthesized at least partially from biobased precursors and that provide the closest matches to PET in terms of the search criteria provided in Table 1 are shown in Fig. 3. Table 3 compares the target value for each property with the value for the candidate providing the closest match and the range over the 20 candidates providing the closest matches.

3.2. Identification of biobased alternatives for BPAPC

Alternatives that can be prepared with a significant percentage (but ideally 100 %) of biobased content were sought for BPAPC. The search criteria (see Section 2.4.1) targeted the identification of candidates expected to provide an excellent match for the thermal and mechanical properties while not being extremely different for some additional properties.

The 20 repeat units in PEARL that can be synthesized at least partially from biobased precursors and that provide the closest matches to BPAPC in terms of the search criteria provided in Table 1 are shown in Fig. 4. Table 4 compares the target value for each property with the value for the candidate providing the closest match and the range over the 20 candidates providing the closest matches.

3.3. Identification of alternatives for PPHP

Alternatives were sought for PPHP. The search criteria (see Section 2.4.2) targeted the identification of candidates expected to provide an excellent match for the thermal and mechanical properties while also ensuring that all candidates were polypropylene-like; namely, lightweight and of low polarity.

The 20 repeat units in PEARL that provide the closest matches to PPHP in terms of the search criteria provided in Table 2 are shown in Fig. 5. Table 5 compares the target value for each property (excluding the properties for which only a pass-fail criterion is imposed) with the value for the candidate providing the closest match and the range over the 20 candidates providing the closest matches.

3.4. Identification of alternatives for PP10GF

Alternatives were sought for PP10GF. The search criteria (see Section 2.4.2) targeted the identification of candidates expected to provide an excellent match for the thermal and mechanical properties while also ensuring that all candidates were 10 % glass fiber reinforced polypropylene-like; namely, lightweight and of polarity not far exceeding that of PP10GF.

The 20 repeat units in PEARL that provide the closest matches to PP10GF in terms of the search criteria provided in Table 2 are shown in Fig. 6. Table 6 compares the target value for each property (excluding the properties for which only a pass-fail criterion is imposed) with the value for the candidate providing the closest match and the range over the 20 candidates providing the closest matches.

3.5. Identification of polymers that may provide unusually high dielectric constants

High dielectric constant polymers are highly desirable for use in new applications such as gate dielectrics for printable electronics and polymer film capacitors [39]. The numbers and percentages of repeat units in PEARL that provide polymers with predicted dielectric constants in different ranges are listed in Table 7. It is seen that 4900 (0.445 %) of the repeat units are predicted to provide a dielectric constant of ≥ 4.5. The 10 repeat units in PEARL that provide the highest predicted dielectric constant are shown in Fig. 7.

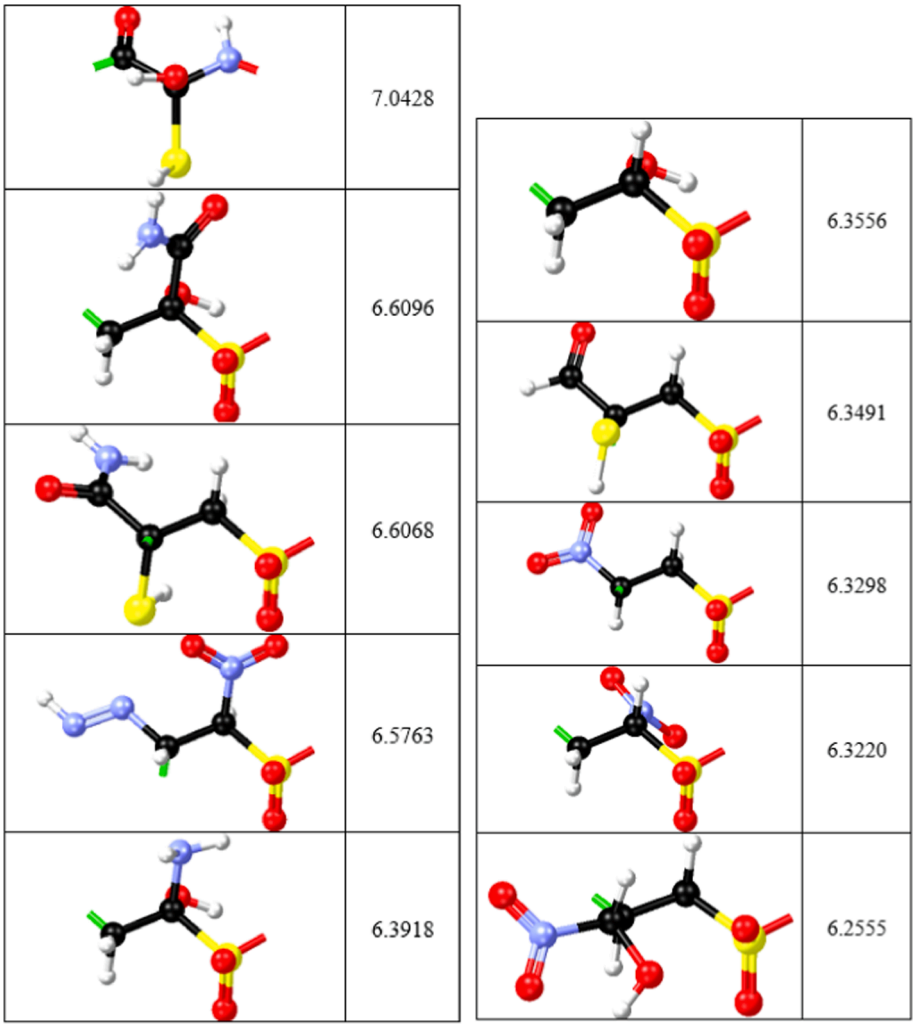

Fig. 7. The 10 repeat units in PEARL that provide the highest predicted dielectric constant are shown. The predicted dielectric constant is shown to the right of each repeat unit.

4. Future work

Future work will focus on improving the quality of candidate repeat units by refining the QSPR method, enhancing the diversity of candidate repeat units by expanding PEARL, providing additional interactive search options, and converting Polymer Expert into a versatile R&D platform that users can customize for their own needs.

The top priority in refining the QSPR method is likely to be given to improving the equations used for the small-strain (elastic) behavior of isotropic (unoriented) glassy (below the glass transition temperature) amorphous thermoplastics at room temperature (T = 298 K).

The top priority in expanding PEARL is likely to be given to using the algorithm described in Section 2.2 to create hundreds of thousands of additional Generation 2 repeat units and then add these repeat units and their predicted properties to PEARL.

The additional interactive search options will enable users to explore regions of interest in the polymer design space visually rather than being limited to entering property targets into pulldown menus. Enabling users to create Ashby diagrams from pairs of properties listed in PEARL and to then select points or entire regions of those diagrams to explore repeat units at those points or in those regions interactively is under consideration, as is the option of providing users the ability to visualize three properties in three-dimensional diagrams.

Improvements under consideration to enable customization, to be prioritized based on the extent of interest from users for each improvement, include providing users the ability to:

1. Rather than being limited to the repeat units in PEARL, explore user-defined polymer design spaces in more detail by specifying user-selected fragments to derive candidates either via combinatorial or via stochastic fragment substitutions on a “seed” repeat unit.
2. Edit PEARL to create customized versions substituting predictions made with correlations developed by the user for the general-purpose correlations of the built-in QSPR method.
3. Rather than being limited to selection based on properties predicted by QSPR, incorporate proprietary repeat units and proprietary data in user-defined polymer design spaces.
4. Use the method implemented in PEARL as a standalone polymer informatics software tool to develop proprietary repeat unit and predicted property libraries separate from PEARL.

5. Conclusions

Polymer informatics is 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. Polymer informatics will greatly accelerate the exploration of polymer design spaces as its capabilities are enhanced and its use becomes widespread. This paper presents the first stage of our ongoing work to implement polymer

informatics methods for research and development.

A versatile and user-friendly "expert system" for *de novo* polymer design, named Polymer Expert, was developed and implemented. Polymer Expert can be used to rapidly generate novel candidate polymer repeat units to meet desired performance targets.

For the initial implementation, we (1) generated an initial repeat unit database, (2) expanded this initial database into a large analog repeat unit database, (3) performed QSPR calculations for all repeat units in the large analog database, and (4) integrated the resulting searchable library of repeat units and their predicted properties as a new module in a materials modeling and simulation software suite which provides a broad range of capabilities.

Applications were illustrated by identifying biobased alternatives for poly(ethylene terephthalate) (PET) and bisphenol-A polycarbonate (BPAPC), alternatives for highly crystalline polypropylene homopolymer (PPHP) and 10 % glass fiber containing polypropylene (PP10GF), and polymers that may provide unusually high dielectric constants. Many promising candidates were unobvious and unlikely to have been identified without using a polymer informatics approach.

Future work will focus on improving the quality of candidate repeat units by refining the QSPR method, enhancing the diversity of candidate repeat units by expanding PEARL, providing additional interactive search options, and converting Polymer Expert into a versatile R&D platform that users can customize for their own needs.

Declaration of interest

BL and JA are employed by Materials Design SARL. DR and CF are employed by Materials Design, Inc. BL, JA, DR, and CF are shareholders of Materials Design, Inc. JB is an independent consultant on polymers and composites, collaborating with Materials Design, Inc.

CrediT authorship contribution statement

Jozef Bicerano: Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Project administration, Resources, Validation, Visualization, Writing – original draft, Writing – review & editing. **David Rigby:** Data curation, Formal analysis, Investigation, Methodology, Validation, Visualization. **Clive Freeman:** Data curation, Formal analysis, Investigation, Methodology, Project administration, Supervision, Validation, Visualization. **Benoit LeBlanc:** Software. **Jason Aubry:** Software.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

I am providing a file containing supplementary information with details for interested readers to download from the journal website.

Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.commatsci.2024.112810.

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