

PRF #57150-ND7

Project Title: Functionalized Polydicyclopentadiene
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Polydicyclopentadiene (PDCPD) is an industrially important ROMP polymer valued for its light weight and impressive material strength, as well as for its good performance at both high and low temperatures. PDCPD body panels are widely used in heavy-duty construction equipment and transport trucks. However, PDCPD has four important disadvantages that have limited its broader utility: (1) entrapped dicyclopentadiene monomer lends an unpleasant odor to PDCPD parts; (2) the polymer has an intrinsically low surface energy, which makes it difficult to apply paints or adhesives to PDCPD components; (3) the properties of PDCPD (e.g. surface energy, glass transition temperature, modulus, etc.) are not chemically tunable; and (4) the material is not recyclable because the chemical crosslinks that form during polymerization cannot be undone.

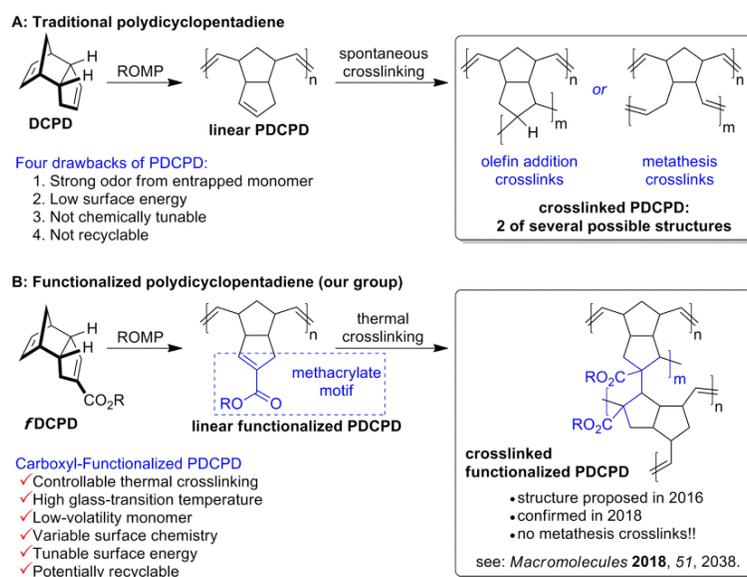


Figure 1. Comparison of traditional and functionalized polydicyclopentadiene polymers.

In preliminary data for our PRF proposal, we demonstrated the synthesis of a novel C-linked methyl ester-functionalized polydicyclopentadiene (*f*PDCPD), and showed that this could be successfully polymerized. We hypothesized that thermal curing of the resulting linear polymer would lead to a particular type of chemical crosslink arising from specific head–tail olefin-addition polymerization through the embedded methacrylate motif (see Figure 1). This is significant because the structure of the chemical crosslink in regular (i.e. unfunctionalized) PDCPD remains a matter of considerable debate, despite the fact the polymer has been used industrially for over two decades. Our characterization studies would thus not only shed light upon our own material, but could also provide important insight into structural aspects of the existing thermoset.

We further hypothesized that we could tune the properties of our new *f*PDCPD material in two important ways: either by saponifying the methyl ester to produce a surface carboxylic acid group (which would substantially increase the surface energy), or by incorporating different ester groups either before or after the polymerization step (which would not only change the surface energy but would affect T_g and modulus). Indeed, the first of these hypotheses proved very easy to verify, and we were able to publish our first manuscript from this research program before we were notified of the PRF award (see: *ACS Omega* **2016**, *1*, 532-540).

In addition to solving the surface energy and chemical tunability challenges described above, our ester-bearing monomer has a pleasant smell and should provide a chemical handle to undo the molecular crosslinks formed during thermal curing – if our hypothesized crosslink structure in Figure 1 is correct! Thus our inclusion of a functional group within the PDCPD structure has the potential to solve all of the principal challenges associated with the current use of the polymer.

Shortly after receiving notification of the PRF award, we were also awarded an NSERC I2I grant aimed at commercialization of our first-generation methyl-ester functionalized PDCPD. In consultation with the PRF program officer, we established that there was no overlap between these projects – the I2I money would be used to support scale-up and commercialization efforts of the original methyl-ester homopolymer while the PRF funds would be used exclusively for non-commercial discovery-based research into: (1) rigorously establishing the structure of the molecular crosslink in *f*PDCPD by spectroscopic means; (2) developing new homopolymers bearing different ester functional groups; (3) developing new copolymers comprised of two different functionalized dicyclopentadiene monomers; and (4) taking steps toward the development of a “de-crosslinking” method that could be used to establish an *f*PDCPD recycling process.

With PRF funding, we have completed the first of these aims (see: *Macromolecules* **2018**, *51*, 2038-2047), and have a manuscript currently in preparation describing the successful conclusion of the second aim (see Figure 2 for summary). The third aim is also mostly complete, and we hope to have another manuscript in preparation soon (see Figure 3 for summary). As evidence for the impact of this research, we are pleased to note that our 2018 *Macromolecules* paper was selected for a highlight article in *Advances in Engineering*. This can be accessed at: <https://advanceseng.com/understanding-molecular-structure-understand-polymer-properties/>.

In parallel work (funded by our NSERC I2I, but very much informed by the insight we gain from our PRF-funded research) we developed an improved synthesis of our functionalized dicyclopentadiene monomer mixture on half-kilo scale, and invented a laboratory-scale reaction injection molding protocol suitable for the preparation of macro-scale *f*PDCPD objects (Figure 4; see: *ACS Appl. Polym. Mater.* **2019**, *1*, 2460-2471). Dynamic mechanical analysis (DMA) studies on these objects established for the first time that our *f*PDCPD polymer has equivalent modulus to that of the parent PDCPD material. In our view, these data provide the most compelling support to date for the incorporation of functionality into commercial PDCPD products.

With the mechanical properties of our material thus established, we have now turned our attention to how to produce it on greater scale, to facilitate greater collaboration with industrial partners. In ongoing work, therefore, we are re-designing the functionalized monomer to allow it to be produced with greater regiochemical control. As an added benefit, this redesigned material will undergo crosslinking more quickly (and at lower temperature), improving performance in the reaction injection molding protocols that our industrial colleagues are most interested in.

I am a small-molecule synthetic organic chemist by training, and prior to taking on this project I'd never even used the word 'polymer' in a grant proposal. Thanks to this PRF New Directions grant, my students and I have been able to make inroads into an entirely new research area. Our newfound expertise in the field of thermoset polymers has already led us to obtain a CDN \$259,000 Mitacs Accelerate grant for a different – but somewhat thematically related – project aimed at the invention of novel chemical crosslinkers. This was supplemented by a further CDN \$160,000 in funding from the Canadian Department of Defense to apply our crosslinkers in antiballistic applications, and then further support through a CDN \$1.5M team grant aimed at developing comfortable and breathable armor solutions for the Canadian military. Most gratifyingly, the first manuscript from our Mitacs-funded research was recently accepted for publication in *Science*. It is evident that the PRF funds have been enormously successful into leading us in a bold new research direction, and we are extremely grateful to the donors of the American Chemical Society Petroleum Research Fund for the opportunities provided.

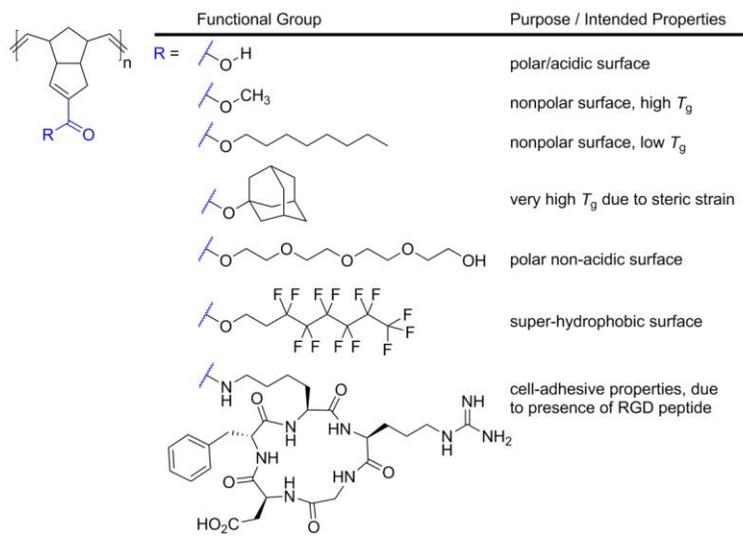


Figure 2. Novel homopolymers synthesized and characterized in PRF-funded research. Characterization experiments include surface energy measurements, TGA/DSC analysis and tumor cell adhesion assays.

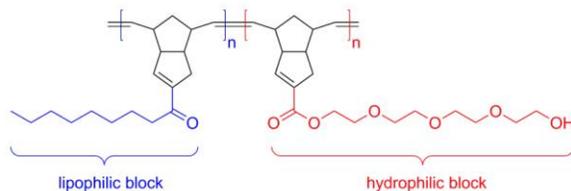


Figure 3. Representative amphiphilic block copolymer synthesized in PRF-funded research. Self-assembly experiments are confirm nanoparticle formation.



Figure 4. Macro-scale functionalized PDCPD objects produced in a reaction injection molding process.