

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 leads 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.

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 (a manuscript based on these studies is currently in preparation for *OPRD*) 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.

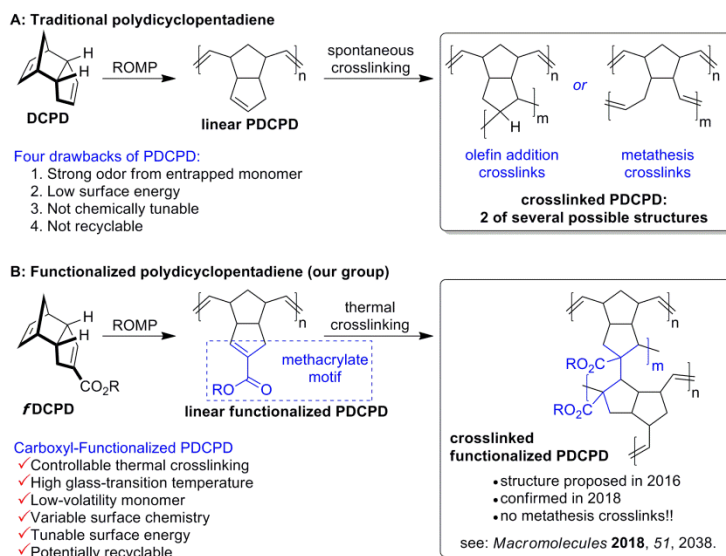


Figure 1. Comparison of traditional and functionalized polydicyclopentadiene polymers.

Thus far, we have completed the first of these aims (see: *Macromolecules* **2018**, *51*, 2038-2047), and mostly completed the second (manuscript in preparation; see Figure 2 for summary). The third aim is also well underway (see Figure 3), and will be the principal focus of our second year's research. By knowing the structure of our molecular crosslink, we also lay the groundwork for our ultimate goal of a recycling process, and so we expect to make progress on this fourth and final aim during our second year of research as well.

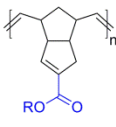
Our detailed spectroscopic study of the molecular crosslink in *f*PDCPD is arguably our most important advance during the first term of our PRF award, and so merits further comment here. Characterizing crosslinked thermoset polymers like PDCPD is extremely challenging because the materials are inherently heterogeneous and are also totally insoluble. Therefore, standard characterization methods employed for uniform (macro)molecular species are of limited value. This is one of the reasons that the structure of the unfunctionalized PDCPD crosslink is still so poorly understood. In this regard, our appended ester functional group provides a convenient “handle” for spectroscopic studies: NMR, IR and Raman signals will all be affected by changes that happen near the carbonyl functional group. Thus, in addition to engendering polydicyclopentadiene with novel properties, our newly added ester group can also be viewed as a chemical probe that can be used to reveal deep-seated structural information.

In order to conclusively establish the structure of the crosslink in *f*PDCPD, we conducted solid state NMR, IR and Raman experiments on materials that had been thermally crosslinked for different amounts of time. These data revealed that we could tune the degree of crosslinking – high temperature curing “froze” the system at a relatively low crosslink density while longer times at a lower temperature encouraged more chain mobility within the sample, ultimately affording a nearly quantitative chemical crosslinking. This is the first time that such tunability in the *degree of crosslinking* has been demonstrated for any polydicyclopentadiene material.

We considered 5 different crosslinking scenarios: olefin addition through the backbone alkene only; olefin addition through the pendent methacrylate motif; mixed-mode olefin addition reactions occurring through both types of alkenes; oxidative crosslinking resulting from autoxidation; and metathesis-based crosslinks. In addition to the spectroscopic methods discussed above, conclusive identification of the crosslink structure required the synthesis of isotope-labeled analogs of our functionalized polymer, as well as the synthesis of selectively reduced congeners for more extensive TGA/DSC studies. We were ultimately able to confirm that head–tail polymerization through the methacrylate moiety was responsible for the vast majority of crosslinks within the material. Critically, no evidence whatsoever could be found for metathesis-based crosslinks – despite the fact that most authors assume (erroneously, we believe) that this is the dominant crosslink within traditional PDCPD materials. Once again, knowing the structure of the thermally-induced crosslink is an absolute requirement for us to be able to uncouple these bonds in a future *f*PDCPD recycling process.

By way of addressing the impact of this research, we are pleased to note that our *Macromolecules* paper on this work was selected for a highlight article in *Advances in Engineering*. This can be accessed at: <https://advanceseng.com/understanding-molecular-structure-understand-polymer-properties/>.

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 this field of thermoset polymers has already led us to obtain a \$259,000 MITACS Accelerate grant for a different – but somewhat thematically related – project aimed at the invention of novel chemical crosslinkers. We are extremely grateful to the donors of the American Chemical Society Petroleum Research Fund for the opportunities provided to us through this funding.




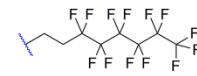
Functional Group	Purpose / Intended Properties
R = H	polar/acidic surface
CH ₃	nonpolar surface, high <i>T_g</i>
CCCCCCCC	nonpolar surface, low <i>T_g</i>
	very high <i>T_g</i> due to steric strain
CCCCOCCOCCOCCOCCO	polar non-acidic surface
	super-hydrophobic surface

Figure 2. Novel homopolymers synthesized and characterized so far. Characterization experiments include surface energy measurements, TGA/DSC analysis and tumor cell adhesion assays.

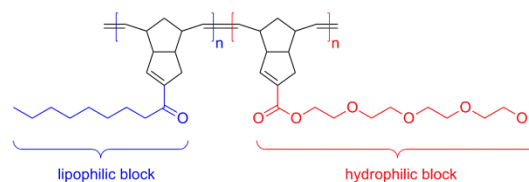


Figure 3. Representative amphiphilic block copolymer synthesized recently. Additional block copolymer synthesis and self-assembly experiments are underway.