DOI: 10.1021/ma901123p

Macromolecules
COMMUNICATION TO THE EDITOR

Staudinger's Poly(cyclopentadiene): Sintering Processing of Poly(Diels−Alder cyclopentadiene)

Brittnee Veldman,[†,‡] Tamar Kaully,[†,‡] Russell K. Feller,[§] Eduardo Falcao,[§] and Fred Wudl*[,†,‡,§]

[†]*Department of Chemistry and Biochemistry and* [‡]*Center for Polymers and Organic Solids and* [§]*Materials Research Laboratory, University of California, Santa Barbara, California 93106*

Received June 4, 2009
Revised Manuscript Received August 24, 2009

Introduction. In principle, there are at least four ways of linking cyclopentadiene units in a polymer: poly(cyclopentadiene) could be the result of 1,4-linking, 1,2-linking, and [2 + 4] addition reactions as well as ring-opening metathesis polymerization of dicyclopentadiene.[1] A quick literature check under "polycyclopentadiene" yields a large number of references to essentially only the first two forms of the polymer. However, a more thorough examination revealed that in 1926 the father of polymer science, H. Staudinger, described a poly([2 + 4]-cyclopentadiene).[2] Staudinger and Bruson concluded by a rather interesting correlation of molecular weight with melting point that their polymer was only a hexamer.[2] Because their initial work was performed before the publication of the "diene synthesis" (Diels−Alder reaction), Staudinger and Bruson actually had the incorrect mode of bonding that was later corrected by Alder and Stein.[3] These authors went on to fully characterize the dimer, trimer, and tetramer.

We have revisited PDACp that, to the best of our knowledge, has remained dormant since it was last mentioned in a 1944 review.[4] Here we present the characterization and mechanical properties of poly(Diels−Alder cyclopentadiene) (PDACp), which is processable by sintering.

A working definition of sintering for amorphous polymers involves heat-treating a sample to a temperature at, or above, the glass transition temperature (T_g) and near, or above, the melting temperature (T_m), if semicrystalline.[5] It has also been shown that polymers that are semicrystalline such as PTFE respond well to compaction, especially if processed at, or just above, the melting temperature.[6]

Results and Discussion. Following the Staudinger protocol[2] (see Supporting Information), the polymer was obtained as a slightly off-white fine powder that, by mass spectroscopy, was at least an octadecamer [(Cp)18].[7] A hot ODCB (*o*-dichlorobenzene)-soluble fraction revealed an H NMR spectrum that was very similar to that of the pentamer (essentially the same number of resonances of similar multiplicity and chemical shift). It was clear from the complexity of the spectra that the pentamer was isolated as a mixture of multiple exo and endo isomers, already observed by Alder and Stein for the trimer and tetramer, before the advent of NMR. Semiempirical energy minimization calculations reveal that if the polymer were composed of 19 strictly endo-linked units, the macromolecule would form a toroid.[8] It is likely coincidental that the maximum molecular weight, determined by mass spectroscopy, corresponded to the octadecamer.

To determine whether PDACp was a good candidate for compaction and sintering, it was examined by X-ray diffraction, termogravimetric analysis (TGA), and differential scanning calorimetry (DSC). From the diffraction pattern in Figure 1, PDACp can qualitatively be classed as a semicrystalline polymer because of the peak definition and multiple reflections (main reflection: 16.58 2θ, 1.58 fwhm).[9,10] Once PDACp was established to be semicrystalline, its thermal properties were explored. The TGA trace for PDACp exhibited a mass loss of 2.5% at 215 °C, followed by decomposition. The trimer and tetramer began to decompose at 80 and 130 °C, respectively. In the DSC plots of the three compounds only the trimer displayed a thermal transition (melting point of 66 °C). No thermal transitions were detected up to 200 °C in the DSC of PDACp. In addition, the density of the powders of all three compounds was determined by helium picnometry. The densities of the pure powders were used to calculate the theoretical maximum density (TMD) of each of the composite powders and to serve as an upper bound density for the pellets.[6] Because of PDACp's very rigid structure and the possibility of retro addition at high temperatures, typical sintering protocols could not be applied in this case. However, the possibility of retro-Diels−Alder reactivity, applicable to remending polymers by us,[11] could be exploited in future work on high-temperature processing that, strictly speaking, would not be sintering. Instead, small percentages of tricyclopentadiene (trimer) or tetracyclopentadiene (tetramer) were added to the PDACp to act as a potential lubricant and/or liquid phase during compaction and sintering. Hence, 10 wt % of either trimer or tetramer was added to the PDACp to ease compaction.

Following the characterization of the three materials, compaction and sintering regimes were established. When choosing parameters, the intent was to keep to a brief comparative survey rather than an optimization. To this end, one compaction load of 3770 kg/cm^2 was chosen, as it was more than sufficient to create robust and coherent pellets and compressions test samples. On the basis of the decomposition temperature of 215 °C, the compaction and sintering temperature of 200 °C was selected for the pure polymer. For the composites, the sintering temperature was based on thermal transitions of the additives. To determine whether incorporating a melting phase was beneficial, 70 °C was chosen because it exceeded the melting point of the trimer but was safely below its degradation temperature.

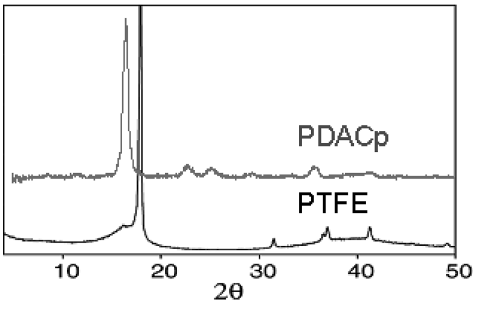

Figure 1. Powder XRD patterns of PADCp, overlaid on a pattern of PTFE from ref 9. Relative vertical scaling is arbitrary.

*Corresponding author. E-mail: wudl@chem.ucsb.

 Published on Web 08/28/2009

Table 1

sample	thermal transition[a] (°C) melt	thermal transition[a] (°C) decomposition	powder density[b] (g/cm^3)	pellet density[c] (g/cm^3)	TMD[d] (%)	Vickers hardness[e] (MPa)	Young's modulus (GPa)
powders							
trimer	66	80	1.169		100.00		
tetramer		130	1.253		100.00		
polymer		215	1.303		100.00		
pellets							
polymer (25 °C)			1.303	1.204	92.4	363 ± 56	1.56 ± 0.48
polymer (70 °C)			1.297	1.223	94.3	354 ± 44	1.70 ± 0.25
polymer (200 °C)			1.293	1.255	97.1	336 ± 35	2.54 ± 0.28
10% trimer blended (70 °C)			1.285	1.225	95.3	265 ± 33	2.16 ± 0.30
10% tetramer blended (70 °C)			1.293	1.219	94.3	273 ± 27	2.94 ± 0.15

[a] Temperatures determined by TGA and DSC. [b] Powder density of the three pure powders was collected via helium picnometry. For the pellets, a weighted average of the densities for the two components was taken to be the powder density. These powder densities were taken to be the theoretical maximum density of each pellet. [c] The bulk density is that of the pellets measured by the Archimedean method. [d] TMD percentage relates the bulk density to the powder density (bulk/powder) × 100 = %TMD. [e] All Vickers hardness values were collected under a load of 0.185 kg/mm^2 for 30 s compression.

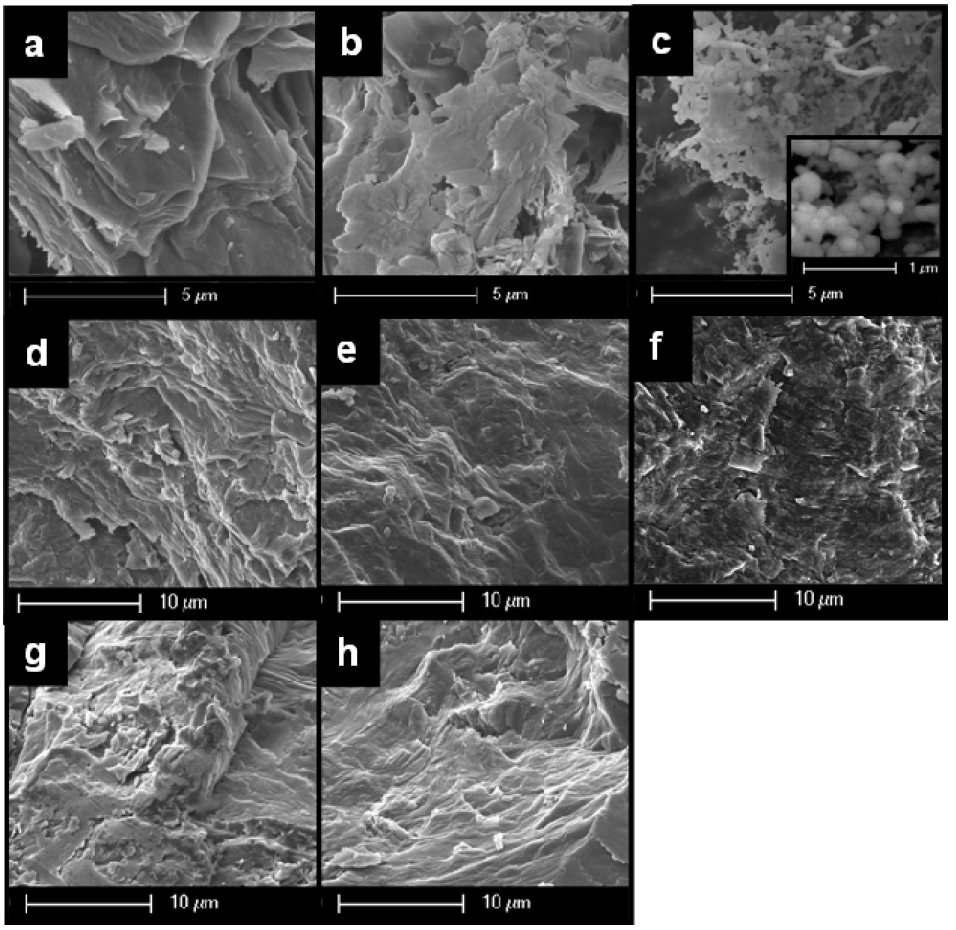

Figure 2. Electron micrographs of the pure powders of (a) PDACp, (b) tetramer, and (c) trimer under 5000× magnification. The inset at 20 000× reveals the nanostructure of the trimer. The fractured pellet surfaces at 2000× magnification of (d) pure PDACp pressed without sintering, (e) pure PDACp pressed and sintered at 70 °C, (f) pure PDACp pressed and sintered at 200 °C, (g) PDACp blended with 10% trimer pressed and sintered at 70 °C, and (h) PDACP blended with 10% tetramer pressed and sintered at 70 °C.

Analysis of the pellets began with Archimedes density measurements, from which the bulk pellet density and the TMD percentage were obtained (Table 1).[12] All samples were found to have densities ranging from 1.204 to 1.25 g/cm^3 and TMD figures above 90%. When compared with the control pellet, pressed at 25 °C, the sintered samples had slightly increased bulk densities but were within experimental error of one another.

Morphology. The powders of the three compounds have a distinctive morphology (Figure 2a−c). The PDACp has a very dense and compact form, which, on closer inspection, is comprised of fine layers. This would not be unreasonable from a material with a rigid backbone and weak intermolecular forces. The tetramer is quite reminiscent of the polymer yet with much more pronounced flaking. The morphology of the trimer is very different, exhibiting a few sheets interconnected by fibrous nanometer-sized strings of crystallites.

Scanning electron microscopy of the pellet fracture surfaces yielded support for the observed mechanical properties (Figure 2d−h). Though the surface of the nonsintered

polymer pellet was more coherent than the polymer powder, the layered structure is easily recognized, as is the submicrometer porosity of the sample. It is clear from the comparison of Figures 1d−f that sintering at 70 and 200 °C shows an increase in compaction with increasing temperature. In addition, surface features become smaller with increasing temperature, possibly implying increasing brittleness. Comparing Figures 1f−h, it appears that there is fusion between surface features on going from part f to part h—the latter also having the largest modulus (Table 1).

Mechanical Properties. Vickers hardness was measured to see whether the density and morphology were true indications of mechanical performance (Table 1). Regardless of processing condition, the pellets were found to be quite hard for organic polymeric materials, easily surpassing the hardness of PMMA and polycarbonate.[13] Here the discrepancy between samples was not due to sintering temperature but additive. Both pellets without additives have a substantially greater compressive hardness. Though hardness does not correlate with the trend in density, it is not unreasonable for a second phase to lower the hardness of a material. The hardness also does not correlate with Young's modulus.

Conclusion. We have shown that even a mild heat treatment can increase the density and modulus of an already very compactable polymer. The density and the morphology show that heat treatment is favorable for compaction; nevertheless, the hardness measurements show quite clearly that the additives decrease the surface hardness of the polymer. From the findings it is possible that these particular coordinates of parameter space are not suited to give the optimum performance for the additives, though their low degradation temperatures do limit the available processing conditions. It is also possible that a higher processing temperature and pressure would only help to improve the properties of PDACp, assuming higher pressure would prevent reverse Diels−Alder processes.

Acknowledgment. We thank Prof. Paul Smith (ETH Materials) and Mr. Kirk A. Fields, P.E., for their helpful discussions.

Supporting Information Available: Experimental details;[12] synthesis of tricyclopentadiene, tetracyclopentadiene, and poly(Diels−Alder cyclopentadiene).[7] This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) (a) Woodson, C. S.; Grubbs, R. H. Cont.-in-part of U.S. 5,939,504, **2000**; 12 pp. (b) Grubbs, R. H.; Hillmyer, M.; Benedicto, A.; Wu, Z. *Polym. Prepr.* (*Am. Chem. Soc., Div. Polym. Chem.*) **1994**, *35*, 688.
(2) Staudinger, H.; Bruson, H. A. *Justus Liebigs Ann. Chem.* **1926**, *446*, 97–110.
(3) (a) Alder, K.; Stein, G. *Justus Liebigs Ann. Chem.* **1931**, *485*, 223–246. (b) **1932**, *496*, 204−251. (c) *Chem. Ber.* **1934**, *67*, 613−627.
(4) Wilson, P. J.; Wells, J. H. *Chem. Rev.* **1944**, *34*, 1–50.
(5) Vick, L. W.; Kander, R. G. *Polym. Eng. Sci.* **1998**, *38* (11), 1824–1996.
(6) Bigg, D. M., Epstein, M. M., Eds.; Suh, N. P.; Sung, N.-H. *Sci. Technol. Polym. Process., Proc. Int. Conf.*, **1979**, 897−919.
(7) Lao, L. Master of Science Thesis, UCLA, **2001**.
(8) We thank our former colleague Prof. Y. Rubin for the results of MM calculations at the MM3 level.
(9) Note: the DuPont PTFE 7C, in ref 9, which was found to be 76% crystalline, had a fwhm of 0.5. Though the full width at half-maximum is a measure of correlation length, it can be used as an approximation for crystalline domain size.
(10) Rae, P. J.; Dattelbaum, D. M. *Polymer* **2004**, *45*, 7615–7625.
(11) Murphy, E. B.; Bolanos, E.; Schaffner-Hamann, C.; Wudl, F.; Nutt, S. R.; Auad, M. L. *Macromolecules* **2008**, *41*, 5203−5209, and references therein.
(12) ASTM C373-88(2006) Standard Test Method for Water Absorption, Bulk Density, Apparent Porosity, and Apparent Specific Gravity of Fired Whiteware Products.
(13) Commercially available samples of PMMA and polycarbonate were indented under the same conditions as the pellets to yield hardness values of 157 and 243 MPa, respectively.