# Photoinitiated Thermoset Polymerization Through Controlled Release of Metathesis Catalysts Encapsulated in Poly(phthalaldehyde)

Oleg Davydovich,[1] Josephine Lewis,[1] Mikayla Romero,[1] Julia Deitz,[1] Francesca C'deBaca,[1] Jared M. Schwartz,[2] Anthony C. Engler,[3] Paul A. Kohl,[2] Samuel C. Leguizamon,[1] and Brad H. Jones[1]*

[1]Sandia National Laboratories, Albuquerque, NM 87185, USA

[2]Chemical and Biomolecular Engineering, Georgia Institute of Technology, Atlanta, GA 30332, USA

[3]Cain Department of Chemical Engineering, Louisiana State University, Baton Rouge, LA 70803, USA

*Corresponding Author: mailto:bhjones@sandia.gov; P.O. Box 5800, MS 0888, Albuquerque, NM 87185, USA

# SUPPLEMENTARY INFORMATION

*Table 1*. DCPD/PMP dispersion compositions tested and corresponding PIT measured by photorheology. The catalyst content of all PMPs is 12:88 catalyst:cPPA by wt.

| Sample | MBTT Content in PMP (wt % relative to cPPA) | Catalyst Type | Temperature (°C) | PMP Loading (mg PMP/ml DCPD) | PIT (min) |
|---|---|---|---|---|---|
| **1** | 0 | **HG2** | 25 | 8 | N/A |
| **2** | 2 | **HG2** | 25 | 8 | N/A |
| **3** | 5 | **HG2** | 25 | 8 | 6.8 |
| **4** | 10 | **HG2** | 25 | 8 | 3.9 |
| **5** | 5 | **HG2** | 25 | 4 | 7.5 |
| **6** | 5 | **HG2** | 25 | 16 | 5.0 |
| **7** | 5 | **HG2** | 30 | 8 | 4.9 |
| **8** | 5 | **HG2** | 35 | 8 | 3.3 |
| **9** | 5 | **HG2** | 40 | 8 | 2.7 |
| **10** | 5 | **HG2** | 45 | 8 | 2.0 |
| **11** | 5 | **HG2** | 50 | 8 | 1.5 |
| **12** | 5 | **GC2** | 25 | 8 | 7.9 |
| **13** | 5 | **Nitro-Grela** | 25 | 8 | 4.0 |

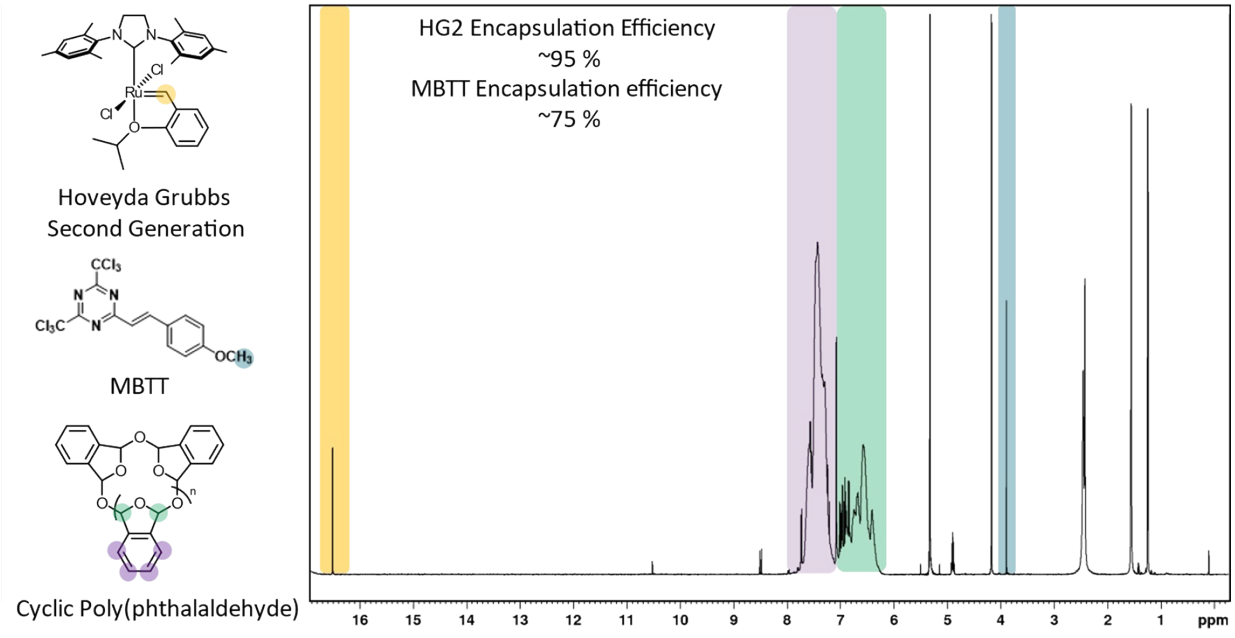


*Figure 1*. Representative example of NMR spectrum (in $d_2$-dichloromethane) of PMP. This specific example shows Sample **3** in Table 1. The encapsulation efficiency was determined to be 95% relative to the target loading of 12:88 **HG2**:cPPA (by wt). Encapsulation efficiency was determined by comparing the integration of the peaks corresponding to the carbene proton from **HG2** (yellow highlight, 16.56 ppm) and three protons in the methoxy group attached to the phenyl ring from MBTT (blue highlight, 3.83 ppm). against six backbone protons of cPPA (green and purple highlight, 8.0 - 6.2 ppm).

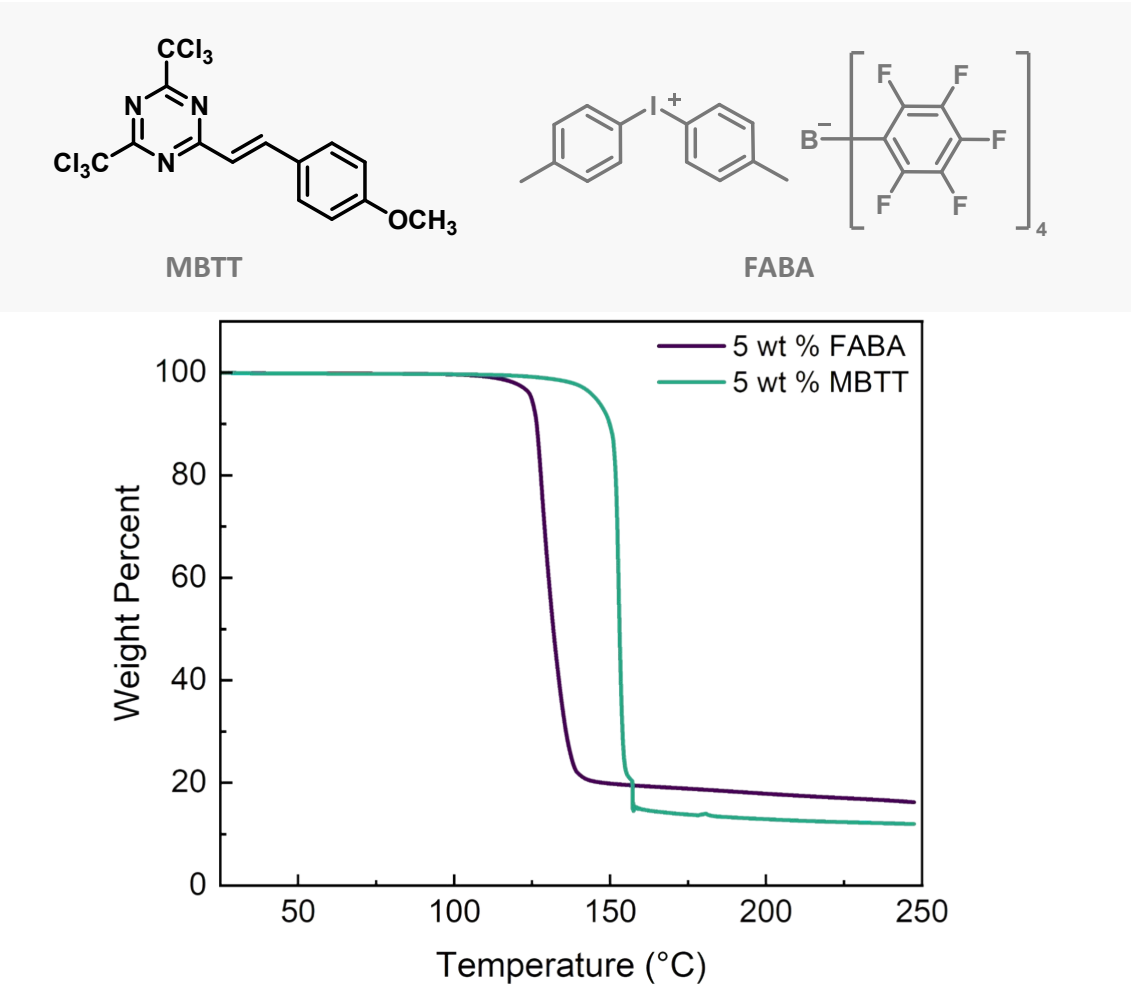


*Figure 2*. TGA of cPPA PMPs containing **HG2** (12:88 by wt **HG2**:cPPA) and PAG (FABA or MBTT, 5:100 by wt PAG:cPPA), heating rate 10 °C/min. Chemical structures of MBTT and FABA are shown above the plot.

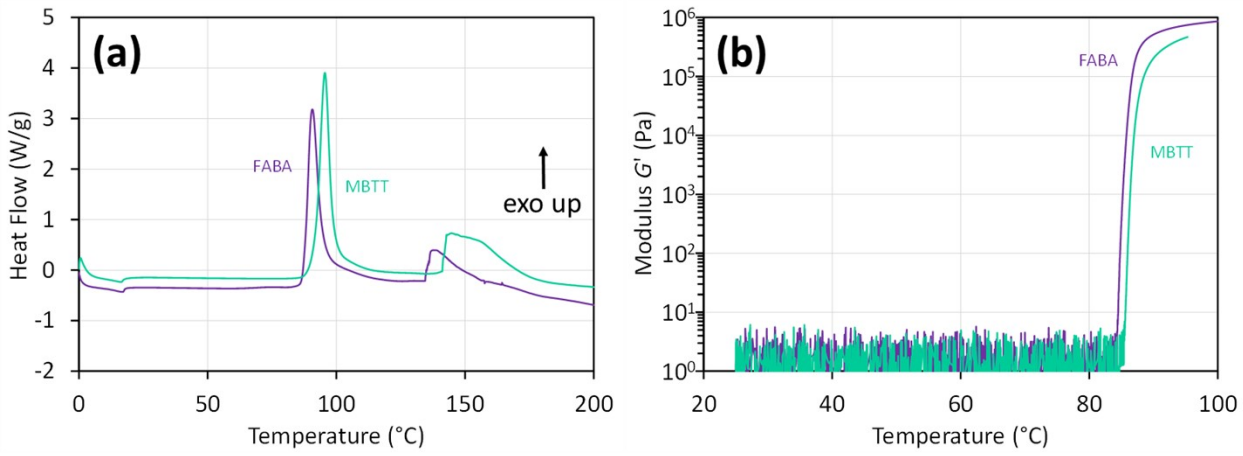


*Figure 3*. **(a)** DSC and **(b)** rheology of DCPD/PMP dispersions heated at 10 °C/min and 3 °C/min, respectively. The PAG (FABA or MBTT) and metathesis catalyst (**HG2**) are present in the PMPs at 5:100 PAG:cPPA and 12:88 **HG2**:cPPA by wt and the PMPs are added to DCPD at 8 mg/ml.

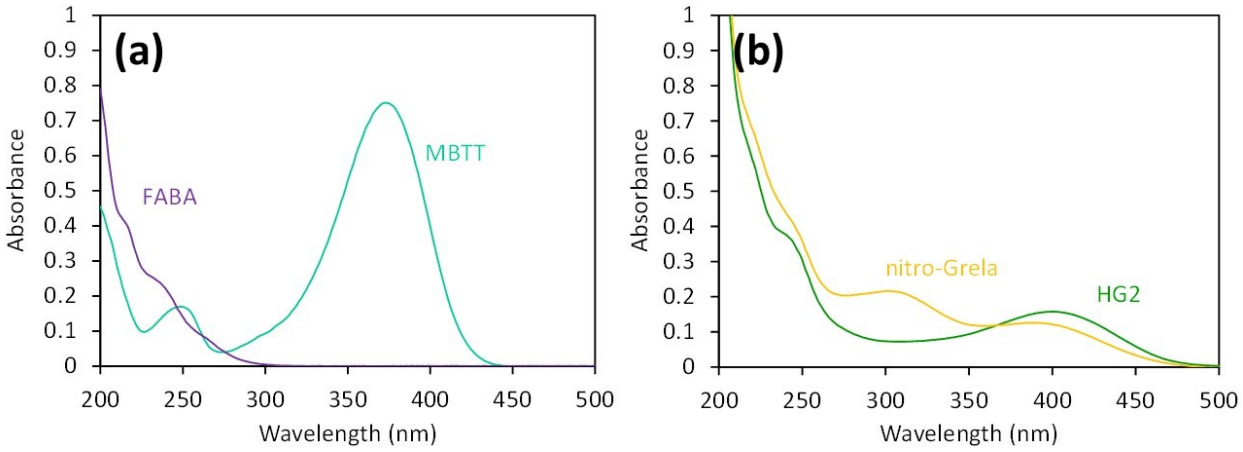


*Figure 4.* UV-visible absorption spectra of PMP constituents: **(a)** PAGs Rhodorsil-FABA and MBTT, **(b)** metathesis catalysts **HG2** and **nitro-Grela**. All spectra are collected in acetonitrile at 0.01 mg/ml.

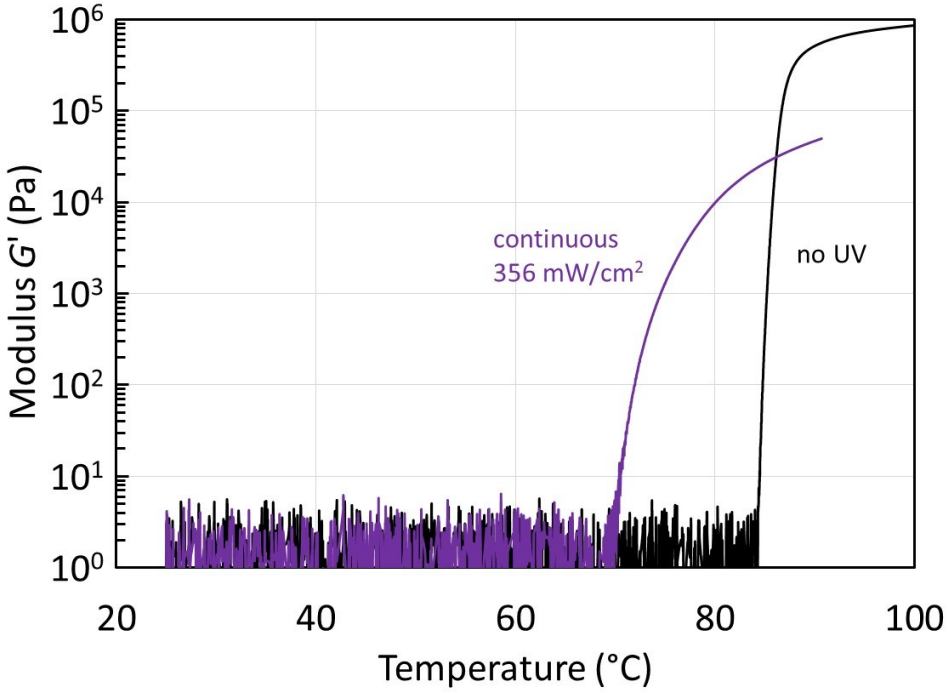


*Figure 5*. Rheology of DCPD/PMP dispersion during heating at 3 °C/min with and without simultaneous illumination by a broadband light source. The PMPs contain Rhodorsil-FABA as PAG (5:100 PAG:cPPA by wt) and **HG2** (12:88 **HG2**:cPPA) as catalyst. PMP concentration in DCPD: 8 mg/ml. Sample thickness: 0.5 mm.

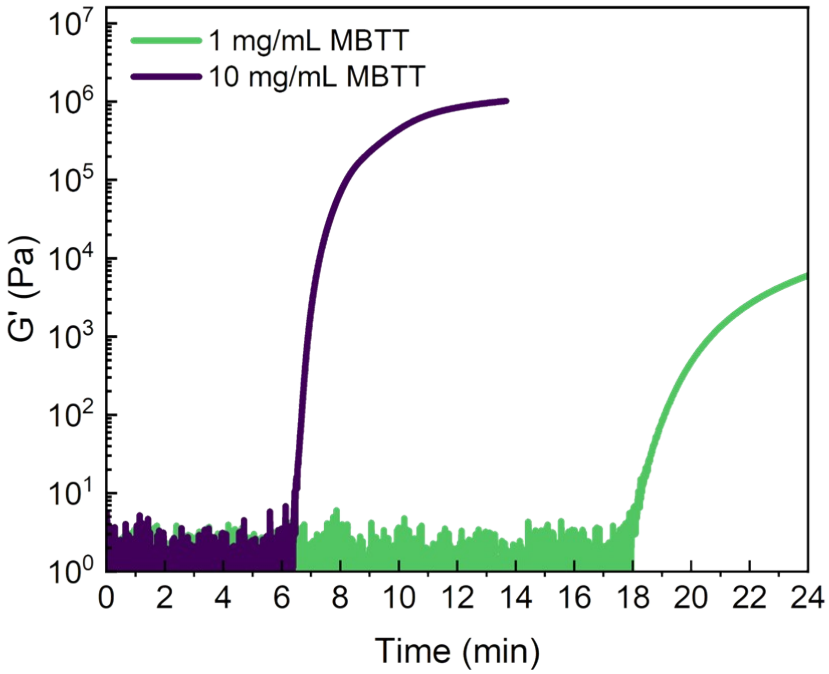


*Figure 6*. Photorheology of DCPD/PMP dispersions with external MBTT (dissolved in DCPD as opposed to encapsulated within PMP). The PMPs, consisting of only **HG2** encapsulated in cPPA at 12:88 **HG2**:cPPA by wt, are added at 8 mg/ml. For comparison, the overall concentration of MBTT at 10 mg/ml external addition is roughly 30x that of the 5 phr curve in Figure 2A of the main text, which exhibits similar PIT. Other conditions: 365 nm, 27 mW/cm$^2$, 25 °C.

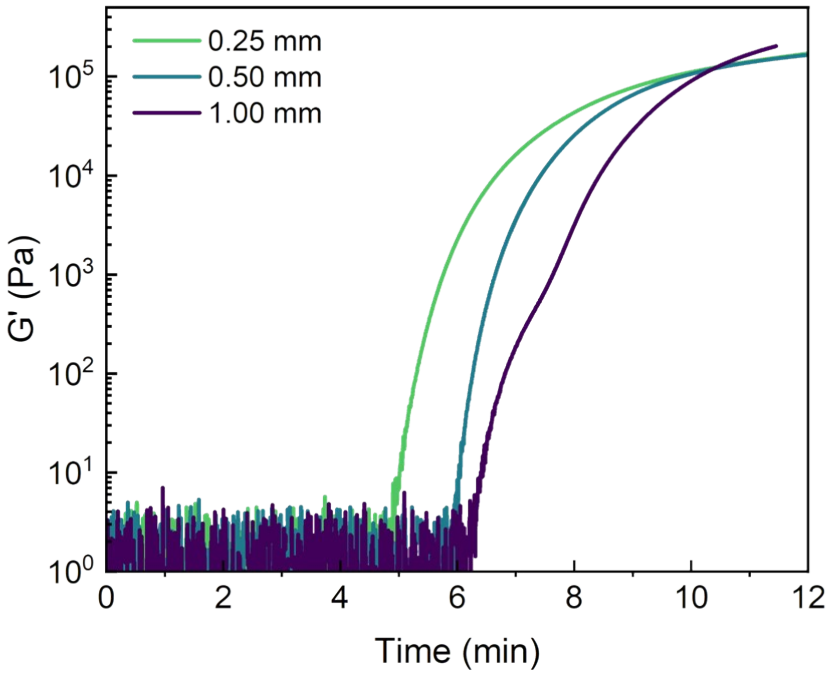


*Figure 7.* Photorheology of DCPD/PMP dispersions with different sample thicknesses. Other conditions: 365 nm, 27 mW/cm$^2$, 5:100 MBTT:cPPA by wt, 12:88 **HG2**:cPPA by wt, 8 mg PMP/ml DCPD, 25 °C.

*Table 2.* Enthalpy of reaction of PMPs containing **HG2** (12:88 by wt **HG2**:cPPA) and MBTT (5:100 by wt MBTT:cPPA) over the course of one month of storage in the absence of light at room temperature. Enthalpy is determined via the integration of the heat flow values from DSC traces.

| Time | Enthalpy (J/g) |
|---|---|
| Initial | 376 |
| Week 1 | 377 |
| Week 2 | 372 |
| Week 3 | 366 |
| Week 4 | 284 |

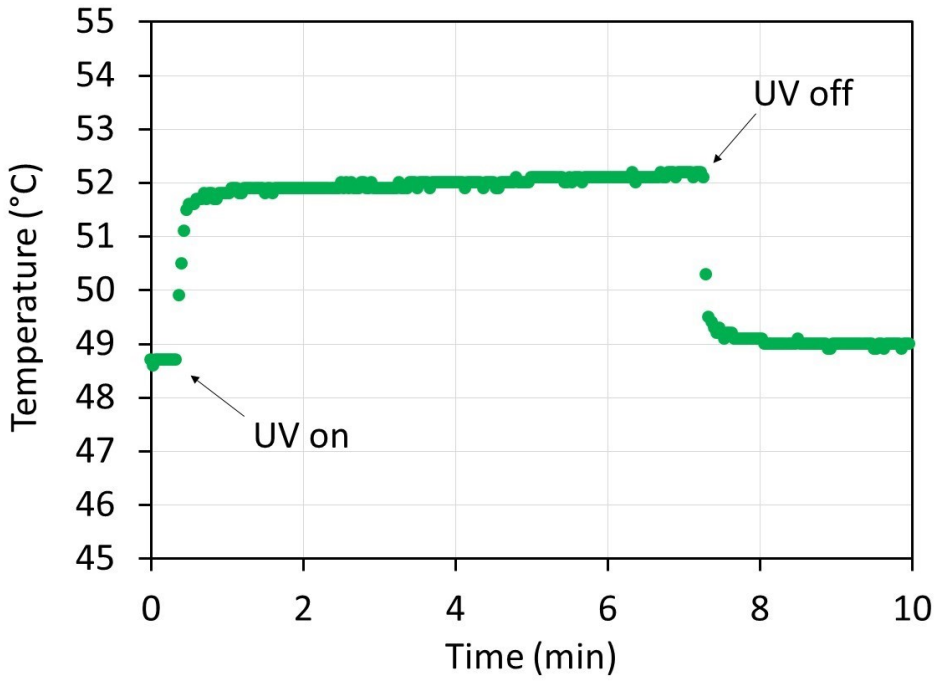


*Figure 8.* Temperature measured via thermocouple inserted into 1 mm thick sample of DCPD during irradiation at 356 mW/cm$^2$ with sample held at a nominal 50 °C. The temperature rise due to irradiation is limited to *ca*. 3 °C.

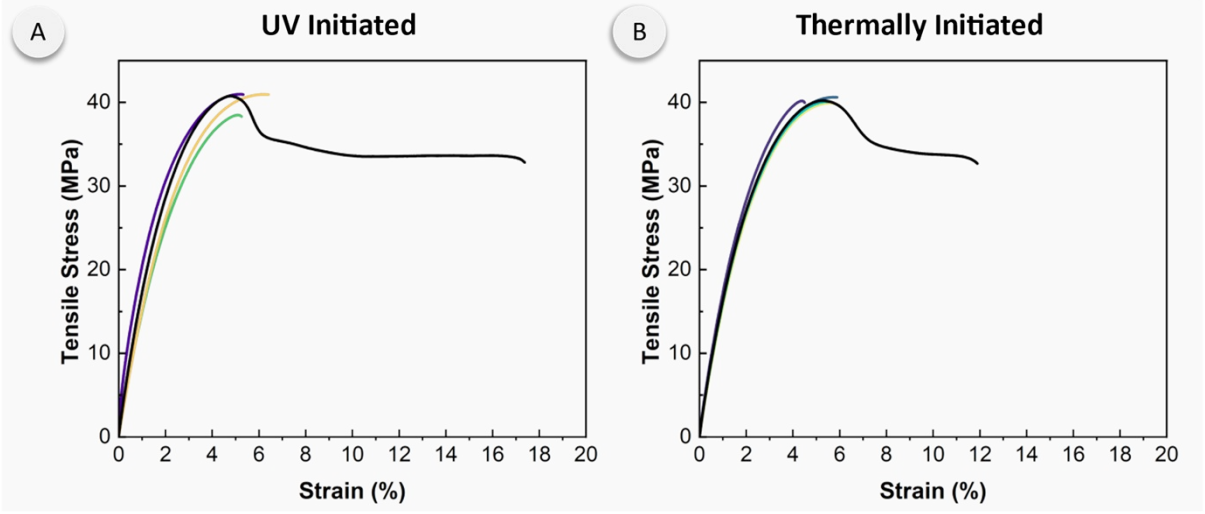


*Figure 9*. Uniaxial tensile response of all specimens generated by (A) photo- and (B) thermal-initiation of DCPD/PMP dispersions. UV Initiated refers to specimens generated by local illumination at one end of the sample area.

*Table 3.* Monomer conversion back-calculated by DSC post-cure analysis of specimens generated by photo- and thermal-initiation of DCPD/PMP dispersions. UV Initiated and Thermally Initiated refer to specimens generated by local illumination or heating, respectively, at one end of the sample area.

| Sample | Enthalpy (J/g) | Monomer Conversion (%) |
|---|---|---|
| Initial | 376.7 ± 14 | N/A |
| UV Initiated | 35.4 ± 10.9 | 92.1 ± 2.9 |
| Thermally Initiated | 29 ± 29.1 | 92.3 ± 2.9 |

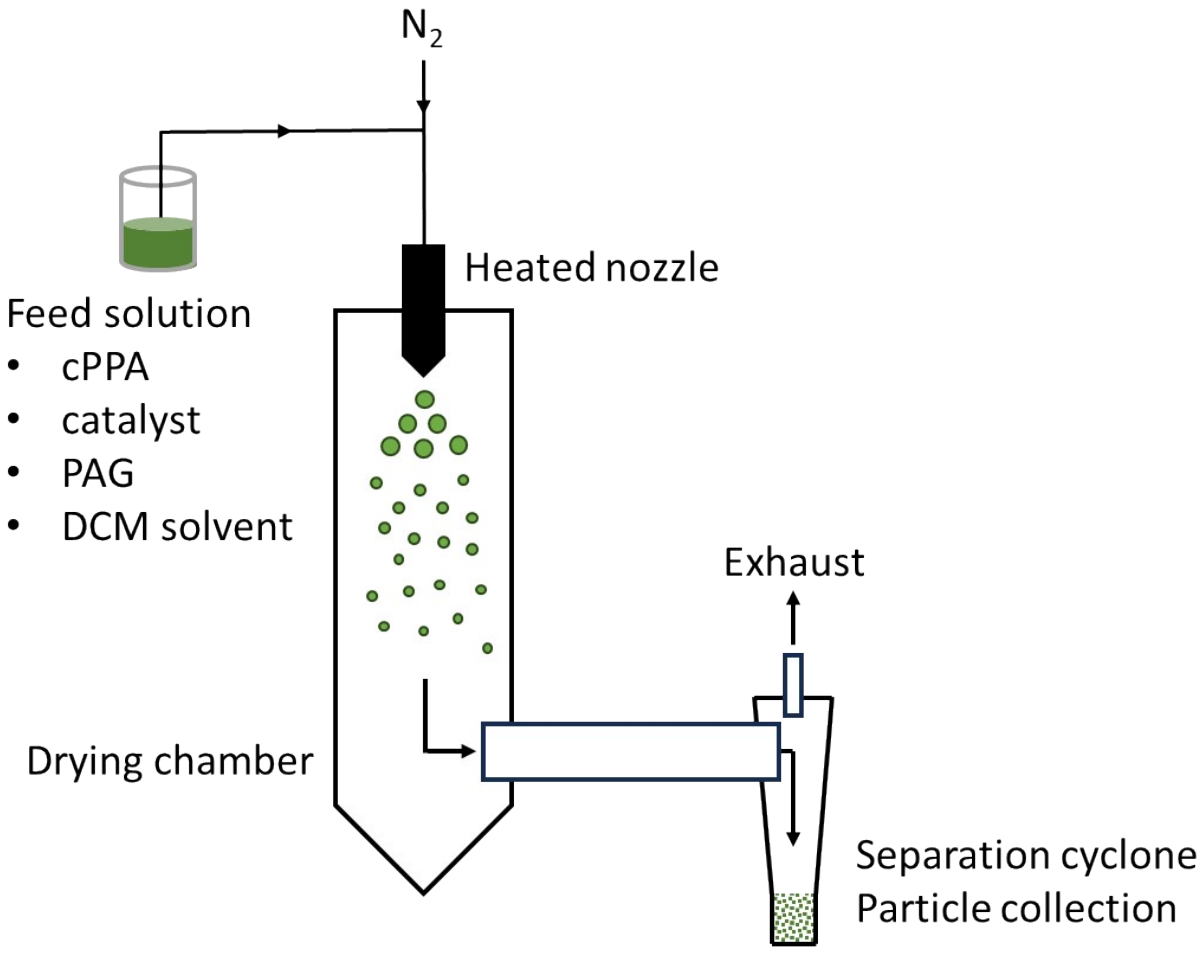


*Figure 10*. Schematic diagram illustrating spray drying process used for microencapsulation of catalyst and PAG within cPPA.