



Fabrication and Properties of 3D Printable Dental Composite Containing Catechol Polymer

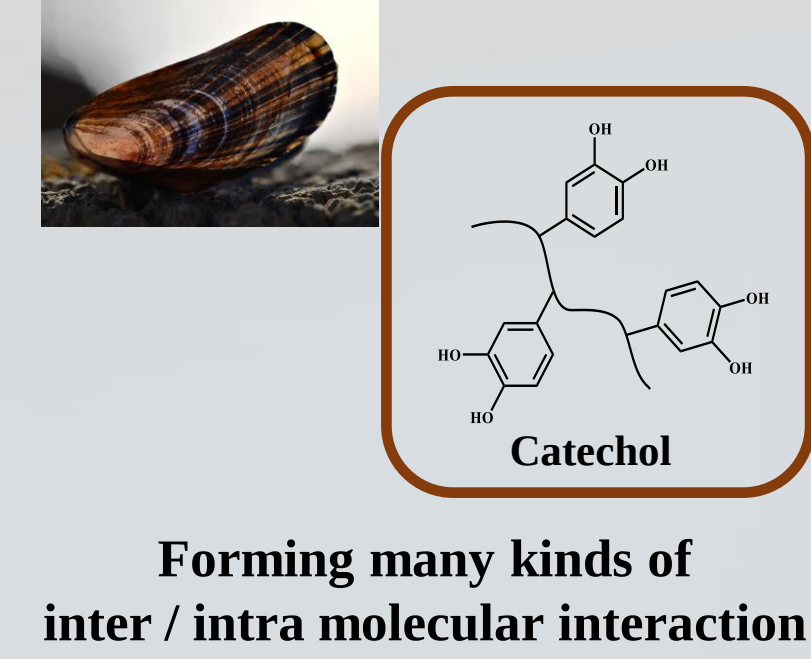
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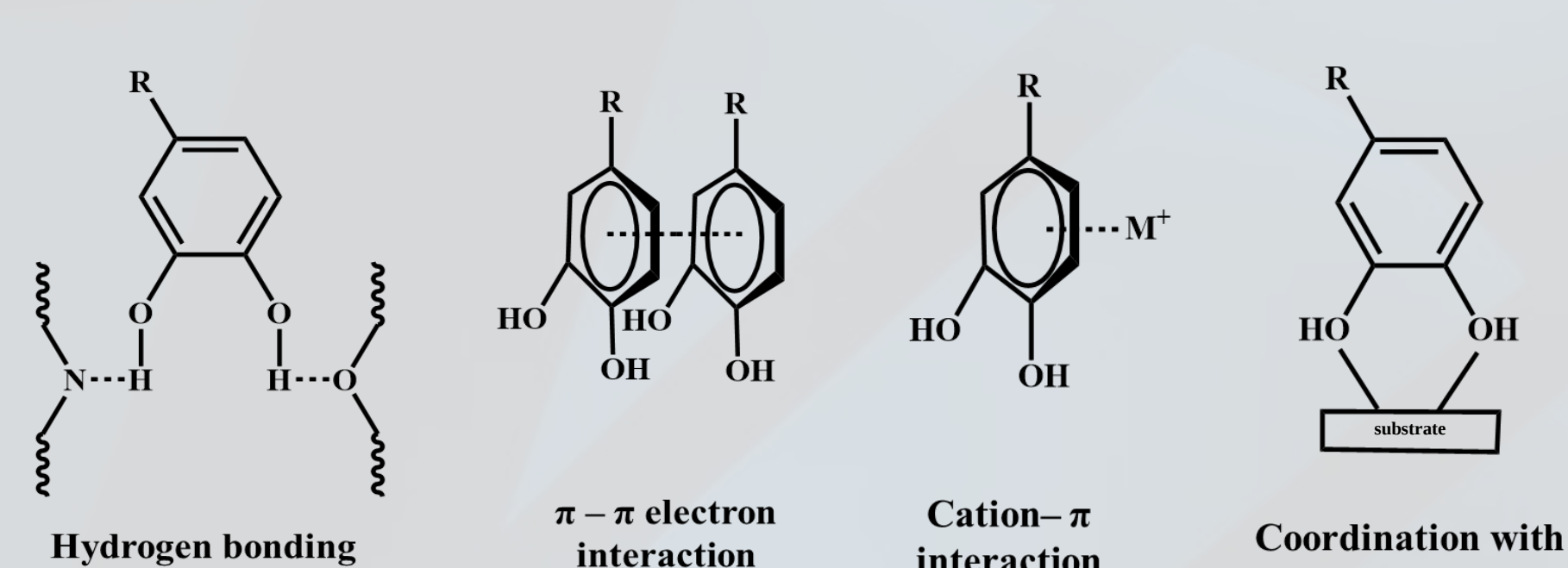
Abstract & Introduction

Catechol-containing polymers, which have excellent adhesion function derived from mussels, have recently attracted much attention. Strong interaction between interfaces due to the catechol group with the hydrogen bond allows to apply to various field. Dopamine, 3,4-dihydroxyphenylalanine (DOPA) with catechol moieties, were selected as a starting material to synthesize polymerizable monomer by reacting with methacrylic anhydride. The synthesized dopamine methylacrylamide (DMA) was characterized through FT-IR, ¹H-NMR and ¹³C-NMR spectroscopies and mixed with ethoxylated bis-GMA (EBPDMA) with various compositions to 3D print by DLP technique. Catechol-functionalized polymers are synthesized by free radical polymerization of dopamine methylacrylamide (DMA) and methyl methacrylate (MMA) in DMF. The polymer with the crosslinked structure was characterized through GPC, FT-IR and ¹H-NMR spectroscopies. The mechanical properties of fabricated specimens such as compressive and flexural strengths were evaluated by UTM.

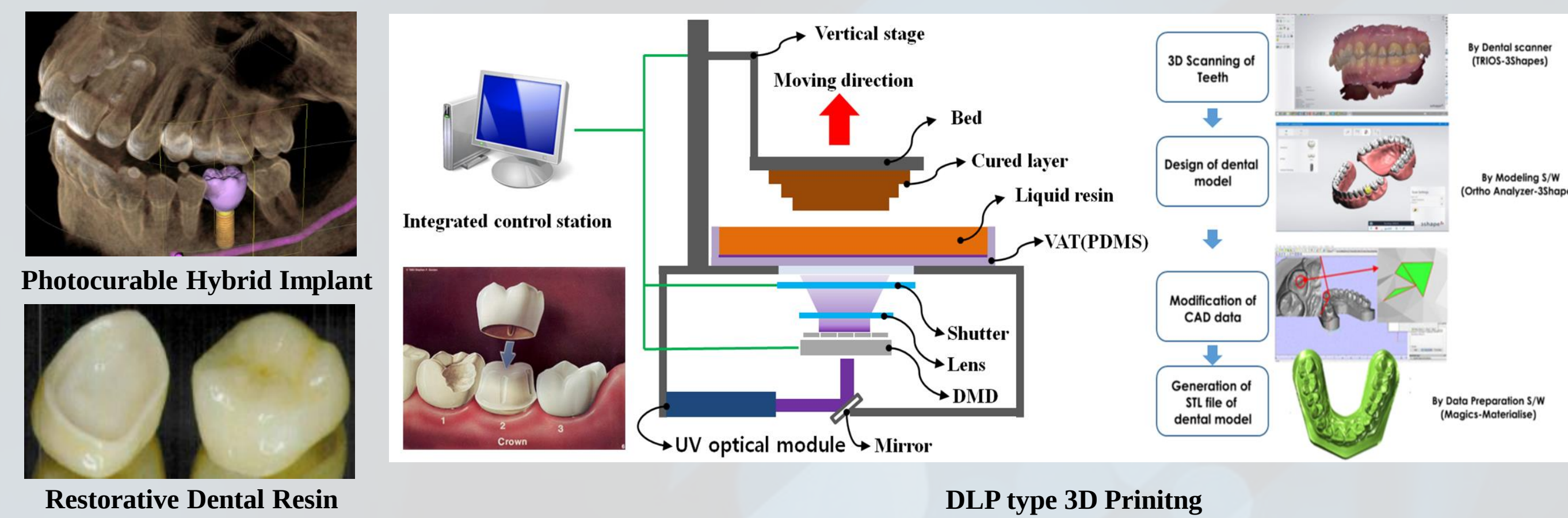
• Catechol functional group



• Non-Covalent Interaction of Catechol



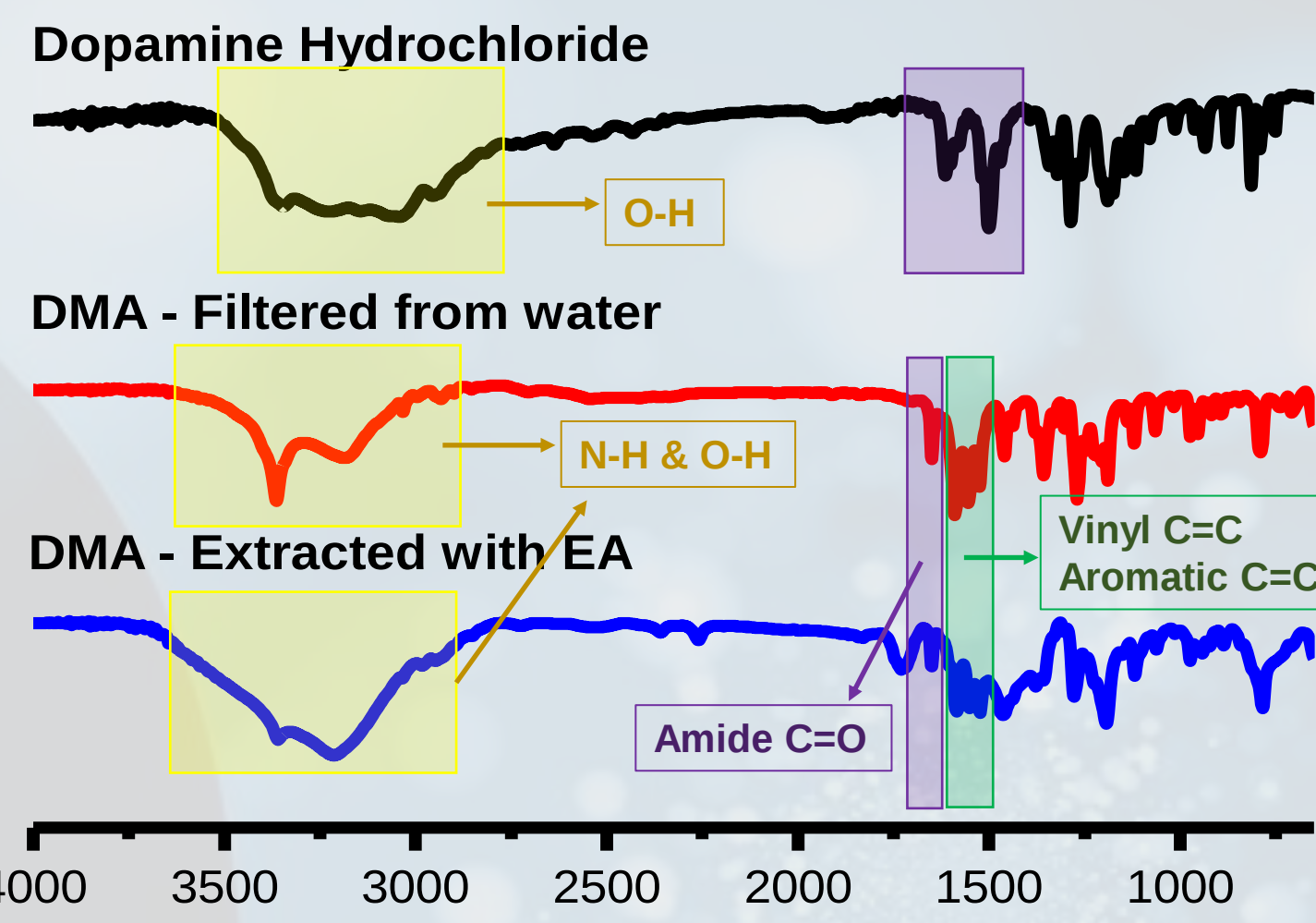
• Dental application – 3D Printing



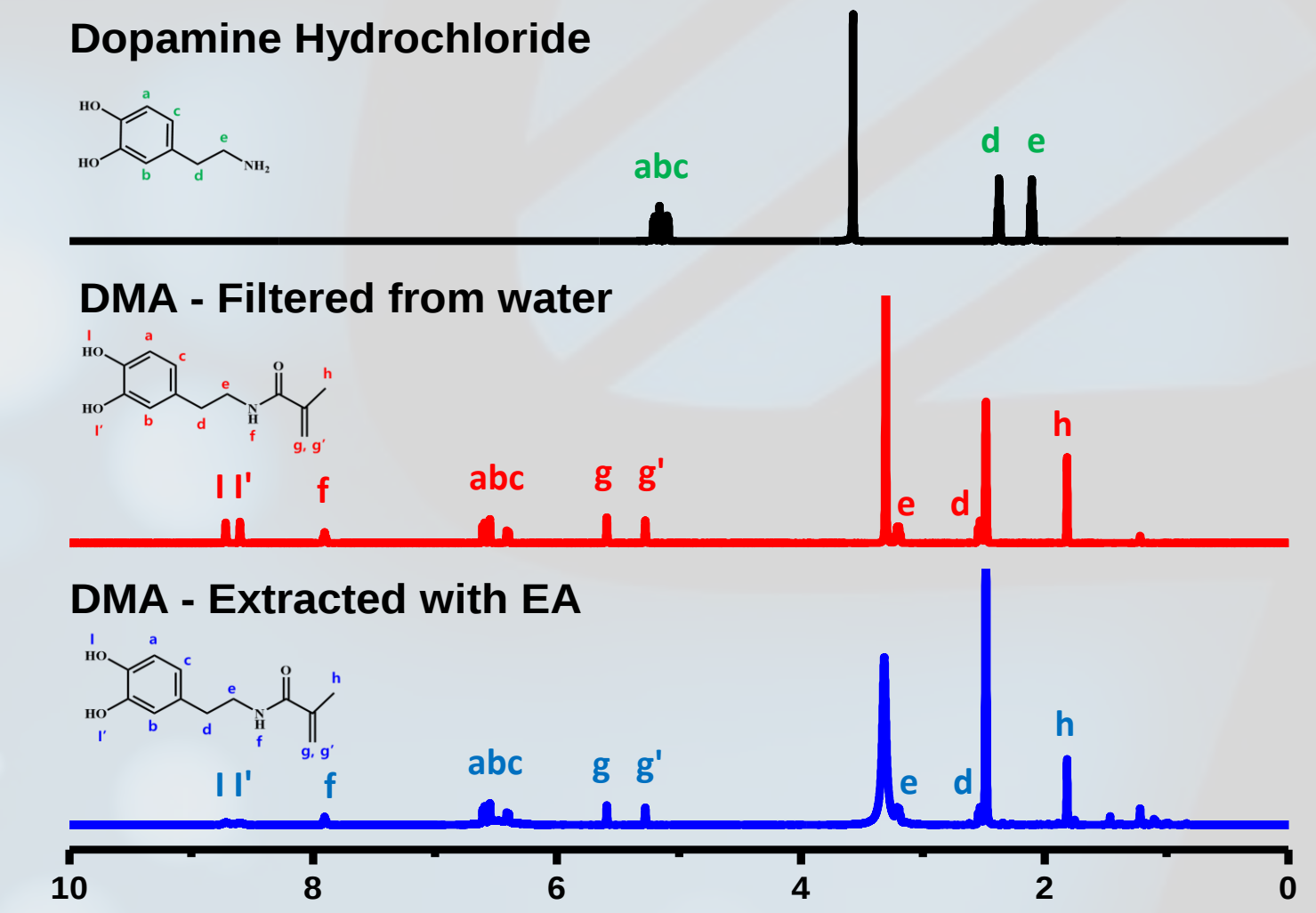
Result & Discussion

→ DMA

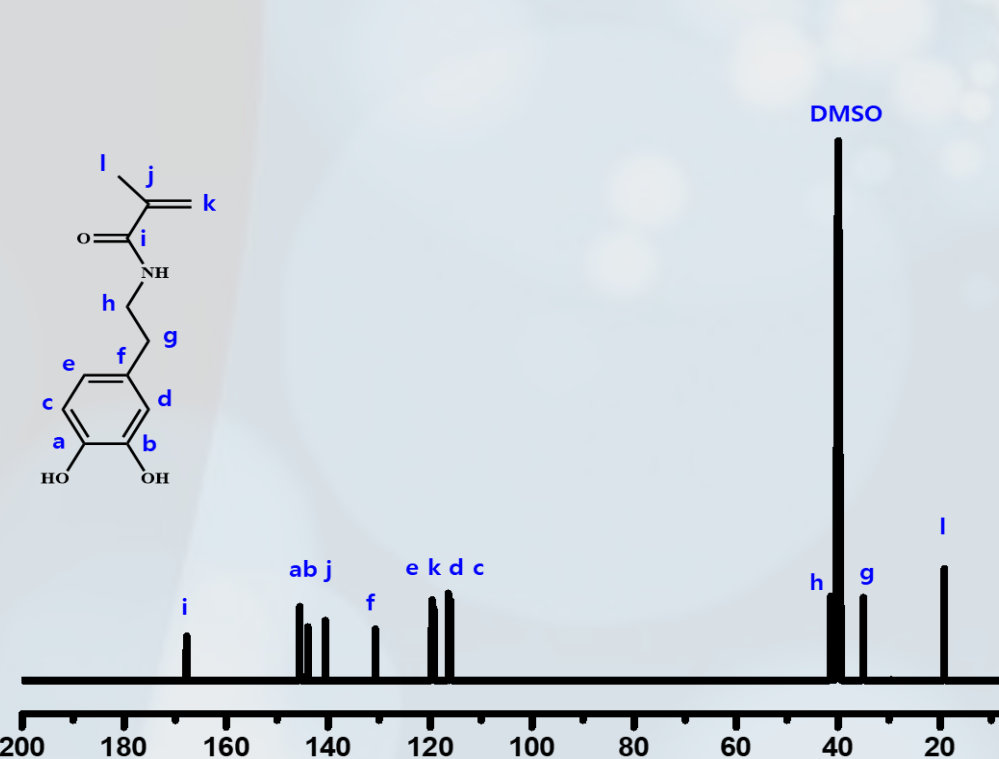
• FT-IR



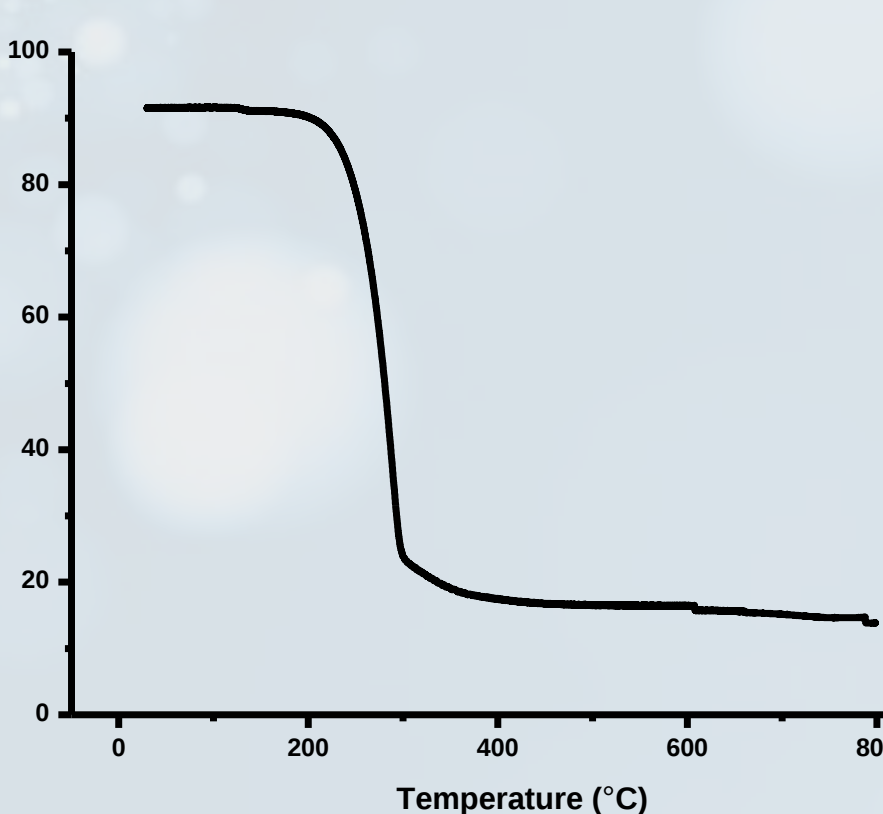
• ¹H-NMR



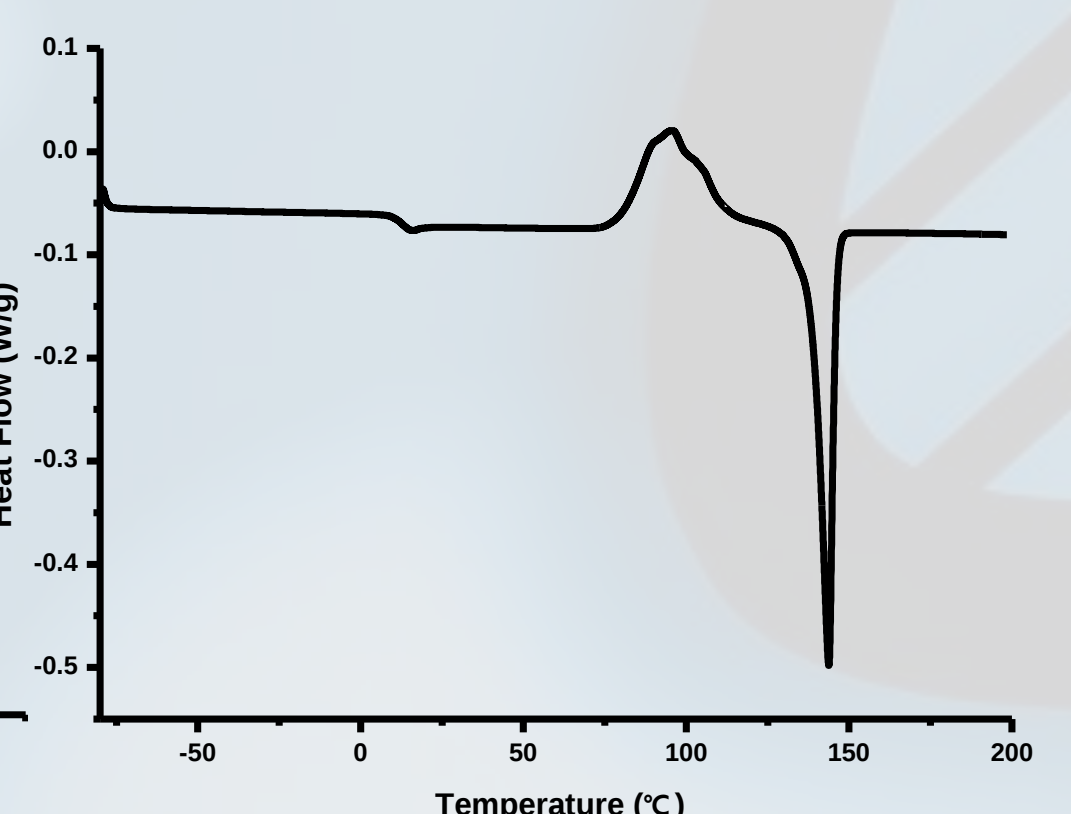
• ¹³C-NMR



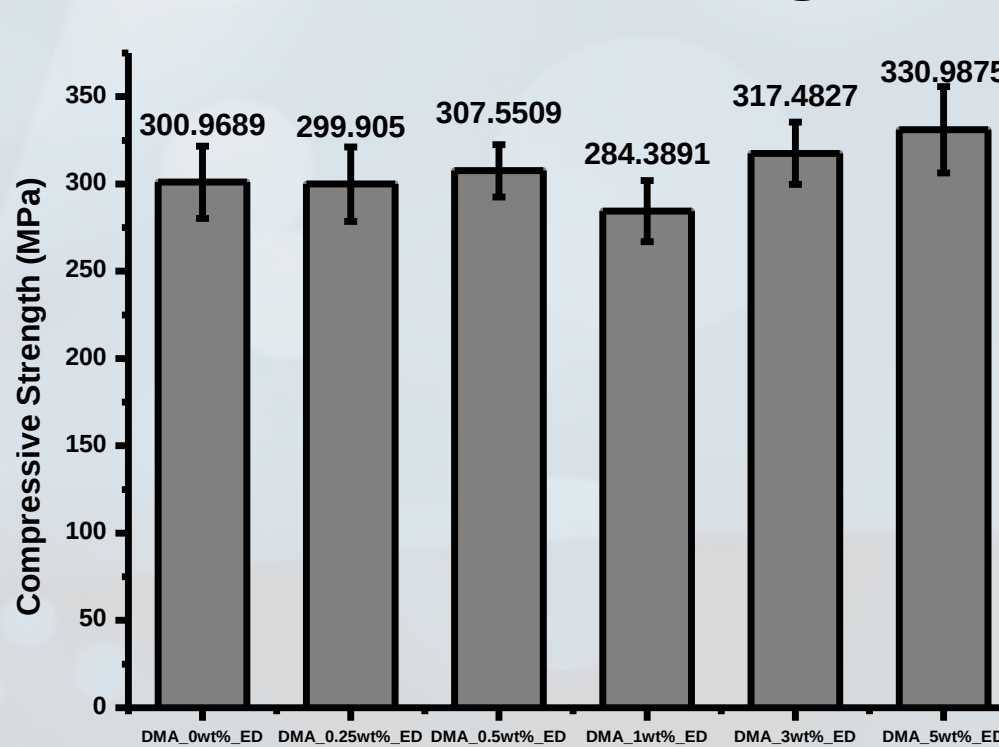
• TGA



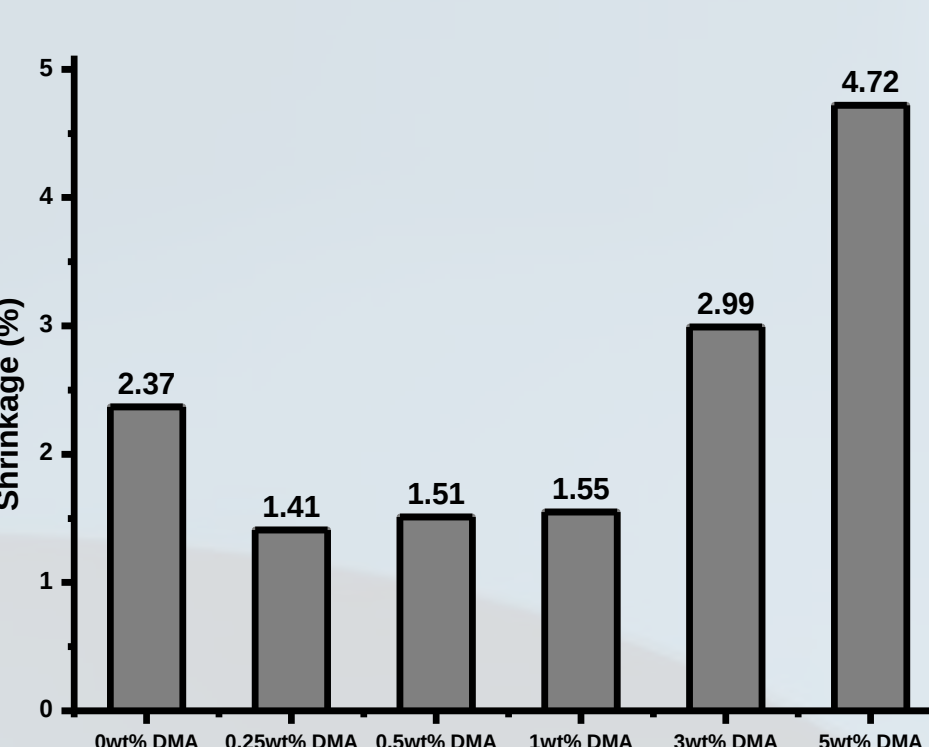
• DSC



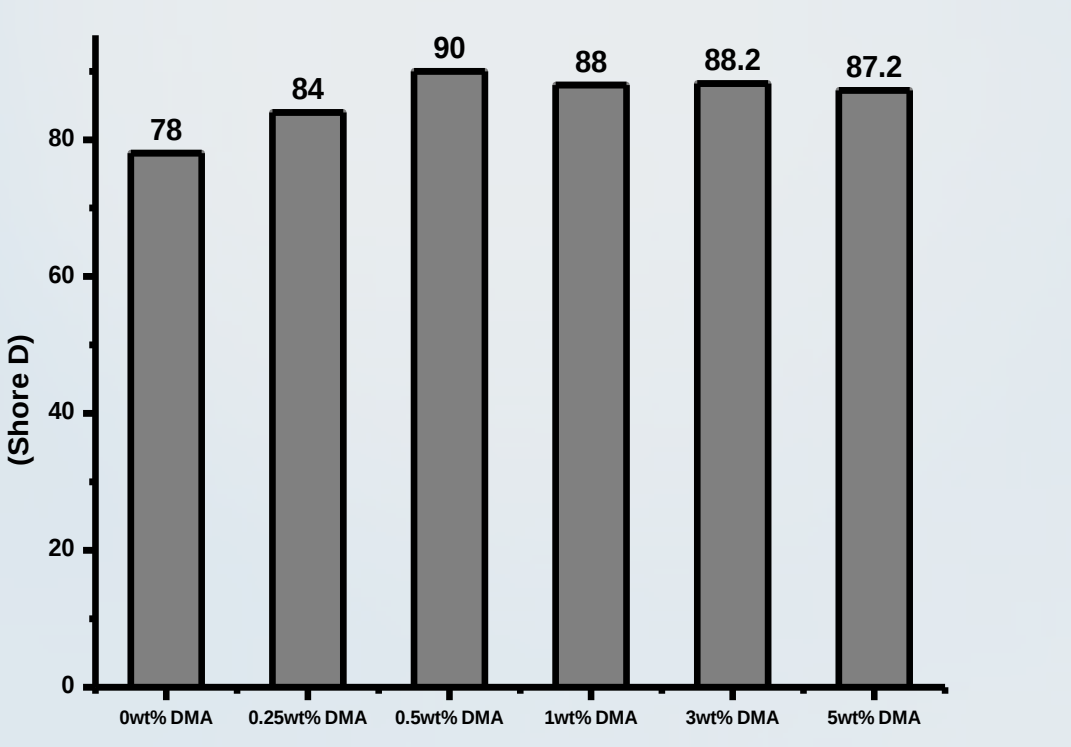
• Compressive Strengths



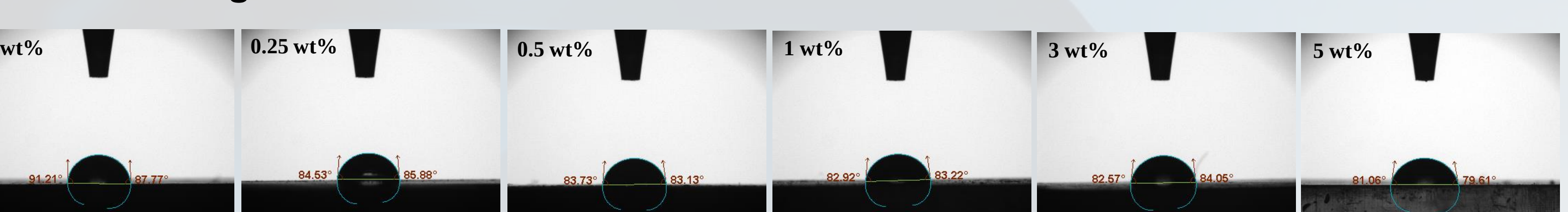
• Shrinkage Strengths



• Hardness

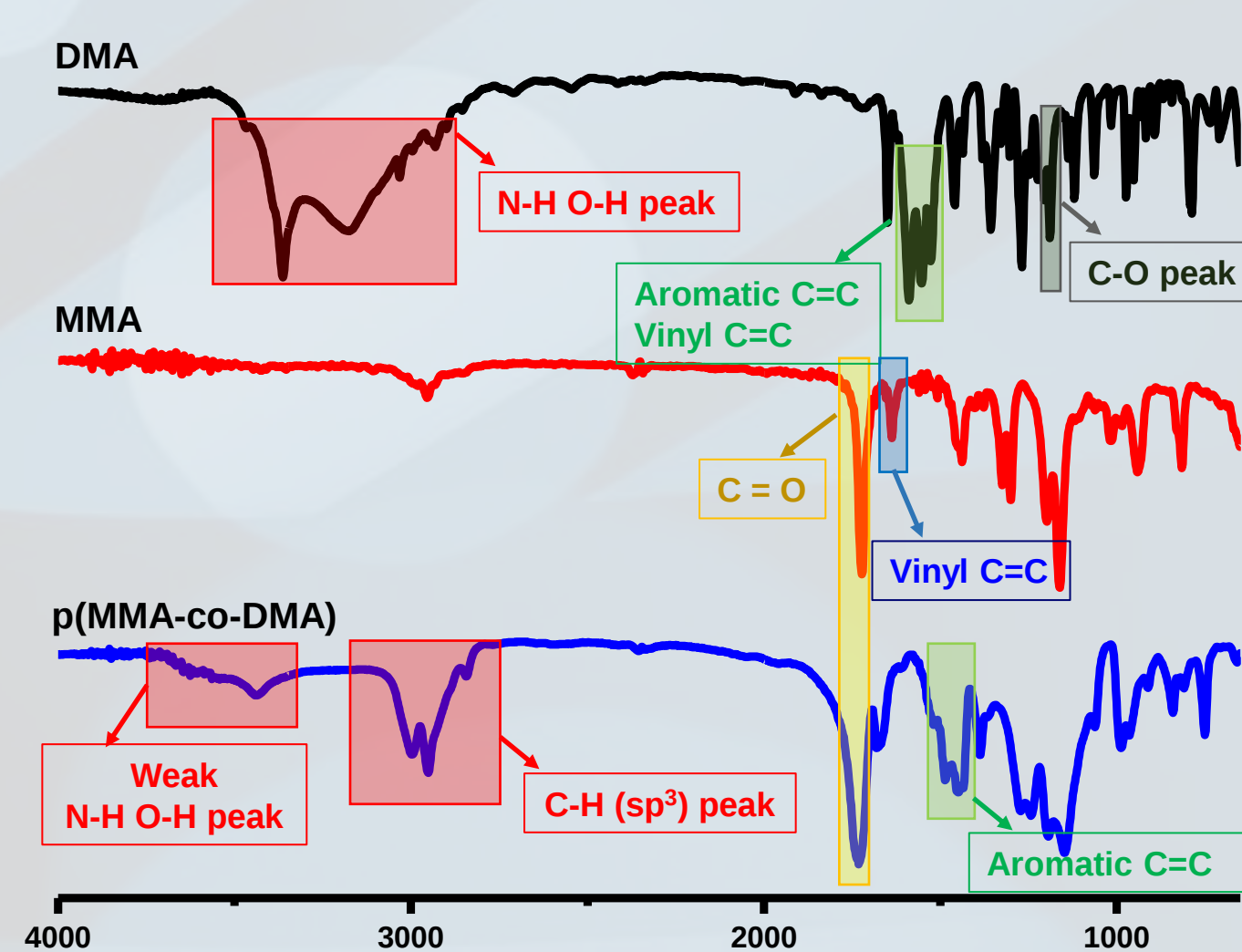


• Contact Angle

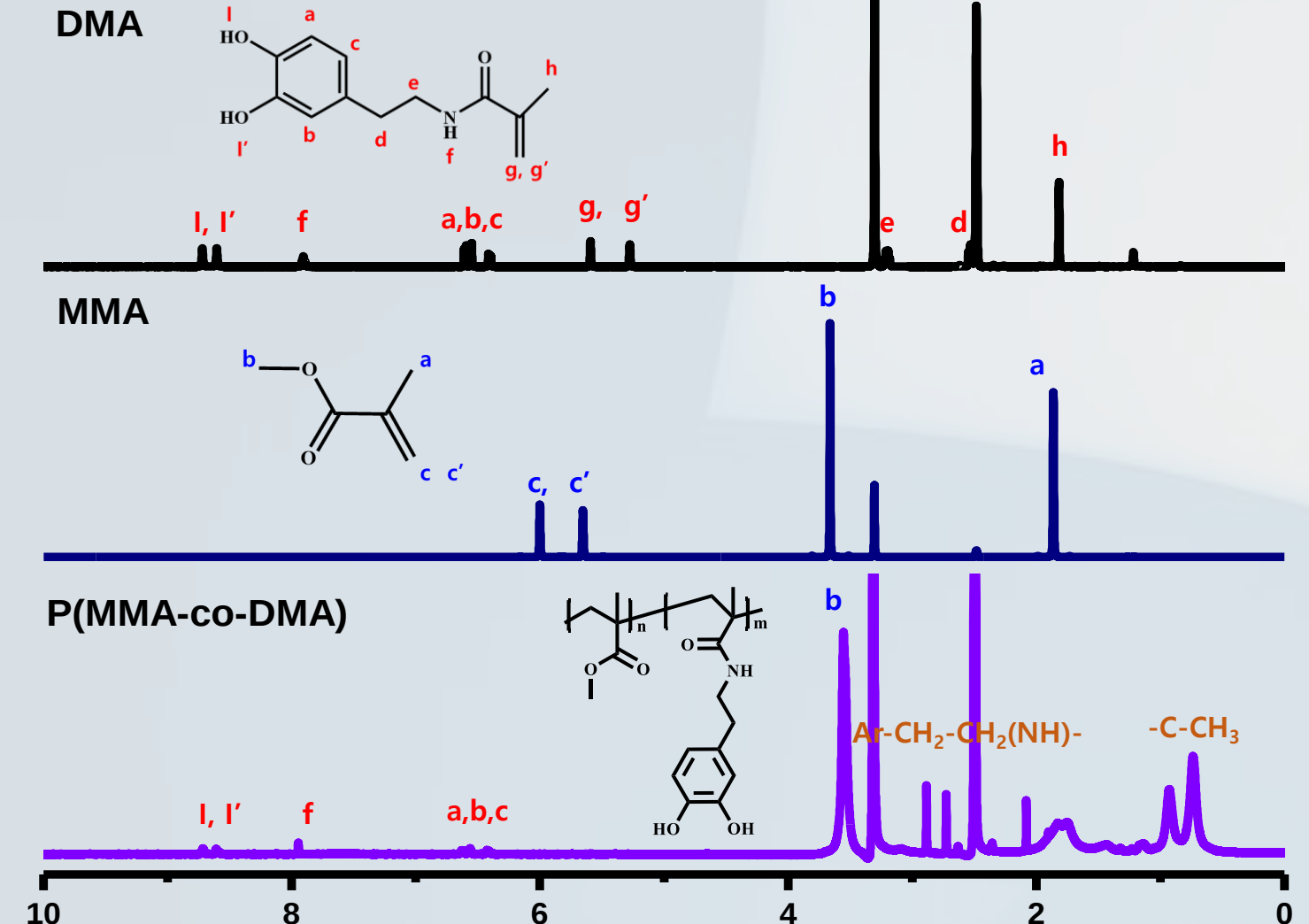


→ p(MMA-co-DMA)

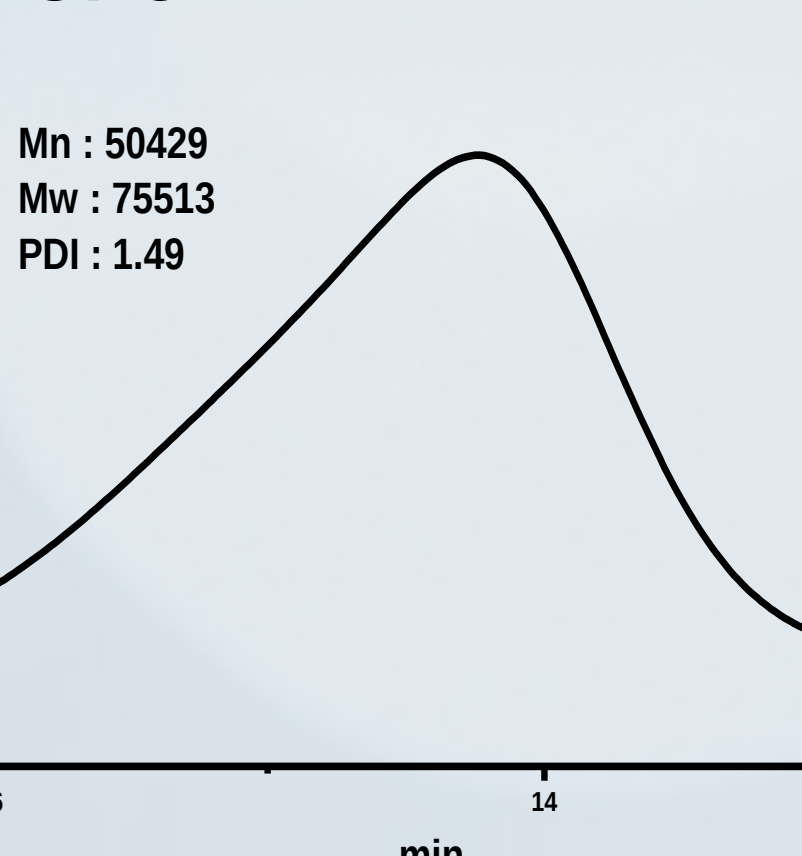
• FT-IR



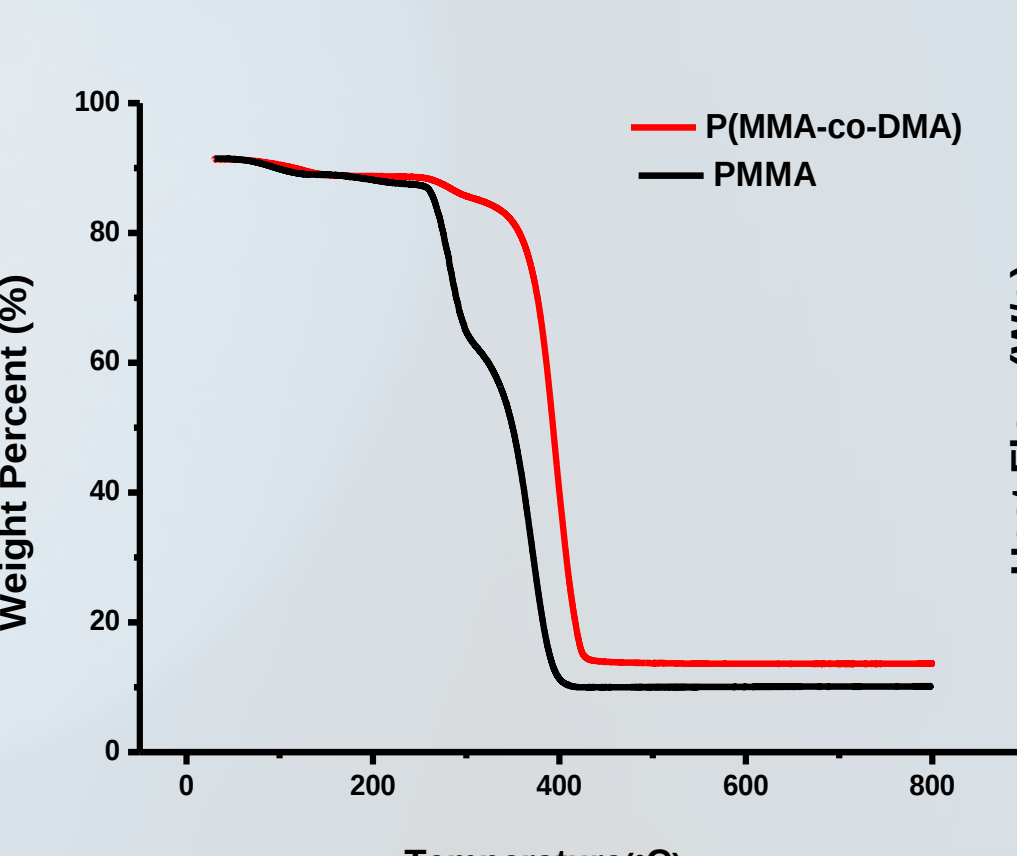
• ¹H-NMR



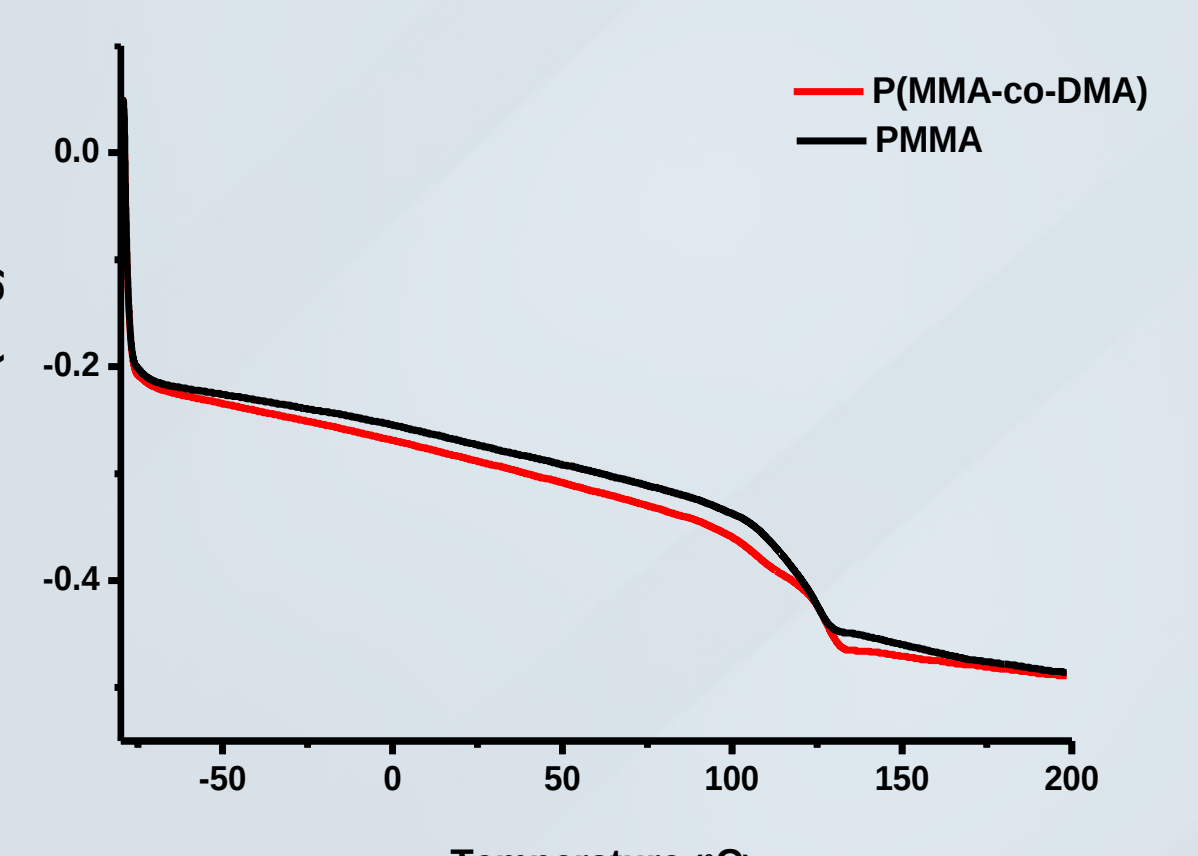
• GPC



• TGA



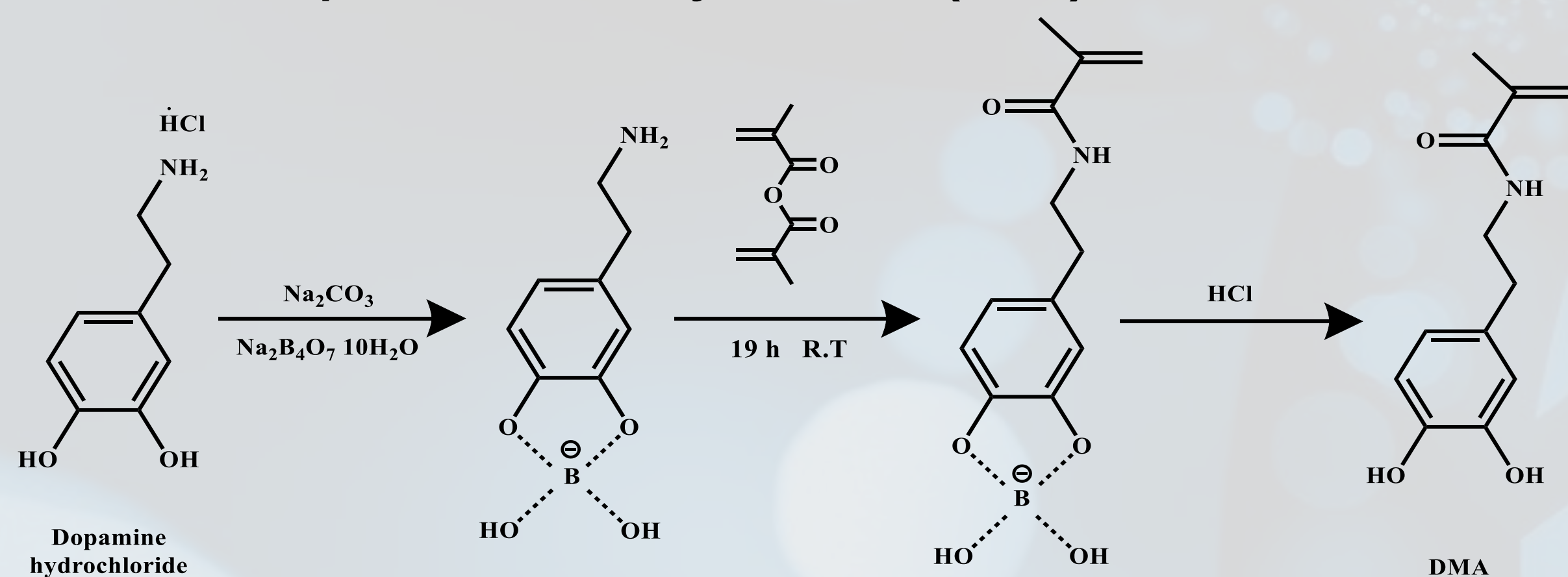
• DSC



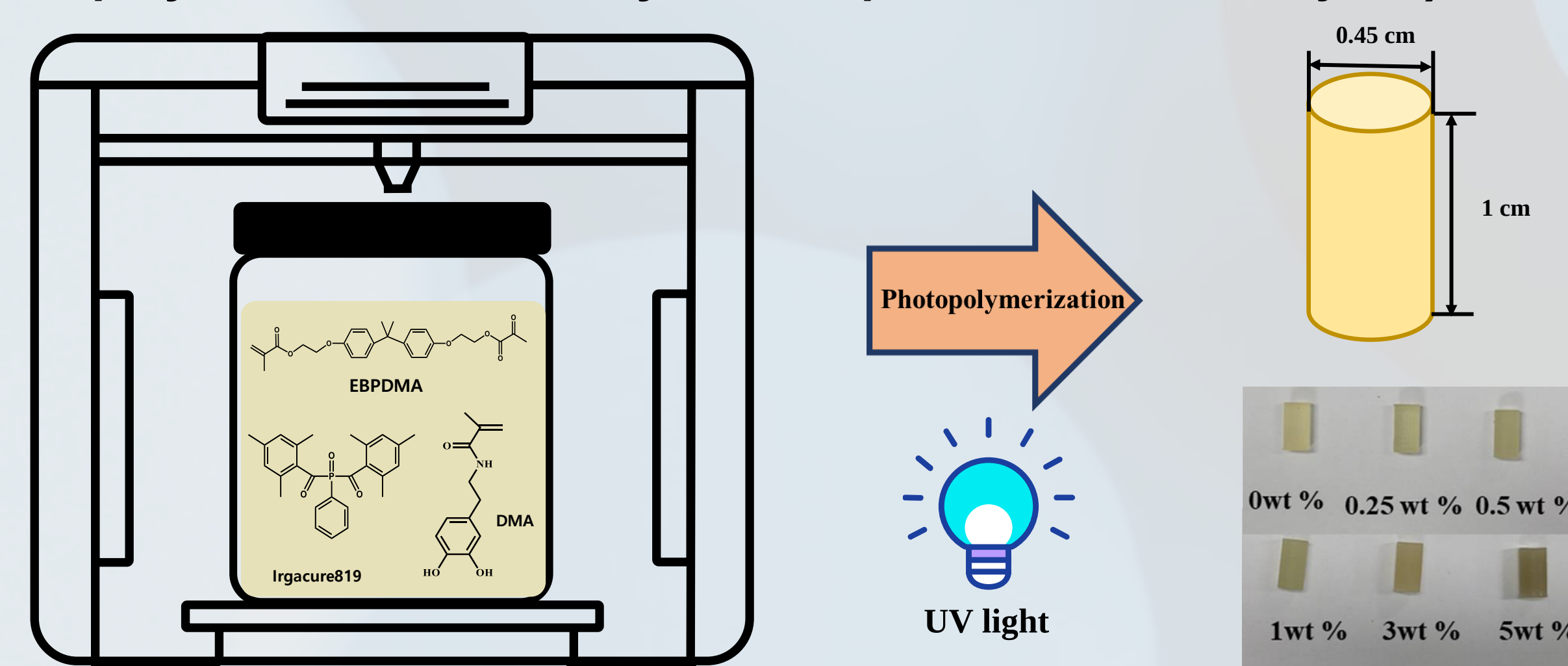
Experimental

The synthesized dopamine methylacrylamide (DMA) was characterized through FT-IR, ¹H-NMR and ¹³C-NMR spectroscopies and mixed with ethoxylated bis-GMA (EBPDMA) and Irgacure 819 with various compositions to 3D print by DLP technique. Catechol-functionalized polymers are synthesized by free radical polymerization of dopamine methylacrylamide (DMA) and methyl methacrylate (MMA) in DMF. The polymer with the crosslinked structure was characterized through GPC, FT-IR and ¹H-NMR spectroscopies. The mechanical properties of fabricated specimens such as compressive and flexural strengths were evaluated by UTM.

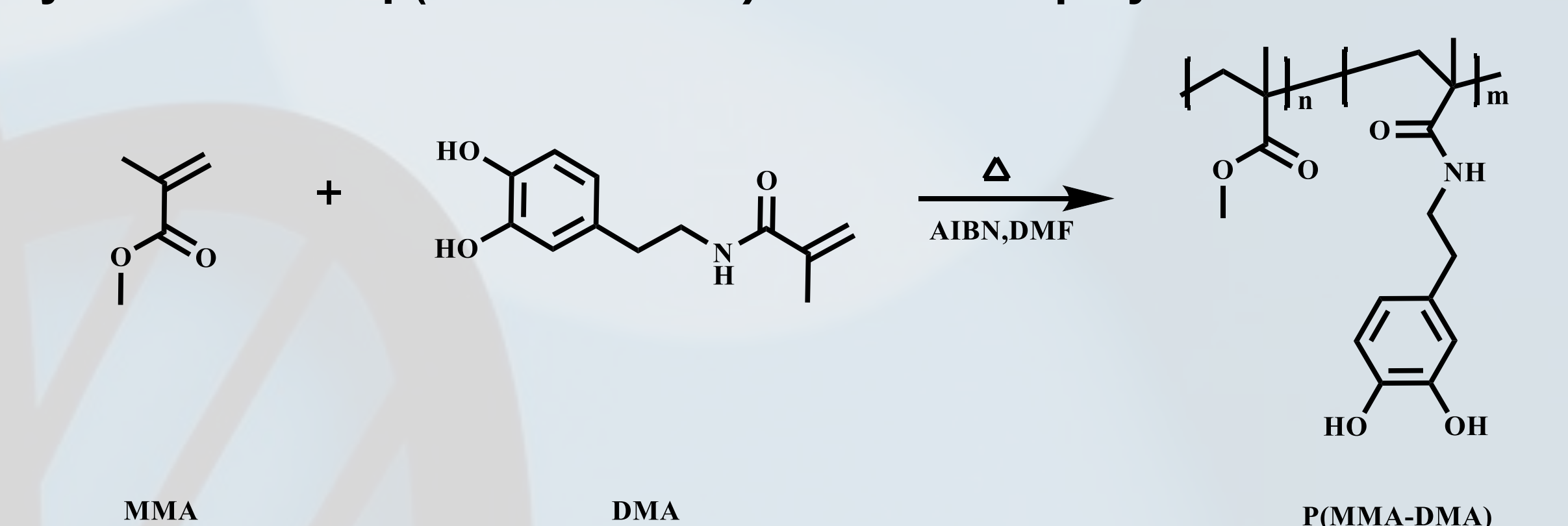
• Synthesis of Dopamine Methacrylic Amide (DMA)



• Photopolymerization of ethoxylated bisphenol-A dimethacrylate) with DMA



• Polymerization of p(MMA-co-DMA) with radical polymerization



Conclusion

In this study, dopamine methylacrylamide containing catechol group and vinyl group was analyzed using FT-IR, NMR spectroscopy. The N-H, O-H and aromatic C=C peaks of dopamine hydrochloride were represented in DMA. DMA showed C=O peak at 1652 cm⁻¹, aromatic C=C peak at 1603 cm⁻¹ and 1439 cm⁻¹, and vinyl C=C peak at 1533 cm⁻¹. The peaks from the products show that the C=O peak of amide and vinyl C=C peak of amide were newly created. In the case of ¹H-NMR spectroscopy, amine group peak of dopamine hydrochloride was appeared at near 1.6 ppm, and was converted to amide and appeared as amide peak near 8 ppm of DMA. Near 5.5 ppm, the signals of alkene hydrogens of DMA were appeared. Also, the signals of methyl group were appeared at near 1.9 ppm. These results show that DMA has been successfully synthesized. As for compressive strength, 0 wt%, 0.25 wt%, 0.5 wt%, 1 wt%, 3 wt%, and 5 wt% of DMA were dissolved in EBPDM resin to produce a specimen through DLP type 3D printing. The compression strength generally increased as the content of DMA increased, and the maximum value of 330.9875 was obtained for a sample of 5wt% DMA. The strength of EBPDM at 0 wt% DMA was 78 shore D, and overall, the values of all samples increased compared to those of EBPDM at 0 wt% DMA. In general, the hardness value increased as the content of DMA increased up to 0.5 wt%, but the hardness value gradually decreased from 1 wt% or more, so it was determined that 0.5 wt% DMA was the best. In samples containing less than 1 wt% of DMA, shrinkage occurred, and the lowest shrinkage rate value was shown at 0.25 wt%. The synthesized DMA was polymerized with MMA through radical polymerization to produce p(MMA-co-DMA). p(MMA-co-DMA) was characterized through FT-IR and NMR. In the IR spectra, p(MMA-co-DMA) showed a C-H (sp³) peak near 3000cm⁻¹, which did not appear in the monomer, and vinyl peak in the monomer disappeared. In the NMR spectrum vinyl peak appearing near 5.5ppm in DMA and 5.7ppm in MMA did not appear in p (MMA-co-DMA). Characteristic peaks of the monomers were also well observed in polymer, and peaks for a vinyl group appeared anew at around 0.8 - 1 ppm.