



# Synthesis, Characterization and Thermal Properties of Fluorinated Bisphenol Compounds and Their Copolymers

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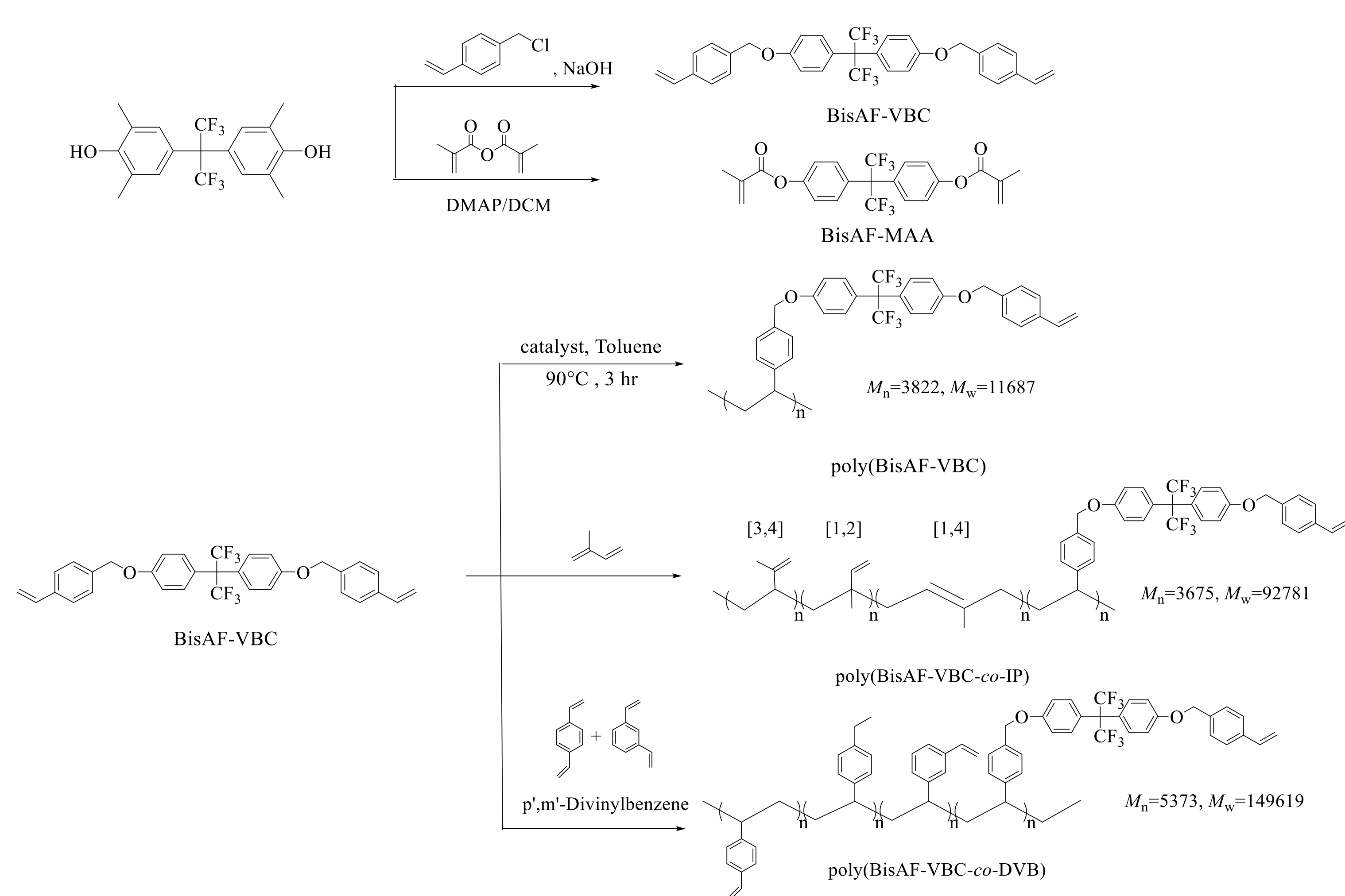
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## Abstract

Fluorinated polymers have attracted significant attention due to their exceptional thermal and chemical stability, hydrophobicity, and insulating properties. In this study, we report the synthesis of fluorine-containing bisphenol compounds with various functional groups, which were subsequently copolymerized with different dienes via cationic polymerization to produce novel heat-resistant resins. The structures and properties of these fluorinated bisphenol monomers and copolymers were characterized using  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR,  $^{19}\text{F}$  NMR, and differential scanning calorimetry (DSC). HSQC NMR analysis revealed that the chemical shift at 3.86 ppm corresponds to the methine protons on the fluorinated polymer backbone, while the fluorine atoms exhibit a chemical shift around -64.19 ppm in  $^{19}\text{F}$  NMR spectroscopy. When crosslinked with polyphenylene ether, the vinylbenzyl-functionalized compounds exhibited significantly improved thermal properties, including higher glass transition temperatures ( $T_g$ ) and thermal decomposition temperatures ( $T_d$ ), compared to their methacryloyl-functionalized counterparts.

## Experimental



## Result

The fluorine-containing vinyl monomer was synthesized through a nucleophilic substitution reaction between vinylbenzyl chloride and hexafluorobisphenol-A. The resulting monomer, BisAF-VBC, was then copolymerized with various dienes via cationic polymerization to produce novel heat-resistant resins. Random copolymerization was carried out by reacting BisAF-VBC with isoprene or divinylbenzene using  $\text{SnCl}_4$  as the catalyst and benzyl bromide as the initiator. The chemical structures and thermal properties of the resulting polymers were characterized using  $^1\text{H}$  NMR, FT-IR, DSC, GPC, and TGA analyses.

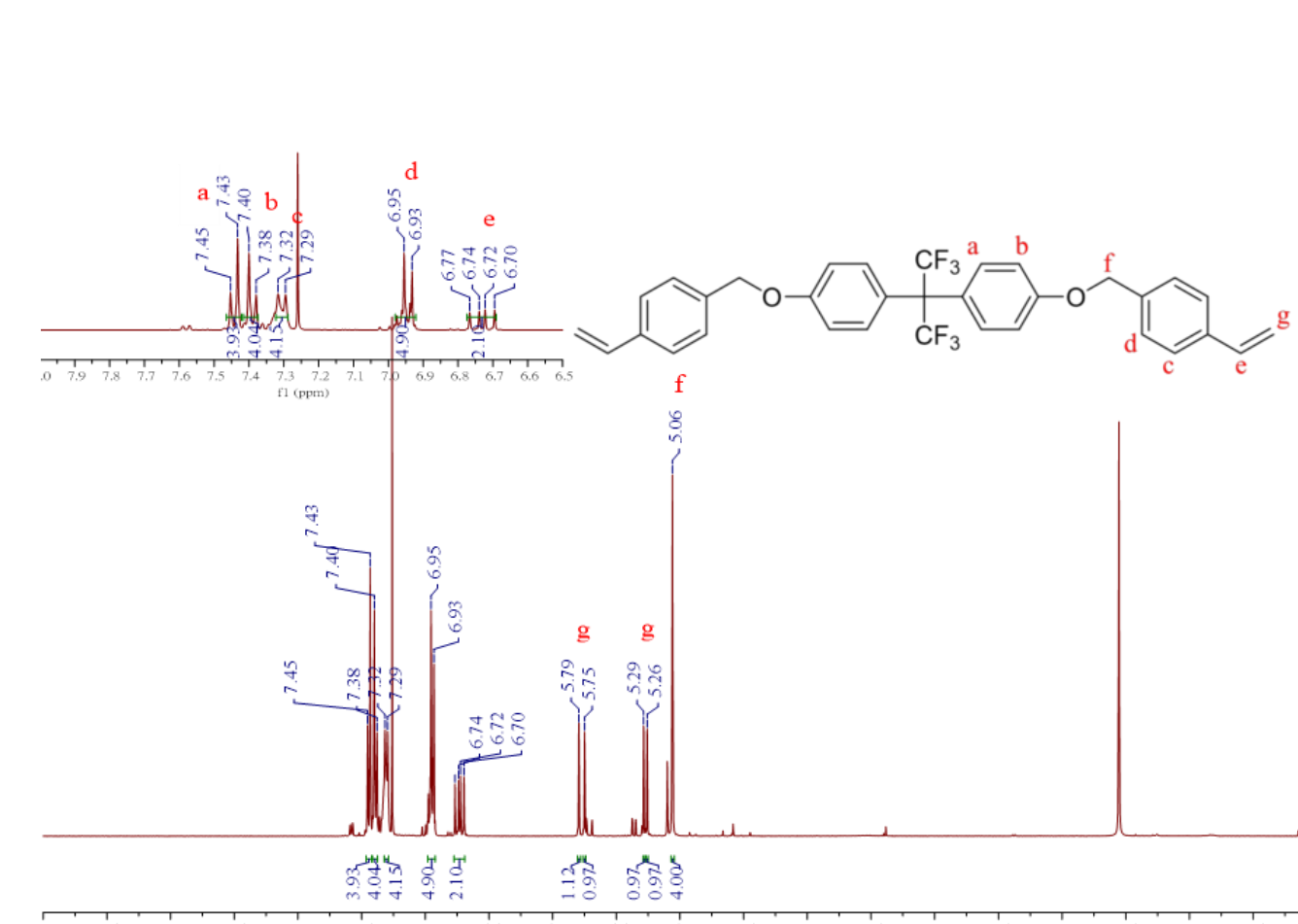


Fig 1.  $^1\text{H}$  NMR-BisAF-VBC

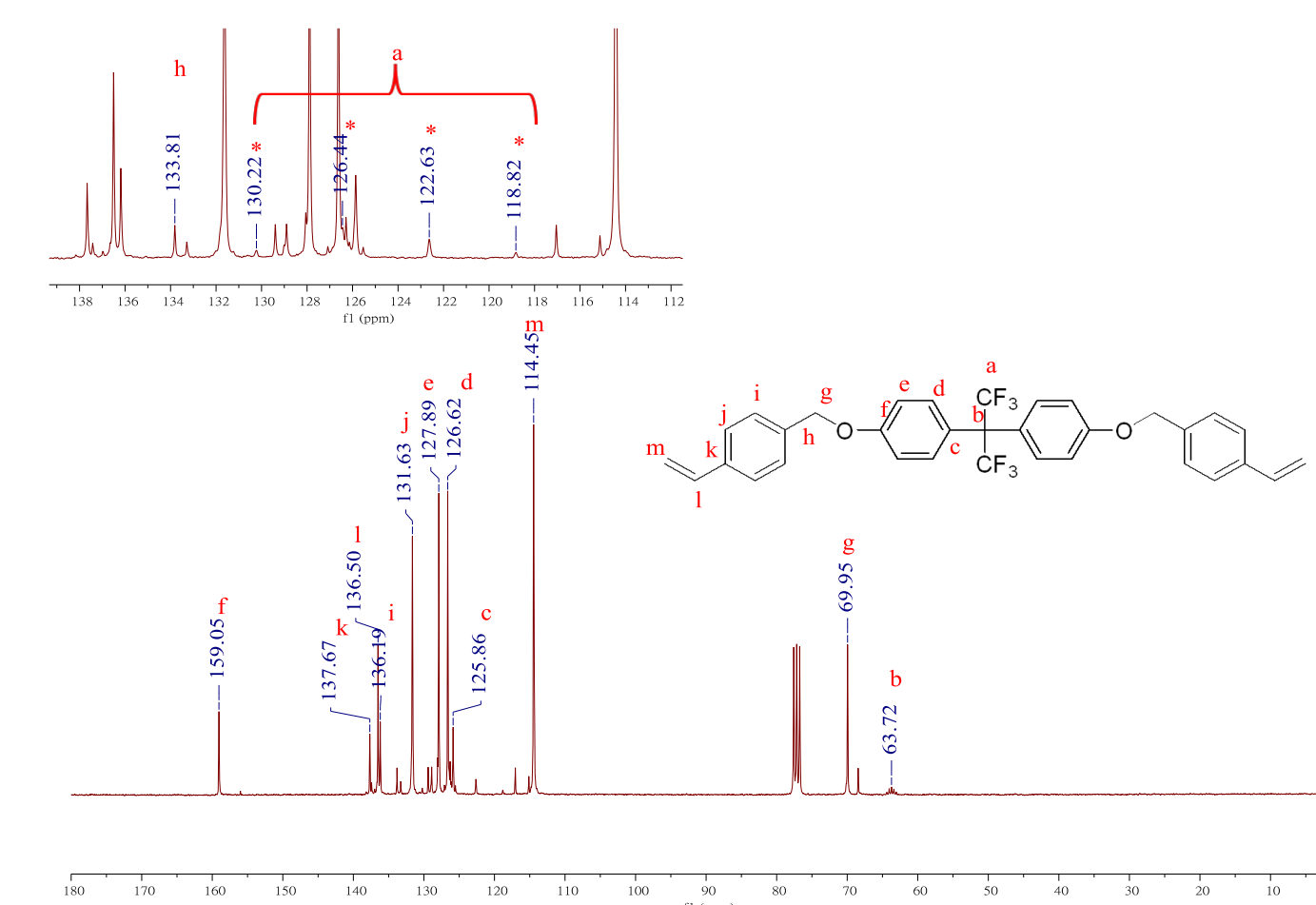


Fig 2.  $^{13}\text{C}$  NMR-BisAF-VBC

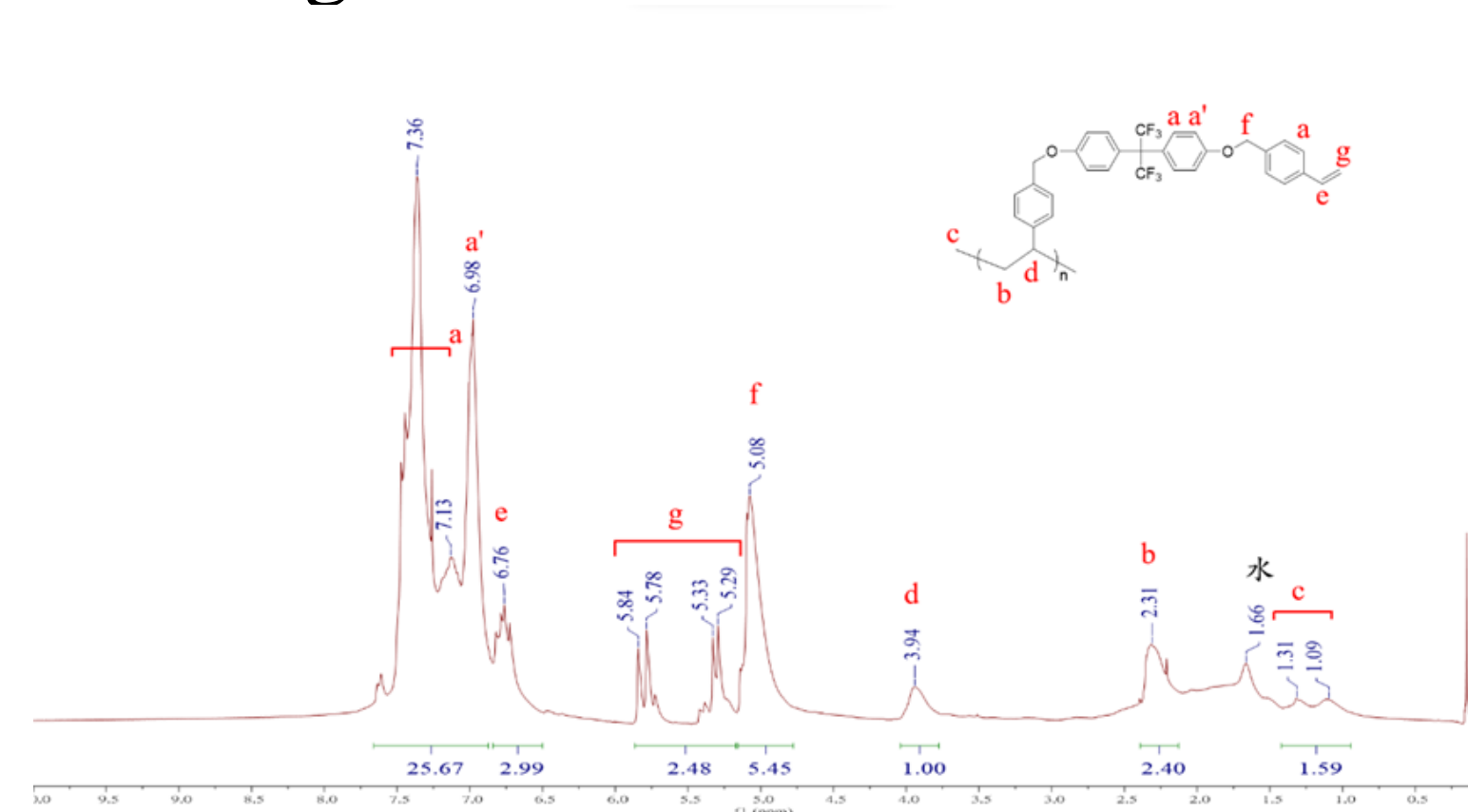


Fig 3.  $^1\text{H}$  NMR-poly(BisAF-VBC)

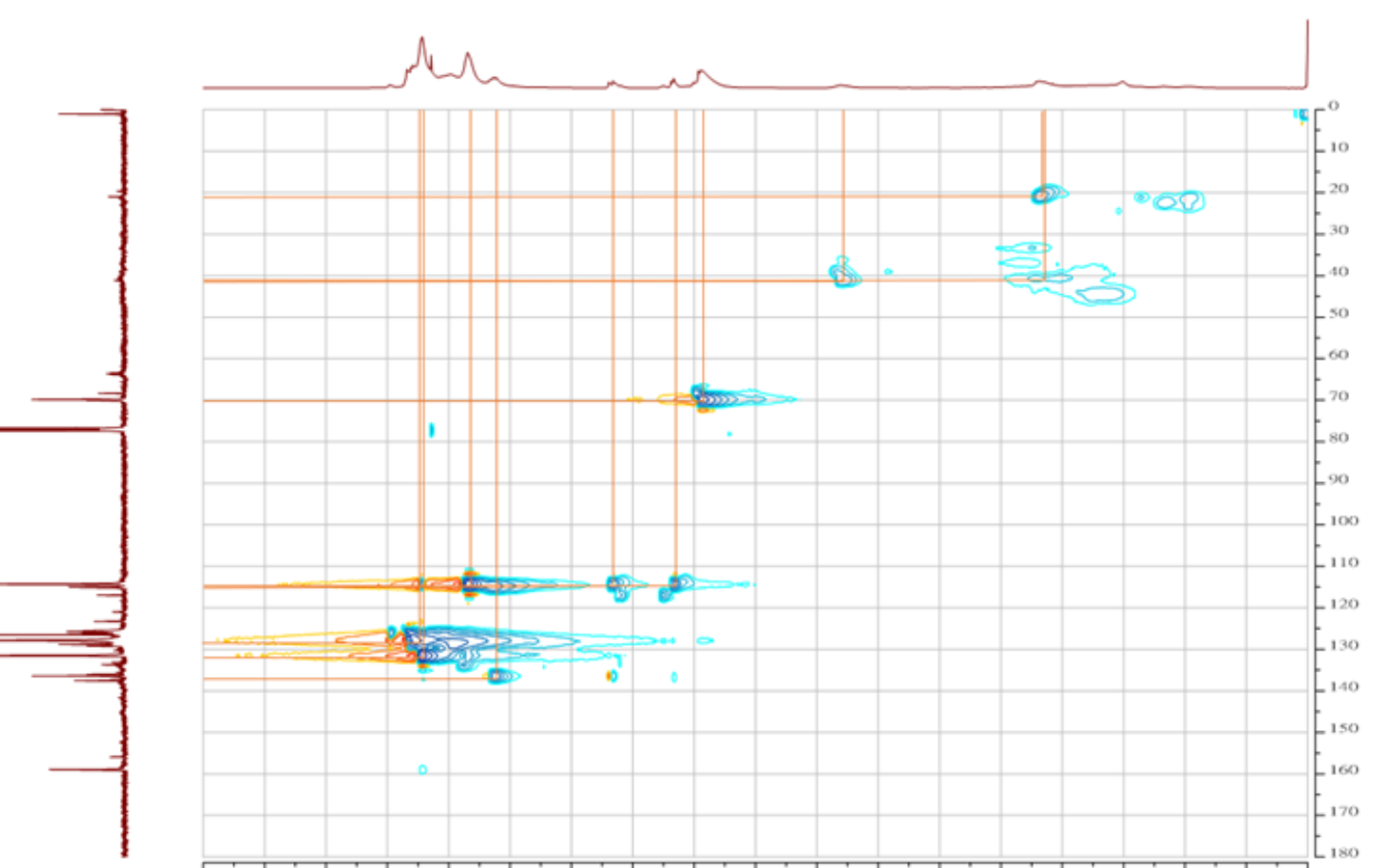


Fig 4. HSQC of poly(BisAF-VBC)

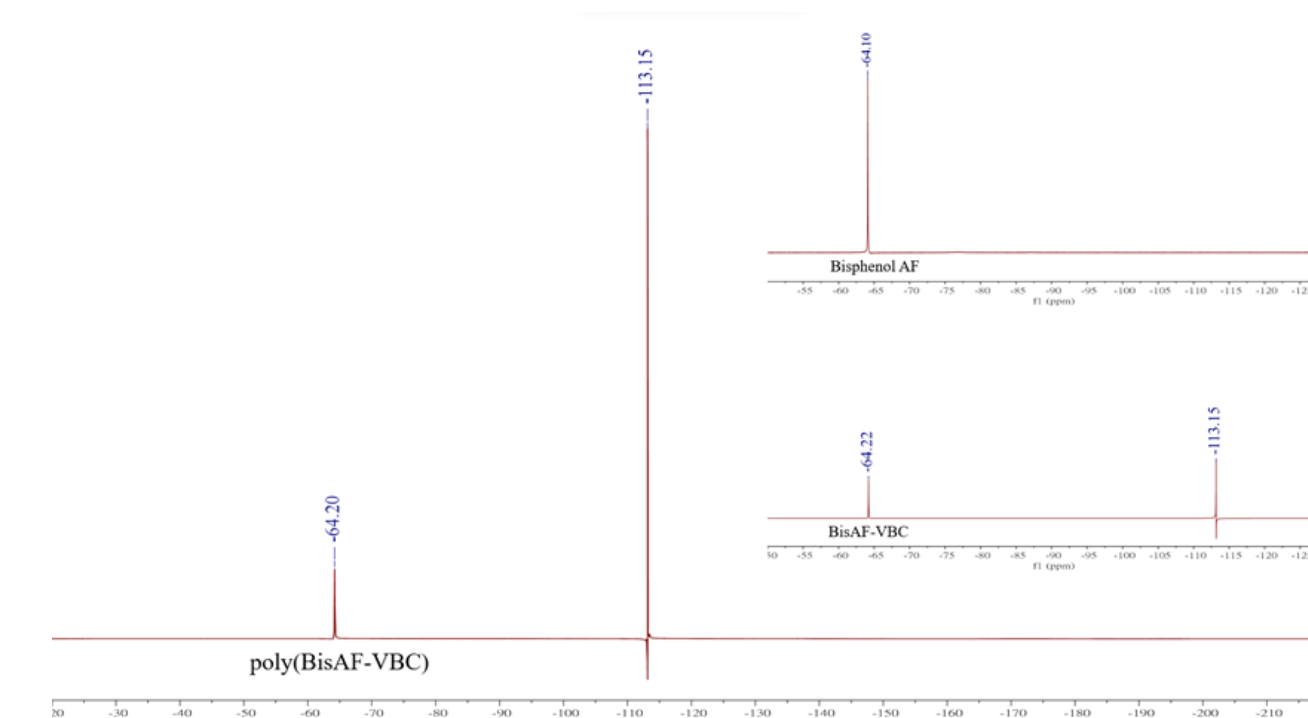


Fig 5.  $^{19}\text{F}$  NMR-poly(BisAF-VBC)

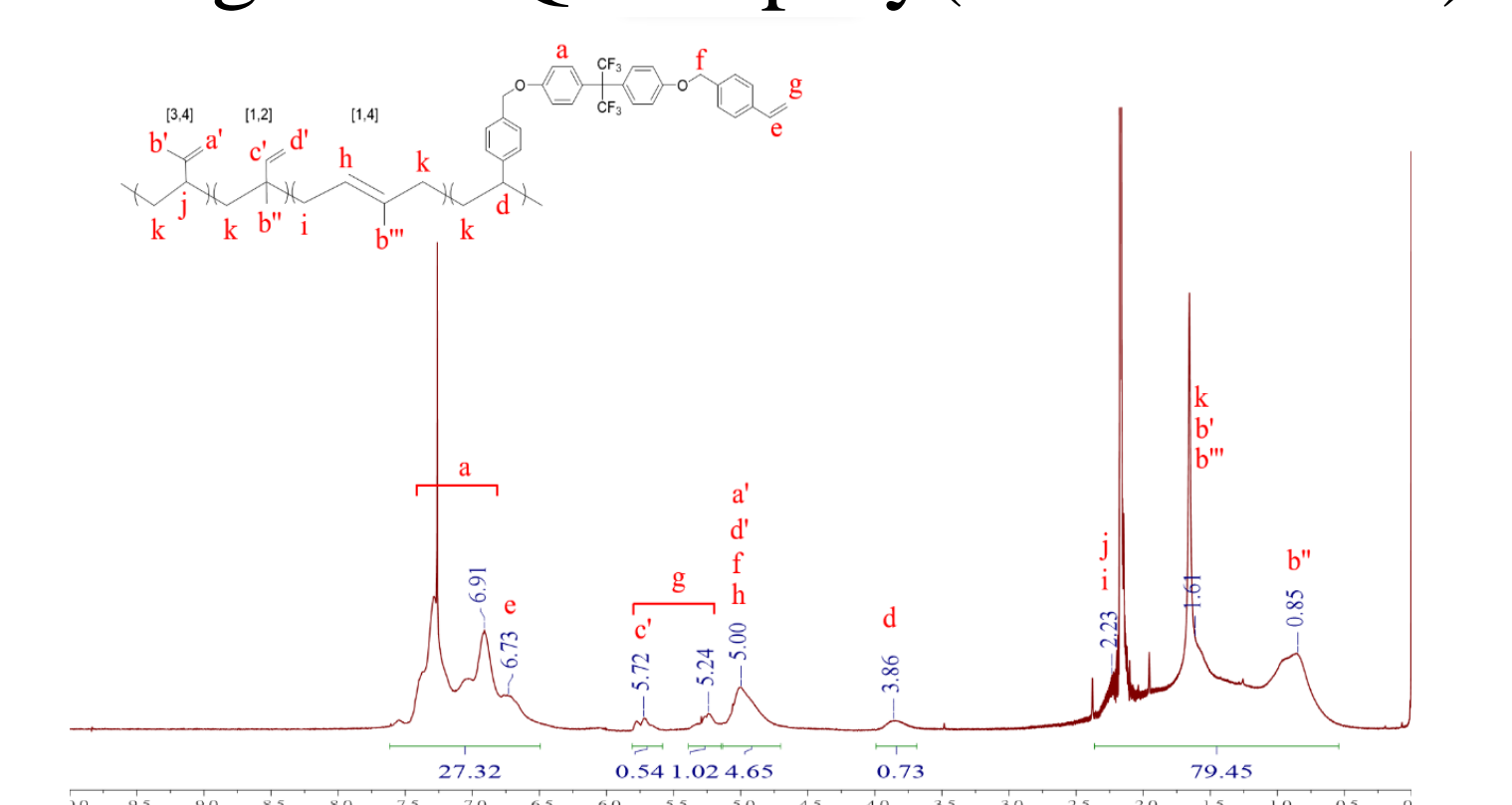


Fig 6.  $^1\text{H}$  NMR-poly (BisAF-VBC-co-IP)

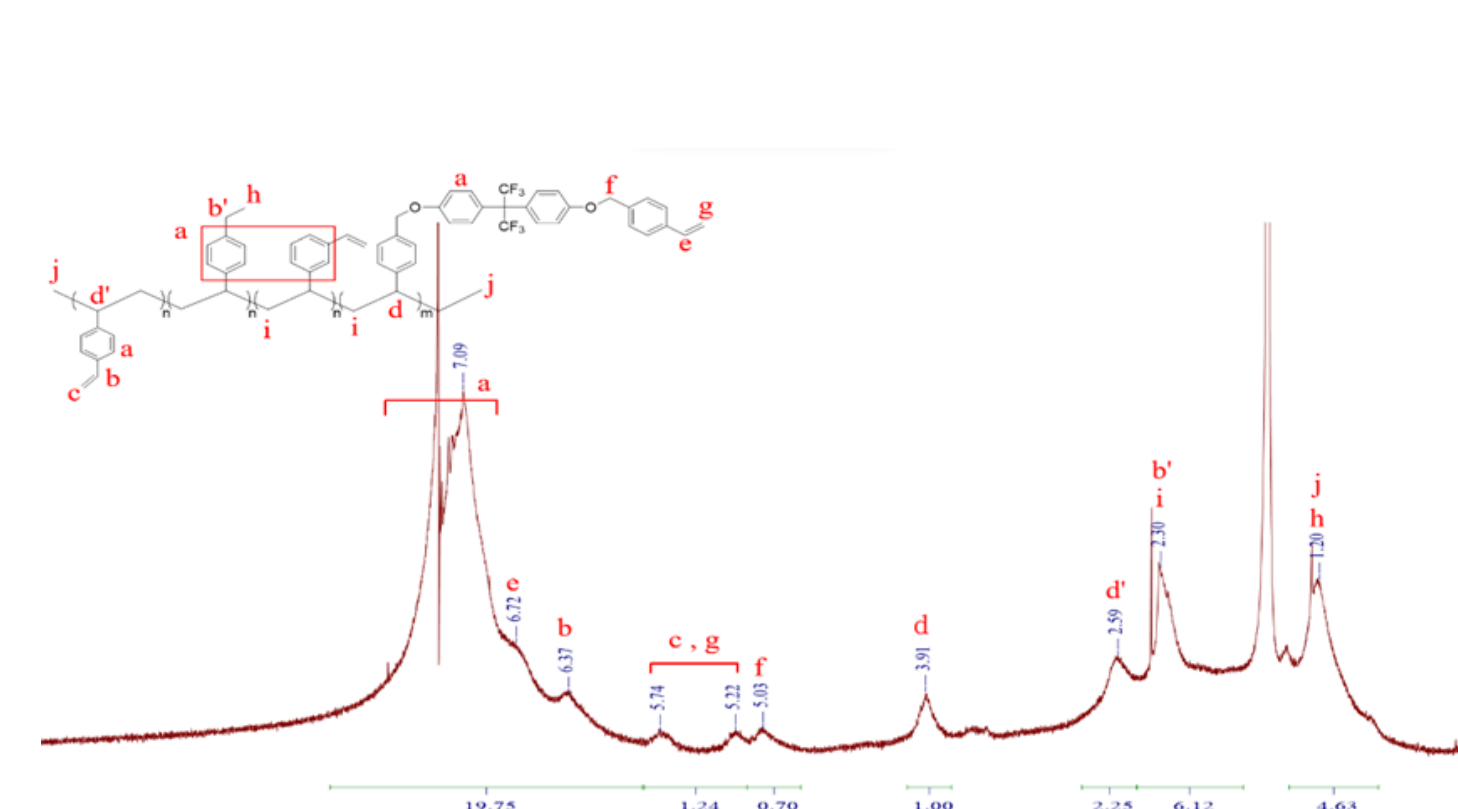


Fig 7.  $^1\text{H}$  NMR-poly (BisAF-VBC-co-DVB)

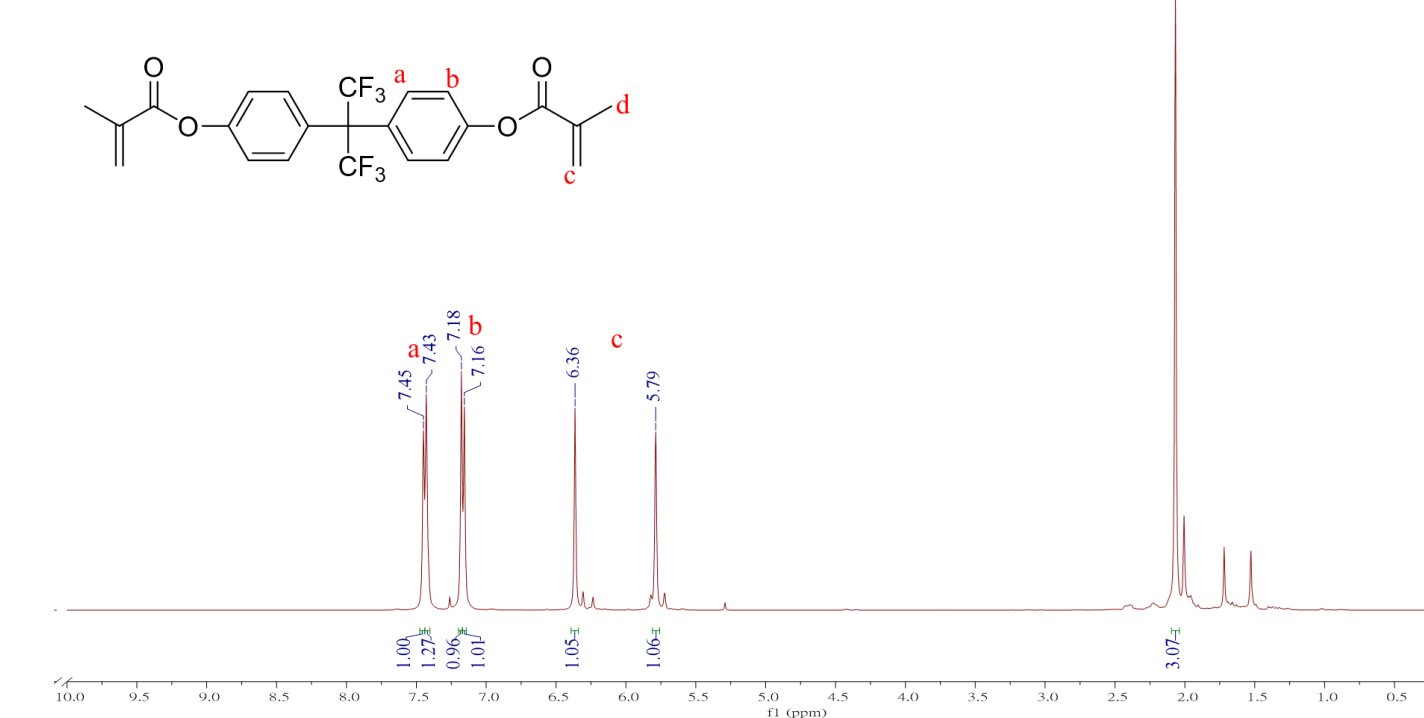


Fig 8.  $^1\text{H}$  NMR-BisAF-MAA

Table 1. Thermal Property Analysis of BisAF-VBC polymer

Sample	Before DHBP Curing						
	Initial $T_g$ (°C)	Enthalpy (J/g)	Curing Temp (°C)	$T_d, 2\%$ (°C)	$T_d, 5\%$ (°C)	$T_d, \text{max}$ (°C)	Char yield (%)
poly(BisAF-VBC)	116.31	4.782	142.35	263.46	292.98	589.19	0.8723
poly(BisAF-VBC-co-IP)	133.30	2.260	102.06	242.40	268.77	563.04	1.983
poly(BisAF-VBC-co-DVB)	---	4.162	128.71	296.63	319.56	555.20	3.290
After DHBP Curing							
poly(BisAF-VBC)	---	265.0	195.13	285.74	310.01	592.17	2.905
poly(BisAF-VBC-co-IP)	---	30.54+	181.11+	246.89+	291.98+	576.79+	3.652
poly(BisAF-VBC-co-DVB)	---	135.8	197.99	325.69	343.19	568.85	3.769

Table 2. Crosslinking results with PPO

Crosslinking	Ratio (by wt.)	Peroxide (0.5%)	$T_g$
			°C
BisAF-MAA + PPO	9:1	DHBP	204.4
BisAF-MAA + PPO	8:2	DHBP	200.9
BisAF-VBC + PPO	9:1	DHBP	231.5
BisAF-VBC + PPO	8:2	DHBP	230.9

## Conclusion

In this study, a fluorine-containing vinyl monomer and its corresponding polymers, which are diene copolymers with different backbone structures, were successfully synthesized. After the cross-linking reaction, the thermal decomposition temperature of the resulting polymers significantly increased. The thermal stability followed the order: poly(BisAF-VBC-co-DVB) > poly(BisAF-VBC) > poly(BisAF-VBC-co-IP), which is attributed to the increasing benzene content within the polymer backbone.

## References

- Zhang, H.; Weber, S. G. *Fluorous chemistry* **2012**, 307-337.
- Chen, Y. C.; Reddy, K. S. K.; Lin, Y. A.; Wang M. W.; Lin, C. H.; *ACS omega*, **2022**, 7(30), 26396-26406.