

Frontal Ring-Opening Metathesis Copolymerization: Deviation of Front Velocity from Mixing Rules

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ABSTRACT: Frontal ring-opening metathesis polymerization (FROMP) of dicyclopentadiene (DCPD) shows promise for rapid, energy-efficient manufacturing of high-performance polymers and composites. Copolymerization in FROMP allows for systematic modification of materials properties while retaining the benefits of the DCPD system such as low cost of the monomer and excellent mechanical properties of the resulting polymer. While the copolymerization reactivity and copolymer properties generally exhibit monotonic dependence on monomer composition as predicted by simple, empirical mixing rules, we discovered that the frontal copolymerization behavior of DCPD with a dinorbornenyl (di-NBE) cross-linker deviates significantly from that expected relationship. As the comonomer content increases, the FROMP reaction shows a non-monotonic increase in front velocity with intermediate compositions 40% faster than either pure component. We then studied the behavior of a series of comonomers, analyzed several factors (such as thermodynamic and kinetic properties) that might influence front velocity, and found that the non-monotonic trend mainly results from the cross-linked structure. This copolymerization system provides a promising strategy to tune materials properties (such as glass transition temperature) and simultaneously improve the efficiency in FROMP-based materials manufacturing.

Thermally-initiated frontal polymerization (FP) is a process that forms a propagating reaction zone where monomer transforms to polymer. Many FP chemistries have been developed, which enables a wide variety of applications such as out-of-autoclave curing of large composites and cure-on-demand repair.^{1–4} Radical FP is by far the most investigated method due to the high exothermicity of addition polymerization and the readily available monomers and initiators.¹ However, the limiting aspects of radical FP include short pot life when combined with highly reactive monomers and inferior mechanical properties of the resulting polymers. Recently, Robertson et al. demonstrated that phosphite-inhibited frontal ring-opening metathesis polymerization (FROMP) of *endo*-dicyclopentadiene (*endo*-DCPD) substantially extends the pot life up to 30 hours,⁵ which allows manufacturing high performance thermosets and fiber-reinforced polymer composites (FRPC).⁴ This strategy dramatically reduces, by several orders of magnitude, the energy required for curing and yields FRPCs with similar mechanical properties to those from conventional autoclave curing. *endo*-DCPD is an excellent monomer in FROMP owing to its high strain energy and commercial availability, and the resulting polydicyclopentadiene (pDCPD) exhibits outstanding mechanical properties.^{4,6,7} Despite the advantages of *endo*-DCPD, there are still challenges in the current system including poor interfacial shear strength in FRPCs and low cross-linking density of pDCPD.⁴ One approach to mitigate this problem is by copolymerization with other functional monomers.

Copolymerization is a common strategy to tailor polymeric materials with desired properties by modifying the chemical structure and comonomer feed ratio. In radical FP, copolymerization has been largely explored to synthesize functional materials,^{8,9} interpenetrating networks,¹⁰ gradient polymers,¹¹ hydrogels,^{12,13} and consolidants.¹⁴ Front velocity (v_f) is systematically controlled, being a monotonic function of the comonomer composition, initiator concentration, and initial reactant temperature.^{1,15–18} Copolymerization in FROMP, however, is underexplored due to the limited availability of functionalized monomers with sufficient ring strain. Since FP is directly related to the amount of heat released during polymerization, we envisioned that norbornene (NBE) derivatives are excellent FROMP comonomer candidates as they possess similar ring strain to *endo*-DCPD.¹⁹ Thus, copolymerization of *endo*-DCPD with NBE-based monomers would systematically modify the properties (e.g., mechanical and interfacial) of pDCPD without sacrificing v_f . Here we studied the copolymerization behavior in FROMP and discovered an unusual non-monotonic increase in v_f upon copolymerizing with di-NBE monomers, which contradicts the intuitive predictions of the mixing rule.

The mixing rule is an empirical prediction of properties of a multicomponent system over a wide range of chemical composition. In materials science, the “rule of mixtures” is commonly used as a simple method that yields acceptable predictions compared to experimental values.²⁰ The mixture property is predicted to have an upper bound defined by the weighted arithmetic mean (WAM) and a lower bound based on the weighted harmonic mean (WHM)

of each individual component. Thus, the reactivity and materials properties at any composition are expected to lie between those of the pure components.²¹ In free-radical frontal copolymerization, while v_f showed monotonic dependence on composition,^{15,16} exceptions have been noted. Pojman et al. observed an interesting relationship in a system of binary FP reactions that consisted of free-radically polymerized diacrylate and an amine-cured epoxy. v_f exhibited a minimum or maximum value at intermediate compositions.^{10,22} They suggested that this behavior is related to the independent mechanism of each polymerization. In another study from their group on multifunctional thiol-ene systems, v_f reached a maximum value when the thiol and ene were stoichiometrically equivalent due to the complete consumption of both monomers.^{23,24} For copolymerization in FROMP, the above scenarios are not expected when two comonomers are both strained rings. Intuitively, the weighted means would predict FROMP performance (such as v_f) with acceptable accuracy. Thus, monomers that homopolymerize at a v_f comparable or even faster than v_f (*endo*-DCPD) in FROMP are ideal candidates for copolymerization.

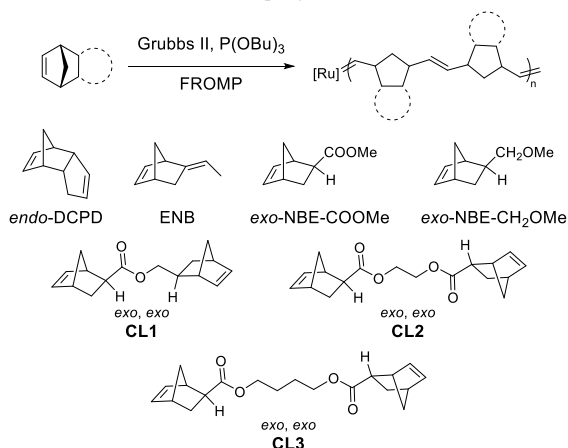


Figure 1. FROMP monomers investigated in this study. Second generation Grubbs' catalyst (Grubbs II) was used as the metathesis catalyst, and tributyl phosphite was employed as the inhibitor.

To identify potential comonomers, we first investigated homopolymerization reactivity in FROMP of mono-NBEs where the substituents are in the *exo* position (Figure 1) as these isomers exhibit higher reactivity than the corresponding *endo*-isomers.^{19,25} These *exo*-monomers propagate at a stable velocity, characterized by linear plots of front position over time (Figure S1). The amount of heat released (ΔH_p) was also quantified by differential scanning calorimetry (DSC) (Figure S5). The efficacy of FROMP was based on v_f and ΔH_p . As summarized in Table 1, v_f is sensitive to the linking group (i.e., functional group that attaches to the NBE ring). Monomers with smaller groups such as ethylidene norbornene (ENB) release the highest amount of heat upon ring-opening and thus possess a faster v_f compared to the other monomers studied. Despite similar ΔH_p of *exo*-NBE-COOMe and *exo*-NBE-CH₂OMe, the former monomer exhibits almost twice as fast v_f as the latter one. We envisioned that a di-NBE cross-linker (**CL1**) with an

ester linking group would have better performance in FROMP than the one with a methylene ether group. Gratifyingly, **CL1** polymerizes at $v_f = 0.96$ mm/s, which makes it an ideal cross-linker in FROMP since it modulates cross-linking density without adversely affecting v_f .

For copolymerization in FROMP, we initially studied the v_f dependence by varying the weight percentage of ENB upon copolymerizing with *endo*-DCPD. As expected, v_f shows a steady increase as ENB loading increases (Figure 2a). The same trend was observed with ΔH_p (Figure 2b). Although v_f exhibits a slightly negative deviation from WHM of each individual monomer, similar to the observation in previous frontal radical copolymerization,¹⁵ the weighted means predict the copolymerization performance with acceptable errors. However, upon copolymerization of *endo*-DCPD and **CL1**, v_f exhibits a non-monotonic behavior as the content of **CL1** increases with a significant deviation from WAM or WHM (Figure 3a). The highest v_f was observed to be 1.4 mm/s at 40 wt. % loading of **CL1**. The maximum v_f is 40% higher than v_f of each individual monomer. Copolymerization with **CL1** not only leads to faster front propagation but also increases the cross-linking density of the resulting thermosets. Introducing 10 and 20 wt. % of **CL1** elevates glass transition temperatures from 100 °C to 116 °C and 138 °C, respectively (Figure S11).

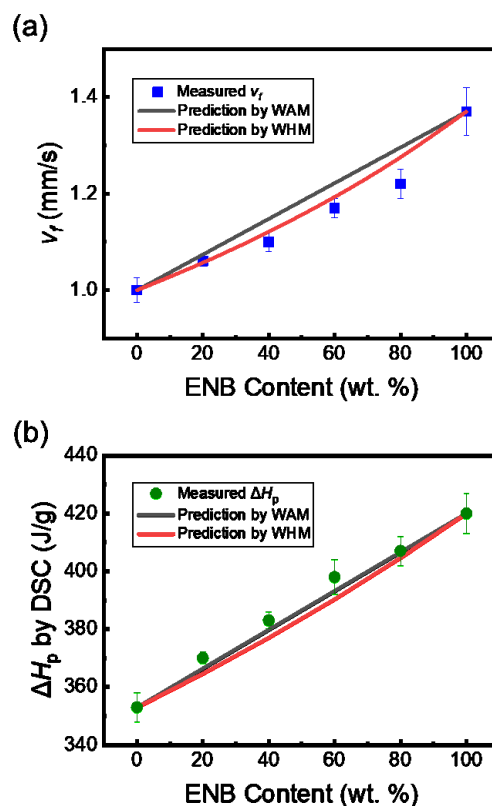


Figure 2. (a) Front velocity and (b) heat released data for the copolymerization of *endo*-DCPD and ENB. FROMP was performed in the presence of 100 ppm Grubbs II catalyst and 1.0 equiv (per mole ruthenium) P(OBu)₃ at 20 °C. WAM and WHM represent weighted arithmetic mean and weighted harmonic mean, respectively.

Table 1. v_f and ΔH_p of investigated monomers upon homopolymerization.

Monomer	<i>endo</i> -DCPD	ENB	<i>exo</i> -NBE-COOMe	<i>exo</i> -NBE-CH ₂ OMe	CL1	CL2	CL3
v_f (mm/s) ^a	1.00 ± 0.03	1.37 ± 0.05	1.12 ± 0.06	0.65 ± 0.03	0.96 ± 0.06	0.62 ± 0.04	0.47 ± 0.04
ΔH_p (J/g) ^b	353 ± 5	420 ± 7	320 ± 10	325 ± 5	273 ± 7	260 ± 5	250 ± 8

^a FROMP was performed in NMR tubes and proceeded in a descending mode. v_f was measured with the formulation of 100 ppm Grubbs II per norbornenyl C=C, 1.0 equiv. P(OBu)₃ and 500 mg neat liquid monomers at 20 °C. ^b ΔH_p (J/g) was measured by DSC with a ramping rate of 10 °C/min. The error bar was obtained from three trials.

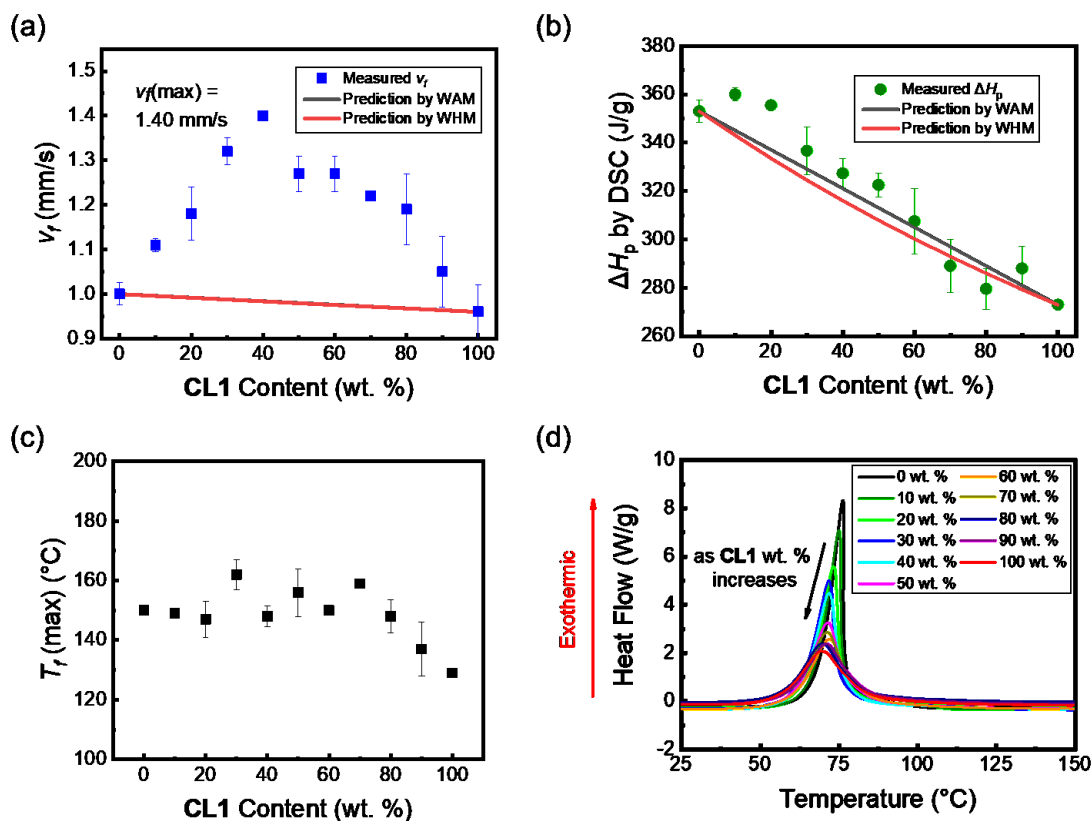


Figure 3. (a) Front velocity, (b) heat released, (c) maximum front temperature and (d) DSC traces for the copolymerization of *endo*-DCPD and CL1. FROMP and DSC experiments were performed in the presence of 100 ppm Grubbs II catalyst per norbornenyl C=C and 1.0 equiv (per mole ruthenium) P(OBu)₃. FROMP experiments in (a) and (c) were thermally initiated on samples equilibrated at 20 °C. DSC data in (b) and (d) were collected with a ramping rate of 10 °C/min. WAM and WHM represent weighted arithmetic mean and weighted harmonic mean, respectively. Prediction by WAM in (a) overlaps with prediction by WHM due to the fairly close v_f values of *endo*-DCPD and CL1.

To understand the unusual non-monotonic behavior, we analyzed factors that influence v_f such as thermodynamic and kinetic properties. In thermally initiated FP, one essential criterion is that the monomer releases enough heat at a fast enough rate to compensate for the heat loss to the environment.¹ Thus, ΔH_p directly affects v_f , and larger ΔH_p is expected to afford faster v_f as observed in Figure 2. ROMP of pure CL1 releases lower amount of heat per gram than *endo*-DCPD, and ΔH_p values upon copolymerization exhibit a decreasing trend as the content of CL1 increases (Figure 3b). This trend of ΔH_p , however, does not correlate with the variance in v_f . It is also known that v_f is affected by the front temperature (T_f) since the kinetics are accelerated by elevated temperatures,⁴ so the temperature profile was

then evaluated at different CL1 compositions. As shown in Figure 3c, the maximum T_f does not show strong correlation with v_f . Thus, the non-monotonic increase in v_f does not result from generating more heat nor elevating T_f by introducing CL1 into FROMP.

We noticed that as the wt. % of CL1 increases, the exothermic peak becomes broader and polymerization initiates at an earlier temperature as shown in Figure 3d. We then hypothesized that the increase in v_f results from a better initiation of the catalyst upon mixing with ester-functionalized monomers. To test this hypothesis, *exo*-NBE-COOMe was employed as a comonomer. It was selected because it not only polymerizes at a lower temperature than

endo-DCPD but also contains an ester functional group that might contribute to the v_f increase. As shown in Figure 4b, the DSC curves of copolymerization systems shift to a lower temperature with broadening of the peak shape as the comonomer wt. % increases. Even though pure *exo*-NBE-COOMe possesses a higher v_f than *endo*-DCPD, comonomer mixtures do not exhibit a non-monotonic increase in v_f (Figure 4a). Similar observation was made in the copolymerization of *endo*-DCPD and *exo*-NBE-CH₂OMe where v_f and ΔH_p show monotonic dependence on composition (Figure S2 and Figure S6). Overall, neither more efficient catalyst initiation nor the ester functional group are the origins of non-monotonic behavior.

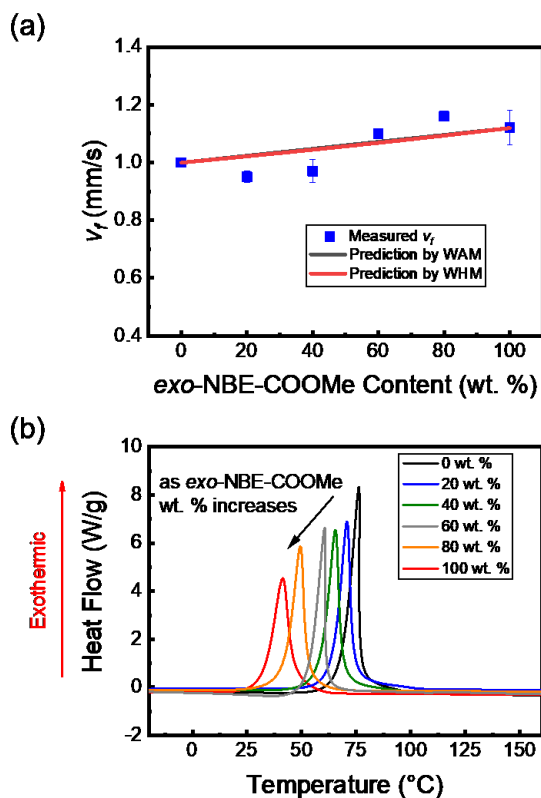


Figure 4. (a) Front velocity and (b) DSC traces for the copolymerization of *endo*-DCPD and *exo*-NBE-COOMe. FROMP and DSC were performed in the presence of 100 ppm Grubbs II catalyst and 1.0 equiv (per mole ruthenium) P(OBu)₃. FROMP experiments were thermally initiated on samples equilibrated at 20 °C. DSC data were collected with a ramping rate of 10 °C/min. WAM and WHM represent weighted arithmetic mean and weighted harmonic mean, respectively. Prediction by WAM in (a) overlaps with prediction by WHM due to the fairly close v_f values of *endo*-DCPD and *exo*-NBE-COOMe.

Since the non-monotonic increase was only observed with the di-NBE comonomer that forms a cross-linked structure, we further tested **CL2** which can be regarded as the “dimer” of *exo*-NBE-COOMe owing to a doubling of molecular weight (MW). Despite the lower v_f of **CL2** (0.62 mm/s), its copolymerization with *endo*-DCPD shows similar non-monotonic behavior with the maximum v_f observed at 40 wt. % (Figure 5a, Figure S7). This implies that v_f shows acceleration when two NBE rings are physically linked together. This covalent link leads to a higher neat NBE C=C concentration ($[M]_{\text{neat}}$) which is calculated as density

divided by MW per NBE moiety (Table S1). To be more specific, even though **CL2** and *exo*-NBE-COOMe have almost the same MW per NBE, the former monomer possesses a higher $[M]_{\text{neat}}$ (7.6 mol/L) than the latter one (7.1 mol/L) because **CL2** has a higher density (1.15 g/mL). Thus, for the same total mass, comonomer with a higher $[M]_{\text{neat}}$ affords more reactive C=C bond per unit volume, which accelerates the front propagation. This is further supported by copolymerization with **CL3** which has a larger MW but similar $[M]_{\text{neat}}$ (6.9 mol/L) as *exo*-NBE-COOMe. A steady decrease in v_f was observed when **CL3** was copolymerized with *endo*-DCPD (Figure 5b, Figure S8). Among all the cross-linkers investigated, **CL1** has the largest $[M]_{\text{neat}}$ of 9.0 mol/L, and thus it exhibits the largest deviation from the weighted means.

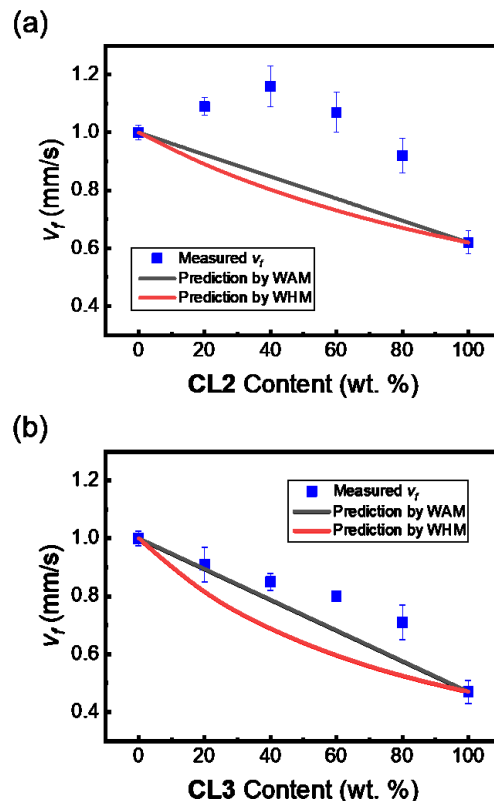


Figure 5. Front velocity of copolymerization of (a) *endo*-DCPD and **CL2**, (b) *endo*-DCPD and **CL3**. FROMP experiments were performed in the presence of 100 ppm Grubbs II catalyst, 1.0 equiv (per mole ruthenium) P(OBu)₃ and thermally initiated on samples equilibrated at 20 °C. WAM and WHM represent weighted arithmetic mean and weighted harmonic mean, respectively.

While $[M]_{\text{neat}}$ is a key determinant for the v_f acceleration, the degree of cross-linking also greatly contributes to the non-monotonic dependence. To eliminate the effect of $[M]_{\text{neat}}$, the total NBE C=C bond concentration was fixed at 7.1 mol/L using toluene as a solvent additive in the copolymerization of *endo*-DCPD and **CL1**. In this case, the non-monotonic dependence on composition was still observed but with much smaller deviations from WAM and WHM (Figure S3, Figure S9). This effect suggests that cross-linking renders close proximity of two NBE rings and allows for more rapid approach of the propagating [Ru] carbenes. The toluene molecules act as diluents and weaken the

proximity effect by cross-linking. A similar conclusion was reached in a recent radical FP study on the effect of acrylate functionality where v_f increases from monofunctional to difunctional acrylate due to autoacceleration.¹⁸

As the cross-linker loading further increases, the front propagation is decelerated presumably due to limited chain mobility at high cross-linking. Such phenomena are known, especially in bulk polymerization where diffusion is a key factor.^{18,26–28} In the copolymerization of *endo*-DCPD and **CL1**, the deceleration effect dominates when the cross-linker loading is larger than 40 wt. %. It is important to remember that *endo*-DCPD also generates a small degree of cross-linking itself by ring-opening of the cyclopentenyl ring. Thus, we also studied ENB, which can only form linear polymers under homopolymerization conditions. In copolymerizations of ENB and **CL1**, we observed similar non-monotonic dependence on **CL1** wt. %, but the maximum v_f shifts to 60 wt. % (Figure S4, Figure S10). Since ENB does not induce any cross-linking by itself, higher loading of **CL1** is required to reach the threshold where high cross-linking density adversely affects v_f . The effect of cross-linking degree on v_f is further supported by the concentration dependence study. While **CL1** forms a highly cross-linked polymer, *endo*-DCPD can only minimally cross-link due to the low-strain cyclopentene ring.^{29,30} Thus, FROMP of *endo*-DCPD demonstrates a linear relationship between v_f and NBE C=C concentration while FROMP of **CL1** reaches a maximum v_f of 1.04 mm/s at 7.7 mol/L C=C concentration (Figure S12, Figure S13). We reasoned that beyond this critical point, high cross-linking density limits the accessibility of monomer to active propagating chains and decelerates FROMP for the **CL1** system. While cross-linking modulates the rate of propagation, it has minimal effect on the thermodynamic parameter, and thus ΔH_p exhibits monotonic dependence as predicted by weighted means in all cases.

In conclusion, we investigated the copolymerization behavior in FROMP and discovered the non-monotonic increase in v_f when DCPD is copolymerized with a di-NBE monomer. This unusual behavior is mainly attributed to the nature of the cross-linked structure, which leads to larger $[M]_{\text{neat}}$ and brings the reactive NBE moieties into closer proximity. As a result of this high effective molarity, the active $[\text{Ru}]$ species propagate faster compared to less cross-linked cases. However, as the cross-linking density increases too much, v_f decreases owing to lower ΔH_p of di-NBE and limited chain mobility. As far as we are aware, this phenomenon has not been observed in other frontal copolymerization systems where monomers polymerize with the same mechanism. With v_f accelerated by copolymerization, it offers a potential approach to increase fiber content and simultaneously improve the interfacial and mechanical properties in FRPC manufacturing.⁴ FROMP with di-NBE comonomers opens up new possibilities for more rapid, energy-efficient fabrication of thermosets and composite materials with tunable properties.

ASSOCIATED CONTENT

The Supporting Information is available free of charge on the ACS Publications website. General experimental details,

synthesis of norbornenyl monomers, front velocity measurement, and DSC characterization.

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Notes

The authors declare no competing financial interest.

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