

Fundamental Investigations into the Free-Radical Copolymerization of *N*-Phenylmaleimide and Norbornene

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ABSTRACT: A fundamental investigation into the copolymerization of *N*-phenylmaleimide and norbornene via conventional free-radical polymerization techniques was conducted. Reaction conditions were optimized for molecular weight and percent yield by tuning overall concentration and initiator loading. The copolymerization kinetics were monitored using *in-situ*, variable temperature nuclear magnetic resonance and first-order behavior was observed with respect to each monomer. Although the related copolymerization of norbornene and maleic anhydride was well-known to proceed in a perfectly alternating manner, the copolymerization of norbornene and *N*-phenylmaleimide was found to deviate from strictly alternat-

ing copolymerization behavior, producing significant amounts of sequentially enchainned *N*-phenylmaleimide units within the polymeric backbone. This deviation from perfectly alternating behavior was confirmed by analysis of individual monomer conversion rates and by measurement of monomer reactivity ratios using the Mayo–Lewis graphical analysis method. © 2015 Wiley Periodicals, Inc. *J. Polym. Sci., Part A: Polym. Chem.* **2015**, *00*, 000–000

KEYWORDS: copolymerization; free-radical; kinetics; Mayo–Lewis; norbornene; *N*-phenylmaleimide; reactivity ratio

INTRODUCTION In the late 1990s, perfectly alternating copolymers consisting of norbornene and maleic anhydride were extensively investigated as promising materials for 193 nm photolithography.^{1–5} Although these alternating copolymers possessed several desirable properties such as good thermal stability, high glass transition temperatures, optical transparency at the wavelength of interest, and the ability to form exceptional films for device fabrication,⁵ they ultimately reached their figurative limits while attempting to balance the inherent trade-off between etching resistance and overall lithographic performance.¹

Despite never reaching commercial use as 193 nm lithographic resists, such alternating copolymers continue to be of interest for a variety of applications today. Particularly, because of the remarkable film-forming properties and the highly rigid backbone of norbornene-*alt*-maleic anhydride copolymers, these unique polymeric materials piqued our interest as possible candidates for advanced gas separation membranes. Polymers with rigid backbones have been repeatedly shown to form membranes with remarkably high gas permeabilities.^{6–12} Likewise, the ability to modify either monomer to incorporate functionalities that favorably interact with gases such as CO₂ are extremely desirable as the efficient separation of CO₂ from non-harmful gases such as

N₂ is currently a grand-challenge within the field of gas-separations.¹³

In an effort to tailor the chemical structure of these sequence-controlled copolymers for membrane-based gas separation applications, and while avoiding sometimes problematic post-polymerization modifications of the anhydride functionalities, we hypothesized that replacing the maleic anhydride units with structurally related co-monomers, such as *N*-substituted maleimides, would be an ideal pathway toward the development of those materials. A wide variety of *N*-substituted maleimides are commercially available or are easily synthesized from readily available and cheap starting materials, thereby making them ideal monomeric targets. Furthermore, it has been shown that changes in maleimide's *N*-substituent (Fig. 1) can lead to significant changes in its resultant polymer's physical properties^{14–16} while the rigid cyclic nature of the maleimide, in similarity to maleic anhydride, generally increases thermal stability upon incorporation into the polymeric backbone.^{15,17}

Although the radical homopolymerization of *N*-substituted maleimides, as well as its copolymerization with electron-rich olefins such as styrene, *n*-butyl vinyl ether, 3-methylenecyclopentene, and isobutene monomers have been

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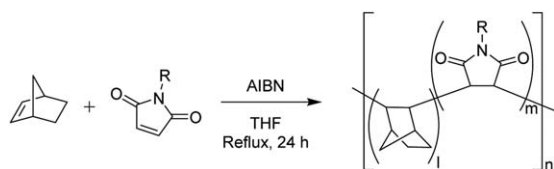


FIGURE 1 Free-radical copolymerization of norbornene and *N*-substituted maleimides.

investigated,^{15–23} no such systematic and fundamental investigations into the free-radical copolymerization behavior of norbornene and *N*-substituted maleimides has ever been reported to the best of the author's knowledge. Additionally, given that certain controlled radical copolymerizations of *N*-substituted maleimides and electron-rich olefins have been reported to proceed in a predominantly alternating manner, but not in a strictly alternating fashion,^{14,15,19,21} a fundamental study into the polymerization kinetics and relative reactivity ratios for this particular pair of monomers is needed to fully understand the structure of their resultant copolymers.

Herein, we report a fundamental investigation into the copolymerization behavior of *N*-substituted maleimide and norbornene using conventional free-radical polymerization techniques. Polymerization parameters such as concentration and initiator loading were systematically studied to ascertain their effects on polymer yield and molecular weight. Likewise, we will demonstrate that the free-radical copolymerization of norbornene and *N*-phenylmaleimide follows the aforementioned observation that changing the electron-deficient co-monomer from maleic anhydride to *N*-substituted maleimide leads to a structure that is predominantly alternating, but not perfectly alternating, and displays a significant propensity to incorporate sequential *N*-phenylmaleimide units into the copolymer chain. We will show that this deviation from perfectly alternating behavior is related to differences in the comonomers inherent reactivity ratios and individual rates of incorporation into the polymer. The reaction kinetics of these copolymerizations were followed using high temperature, *in-situ* ¹H nuclear magnetic resonance (NMR), which facilitated real-time monitoring of monomer consumption as the polymerizations progressed.

EXPERIMENTAL

Materials and Methods

Norbornene was purchased from Sigma Aldrich and sublimed *in-vacuo* at room temperature onto a cold finger at 0 °C prior to use. *N*-phenylmaleimide was purchased from TCI chemicals and recrystallized in cyclohexane prior to use. Azobisisobutyronitrile (AIBN) radical initiator was purchased from Sigma Aldrich and recrystallized prior to use by recrystallizing from a supersaturated solution in hot methanol to produce white needles that were stored at –35 °C. 1,3,5-Tri-methoxybenzene was purchased from Acros Organics and recrystallized three times in diethyl ether prior to use. Anhydrous THF-*d*₈ was purchased from Cambridge Isotopes Laboratories in ampoules and used as received. Polymerization

kinetics were monitored by *in-situ* high-temperature NMR on a Bruker 400 MHz NMR Spectrometer using a broad-band inverse probe set at 75 °C. Molecular weights were determined using an Agilent EcoSEC GPC and molecular weights are reported relative to polystyrene standards. Differential scanning calorimetric measurements were performed on a TA Instruments Q2000 using a standard heat/cool/heat cycle with a heating rate of 10 °C/min and a cooling rate of 5 °C/min.

General Procedure for Copolymerizations

In a typical polymerization, norbornene (2.720 g, 28.87 mmol), *N*-phenylmaleimide (5.000 g, 28.87 mmol), and AIBN (0.047 g, 0.287 mmol) were added to a Schlenk tube. The reaction vessel was purged with dry N₂ gas and 5.82 mL of dry/degassed THF was added via syringe. The Schlenk tube was then sealed and the polymerization was heated to 66 °C for 24 h. After 24 h, the mixture was cooled to room temperature, an additional 15 mL of THF was added and the polymer completely dissolved. The polymer is then precipitated into 200 mL of stirred methanol, filtered, and dried under vacuum at 75 °C.

General Procedure for the NMR-Scale Copolymerizations

In a J. Young NMR tube, norbornene (0.151 g, 1.593 mmol), *N*-phenylmaleimide (0.276 g, 1.593 mmol), and AIBN (0.052 g, 0.319 mmol) were added to 0.75 mL of anhydrous THF-*d*₈. Additionally, 1,3,5-trimethoxybenzene (0.054 g, 0.319 mmol) was added as an internal standard for determining NMR integration values. The reaction mixture was degassed (within the J. Young NMR tube) via the freeze, pump, thaw method (×3) and back-filled with dry N₂ gas. The polymerizations were run for 24 h at 75 °C and terminated by precipitation of the polymer into 20 mL of methanol. The polymer was filtered and dried under vacuum at 75 °C for 24 h.

RESULTS AND DISCUSSION

In an effort to develop a deeper understanding of the factors that influence the free-radical copolymerization of *N*-phenylmaleimide and norbornene, a systematic series of copolymerizations were conducted. There, the effects of monomer concentration and radical-initiator loading were both studied with respect to the molecular weights obtained and yield of the polymer produced (Fig. 2). To study the effects of thermal initiator loading, solution state polymerizations containing 60 wt % solids were polymerized using varying ratios of AIBN initiator in THF [Fig. 2(a,b)]. THF was chosen due to the limited solubility of *N*-phenylmaleimide in common organic solvents such as benzene, which have been previously used.²⁴ Those trials revealed that polymer yield increased rapidly as a function of AIBN loading, reaching approximately 60%–70% yield at an AIBN loading of 1–2 mol %, but then remained relatively constant at higher initiator concentrations. Initially, the inability to reach percent conversions greater than 70% was concerning; however, we can now attribute this behavior to the fact that *N*-phenylmaleimide is consumed more rapidly than norbornene due to inherent differences in reactivity ratios, thereby preventing

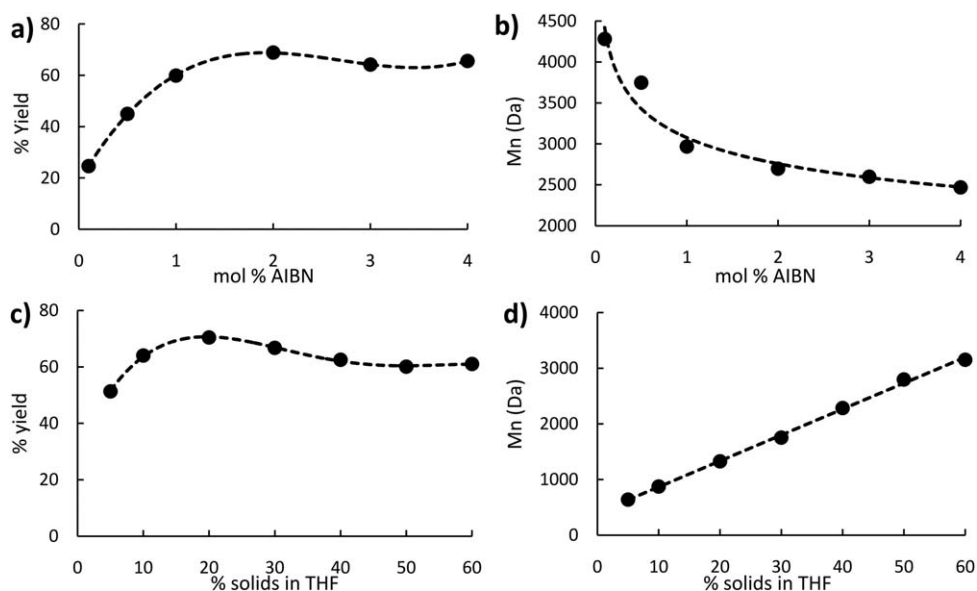


FIGURE 2 The effects of initiator loading as a function of (a) % yield and (b) molecular weight (60 wt % solids, 50/50 *N*-phenylmaleimide/norbornene, 66 °C, 24 h), and the effects of weight % solids as a function of (c) % yield and (d) molecular weight (3 mol % AIBN, 50/50 *N*-phenylmaleimide/norbornene, 66 °C, 24 h).

further polymerization. This result will be discussed in greater detail later within this report. In contrast to polymer yield, molecular weights of the resultant polymers were found to decrease logarithmically as AIBN loadings were increased yielding molecular weights as low as 2500 g/mol at 4 mol % AIBN [Fig. 2(b)] and as high as 4300 g/mol at 0.1 mol % AIBN.

To study the effect of concentration on polymerization behavior, a series of reactions in which initiator loading was held constant (3 mol % AIBN relative to monomer) were performed [Fig. 2(c,d)]. As the weight % solids in tetrahydrofuran (THF) was increased from 5 to 20 wt % a notable increase in isolated polymer yield was observed. However, as the solids content was further increased from 20 to 60 wt %, the yields remained relatively constant and never exceeded approximately 70%. In comparison, when monitoring molecular weight as a function of weight % solids in THF, a linear relationship was observed reaching a molecular weight (M_n) of approximately 3200 g/mol at 60 wt % solids, which was the limit of *N*-phenylmaleimide solubility.

In order to probe the mechanistic behavior of this copolymerization, *in-situ* high temperature NMR was used to monitor individual monomer concentrations during the course of the polymerization. In this work, copolymerizations were performed in sealed J. Young NMR tubes using THF- d_8 as solvent and 1,3,5-trimethoxybenzene as an inert internal standard (aryl C-H resonance at 6.05 ppm). Monomer consumption was measured by monitoring the disappearance of the baseline-resolved signals for the olefinic norbornene resonance at 5.94 ppm and the olefinic *N*-phenylmaleimide resonance at 6.73 ppm (Fig. 3). The data collected from these spectra was used to produce the plots shown in Figure 4. Careful analysis of Figure 4(a) clearly demonstrated that

N-phenylmaleimide was consumed at a greater rate than norbornene, and that all *N*-phenylmaleimide was consumed after eight hours, at which time norbornene consumption ceased (~70% consumed) and its concentration remained constant for all reaction times extending beyond this point. This observation was consistent with previous literature

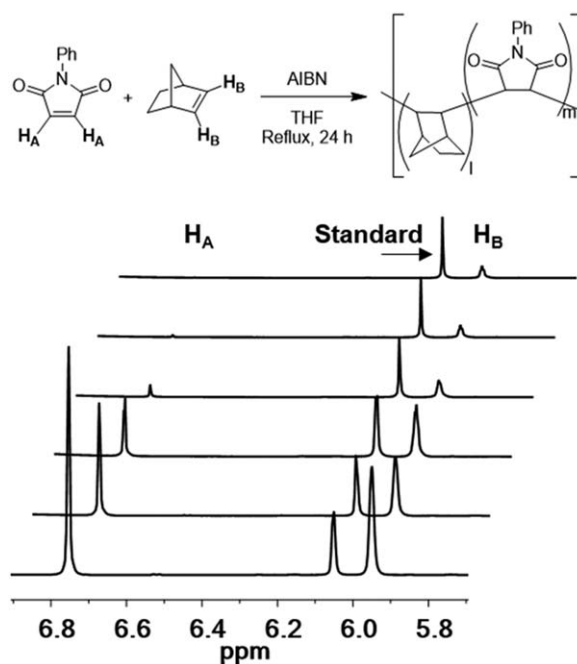


FIGURE 3 Stacked *in-situ* ^1H NMR spectra taken over the course of the polymerization at 75 °C in THF- d_8 . (Note: the vinylic protons of *N*-phenylmaleimide are at 6.76 ppm, the vinylic protons of norbornene are at 5.95 ppm, and the aromatic protons of the trimethoxybenzene internal standard are at 6.06 ppm).

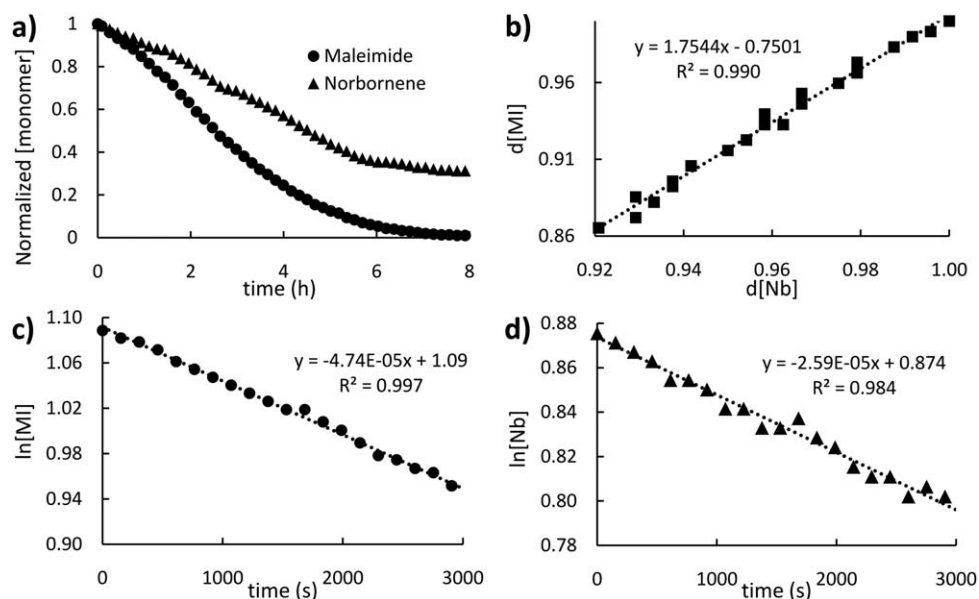


FIGURE 4 Plots of (a) normalized [monomer] versus time for a polymerization of *N*-phenylmaleimide (MI, circles) and norbornene (Nb, triangles), and (b) $d[MI]$ versus $d[Nb]$ for the copolymerization of 50/50 *N*-phenylmaleimide/norbornene, monitored via *in situ* 1H NMR up to 10% total monomer conversion. Also, first-order kinetic analysis of (c) *N*-phenylmaleimide and (d) norbornene as a function of time for the copolymerization of 50/50 *N*-phenylmaleimide/norbornene, monitored via *in situ* 1H NMR analysis up to 10% total monomer conversion.

reports in which norbornene is well known to be incapable of radically homopolymerizing in the absence of an electron-deficient comonomer.²⁵ Furthermore, this result is reinforced by Figure 4(b) in which the change in monomer concentration is plotted with respect to its comonomer, yielding a slope of 1.7544 ($d[MI]/d[Nb]$). For perfectly alternating copolymerizations, a slope equal to 1 should be observed. Deviation from that value of 1 strongly indicates that *N*-phenylmaleimide concentration is changing roughly 1.75 times faster than norbornene concentration for free-radical copolymerizations of *N*-phenylmaleimide and norbornene. This indicated that an inherent difference in reactivity ratios must be present between these two monomeric species, and suggested that a strictly alternating polymerization mechanism was not possible.

Further analysis revealed that first-order polymerization kinetics was observed with respect to each monomer, which was evidenced by the linear relationship between $\ln[\text{monomer}]$ versus time for both *N*-phenylmaleimide and norbornene [Fig. 4(c,d)]. Such analyses were performed at multiple monomer ratios (see Supporting Information) and were monitored up to 10% total monomer consumption. Figure 4 shows the results of a 50/50 copolymerization of *N*-phenylmaleimide/norbornene where the rate constant for *N*-phenylmaleimide incorporation was found to be $k = 4.74 \times 10^{-5}$ [Fig. 4(c)], and the rate constant for norbornene incorporation was $k = 2.59 \times 10^{-5}$ [Fig. 4(d)]. This difference in rate constants likewise suggests that *N*-phenylmaleimide is consumed at approximately 1.83 times faster than norbornene, which is in strong agreement with the relationship found in Figure 4(b) (~ 1.75 times faster).

Graphical Analysis Using the Mayo–Lewis Equation

Based on the observations described above, which demonstrate that copolymerizations of *N*-phenylmaleimide and norbornene are not perfectly alternating, we chose to investigate the differences in monomer reactivity ratios to better understand the mechanistic details of this polymerization and its resultant polymer structures. To do this, we utilized the well-known Mayo–

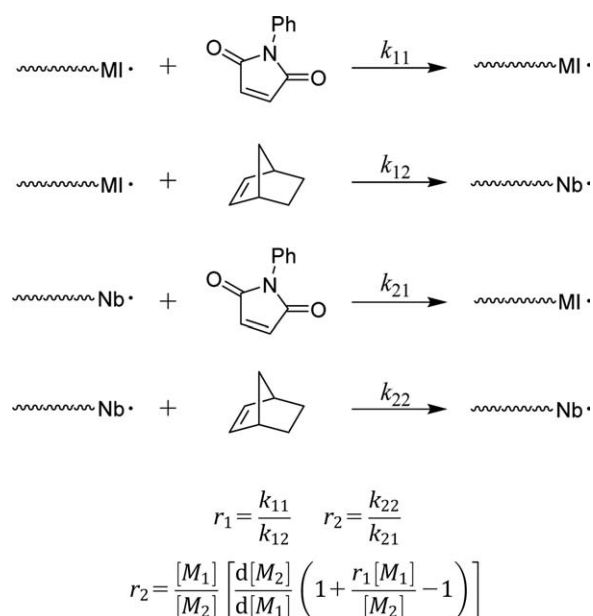


FIGURE 5 The terminal copolymer model, definitions of reactivity ratios ($r_1 = N$ -phenylmaleimide, $r_2 =$ norbornene), as well as a re-arranged Mayo–Lewis copolymer equation.

TABLE 1 Polymerization Data for the Polymers Produced During the Mayo–Lewis Experiments

Entry	[MI]/[Nb] ^a	M_n^b (g/mol)	M_w/M_n^b	d[MI]/d[Nb] ^c	k_{obs}^c	T_g^d (°C)
1	40/60	2,300	1.55	2.16	2.65	253
2	50/50	2,700	1.46	1.75	3.76	266
3	60/40	2,100	1.55	1.58	4.90	255

^a Initial monomer feed ratio.

^b Determined using gel permeation chromatography in THF at 40 °C relative to polystyrene standards.

^c Observed rate constant, determined using *in situ* ¹H NMR up to 10% total monomer conversion.

^d Determined using differential scanning calorimetry on the second heating cycle.

Lewis graphical analysis method for the free-radical copolymerization of norbornene and *N*-phenylmaleimide.²⁵ Although numerous methods for determining reactivity ratios may be employed, such as the Jaacks,^{26,27} Fineman–Ross,²⁸ and Tidwell–Mortimer^{29,30} methods, the Mayo–Lewis method was chosen due to monomer solubility limitations (Jaacks) and complications in obtaining accurate mole fractions of each monomer within the resultant polymers (Fineman–Ross, Tidwell–Mortimer), which are required for most other reactivity ratio calculations.^{14,31,32} Additionally, the Mayo–Lewis method has classically been used to determine reactivity ratios for perfectly alternating norbornene/maleic anhydride copolymerizations.³² The Mayo–Lewis graphical analysis presented herein follows the terminal copolymer model shown in Figure 5, and the reactivity ratios determined are defined as $r_1 = k_{11}/k_{12}$ (*N*-phenylmaleimide) and $r_2 = k_{22}/k_{21}$ (norbornene). The rearranged Mayo–Lewis equation, which was used for this graphical analysis is also described in Figure 5.

In order to perform this graphical analysis, three copolymerizations of *N*-phenylmaleimide and norbornene with different initial monomer feed ratios were monitored via *in-situ* NMR up to 10% total monomer conversion. The results of those polymerizations are shown in Table 1, in which molecular weights, molecular weight distributions (M_w/M_n), and glass transition temperatures (T_g) were recorded. As expected from the optimization studies conducted in Figure 2, the molecular weights of the resultant polymers were low ($M_n < 3000$ g/mol), however, they demonstrated high glass transition temperatures ($T_g > 250$ °C) in similarity to alternating norbornene/maleic anhydride copolymers. The values of d[MI]/d[Nb] were found to decrease as the *N*-phenylmaleimide/norbornene ratio was varied from 40/60 to 60/40 while the observed rate constants (k_{obs}) were found to increase. These trends intuitively make sense as small changes in *N*-phenylmaleimide concentration are minimized as its loading was increased, yet higher *N*-phenylmaleimide concentrations increased the rate of polymerization as a result of its ability to homopolymerize in addition to its propensity to propagate with norbornene. The graphical analysis was performed by assuming reactivity ratio values of -1 to $+1$ for *N*-phenylmaleimide (r_1) and calculating the reactivity ratio of norbornene (r_2) (see Supporting Information) using the rearranged Mayo–Lewis copolymerization equation (Fig. 5). Those reactivity ratio values are plotted in Figure 6, and a clear intersection point was observed. Via the Mayo–Lewis method, the

calculated intersection point is related to the reactivity ratios of each monomer. For perfectly alternating copolymerizations, a reactivity ratio of approximately 0 is predicted for each monomer, which originates from the definition of monomer reactivity ratios in the terminal model presented in Figure 5.³³ The average intersection point for the copolymerizations of *N*-phenylmaleimide and norbornene was found to be $r_1 = 0.17$ and $r_2 = -0.33$. Because these values are non-zero, we can safely conclude that the mechanism by which this polymerization proceeds is not strictly alternating, yet their small magnitude strongly supports that these copolymerizations do in fact have strong alternating tendencies. Although negative reactivity ratio values have been previously reported in the literature, a negative value for r_2 has no physical interpretation due to the reactivity ratio definitions highlighted in Figure 5, and therefore do not provide any additional mechanistic insight into this copolymerization.^{34–37}

Furthermore, though the removal of unreacted monomer impurities from the resultant polymers proved to be problematic, the resultant polymers' compositions were analyzed at various initial monomer ratios (Fig. 7). To do this, the

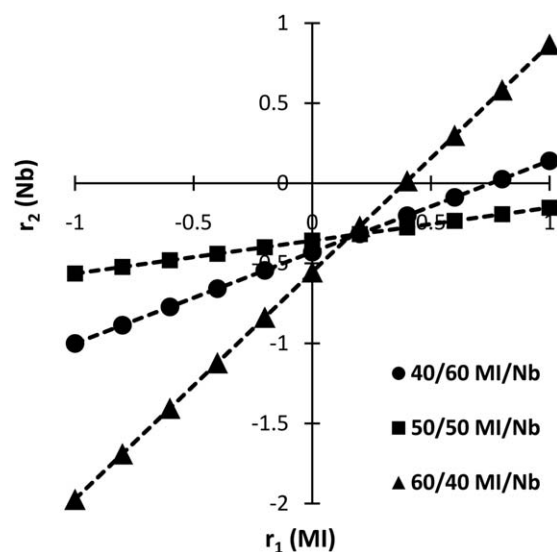


FIGURE 6 Mayo–Lewis graphical analysis for the free-radical copolymerization of *N*-phenylmaleimide (MI) and norbornene (Nb) at respective monomer loadings of 40/60 (circles), 50/50 (squares), and 60/40 *N*-phenylmaleimide/norbornene (triangles).

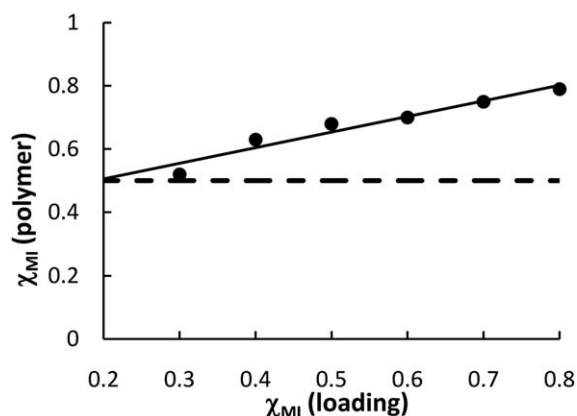


FIGURE 7 Graphical depiction of the mole fraction of *N*-phenylmaleimide units present in the polymer (at 10% total monomer conversion) versus initial *N*-phenylmaleimide loading for various monomer feed ratios (circles). χ_{MI} (polymer) was estimated using monomer conversion data obtained via ^1H NMR spectroscopy. Dashed line represents expected χ_{MI} for a strictly alternating copolymerization.

mole fraction of *N*-phenylmaleimide units within the resultant polymer [χ_{MI} (polymer)] was estimated using the monomer conversion data obtained via ^1H NMR spectroscopy. From Figure 7, a linear trend was observed in which deviation from perfectly alternating behavior [χ_{MI} (polymer) = 0.5] was witnessed as *N*-phenylmaleimide initial *N*-phenylmaleimide loading ratios [χ_{MI} (loading)] were increased. As previously noted, this behavior was attributed to *N*-phenylmaleimide's ability to radically homopolymerize, thereby allowing for increased frequency of subsequent *N*-phenylmaleimide units incorporated within the polymer backbone as a function of increasing *N*-phenylmaleimide concentration. For example, at initial monomer loadings of 80 mol % *N*-phenylmaleimide to 20 mol % norbornene, polymer compositions containing up to 79 mol % *N*-phenylmaleimide units were observed.

CONCLUSIONS

The free-radical copolymerization of *N*-phenylmaleimide and norbornene was optimized to maximize either percent yield or molecular weight. Polymers with molecular weights up to approximately 4300 g/mol were synthesized when using 0.1 mol % initiator and at a concentration of 60 wt % total solids dissolved in THF. Although these polymers are of low molecular weight, their rigid nature, high glass transition temperatures ($T_g > 250$ °C), and possibilities for functionalization make them attractive candidates for a number of potential applications. Mechanistic details of these copolymerizations were investigated using high-temperature, *in-situ* ^1H NMR analysis. Careful examination of the kinetic polymerization data and Mayo–Lewis graphical analysis conclusively showed that the copolymerization does not follow a strict alternating mechanism, but instead is a predominately alternating copolymerization that displays a strong tendency to

incorporate sequential maleimide units within the polymeric backbone. These results conclusively demonstrate that when utilizing free-radical copolymerizations of electron-rich cycloolefins with electron deficient comonomers, subtle changes in electronic character of the electron-deficient comonomer can lead to significant changes in copolymer structure.

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