Master's Thesis

Design of Gradient Copolymer Platform toward Advanced Optical Applications

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(Chemical Engineering)

Ulsan National Institute of Science and Technology

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Abstract

Research has been continuously conducted to achieve sequence-controlled polymers through various methods, with the goal of synthesizing perfect sequence-controlled materials such as DNA and proteins. In particular, gradient structures exhibit unique properties depending on the gradual changes in monomer composition in the polymer chain. By utilizing the differences in monomer reactivity ratios, copolymers with gradient structures can be synthesized. One example is cyclic olefin copolymers (COCs) synthesized using vinyl-addition polymerization. COCs can be polymerized using cyclic olefin monomers, with many cases involving norbornene (NB), which has a bicyclic structure. COCs synthesized through addition-type polymerization can maintain their bicyclic structure after polymerization. This results in key characteristics such as high transmittance, high thermal stability, and low birefringence. In this study, polymerization was carried out with NB-based monomers and methyl vinyl ketone (MVK) as the polar olefin monomer. Additionally, post-polymerization modification can be conducted in the ketone group in MVK within the polymers, allowing the polymers to be tailored for use in various fields and demonstrating their potential as upcyclable and recyclable materials.

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Chapter I.

Synthesis and Characterization of Polymer Platforms with Different Monomer Sequences via Polymerization Temperature

1.1. ABSTRACT

Norbornene (NB), butyl-norbornene (BuNB), and methyl vinyl ketone (MVK) were utilized for terpolymerization under palladium catalyst systems. By using the Fineman-Ross equation, the reactivity ratios of NB and MVK were determined, confirming the presence of gradient structures in the polymers. Interestingly, although we only changed the reaction temperature, the monomer sequence in the polymer chain was dramatically changed, resulting in polymers with gradient structures containing block-like segments. Through IG-mode ^{13}C NMR analyses, it was found that the two terpolymers were composed of up to approximately 37% MVK., and the films of the terpolymers exhibited high visible light transmittance of up to 93%. Through the comparison of thermal properties, it was found that the gradient polymers exhibited a broad range of glass transition temperatures, while the gradient-block polymers showed two peaks similar to block copolymers. In terms of mechanical properties, the gradient polymers demonstrated better stretchability even under the same force compared to the gradient-block polymers.

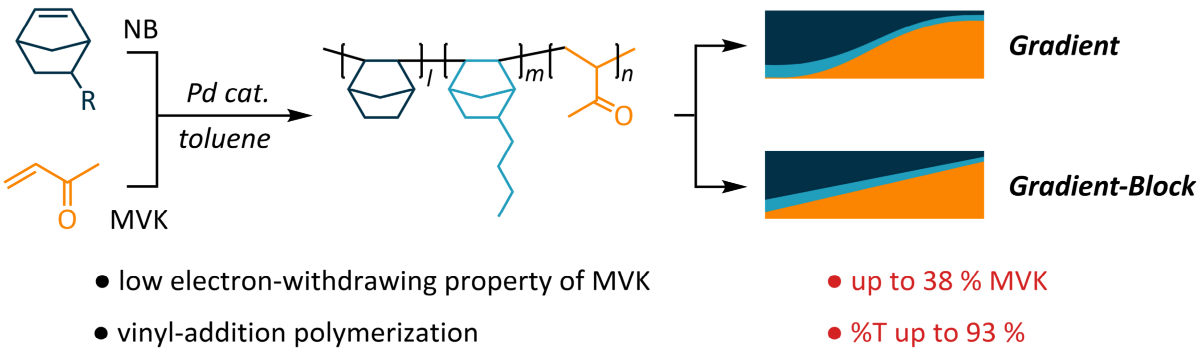

Figure 1.1. This work for the design of polymer platforms using monomer reactivity ratios.

1.2. INTRODUCTON

DNA, well known as the material containing unique genetic information in the natural world or within organisms, is determined by the sequence order of bases composing it. Furthermore, proteins exhibit distinct characteristics based on the varied combinations and arrangements of the 20 different amino acids. The properties of these biomolecules are governed by precise control over their sequences, playing a crucial role in the structure and function of biological molecules. These molecules synthesized within organisms are under perfect control of their sequences, which constitutes a fundamental factor in determining the characteristics of biomolecules within living organisms.

Based on the highly organized molecular precision observed in nature, various studies have been conducted for the synthesis of "sequence-controlled polymers”.[1-5] This has been largely facilitated by the advancement of living polymerization techniques, particularly the emergence of controlled radical polymerization methods. Specifically, techniques such as Nitroxide-Mediated Polymerization (NMP),[6-7] Atom Transfer Radical Polymerization (ATRP),[8-9] and Reversible Addition-Fragmentation Chain Transfer (RAFT)[10-11] provide excellent platforms for the synthesis of sequence-controlled polymers. Successful synthesis of polymers with specific monomer sequences, such as alternating copolymers,[12-13] block copolymers,[14-15] and gradient copolymers,[16] has become possible through these methods. Furthermore, the diversification of polymer synthesis methods has significantly advanced the precision and control capabilities of polymer synthesis through enhanced synthetic approaches pioneered by researchers such as Kamigaito[17-18] and Sawamoto.[19-20]

Among various polymer structures, gradient copolymers are polymers where the composition gradually changes from one end to the other end. Due to this unique fine structure, gradient copolymers possess distinct properties compared to statistical copolymers, alternating copolymers, and block copolymers.[21-24] These properties make gradient copolymers advantageous for applications such as emulsions, cosmetic additives, compatibilizers in polymer blends, dispersants in nanocomposite materials, and effective stabilizers in sound damping materials.

Materials for optical applications such as displays, lenses, and optical fibers require various properties including high transparency, low birefringence, excellent heat and chemical resistance, and low density. Meeting these requirements, specific cyclic olefin copolymers (COCs) and cyclic olefin polymers (COPs) synthesized from norbornene-based monomers have attracted attention in the field of optics.[25-27] The three main processes for commercially synthesizing COPs or COCs are as follows: (1) ring-opening metathesis polymerization (ROMP) of cyclic olefins and subsequent hydrogenation,

(2) vinyl-addition polymerization of α-olefins with cyclic olefins, and (3) cationic polymerization of cyclic olefins.

In particular, COCs synthesized through vinyl addition polymerization maintain bicyclic structures even after polymerization, exhibiting excellent transparency due to high amorphousness. Additionally, it is possible to copolymerize with various alpha-olefins and control the monomer sequence to synthesize polymers with diverse structures, depending on the reactivity ratio between monomers. Currently, the most widely used type of COCs is a copolymer of norbornene and ethylene, employed as an engineering thermoplastic material.[28-29] Despite numerous studies on COCs, including copolymerization with NB/higher alpha-olefins,[30-31] COCs with non-polar characteristics still faces limitations. Consequently, research has been conducted to introduce polar functional groups into the COCs backbone to enhance polymer performance in terms of adhesion, dye retention, and compatibility.[32-36] However, in many cases, polar functionaal groups were either attached to norbornene or were significantly distant from the polymer backbone even if present in alpha-olefins. It has been revealed that there should be sufficient distance between the polymer backbone and polar groups, as proximity may hinder synthesis due to interactions between the polar functional groups and the polymer backbone.

In this study, while avoiding the use of gas-phase polymerization and aiming to design alpha-olefin monomers with polar groups closer to the backbone, we decided to utilize methyl vinyl ketone. Compared to other polar groups like ester or carboxylic groups, the ketone group has weaker electron-withdrawing properties. Thus, it was determined that there would be sufficient electron density in the polymer backbone during the polymerization process, enabling successful polymerization. Additionally, the ketone group in methyl vinyl ketone can be functionalized through various post-polymerization processes such as hydrosilylation, oxime formation, imine formation, and hydrazone formation, providing flexibility in the synthesis of multifunctional polymers.

This paper focuses on the copolymerization reaction of norbornene-based monomers with methyl vinyl ketone, investigating the influence of polymerization temperature on the monomer sequences within the polymer. Structural differences in the polymer were observed depending on the polymerization temperature, and the impact of these differences on the physicochemical properties of the polymer was analyzed.

1.3. EXPERIMENTAL SECTION

Materials

bicyclo[2.2.1]hept-2-ene (Sigma-Aldrich; purity ≥99%, NB), 3-buten-2-one (Sigma-Aldrich; purity ≥90%, MVK), butyl-norbornene (NH chemicals; purity ≥95%, BuNB), palladium(II) acetate (Sigma-Aldrich; purity ≥98%), tricyclohexylphosphine (Sigma-Aldrich; purity ≥95%, PCy_3), dioctadecynilinum tetrakis(pentaflorophenyl)borate (SPCI; purity ≥50%, borate)

Synthesis of Poly(NB-co-MVK) having gradient structure. (NB/MVK_G)

At room temperature, palladium acetate (1.0 mM), tricyclohexylphosphine (2.0 mM), and dioctadecynilinum tetrakis(pentaflorophenyl)borate (2.0 mM) were added to a 50 mL round-bottom flask. The flask was purged with argon, and then 5 mL of purified toluene was added and stirred for 1 hour. Simultaneously, another 50 mL round-bottom flask was purged with argon, and norbornene (1000 mM) was added along with 5 mL of purified toluene and stirred for 30 minutes. Subsequently, methyl vinyl ketone (1000 mM) was injected into the flask containing norbornene, and the solution from the flask containing the catalyst was slowly added. The reaction was carried out at 60 °C for 14 days. The reaction was terminated by adding a small amount of hydrochloric acid/methanol (v/v = 1/9) solution to the reaction mixture, and the reactant was slowly added to excess methanol to precipitate it. The precipitate was vacuum-dried at 70 °C for 12 hours to obtain a white powder of NB/MVK_G (Yield = 78%).

Synthesis of Poly(NB-co-MVK) having gradient-block like structure. (NB/MVK_GB)

The synthesis procedure for NB/MVK_GB was conducted following the same steps as before, except for altering the polymerization conditions to 80 °C for a duration of 4 days. (Yield = 73.5%)

Synthesis of Poly(NB/BuNB/MVK) having gradient structure. (NBM5_G)

At room temperature, palladium acetate (1.0 mM), tricyclohexylphosphine (2.0 mM), and dioctadecynilinum tetrakis(pentaflorophenyl)borate (2.0 mM) were added to a 50 mL round-bottom flask. The flask was purged with argon, and then 5 mL of purified toluene was added and stirred for 1 hour. Simultaneously, another 50 mL round-bottom flask was purged with argon, and norbornene

(750 mM) was added along with 5 mL of purified toluene and stirred for 30 minutes. Subsequently, butyl-norbornene (250mM) and methyl vinyl ketone (1000 mM) were injected into the flask containing norbornene, and the solution from the flask containing the catalyst was slowly added. The reaction was carried out at 60 °C for 14 days. The reaction was terminated by adding a small amount of hydrochloric acid/methanol (v/v = 1/9) solution to the reaction mixture, and the reactant was slowly added to excess methanol to precipitate it. The precipitate was vacuum-dried at 70 °C for 12 hours to obtain a white powder of NBM5_G (Yield = 74.8%).

Synthesis of Poly(NB/BuNB/MVK) having gradient-block like structure. (NBM5_GB)

The synthesis procedure for NBM5_GB was conducted following the same steps as before, except for altering the polymerization conditions to 80 °C for a duration of 4 days. (Yield = 72.2%)

Measurements.

GPC was conducted to analyze the M_w and M_w/M_n of polymers with chloroform ($CHCl_3$) as the eluent at 40 °C and the flow rate was maintained at 1.0 mL/min. For chloroform-GPC, three polystyrene columns from Agilent [two LF-804 (from Shodex); 6 µm pore size; 8 mm i.d. × 300 mm, one KF-802.5 (from Shodex); 6 µm pore size; 8 mm i.d. × 300 mm] were connected to a 1260 ISO pump, a 1260 vialsampler, a multicolumn thermostat (MCT), and a 1260 refractive index (RI) detector. To obtain the information about molecular weight of obtained polymers, 10 standard polystyrene (PS) samples were used to calibrate the columns (Agilent Technologies; M_p = 1,230–1,740,000; M_w/M_n = 1.02–1.08). ^{1}H NMR spectra were acquired using a 300 MHz Bruker Ultrashield spectrometer, while IG-mode ^{13}C NMR spectra were analyzed using a 600 MHz Bruker Ultrashield spectrometer. All spectra were recorded in ppm units using $CDCl_3$ as the solvent at room temperature. Fourier-transform infrared (FT-IR) spectra were recorded using a Thermo Scientific NOCOLET 6700 FT-IR spectrometer equipped with an attenuated total reflection (ATR) module. Thermal gravimetric analysis (TGA) was performed using a Q500 calorimeter (TA Instruments) under a dry nitrogen flow from 35 °C to 800 °C at a heating rate of 10 °C/min. The glass transition temperatures were observed using a Q2000 calorimeter (TA Instruments) under a dry nitrogen flow at a heating or cooling rate of 20 °C min^{-1} by differential scanning calorimetry (DSC). For tensile testing, the polymers were completely dissolved in toluene at a concentration of 20 wt.%, poured into dog-bone-shaped molds, and allowed to solidify. The obtained dog-bone-shaped films were elongated at a rate of 10 mm/min at 25 °C using a universal testing machine (UTM) for tensile testing. All tensile tests were conducted three times.

Transmittance test.

For sample preparation, the polymers were completely dissolved in toluene at a concentration of 10 wt.%. Subsequently, the solution was filtered through a 0.45 μm syringe filter to obtain a clean solution, and then poured into a 5×5 cm glass petri dish. The film was cast by gradually raising the temperature while ensuring sufficient solvent was present for 6 hours. The remaining solvent was removed by placing the petri dish in a 70 °C vacuum oven overnight. The resulting polymer films were then used to measure the transmittance in the visible light range (300 nm to 700 nm) using a UV-visible spectrometer (JASCO V-700).

1.4. RESULTS and DISCUSSIONS

Synthesis of poly(NB-*co*-MVK) to calculate the monomer reactivity ratios

Prior to synthesizing the terpolymer, copolymerization with NB and MVK was conducted as model reaction to analyze the monomer sequence within the polymer. The polymerization reaction was carried out at 60 °C for 30 minutes using the $[Pd(OAc)_2]/[PCy_3]/[borate]$ catalyst system (**Figure 1.2**). The reactivity ratios of NB and MVK were estimated from various supplied monomer compositions (**Table 1.1**). To utilize the Fineman-Ross equation, the yield of the polymer needed to be maintained at less than 10%.[37] Consequently, the reactivity ratios of NB and MVK were calculated as $r_{NB} = 14.41$ and $r_{MVK} = 0.318$, respectively (**Figure 1.3**). These values, with $r_1 > 1 > r_2$, were consistent with those typically observed in gradient copolymers, ultimately providing support for the presence of a gradient structure in NB/MVK. Subsequent polymerization experiments were conducted using NB and MVK.

Using the previously employed $[Pd(OAc)_2]/[PCy_3]/[borate]$ system, NB/MVK copolymer was synthesized. With a 1000:1000 molar ratio of NB/MVK in toluene and a reaction temperature of 60 °C, both monomers exhibited over 80% conversion after 14 days (**Figure 1.4 a**). In the graph showing the conversion rate of monomers over time, it was observed that the consumption of NB occurred first, followed by an increase in the consumption of MVK as time progressed. Furthermore, when plotting with the normalized chain length set to 1, an ideal linear gradient structure showing a gradual transition in composition from NB to MVK was illustrated.

Subsequently, to reduce the polymerization time, the experiment was conducted at 80 °C under the same polymerization conditions. After 4 days, both monomers exhibited over 80% conversion (**Figure 1.4 b**). Interestingly, although we only change the reaction temperature, monomer sequence in polymer chain was dramatically changed. In the graph showing the conversion rate of monomers over time, NB was consumed too quickly at the beginning, resulting in a pattern where almost only MVK remained towards the end. When the conversion rate was plotted based on the normalized chain length, a gradient structure was observed, but it appeared as if there were block segments of each monomer on either side. Therefore, the copolymer synthesized at 60 °C, possessing a complete gradient structure, was named NB/MVK_G, whereas the copolymer synthesized at 80 °C, possessing a gradient-block like structure, was named NB/MVK_GB.

FT-IR analysis revealed carbonyl peaks at 1750 cm^{-1} in both NB/MVK_G and NB/MVK_GB, indicating the sufficient presence of MVK within the polymer (**Figure 1.5**).

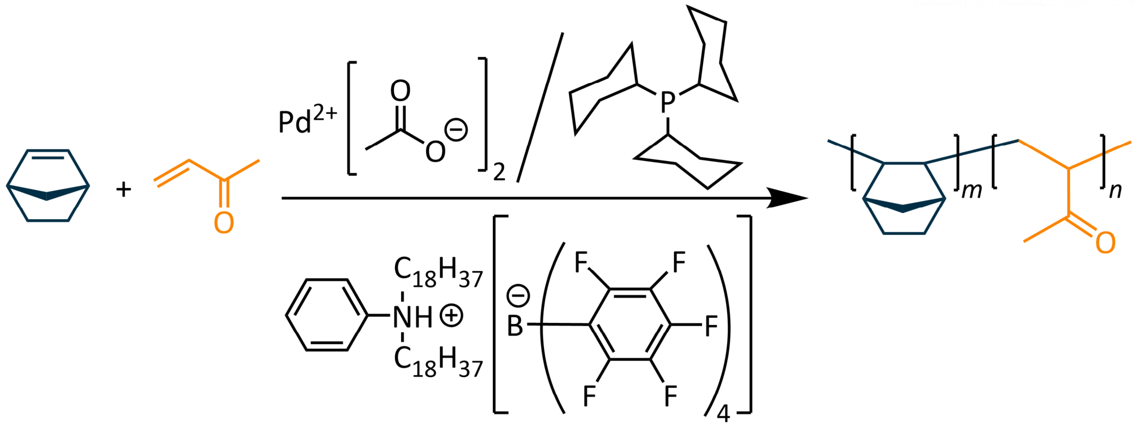

Figure 1.2. Scheme of the copolymerization NB and MVK under the palladium catalyst system.

Table 1.1. Results of NB/MVK copolymerization using $[Pd(OAc)_2]/[PCy_3]/[borate]$ with different monomer ratios in the feed.

Entry	NB (mM)	MVK (mM)	Ratio	Yield[b] (%)	Cont.$_{NB}$[c]
1	1000	500	1/0.5	10.28	97.2
2	1000	1000	1/1.0	4.66	96.3
3	1000	1500	1/1.5	4.85	95.1
4	1000	2000	1/2.0	6.56	94.5

[a] Conditions: $[Pd\ Cat.]_0 : [PCy_3]_0 : [borate]_0 = 1\ mM : 2\ mM : 1\ mM$ in toluene at 60 ˚C for 30 min.

[b] Calculated based on the weight of the obtained copolymer.

[c] Contents of NB (in mol%) calculated from the 13C NMR spectra of the copolymer.

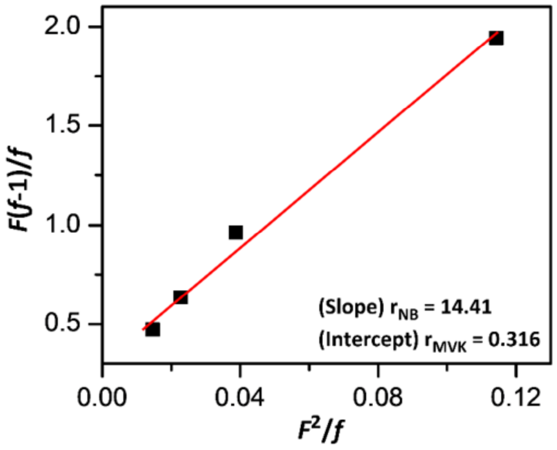

Figure 1.3. Fineman-Ross plots for NB/MVK copolymerization.

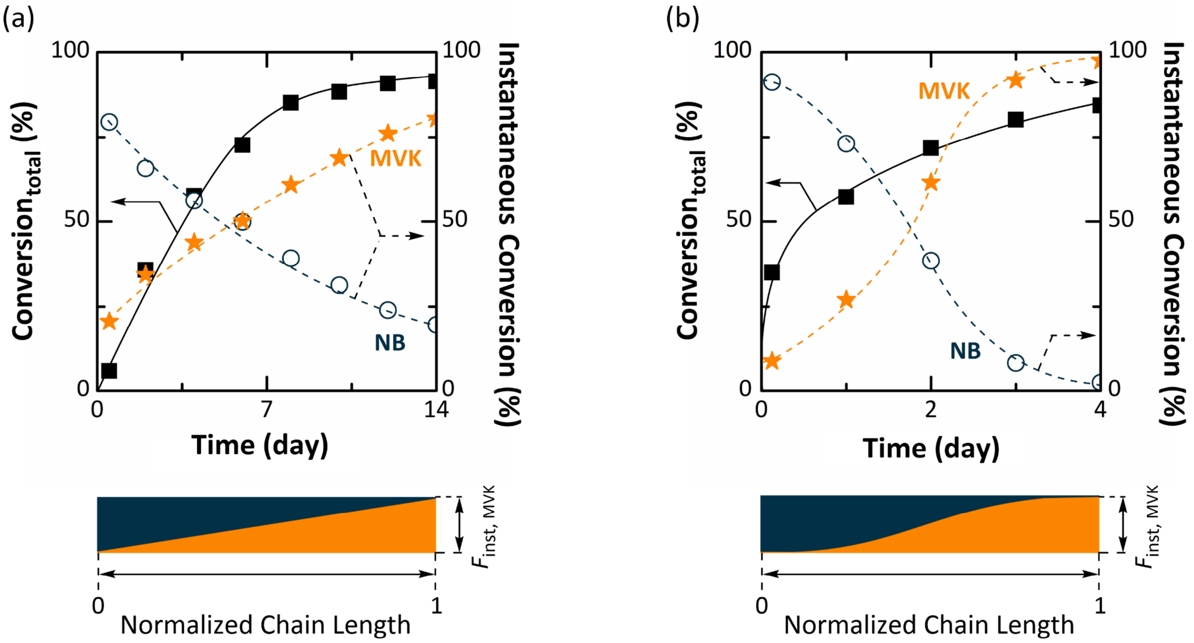

Figure 1.4. Copolymerization of NB and MVK (top) having (a) gradient structure, (b) gradient-block-like structure. Monomer compositions via $F_{\text{inst, MVK}}$ in normalized polymer chain (bottom): $[NB]_0$ = 1000 mM; $[MVK]_0$ = 1000 mM in toluene at (a) 60 °C for 14 days, (b) 80 °C for 4 days.

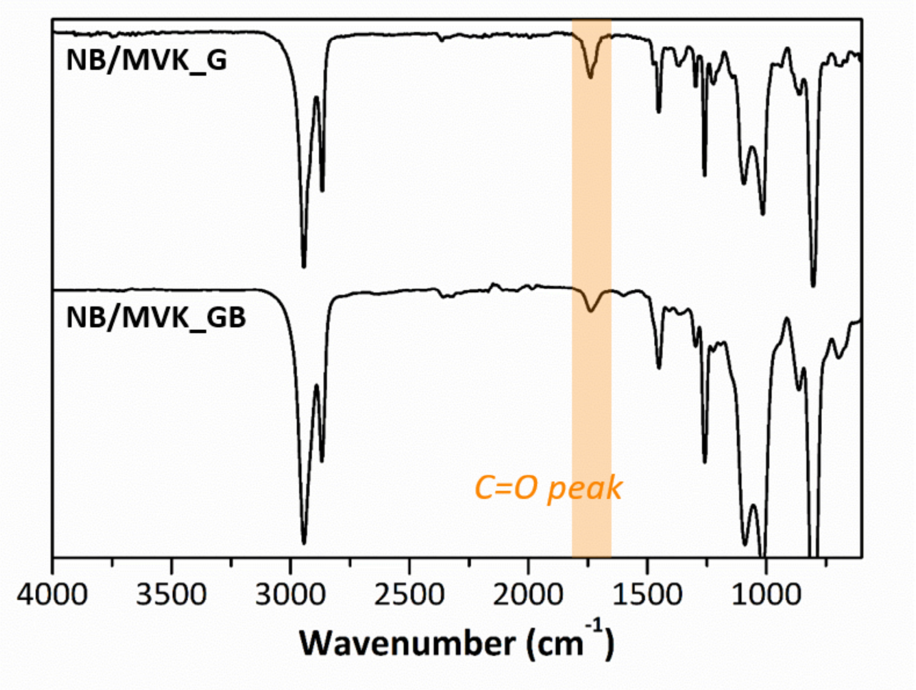

Figure 1.5. FT-IR spectra of copolymers polymerized at (top) 60 °C; NB/MVK_G, and (bottom) 80 °C; NB/MVK_GB.

Synthesis of poly(NB/BuNB/MVK) having gradient and gradient-block like structure.

In this study, polymerization reactions were performed using butyl-norbornene (BuNB) introduced to enhance the solubility of NB, MVK, and the polymer. Various feed ratios of the monomers were attempted (**Table 1.2**), and it was observed that when the ratio of MVK relative to NB and BuNB was relatively low, the presence of MVK within the polymer was hardly detected. When keeping MVK constant at 1000 mM and supplying NB/BuNB/MVK at a ratio of 750/250/1000 mM, the highest yield was observed. At this ratio, the polymer synthesized exhibited the largest carbonyl peak at 1750 cm^{-1} in FT-IR analysis, confirming sufficient incorporation of MVK within the polymer (**Figure 1.6**). Thus, this ratio was deemed the most ideal, and based on this, further experiments were conducted with the NBM5 polymer.

Referring to the model reaction from the previous experiment, polymerizations were performed for the same NBM5 polymer at 60 °C for 14 days and at 80 °C for 4 days to manufacture polymers under two conditions. When the polymerization was conducted at 60 °C, it was observed that initially, consumption of NB-based monomers predominated, followed by gradual consumption of MVK over time, eventually forming a ideal gradient structure (NBM5_G) (**Figure 1.7 a**). Conversely, when polymerization was performed at 80 °C, excessive consumption of NB-based monomers occurred initially, resulting in the formation of a gradient-block structure with MVK predominantly present at the chain ends (NBM5_GB) (**Figure 1.7 b**). FT-IR analysis confirmed the presence of carbonyl peaks at 1750 cm^{-1} in both polymers, indicating sufficient incorporation of MVK within the polymers (**Figure 1.8 a**). Through GPC analyses, it was found that two terpolymers exhibited similar molecular weights, approximately around 80,000 (**Figure 1.8 b**).

IG-mode ^{13}C NMR analyses were used to determine the contents of MVK in the terpolymers. The incorporations of MVK could be obtained through the integral values of the C=O peak observed around 210 ppm and the aliphatic parts. The analyses revealed that NBM5_G contained approximately 38% MVK and NBM5_GB contained approximately 34% MVK (**Figure 1.9 and 1.10**). Therefore, it appears that the proportion of polar monomers in the terpolymer was sufficient, which raises the expectation that large changes will be observed when the polymer properties are modified later through post-polymerization modification.

Table 1.2. Results of terpolymerization NB/BuNB/MVK at 60 °C for 14 days.

Polymer[a] code	**$[NB]_0$ (mM)**	**$[BuNB]_0$ (mM)**	**$[MVK]_0$ (mM)**	**Yield (%)**	**M_w[c] (kg/mol)**	**M_w/M_n[c]**	**$T_{d,3}$[d] (°C)**	**T_g[e] (°C)**
NBM1_G	0	1000	500	21.2	43	2.02	289	226
NBM2_G	0	1000	1000	31.1	54	1.90	300	234
NBM3_G	500	500	500	26.3	49	2.02	308	229
NBM4_G	500	500	1000	34.5	65	1.65	368	236
NBM5_G	750	250	1000	74.8	78	1.51	393	255

[a] Conditions: $[\text{Pd Cat.}]_0$:$[\text{borate}]_0$:$[\text{PCy}_3]_0$ = 1 mM : 1 mM : 2 mM in toluene at 60 ˚C for 14 days.

[b] Calculated based on the weight of the obtained copolymer.

[c] Measured by GPC calibrated with PS standard in chloroform (45 ˚C, flow rate 1.0 mL/min).

[d] $T_{d,3}$ (temperature at which 3% weight loss occurs) was determined by TGA at a rate of 10 °C/min.

[e] Glass transition temperature (T_g) was determined by DSC at a rate of 20 °C/ min.

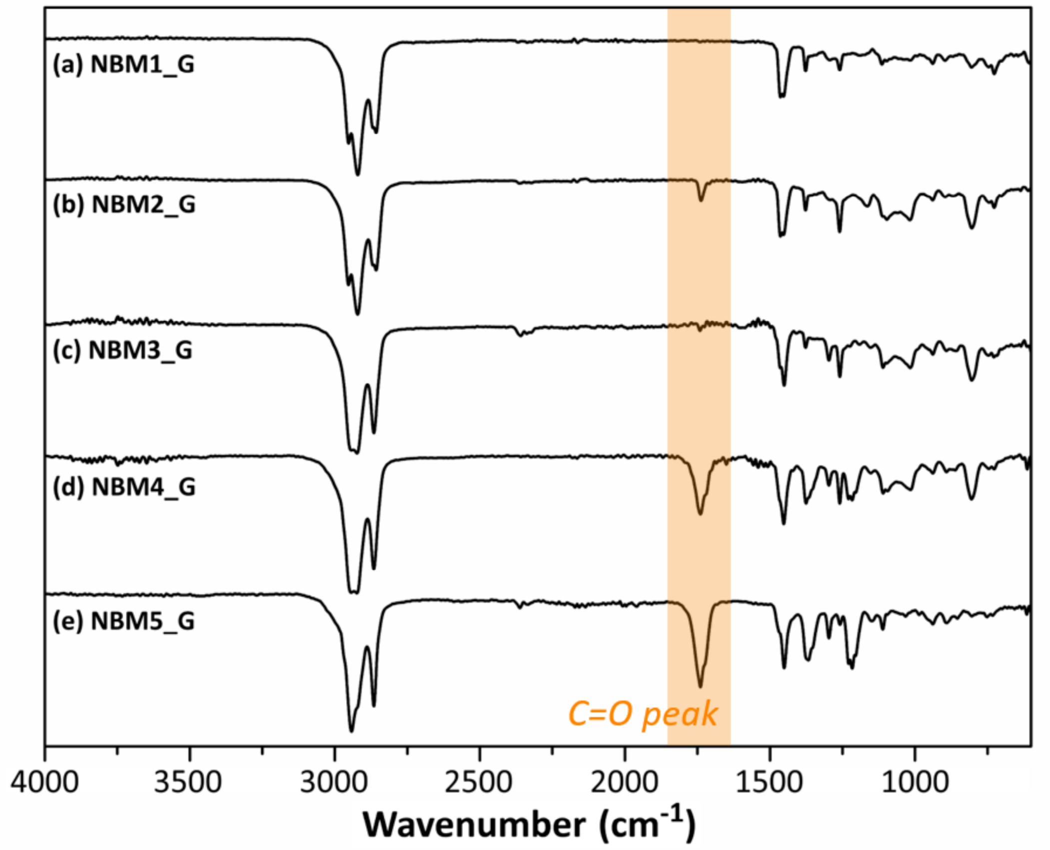

Figure 1.6. FT-IR spectra of polymers synthesized at 60 ℃ for 14 days (a) NBM1_G, (b) NBM2_G, (c) NBM3_G, (d) NBM4_G, (e) NBM5_G.

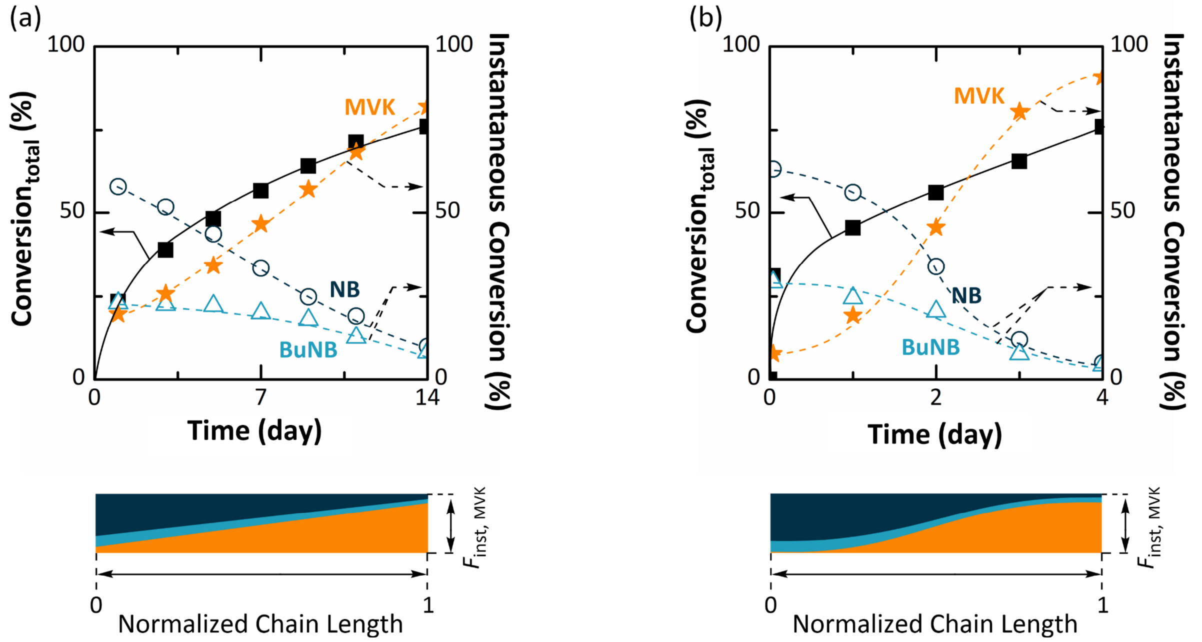

Figure 1.7. Terpolymerization of NB, BuNB and MVK (top) (a) having gradient structure, (b) having gradient-block-like structure. Monomer compositions were expressed via $F_{\text{inst, MVK}}$ in normalized polymer chain length (bottom): [NB]$_0$ = 750 mM; [BuNB]$_0$ = 250 mM; [MVK]$_0$ = 1000 mM in toluene at (a) 60 °C for 14 days, (b) 80 °C for 4 days.

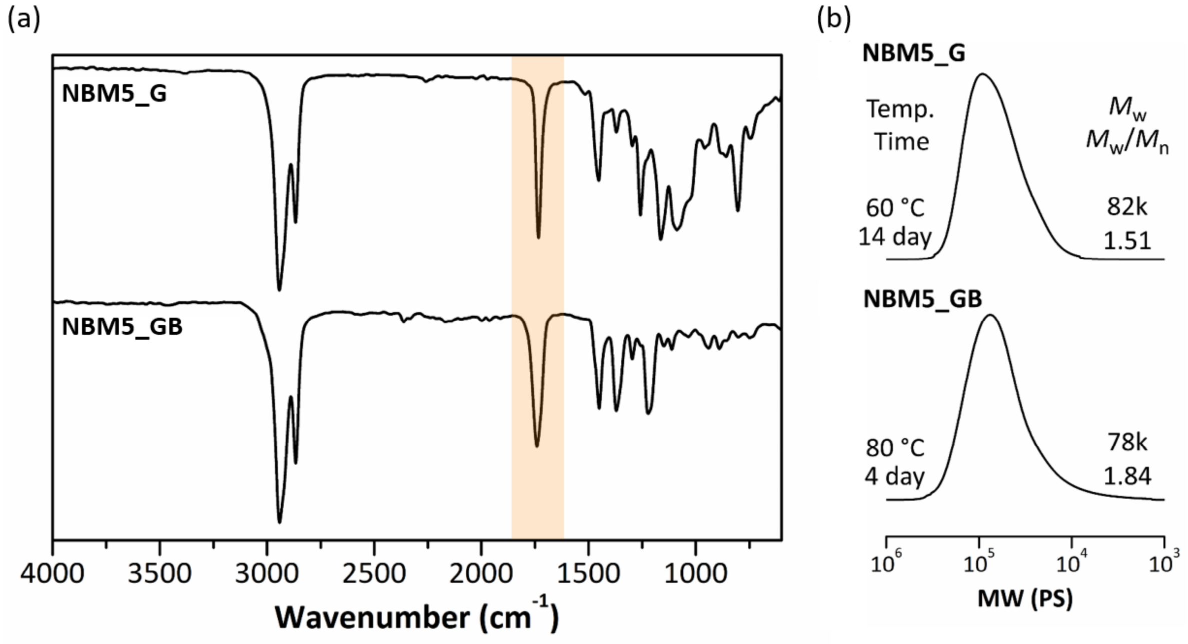

Figure 1.8. (a) FT-IR spectra of NBM5_G and NBM5_GB. (b) GPC graphs of NBM5_G and NBM5_GB.

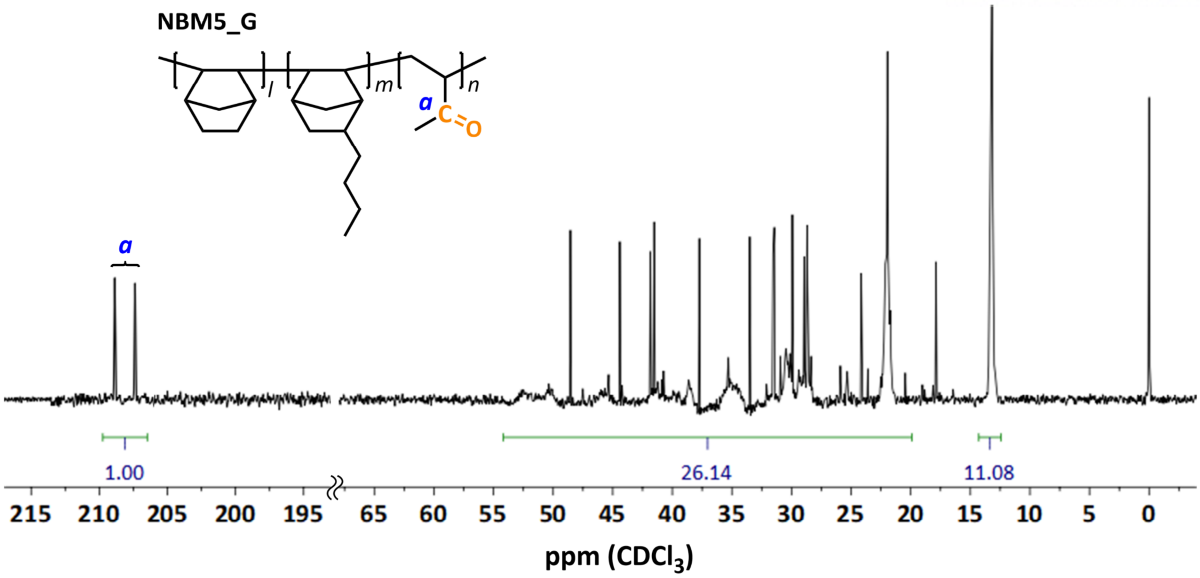

Figure 1.9. IG-mode ^{13}C NMR spectra of NBM5_G.

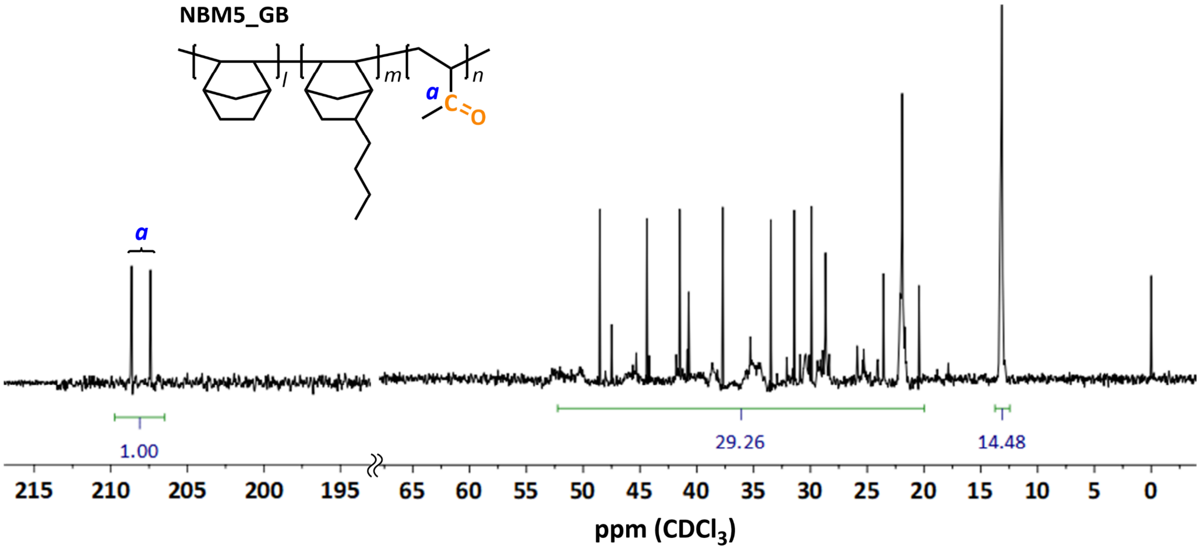

Figure 1.10. IG-mode ^{13}C NMR spectra of NBM5_GB.

*** Calculation of MVK incorporation in NBM5_G and NBM5_GB**

The incorporation (mol%) of MVK in the terpolymer

$$\text{Incorporation of MVK (\%)} = \frac{I_{\text{MVK}}}{I_{\text{MVK}} + \dfrac{I_{\text{aliphatic}} - I_{\text{MVK}} \times 3}{21}} \times 100\% = \frac{21\, I_{\text{MVK}}}{I_{\text{aliphatic}} + 18\, I_{\text{MVK}}} \times 100\%$$

I_{MVK} - Integration of MVK (C=O) in terpolymer

I_{MVK} - Integration of aliphatic-C in terpolymer

Comparison of thermal and mechanical properties based on polymer structures.

In general, gradient polymers exhibit a wide range of phase transitions within the glass transition temperature (T_g) range typical for homopolymers of the monomers.[38] In this study, NBM5_G, which ideally possesses a gradient structure, showed a very wide glass transition temperature range ($\triangle T_g$) of approximately 33.4 °C (**Figure 1.11 b and 1.11 c**). On the other hand, the gradient-block structure polymer exhibited two glass transition temperatures, similar to those observed in block copolymers: one in a relatively narrow range of about 9.6 °C and the other in a slightly broader range of about 13.6 °C (**Figure 1.11 e and 1.11 f**). These results indicated that the coexistence of gradient and block segments within the NBM5_GB polymer, resulting in unique glass transition behaviors.

Tensile tests were conducted using a Universal Testing Machine (UTM) to investigate the correlation between monomer sequence and mechanical properties. The tensile strength of NBM5_G and NBM5_GB polymers showed almost identical values. But, interestingly, the elongation at break of NBM5_G was approximately 1.5 times higher than that of NBM5_GB (**Figure 1.12 a**). Generally, block structures typically exhibit very distinct interfaces, resulting in significant modulus changes, while polymers with gradient structures effectively alleviate stress concentration due to the gradual change in local modulus. Therefore, NBM5_G, which possesses an ideal gradient structure, experiences less stress concentration compared to NBM5_GB, which contains block segments.[39] However, the Young's modulus of NBM5_G was lower than that of NBM5_GB (**Figure 1.12 b**). When tension applied in the block copolymers, causing them to separate the domain and break more easily. But, in gradient copolymers, the domains are dispersed a lot, so when stretched, they align parallel and extend instead of simply separating. Consequently, the blocky structure stretches less compared to the gradient one under the same force, leading to relatively lower Young's modulus values for NBM5_G, which possessed a complete gradient structure.

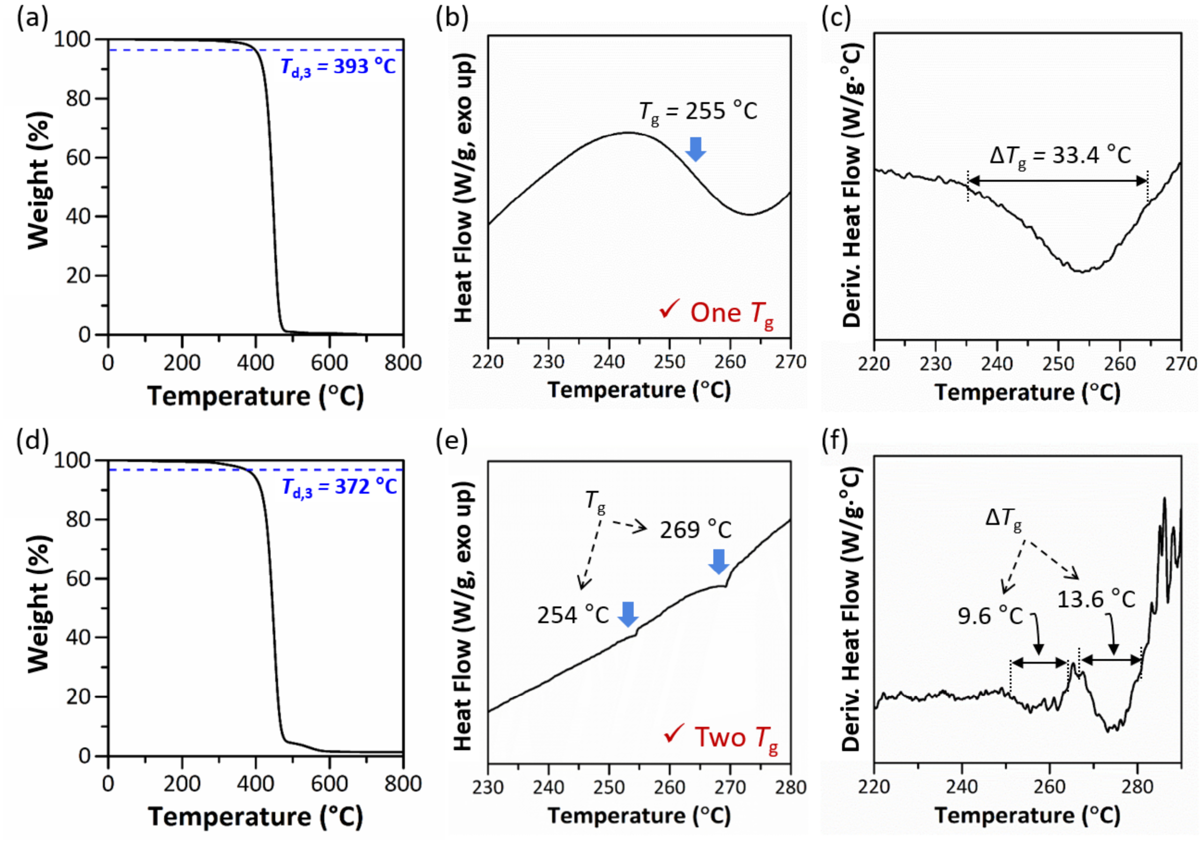

Figure 1.11. (a) TGA, (b) DSC, (c) differentiated DSC curves of NBM5_G. (d) TGA, (e) DSC, (f) differentiated DSC curves of NBM5_GB. DSC thermograms were obtained at 2nd heating process at 20 °C/min.

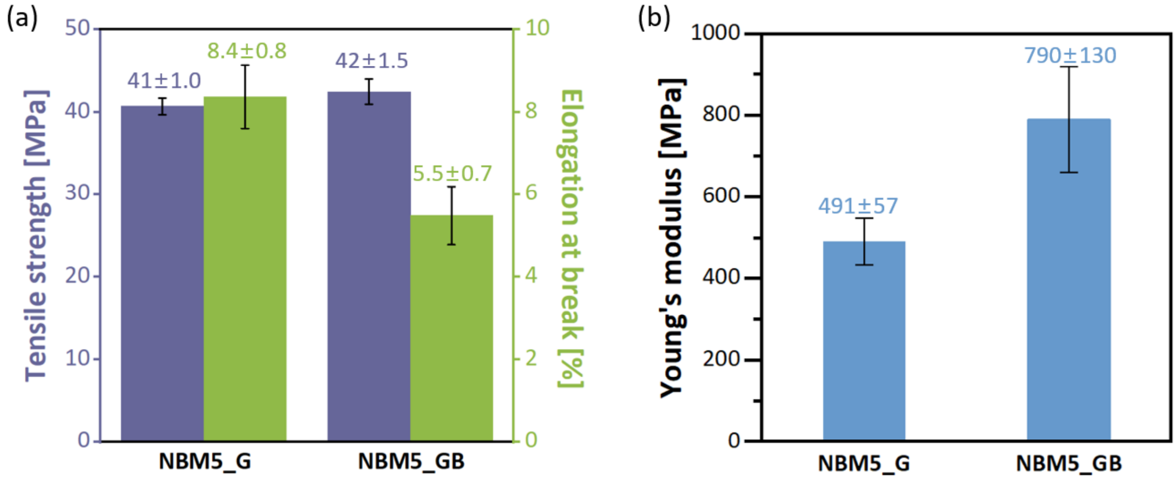

Figure 1.12. (a) Tensile strength and elongation at break of NBM5_G and NBM5_GB films. (b) Young's modulus of NBM5_G and NBM5_GB.

Optical properties of terpolymers

Finally, in this study, thin films with a thickness of approximately 30 µm were produced using the two polymers, and their optical properties were evaluated. Both produced films exhibited high transparency with over 88% in the visible light range of 300-700 nm (**Figure 1.13**). Notably, the gradient film displayed about 3% higher transmittance than the gradient-block film. This gap likely came from the superior structural integrity of the gradient structure, reducing interference from phase separation.

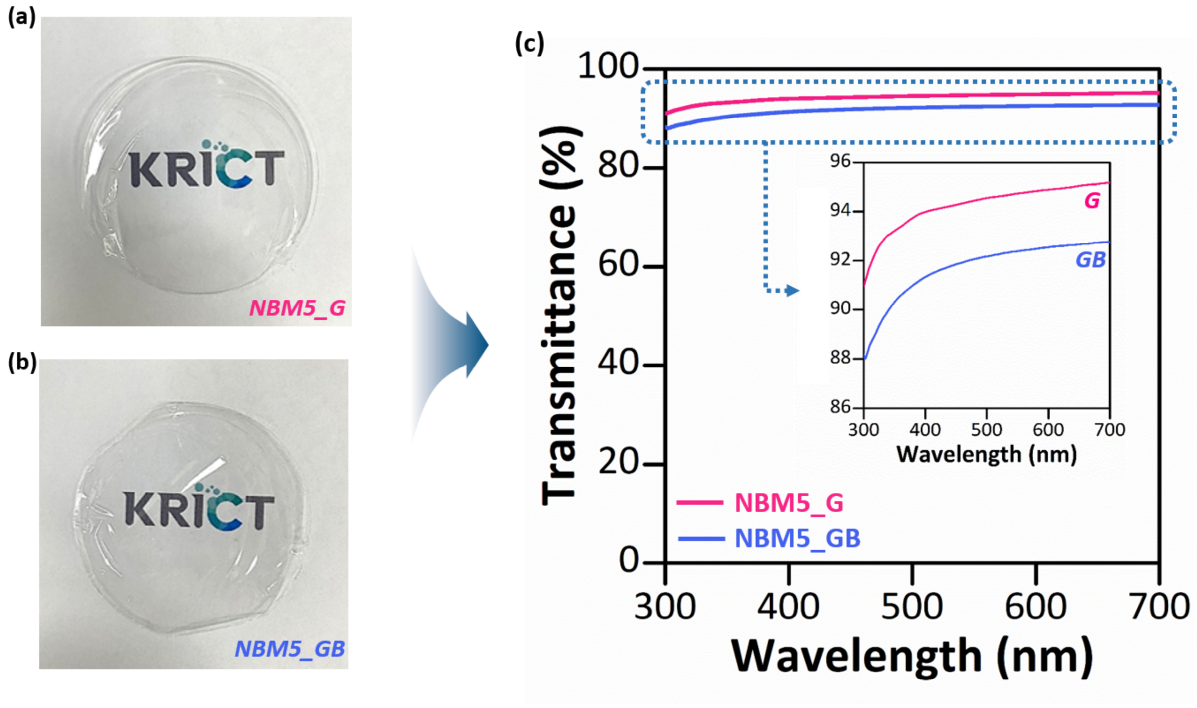

Figure 1.13. Photos of the films of (a) NBM5_G, (b) NBM5_GB. The films were prepared using the solution-casting method (30 ㎛) after dissolving them in toluene at 10 wt.%. (c) UV-vis graph of the films of NBM5_G and NBM5_GB.

1.5. CONCLUSIONS

In this study, successful copolymerization of NB and MVK was achieved via vinyl-addition polymerization under a palladium catalytic system. The monomer reactivity ratios of NB/MVK polymerization (r_{NB} = 14.41; r_{MVK} = 0.31) confirmed that the synthesized polymer had a gradient structure. Furthermore, effective polymerization was observed when NB, BuNB, and MVK monomers were polymerized, and by varying the temperature during polymerization, it was observed that polymers with an ideal gradient or gradient-block like structure were synthesized. These two terpolymers with different polymer structures, NBM5_G with a gradient structure and NBM5_GB with a gradient block structure, were characterized through detailed studies comparing their thermal properties (glass transition temperature), as well as their mechanical and elastic properties. Films of the two terpolymers produced by the solution-casting method exhibited excellent visible light transmittance of up to approximately 93%, indicating high potential in optical applications. Through IG-mode ^{13}C NMR analyses, it was observed that the synthesized terpolymers contained a high content of MVK, up to 38%. This demonstrated the potential to generate versatile polymers suitable for various applications through post-polymerization modification of the polar functional groups.

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Chapter II.

Functionalization of Terpolymer via Post-Polymerization Modification towards Sustainable and Versatile Materials

2.1. ABSTRACT

Among the various methods to improve the structure and properties of polymers, post-polymerization modification (PPM) is a way to easily provide the desired functionality. In previous research, we synthesized terpolymers using NB/BuNB/MVK and confirmed that MVK made up more than 30% of the terpolymer. In particular, the ketone group can be easily modified into polymers usable in various fields through PPM using silanes and nitrogen-containing functional groups like oxime, imine, or hydrazone. In this study, various silanes, from silane monomers to silane oligomers, were introduced to the NBM5_G sample through a hydrosilylation reaction. The modified polymers showed improved fluidity compared to the unmodified polymers, which was confirmed through comparisons of thermal and optical properties. Additionally, these polymers can be degraded through hydrolysis reactions, demonstrating their potential as recyclable and upcyclable polymer platforms and highlighting their potential as sustainable polymers.

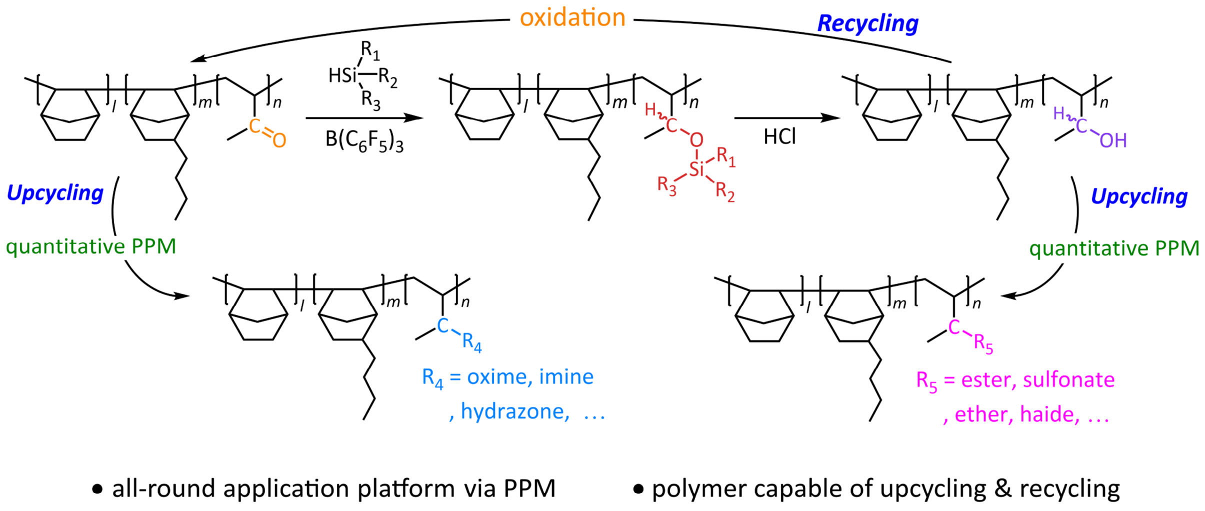

Figure 2.1. This work for enhancing recyclability and upcycling via post-polymerization modification of ketone-functionalized terpolymers.

2.2. INTRODUCTON

To enhance the structure and properties of polymers, complex and delicate chemical processing is required. Among these methods, post-polymerization modification (PPM) is one approach used to improve polymer performance, allowing for the addition of various functional groups to existing polymer precursors or the modification of polymer chain structures.[1-5] Key techniques of PPM include Functionalization, which introduces functional groups into polymers, cross-linking to form three-dimensional network structures, and grafting or creating block copolymers. Since its introduction in 2001, PPM, facilitated by click reactions, has paved the way for the straightforward synthesis of diverse functional polymers, characterized by readily available reagents, mild reaction conditions, and easily removable byproducts.[6]

Notably, polymers containing highly reactive ketone groups offer new materials that can be applied in various fields through PPM. The catalytic transformation of the C=O group double bond into a C-O-R structure allows for the manifestation of various properties depending on the functional groups. Through hydrosilylation reactions with silanes, silicon compounds can be synthesized, while modification into oxime, imine, or hydrazone structures enables the incorporation of nitrogen into the polymer.[7-10]

One of the PPM methods used to enhance the structure and properties of polymers is the hydrosilylation reaction, which proceeds by adding silane ($H\text{-}SiR_3$) to the C=O bond. Polymers modified through this reaction with silicon exhibit improved physical and chemical properties, particularly high temperature stability, excellent resistance to organic solvents, and low moisture absorption due to the formation of Si-O bonds.[11-12] These characteristics provide the advantage of easily designing tailored polymers for various applications through the modification of silane functional groups. Traditionally, platinum-based catalysts have been used for this reaction,[13-14] but they pose issues such as high cost, toxicity, and low reusability. To overcome these challenges, non-metal based tris(pentafluorophenyl)borane (BCF) catalyst has recently been investigated as alternatives. BCF catalyst not only offers low toxicity to humans and the environment and high reusability, but also provides flexibility in reaction conditions, thus opening up possibilities for versatile applications.[15-18]

In our previous study, we synthesized a polar cyclic olefin terpolymers (COTs) containing ketone groups using norbornene (NB), butyl-norbornene (BuNB), and methyl vinyl ketone (MVK). We observed the diversity of monomer sequences within the polymer depending on the polymerization conditions, noting an ideal gradient structure at 60 °C and a gradient-block-like structure at 80 °C. In this study, we conducted hydrosilylation reactions on the gradient-structured polymer synthesized in the previous study and compared the resulting changes in properties with the initial polymers. By using various silane monomers and oligomers in the reaction, we investigated the differences depending on the type of silane. We confirmed that PPM could be easily performed at room temperature without the application of metal catalysts by using BCF catalysts. The polymers after PPM exhibited enhanced transparency compared to the initial polymers, and we explored the potential for sustainable environmental management by applying hydrolysis reactions to the polymers after the hydrosilylation reaction.

2.3. EXPERIMENTAL SECTION

Materials

bicyclo[2.2.1]hept-2-ene (Sigma-Aldrich; purity ≥99%, NB), 3-buten-2-one (Sigma-Aldrich; purity ≥90%, MVK), butyl-norbornene (NH chemicals; purity ≥95%, BuNB), palladium(II) acetate (Sigma-Aldrich; purity ≥98%), tricyclohexylphosphine (Sigma-Aldrich; purity ≥95%, PCy_3), dioctadecynilinum tetrakis(pentaflorophenyl)borate (SPCI; purity ≥50%, borate), tris(pentafluorophenyl)borane (Sigma-Aldrich; purity ≥95%, BCF), cyclohexyl dimethyl silane (Sigma-Aldrich; purity ≥98%, CHDS); dimethyl phenyl silane (TCI; purity ≥97.0%, DPS), triethyl silane (TCI; purity ≥98.0%, TES), poly(methylhydrosiloxane) (Sigma-Aldrich; M_n = 1700-3200, PMHS), (3-4% methylhydrosiloxane) - dimethylsiloxane copolymer (Gelest; M_n = 1900-2000, HMS-031), (6-7% methylhydrosiloxane) - dimethylsiloxane copolymer (Gelest; M_n = 1900-2000, HMS-071)

Synthesis of NBM_G

At room temperature, palladium acetate ($Pd(OAc)_2$, 1.0 mM), tricyclohexylphosphine (PCy_3, 2.0 mM), and Dioctadecynilinum tetrakis(pentaflorophenyl)borate (borate, 2.0 mM) were added to a 50 mL round-bottom flask equipped with a magnetic stir bar. The flask was purged with argon, and then 5 mL of purified toluene was added, followed by stirring for 1 hour. Concurrently, another 50 mL round-bottom flask was purged with argon, and then norbornene (NB, 750 mM) was added, followed by 5 mL of purified toluene and stirring for 30 minutes. Subsequently, immediately after injecting butyl-norbornene (BuNB, 250 mM) and methyl vinyl ketone (MVK, 1000 mM) into the flask containing norbornene, the solution from the flask containing the catalyst was slowly added, and the reaction was carried out at 60 °C for 14 days. The reaction was terminated by adding a small amount of hydrochloric acid (Hydrochloric acid)/methanol (Methanol) (v/v = 1/9) solution to the reaction mixture, and the reactant was slowly added to excess methanol to precipitate it. The precipitate was vacuum-dried at 70 °C for 12 hours to obtain white powder NBM5_G. (Yield = 74.8%)

Hydrosilylation of NBM5_G

At room temperature, NBM5_G (100 mM) and toluene were added to a 10 mL round-bottom flask and stirred until fully dissolved. Then, BCF (1 mM) was added, followed by the addition of silane (100 mM) after thorough mixing of BCF. After one hour of stirring, chloroform was added to the flask to dilute the solution, and then the solution was slowly dropped into hexane to precipitate the polymer. The precipitate was collected, and then vacuum-dried at 70 °C for 12 hours to obtain white powder, the polymer.

Measurements

GPC was conducted to analyze the M_w and M_w/M_n of polymers with chloroform ($CHCl_3$) as the eluent at 40 °C and the flow rate was maintained at 1.0 mL/min. For chloroform-GPC, three polystyrene columns from Agilent [two LF-804 (from Shodex); 6 µm pore size; 8 mm i.d. × 300 mm, one KF-802.5 (from Shodex); 6 µm pore size; 8 mm i.d. × 300 mm] were connected to a 1260 ISO pump, a 1260 vialsampler, a multicolumn thermostat (MCT), and a 1260 refractive index (RI) detector. To obtain the information about molecular weight of obtained polymers, 10 standard polystyrene (PS) samples were used to calibrate the columns (Agilent Technologies; M_p = 1,230–1,740,000; M_w/M_n = 1.02–1.08). To obtain the information about molecular weight of obtained polymers, 10 standard polystyrene (PS) samples were used to calibrate the columns (Agilent Technologies; M_p = 1,230–1,740,000; M_w/M_n = 1.02–1.08). ^{1}H NMR spectra were acquired using a 300 MHz Bruker Ultrashield spectrometer. All spectra were recorded in ppm units using CDCl3 as the solvent at room temperature. Fourier-transform infrared (FT-IR) spectra were recorded using a Thermo Scientific NOCOLET 6700 FT-IR spectrometer equipped with an attenuated total reflection (ATR) module. Thermal gravimetric analysis (TGA) was performed using a Q500 calorimeter (TA Instruments) under a dry nitrogen flow from 35 °C to 800 °C at a heating rate of 10 °C/min. The glass transition temperatures were observed using a Q2000 calorimeter (TA Instruments) under a dry nitrogen flow at a heating or cooling rate of 20 °C/min by differential scanning calorimetry (DSC).

Transmittance test

To prepare the samples for film formation, the polymers were completely dissolved in toluene at a concentration of 10 wt.%. Subsequently, a clean solution was obtained using a 0.45 µm syringe filter, and the solution was poured onto a 5×5 cm glass petri dish. The film was cast for 6 hours while gradually increasing the temperature in a situation where the solvent was sufficient. The dish was then placed in a 60 °C vacuum oven overnight to remove any remaining solvent. The resulting polymer films were used to measure transparency in the visible light range from 300 nm to 700 nm. UV-visible spectrometer was used to determine the transmittance of polymer films (JASCO V-700).

2.4. RESULTS and DISCUSSIONS

Hydrosilylation of NBM5_G

In this study, a method for diversifying the characteristics of polymers was proposed through the introduction of various functionalized silanes into the polymer via hydrosilylation reactions catalyzed by the BCF catalyst **(Figure 2.2)**. To compare the properties of the modified polymers after hydrosilylation based on the functional groups within the silane monomers, three types of silane monomers were selected: cyclohexyl dimethyl silane (CHDS), dimethyl phenyl silane (DPS), and triethyl silane (TES). After synthesizing the polymer through the reaction with silane oligomers containing siloxane, we aimed to compare the differences in properties compared to those observed when synthesizing the monomer. These various silanes were synthesized with previously synthesized gradient terpolymers via hydrosilylation reactions and characterized through thermal and optical analyses. The advantage of BCF, a catalyst used for hydrosilylation reactions, in that the reaction proceeded easily at room temperature and under atmospheric conditions, was utilized in this study.

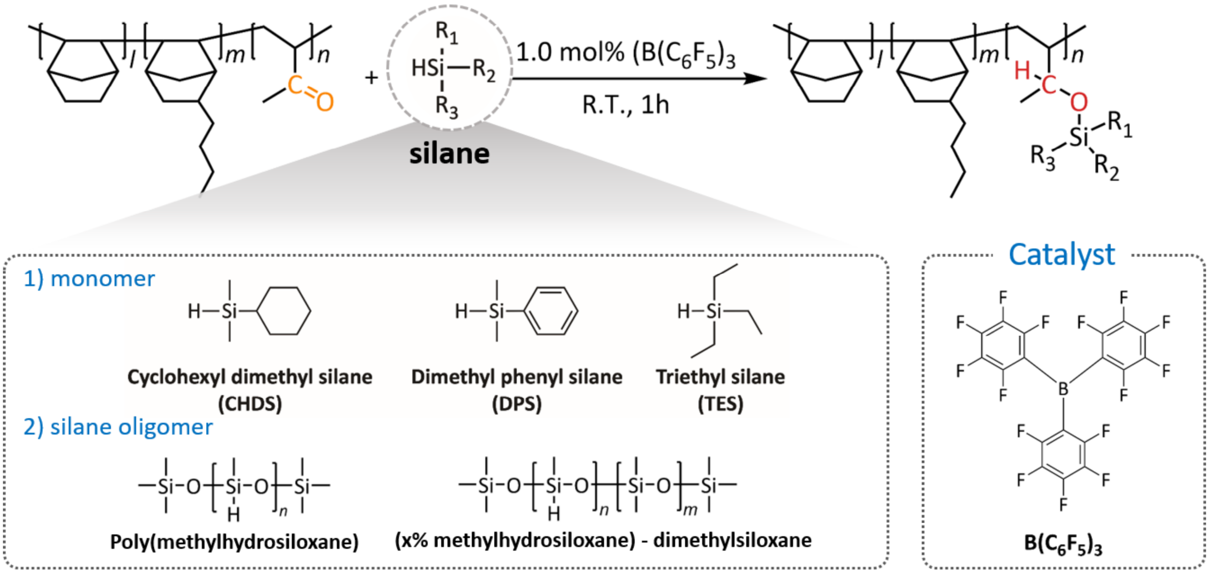

Figure 2.2. Schematic diagrams illustrating post-polymerization modification on the ketone group in the synthesized terpolymer with various silanes.

Structural analyses of hydrosilylation reactions of NBM5_G with various silanes

First, the hydrosilylation reaction using silane monomers including CHDS, DPS, and TES was carried out, and complete modification to silyl ethers was achieved by using a sufficient amount of silane relative to the ketone content in the polymer. NMR analyses showed silane peaks near 0 ppm and hydrogen peaks around 3.5 ppm, indicating successful polymerization through the breaking of carbonyl peaks (**Figure 2.3**). Through FT-IR analyses, it was observed that the carbonyl peak of the original polymer, which is typically found around 1750 cm^{-1}, completely disappeared after the hydrosilylation reaction (**Figure 2.4**). Additionally, peaks corresponding to the functional groups in each silane were well observed at 1250 cm^{-1} and 850-750 cm^{-1}.

Based on the successful reaction with monomers, further reactions using silane oligomers were attempted. Through NMR analyses, it was confirmed the presence of silane functional groups in silane oligomer at specific ppm (**Figure 2.5**). The complete disappearance of the carbonyl peak at 1750 cm^{-1} and a relatively larger peak ratio of 1000-1100 cm^{-1} and 2100-2300 cm^{-1} (**Figure 2.6**), corresponding to the Si-O-Si and Si-H functional group, indicated the effective polymerization of silane oligomers. Analyses by GPC confirmed an increase in the relative molecular weight of the polymer after polymerization.

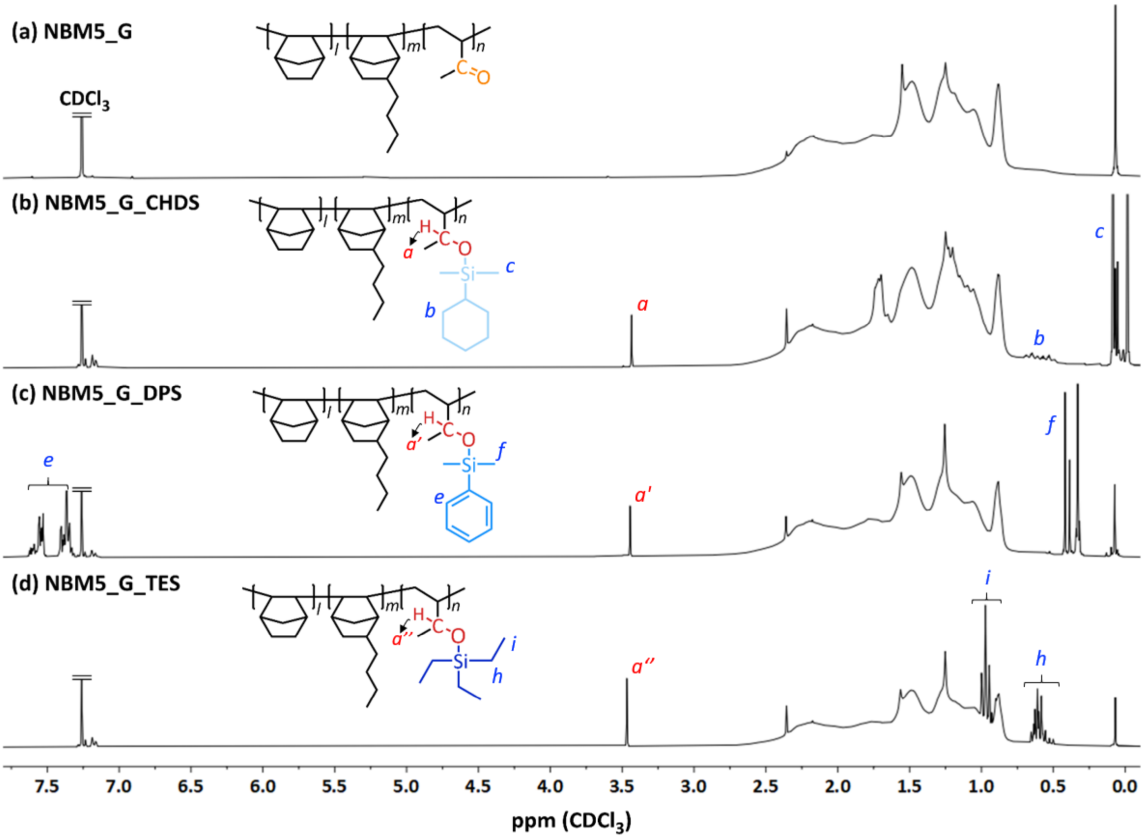

Figure 2.3. ^{1}H NMR spectra of NBM5_G (a) before hydrosilylation, (b) after hydrosilylation with CHDS, (c) after hydrosilylation with DPS, (d) after hydrosilylation with TES.

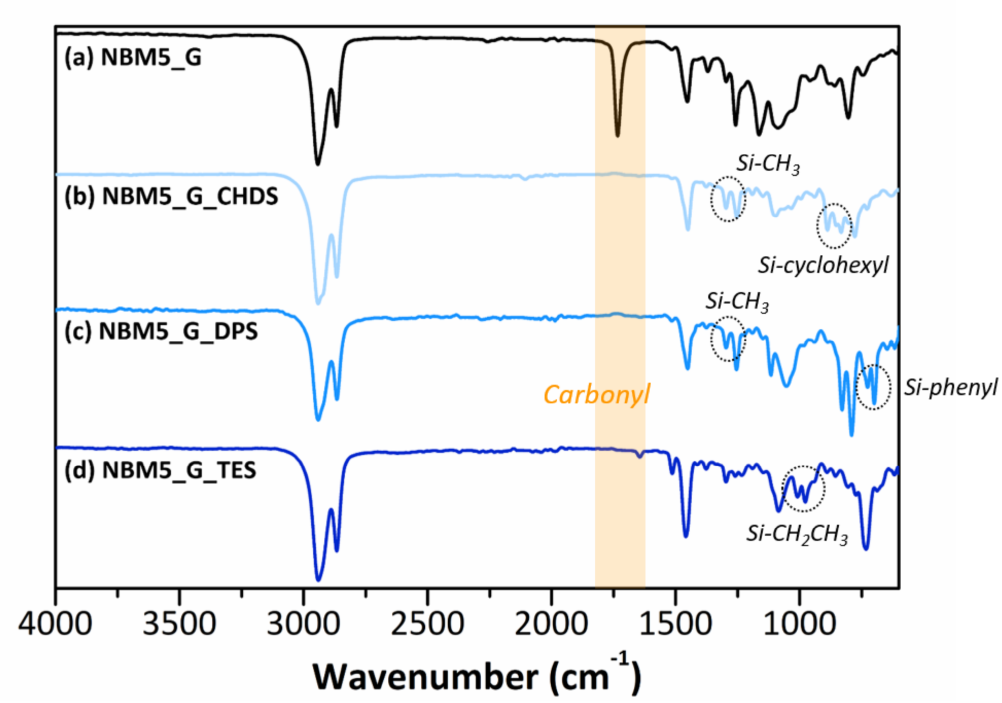

Figure 2.4. FT-IR spectra of NBM5_G (a) before hydrosilylation, (b) after hydrosilylation with CHDS, (c) after hydrosilylation with DPS, (d) after hydrosilylation with TES.

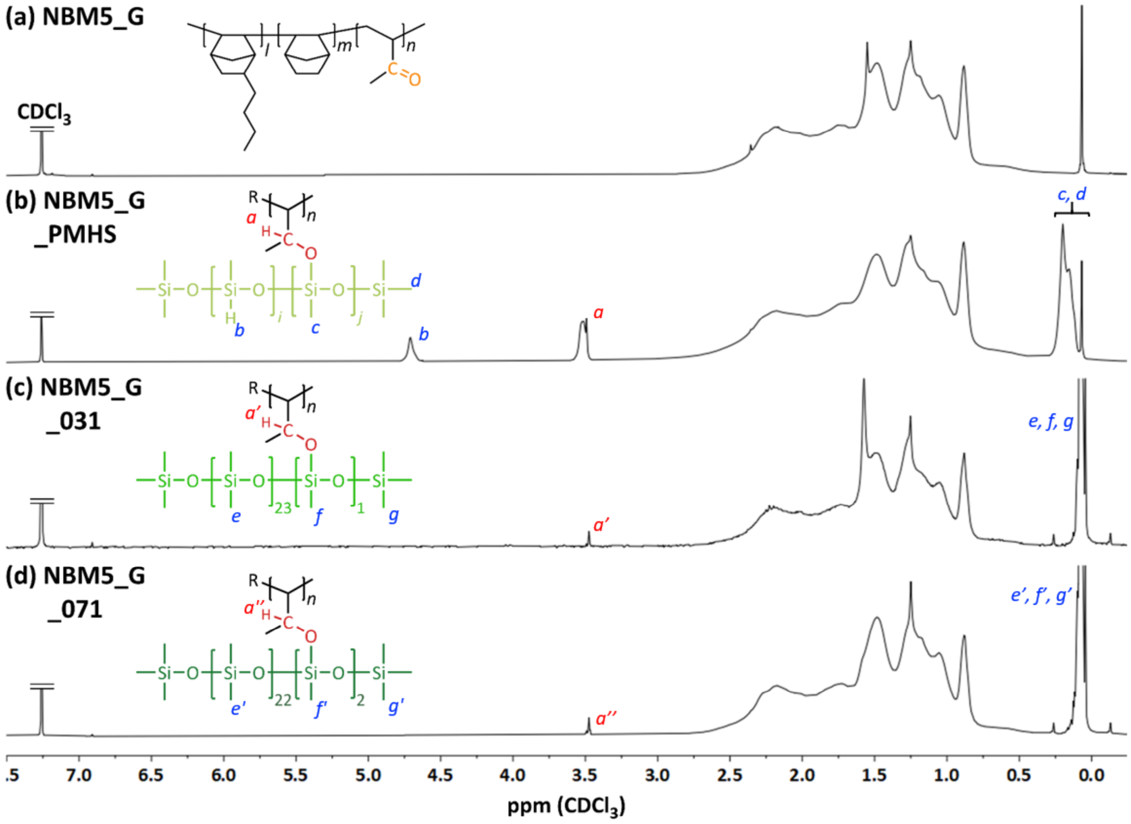

Figure 2.5. ^{1}H NMR spectra of NBM5_G (a) before hydrosilylation, (b) after hydrosilylation with PMHS, (c) after hydrosilylation with HMS-031, (d) after hydrosilylation with HMS-071.

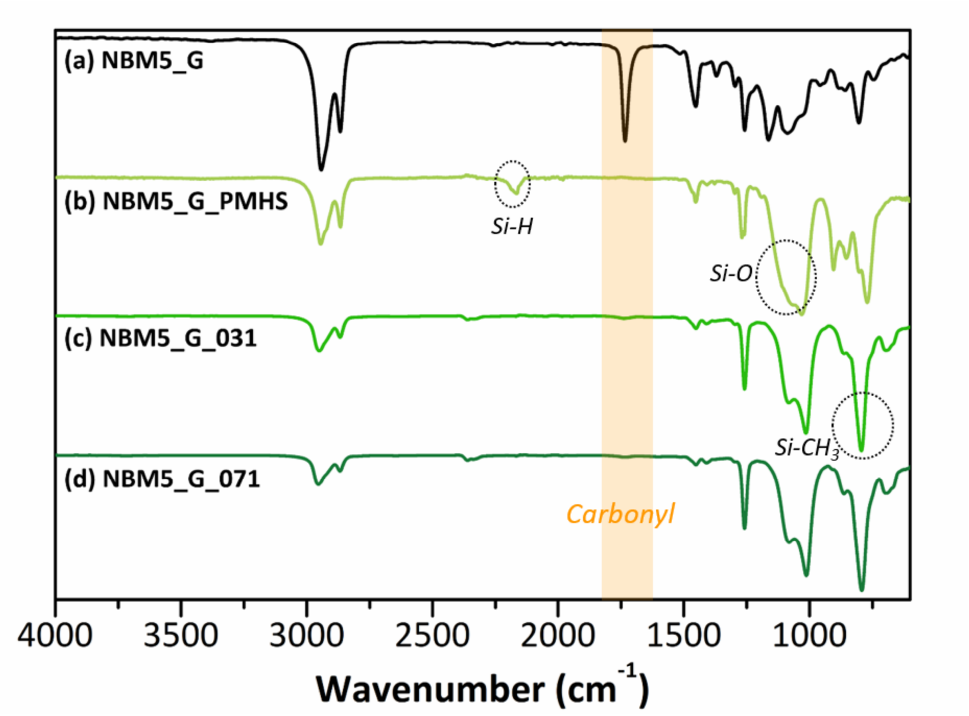

Figure 2.6. FT-IR spectra of NBM5_G (a) before hydrosilylation, (b) after hydrosilylation with PMHS, (c) after hydrosilylation with HMS-031, (d) after hydrosilylation with HMS-071.

Thermal and Optical properties

The thermal properties of the polymers before and after modification were compared using TGA and DSC analyses. It was observed that polymers with introduced silicon generally exhibited lower decomposition temperatures compared to the original polymers. This was attributed to the introduction of C-O-Si bonds, which increased the mobility compared to the existing bonds in the polymer.[19-20] Polymers with higher mobility allowed for more efficient heat transfer as the internal bonds could move more freely, facilitating decomposition at lower temperatures.

Similar trends were observed in the analysis of glass transition behavior through DSC. Polymers subjected to hydrosilylation reactions showed lower glass transition temperatures (Tg), particularly when silane oligomers were introduced (**Table 2.1**). This significant reduction in glass transition behavior was attributed to the presence of flexible silane oligomers, which reduced the energy required for transitioning into a liquid state, thus making the polymer structure more flexible. These results clearly demonstrated the impact of silane-based modification on the thermal stability and glass transition characteristics of the polymers.

Thin films with a thickness of approximately 30μm were prepared using a solution casting method for both the original polymer NBM5_G and polymers after the introduction of silane monomers and oligomers (**Figure 2.7 a**). Optical anaylses revealed that NBM5_G exhibited high transparency in the visible light range, ranging from 91% to 93% (**Figure 2.7 b**). In contrast, polymer films with introduced silane monomers showed a slight improvement in transparency of about 1% in the range of 92% to 95%. Particularly, films of polymers with introduced silane oligomers demonstrated excellent light transmittance of 94% to 96%, proving suitable for advanced optical applications. This clearly demonstrates that polymers synthesized through post-polymerization modification with silane-based functionalities exhibit superior transparency compared to the original polymer NBM5_G.

Table 2.1. Results of hydrosilylation of NBM5_G.

Polymer code	M_w **(kg/mol)**	$M_\mathrm{w}/M_\mathrm{n}$	$T_\mathrm{d,3}$ **(°C)**	T_g **(°C)**
NBM5_G	82	1.33	393	255
NBM5_G_CHDS	86	1.37	413	221
NBM5_G_DPS	87	1.34	394	219
NBM5_G_TES	91	1.31	397	228
NBM5_G_PMHS	90	1.40	317	253
NBM5_G_031	95	1.33	299	158
NBM5_G_071	108	1.31	321	168

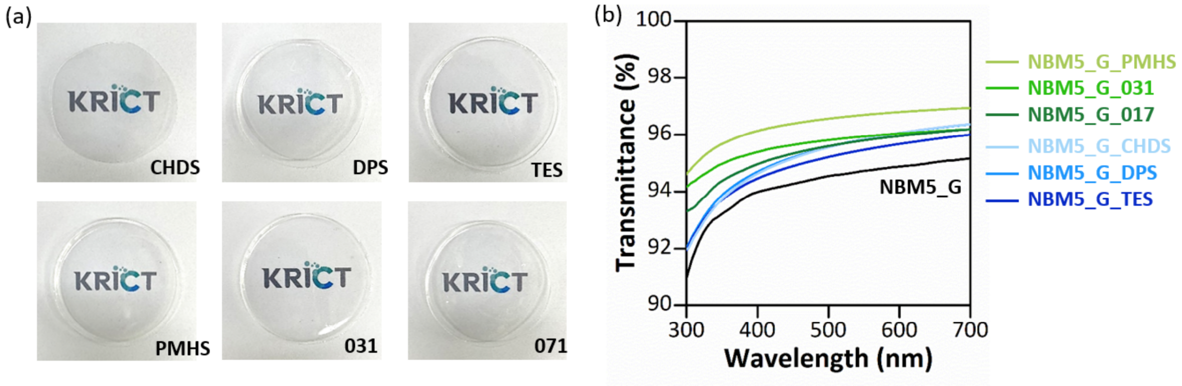

Figure 2.7. (a) Photos of the films of NBM5_G after hydrosilylation with CHDS, DPS, TES, PMHS, HMS-031, HMS-071. The films were prepared using the solution-casting method (30 ㎛) after dissolving them in toluene at 10 wt.%. (b) UV-vis graph of the films.

Hydrolysis reaction to evaluate the recyclability of polymers

Si-O-C bonds created through BCF-catalyzed carbonyl addition reactions were shown to have less stability against hydrolysis than conventional Pt catalyst-cured silicones.[18] This garnered significant attention due to the increasing demand for materials requiring rapid degradation in the environment. In this study, a hydrolysis experiment was performed on the NBM5_G_PMHS sample in a chloroform solution containing HCl (1 mM) for 3 hours. The experimental results showed that the sample was completely dissolved and separated into distinct layers, indicating that the Si-O-C bond was dissociated and the Si-OH bond and C-OH bond were formed in the chloroform layer. Through NMR analysis, it was confirmed that the existing Si-H bond was lost, and that silane was completely removed from the precipitate after hydrolysis (**Figure 2.8**). GPC analyses showed a decrease in the molecular weight of the degradation products compared to the initial material, confirming that the siloxane backbone was completely separated from the polymer (**Figure 2.9**).

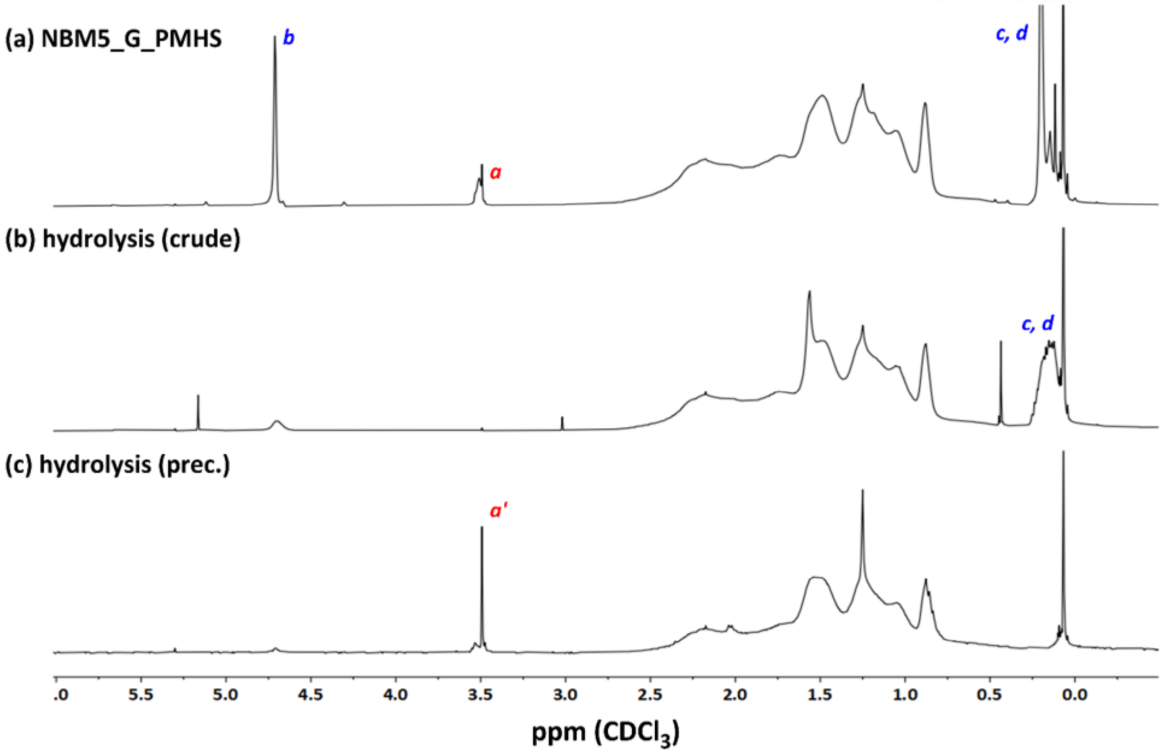

Figure 2.8. Hydrolysis reaction with NBM5_G_PMHS. ^{1}H NMR spectra of the (a) before hydrolysis, (b) crude sample after hydrolysis for 3 h, (c) precipitated sample after hydrolysis for 3h.

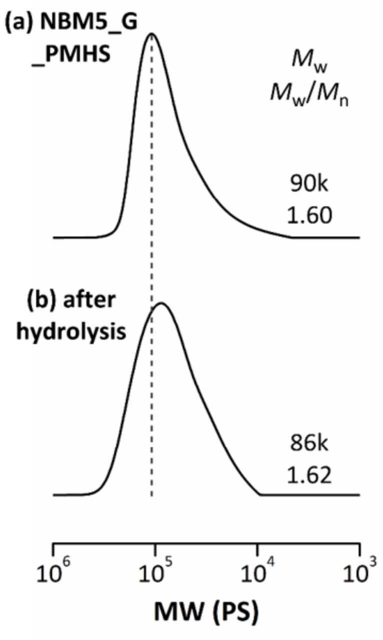

Figure 2.9. GPC graphs of (a) starting sample; NBM5_G_PMHS, (b) product after hydrolysis.

CONCLUSIONS

In this study, post-polymerization modification (PPM) via hydrosilylation reaction was conducted on terpolymers polymerized using three monomers, NB/BuNB/MVK, as precursors. The reactions were performed using a BCF catalyst, allowing PPM under ambient conditions without the need for metal catalysts. Previously synthesized gradient structure terpolymers were reacted with various silanes, ranging from silane monomers to silane oligomers. Structural analyses confirmed the complete disappearance of ketone bonds within the polymer and verified the formation of C-O-Si bonds. The polymer with introduced silicon showed enhanced chain flexibility due to the functional groups in the silanes, resulting in a reduced glass transition temperature. Furthermore, analyses of the transparency of films made from the modified polymers showed improved transmittance compared to the original polymer, with particularly high transparency of 94-96% observed when silane oligomers were introduced. To evaluate the recyclability of the polymer, hydrolysis reactions were conducted, confirming the complete removal of siloxane groups from the polymer backbone. Through subsequent oxidation and various quantitative modifications, we believe that our polymer platform has the potential to contribute to sustainable practices as an upcyclable and recyclable polymer.

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