Conformational Conversion and Local Packing of Cyclic Olefin Copolymers

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ABSTRACT: Cyclic olefin copolymer (COC, poly(norbornene-co-ethylene)) catalyzed by ansa-ethylidenebis(indenyl)zirconium dichloride (Et(Ind)2ZrCl2)/methylaluminoxane (MAO) gives rise to phenomenal increase of Tg upon annealing. Unaveraged solid-state 13C NMR resonance of the CH carbons in the norbornene (53 and 49 ppm) evidenced the conformation conversion from T[X]T and G[X]G to more stable T[X]G conformers (where [X] = [T] or [G] represent the norbornene chain conformation). As the persistent length increases with the conversion, local packing of the rigid chain subsequently occurs. Synchrotron source X-ray diffraction provides clear evidence of the averaged interchain contraction from 12.0 to 8.5 Å and a tighter distribution in the spacing after annealing. In the preannealed state, T1p relaxation time revealed both mobile (where conformer converts) and rigid components (where conformation is frozen), which coalesce into a further rigid component after extended annealing. The mechanisms governing the packing in amorphous COC are likely by the random chain diffusion and not from cooperative motion as described by the bundle-packing model.

Introduction

Cyclic olefin copolymers (COC) synthesis and characterization have been the subject of many researches. The copolymers receive new thrust with recent developments of metallocene technologies.1-9 Prior studies have shown that Tg up to 260 °C and a melting temperature (Tm) near 400 °C can be reached for polynorbornene homopolymer.6-8 Fink et al. reported that COC with the norbornene (NB) microblock varying from isolated, alternating NB and longer NB block structures can be produced by tailoring metallocene and half-sandwich catalysts.9 In this study, we present the structural characterization of a series of COC’s synthesized with ansa-ethylidenebis(indenyl)zirconium dichloride (rac-Et(Ind)2ZrCl2). Because of the rigidity of the NB unit, the conformation conversion is highly restricted, and the conformers were “frozen” after polymerization. Previous 13C solid-state NMR studies had identified unaveraged chain conformations in the condensed phase.10 Heating provided the energy to convert to the most energetically favored conformer which leads to an increase of the persistent length and a more rigid chain segment. Amorphous polymers containing rigid monomer unit, such as polycarbonate (PC),11 poly(phenylene sulfide) (PPS),12 poly(ethyl ether ketone) (PEEK),13 and polyimide (PI),14 are reported to exhibit ordered local packing. Capable of rearranging into higher ordered local packing, COC from norbornene and ethylene was synthesized according to the procedure described previously using ansa-metallocene catalyst Et(Ind)2ZrCl2/MAO.2-8 Co-catalyst/catalyst mole ratio of 3000-7000 were employed. The polymerization temperature was maintained at ~70 °C with constant ethylene pressure of 19-21 psi (ca. 1.5 bar). The ethylene pressure is much lower and the reaction temperature higher than those used by Ruchatz et al. where ethylene pressure is 1-10 bar and the reaction temperature is 30-40 °C.10 Micro-structures of these copolymers were characterized by solution 13C NMR (νc = 50 MHz) using 5 wt % solution in trichlorobenzene (TCB) at elevated temperature (120 °C). The alternating, isolated, and block norbornene contents are determined following the prescribed characterization procedures with 13C NMR.15-16 Glass temperatures were determined by DSC (Perkin-Elmer DSC-7) with a heating rates of 10 °C/min. The scanning temperature was limited from 30 to 220 or 300 °C to avoid sample degradation. Sample annealing was conducted on a vacuum oven at 30 °C above the initial Tg for controlled duration. Solid-state 13C NMR (νc = 100.24 MHz) spectra were recorded with strong proton decoupling (H1 = 85 kHz) with a spinning rate close to 8 kHz. Proton spin–lattice relaxation time in the rotating frame, T1p, measured indirectly from carbon signals with strong spin-lock field.

Experimental Section

COC from norbornene and ethylene was synthesized according to the procedure described previously using ansa-metallocene catalyst Et(Indenyl)2ZrCl2/MAO.2-8 Cocatalyst/catalyst mole ratio of 3000-7000 were employed. The polymerization temperature was maintained at ~70 °C with constant ethylene pressure of 19-21 psi (ca. 1.5 bar). The ethylene pressure is much lower and the reaction temperature higher than those used by Ruchatz et al. where ethylene pressure is 1-10 bar and the reaction temperature is 30-40 °C.10 Micro-structures of these copolymers were characterized by solution 13C NMR (νc = 50 MHz) using 5 wt % solution in trichlorobenzene (TCB) at elevated temperature (120 °C). The alternating, isolated, and block norbornene contents are determined following the prescribed characterization procedures with 13C NMR.15-16 Glass temperatures were determined by DSC (Perkin-Elmer DSC-7) with a heating rates of 10 °C/min. The scanning temperature was limited from 30 to 220 or 300 °C to avoid sample degradation. Sample annealing was conducted on a vacuum oven at 30 °C above the initial Tg for controlled duration. Solid-state 13C NMR (νc = 100.24 MHz) spectra were recorded with strong proton decoupling (H1 = 85 kHz) with a spinning rate close to 8 kHz. Proton spin–lattice relaxation time in the rotating frame, T1p, measured indirectly from carbon signals with strong spin-lock field.

X-ray diffraction was conducted using a synchrotron source (Synchrotron Radiation Research Center, Hsin-Chu, Taiwan) on a J apan MacScience Co. (M18XHF-SRA) diffractometer with a scanning rate of 2°/min at room temperature.

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Results and Discussion

The microstructure and the mole fraction of the three main NB microblock signatures (alternating, isolated, and block) for the COC studied are summarized in Table 1. Different norbornene feed ratios lead to copolymers with varying NB and ethylene segmental lengths. The higher reaction temperature used in this study raises the norbornene activity ratio, and the two-carbon bridge in the catalyst created an opening wide enough for more continuous norbornene (NB) units to be included. The COC produced here contains a higher amount of NB than the COCs produced previously.

Table 1. High-Resolution $^{13}$C NMR Analysis Results of Cycle Olefin Copolymers (COC’s)$^a$

<table>
<thead>
<tr>
<th>run</th>
<th>NB content (mol %)</th>
<th>block (--N--N-- and higher)</th>
<th>alternating</th>
<th>isolated</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>100.0</td>
<td>100.0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>58.36</td>
<td>40.16</td>
<td>51.85</td>
<td>7.99</td>
</tr>
<tr>
<td>4</td>
<td>47.63</td>
<td>50.21</td>
<td>40.55</td>
<td>9.25</td>
</tr>
<tr>
<td>5</td>
<td>43.51</td>
<td>17.33</td>
<td>66.60</td>
<td>16.07</td>
</tr>
<tr>
<td>6</td>
<td>24.88</td>
<td>21.02</td>
<td>51.04</td>
<td>27.98</td>
</tr>
</tbody>
</table>

$^a$ Polymerization conditions: ethylene pressure = 20 psi, 70°C; total volume = 60 mL; [Al]/[Zr] = 8000–4000; catalyst = 1–2 mg.

Figure 1 displays normal solid-state $^{13}$C NMR CP/MAS spectra of run 3 to run 7.

Figure 1. Solid-state NMR $^{13}$C NMR cross-polarization with magic angle spinning (CP/MAS) spectra of run 3 to run 7.

For samples containing over 47.63 mol % norbornene content (runs 1, 3, and 4), a rapid $T_g$ jump (over 32 °C) during initial annealing stage is apparent. (Figure 2 and Table 2). In those samples, solid-state $^{13}$C NMR unravels systematic changes with heat treatment. Shown in Figure 3 are the $^{13}$C spectrum of run 1 (PNB), run 4 ($[NB]$ = 47.63 mol %), and run 6 ($[NB]$ = 24.88 mol %). For both run 1 and run 4, partially resolved peaks are detected. The split feature is most prominent for the CH backbone carbons on NB monomer (peak 1) where two major groups of chemical shifts at 49 and 53 ppm are identified. Notice that the 53 ppm peak, which is absent in the solution spectrum, diminishes upon annealing. The different conformers established between consecutive single bonds in polymers comprise a variety of chemical shifts and broadens the individual resonance. Rapid

Table 2. Characteristics of Cycle Olefin Copolymers Studied

<table>
<thead>
<tr>
<th>run</th>
<th>NB content (mol %)</th>
<th>$T_g$ (°C) before annealing</th>
<th>$T_g$ (°C) after annealing$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>100</td>
<td>136.2</td>
<td>216.9 (252*)</td>
</tr>
<tr>
<td>3</td>
<td>58.38</td>
<td>102.5</td>
<td>179.9</td>
</tr>
<tr>
<td>4</td>
<td>47.63</td>
<td>81.3</td>
<td>154.5</td>
</tr>
<tr>
<td>5</td>
<td>43.51</td>
<td>86.8</td>
<td>119.6</td>
</tr>
<tr>
<td>6</td>
<td>24.88</td>
<td>68.1</td>
<td>98.0</td>
</tr>
</tbody>
</table>

$^a$ Pure PE. $^b$ Plateau value from the uppermost curve in Figure 2.

$T_g$ Variation with Annealing. As seen in Figure 2, substantial increases of $T_g$ for all COC samples are observed with heat treatment at 30 °C above initial $T_g$. Depending on the NB content (mole percent), the degree of changes in $T_g$ before and after annealing occurs in the range of 15–35 °C (Table 2). In addition, the final $T_g$ where equilibrium is reached increases with increasing NB. Interestingly, pure PNB shows an initial $T_g$ of 135 °C which increases to 252 °C (the plateau value), with nearly 120 °C jump after annealing. This value is comparable with $T_g$ of compression-molded COC products (~250 °C) where [NB] content is 98 mol %, for other COCs examined, $T_g$ variation occurred on the order of 30–80 °C. The unusual $T_g$ variation is indicative of the metastable state in the as-prepared glassy COC and PNB samples. Although other amorphous polymers containing rigid repeating unit have also displayed $T_g$ variation on the order of 5–8 °C after heat treatment, a substantial change as observed here is rather unusual.

Conformation Conversion. For samples containing over 47.63 mol % norbornene content (runs 1, 3, and 4), a rapid $T_g$ jump (over 32 °C) during initial annealing stage is apparent. (Figure 2 and Table 2). In those samples, solid-state $^{13}$C NMR unravels systematic changes with heat treatment. Shown in Figure 3 are the $^{13}$C spectrum of run 1 (PNB), run 4 ([NB] = 47.63 mol %), and run 6 ([NB] = 24.88 mol %). For both run 1 and run 4, partially resolved peaks are detected. The split feature is most prominent for the CH backbone carbons on NB monomer (peak 1) where two major groups of chemical shifts at 49 and 53 ppm are identified. Notice that the 53 ppm peak, which is absent in the solution spectrum, diminishes upon annealing. The different conformers established between consecutive single bonds in polymers comprise a variety of chemical shifts and broadens the individual resonance. Rapid
interconversions between rotation isomers yield averaged absorption with breadth dependent upon the conversion rate. However, when the conversion is restricted, the conformers can be frozen at the local energy minimum. For example, the all-trans and \( t(g)g \), conformers in the crystalline syndiotactic polystyrene (identified by the resolved \( ^{13}C \) NMR separated energy minimum. For example, the all-trans and \( t(g)g \), conformers in the crystalline syndiotactic polystyrene (identified by the resolved \( ^{13}C \) NMR separated energy minimum.)

When including the \( C-C \) bond adjacent to the central norbornene unit, we have the following six basic conformations: \( T[T][T] \), \( T[G][T] \), \( T[T][G] \), \( T[G][T] \), \( G[T][G] \), and \( G[G][G] \). Here \( [X] \) = \( [G] \) or \( [T] \) has been determined during polymerization, as mentioned previously. For \( -N-N-N- \) and \( -N-N- \) sequences the conversion within the \( X[T][Y] \) and the \( X[G][Y] \) group experiences greater restriction than those in the isolated or alternating NB segments due to their less steric hindrance. The unaveraged conformation observed here would mostly be attributed to the NB dyad and triad sequence. Although the block is most possible in \( -N-N-N- \) dyad in reality, Schemes 2 and 3 illustrate with \( -N-N-N- \) triad sequence all possible conformations in syndiotactic and isotactic polynorbornene. In the syndiotactic case, it is impossible for norbornene to have all gauche configurations. Similarly, it is also impossible for the isotactic polynorbornene chain to bear consecutive trans configurations. The tacticity, meso \( (m) \) and racemo \( (r) \) with regards to the three-membered ring, is consistent with erythro \( (E) \) and threo \( (Z) \) nomenclature where three triad configurations, \( (E,E) \), \( (E,Z) \), and \( (Z,Z) \), are defined.

Despite its importance, little attention has been given to the conformational analysis of norbornene polymer and copolymers. Provasoli et al. have determined the conformer populations with the rotational-isomeric-state (RIS) approximation, where the distinct bond dihedral angles are determined by assuming nondistorted norbornene structure with molecular mechanics (MM3) minimization. However, the study also found large conformational differences in the \( -N-N-N- \) or \( -N-N- \) sequence where strong effects arising from distortions of the norbornene rings superposed to the pure conformational effects. Because of this complexity, the \( ^{13}C \) NMR chemical shift calculation was not performed. A similar calculation also concluded that it is not possible to have chemical shift higher than 46 ppm for \( C2 \) and \( C3 \) carbons in all possible conformations in \( -N-E-N-E- \), \( -E-N-E- \), or \( -N-N-N- \) configurations.20
To make qualitative assignment of the shifts in PNB and COC with $-N-N-N-N-$ and $-N-N-$ blocks, simple counting of the $\gamma$-gauche effect is performed, where we have assumed also the norbornene ring is not distorted. The shift calculations are demonstrated in two extreme cases shown in Scheme 4 for the norbornene CH carbons on the main chain (peak 1, designated by the arrow). The strongest $\gamma$-gauche effects are labeled as “s” and the weaker one by “w”. The simple structure model also shows, except for the [G] configurations in NB units, that isotactic PNB experiences unusually high steric hindrance between the adjacent norbornene units (intrachain crowding and strenuous C–C single bond length). Although the catalyst rac-Et(Ind)$_2$ZrCl$_2$ bears a symmetry suitable for isotactic stereoregulation, a low amount of NB block with meso configuration is expected for this reason.

Table 3 lists the number of the $\gamma$-gauche effect calculated for all possible conformations with erythro-disyndiotactic and threo-disyndiotactic triad conformers considered for the 18 possible conformers. The result shows the T[T]T conformer bears three strong and one weak $\gamma$-gauche effect while T[T]T and G[T]G conformers, two strong and one weak $\gamma$-gauche effects on the backbone carbon in norborne (peak 1). Similarly, the G[G][G]G conformer yields the greatest $\gamma$-gauche effects in the X[G][Y] group. Although the final $^{13}$C NMR shift value depends on the exact knowledge of the conformer potential energies, an estimation can still be made by recognizing that the X[G][Y] conformer has a higher potential energy than the X[T][Y] counterpart. This would lead to several resonances centered at two groups with a chemical shift separated slightly larger than one $\gamma$-gauche effect (~2.8 ppm) on the order of 3–4 ppm. This result concurred with the ca. 2–4 ppm shift difference observed experimentally. The T[T]T and G[T]G groups, with the strongest $\gamma$-gauche contribution, is reasonably assigned to the most upfield shift, while the 53 ppm peak is tentatively assigned to T[T]T and G[T]G groups of conformers. Other less populated conformers and possibly the isolated and alternating unit would locate between the two peaks.

Scheme 4 shows the NB rings experience severe crowding, and distortion in the three- and four-member rings on NB is necessary to accommodate neighboring NB units. However, the internal strain within norborne is not likely to create a shift difference as high as 4 ppm, though it can modify slightly the calculated results. On the other hand, the tendency to release the internal strain served as the driving force for the conversion to a least restraint conformer, T[T]G.

Dual-component Gaussian decomposition (shown as the dashed curve) resolves the weight percentage of the two major groups of conformer being T[T]T + G[T]G = 55% and T[T]T + G[T]G = 45%. Similar calculation yields 40% and 60% for run 4 and 20% and 80% for run 3 respectively for T[T]T + G[T]G and T[T]T. A more quantitative calculation can be achieved with a suitable model developed to account for the NB ring internal strain, but for the present purpose, we retain the simplicity of the description to avoid a complicated situation.

For runs 1, 3, and 4, two groups of resonances are more clearly resolved with increasing fraction of block NB, where the NB block content is also high. However, in the case of low NB content (runs 5 and 6, [NB] < 45 mol %), where there are fewer NB block units, the downfield shoulder (at 53 ppm) becomes barely observable for runs 5 and 6. In alternating and isolated structures, cis-2,3-exo enchantment would be the major configuration as reported previously. However, such an enchantment does not predict any shift above 46 ppm, as mentioned previously.

Scheme 5 shows one example of the one-bond conversion from T[T]T into the G[T]T T conformer. In reality, cooperative conversion over several bonds occurs. These conversions are irreversible in the heat–melt cycle since the reverse process faces great resistance from increasing NB internal ring strain. The downfield portion in NMR does not recover either after quenching the annealed sample to liquid nitrogen temperature. In contrast with semicrystalline polymers where melt–
quench cycle retrieves the amorphous state, the stable conformation in COC appears frozen permanently once converted.

Run 3 (high NB content) and PNB (run 1) show similar conversion to the most thermodynamically stable T[T]G conformers with annealing. Nevertheless, complete removal of the T[T]T + G[T]G conformer is not possible, even after extensive annealing. It is plausible that a small amount of X[G]Y conformers or isolated and alternating NB has contributed to these absorptions. Recovery of the less stable conformer from quenching the extensively annealed sample is also not detected for these samples.

**Densification.** In the process of reaching the stable conformation, the persistent length increases and adjacent polymer fibrilar begin to self-assemble into short-range higher ordered arrangements. The net results of local packing are a decrease of the free volume with elevated \( T_g \). Figure 4 shows the \(^{13}\text{C} \) CP/MAS spectrum of run 4 at different stages of thermal treatments. When the original sample (Figure 4a) is annealed for 8 h, the downfield resonance of peak 1 (mainly T[T]T + G[T]G conformers, \( \delta = -53 \text{ ppm} \)) is substantially suppressed (Figure 4b) where the most thermodynamically stable conformation (T[T]G) was identified. Although there is no clear sign of conversion beyond this stage, the densification persists as the \( T_g \) continues to increase until annealing for 200 h (Figure 4c).

Previous wide-angle X-ray diffraction of poly(norbornene) homopolymer by Haselwander et al. found two diffraction peaks located at \( 2\theta = 10^\circ \) and \( 19^\circ \). The large angle scattering is assigned to the norbornene repeating unit, but the smaller diffraction with much larger \( d \) spacing remains unaccounted for. Later, a WAXD study of COC by MacKnight also revealed two halos which become more pronounced when NB content reaches 79 mol \%. The large scattering (\( 2\theta \sim 17^\circ \)) is assigned to the ethylene block and the norbornene alternating sequence, and the low angle peak (\( 2\theta \sim 11^\circ \)) has been assigned to the norbornene block unit since its intensity increases with increasing norbornene content. Closer examination of their results shows the low angle peak shift further to lower diffraction angles with increasing norbornene content. However, none of the studies reported scattering peak shifts with heat treatment. In the current study, X-ray diffraction (Figure 5), using run 4 as an example, also shows resolved double diffraction halos located at \( 2\theta = 20^\circ \) and \( 11^\circ \). Here the norbornene content is lower than that in ref 21. The larger angle scattering (\( d = 3.6 \text{ Å} \)) is attributed to the norbornene and ethylenes repeat unit length, which is consistent with all previous observations. However, the weaker halo at smaller scattering angle (\( d = 12 \text{ Å} \)) sharpens and shifted to higher diffraction angle (\( d = 8.5 \text{ Å} \)) with increasing degree of annealing. The present assignment explains the presence of the low angle peak in Haselwander’s results, since there is no well-defined NB block length in PNB. It also accounts for the gradual lower angle shift with NB content reported by MacKnight since interchain spacing will increase with the presence of a more rigid NB block. Previous assignment of the low angle diffraction being attributed to NB block may be erroneous. The shift to higher angle with annealing readily evidenced that local chain packing in COCs occurred, and the peak sharpening indicated tighter distribution in the interchain spacing with greater ordering. For other COC samples with NB content below 47%, the low angle diffraction is less apparent, and the densification is harder to identify by this measurement. Nevertheless, densification is evidenced from the large \( T_g \) elevation for all COC samples.

The proton spin relaxation time in the rotating frame, \( T_{1pH} \), provides the information regarding the change of dynamics during densification. Based on a crude estimation of proton spin diffusion, this measurement is...
subjected to a limited domain resolution of ~50 Å. Figure 6 shows the variation of $T_1^p$ relaxation time for the COC (run 5) with annealing where the decay is taken from the integrated intensity of signals occurring between 28 and 32 ppm (ethylene CH$_2$ and norbornene CH$_2$ resonances). Two $T_1^p$ exponential decays are apparent at the initial stage of annealing, which gradually coalesce to a single relaxation after annealing. In contrast, DSC shows only single $T_g$ throughout all stages of annealing for all samples. Figure 7 summarized the changes of both $T_1^p$ and $T_g$ (run 5) with annealing. The two dynamic heterogeneous domains identified by $T_1^p$ should therefore be smaller than can be differentiated by $T_g$. The coalescence of relaxation after extended annealing suggested that homogenization in either the composition or the mobility has occurred. Most interestingly, the time where the two relaxation values coalesce coincide with the instant when conformation conversion ceases. Other COC samples (runs 1, 3, and 4) also indicated coalesces of dual relaxation after extended annealing. These observations are not consistent with the possibility of the presence of separated PE-rich and PNB-rich domains (with size larger than 50 Å). Besides, PE crystallization is not found for those samples. The two $T_1^p$'s are more reasonably attributed to domains with different mobility, carrying similar chemical composition. Knowing that the short $T_1^p$ originates from more mobile COC, the result provide the microscopic understanding that extended annealing (run 5, roughly 60% of the mobile fraction and 40% of the rigid fraction) has homogenized chain mobility which led to greater overall rigidity with longer averaged $T_1^p$. This understanding is consistent with the picture that conformation conversion has converted the relatively softer domain to more rigid domain segment and led to the increase of the hard domain fraction. The detailed morphology of micro-domain phase separation on the order smaller than 50 Å would be the subject of a separate study using small-angle neutron scattering techniques.

Figure 8 summarizes with run 4 of the $T_g$ elevation and the change of conformation from $^{13}$C NMR spectra during different stages of annealing. The result suggested that the initial rapid rise of $T_g$ originated from the conformation conversion, which produced longer rigid length with lower entropy in the amorphous polymer, and the subsequent $T_g$ increase corresponds to the densification with more ordered local packing. This phenomenon has not been reported in previous COC studies, possibly due to an insufficient amount of long NB block unit as it is in the current samples, or the densification has already been reached with prior heat treatments.

Since all trans or $T[TG][G]$ chain conformations in COC are not energetically favored (vide supra), crystallization of COC is extremely difficult even in the highly stereoregulated case. This argument is further supported by the understanding that periodical $TTG[G]$ or all $TTT[T]$ conformations in COC, required for crystallization, is difficult if not impossible to reach. The few characteristics associated with the local packing in COC (poly(norbornene-co-ethylene) are sum-
marized: (i) phenomenal glass temperature variations, (ii) dense packing, (iii) conformation ordering, (iv) smaller distribution in interchain spacing, and (v) reduction of the nearest-neighbor COC chain spacing to about 6 Å.11 For polycarbonate-like polymer, the in the nearest-neighbor interchain distance is shortened model where the carbonyl carbon to quarternary carbon the tataional order and has been described by the bundle reduction of the nearest-neighbor COC chain spacing barrier. However, for COC the densification continues after the stable conformation is reached, and there is no apparent τ-flip mechanism available in COC. Furthermore, there are no specific interchain interactions, apart from the fundamental London dispersion force, to adhere the bundle. The possible densification mechanism in COC may involve that proximal NB unit stiffens the chain first by the converted conformation, which reduced the entropy of the nearby fibular rigid segment. The reduction of interchain barrier which leads to the later stage of local packing in COC is not consistent with the cooperative motion given by the bundle model.15 Instead, it is more likely due to random sources achieved through chain diffusion.15 As far as the kinetics is concerned, the later process would be much slower in comparison.

**Conclusions**

Cyclic olefin copolymer (COC), made by ethylene and norbornene catalyzed by ansa-ethylene bis(indenyl) zirconium dichloride (Et[Ind]2ZrCl2)/methyl aluminoxane (MAO), shows higher concentration of norbornene block (−N−N−N− and −N−N−). Annealing has raised the Tg of the nominally amorphous PN and COC’s to nearly 120 and 30–80 °C, respectively. The study shows these COC exhibited conformation conversion which increases the persistent length and facilitated local packing into more ordered morphology. Unlike most amorphous polymers, where conformers are freely converted via rapidly chain orientation, norbornene chain reorientation is highly restricted. Failure to sample all conformations within the NMR time scale produced two resolved groups of resonances at 53 and 49 ppm in the 13C spectrum of the CH carbon in the norbornene unit which are assigned to T[T]T + G[T]G and T[T]G conformers after counting all possible γ-gauche effects. Two separate relaxations coalesce to a longer relaxation component with progressive annealing in T1,11 measurements, suggesting that the local packing has averaged the chain mobility leading to single and more rigid overall structure. The low angle diffraction halos in synchrotron source X-ray data provide direct identification that a contraction in the averaged spacing is reduced from ca. 12 to 8.5 Å, and the distribution of the interchain spacing becomes tighter upon extensive annealing.

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**References and Notes**

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(27) Huang, J. -M.; Chu, P. P.; Chang, F.-C. Polymer 2000, 41, 1741.
(28) Sticky speaking, there is no well-defined trans or gauche conformation for the NB single bond on the main chain. The [T] or [G] symbols are used here for convenience to differentiate the possible geometries in NB as defined in Scheme 1. This conformation for the single bonds adjacent to NB follows the conventional definition.

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