Solid-State NMR Study of Cyclo-Olefin Copolymer (COC)

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ABSTRACT: In this article, we have applied solid-state ^{13}C NMR techniques, cross-polarization/magic-angle spinning (CP/MAS), and single-pulse ^{13}C NMR to characterize the NB conformation of the cyclo-olefin copolymer. The copolymers containing higher NB contents produce more NB blocks according to ^{13}C CP/MAS spectral analysis. In addition, NB-dyad-based conformations are able to induce peak splitting in the region of 49–52 ppm. © 2000 John Wiley & Sons, Inc. J Polym Sci B: Polym Phys 38: 2554–2563, 2000

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INTRODUCTION

Cyclo-olefin copolymer (COC) contains cyclo-olefin and α-olefin monomer units. COC possesses excellent properties: it is totally amorphous and has a density 20% lower than polycarbonate (PC), a high light transparency ($\leq$92% for 100-mm thin film), and a high glass-transition temperature (T_g; $\leq$338 °F).[1] Although the price of cyclo-olefin monomers is about six times higher than the price of acrylate monomers, the lower density and lower moisture absorption aspects or points of COC makes it a potential replacement for polymethyl methacrylate (PMMA) or PC. The excellent optical transparency and low refraction index of COC are also advantages for applications in optical devices and optical fibers. Its potential applications include super twisted nematic displays, high-performance capacitors, and optical disks.

In a previous report, we demonstrated that polynorbornene (PNB) and its copolymer with ethylene (COC) can undergo conformational con-version into a more stable T(T)G conformer from T(T)T and G(T)G by thermal annealing based on the PNB triad sequence.[1] Subsequent chain reordering following the conformational conversion leads to densification of the COC bulk and raises the T_g substantially.[1]

The conformational conversion is the nascent stage for the reordering process of the COC.[1] For the first time, two major chain conformers of COC leading to two groups of solid-state ^{13}C NMR resonances have been observed that correspond to the CH carbon in the norbornene (NB) chain at 53 ppm [T(T)T + G(T)G] and 49 ppm [T(T)G]. Recently, results from the molecular simulation and ^{13}C NMR of COC indicated that only the erythro-diisotactic of the NB configuration can be formed and that the triad NB sequence may not be produced during the polymerization stage.[2]

In this article, we attempt to analyze the ^{13}C NMR cross-polarization with magic-angle spinning (CP/MAS) spectra of PNB and its copolymers with ethylene (COC). The conformational conversion caused by thermal annealing is reflected in the spectra. Because the results obtained for a polymer with an NB content of 47.63 mol % have already been reported elsewhere,[1] this article is a full report of our work on the ^{13}C CP/MAS NMR of the polymers.

Table I. High-Resolution ^{13}C NMR Analysis Results of COCs[a]

Run	NB Content (mol %)	T_g (°C) As Prepared	NB Sequence (mol %)		
			Block	Alternative	Isolate
1	100.0	136.2	100	0	0
3	58.36	102.5	40.16	51.85	7.99
4	47.63[b]	81.3	>50[b]	—	—
5	43.51	86.8	17.33	66.60	16.07
6	24.88	68.1	21.02	51.04	27.98
7	0	<0	—	—	—

[a] Polymerization conditions: ethylene pressure = 20 psi at 70 °C; total volume = 60 mL; [Al]/[Zr] = 8000–4000; catalyst = 1–2 mg.
[b] Estimated from ^{1}H NMR. [3]

EXPERIMENTAL

Material Preparation

COC was polymerized from NB and ethylene with an ansa-metallocene catalyst, Et(Indenyl)$_2$ZrCl$_2$, and a methyl aluminoxide (MAO) cocatalyst.[3–10] The polymerization temperature was controlled at 66 °C with a catalyst/cocatalyst ratio ranging from 3000 to 7000, and the ethylene pressure was maintained at 19–21 psi. The total volume of the system was 60–65 mL during the 2 h of polymerization time. The amount of metallocene catalyst was kept at about 2 mg. Acidic methanol (10 mL) was used to terminate the polymerization. The polymer was precipitated through the addition of an excessive amount of acetone nonsolvent and was dried for 8 h at 50 °C *in vacuo*.

NMR Measurements

The microstructure of the COC polymer was determined by a Bruker ADX-300 solution NMR (ν_C = 75 MHz) with trichlorobenzene as the solvent and C$_2$D$_2$Cl$_4$ as the lock solvent at 70 °C. Solid-state ^{13}C NMR was also performed on the Bruker ADX-300 with strong proton decoupling (H$_1$ = 85 kHz) at ν_C = 75 MHz, with spinning rates of 1.3 and 7 kHz at room temperature.

The NB content and the corresponding microstructure in the COC depend on the feed ratio and the results in the reactivity ratio of the two monomers. Changing the NB feed ratio results in copolymer structures with various NB and ethylene segmental lengths. The microstructure of the NB–ethylene copolymer can be conveniently derived from the high-temperature liquid-state ^{13}C NMR. Following previous ^{13}C NMR chemical-shift assignments,[4–10] we determined the NB content and molar fraction of three main NB-microblock structures (alternative, isolate, and block) and summarized them in Table I.

For ^{13}C CP/MAS NMR experiments, the contact time and the number of scans were set at 1.5 ms and 512 scans, respectively. For single-pulse ^{13}C NMR experiments, the 90° pulse-duration time was set at 3.8 μs, and the recycle delay time was varied from 0.5 to 20 s.

RESULTS AND DISCUSSION

CP/MAS Spectra of Synthesized COCs

Figure 1 shows the solid-state ^{13}C CP/MAS NMR spectra of samples from runs 3–7 together with a liquid ^{13}C NMR spectrum of run 4. The assignments for the major resonances are indicated in the insert corresponding to the backbone carbon (CH, peak 1), bridgehead carbon, (CH, peak 2), and one and two carbon bridges (CH$_2$, peaks 3 and 4). Peaks 1–4 appear at chemical shifts similar to those observed in solution NMR, except that overlapping of peaks 3 and 4 was observed because of poor resolution in the solid-state NMR. The breadth in the solid-state NMR spectrum can be attributed to the strong dipolar–dipolar interaction and the inhomogeneous chemical-shift distribution in the amorphous state. Because we utilized a relatively high decoupling power in the ^{1}H channel, the stronger dipolar–dipolar interaction between protons should be entirely suppressed and the breadth of the ^{13}C peaks should be only caused by the inhomogeneous chemical-shift distribution in the amorphous state.

^{13}C CP/MAS NMR is the most efficient technique for identifying configurations of the polymeric condensed phase.[11–13] Figure 2 shows the
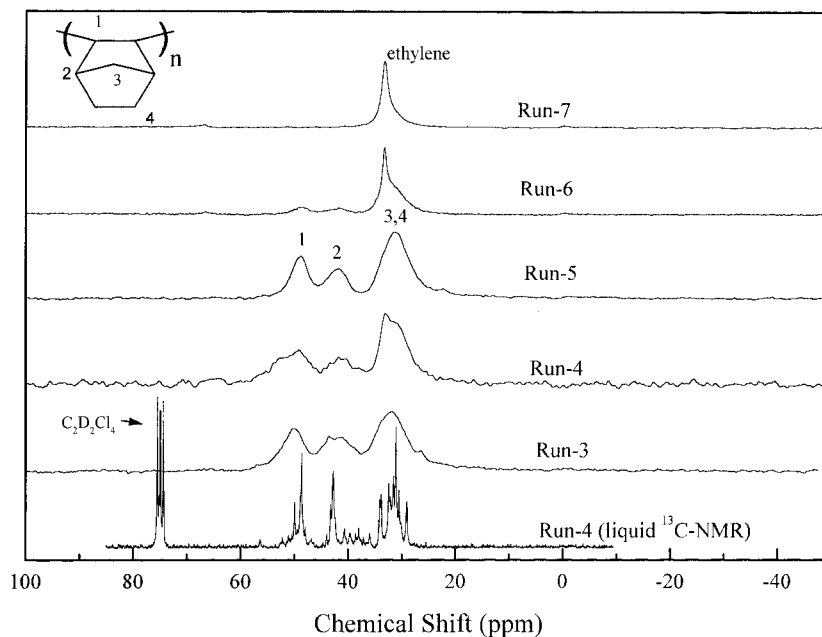
Figure 1.   Solid-state ^{13}C NMR CP/MAS and liquid-state NMR spectra of runs 3–7. The peak near 30 ppm increases with increasing polyethylene content.

^{13}C CP/MAS NMR spectra of run 1 (PNB), run 4 ([NB] = 47.63 mol %), and run 6 ([NB] = 24.88 mol %). In runs 1 and 4, these resonance peaks are only partially resolved. This feature is partic-

ularly prominent for the CH backbone carbons of the NB segment (peak 1) where two major groups of chemical shifts at 49.9 ppm (peak I′) and 53 ppm (peak I′) are identified. The spectrum of run
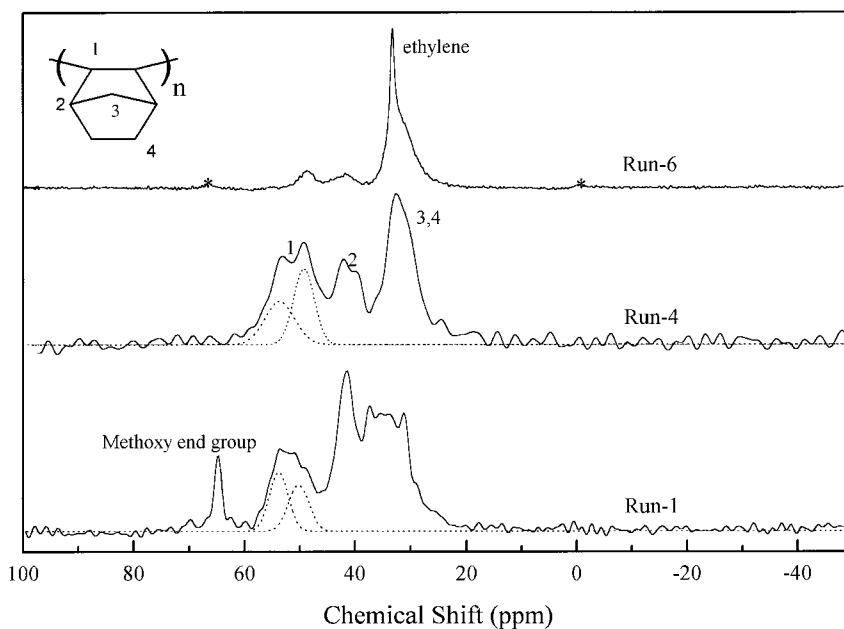

Figure 2.   Solid-state ^{13}C NMR CP/MAS spectra for runs 1, 4, and 6. The assignment is indicated in the insert. The dashed curve represents the best fit with two Gaussian components.
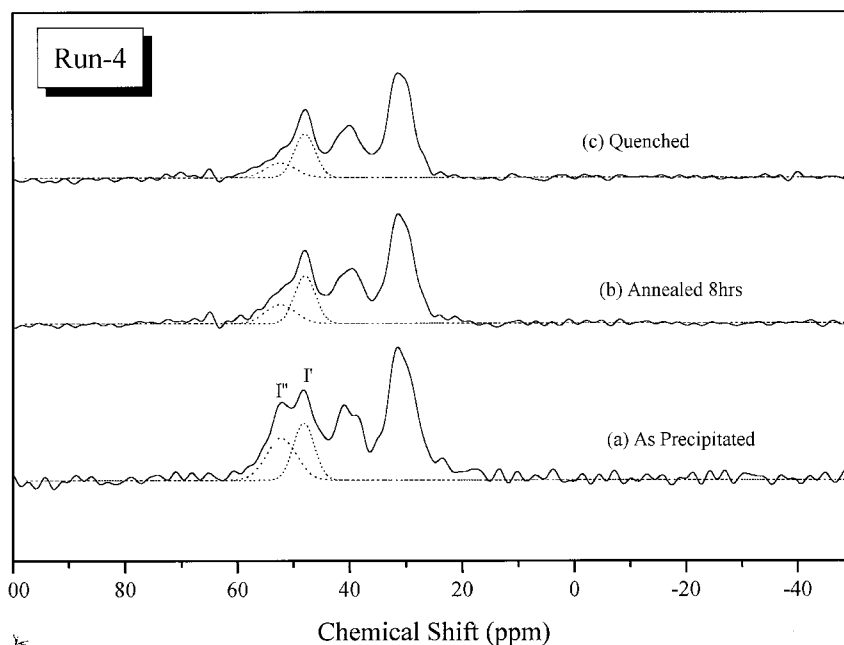
Figure 3. ^{13}C CP/MAS NMR spectra of run 4 with different thermal treatments: (a) as precipitated, (b) annealed for 8 h, and (c) quenched.

4 in Figure 1 looks different from the spectrum of the same sample in Figure 2. The spinning rate used in Figure 1 was 1.3 kHz, and the experiment was performed on our own instrument (6 years old); in Figures 2 and 3, the spinning rate was 7 kHz, and the experiments were performed at a regional instrument center in Taiwan (1 year old) with the same magnetic field strength.

Conformers associated with consecutive single bonds in polymers comprise a variety of chemical shifts and tend to broaden the individual resonances. In an amorphous polymer, the rapid interconversions between conformers leads to an average absorption with breadth that is dependent on the conversion rate. A lower conversion rate results in a broader peak, and a high conversion rate produces a sharper peak. In a few cases, chemical shifts in amorphous and crystalline phases can actually be resolved.[12] The well-resolved spectrum (spaced 2–4 ppm) shown in Figure 2 is rather unusual because the crystalline phase is absent, and only a single resonance is expected from an amorphous polymer. The chemical-shift separation is also too large as the result of a microstructural difference, which is usually less than 1 ppm according to solution NMR.[3,13] The only possible cause of the multiple absorption peaks is those unique conformations that are not completely motion-averaged in the amorphous phase.
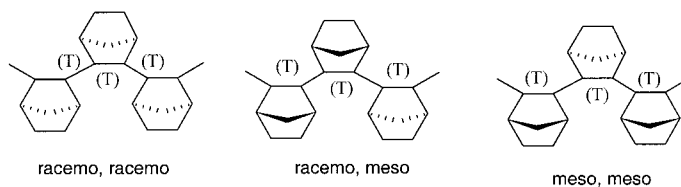
Annealing-Induced Conformation Conversion

For COC samples containing over 47.63 mol % NB (runs 1, 3, and 4), a rapid T_g jump during initial annealing has been observed.[1] In addition, an unusual conformational conversion of the NB segments is also observed during the process of thermal annealing.[1]

Figure 3(b,c) shows the ^{13}C CP/MAS NMR spectrum of run 4 with different degrees of thermal treatment. In Figure 3(b), the original run 4 sample [shown in Figs. 1 and 3(a)] is annealed for 8 h, and the downfield resonance in carbon position 1 is substantially suppressed. The most thermodynamically stable conformation seems to appear at 48–49 ppm. However, the densification process is still in progress as the T_g continuously increases until 200 h of annealing.[1] Through annealing of the sample at about 200 °C (50 °C higher than the final T_g) for 2 h and then rapid quenching by liquid nitrogen, the downfield portion does not recover, as shown in Figure 3(c).

cis-exo /   cis-endo /   exo/endo /
gauche (G)   gauche (G)   trans (T)
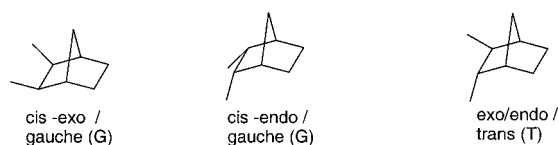
Scheme 1

Scheme 2

Both run 3 (high NB content) and PNB (run 1) show conversions similar to the most thermodynamically stable conformer through thermal annealing.

MODELS OF CHAIN CONFORMATION

Scheme 1 shows the middle NB unit configuration compared to the literature[1,16] assignment of cis-exo, cis-endo, and others. Here, we assign cis as gauche (G) and others as trans (T) conformations. Exo and endo are replaced by (G) and (T) configurations.

Details of Triad-Based and Dyad-Based Conformers of PNB in COC

Because of the high rigidity of the NB ring structure, the six basic conformers of the NB triad microstructure, T(T)T, T(G)T, T(T)G, T(G)G, G(T)G, and G(G)G, are substantially hindered. The parenthetical expression (X) designates the indigenous T or G conformation for the NB unit that has already been determined during copolymerization. Two other C—C bond configurations are the middle NB unit linking to the next ones.
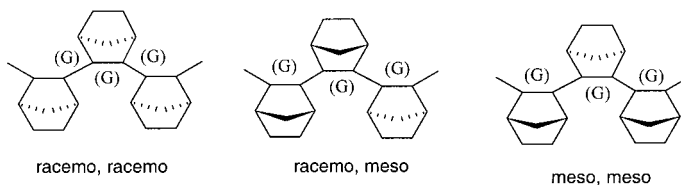
Triad-Based Conformers of PNB

Typical configurations of syndiotactic PNB and isotactic PNB-based NB unit triads are shown in Schemes 2 and 3. The tacticity of the three-member ring is considered erythro (E) and thre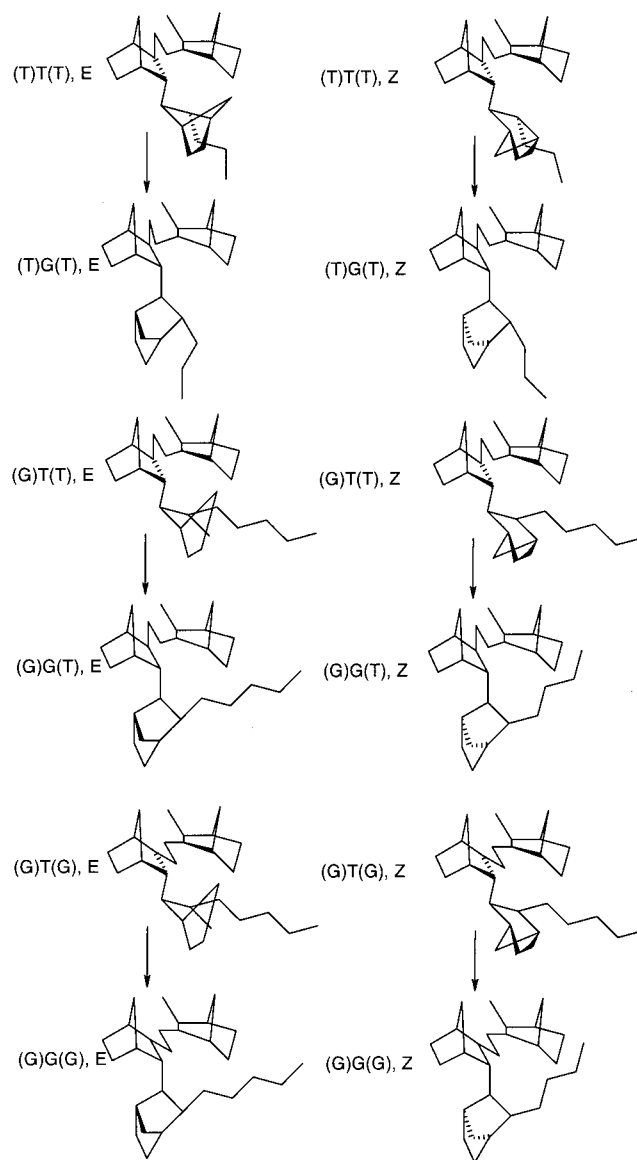o (Z) for the NB-dyad unit according to the usual assign-ment of meso (m) and racemo (r) configurations in the literature.[2,5–7] Three possibilities, (E, E), (E, Z), and (Z, Z), are present for the NB triad unit. It is infeasible that a syndiotactic PNB chain has all (G) configurations and an isotactic PNB chain has all (T) configurations. The sample possesses all possible chain conformations and leads to an incomplete average of conformations in the solid state. This causes the observed multiple absorption peaks instead of a broad and partially averaged amorphous resonance.
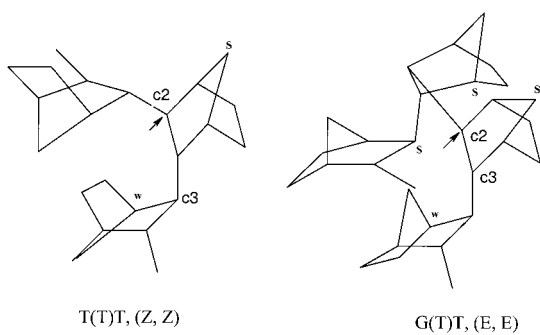
Dyad-Based Conformers of PNB

The basic conformers based on the NB-dyad microstructure are (T)T(T), (T)G(T), (T)T(G), (T)G(G), (G)T(G), and (G)G(G). Again, the parenthetical expression (X), designated the indigenous (T) or (G) configuration for the NB unit, has already been determined during copolymerization. The middle C—C bond configuration is the connection between two NB units. The tacticity of the three-member ring considers only the erythro (E) and threo (Z) for erythodisyndiotactic and erytho-diisotactic PNB sequences. These conformers' interconversions are demonstrated in Scheme 4. To match the identified peak with a particular conformer, simple chemical-shift calculations, through consideration of the γ-gauche effect of only the C—C single bonds of these CH carbons, are performed. Scheme 5 illustrates the counting method of the number of the γ-gauche effect. Table II lists the number of the counted γ-gauche effect on conformations of all erythrodisyndiotactic and threo-disyndiotactic triad conformers. Due to the NB

Scheme 3

(T)T(T), E   (T)T(T), Z

(T)G(T), E   (T)G(T), Z

(G)T(T), E   (G)T(T), Z

(G)G(T), E   (G)G(T), Z

(G)T(G), E   (G)T(G), Z

(G)G(G), E   (G)G(G), Z

Scheme 4

T(T)T, (Z, Z)   G(T)T, (E, E)

Scheme 5

internal strains from great hindrance between norbornene units, intrachain crowding and too short C—C sing bond length of the main chain in forming the (G) conformers, the contribution of (G) conformers to the ^{13}C-NMR intensity is negligible. Table III lists the number of the counted γ-gauche effect on conformations of all erythrodisyndiotactic and threodisyndiotactic dyad conformers. Strong and weak gauche effects are different in the degree of interaction between two gauche carbons. Two gauche carbons having a 60° gauche angle is called a strong effect, whereas gauche carbons having a 120° gauche angle is called a weak effect.

Table II.   γ-Gauche Effect for All Possible NB Triad Configurations

| Tacticity	Ring Tacticity	Conformer	Number of γ-Gauche Effect (Strong/Weak)
Syndiotacticity	(E, E)	T(T)T	2/1
	(E, Z)		1/1
	(Z, Z)		1/1
	(E, E)	T(T)G	3/1
	(E, Z)		3/1
	(Z, Z)		3/1
	(E, E)	G(T)G	2/1
	(E, Z)		2/1
	(Z, Z)		1/1
	(E, E)	T(G)T	1/1
	(E, Z)		2/1
	(Z, Z)		1/1
	(E, E)	T(G)G	1/1
	(E, Z)		1/1
	(Z, Z)		1/1
	(E, E)	G(G)G	2/1
	(E, Z)		2/1
	(Z, Z)		2/1

The isotacticity of NB is not favored in our results.

Conformation Conversion of Triad Conformers

From Table II, the T(T)G conformer has the expected three strong and one weak stronger γ-gauche effects, whereas the T(T)T or G(T)G conformer has the expected two strong and one weak

γ-gauche effects. The γ-gauche effect has been estimated to be about 5.0 ppm for CH carbons in the polymer crystalline or glassy state.[12,13] A considerable conversion between trans and gauche conformations reduces the value to about 2.3 ppm

Table III.   γ-Gauche Effect for All Possible NB Dyad Configurations

Tacticity	Ring Tacticity	Conformer	Number of β-Gauche Effect (Strong/Weak)	Number of γ-Gauche Effect (Strong/Weak)
Syndiotacticity	E	(T)T(T)	—	—
	E	(T)G(T)	—	—
	E	(G)T(T)	—	—
	E	(G)G(T)	—	—
	E	(G)T(G)	—	—
	E	(G)G(G)	—	—
Isotacticity	Z	(T)T(T)	C2: 1/1	C2: 1/0
			C3: 1/0	C3: 2/1
	Z	(T)G(T)	C2: 1/0	C2: 0/1
			C3: 1/0	C3: 1/1
	Z	(G)T(T)	C2: 1/0	C2: 1/0
			C3: 0/0	C3: 0/0
	Z	(G)G(T)	C2: 1/0	C2: 0/1
			C3: 0/1	C3: 0/2
	Z	(G)T(G)	C2: 2/1	C2: 1/0
			C3: 1/0	C3: 1/1
	Z	(G)G(G)	C2: 0/0	C2: 1/1
			C3: 0/0	C3: 0/3

T(T)T, (E, E)   G(T)T, (E, E)
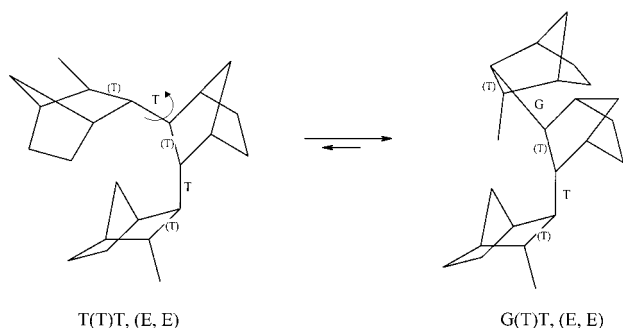
Scheme 6

in the rubbery state.[14] We should predict about a 5-ppm chemical-shift difference between the T(T)G and T(T)T+G(T)G conformers on the basis of only one stronger γ-gauche effect difference. The experimental observation is about a 4.0-ppm chemical-shift difference. Because the conformer of the NB ring (T conformer favored only in the NB triad) has already been fixed during the polymerization process, the conformation conversion takes place only through the rotation of the C—C single bonds adjacent to NB rings. Thermal annealing provides the necessary activation energy for conversion in the condensed phase. Such a conversion is shown in Scheme 6. The chemical-shift difference may be caused by these two ef-

fects. The substantial motional averaging is inhibited because the measurement temperature is far lower than the T_g of the polymer, and the state of the polymer could be seen in glassy state. However, the γ-gauche effect would be weakened by a light equilibrium trans–gauche conversion between NB units that is caused by polymer local motion of the chain (sub-T_g transition) even under the T_g of the copolymer.

Conformation Conversion of Dyad Conformers

From Table III, an approximately 4-ppm chemical-shift difference between the (X)T(X) and (X)G(X) conformers based on the NB dyad is predicted. This result is consistent with the 4-ppm chemical-shift difference observed experimentally. The assignment of the (X)G(X) conformer is based on the 4-ppm downfield peak (located at 49–53 ppm) due to the stronger γ-gauche and β-gauche effects[2] of the (X)T(X). Such a conversion is shown in Scheme 7. The β-gauche effect is related to all carbons via two bonds in comparison to the γ-gauche effect. Based on a theoretical calculation, the population of NB trimer is scarce because of its high instability.[14] Therefore, we correct our previous assignment[1] to Scheme 7. The conversion by an inter-NB ring bond is the
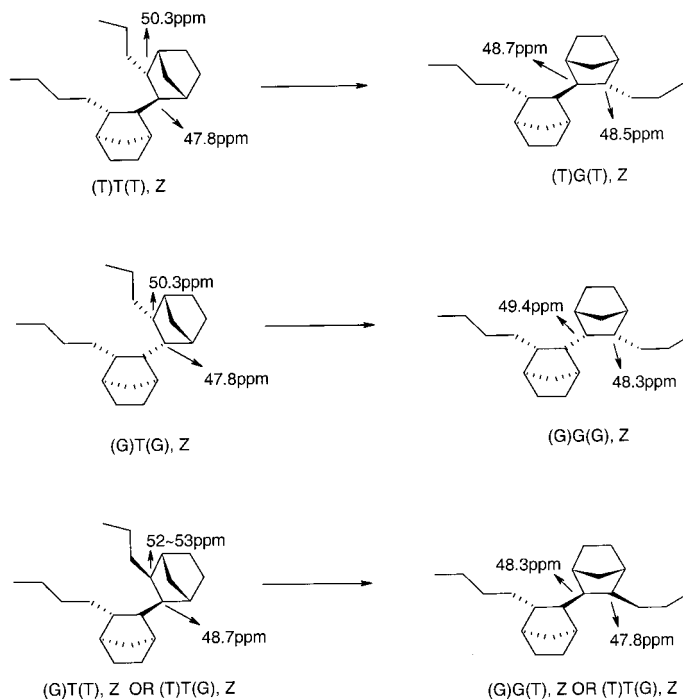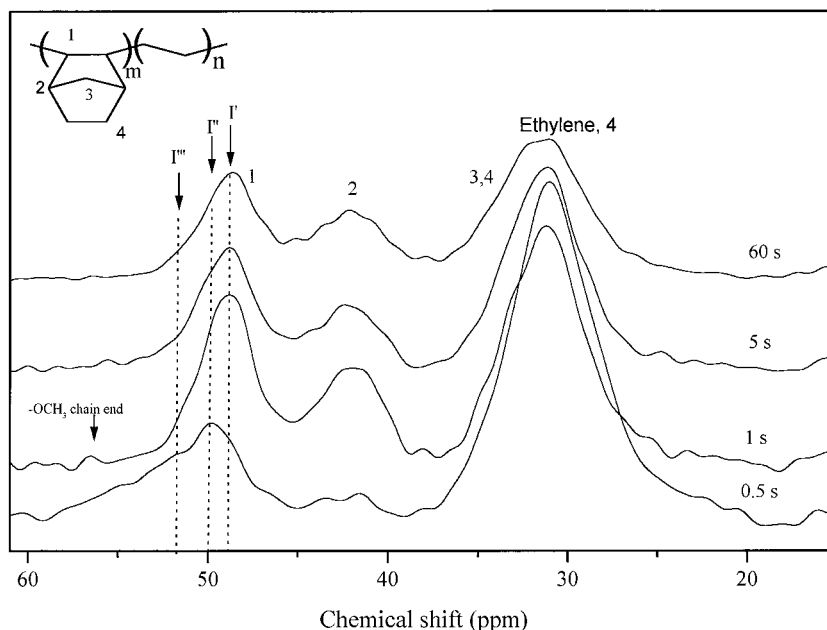

Scheme 7

Figure 4. Series of single-pulse ^{13}C MAS NMR spectra of COC with various recycle delay times.

same in both triad and dyad models. The main difference is their relative abundance in the copolymer; on the basis of our liquid-state NMR data and the literature,[2–10] it is impossible to conclude that the NB trimer is indeed present. However, a complete absence of the downfield peak is unlikely even under the maximum annealing condition; a residual downfield resonance peak is still present. Because the COC sample does not reach a melt state at the annealing temperature and the densification process is irreversible, recovery of the less stable conformer (peak I″) via quenching of the extensively annealed sample (annealed at T_g + 100 °C) is also unobtainable until the sample is recovered freshly from solution.

Single-Pulse ^{13}C NMR of COC

We have searched relative publications about two-dimensional exchange experiments and have found that single-pulse experiment can be used to check the exchangeable signals.[15] Therefore, we ran the same experiment and tried to determine the possibility of similar behavior. The ^{13}C CP/MAS NMR spectra of run 5 shown in Figure 1 do not trace the existence of the conformation of PNB. Figure 4 shows the single-pulse ^{13}C CP/MAS NMR spectra with different recycle delay

times on COC with 23.6 mol % NB and a T_g at 89 °C (run 5). Two additional peaks (peaks I″ and I‴) can be detected and may correspond to other conformers from PNB in the copolymer according to our previous observation.[1]

These new resonance peaks can be traced in the single-pulse MAS experiment for the following reasons. The single-pulse experiment can only observe a very mobile component with a very short spin–lattice relaxation time of carbon (T_1^C). The very mobile component cannot be observed in normal CP/MAS spectra because of its inefficiency in cross-polarization and quick decay in magnetization before the free induction decay acquisition. Because the NMR measurements were performed at room temperature (which is lower than the T_g of the polymer, 89 °C), in the major component there should be a T_1^C much longer than 5 s (peak I′). The new peaks have a shorter T_1^C relaxation time (peaks I″ and I‴) in the region ranging from 50 to 53 ppm during cross-polarization. As shown in Scheme 6, peaks at 50 and 53 ppm represent the (T)T(T) and (G)T(T) conformations, respectively. Converted conformations with (T)G(T) and (G)G(T) have similar chemical shifts in the range of 48–49 ppm. This is why three peaks have been detected by the single-pulse ^{13}C NMR pulse spectrum.

CONCLUSIONS

We have presented solid-state ^{13}C NMR spectra of PNB–polyethylene copolymers and have demonstrated that the conformation based on the NB-dyad structure may involve conformation conversion when the sample is annealed above its T_g. ^{13}C CP/MAS NMR spectra from copolymers of different NB contents show that the higher NB-containing copolymer possesses more NB blocks. Results also show that the NB-dyad-based conformation is able to induce peak splitting in the region of 49–52 ppm in the COC main chain. The conformation conversions of (T)T(T) to (T)G(T) and (G)T(G) to (G)G(G) will cause a chemical-shift change similar to that in the triad-based conformers.

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