polymer

Polymer Communication

Conformational conversion and chain ordering in cyclo olefin copolymer (COC)

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Abstract

Polynorbornene (PNB) or cyclo olefin copolymer (COC) can undergo conformational conversion into the more stable $T(T)G$ conformer from $T(T)T$ and $G(T)G$. The conversion constitutes the nascent stage for the reordering process of the COC. Interconversion between two major chain conformers leads to two groups of ^{13}C NMR resonances corresponding to the CH carbon in the norbornene chain at 53 ppm ($T(T)T + G(T)G$) and 49 ppm ($T(T)G$). Chain reordering following the conversion leads to the condensation of the COC bulk and raises its T_g, substantially. The presence of random PE segment not only improves its segmental motion but also facilitates the conversion into the most stable $T(T)G$ conformation. © 1999 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Copolymerization of norbornene (NB) with ethylene leading to cycle olefin copolymer (COC) with unique physical properties has been reported [1–4]. These products, with highly optically transparent high T_g (glass transition) and high T_d (decomposition temperature), become a potential replacement of polycarbonate as an engineering plastic. Increase of ethylene contents in the COC results in higher melt-flow rate, and can be processed like most thermoplastics in extrusion and injection moulding. Several microstructure characterizations have been reported for the COC using solution NMR, and confirmed that the micro NB block can be controlled by different metallocene catalysts [5]. However, issues regarding the conformation, chain mobility, ordering and crystallization in the solid phase remain unclear. In the present study of COC with long NB block and the polynorbornene (PNB) homopolymer, solid state ^{13}C NMR shows finely resolved spectra for the amorphous COC varying with thermal annealing. In addition, we have also discovered a phenomenal increase of COC T_g ($\sim$70°C) after thermal annealing. This conformational conversion promotes the reordering of the amorphous COC that is believed to be responsible for its drastic T_g change. Relevancy of the conformational conversion with PE segments is also present.

2. Experimental

Polymerization condition was carried out under 20 psi ethylene pressure at 70°C. Total reactant volume was 60 ml with [Al]/[Zr] ratio 8000~4000 using 1–2 mg of catalyst [6]. Microstructure of the COC polymer was determined by solution ^{13}C NMR (ν_C = 50 MHz) using the trichlorobenzene (TCB) as solvent and the $C_2D_2Cl_4$ as the lock solvent at 70°C. Based upon previous studies, the catalyst family with C_2 symmetry is likely to produce a syndiotactic stereo-regulation for norbornene monomer [7]. Thermal transition temperature was determined by the second DSC scan (Perkin–Elmer DSC-7) using a heating and cooling rate of 10°C/min. The scanning temperature was limited from 30 to 300°C to avoid possible degradation. First run removed residual solvent and the large voids of the solvent recovered sample. Solid state ^{13}C NMR are performed with strong proton decoupling (H_1 = 85 kHz) at ν_C = 100 MHz, with spinning rate close to 8 kHz.

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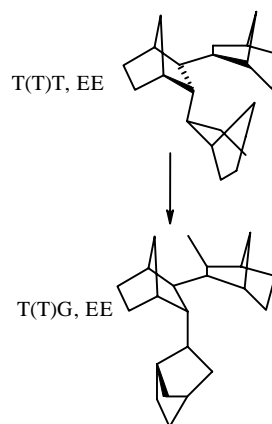*E-mail address:* fcchang@cc.ntcu.edu.tw (F.C. Chang)

Table 1
Characterization of the cyclo olefin copolymer

NB content (mol%)	T_g (°C) before annealing	T_g (°C) after annealing
47.63	81.3	154.5

3. Results and discussion

Characterizations of the COC polymer using 47.63 mol% of norbornene (NB) are summarized in Table 1. For most amorphous polymer, interconversion frequencies among conformers determine the breadth of their ^{13}C resonances. Rapid reorientation and conformational interchange lead to sharper averaged resonance, while the slower reorientation gives rise to a broader line width. In the case of COC with long PNB block length, or in the PNB homopolymer, its CP/MAS spectrum is broader than most amorphous polymers, and the resolved resonances correspond to two major conformers as shown in Fig. 1(a). These results are rather unusual for an amorphous polymer, since a single resonance is normally expected from a chemically distinctive carbon. These two peak gives clear splitting from 2 to 4 ppm which is considered too large by a simple tacticity difference (usually fewer than 1 ppm) [8]. This split-feature is particularly prominent in the well resolved region (chemical shift of 49–53 ppm) corresponding to the CH backbone carbons attached to the NB.

The conformations of *trans* (T) and *gauche* (G) conformers of the backbone single bond in NB ring are actually predetermined during polymerization. Only those single bonds next to NB ring are able to rotate within the triads of the NB structure. Molecular model representing the interconversion of T(G)T to T(T)G conformation is shown in Scheme 1. However, the rigid nature of the NB makes such T–G conversion relatively difficult. The conversion among these basic T(T)T, T(G)T, T(T)G, T(G)G, G(T)G
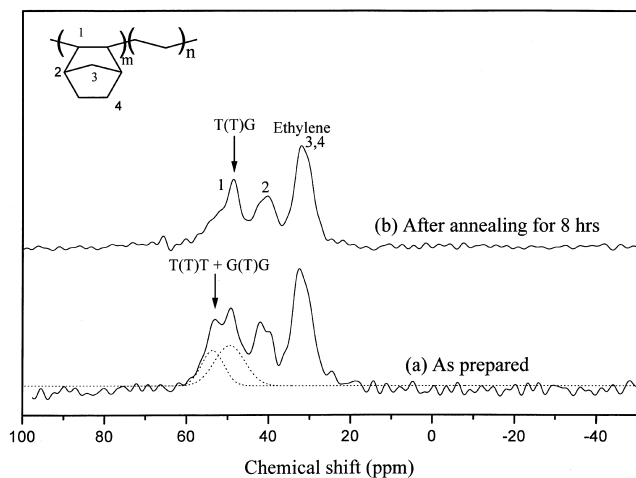

Fig. 1. NMR CP/MAS spectrum of COC with different thermal treatment: (a) as precipitated; (b) after annealing for 8 h.

Scheme 1.

Table 2
γ-*gauche* effect calculation results of COC

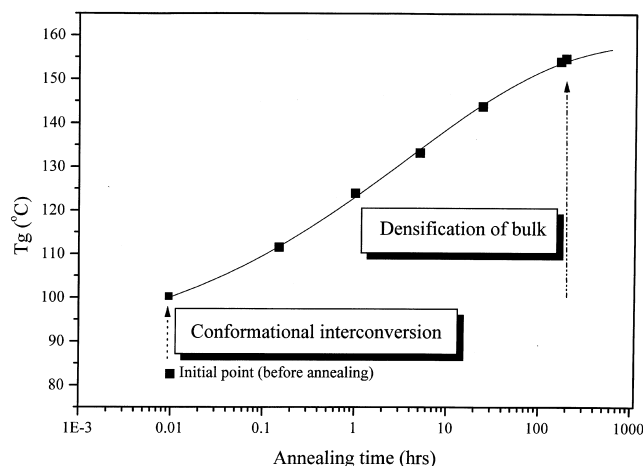| Tacticity	Ring's tacticity	Tetrad conformation	No. of γ-*gauche* effect (strong/weak)
Syndio-	EE	T(T)T	2/1
	EZ		1/1
	ZZ		1/1
	EE	T(T)G	3/1
	EZ		3/1
	ZZ		3/1
	EE	G(T)G	2/1
	EZ		2/1
	ZZ		1/1
	EE	T(G)T	1/1
	EZ		2/1
	ZZ		1/1
	EE	T(G)G	1/1
	EZ		1/1
	ZZ		1/1
	EE	G(G)G	2/1
	EZ		2/1
	EZ		2/1
Iso-	EE	G(T)G	2/1
	EZ		2/1
	ZZ		2/1
	EE	G(G)G	Unfavor
	EZ		Unfavor
	ZZ		Unfavor
	EE	T(T)G	2/1
	EZ		2/1
	ZZ		2/1
	EE	T(T)T	2/1
	EZ		2/1
	ZZ		2/1
	EE	T(G)T	Unfavor
	EZ		Unfavor
	ZZ		Unfavor
	EE	G(G)T	Unfavor
	EZ		Unfavor
	ZZ		Unfavor

Fig. 2. T_g increases with increasing annealing time of COC.

and $G(G)G$ conformers, is substantially hindered. As a result of the difficulty to freely convert among conformers, a multiple absorption line instead of a broad and partially averaged amorphous resonance is detected for a single, but structurally distinct carbon.

A simple chemical shift calculation by considering the γ-*gauche* effect for the C–C single bond of these CH carbons (ca. -2.3 ppm) [9], predicts about 4 ppm chemical shift difference between the $T(T)G$ and $T(T)T + G(T)G$ conformers. The assignment of this $T(T)G$ conformer as the relatively up-field (4 ppm) peak is based on the stronger γ-*gauche* effect (3 strong plus 1 weak *gauche*) compared with the $T(T)T$ (2 strong plus 1 weak) or $G(T)G$ (2 strong plus 1 weak) conformer (Table 2). Because $T(G)T$, $T(G)G$ and $G(G)G$ conformers possess higher internal strain, the contribution from (G) form is less significant, and its contribution to the NMR peak intensity is less prominent. For the same reason, the isotactic stereo-regulation of NB microblock is unfavorable. In addition, the strong *gauche* effect is the dominant factor to stabilize these two major conformers. It is worthy to notice that the ethryl-tacticity of the bridge carbons on the ring have little effect to the conformer's chemical shift.

It is important to know how many conformers possibly exist in the COC and which one bears the lowest conformational energy. Table 2 lists the results of calculated γ-*gauche* effect from various possible conformations by considering all erythrodiisotactic and erythrodisyndiotactic triads conformers [7]. Peak decomposition shown in the dashed traces of the Fig. 1(a) results in weight percentage of $T(T)G = 60\%$ and $T(T)T + G(T)G = 70\%$ of the COC as prepared. These three most plausible conformers are assumed to be kinetically stable at ambient conditions. Upon annealing, the sample at a temperature 15°C above its T_g for 8 h, the down field resonances (~53 ppm mainly $T(T)T$ and $G(T)G$ conformers) are substantially suppressed (as shown in Fig. 1(b)). This result provides strong and direct evidence that the split-resonances originate from

different conformers, and the change is associated with the conformational conversion. Apparently, the thermal treatment facilitates such a conformational conversion among these conformers. Nevertheless, complete conversion to $T(T)G$ peak can not be achieved even after prolonged annealing (over 200 h), as evidenced by the remaining small peaks.

On the contrary, for the COC containing longer PE segment, the down field peak is completely missing [10]. COC sample with a different treatment by annealing, quenching from high temperature and recovery from solution, all results in negligible change in their NMR patterns. It appears that the PE segments in COC, lower the activation energy for the conformational conversion, making PNB segments easier to convert into the most thermodynamically stable $T(T)G$ conformer. Understandably, the chemically fused PE provides greater chain flexibility relative to a long NB block, and facilitates the conformational interconversion. The COC with a high PE content tends to produce mostly the $T(T)G$ conformer that posses higher ordering in chain packing, and T_g increase with annealing. This implies that the main chain reordering occurs in both cases, regardless of the conformational conversion.

Compared with COC, other polymers such as sPS, PP and PET, a single and averaged amorphous peak are usually detected for a chemically distinctive carbon. The conformational interconversion is much easier to achieve due to a low strict chain rigidity. Fig. 2 shows a dramatic T_g increase in the annealing time that is directly related to the extent of the conformational conversion. This phenomenon can be interpreted as the result of the densification of COC main chain following the conformation conversion [11]. Such behavior is quite unique of the COC, and has rarely been observed in other less rigid amorphous polymers.

It is reasonable to conclude that the conformational conversion promotes the reordering process in the COC. Increasing degree of ordering will eventually lead to crystallization. However, it is unlikely for the COC to exist as $T(T)G(G)$ or all trans $T(T)T(T)$ conformations [11] to crystallize. It is unlikely for the adjacent NB unit to have (T) and (G) conformers either alternatively or continuously. In other words, these conformers can not be freely changed with thermal treatment after the polymer is produced.

In summary, we have detected for the first time the existence of the non-averaged conformers in an amorphous COC and the conformational conversion among different conformers in the COC has evidently demonstrated. We believe that the same phenomena may occur in other more bulky main chain copolymers. PNB or COC with long PNB block can undergo conversion to the more stable $T(T)G$ conformation from $T(T)T$ and $G(T)G$, initiated by annealing followed by reordering into a more stable and more densely packing. In contrast, those poly(cyclopentene) based copolymer shows only averaged conformations, which are relatively easier for the conversion between the *cis* conformer on the ring to the more stable *trans* conformer. Similarly,

the presence of random PE segments improves the segmental motion and facilitates the conversion to the most stable $T(T)G$ conformation.

Acknowledgements

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