

Effects of Microstructures on the Viscoelastic and Rheological Properties of Metallocene-Catalyzed Cyclo-Olefin Copolymers: A Preliminary Study

Hsi-Hsin Shih, Po-Ling Shiao, Hsiu-Chin Hsu, Hsin-Ju Liu, Chi-Jou Huang, Chin-Chin Tsai

Union Chemical Laboratories, Industrial Technology Research Institute, 321 Kuang-Fu Road, Section 2, Hsinchu, Taiwan 300, Republic of China

Received 1 May 2001; accepted 25 March 2002

ABSTRACT: We characterized metallocene-catalyzed cyclo-olefin copolymers (mCOCs) with similar heat distortion temperatures but dramatic differences in melt-flow indices to understand how the molecular conformation affected their rheological and viscoelastic properties. The mCOC conformations were identified with ^{13}C -NMR, whereas the viscoelastic and rheological properties were measured with cone-and-plate and high-pressure capillary rheometers. Our preliminary results showed that the mCOC rheological and viscoelastic properties might depend strongly on the conformation rather than the norbornene content, molecular

weight, and molecular weight distribution. mCOCs containing -NNN- locks (where N represents norbornene) exhibited stronger molecular entanglements than those having no -NNN- blocks, as reflected in lower crossover frequencies and higher crossover torque. Furthermore, the existence of larger rigid -NNN- blocks resulted in higher molten viscosities and flow activation energies. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 3695–3701, 2002

Key words: viscoelastic properties; rheology

INTRODUCTION

Cyclo-olefin polymers (COPs), possessing high glass-transition temperatures (T_g 's) and, therefore, improved heat resistance, have been on the market for many years. Such high-heat-resistance polymers are manufactured by ring-opening polymerization (Arton from Japan Synthetic Rubber (Japan) and Zeonex from Nippon Zeon, Japan) and by vanadium-catalyzed addition copolymerization with ethylene (Apo and Apel from Mitsui, Japan). Because of their amorphous nature and excellent optical properties, COPs can be applied for optical uses.

Recently, the metallocene catalyst technology developed by Kaminsky et al.¹ was successfully incorporated into linear and cyclo-olefins; the resulting copolymers are called metallocene-catalyzed cyclo-olefin copolymers (mCOCs) to distinguish between the catalysts used. Unique properties of mCOCs have been reported.² mCOCs also have excellent optical properties, low water absorption, and various T_g 's and are becoming potential replacements for polycarbonates, especially in high density digital versatile disk applications. In addition, more options for tailor-making

the properties of copolymers with metallocene catalysts are becoming possible. For example, Ticona (Germany) first introduced to the market several mCOCs² with a broad range of heat distortion temperatures (HDTs).

Knowledge of the microstructure–rheology–property relationship is important and essential for polymer synthesis and application, especially for metallocene-catalyzed polymers [metallo-catalyzed polyethylene, metallocene-catalyzed ethene/propene/5-ethylidene-2-norbornene (mEPDM), and mCOC]. Studies have been conducted to explore the rheology and properties of mPE and mEPDM with respect to their microstructures.^{3–9} The rheological properties of molten polyethylene homopolymers and copolymers have been shown to depend on the molecular composition, including the molecular weight and molecular weight distribution [MWD, or the ratio of the weight-average molecular weight to the number-average molecular weight (M_w/M_n)], as well as the molecular structure, short-chain and long-chain branching, and distributions. Short-chain branching has little effect on the rheological properties, whereas long-chain branching greatly influences the rheological properties.³ Furthermore, the properties of polyethylene copolymers are dominated by the type of composition distribution rather than the overall content of branching.⁴

Moreover, it is known that the melt viscosity of mEPDM is affected by the amount of the termonomer, that is, 5-ethylidene-2-norbornene, which is the most rigid among the three comonomers. Rigid polymers

Correspondence to: H.-H. Shih (hhshih@itri.org.tw).

Contract grant sponsor: Ministry of Economic Affairs (Taiwan, Republic of China).

TABLE I
Characteristics of mCOCs

	HDT (°C)	MVR ^a (mL/10 min) at HDT + 115°C, 2.16 kg
mCOC-5	130	25
mCOC-6	130	6
mCOC-3	150	5
mCOC-4	170	5

^a *MVR = melt volume flow rate.

have higher melt viscosities than flexible polymers of similar molecular weights, and any factors that increase T_g tend also to increase the melt viscosity.⁵

mCOC microstructures have been characterized with high-resolution NMR by many researchers,^{10–17} although a complete understanding of these microstructures has so far not been achieved. This is at least partially due to the complexity of the ¹³C-NMR spectra and difficulties in the peak assignments of the mCOCs. Furthermore, how the microstructure affects the rheological and viscoelastic properties of mCOCs is rarely discussed. Recently, mCOC storage moduli were found to be dependent on their sequence distributions, alternating or random, without any further explanation given.¹¹ In this article, we present preliminary results aimed at understanding, from a molecular standpoint, how ethylene and norbornene compositions and their distributions affect the rheological and viscoelastic properties of mCOCs.

EXPERIMENTAL

Materials (mCOC-6 and mCOC-5 with similar HDTs and mCOC-3 and mCOC-4 with higher HDTs than

that of mCOC-5) from Ticona Co. were used in this study, and their characteristics² are listed in Table I. The molecular weights and MWDs of the mCOCs were determined with gel permeation chromatography (GPC) with a Waters Styragel (USA) HT column working at 140°C with 1,2,4-trichlorobenzene as a solvent.

¹³C-NMR spectra were obtained with a Bruker (Germany) AMX400 spectrometer with a 10% solution in 1,2-dichlorobenzene-*d*₄/trichlorobenzene (1/2 v/v) at 100°C in 10-mm NMR tubes, and they were referenced to 2.03-ppm hexamethyldisiloxane. The spectra were recorded with an inverse-gated pulse sequence and a 45°C pulse with an 8-s delay.

The mCOCs were first dried at 100°C for 4 h, compression-molded to a thickness of 1 mm at 250°C for 10 min, and cooled to the ambient temperature. Samples 25 mm in diameter, 5 mm wide, and 20 mm long were cut for experiments to determine the molten and solid viscoelastic properties. Storage and loss moduli, as well as loss tangents ($\tan \delta$), measured with a thermal mechanical analyzer (PerkinElmer (USA) 7 series) with the three-point bending method, were recorded at 1 Hz and at 2 and 5°C/min rates.

The molten viscoelastic mCOC properties were obtained with a parallel-plate rheometer (Physica (Germany) UDS200). Samples were proceeded at a 2% strain, 3 Hz, and 20°C/min for temperature-sweep measurements. Frequency-sweep experiments were performed at 0.1–10 Hz and 2% strain. The mCOC molten shear viscosities were obtained with a high-pressure capillary rheometer (Gottfert (Germany) 2003) at various temperatures and shear rates.

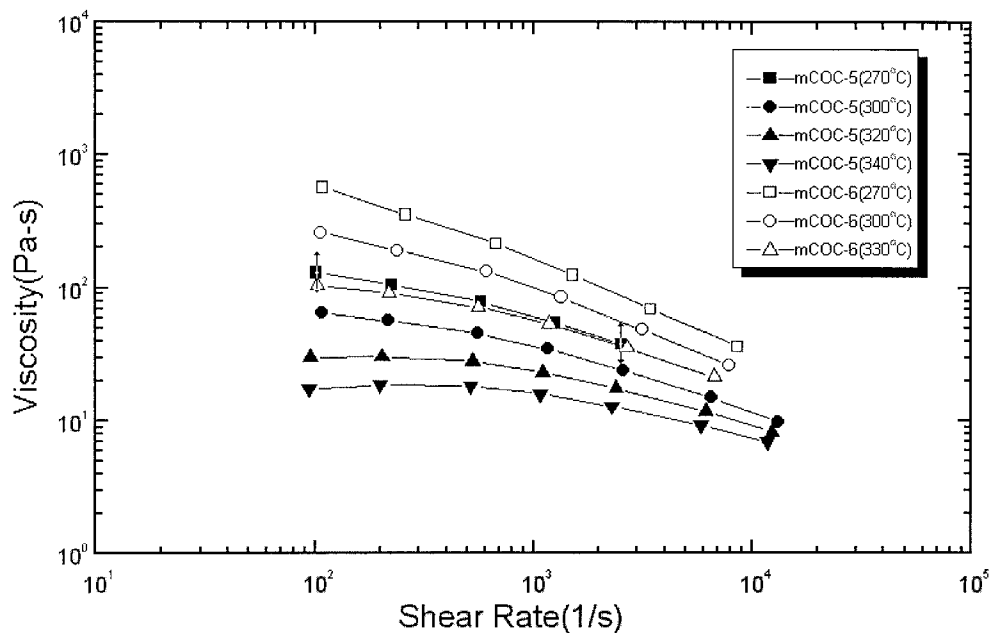


Figure 1 Molten viscosities of mCOCs measured at various temperatures and shear rates.

TABLE II
Viscosity Parameters of mCOCs

	τ^* (Pa)	n	B_0 (Pas)	E_a (cal/g mole)	Measurement range ($^{\circ}$ C)
mCOC-5	7.79×10^4	0.271	2.51×10^{-6}	1.95×10^4	270–340
mCOC-6	9.55×10^4	0.251	9.04×10^{-8}	2.52×10^4	270–330

n = power law index; B_0 = cross model constant.

RESULTS AND DISCUSSION

Rheology and viscoelastic properties of mCOC-5 and mCOC-6

Rheological studies give us some molecular insights into interpreting polymer flow behaviors. Figure 1 shows plots of the viscosities of mCOC-5 and mCOC-6 measured with a high-pressure capillary rheometer at various temperatures and shear rates. As expected, mCOC-5 had lower molten viscosities at various test temperatures and shear rates. Because of an instrument limitation, viscosities in the lower shear rate regions, that is, the regions in which MUR was conducted, could not be detected. However, differences between the two mCOCs at those lower shear rate regions could be distinguished. mCOC-5 and mCOC-6 viscosities versus the temperatures and shear rate were fit into a cross model¹⁸ with a nonlinear regression method to further clarify the rheological phenomena, and the constants for the cross model are listed in Table II. mCOC-5 had a smaller activation energy (E_a) and crossover torque (τ^*) than mCOC-6.

Viscoelastic properties of mCOC-5 and mCOC-6 in the melting state

Viscoelasticity demonstrates polymer molecular responses to the polymer being subjected to external forces. The storage modulus is an index of energy recovery, that is, elasticity, whereas the loss modulus demonstrates the energy dissipation, that is, viscosity. The viscoelasticities of mCOC-5 and mCOC-6 were determined at lower shear rates and strains; therefore, these properties may reflect molecular conformation in much more detail. The storage and loss moduli of the two mCOCs were measured with a parallel-plate rheometer, and the results are plotted in Figure 2. The storage modulus of mCOC-6 decreased sharply around 160 $^{\circ}$ C, almost plateauing or slightly decreasing with increasing temperature. In contrast, the storage modulus of mCOC-5 was falling dramatically at 145 $^{\circ}$ C and not plateauing as the temperature increased. Similar loss modulus results at higher temperatures were found for mCOC-5 and mCOC-6.

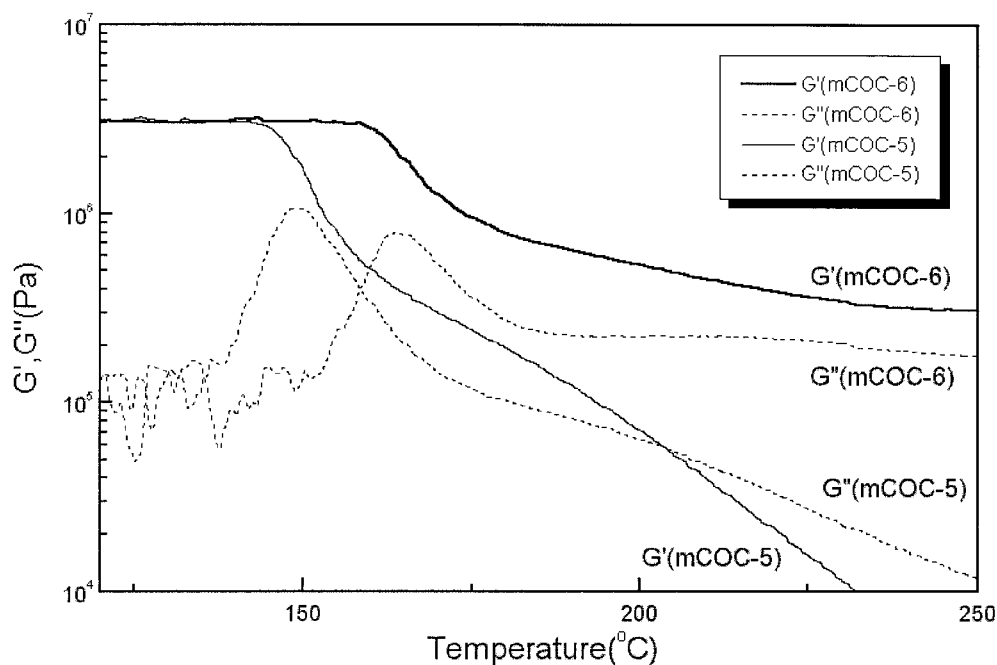


Figure 2 Molten viscoelastic behaviors of mCOCs.

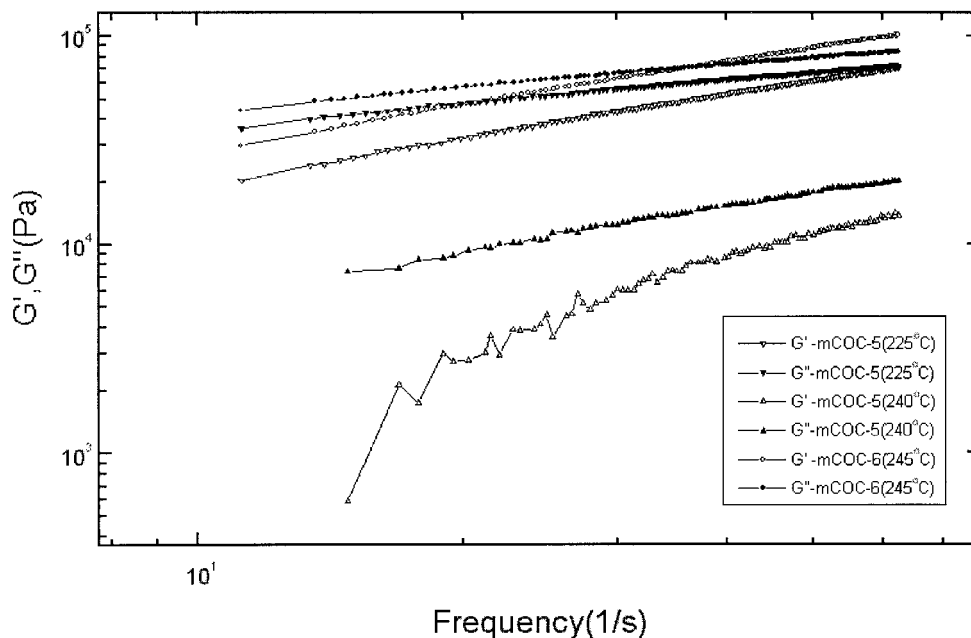


Figure 3 Viscoelasticity of mCOCs measured at $T_g + 100^\circ\text{C}$ and at different frequencies.

The crossover frequency demonstrates the entanglement density. The lower the crossover frequency is, the higher the entanglement density is and the higher the molten elasticity is. Figure 3 shows the crossover frequencies of mCOC-5 and mCOC-6 at temperatures above the respective T_g 's, around 80°C . mCOC-6 had a lower crossover frequency than mCOC-5, and this is consistent with the molten storage modulus observations.

Viscoelastic properties of mCOC-5 and mCOC-6 in the solid state

The mCOC solid-state viscoelastic properties are presented in Figure 4. $\tan \delta$ is the ratio of the loss modulus to the storage modulus. The $\tan \delta$ peak temperature indicates T_g , and it is evident that mCOC-5 had a lower value of T_g than mCOC-6; a higher $\tan \delta$ peak height for mCOC-5 was also observed.

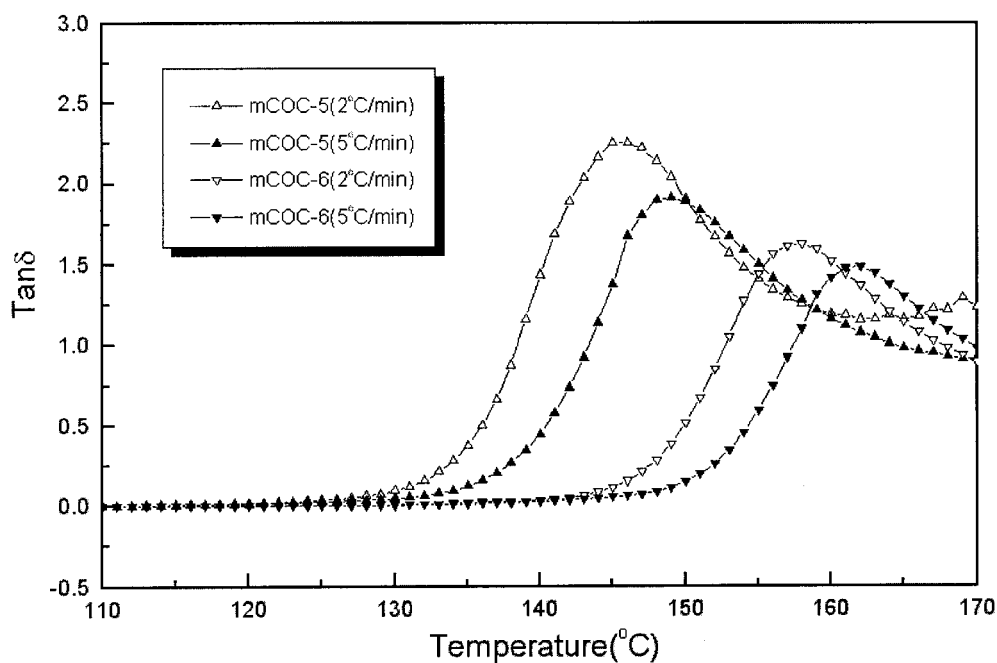


Figure 4 $\tan \delta$ values of mCOCs measured at various heating rates.

TABLE III
Molecular Weight and MWD of mCOCs

	M_n	M_w	M_w/M_n
mCOC-5	42,336	94,653	2.24
mCOC-6	40,840	99,054	2.43
mCOC-3	39,256	91,103	2.32
mCOC-4	40,541	86,031	2.14

Weight-average molecular weight (m_w) and MWD of mCOC-5 and mCOC-6

The molecular weight and MWDs for mCOC-6 and mCOC-5 were determined by high-temperature GPC, and the results are listed in Table III. The two mCOCs had similar molecular weights and MWDs.

Microstructure of mCOC-5 and mCOC-6

The microstructures of mCOC-5 and mCOC-6 were evaluated with ^{13}C -NMR, and their norbornene contents and conformations were calculated according to a method proposed by many authors.^{10,11} NMR spectrograms for mCOC-5 and mCOC-6 are shown in Figure 5, and all relevant norbornene and ethylene contents and conformations are listed in Table IV. mCOC-6 had a have slightly higher norbornene con-

tent (ca. 4 mol %) than mCOC-5. Higher percentages of -NN- blocks were found in mCOC-6, whereas mCOC-5 had higher percentages of -EE- blocks and alternating -NE- blocks (where N represents norbornene and E represents ethylene). Moreover, mCOC-5 did not contain -NNN- blocks, whereas mCOC-6 did have around 10 mol % -NNN- blocks. Furthermore, mCOC-6 had almost twice as much -NNE- and -ENN- than mCOC-5; more -EEE-, -NEN-, -EEN-, or -NEE- triads and fewer -ENE- triads were also found in mCOC-6.

Correlation between the molten viscoelasticity and microstructures of mCOC

It is well known that the molten viscosity strongly depends on the molecular weight at a power of 3.4, as the molecular weight is greater than the critical molecular weight. A broader MWD yields a lower molten viscosity. mCOC-5 and mCOC-6 possessed similar molecular weights and MWDs. Therefore, conventional theory suggests that they should have similar molten viscosities. However, mCOC-5 had much lower molten viscosities than mCOC-6. This strongly suggests that the molecular weight and MWD may have little influence on the molten viscosity and other

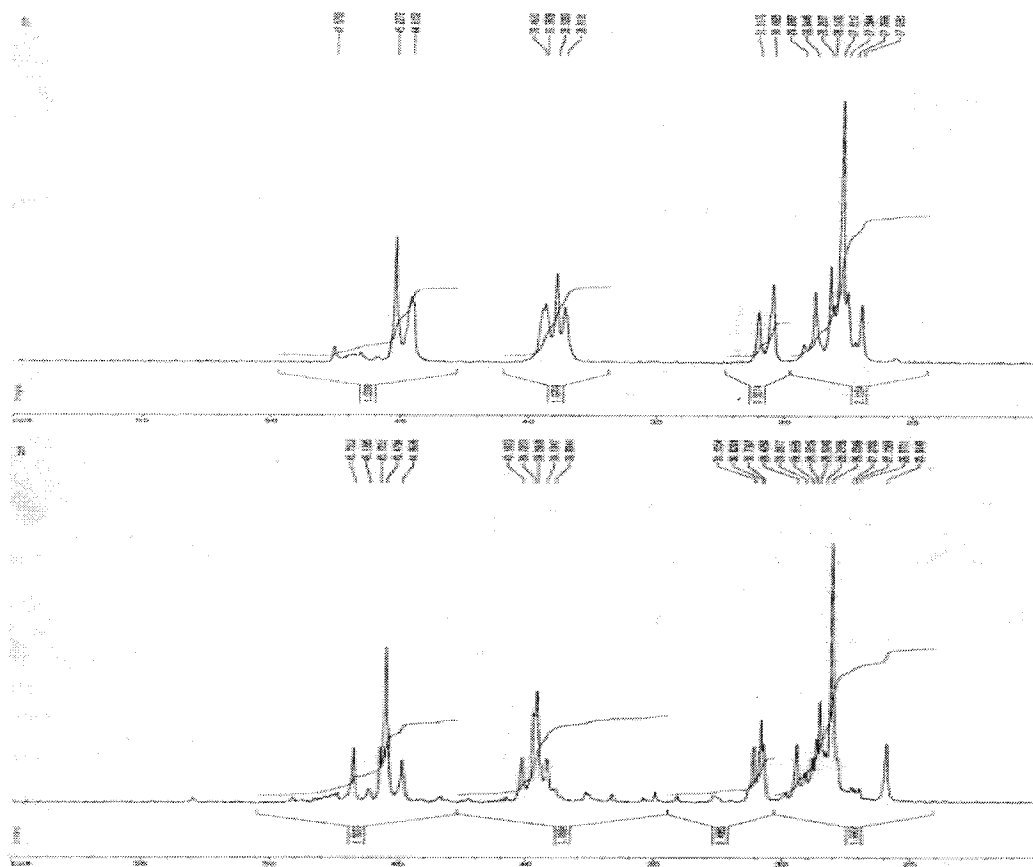


Figure 5 NMR spectra of mCOC-5 and mCOC-6.

TABLE IV
Norbornene Content and Conformation of mCOCs

	N (mol %)	T_g (°C)	Dyad			Triad		
			NN	NE/EN	EE	ENE	NNE/ENN	EEE, NEN, EEN/NEE
mCOC-5	48	133.1	6.7	82.0	11.3	34.3	13.4	52.3
mCOC-6	51.7	146.4	13.9	75.6	10.5	24.0	27.7	48.3
mCOC-3	55.8	160.3	15.6	76.1	8.0	22.2	31.7	46.1
mCOC-4	60.1	175.5	19.7	76.1	4.2	18.3	39.4	42.2

molecular aspects, such as the norbornene content, although the norbornene content of mCOC-5 was only slightly greater than that of mCOC-6, or that the mCOC conformation may control the mCOC rheology.

We now present a possible explanation of why mCOC-5 possessed lower viscosities than mCOC-6. First, there are eight dyad conformations. Among these forms, the -EEE- is the most flexible, whereas -NNN- exhibits the greatest rigidity and the largest pendent group size. Therefore, mCOC with no -NNN- blocks should present much more flexible chain motions, which would result in lower molten viscosities, as shown in Figure 1. Evidence that mCOC-5 did have a lower loss modulus (Fig. 2) and a lower flow activation energy (Table II) further supports this interpretation. In other words, the more rigid and larger sizes of the side groups induce higher flow viscosities and flow activation energies.¹⁹

According to the crossover frequency measured by the parallel-plate rheometer, mCOC-5 had a higher crossover frequency than mCOC-6, as shown in Figure 3. This indicates that mCOC-6 presented a higher entanglement density.²⁰ mCOC-6 also had a much greater molar percentage of rigid -NNN- blocks. Combining the two preceding factors, we may summarize that mCOC-6 needed higher torque to disentangle its molecular entanglements, which led to lower molten viscosities in the non-Newtonian flow region. This is quite consistent with the observation that mCOC-6 had a higher value of τ^* (Table II). The lower $\tan \delta$ peak height (Fig. 4) and higher molten storage modulus of mCOC-6 (Fig. 2) further support this hypothesis.

However, the aforementioned hypothesis still leaves one question unanswered: can only 4% more norbornene, rather than conformation, lead to the huge increments in molten viscosities? To address this concern, we tested the molten viscosities of two more

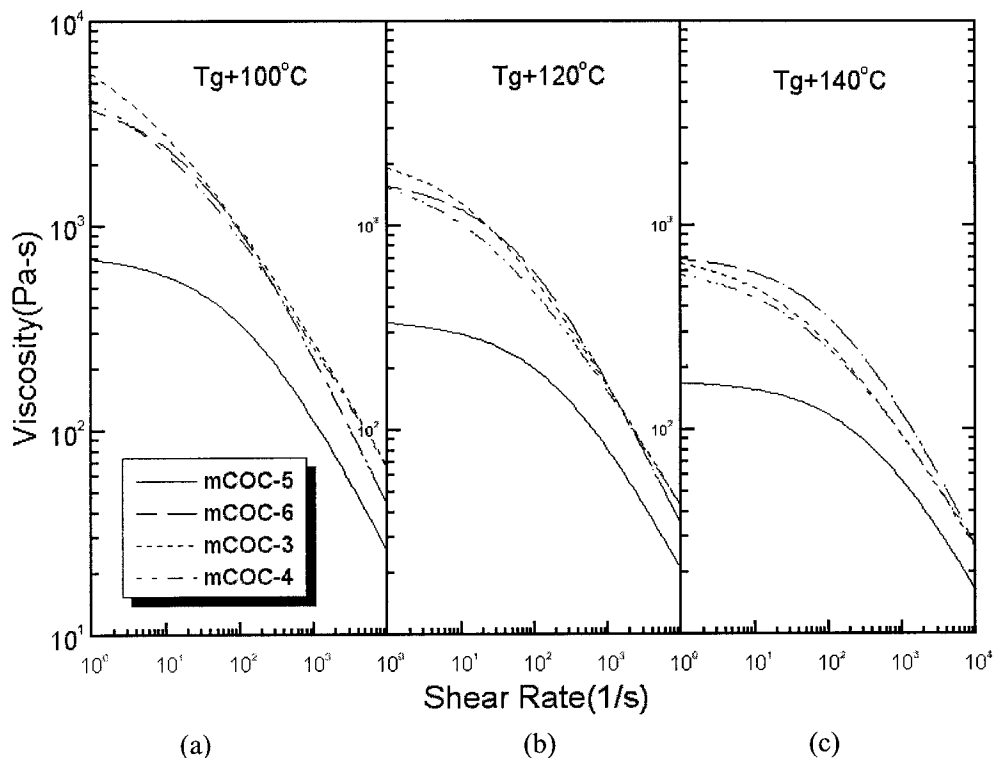


Figure 6 Molten viscosities of mCOCs at T_g shifted at constant temperatures: (a) $T_g + 100^\circ\text{C}$, (b) $T_g + 120^\circ\text{C}$, and (c) $T_g + 140^\circ\text{C}$.

mCOCs (mCOC-3 and mCOC-4) possessing M_w 's, MWDs, and conformations similar to those of mCOC-6 (Table III) but having higher molar percentages of norbornene (as shown in Table IV) at various temperatures (I) and fitted them into the cross model mentioned previously. Ignoring temperature effects, we calculated and compared the viscosities of these four polymers at $T_g + T$. Figure 6 presents the results of this experiment. It is quite surprising that mCOCs (mCOC-6, mCOC-3, and mCOC-4) with similar conformations fell into a group, although there were slight differences among them, and they had higher molten viscosities than mCOC-5. This demonstrates that the molten viscosities of mCOCs are mainly controlled by conformation (the sequence distributions of norbornenes and ethylenes), whereas molecular weights, MWDs, and norbornene contents may have less influence on molten viscosities.

The molecular weights and MWDs determined with high-temperature GPC are relative ones; therefore, the molecular weight values may or may not be different from the absolute molecular weights. Nevertheless, mCOCs with larger norbornene contents may have smaller or no differences between the absolute and relative molecular weights and may present similar solubility characteristics for various norbornene contents. If this hypothesis holds, it can be concluded that the molecular weight and MWD exert little influence on mCOC molten viscosities.

CONCLUSIONS

In this study, several mCOCs were used to establish the relationships among microstructural, rheological, and viscoelastic properties. According to the ^{13}C -NMR spectrogram, mCOC-6 contained -NNN- blocks, whereas mCOC-5 exhibited no such -NNN- blocks. mCOC-5 demonstrated much lower viscosities than mCOC-6. In addition, mCOC-5 also exhibited a lower elasticity, a lower value of $E_{a'}$, a higher crossover frequency, and a lower value of τ^* than mCOC-6. This suggests that the larger pendent -NNN- groups strongly induce a higher degree of molecular entanglements in mCOC chains. Further evidence that mCOC-3 and mCOC-4 had microstructures similar to

that of mCOC-6 is their much higher molten viscosities compared with that of mCOC-5. On the basis of the aforementioned results, we conclude that conformation, rather than norbornene content, molecular weight, and MWD, dominates the rheology and viscoelasticity of mCOCs.

However, studies involving mCOCs with known absolute molecular weights, rather than relative molecular weights measured by high-temperature GPC, of mCOCs with different norbornene contents, and more detailed conformation identifications obtained from ^{13}C -NMR spectrograms, may be required to further clarify this microstructure-rheology relationship.

References

1. Kaminsky, W.; Bark, A.; Arndt, M. *Macromol Chem Macromol Symp* 1991, 47, 83.
2. Ticona Brochure; Germany, 1998.
3. Kim, Y. S.; Chung, C. I.; Lai, S. Y.; Hyun, K. S. *J Appl Polym Sci* 1995, 59, 125.
4. Gelfer, M. Y.; Winter, H. H. *Macromolecules* 1999, 32, 8974.
5. Malmberg, A.; Lófgren, B. *J Appl Polym Sci* 1997, 66, 35.
6. Showaib, E. A.; Moet, A.; Sehanobish, K. *Polym Eng Sci* 1995, 35, 786.
7. Benavente, R.; Perena, J. M.; Bello, A.; Perez, E.; Locatelli, P.; Fan, Z.-Q.; Zucchi, D. *Polym Bull* 1996, 36, 249.
8. Cincu, C.; Chatzopoulos, F.; Montheard, J.-P. *Macromol Rep A* 1996, 33(Suppl. 2), 83.
9. Raebing, D.; Lambla, M.; Wautier, H. *J Appl Polym Sci* 1997, 66, 809.
10. Arndt-Rosenau, M.; Beulich, I. *Macromolecules* 1999, 32, 7335.
11. Tritto, I.; Boggioni, L.; Sacchi, M. C.; Locarelli, P.; Ferro, D. R.; Provaasoli, A. *Macromol Rapid Commun* 1999, 20, 279.
12. Provaasoli, A.; Ferro, D. R.; Tritto, I.; Boggioni, L. *Macromolecules* 1999, 32, 6697.
13. Harrington, B. A.; Crowther, D. *J Mol Catal A* 1998, 128, 79.
14. Rische, T.; Waddon, A. J.; Dickinson, L. C.; MacNight, W. J. *Macromolecules* 1998, 31, 1871.
15. Bergstrom, C. H.; Sperlich, B. R.; Ruotoistenmaki, J.; Seppala, J. V. *J Polym Sci Part A: Polym Chem* 1998, 36, 1633.
16. MacNight, A. L.; Waymouth, R. M. *Macromolecules* 1999, 32, 2816.
17. Chu, P. P.; Huang, W. J.; Chang, F. C.; Fan, S. Y. *Polymer* 2000, 41, 401.
18. Chiang, H. H.; Hieber, C. A.; Wang, K. K. *Polym Eng Sci* 1991, 31, 116.
19. Nielsen, L. E. *Polymer Rheology*; Marcel Dekker: New York, 1977.
20. Aklonis, J. J.; Macknight, W. J. *Introduction to Polymer Viscoelasticity*; Wiley: New York, 1983.