

# Dependence of zero-shear viscosity and steady-state compliance on molecular weight between entanglements for ethylene–cycloolefin copolymers

Toshikazu Takigawa\*, Hidenori Kadoya, Takashi Miki, Takashi Yamamoto, Toshiro Masuda

*Department of Material Chemistry, Kyoto University, Nishikyo-ku, Kyoto 615-8510, Japan*

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## Abstract

Dynamic viscoelastic properties of a series of cyclic olefin copolymers have been investigated. The specimens differ in total molecular weight as well as molecular weight between entanglements. The angular frequency ( $\omega$ ) dependence curves of dynamic storage and loss moduli ( $G'$  and  $G''$ , respectively) of the specimens have shown that  $G' \propto \omega^2$  and  $G'' \propto \omega$  in the terminal region, and a plateau region at high  $\omega$ . On the basis of the experimental results, the dependence of total molecular weight as well as molecular weight between entanglements has been examined for zero-shear viscosity ( $\eta_0$ ) and steady-state compliance ( $J_e$ ). It is shown that  $\eta_0 \propto M_e^{1.5}(M_w/M_e)^{3.5}$  for the melts of the copolymers in the entangled regime,  $M_w$  being the weight-average molecular weight and  $M_e$  the molecular weight between entanglements. The steady-state compliance  $J_e$  for the melts scales with  $M_e$  and  $M_w$  as  $J_e \propto M_e^{0.5}(M_w/M_e)^0$ .

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**Keywords:** Cycloolefin copolymer; Zero-shear viscosity; Steady-state compliance

## 1. Introduction

General-purpose plastics have been used in a wide variety of our daily life. Polyethylene and polypropylene are typical of the general-purpose plastics, and are classified into polyolefin. These polymers are not optically so clear because of their high crystallinity, and mechanical properties of these crystalline polymers in the solid state become complicated because the properties are strongly affected by the brittle crystallites in the specimens. Nevertheless, polyolefin still has a high possibility to extend the applicable fields if the properties such as high crystallinity and optical opaqueness are improved, because polyolefin is supreme in anti-moisture absorption and processability. New catalyst systems discovered and developed by the Kaminsky's group [1] have enabled the synthesis of new types of polyolefin products. Cyclic olefin copolymers (COCs), comprising ethylene and cycloolefin units, have been designed and made to improve the weaknesses of the conventional polyolefin products. The introduction of bulky cycloolefin units

reduces the flexibility of polymer chains and prevents crystallization; hence, the copolymers remain amorphous and transparent, and the glass transition temperature ( $T_g$ ) of the polymers becomes also rather high. Many types of COCs differing in cyclic comonomer species [1,2] have become available, and the polymers are gradually extending the area of use, especially in the field of optical storage media in place of polycarbonate.

The IUPAC Working Party (currently, Subcommittee) in the Polymer Division has started a new project to investigate relationships between structure and properties of commercially available ethylene-based COCs. The molecular characteristics of the COCs used in the project have already been examined carefully and have also become available [3]. Among the COC specimens employed in the project, a series of COCs is very interesting from the viewpoint of melt rheology because the cycloolefin content varies systematically from sample to sample. The introduction of a bulky substituent expands the spacing between entanglements. The samples give a systematic copolymer group differing in total molecular weight as well as molecular weight between entanglements.

Until now many studies have been made to clarify rheological properties of polymer liquids: melts and concentrated solutions. Focusing on the molecular weight dependence, how viscoelastic functions change with total molecular

\* Corresponding author. Tel.: +81 75 383 2453; fax: +81 75 383 2458.

E-mail address: [takigawa@rheogate.polym.kyoto-u.ac.jp](mailto:takigawa@rheogate.polym.kyoto-u.ac.jp) (T. Takigawa).

weight has become well understood. For example, zero-shear viscosity increases linearly with  $M$  ( $M$ ; total molecular weight) at low  $M$ , whereas the viscosity increases in proportion to  $M^{3.5}$  at high  $M$ . A crossover occurs around a critical molecular weight ( $M_c$ ), and  $M_c$  is known to have a close relation to the molecular weight between entanglements ( $M_e$ ). These are summarized in a textbook [4] or the review articles [5–7]. The dependence on total molecular weight is thus well understood, but how the viscoelastic functions for polymer melts depend on  $M_e$  (or  $M_c$ ) is still quite unclear because there was no report on the  $M_e$  dependence of viscoelastic functions. To clarify this point, a series of polymers with  $M_e$  varying systematically must be prepared. A series of the well characterized IUPAC samples is suitable to this purpose. This paper deals with dynamic viscoelasticity of the melts of the COCs as a part of the IUPAC project research. On the basis of the experimental results, the dependence of viscoelastic functions on  $M_e$  is investigated.

## 2. Experimental

Commercially available COCs were supplied from Mitsui Chemical. We call the specimens A-series of COCs, where the cyclic comonomer species for the specimens is tetracyclododecene. The molecular characteristics and structures estimated for the copolymers have been shown in the preceding paper of the IUPAC project [3]. Weight-average molecular weight ( $M_w$ ) and the ratio of  $M_w$  to number-average molecular weight ( $M_n$ ),  $M_w/M_n$ , obtained by gel permeation chromatography (GPC), are summarized in Table 1, together with  $T_g$  determined by differential scanning calorimetry (DSC). The table also contains the cyclic comonomer content ( $f$ ) in mol%. The sample code appearing in this table is also identical to that in the paper covering the details of the molecular characteristics as well as chemical structure of these COCs. Dynamic viscoelastic functions of the melts of COCs were measured with an ARES (Rheometric Scientific) in an angular frequency ( $\omega$ ) sweep mode under dry nitrogen atmosphere. The measurements were made in a cone-plate geometry. Master curves of dynamic storage modulus ( $G'$ ) and loss modulus ( $G''$ ) were well prepared by using the time ( $t$ )-temperature ( $T$ ) superposition principle, and the reference temperature ( $T_r$ ) for the master curves was chosen to be  $T_r/K = (T_g/K + 50)$  for all COC specimens. Only the horizontal shift (the shift factor;  $a_T$ ) was employed for preparation of the master curves.

## 3. Results and discussion

In Fig. 1,  $-(T - T_r)/a_T$  is plotted against  $(T - T_r)$  for A1. The data points fall on a single line, indicating that  $a_T$  can be described by a WLF-type equation [4–6]:

$$\log a_T = -\frac{c_1(T - T_r)}{c_2 + (T - T_r)} \quad (1)$$

The constants,  $c_1$  and  $c_2$ , have the values of  $c_1 = 6.86$  and  $c_2 = 108.7$  at  $T_r = 120$  °C. The shift factor for other specimens also obeyed the WLF-type equation and the variation of the coefficients among specimens was not so large, although we do not show the detailed values of  $c_1$  and  $c_2$  here. Fig. 2 shows the master curves of  $G'$  and  $G''$  vs.  $\omega$  for A1 as an example. On the dispersion curve of  $G'$ , the rubbery plateau is observed in the high  $\omega$  region, indicating that the entanglement coupling occurs in the specimen. In the low  $\omega$  region, the relations  $G' \propto \omega^2$  and  $G'' \propto \omega$  are seen on the dispersion curves. It is well known that in the terminal zone the relation  $G'' \propto \omega$  generally holds even for polymers with broader molecular weight distributions but  $G' \propto \omega^2$  can be hardly seen for the polymers with broader molecular weight distributions [4,5]. As can be seen from Table 1, the  $M_w/M_n$  ratio of A1 is 2.46, which is rather broad, but the relation  $G' \propto \omega^2$  is clearly observed for the sample in the terminal zone. Zero-shear viscosity ( $\eta_0$ ) and steady-state compliance ( $J_e^0$ ) both of which characterize the flow behavior of polymers in the terminal zone are defined by [4–6]:

$$\eta_0 = \lim_{\omega \rightarrow 0} \frac{G''}{\omega} \quad (2)$$

and

$$J_e^0 = \frac{A_G}{\eta_0^2} \quad (3)$$

with

$$A_G = \lim_{\omega \rightarrow 0} \frac{G'}{\omega^2} \quad (4)$$

The values of  $\eta_0$  and  $J_e^0$  for A1 at  $T_r = 120$  °C were, respectively,  $3.3 \times 10^6$  Pas and  $3.6 \times 10^{-5}$  Pa<sup>-1</sup>, as listed in Table 1.

In Fig. 2,  $G'$  in the rubbery region does not show a leveled-off value:  $G'$  slightly increases with increasing  $\omega$ . Because of this weak  $\omega$  dependency the plateau modulus ( $G_N$ ) in this paper

Table 1  
Molecular characteristics and rheological parameters for cyclic olefin copolymers

Sample	$M_w$ ( $10^4$ )	$M_w/M_n$	$f$ (mol%)	$T_g$ (°C)	$\eta_0$ ( $10^5$ Pas)	$J_e$ ( $10^{-5}$ Pa <sup>-1</sup> )	$G_N$ ( $10^5$ Pa)	$M_e$ ( $10^4$ )	$\tau_w$ (s)
A1	13.10	2.46	20.0	70	33	3.6	8.0	0.4 <sub>1</sub>	120
A2	10.8	2.28	21.4	80	14	3.7	6.3	0.5 <sub>4</sub>	52
A3	10.2	2.45	28.8	105	7.9	4.6	4.5	0.8 <sub>2</sub>	36
A4	11.6	2.52	29.6	129	4.9	5.4	3.0	1.3	26
A5	11.9	2.30	32.2	145	3.4	4.4	2.3	1.8	15
A6	9.3	2.40	32.2	139	0.89	5.6	1.9	1.8	5.0

For definitions of variables, see text. Values of the rheological parameters are those at the reference temperature  $T_r = (T_g + 50)$  °C.

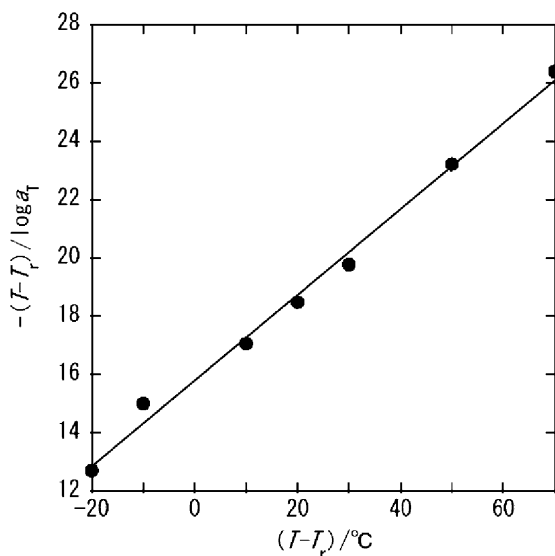


Fig. 1. Plots of  $(T - T_r) / \log a_T$  against  $(T - T_r)$  for A1. Here,  $T_r$  is the reference temperature and  $a_T$  is the shift factor.

was defined as a value of  $G'$  at the point of  $\omega$  where the  $\tan \delta$  ( $= G''/G'$ ) vs.  $\omega$  plot shows a minimum. The  $\tan \delta$  curve for A1 at  $T_r$  (120 °C) is shown as an example in Fig. 3. The curve has a minimum at  $\omega a_T \approx 35 \text{ s}^{-1}$ , giving  $G_N$  of  $8.0 \times 10^5 \text{ Pa}$ . The values of  $G_N$  for the COCs used in this study are tabulated in Table 1. The product of  $\eta_0$  and  $J_e$  corresponds to a characteristic time ( $\tau_w$ ;  $\tau_w = J_e \eta_0$ ), and the value is also listed in Table 1. All COC specimens examined in this study showed the similar  $G'$  and  $G''$  curves to those of A1: the emergence of the rubbery plateau evidencing entanglement coupling and the flow behavior,  $G' \propto \omega^2$  and  $G'' \propto \omega$  in the terminal zone. The values of  $\eta_0$ ,  $J_e$ ,  $G_N$  and  $\tau_w$  for the other COCs are summarized in Table 1. The molecular weight between entanglements  $M_e$  for the copolymers is also listed in the table. The value of  $M_e$  was calculated by using values of the density  $\rho$  and the gas

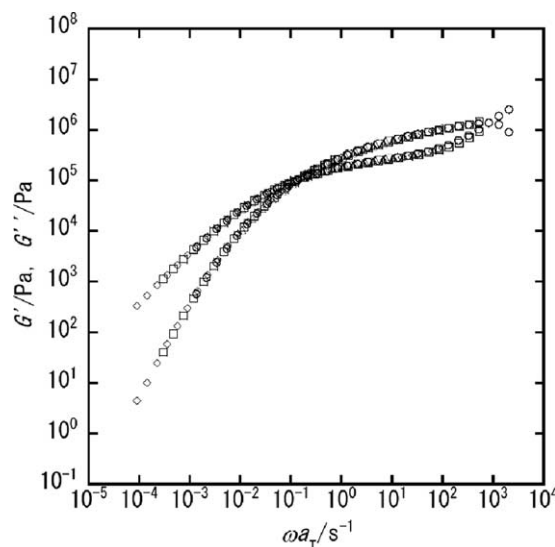


Fig. 2. Master curves of dynamic storage modulus ( $G'$ ) and loss modulus ( $G''$ ) vs. angular frequency ( $\omega$ ) for A1 at the reference temperature ( $T_r$ ;  $T_r = 120 \text{ °C}$ ).

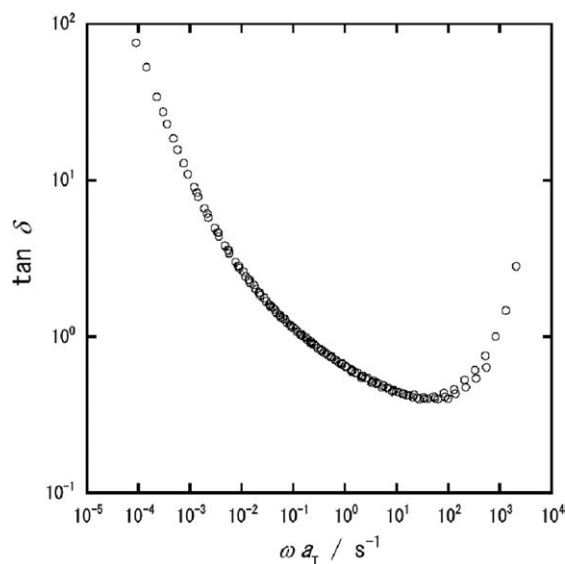


Fig. 3. Plots of  $\tan \delta$  against  $\omega$  for A1 at the reference temperature ( $T_r$ ;  $T_r = 120 \text{ °C}$ ).

constant  $R$  by  $M_e = \rho RT / G_N$ , where  $\rho = 1 \text{ g/cm}^3$  at  $T_r$  was assumed for all copolymers.

Fig. 4 shows  $M_e$  plotted against  $f$  for the A-series specimens. This figure also contains the expected data point for polyethylene:  $f = 0 \text{ mol\%}$  and  $M_e = 1250$  [4]. The quantity  $M_e$  increases with increasing  $f$ , indicating that the introduction of bulky cyclic groups expands the entanglement spacing or the mesh size of a transient network. The slope of the curve is rather small at low  $f$ , but is enhanced at high  $f$  for the copolymers. How the change in  $f$  (or,  $M_e$ ) affects the rheological properties of the copolymers is interesting. It is well known for homopolymers that  $\eta_0$  in the entangled regime is expressed by using  $M_c$  instead of  $M_e$  as [8]

$$\eta_0(M_w) = \eta_R(M_c) \left( \frac{M_w}{M_c} \right)^{3.5} \quad (M_w > M_c) \quad (5)$$

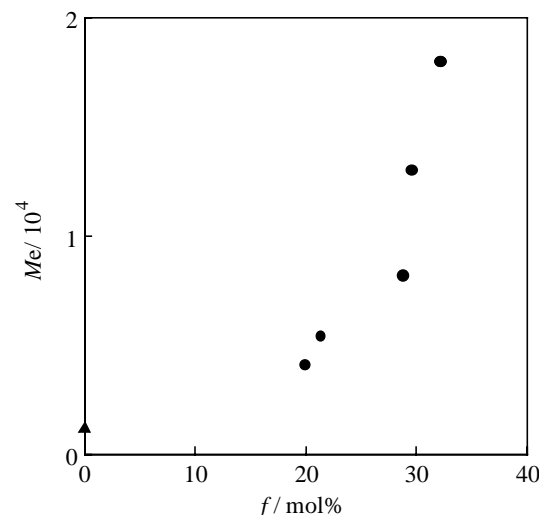


Fig. 4. Plots of  $M_e$  against  $f$  for the COCs.

Here,  $\eta_R(M_w)$  is the zero-shear viscosity in the non-entangled (Rouse) regime and is a linear function of  $M_w$ . The quantity  $M_c$  is a critical molecular weight and is known to have the relation that  $M_c/M_e$  remains constant of 2–3 [4–8]. For  $\eta_0$  of the copolymers in a series at the reference temperature  $T_r$ , we can also expect the relation  $\eta_0 \propto M_w^{3.5}$ , if  $M_e$  is unchanged. The quantity  $\eta_0$  of the present copolymers, however, also depends on  $M_c$ , since  $M_c$  systematically changes. In this case, we must write  $\eta_0$  as  $\eta_0 = \eta_0(M_c, M_w)$ , or equivalently  $\eta_0 = \eta_0(M_c, M_w/M_e)$ . Here, we used here  $M_e$  instead of  $M_c$ , but this is justified because the ratio  $M_c/M_e$  is constant. Following this expression,  $\eta_0$  in the entangled regime for a series of copolymers in this study can be written in the similar form to Eq. (5) as  $\eta_0(M_c, M_w) = \eta_r(M_e)(M_w/M_e)^{3.5}$ . The quantity  $\eta_r(M_e)$  becomes the same as  $\eta_R(M_e)$  when the comparison is made for the copolymers with a fixed  $f$  value, but for the homologous series  $\eta_r(M_e)$  should be considered just a front factor of the viscosity equation for the entangled systems at  $M_w = M_e$ . Fig. 5 shows the plot of  $\eta_r(M_e)$  against  $M_e$  for the copolymer samples. The values of  $\eta_r(M_e)$  in the figure were obtained by dividing the measured  $\eta_0$  data by the known factor  $(M_w/M_e)^{3.5}$ . The data points appear to be approximated by a single line with a slope of 1.5, indicating  $\eta_r(M_e) \propto M_e^{1.5}$ .

The zero-shear viscosity  $\eta_0$  also depends on the monomeric frictional coefficient  $\zeta_0$  as well as  $\rho$  (or concentration) [4–6,9]. Concerning the effects of the local friction, we assumed in this study that  $\zeta_0$  depends only on  $(T - T_g)$ . Namely,  $\zeta_0$  is the same for all copolymers when the comparison is made at  $T_r = (T_g + 50)$  °C. This is based on the experimental results that the WLF coefficients were not so large in variation among the specimens, as stated before. To investigate the effects of  $\rho$  on  $\eta_0$  it is firstly required to measure  $\rho$ . However, such measurements are difficult: the experiments must be made at high temperatures because the values needed are those at high temperatures. We therefore, used  $\rho = 1$  g/cm<sup>3</sup> for all specimens at  $T_r$ . According to Berry and Fox [5], and Berry [9], the front factor  $\eta_r(M_e)$  can be considered to be a function of  $(\hat{a}/M_L^2)$ , with

$\hat{a}$  and  $M_L$  being, respectively, the persistence length and the average mass per unit contour length. For the COCs, the mass per unit length, as well as probably the persistence length, becomes larger with increasing  $M_e$  because the large  $M_e$  in a group results from the introduction of the larger extent of bulky substituents, which might generate the extra  $M_e$  dependence (namely,  $M_e^{0.5}$ ) of  $\eta_r$  for the copolymers.

The steady-state compliance  $J_e$  for homopolymers can be described by [8]

$$J_e = J_R(M_c') \left( \frac{M_w}{M_c'} \right)^0 \quad (M_w > M_c') \quad (6a)$$

$$J_e = J_R(M_c') \left( \frac{M_w}{M_c'} \right) \quad (M_w < M_c') \quad (6b)$$

Here,  $M_c'$  is a constant slightly larger than  $M_c$ :  $M_c'/M_e = 5 \sim 8$  whereas  $M_c/M_e = 2\text{--}3$  [4–7]. The quantity  $J_R$  stands for the steady state compliance in the non-entangled regime, were  $J_R(M_w) \propto M_w$  holds for homopolymers with narrow molecular weight distributions. Generally,  $J_e$  is sensitive to the molecular weight distribution, [4–6] but we neglect here the effects of the polydispersity on  $J_e$  because the values of  $M_w/M_n$  were almost the same for all specimens (see Table 1). The dependence of  $\rho$  on  $J_e$ , which is expressed by  $J_e \sim \rho^{-1}$ , was neglected as in the case of  $\eta_0$ . A reduced compliance  $J_r$  for the entangled COCs is here defined by using again  $M_e$  instead of  $M_c'$  as

$$J_r(M_e) \equiv J_e \left( M_e, \frac{M_w}{M_e} \right) \left( \frac{\rho RT_r}{M_e} \right) \quad (7)$$

because no dependence of  $J_e$  on  $(M_w/M_e)$  can be assumed. In Fig. 6,  $J_r$  for the copolymers is double-logarithmically plotted against  $M_e$ . The data points are a little scattered, but they fall on the line of slope  $-0.5$ ; namely,  $J_r \propto M_e^{-0.5}$ . This indicates  $J_e \propto M_e^{-0.5} (M_w/M_e)^0$  for  $J_e$  of the (entangled) COC melts at  $T = T_r$ . The dependence  $M_e^{0.5}$  in the  $J_e$  expression should be compared with the common relation  $J_R(M_w) \propto M_w$  for homopolymer

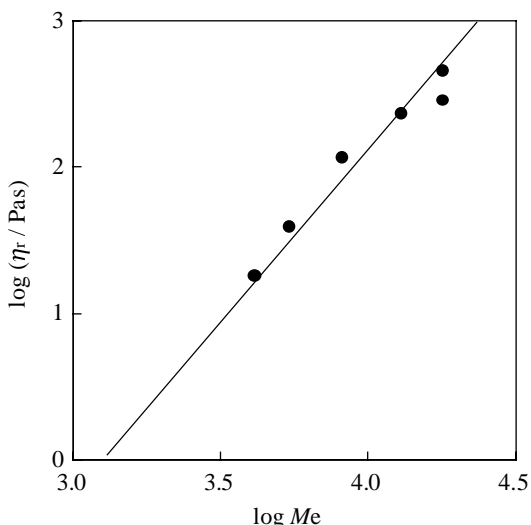


Fig. 5. Double-logarithmic plots of  $\eta_r$  against  $M_e$  for the COCs. The slope of the line is 1.5.

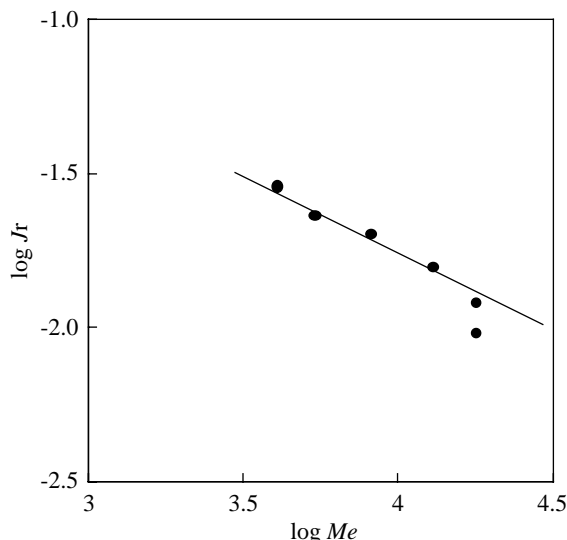


Fig. 6. Double-logarithmic plots of  $J_r$  against  $M_e$  for the COCs. The slope of the line is  $-1.5$ .

melts in the non-entangled regime [4,6,7]. This originates also from the difference in the chain stiffness for the series of polymers. The characteristic relaxation time  $\tau_w$  for the well-entangled COCs is given by

$$\tau_w \left( M_e, \frac{M_w}{M_e} \right) \propto M_e^2 \left( \frac{M_w}{M_e} \right)^{3.5} \quad (8)$$

because  $\eta_0 \propto M_e^{1.5} (M_w/M_e)^{3.5}$  and  $J_e \propto M_e^{0.5} (M_w/M_e)^0$  for the copolymers. This expression indicates that  $\tau_w$  in the non-entangled region ( $\tau_{w,r}$ ) becomes  $\tau_{w,r}(M_e) \propto M_e^2$ , which agrees apparently with the theoretical prediction from the Rouse model [4,6–8].

#### 4. Summary

Dynamic viscoelasticity was measured for melts for a series of ethylene–cycloolefin copolymers. The specimens varied in total molecular weight as well as cycloolefin content, and the difference in cycloolefin content changed the molecular weight between entanglements. The zero-shear viscosity  $\eta_0$  for two series of copolymers was analyzed by assuming that  $\eta_0$  and  $J_e$  are functions of  $M_e$  and  $M_w/M_e$ . It was found for the COCs that  $\eta_0 \propto M_e^{1.5} (M_w/M_e)^{3.5}$  and  $J_e \propto M_e^{0.5} (M_w/M_e)^0$ . These relations were different from those,  $\eta_0 \propto M_e^{1.0} (M_w/M_e)^{3.5}$  and

$J_e \propto M_e^{1.0} (M_w/M_e)^0$ , expected from analogy with entangled homopolymer systems.

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