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Elongational flow birefringence of ethylene–tetracyclododecene copolymer

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Abstract

Simultaneous measurements of transient tensile stress $\sigma(\dot{\epsilon}_0; t)$ and birefringence $\Delta n(\dot{\epsilon}_0; t)$ were conducted under uniaxial elongation with constant Hencky strain rate $\dot{\epsilon}_0$ on new olefin-copolymer of ethylene (E) and tetracyclododecene (TD) of three different TD content from 20 to 41 mol%. For the low TD content copolymer, the extentional viscosity $\eta_E(\dot{\epsilon}_0; t)(\equiv \sigma(\dot{\epsilon}_0; t)/\dot{\epsilon}_0)$ showed only moderate increase with elongation time t or Hencky strain $\epsilon(= \dot{\epsilon}_0 t)$ and the stress optical coefficient $C(\dot{\epsilon}_0; t)(\equiv \Delta n(\dot{\epsilon}_0; t)/\sigma(\dot{\epsilon}_0; t))$ was nearly constant for the whole range of σ examined. On the other hand, for other samples of high TD content ($\geq 30\%$), we observed strong uprising of η_E often referred to as strain-induced hardening, and rapid decrease in C with increasing σ. As the copolymer chains were stretched out from the entangled state, the larger amount of the bulky TD groups in the latter may suppress the flow-induced conformational change to take place and suppress the disentangling of the chains, leading to the increase in σ and decreasing of C. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Cycloolefin copolymer; Elongational viscosity; Stress optical coefficient

Olefin polymers with cycloolefin moieties are expected to be a new class of materials for photonics technology such as optical discs, fibers and lenses, and seem to have a strong potential to replace conventionally used engineering plastics such as polycarbonates. The search for such materials got a momentum when a random copolymer of ethylene (E) and tetracyclododecene (TD) was unveiled and their inherent properties of high chemical resistance and low birefringence became known. Another advantage may lie in their widely ranging glass transition temperature (T_g) which varies just by varying the TD content from nearly $-40.0°C$ for polyethylene (PE) to $170°C$ for 48% TD copolymer. For these E–TD copolymers, the synthetic aspect has been fairly well worked out [1] but their physical properties including optical and rheological behavior are yet to be studied. We have tested the E–TD copolymers of different TD content on our newly developed elongational flow opto-rheometry (EFOR) [2] which enabled us to achieve simultaneous measurements of transient tensile stress $\sigma(\dot{\epsilon}_0; t)$ and birefringence $\Delta n(\dot{\epsilon}_0; t)$ as a function of time under uniaxial elongation with constant Hencky strain rate $\dot{\epsilon}_0$. Additional ex situ characterization such as differential scanning calorimetry (DSC), ^{13}C NMR analysis and wide angle X-ray diffraction (WAXD) were conducted on the copolymers recovered before and after elongation. Through these preliminary experiments, we found interesting features of the elongation behavior of the E–TD copolymer dependent on the TD content. The results will be reported here.

The E–TD random copolymer [1] (Scheme 1) of different TD content (20 to 41 mol%) supplied were prepared with a Ziegler–Natta catalyst. The copolymer samples were characterized by using temperature modulated differential scanning calorimeter (TMDSC, TA2920, TA Instruments) to determine T_g, and high temperature gel permeation chromatograph (GPC: Tosoh HLC-8121 GPC/HT) in o-dichlorobenzene carrier at $140.0°C$ with polystyrene (PS) elution standards. Table 1 summarizes the GPC results together with TD content data provided by the supplier. In each EFOR run, a specimen of $\sim 60 \times 7.0 \times 0.5$ mm^3 in size was annealed at $T_g + 50.0°C$ for 3 min in EFOR and subjected to uniaxial elongation at the same temperature with a constant Hencky strain rate $\dot{\epsilon}_0$ in the range from 1.0 to 0.01 s^{-1}.

Fig. 1 shows time development of $\eta_E(\dot{\epsilon}_0; t)$ and $\Delta n(\dot{\epsilon}_0; t)$ obtained at $T_g + 50.0°C$ for the three copolymers. The thin solid curve in each figure represents three-fold shear

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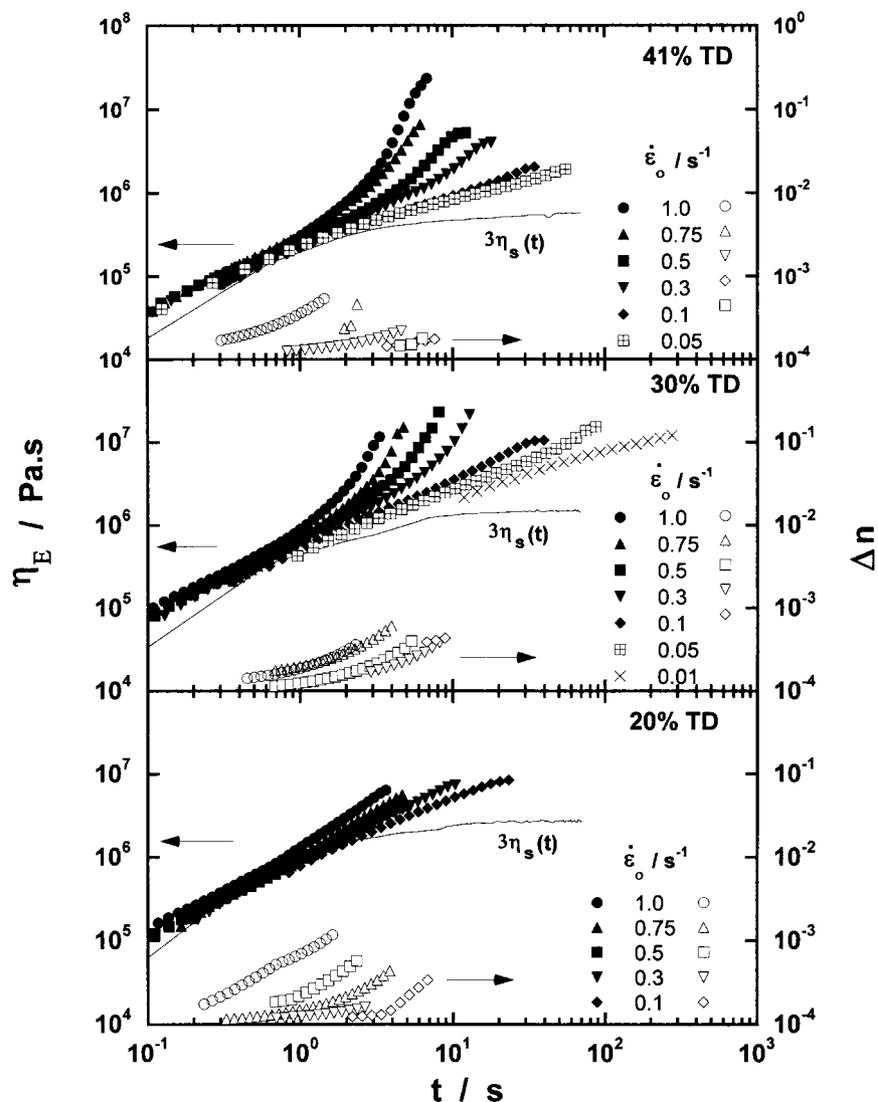*E-mail address:* kotaka@toyota-ti.ac.jp (T. Kotaka).

Fig. 1. Double logarithmic plots of transient elongational viscosity $\eta_E(\dot{\epsilon}_0; t)$ (solid symbols) and birefringence $\Delta n(\dot{\epsilon}_0; t)$ (open symbol) as a function of time for different TD content indicated at $T_g + 50°C$ with various Hencky strain rates $\dot{\epsilon}_0$ as indicated. The solid line represents three times shear viscosity $3\eta_s(t)$ as a function of time, determined at the shear rate $\gamma = 0.001$ s^{-1} at $T_g + 50°C$.

viscosity $3\eta_s(t)$, which agrees roughly with $\eta_E(\dot{\epsilon}_0; t)$ in the so-called linear region where $\eta_E(\dot{\epsilon}_0; t)$ is independent of $\dot{\epsilon}_0$, showing that Trauton's rule is obeyed. For the 20 mol% TD copolymer $\eta_E(\dot{\epsilon}_0; t)$ shows relatively moderate strain-induced hardening in all strain rates measured, and $\Delta n(\dot{\epsilon}_0; t)$ shows moderate increase with time t and hence
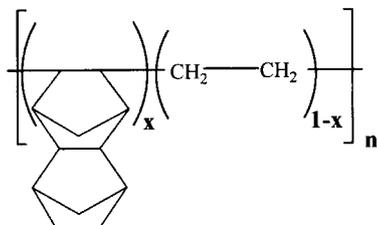
with Hencky strain $\epsilon = \dot{\epsilon}_0 t$. On the other hand, for the copolymers of higher TD content, we see more enhanced strain-induced hardening in $\eta_E(\dot{\epsilon}_0; t)$ especially at higher $\dot{\epsilon}_0$, while the increase in $\Delta n(\dot{\epsilon}_0; t)$ with t or ϵ is rather slow.

Fig. 2 shows plots of the stress optical coefficient $C(\dot{\epsilon}_0; t)$ [$\equiv \Delta n(\dot{\epsilon}_0; t)/\sigma(\dot{\epsilon}; t)$] against $\sigma(\dot{\epsilon}_0; t)$ for the three copolymers obtained at the respective $T_g + 50.0°C$ shown in

Scheme 1.

Table 1
Characteristics of the copolymer

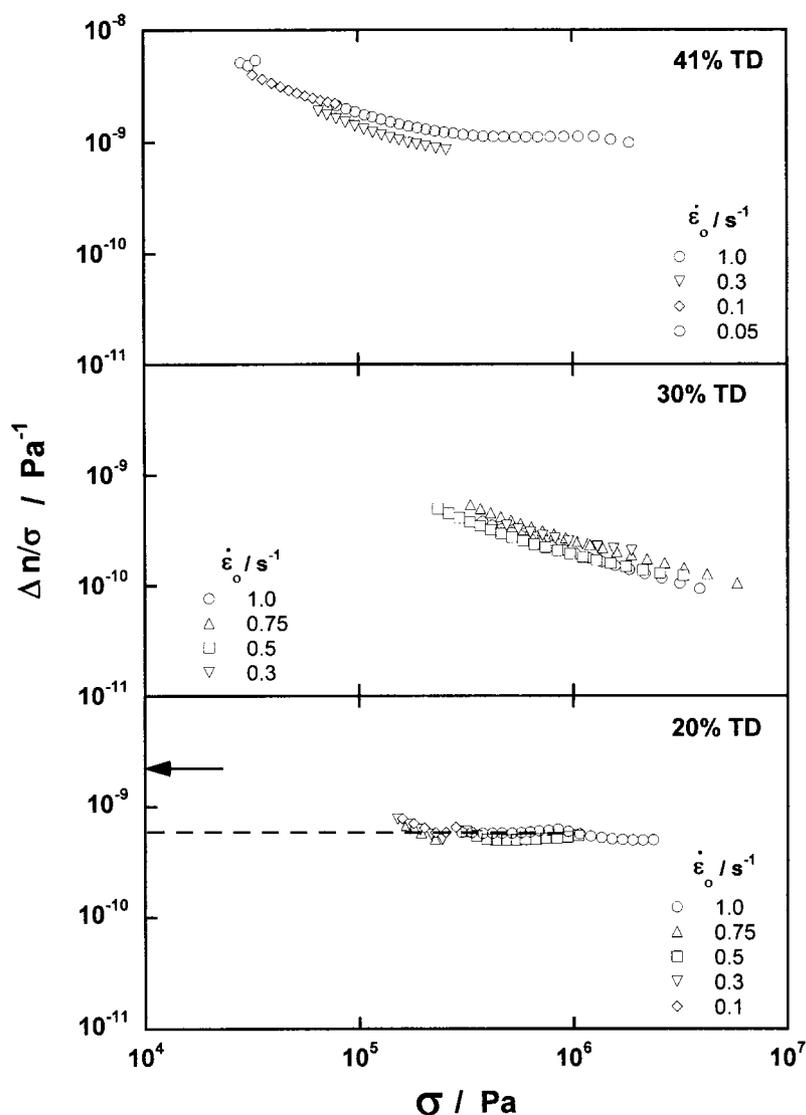| %TD (mol)	$M_w \times 10^{-4}$	M_w/M_n	$T_g/°C$
20	12.5	2.7	64
30	10.0	3.1	103
41	10.4	2.4	146

Fig. 2. Stress optical coefficient $C(\dot{\epsilon}_0; t) \equiv \Delta n(\dot{\epsilon}_0; t)/\sigma(\dot{\epsilon}_0; t)$ for indicated copolymer at $T_g + 50°C$. The dashed line indicates the constant $C(t)$ of 20% TD and the arrow indicates the reported value of $C(t)$ for LDPE.

Fig. 1. As we see in this figure, the values of C for the low TD content copolymer stay nearly constant at 5.7×10^{-10} Pa^{-1}, which is about one-fourth of the value [3] $(2.2 \times 10^{-9}$ Pa$^{-1})$ reported for low density polyethylene (LDPE). The stress-optical rule (SOR) roughly holds. However, for those of higher TD content $C(\dot{\epsilon}_0; t)$ decreases with increasing σ so that the SOR is invalid. At lower temperatures, say, $T_g + 40.0°C$, the tendency of strain-induced hardening becomes more pronounced but SOR remains valid for the 20% TD copolymer. On the other hand, for the 41% TD copolymer the tendency becomes more pronounced and SOR remains invalid even though at higher temperature, $T_g + 60.0°C$.

The strong elongational flow field might induce conformational transition in the individual chains of the E–TD copolymer as we have seen in supercooled liquid of semicrystalline syndiotactic polystyrene (s-PS) [4] and/or nematic ordering of the local chain segments among the neighboring chains.

Fig. 3 indicates some typical examples of WAXD patterns of the copolymers determined before and after elongation at different conditions. The WAXD patterns for the samples before elongation always show a liquid-like hallow with a broad peak corresponding to the correlation length of 0.51 nm, while for those after elongation, beside the broad peak from the hallow a small side peak always appears at the position of 0.76 nm, implying that local ordering of the segments might have taken place.

For the possibility of elongational flow induced conformation change in the copolymer, the evidence is still not quite convincing. However, an interesting implication can be found in, for example, ^{13}C NMR spectra — for the copolymer of 20% TD content, which obeyed SOR, the NMR spectra exhibited a small but a significant difference
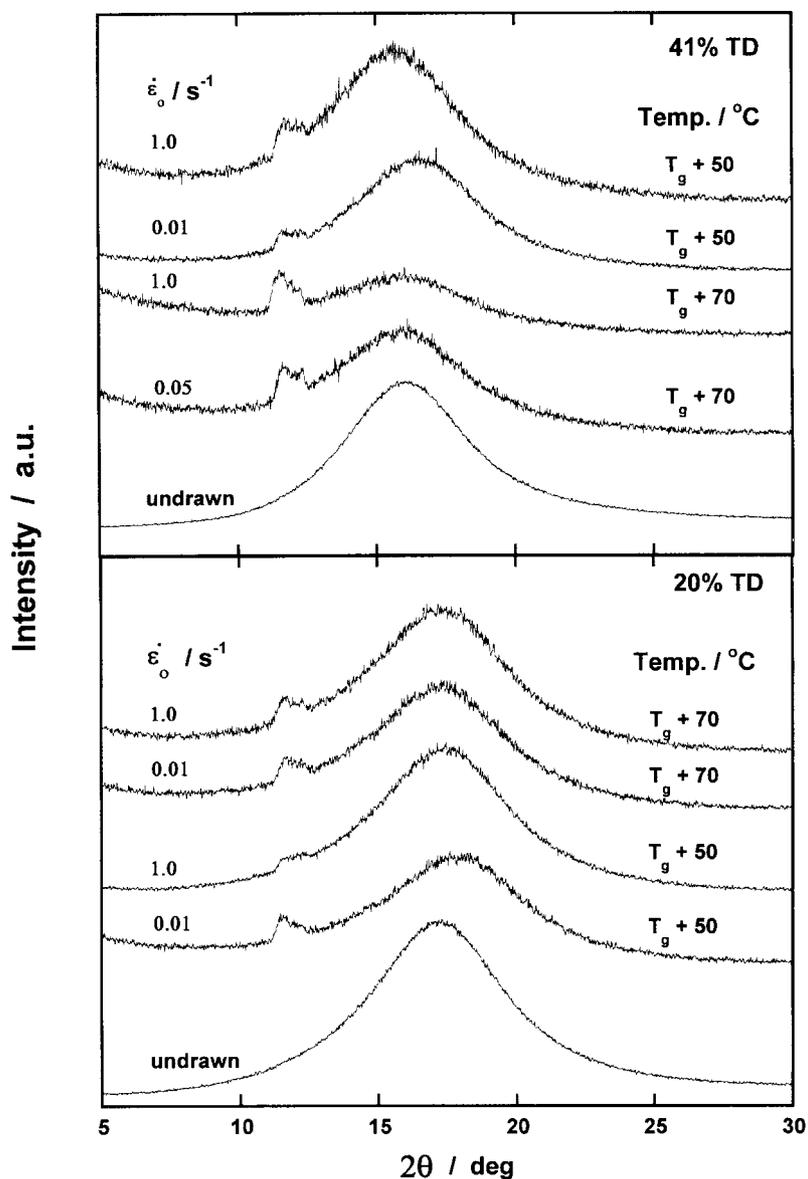
Fig. 3. WAXD patterns of two different TD content copolymers before and after elongation at various Hencky strain rates of two different temperatures.

between the sample before and after elongation. However, for those of 41% TD content, which always violated SOR and exhibited significant strain-induced hardening behavior, we saw virtually no difference in the NMR spectra before and after the elongation.

What are responsible for the strong strain-induced hardening behavior?

The violation of SOR and the tendency of strain-induced hardening are presumably because the bulkier TD groups in the main chain make it more difficult for the chains of higher TD content to be stretched out and disentangled, especially under high-strain rate elongation. More detailed data and the

results of the conformational change concerned with strain-induced hardening will be discussed later [5].

References

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