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Elongational Flow Birefringence of Reactor-Made Linear Low-Density Polyethylene

Masami Okamoto, Akira Kojima, and Tadao Kotaka*

Advanced Polymeric Materials Engineering, Graduate School of Engineering, Toyota Technological Institute, Hisakata 2-12-1, Tempaku, Nagoya 468-8511, Japan

Helmut Münstedt*

Institute of Polymer Materials, Department of Materials Science, University of Erlangen-Nüernberg, Martensstrasse 7 D-91058 Erlangen, Germany

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A recently established technique of polyolefin fractionation called "*temperature rising elution fractionation* (TREF)"[1] revealed an intriguing feature of new generation polyethylenes (PEs); that is, they are, in fact, blends of closely related chemical species. A typical example is commercial linear low-density PE which was claimed via TREF to be a blend of 84% linear low-density PE (LLDPE) of ~ 10 short methylene branchings/1000 carbon atoms with 16% high-density PE (HDPE) with virtually no branchings.[2] Then this finding created a crucial problem of miscibility−immiscibility and/or phase segregation of the chemically akin species in the polymer.[2] For the blend immiscibility problem,[3] commonly used techniques are optical and electron microscopy, thermal analysis, and some scattering methods. However, on dealing with blends of PEs, these methods inevitably run into difficulty in distinguishing the components because of their small contrast factors or close proximity in their glass transition temperatures.[3] The most powerful method may be small angle neutron scattering (SANS) on blends of deuterated and undeuterated species. For example, such a study on blends of fully deuterated HDPE (*d*-HDPE) with LLDPE (*h*-LLDPE) was conducted by Schelten et al.[4] some 20 years ago. Recently, Tashiro et al.[5] also reported the results on blends of *d*-HDPE with *h*-LLDPE that has ~41 ethylene branchings/1000 carbon atoms and concluded that they are fully miscible in the molten state. However, deuteration itself might have altered the chemistry and physics of the components.

Recently we developed a new techique, "*elongational flow opto-rheometry* (EFOR)", which enabled us to make simultaneous measurements of transient tensile stress σ and birefringence Δn for polymer melts under elongational flow at constant tensile strain rates.[6] In our previous studies[6−8] we applied EFOR to several polymers and found that the stress optical rule (SOR)[9,10] was surprisingly well obeyed even during high strain-rate elongation,[5,7] except for those possessing deformable microdomains of different refractive indices such as semicrystalline polymer liquids[7] and block copolymer liquids below (or above) its order−disorder transition temperature (ODT). In fact, a recent EFOR test on elongation of A−B-A type triblock copolymer melts revealed that SOR was violated due to the contribution of form-birefringence of deforming microdomains.[11] Thus EFOR might be a promising means to test the immiscibility of the components having a very small but nontrivial optical contrast by checking whether the blend exhibits form birefringence. This communication reports a preliminary result of such a test on a blend of a low-density PE (LDPE) with a ultrahigh molecular weight PE (UHMWPE) and on a *reactor-made* LLDPE, which was claimed via TREF to be a blend of 16 wt % HDPE of no branchings and 84 wt % LLDPE produced spontaneously during the synthesis.

The *reactor-made* LLDPE (coded as LLD-HDPE) used has $M_w = 10.7 \times 10^4$ and $M_w/M_n = 3.14$ as determined by gel permeation chromatography in trichlorobenzene at 140 °C using polystyrene elution standards and a melting temperature T_m of ~120 °C. Its TREF chromatogram shows that LLD-HDPE is a blend of 16 wt % HDPE of no branchings and 84 wt % LLD-PE of average 10 short branchings/1000 carbon atoms. The details of TREF analysis were described elsewhere.[2]

For EFOR, sample pellets were preheated to 160 °C for 3 min and hot-pressed at 5 MPa for 3 min, and test specimens of $60 \times 7.0 \times 2.0$ mm^3 were cut out from the sheet. In EFOR run, a sample specimen was set at 140 °C ($> T_m$ of LLD-HDPE) and annealed in situ for 150 s long enough for melting the strip to obtain a clear transparent specimen before starting the run. The details of the EFOR were described elsewhere.[6,8] The EFOR data were compared with our previous results on *laboratory-made* blends (up to a ratio of 90/10 by weight) of an LDPE (Asahi Chemical Co.; melt flow index MFI = 0.4 g/10 min, bulk density at 25 °C = 0.919 dl/g, and melting temperature $T_m = 109.3$ °C) and a UHMWPE (Mitsui Petrochemical Co.; $M_w = 2000$K and $T_m = 144$ °C).

First we examined the linear viscoelastic behavior of LLD-HDPE and the LDPE/UHMWPE blend by measuring frequency ω dependence of storage $G'(\omega)$ and loss $G''(\omega)$ moduli at 140−150 °C. For both systems we found $G'(\omega) \propto \omega^2$ and $G''(\omega) \propto \omega$ in the low ω tails, which are similar to those of narrow MW distribution homopolymer melts.

According to the Palierne[12] theory on the immiscible viscoelastic emulsions, the secondary plateau of the modulus can be predicted from the geometric relaxation of the dispersed droplet phase. However, these samples did not show any shoulder or secondary plateau. There are two possibilities to explain these results: One is that the systems are completely miscible, and the other is that the interfacial energy parameter between the chemically similar components is too small for the secondary plateau of the modulus to become appreciable.[12] Anyway, viscoelastic spectroscopy alone cannot tell for sure the miscibility/immiscibility and/or phase segregation behavior of such blends.

Then we proceeded to the EFOR test especially to see if the SOR[9,10] is valid for these systems under elongation and if the stress optical coefficient $C(\dot{\epsilon}_0;t)$ [$\Delta n(\dot{\epsilon}_0;t)/\sigma(\dot{\epsilon}_0;t)$] is independent of Hencky strain rate $\dot{\epsilon}_0$, strain ϵ or $\sigma(\dot{\epsilon}_0;t)$ and also of molecular weight (MW) and its distribution (MWD) or the blend ratio. In our previous experiments on LDPE/UHMWPE[6,8] blends, this was found to be the case as we will demonstrate shortly.

Figure 1 shows double logarithmic plots of transient elongational viscosity $\eta_E(\dot{\epsilon}_0;t)$ ($=\sigma(\dot{\epsilon}_0;t)/\dot{\epsilon}_0$) and birefrin-

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* To whom correspondence should be addressed.

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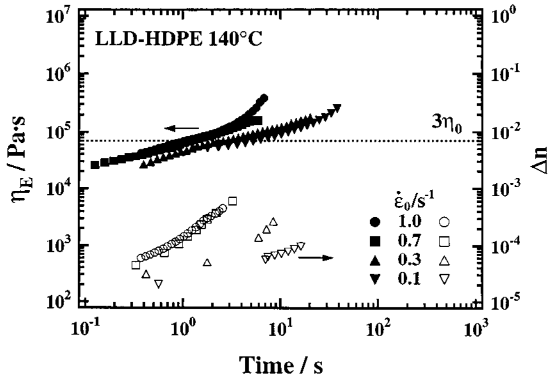

Figure 1. Double logarithmic plots of transient elongational viscosity $\eta_E(\dot\epsilon_0;t)$ $(= \sigma(\dot\epsilon_0;t)/\dot\epsilon_0)$ (solid symbols) and birefringence $\Delta n(\dot\epsilon_0;t)$ (open symbols) as a function of time t for LLD-HDPE elongated at 140 °C with various Hencky strain rates $\dot\epsilon_0$ as indicated. The dotted line indicates 3 times the shear viscosity, $3\eta_0$, determined at the shear rate $\dot\gamma = 0.01$ s^{-1} at 140 °C.

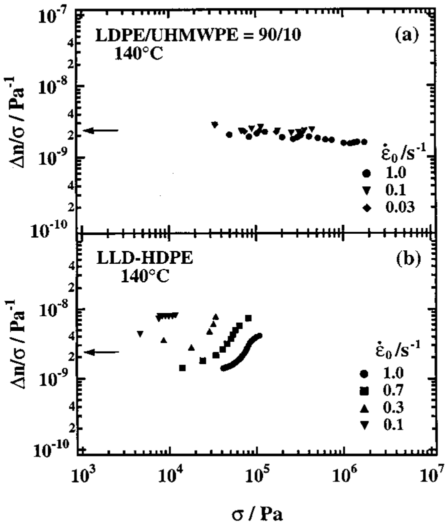

Figure 2. Stress optical coefficient $C(t) \equiv \Delta n(\dot\epsilon_0;t)/\sigma(\dot\epsilon_0;t)$ for (a) LDPE/UHNWPE 90/10 blend and (b) LLD-HDPE obtained at 140 °C. The arrow in each panel indicates C/Pa^{-1} = 2.2 × 10^{-9} reported for shear flow experiments.[9]

gence $\Delta n(\dot\epsilon_0;t)$ against time t observed for LLD-HDPE at 140 °C with different Hencky strain rates $\dot\epsilon_0$ ranging from 0.1 to 1.0 s^{-1}. The dotted line in the figure is the 3-fold zero-shear viscosity $3\eta_0$ obtained at 140 °C. We see that $\eta_E(\dot\epsilon_0;t)$ exhibits a tendency toward so-called *strain-induced-hardening*[13] that is an upward deviation or *up-rising* from $3\eta_0$ at a different *up-rising* time depending on $\dot\epsilon_0$. On the other hand, time development $\Delta n(\dot\epsilon_0;t)$ of increases with t rather faster than $\eta_E(\dot\epsilon_0;t)$.

Figure 2 now shows double logarithmic plots of $C(\dot\epsilon_0;t)$ vs $\sigma(\dot\epsilon_0;t)$ for (a) LDPE/UHMWPE blends and (b) LLD-HDPE both at 140 °C. Also compare our data with the reported value of $C(=\Delta n_{13}/[\sigma_{11} - \sigma_{33}])$ $(=2.2 \times 10^{-9}$ Pa$^{-1})$ for PE melts under the shear flow[9] indicated with an arrow in the figure. We clearly see that the SOR is valid for LDPE/UHMWPE blends, and $C(\dot\epsilon_0;t)$ $[\equiv\Delta n(\dot\epsilon_0;t)/\sigma(\dot\epsilon_0;t)]$ nicely agreed with that reported for shear flow experiments ($C = 2.2 \times 10^{9}$ Pa^{-1}), as seen in the $C(\dot\epsilon_0;t)$ vs $\sigma(\dot\epsilon_0;t)$ plots reproduced in Figure 2a. On the other hand for LLD-HDPE, depends on both $\dot\epsilon_0$ and $\sigma(\dot\epsilon_0;t)$. The value of $C(\dot\epsilon_0;t)$ starts from the reported C $(=2.2 \times 10^{-9}$ Pa$^{-1})$ value and rapidly increases as the specimen is stretched to a large extent. The SOR is clearly violated, implying that the contribution of form birefringence of HDPE domains is nontrivial.

This result is very similar to our recent unpublished results obtained on a styrene–ethylene-*co*-butylene–styrene (SEBS) triblock copolymer with spherical S-microdomains elongated at the temperature between T_g of S-domains and ODT.[11] In SEBS under elongation the increase in $C(\dot\epsilon_0;t)$ with $\sigma(\dot\epsilon_0;t)$ may arise from the increase in the form birefringence of S-microdomains. Observation of the deformed domain morphology in SEBS and/or crystalline morphology in LLD-HDPE specimens after elongation is now in progress to confirm if the contribution of form birefringence does exist or not.

Through the above approaches, we can hopefully clarify the miscibility/immiscibility and/or phase segregation behavior of molten blends without introducing deuterated species. More detailed data and the results of their analyses will be published later.

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