

A Study of the Degradation of Polyethylene by High-Temperature Dynamic Light-Scattering

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SYNOPSIS

After passing through an extruder, a small amount of degradation normally occurs in the high molecular weight tail of a broadly distributed polymer sample. This small amount of degradation could dramatically affect the polymer viscoelastic properties. It is difficult to detect this type of degradation by using conventional analytical methods, such as high-temperature size exclusion chromatography. An investigation of this type of degradation in a broadly distributed polyethylene sample was accomplished by using high-temperature dynamic light-scattering (HTDLS). We have shown that the measured line-width (or the translational diffusion coefficient) distribution in the HTDLS is proportional to M^α with $\alpha = 3.580 \pm 0.005$, so that the HTDLS is a very sensitive technique for detecting a very small amount of degradation in the high molecular weight tail. Another advantage of using the HTDLS is that the study does not introduce further stress or perturbation into the sample. In this study, we also investigated the thermal degradation of the polyethylene sample in trichlorobenzene at high temperatures. We found that the polyethylene sample *after* the extrusion undergoes a thermal degradation more easily. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

The correlation of macromolecular parameters to macroscopic properties of a bulk polymer is very important. In practice, the most important macromolecular parameters are molecular weight and its distribution, which have already been correlated to various macroscopic properties, such as elongation at yield and flexural modulus of elasticity.¹ Several models are proposed to predict mechanical properties as a function of molecular weight.^{2,3} Laser light-scattering (LLS) together with other analytical techniques, such as size exclusion chromatography (SEC) or gel permeation chromatography (GPC), have been used to characterize polyethylene in various solvents, including trichlorobenzene (TCB), to obtain the weight average molecular weight (M_w) or the molecular weight distribution (MWD).⁴⁻⁸

It is well-known that, usually, both the mechan-

ical and thermal degradations occur when polyethylene is processed, which affects the macroscopic properties of the finished products, such as the surface smoothness. Therefore, it is important in practice to detect the degradations and investigate how they occur at various experimental conditions. Since only a very small amount of degradation occurs in the high molecular weight tail under normal processing conditions, or, say that the molecular weight distribution just becomes slightly narrower, it is difficult in practice to detect such a small amount of degradation. In the case of polyethylene, it is even more difficult to detect this type of degradation because polyethylene only dissolves in certain special solvents at high temperature. Therefore, a sensitive technique for detecting this type of degradation in polyethylene is urgently needed for quality control and product development.

In this article, we will demonstrate that the HTDLS as an analytical method is very sensitive for investigating the mechanical and thermal degradations of polyethylene.

BASIC PRINCIPLES

In dynamic light-scattering (DLS), an intensity-intensity time correlation function $G^2(t, q)$ in the self-beating mode is normally measured, which has the following form^{9,10}

$$G^2(t, q) = A[1 + \beta |g^1(t, q)|^2] \quad (1)$$

where A is a measured baseline; β , a parameter depending on the coherence of the detection; and t , the delay time. The $g^1(t, q)$ is the normalized first-order electric-field time-correlation function which can be calculated from the measured $G^2(t, q)$ and A , where $q = 4\pi n \sin(\theta/2)/\lambda_0$ with n , θ , and λ_0 being the solvent refractive index, the scattering angle, and the wavelength of light in vacuum, respectively. In our correlation function measurements, instead of using A as an adjustable parameter, we insisted on having A and $\lim_{t \rightarrow \infty} G^2(t, q)$ (the calculated baseline) agree to within 0.1%. For a polydisperse sample, $g^1(t, q)$ is related to the line-width distribution $G(\Gamma)$ by^{9,10}

$$g^1(t, q) = \int_0^\infty G(\Gamma) e^{-\Gamma t} d\Gamma \\ \propto \langle E(t, q) E^*(0, q) \rangle \quad (2)$$

where the line-width Γ usually depends on both concentration C and q . At $C = 0$ and $q = 0$, Γ can be related to the translational diffusion coefficient D by $\Gamma = Dq^2$. By doing a Laplace inversion of eq. (2), we are able to calculate $G(\Gamma)$ or $G(D)$. In this study, the Laplace inversion was done by a computer program called CONTIN,¹¹ which was kindly furnished by S. W. Provencher. Based on eq. (2), as both $t \rightarrow 0$ and $q \rightarrow 0$, we have

$$\int_0^\infty G(\Gamma) d\Gamma \propto \langle E(0, 0) E^*(0, 0) \rangle \\ = I(q = 0) \quad (3)$$

On the other hand, according to the light-scattering theory, as both $C \rightarrow 0$ and $q \rightarrow 0$, we have

$$I(q = 0) \propto \int_0^\infty f_n(M) M^2 dM \quad (4)$$

where $f_n(M)$ is the number distribution; M , molecular weight. It is known that in general M can be scaled to D by using^{6,8}

$$D = k_D M^{-\alpha_D} \quad (5)$$

with k_D and α_D being two scaling constants. Theoretically, the value of α_D ranges from $\frac{1}{3}$ for a hard sphere to 1 for a rigid, thin rod. In previous study, we have found that $\alpha_D \cong 0.580 \pm 0.005$ for polyethylene in trichlorobenzene at 135°C.⁸ A combination of eqs. (3) and (4) leads to the following relation:

$$G(\Gamma)\Gamma \propto f_n(M)M^3 \quad \text{or} \\ G(D)D \propto f_n(M)M^3 \quad (6)$$

By using eq. (5) and $\alpha_D = 0.58$, we can rewrite eq. (6) as

$$G(\Gamma) \propto f_n(M)M^{3.58} \quad \text{or} \\ G(D) \propto f_n(M)M^{3.58} \quad (7)$$

It shows that $G(\Gamma)$ or $G(D)$ is very sensitive to the molecules with higher molecular mass in a broad distribution even though their number $f_n(M)$ may be very small. The detailed principle of DLS can be found elsewhere.⁸⁻¹⁰

EXPERIMENTAL

Samples

One very broadly distributed commercial polyethylene ($M_w \sim 8 \times 10^5$, $M_w/M_n > 20$, BASF, Ludwigshafen, Germany) was used without further purifications. The mechanic degradation was induced by forcing the sample through a 5-mm hole by an extruder at a speed of 300 rpm and 200°C. The same sample *before* and *after* the extrusion was investigated. Trichlorobenzene (TCB, synthesis-grade) and 0.05 wt % of 2,6-di-tert-butyl-4-methylphenol (antioxidant) was used as solvent without further purification.

Solution Preparation

The polyethylene concentrations were about 5×10^{-4} g/mL. All solutions were made and clarified at 145°C to ensure a complete dissolution of polyethylene. The solutions were filtered by a 25-mm glass-fiber filter with a pore size of 0.5–1.49 μm (no. 6, 370018, Schleicher & Schuell, Dassel, Germany).

DLS Measurements

The sample holder of an ALV commercial laser light-scattering spectrometer (ALV/SP-86, Langen in Hessen, Germany) was modified so that DLS could be done at a temperature as high as 350°C. An argon

ion laser (Coherent INNOVA 300, operated at wavelength 488 nm and 300 mw) was used as the light source. The primary beam was vertically polarized. By placing a polarizer in front of the detector, we measured only the vertically polarized scattered light. An ALV-3000 correlator was used to measure the intensity-intensity time-correlation functions. The details of the HTDLS instrumentation can be found elsewhere.^{8,12} For comparison, we also used a high-temperature size exclusion chromatography (SEC) or gel permeation chromatography (GPC) to investigate the degradation of the same polyethylene sample *before* and *after* the extrusion because SEC as an analytical method has been widely used in both academic research and industrial applications for the characterization of molecular weight distribution. A commercial high-temperature SEC (Waters 150C) with an infrared detector operated at 3.5 μm was used and the measurements were done according to a standard procedure, whereby the same TCB was used as eluent. Both DLS and SEC measurements were performed at 135°C.

RESULTS AND DISCUSSION

Figure 1 shows the semilogarithmic plots of two typical "normalized" intensity-intensity time-correlation functions of the polyethylene sample *before* and *after* the extrusion. It is known that for a poly-

mer with a smaller molecular weight, the diffuse or the relaxation will be faster. It is exactly as we have expected that in Figure 1, the sample after extrusion decays faster because of the degradation of the high molecular weight tail in the molecular weight distribution. For these broadly distributed samples, to avoid the arbitrary error introduced in the choice of the sample time, we intentionally selected the *same* sample time for both samples because we are only interested in the relative change in the relaxation.

According to eq. (2), it is known theoretically that for a monodisperse sample, the semilogarithmic plot should be exactly a straight line and the slope corresponds to Γ or D . The curvatures in Figure 1 clearly show that the samples are very broadly distributed. Therefore, it is expected that the calculated distribution $G(D)$ from the measured time-correlation function, or equivalently, the z -averaged diffusion coefficient ($\bar{D} = \int_0^\infty G(D) D dD$) will depend strongly on which part of the time-correlation function is analyzed. The initial part of the time-correlation function contains more information about the smaller molecular weight portion in the molecular weight distribution; the tail part, more information about the higher molecular weight tail in the distribution. It is obvious that we are more interested in the tail part of the time-correlation function because the degradation occurs there. By intentionally taking away some initial data points, we only analyzed the rest of the measured time-correlation function.

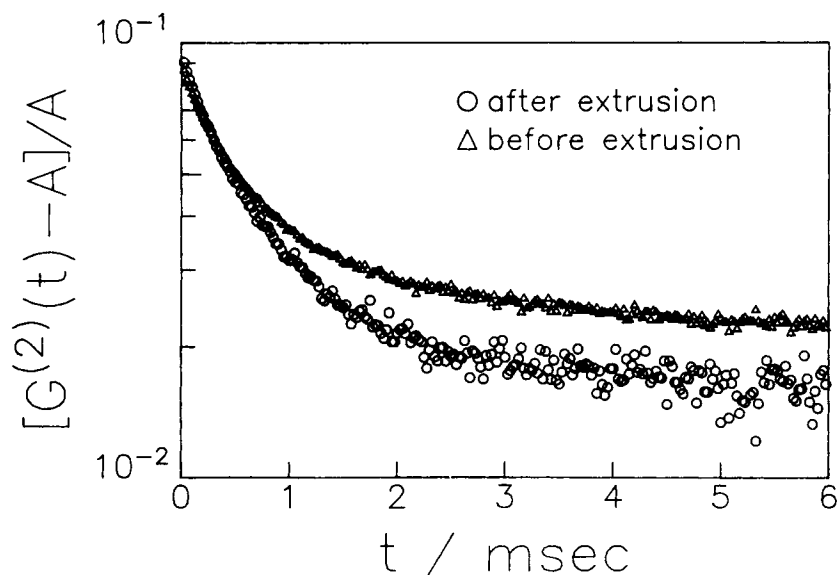


Figure 1 Semilogarithmic plots of the same two correlation functions presented in Figure 1. The clear curvature indicates that the samples are very broadly distributed.

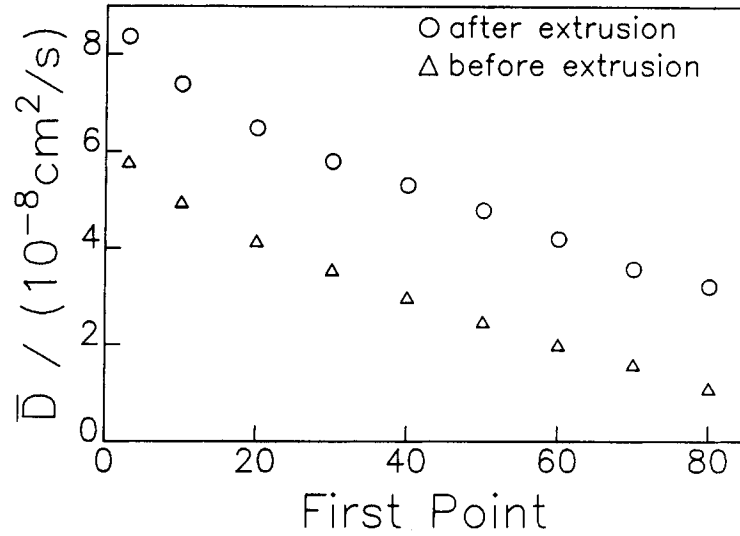


Figure 2 Plot of the average diffusion coefficient \bar{D} vs the “first point,” where the number of “first points” should be read as the number of initial data points which have been intentionally taken away from the measured correlation function before we analyzed $g^2(t, q)$ to obtain \bar{D} .

Figure 2 shows how the average translational diffusion coefficient, $\bar{D} = \int_0^\infty G(D) D dD$, changes with the “first point,” where the number of the “first point” should be read as the number of initial data points which have been taken away from the correlation function. When the “first point” is large, we actually analyzed only the tail part of the time-correlation functions. It can be seen in Figure 2 that the absolute difference between \bar{D} of the two poly-

ethylene samples *before* and *after* extrusion at different “first points” is about a constant, and the relative difference between \bar{D} increases dramatically from less than half at the “first point” $\cong 3$ to more than 2.5 times at the “first point” $\cong 80$. This means that the absolute amount of the degradation is *constant* for our given sample, and the relative amount of the degradation is much higher if we only consider the high molecular weight portion in the distribu-

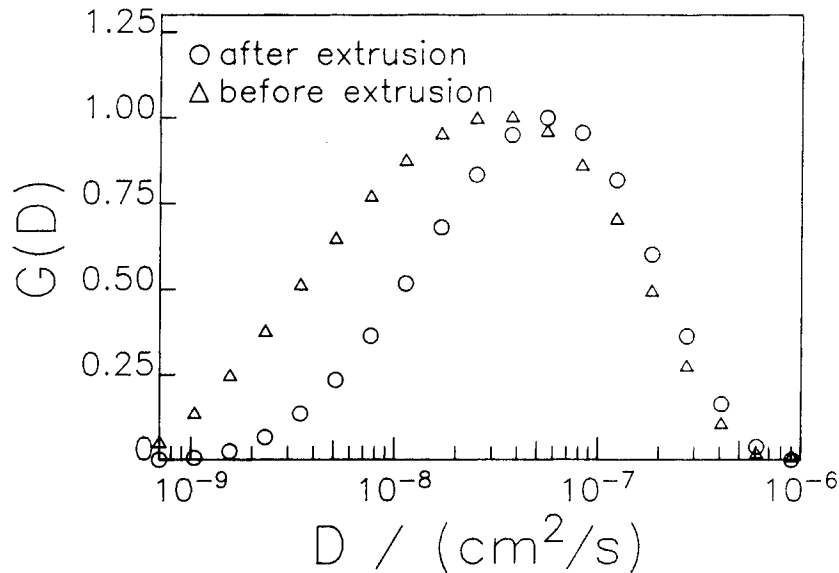


Figure 3 Typical diffusion coefficient distributions $G(D)$ calculated from the measured time-correlation functions presented in Figure 1 without taking away any initial data points.

tion. Therefore, \bar{D} obtained from the tail part of the measured time-correlation function is very sensitive even to a small amount of degradation in the high molecular weight tail.

Figure 3 shows two translational diffusion coefficient distributions $[G(D)]$ calculated from the measured correlation functions presented in Figure 1 without taking away any data points. It is obvious that the two distributions are mainly different in the portion with smaller diffusion coefficient, which corresponds to the higher molecular weight portion in the molecular weight distribution. In comparison with $G(D)$ obtained from the sample *before* extrusion, the lack of a portion with smaller diffusion coefficient in $G(D)$ obtained from the sample *after* extrusion clearly shows the degradation of the high molecular weight tail.

Figure 4 shows two typical molecular weight distributions *before* and *after* degradation, which were obtained by using high-temperature SEC. The two molecular weight distributions are very similar to each other, i.e., we are unable to tell whether there is a degradation in the high molecular weight tail. Thus, it would be rather difficult to use the high-temperature SEC in practice to distinguish between two unknown samples *with* and *without* degradation. This difficulty is caused by the two following facts: first, the detected signal $C(V)$ (the elution volume distribution) in SEC is proportional to the weight concentration $f_n(M)M$, so that the signal from a small amount of the high molecular weight tail is

buried within the baseline noise; second, the resolution of SEC is not very high when $M > 5 \times 10^6$ g/mol. In principle, if a small-angle laser light-scattering (SALLS) detector is used, SEC is more sensitive to the high molecular weight tail because the scattered intensity (I) is proportional to $f_n(M)M^2$. However, it is not trivial to set up and use a high-temperature SALLS detector in practice. Even we could do so, SEC is still less sensitive than the high-temperature DLS because $G(D) \propto f_n(M)M^{3.58}$.

Figure 5 shows the time-dependence of \bar{D} in TCB at 135°C, where the values of \bar{D} were obtained by the second-order cumulant method instead of the time-consuming CONTIN method used in Figure 2. In comparison with the CONTIN method, the cumulant method emphasizes the initial part of the correlation function more, i.e., the faster motion. This is why the values of \bar{D} in Figure 5 are larger than in Figure 2. Here, we are only interested in the relative change in \bar{D} . During the experiments, we observed no change in \bar{D} for the first 4–5 h (data not shown), which is longer than our typical experimental time for one dynamic light-scattering experiment (including the sample preparation). Therefore, we are very sure that there is no significant thermal degradation during our typical DLS experiments. But, Figure 5 shows that \bar{D} increases slightly with time. This indicates a slow thermal degradation of polyethylene in TCB at 135°C even with the presence of the antioxidant (0.05 wt % of 2,6-di-tert-butyl-4-methylphenol). This slow deg-

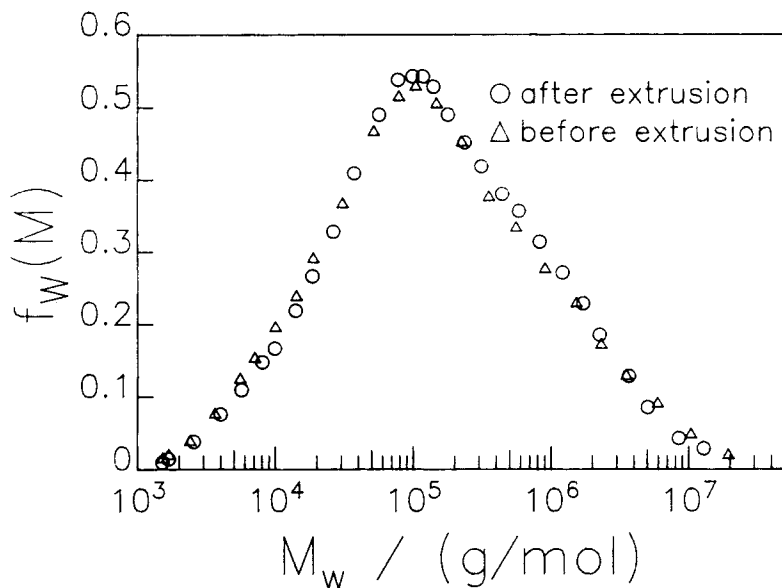


Figure 4 Two typical molecular weight distributions of the polyethylene sample *before* and *after* the degradation, which were obtained by using high-temperature SEC at 135°C.

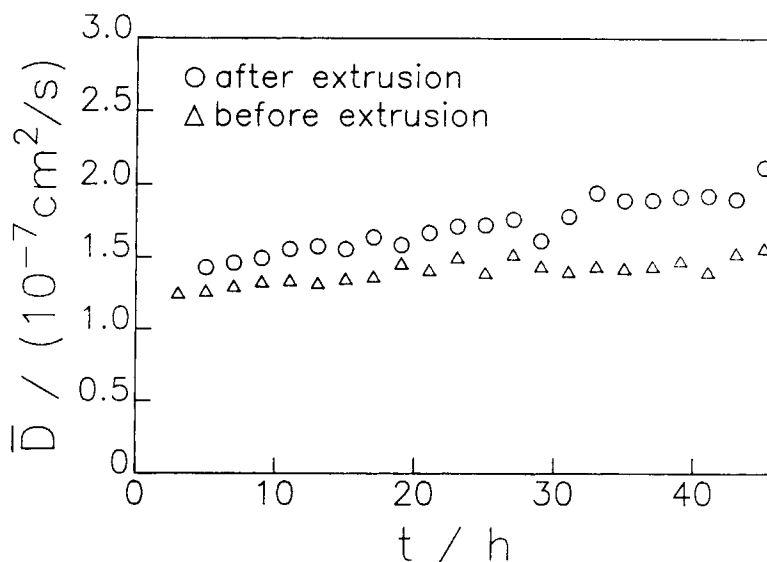


Figure 5 The time-dependence of the average translational diffusion coefficient \bar{D} of the polyethylene sample *before* and *after* the degradation in trichlorobenzene at 135°C.

radiation has been overlooked in the past. Our results suggest that a special attention should be given to this slow thermal degradation whenever an investigation is carried out at high temperature for a time period longer than 5 h. The results in Figure 5 also show that the degradation of the polyethylene sample after extrusion at 135°C is slightly faster, i.e., it has a slightly larger slope. Normally, we would expect that the degradation of the sample *before* extrusion should be *faster* because the degradation of the high molecular weight tail in the sample is *easier*. It is unclear to us why our results contradict a normal expectation. One possible explanation is that the extrusion has introduced *stress* on some polymer chains so that these polymer chains are easier to break at high temperatures.

CONCLUSION

We have shown that the high-temperature DLS, a very sensitive analytical method, can be used to detect a very small amount of degradation in the high molecular weight tail of a broadly distributed polyethylene sample, where the high-temperature SEC was unable to clearly show the degradation. The sensitivity of the HTDLS is intrinsic because the line-width distribution $G(\Gamma)$ measured in DLS is proportional to M^α with $\alpha = 3.580 \pm 0.005$. Besides the sensitivity, we have shown that in the HTDLS, we can look into one particular part of a broad distribution by choosing one proper sample time or by analyzing one part of the measured time-correlation function. Because of its nondestructive nature, the

use of the HTDLS will introduce no further *stress* and no perturbation to the test sample, which is certainly an additional advantage over other analytical methods, such as the high-temperature SEC and the rheology methods.

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