Linear Stress Relaxation Behavior of Amorphous Ethylene−Styrene Interpolymers

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ABSTRACT: Amorphous ethylene−styrene interpolymers (ESIs) provide an excellent model system for testing contemporary concepts of molecular dynamics. Moreover, the results can be extrapolated to the chain reptation dynamics of amorphous polyethylene at ambient temperature which cannot be assessed by direct experimental techniques. Previous studies of creep and nonlinear stress relaxation were extended to test theoretical relaxation functions for monodisperse polymers and proposed combining rules against the linear stress relaxation behavior of ESIs in the plateau and terminal regions. Master curves were constructed by time−temperature superposition of data at temperatures from T_g to $T_g + 30$. The temperature dependence of the shift factor was independent of molecular weight and styrene content and was well described by the WLF equation. The master curves were satisfactorily fit by the empirical KWW equation. Relaxation master curves were modeled with theoretical relaxation functions for monodisperse polymers, appropriate combining rules, and known molecular weight distributions. The Doi−Edwards single reptation model did not give satisfactory results. However, the des Cloizeaux double reptation approach successfully described the relaxation master curves. Excellent agreement was found between the resulting plateau moduli and those from a previous study of creep in the glass transition region. The calculated entanglement molecular weight (1250−2290 g mol^{-1}) was much closer to that of polyethylene (480−860 g mol^{-1}) than to that of polystyrene (13 500 g mol^{-1}) due to the unique chain microstructure of these ESIs with no head-to-tail styrene chain insertions.

Introduction

Past studies of creep and stress relaxation suggest that amorphous ethylene−styrene interpolymers (ESIs) provide an excellent model system for examining the molecular dynamics underlying polymer viscoelastic behavior.[1−3] The copolymers used in these studies have substantially random incorporation of styrene except that successive head-to-tail styrene chain insertions are shown by ^{13}C NMR analysis to be absent, even with high levels of styrene incorporation.[4] This feature differentiates interpolymers from truly random copolymers of ethylene and styrene. Probably because of this unique aspect of the chain microstructure, which means that all carbons with pendant phenyl groups are separated by at least two methylene groups, the entanglement molecular weight obtained from the retardation time spectrum and the plateau compliance is found to be much closer to polyethylene than to polystyrene.[2] Thus, regarding chain flexibility and entanglement network, ESIs provide an unusual opportunity to approach the amorphous state of polyethylene without the constraints of the inevitable crystallinity.

By strongly affecting both stress relaxation and recovery, changing ESI comonomer content reveals the different mechanisms of molecular relaxation for chemically similar materials on the laboratory time scale at temperatures close to ambient.[3] Pronounced nonlinearity of the relaxation modulus in the plateau and terminal regions at large imposed strains was amenable to interpretation in terms of the Doi−Edwards tube theory. Experimental values of the strain dependence (damping function) obtained by superposition of nonlinear relaxation curves fit the theory well. Furthermore, although comonomer content and molecular weight influenced the relaxation dynamics, neither affected the strain dependence, again consistent with theoretical predictions. This study is now extended with an examination of the linear stress relaxation behavior in the plateau and terminal regions.

Interest of researchers in the linear viscoelastic behavior of polymers dates at least to the 1940s when the most successful descriptions of the relaxation spectrum were based on phenomenological spring and dashpot models. Major advances in mechanistic understanding of polymer viscoelasticity occurred in the past two decades with the development of molecular dynamics theories. Doi and Edwards[5] employed the reptation concept of de Gennes[6] to model the viscoelastic behavior as a diffusion process of a chain in a network of surrounding chains. Although this model only qualitatively describes the relaxation behavior of monodisperse polymers, it was a major step forward in understanding of viscoelastic behavior and the basis for subsequent developments. The long-standing problem with the original reptation theory was the predicted cubic dependence of melt viscosity on molecular weight of a monodisperse polymer in contrast to the observed 3.4 power dependence. Later modifications of the theory to incorporate additional relaxation mechanisms, such as contour length fluctuations and constraint release, resolved the problem.[7,8] In an alternative approach that describes the relaxation in the terminal region within the framework of the reptation concept, des Cloizeaux

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Table 1. Materials

designation	styrene (wt %)	styrene (vol %)	a-PS (wt %)	T_g (°C)	M_w (kg mol^{-1})	M_w/M_n	density (g cm^{-3})
ES52	52	47	1.5	−2	219	2.4	0.9678
ES60-250	60	55	0.5	8	252	2.4	0.9874
ES68	68	63	0.7	23	239	2.0	1.0123
ES60-350	61	56	0.7	10	349	2.4	0.9874
ES60-250	60	55	0.5	8	252	2.4	0.9874
ES60-160	58	53	0.5	6	164	2.4	0.9874
ES60-120	58	53	0.6	6	119	2.4	0.9874

considered the “double reptation” of a pair of entangled chains with the reptation modeled with a time-dependent diffusion coefficient.[9−13] This approach may indirectly take into account contour length fluctuations.[8] The “double reptation” theory provides an explicit explanation for the 3.4 power dependence of melt viscosity on molecular weight of a monodisperse polymer.[12,13] The theory also takes into account cooperativity in the chain motion, which is useful in describing the viscoelastic behavior of a polydisperse polymer.

Because of the strong molecular weight dependence of chain dynamics in the plateau and terminal regions, the molecular weight distribution is an important factor in the relaxation behavior of real polymers. The Doi−Edwards model suggested that the relaxation function of a polydisperse polymer is a linear combination of the relaxation function of each molecular weight component.[5] However, this linear combining rule was found to be unsatisfactory even for two-component monodisperse polymer blends.[9] When this combining rule was modified to take into account other relaxation mechanisms,[5] it still did not fully describe the relaxation behavior of polymer blends.[14,15] An alternative combining rule from double reptation theory worked well for binary polybutadiene blends, multicomponent polystyrene blends, and real polymers such as polystyrene, polyisobutylene, ethylene−propylene copolymer, polyethylene, and polypropylene.[16,17]

The various relaxation functions for monodisperse polymers and proposed combining rules are now tested against the linear relaxation behavior of ethylene−styrene interpolymers of typical molecular weight and molecular weight distribution in the plateau and terminal regions. Because the Doi−Edwards model described the nonlinear strain dependence well, the relaxation function and combining rule from this model serve as the starting point. The double reptation theory of des Cloizeaux is then considered as an alternative description. From this analysis of well-characterized copolymers, we can approach understanding of the effect of chain architecture on linear chain reptation dynamics. This allows us to extrapolate to the chain reptation dynamics of amorphous polyethylene at ambient temperature which cannot be assessed by direct experimental techniques.

Experimental Section

Materials. The ESIs synthesized by the INSITE technology from The Dow Chemical Company are described in Table 1. The polymers contained a very small amount of atactic styrene homopolymer (aPS). The weight percent styrene in the copolymer and the amount of aPS, as determined by NMR, were provided by Dow. The volume percent styrene in the copolymer was calculated from the weight percent using molar volumes of 99 cm^3 for styrene and 33 cm^3 for ethylene.[18] The molecular weight and molecular weight distribution as determined by GPC were also provided by Dow. The molecular weight distribution of four polymers with approximate styrene content of 60 wt % is shown in Figure 1. Generally, the polymers have similar molecular weight distribution with polydispersity of about 2.4.

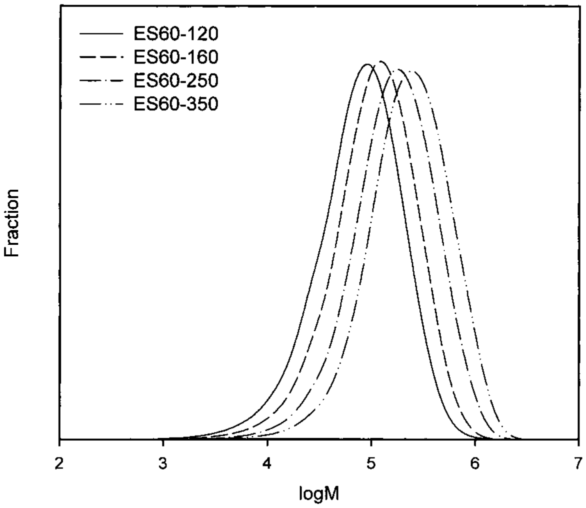

Figure 1. Molecular weight distribution of ES60 polymers.

The polymers are designated by the prefix ES, followed by the weight percent styrene in the copolymer and the weight-average molecular weight for those polymers used in the molecular weight study. The glass transition temperature (T_g) was measured by dynamic mechanical thermal analysis (DMTA) at a frequency of 1 Hz with a tensile strain less than 0.2%. The temperature was raised from 50 °C below T_g to 30 °C above T_g at a scanning rate of 3 °C min^{-1}. The glass transition temperature was taken as the maximum in the loss tangent peak. The T_g was also determined by differential scanning calorimetry (DSC) using a heating rate of 10 °C min^{-1}. The glass transition temperature was taken from the inflection point on the heat capacity curve.

Methods. Plaques 1.3 mm thick were molded from pellets at 190 °C and cooled at about 15 °C min^{-1} using conditions described previously.[2,3] A rectangular specimen was cut from the plaque. Ink reference lines were drawn on the center of the specimen to obtain the real draw ratio defined as the ratio of the length after loading to the initial length.

The stress relaxation response was measured in uniaxial extension with an Instron tensile tester. Specimens were stretched at a maximum speed of 500 mm min^{-1} to the desired draw ratio. The sample length was varied to maintain the stretching time at about 1 s. Data collection began approximately 5 s after stretching in order to avoid initial instabilities. The deformation was recorded with a video camera with a telescopic lens attachment to obtain the real draw ratio. The temperature variation inside the Instron environmental chamber was less than 0.2 °C during an experiment, and the temperature gradient inside the chamber was also less than 0.2 °C. All the measurements were carried out at or above T_g.

Stress relaxation data are presented as the relaxation modulus $E(t,\lambda)$ defined as

$$E(t,\lambda) = 3\sigma(t)/(\lambda^2 - \lambda^{-1}) \qquad (1)$$

where $\sigma(t)$ is the true tensile stress and λ is the applied draw ratio during relaxation. When the draw ratio was 10% or less,

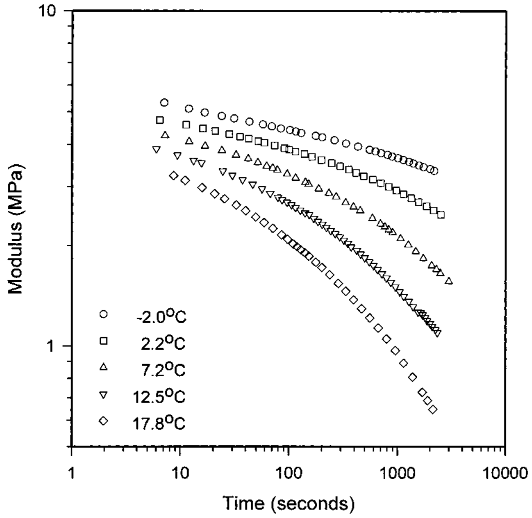

Figure 2. Stress relaxation of ES52 at various temperatures.

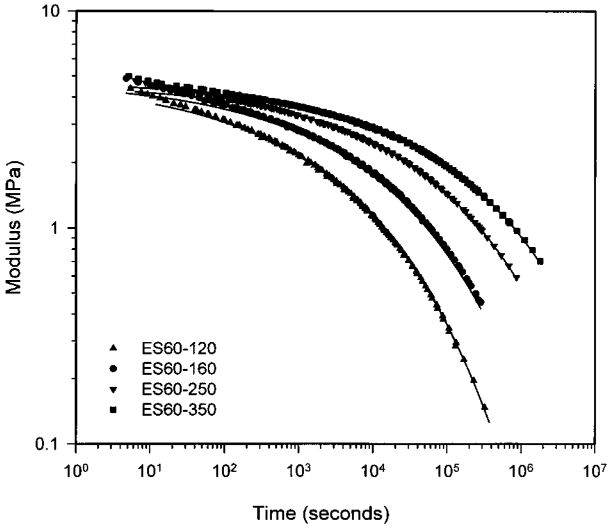

Figure 3. Stress relaxation master curves of ES60 polymers of different molecular weight. The KWW fit is given by the solid lines.

the modulus was independent of the applied strain, and the ESIs exhibited linear stress relaxation behavior. The strain limit for linear viscoelastic behavior was between 10 and 30%.[3] Therefore, to ensure linear behavior, all the experiments were performed at strains less than 10%.

Results and Discussion

Time–Temperature Superposition. The relaxation modulus of ES52 at several temperatures is shown in Figure 2. At lower temperatures and shorter times, the curves were flat, which indicated that the material was in the rubbery plateau region. A rapid drop in modulus with increasing temperature marked the terminal region. Generally, relaxation of all the polymers showed a gradual transition from the plateau region to the terminal region with increasing temperature.

A master curve was obtained for each copolymer by horizontal shifts of the relaxation curves to a reference glass transition temperature T_0 which was chosen as the temperature of the DMTA loss tangent peak at 1 Hz. No vertical shift was required to obtain the master curves in Figures 3 and 4.

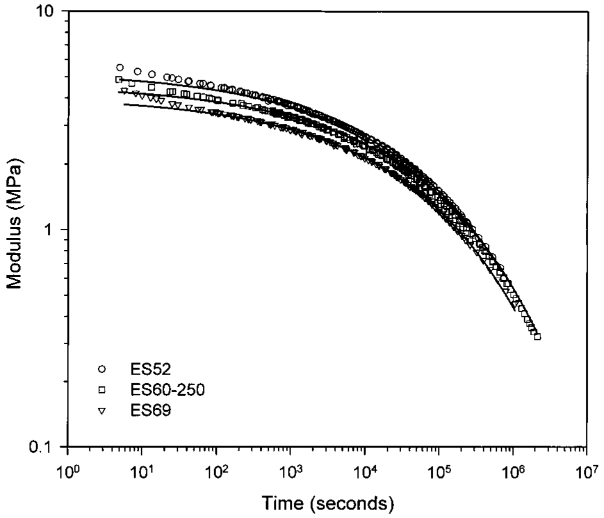

Figure 4. Stress relaxation master curves of ESIs with different styrene content and approximately the same molecular weight. The KWW fit is given by the solid lines.

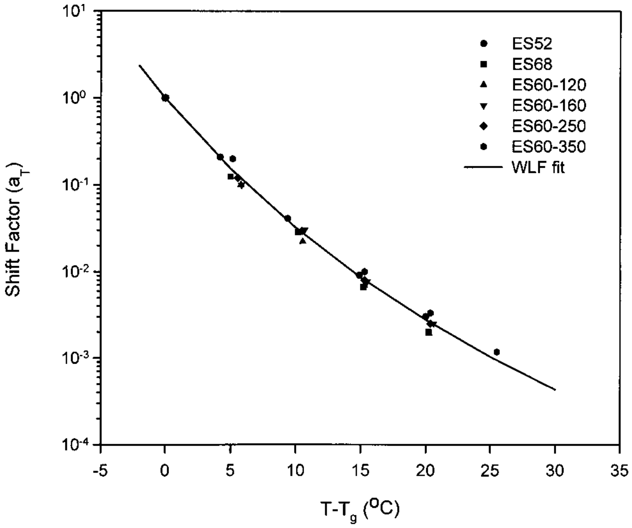

Figure 5. Temperature dependence of the shift factor for all ESIs. The WLF fit is given by the solid line.

The shift factors used to construct the relaxation master curves are presented in Figure 5 as a function of temperature. Styrene content and molecular weight did not significantly affect the relationship. This temperature dependence for all ESIs was fit to the WLF equation with the reference temperature T_0

$$\log a_T = \frac{-C_1(T - T_0)}{C_2 + (T - T_0)} \tag{2}$$

The fitting parameters C_1 and C_2 are listed in Table 2. The values of C_1 and C_2 were independent of the molecular weight and styrene content and were close to those determined in previous creep experiments.[2]

To compare the values of C_1 and C_2 with those in the literature for polystyrene, it was necessary to use comparable reference temperatures. Usually, the glass transition temperature measured by a slow technique such as dilatometry or DSC is used as the reference. Using the glass transition temperature determined by

Table 2. WLF Parameters

	stress relaxation			stress relaxation			creep		
designation	ref temp (DMTA T_g) (°C)	C_1	C_2 (K)	ref temp (DSC T_g) (°C)	C_1'	C_2' (K)	ref temp (DSC T_g) (°C)	C_1'	C_2' (K)
ES52	−2	8.8	49	−10	10.5	41			
ES60-250	8	9.1	52	0	10.8	44			
ES68	23	9.4	51	15	11.1	43	15	10.8	36
PS[a]				102	10.0	36			
ES60-120	6	9.2	51	−2	10.9	43			
ES60-160	6	8.5	48	−2	10.2	40			
ES60-250	8	9.1	52	0	10.8	44			
ES60-350	10	9.1	52	2	10.8	44			

[a] From ref 20.

DSC as the new reference temperature, T_0', the corresponding values C_1' and C_2' are given by[19]

$$C_1' = \frac{C_1 C_2}{C_2 + T_0' - T_0} \tag{3a}$$

$$C_2' = C_2 + T_0' - T_0 \tag{3b}$$

The value of C_1' agrees well with the result from creep in the glass transition region (Table 2). However, C_2' is slightly higher than in the creep study. The values of C_1' and C_2' are very similar to those reported for polystyrene, 10 and 36 K,[20] respectively, and are also in the range reported for many polymers, 8−18 for C_1' and 30−70 for C_2'.[19,20] It has been suggested that C_1' and C_2' are universal constants and therefore do not depend strongly on polymer structure.[21] They are often related to free volume parameters: C_1' to the fractional free volume at T_g and C_2' to the difference between T_g and the thermodynamically defined transition temperature T_∞ where the free volume is zero.

Phenomenological Analysis. Master curves of ES60 polymers with different molecular weights are compared in Figure 3. Convergence of the curves at short times indicated that the plateau modulus was not affected by molecular weight. This is consistent with the general understanding that the plateau modulus is determined by the entanglement molecular weight.[5] The more rapid decline in modulus at longer times with decreasing molecular weight reflected the decrease in characteristic relaxation time.

In contrast, the effect of styrene content on the relaxation behavior is shown in Figure 4. The decreasing plateau modulus with increasing styrene content confirmed the effect of composition on entanglement molecular weight reported previously.[2] However, because the three polymers in this plot had similar molecular weights and molecular weight distributions, the decline in relaxation modulus at longer times was about the same.

To quantify the relaxation behavior in the terminal region, the modulus is often fit to the phenomenological Kohlrausch−Williams−Watts (KWW) equation[22]

$$E(t) = E_0 \exp[-(t/\tau_{\mathrm{KWW}})^n] \tag{4}$$

The plateau modulus, E_0, a characteristic relaxation time, τ_{KWW}, and a parameter, n, can be extracted. In fitting this equation to the relaxation data, only data at longer times were considered in order to avoid the effects of the glass transition at shorter times.[23] The fits are included in Figures 3 and 4, and the fitting parameters are presented in Table 3. The plateau modulus, E_0, was independent of the molecular weight and decreased with increasing styrene content. For the one material included in both studies, the plateau modulus obtained from stress relaxation in the plateau and terminal regions agreed well with that obtained from creep in the glass transition region.[2]

Table 3. KWW Parameters

designation	M_w (kg mol^{-1})	M_w/M_n	E_0 (MPa)	τ (s)	n	J_0^{-1} (MPa) (creep)
ES52	219	2.4	5.3	40 000	0.26	
ES60-250	252	2.4	4.6	56 000	0.27	
ES68	239	2.0	4.1	50 000	0.27	4.0
ES60-120	349	2.4	4.8	145 000	0.26	
ES60-160	252	2.4	4.6	56 000	0.27	
ES60-250	164	2.4	4.8	11 000	0.26	
ES60-350	119	2.4	4.8	2 400	0.26	

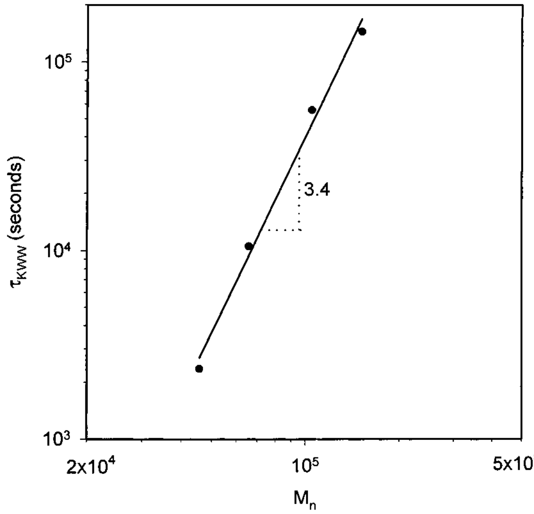

Figure 6. Dependence of the characteristic time on number-average molecular weight.

The characteristic time, τ_{KWW}, increased with number-average molecular weight proportionally to $M_n^{3.4}$ (Figure 6). This is a reasonable result. Tobolsky also found that τ_{KWW} followed a 3.4 power dependence on M_n irrespective of polydispersity when the KWW analysis was performed on stress relaxation data for polystyrene.[24,25] Indeed, it is well-known that the zero-shear viscosity, which is obtained by averaging over the relaxation time spectrum in the terminal region, follows a 3.4−3.7 power dependence on molecular weight.[26]

The rate-of-decay parameter n relates to the width of the relaxation spectrum in the terminal region[27] and hence to the molecular weight distribution.[28] For a monodisperse polymer, n was found to be in the range 0.57−0.60.[23] Therefore, n for a polydisperse polymer should be less. Values of 0.277–0.330 were reported for polystyrene with polydispersity 2.0–2.5.[24,25] The value of 0.26 for ESIs compares closely. Because all the ESIs had similar molecular weight distributions, it was not surprising that *n* was almost a constant.

Molecular Reptation Theories. Although the empirical KWW equation adequately described the relaxation curves, the parameters lack molecular interpretation. For a molecular description of linear relaxation behavior, it is necessary to consider the concepts of the Doi–Edwards tube theory.[5] In this theory, each chain is confined in a tube which forms a primitive path for the chain. Stress relaxes by diffusion of the chain from the original tube by a reptation motion. The residual stress on the chain is proportional to $p_i(t,M_i)$, the fraction of the chain that remains confined in the deformed original tube at time *t*, which is given as

$$p_i(t,M_i) = \frac{8}{\pi^2}\sum_{n=0}^{\infty}\frac{1}{(2n+1)^2}\exp(-(2n+1)^2 t/\tau_i) \qquad (5)$$

and

$$\tau_i = k_s M_i^3 \qquad (6)$$

where M_i is the molecular weight of the chain and τ_i is the characteristic time of the reptation motion, which scales with M_i^3 by a factor of k_s.

For a polymer with a distribution of molecular weights, the total residual stress at time *t* is assumed to be proportional to the sum of all the fractional chains that remain confined in their deformed original tube. This is represented by the linear combining expression

$$\frac{E(t)}{E_0} = \sum_i \varphi_i p_i(t,M_i) \qquad (7)$$

where $E(t)$ is the relaxation modulus at time *t*, E_0 is the plateau modulus, and φ_i is the volume fraction of polymer chains with molecular weight of M_i.

Using the known molecular weight distribution, the relaxation curves were fit to eqs 5–7 to determine the model parameters. To avoid effects of the glass transition at short times, only long time relaxation data were fit. The fitting curves are shown in Figure 7a, and the fitting parameters E_0 and k_s are presented in Table 4. The plateau modulus, E_0, was independent of molecular weight and decreased with increasing styrene content; however, the values were lower than those obtained from the KWW analysis by about 30%. The scaling parameter between characteristic time and molecular weight, k_s, was independent of styrene content and molecular weight.

To better reveal the quality of the fit, the data and the fitting curves were compared in terms of the relaxation spectrum. The relaxation time spectrum $H(\tau)$ was calculated from the relaxation modulus master curves by the approximation method of Schwarzl and Staverman[29]

$$H(\tau) = -\mathrm{d}E(t)/\mathrm{d}\ln t + \mathrm{d}^2E(t)/\mathrm{d}(\ln t)^2|_{t=2\tau} \qquad (8)$$

Relaxation time spectra obtained from the experimental master curves are presented in Figure 7b. The shift in the terminal peak to longer times with increasing molecular weight reflected the $M^{3.4}$ dependence of the characteristic time. Comparison of the relaxation time spectra calculated from the fitting curves, shown as solid lines in Figure 7b, revealed the poor fit, especially on the short time side of the terminal peak. This suggested that alternative formulations should be tested.

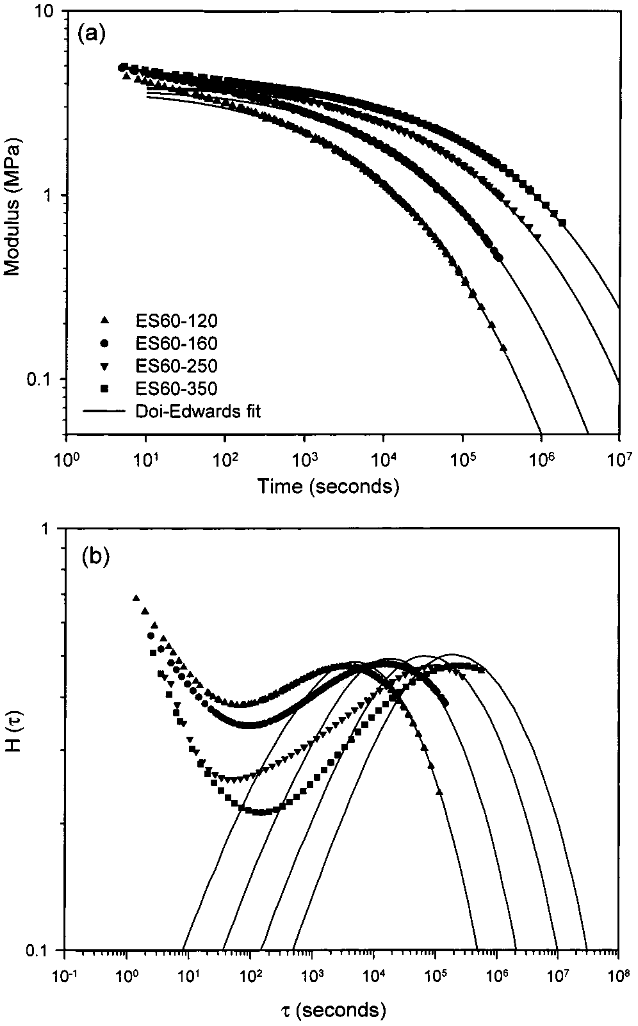

Figure 7. Fit of the Doi–Edwards model (solid lines) for ES60 polymers of different molecular weight: (a) to the stress relaxation master curves and (b) to the relaxation time spectra.

Some new approaches to tube models and reptation have met with reasonable success when tested against dynamic modulus measurements in the plateau and terminal regions.[13,16] Des Cloizeaux considered the "double reptation" of a pair of entangled chains.[9] The entanglement persists as a stress point until one of the chains slips through. If $p_i(t,M_i)$ is the probability that one of the chains did not slip through the stress point, the relaxation function takes the form

$$\frac{E(t)}{E_0} = [\sum_i \varphi_i p_i(t,M_i)]^2 \qquad (9)$$

Des Cloizeaux provided an explicit expression for the probability function based on a modified version of the reptation concept.[13] In addition to diffusion of one chain out of the tube with characteristic reptation time $\tau_i \propto M_i^3$, he considered diffusion of the stress point along the chain by Rouse-type relaxation motion with characteristic time $\tau_a \propto M_i^2$. This resulted in a time-dependent

Table 4. Reptation Parameters

	Doi−Edwards		des Cloizeaux			KWW	creep[a]
designation	E_0 (MPa)	$-\log k_s$	E_0 (MPa)	$-\log k_d$	$M_0 \times 10^{-4}$	E_0 (MPa)	E_0 (MPa)
ES52	4.4	10.6	5.5	9.4	4.0	5.3	
ES60-160	3.8	10.7	5.0	9.6	2.8	4.6	
ES68	3.2	10.7	4.0	9.5	4.6	4.1	4.0
ES60-120	3.7	10.9	5.1	9.8	2.5	4.8	
ES60-160	3.8	10.7	5.0	9.6	2.8	4.6	
ES60-250	3.8	10.7	4.7	9.5	3.1	4.8	
ES60-350	3.8	10.6	4.8	9.5	5.5	4.8	

[a] From ref 2.

diffusion coefficient for diffusion of the chain out of the tube and led to the expression

$$p_i(t,M_i) = \frac{8}{\pi^2}\sum_{n=0}^{\infty}\frac{1}{(2n+1)^2}\exp[-(2n+1)^2U_i(t)] \quad (10)$$

where

$$U_i(t) = \frac{t}{\tau_i} + \frac{1}{H_i}g(H_it/\tau_i) \quad (11)$$

$$g(x) = \sum_{m=1}^{\infty}\frac{1-\exp(-m^2x)}{m^2} \quad (12)$$

$$\tau_i = k_dM_i^3 \quad (13)$$

$$H_i = \tau_i/\tau_a = M_i/M_0 \quad (14)$$

where k_d has the same physical meaning as k_s as in the Doi−Edwards model and M_0 is a scaling parameter.

The fits of eqs 9−14 to the relaxation modulus master curves are shown in Figure 8a. The fit was much better than the Doi−Edwards model in Figure 7a, especially at shorter times, and also better than the KWW fit in Figure 4. The excellent fit to the terminal peak was confirmed by comparing the relaxation time spectra (Figure 8b).

Because the Doi−Edwards model described the nonlinear strain dependence well in the terminal region where the relaxation modulus can be factorized as strain and time functions, this model served as the starting point for the present investigation of linear stress relaxation. The original approach was sufficient for describing the chain retraction mode which is responsible for the deviation from linear behavior at increased strains, as shown by the agreement of predicted damping function with experiment. However, the chain reptation concept employed in the Doi−Edwards model to describe the underlying linear viscoelastic behavior only qualitatively fits the experimental relaxation modulus. A better approach requires consideration of additional relaxation mechanisms such as contour length fluctuation and cooperativity of chain motion. In the present study, the double reptation model satisfactorily met this need.

The fitting parameters E_0, k_d, and M_0 are presented in Table 4. The plateau modulus, E_0, was higher than that obtained from the Doi−Edwards model and was very close to that obtained from the KWW analysis. The parameter M_0, which scales between H_i and M_i, had a weak dependence on molecular weight and styrene content. Because H_i is interpreted as proportional to the number of steps in the primitive chain,[5,12] M_0 should relate to the entanglement molecular weight M_e.[16] The values of M_0 were 15−30 times higher than the entanglement molecular weight, M_e. Similarly, M_0 was found to be 13 times higher than M_e for polybutadiene.[13,16]

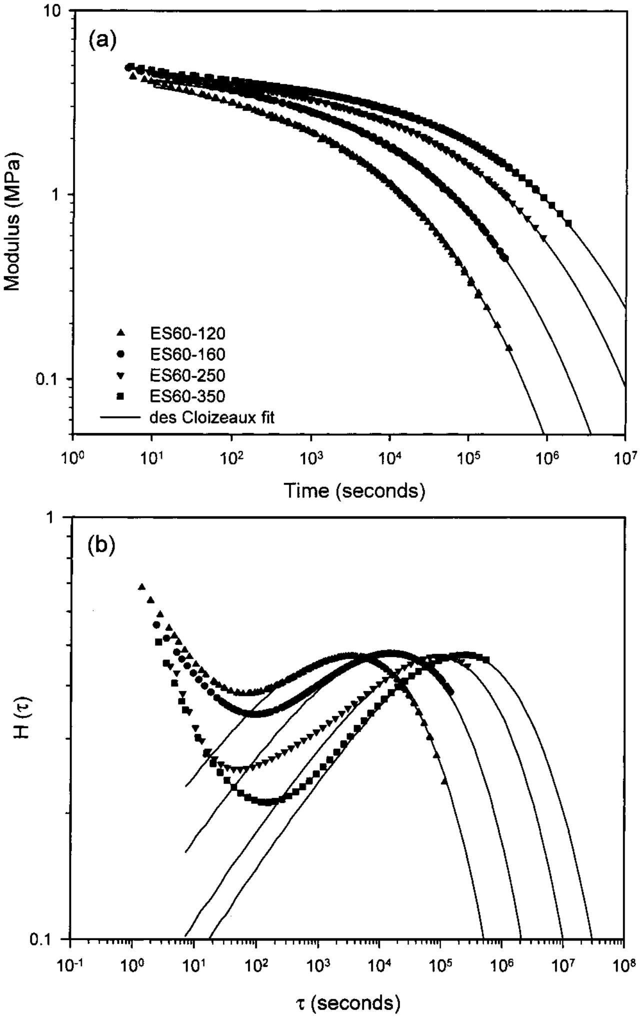

Figure 8. Fit of the des Cloizeaux double reptation model (solid lines) for ES60 polymers of different molecular weight: (a) to the stress relaxation master curves and (b) to the relaxation time spectra.

The parameter k_d scales between the characteristic time τ and M^3. The fact that it was found experimentally to be independent of molecular weight confirmed the relevancy of the theory to this polymer system. The parameter k_d was also independent of styrene content. Because k_d is related to the tube structure of the entangled network, this result was consistent with the small variation in entanglement molecular weight among copolymers of different composition.[2]

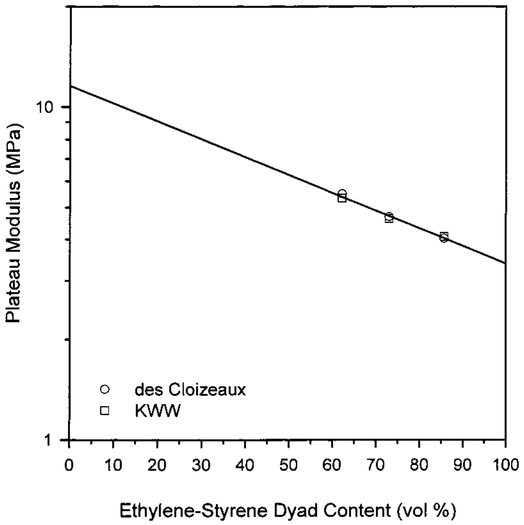

Figure 9. Composition dependence of the plateau modulus.

Entanglement Molecular Weight. The dependence of plateau modulus on composition of random copolymers is usually described by[30]

$$\log E_0 = v_1 \log E_1 + v_2 \log E_2 \tag{15}$$

where E_0 is the plateau modulus of the copolymer, E_i is the plateau modulus of the homopolymer of comonomer i, and v_i the volume fraction of comonomer i. The normal approach would be to analyze the ESIs as random copolymers and take polystyrene and polyethylene as the component homopolymers. However, extrapolation of log E_0 as a function of styrene content resulted in an unrealistically high value for the plateau modulus of polystyrene.

The ESIs in this study do not meet the assumption of true randomness. In the absence of successive head-to-tail styrene insertions, it is more appropriate to consider ESIs as random copolymers of ethylene and ethylene–styrene (ES) dyads. Accordingly, the data should be described by

$$\log E_0 = v_{\mathrm{E}} \log E_{\mathrm{E}} + v_{\mathrm{ES}} \log E_{\mathrm{ES}} \tag{16}$$

where E_{E} is the plateau modulus of polyethylene, v_{E} the volume fraction of ethylene, E_{ES} is the plateau modulus for the alternating ethylene–styrene copolymer (PES), $v_{\mathrm{ES}} = (V_{\mathrm{ES}}/V_{\mathrm{S}})v_{\mathrm{S}} = 1.33v_{\mathrm{S}}$ where v_{ES} is the volume fraction of ES dyads, V_{ES} is the molar volume of an ES dyad assumed to have additive contributions of ethylene and styrene, V_{S} is the molar volume of a styrene unit, and v_{S} is the volume fraction of styrene in the polymer. Extrapolation of plateau modulus values from the KWW analysis and the double reptation analysis gave the plateau modulus of polyethylene as 11.6 MPa (Figure 9). This is similar to the reported value of 10.5 MPa at 25 °C.[31,32] The corresponding plateau modulus of PES, the alternating ethylene–styrene copolymer, was 3.3 MPa.

The plateau modulus is generally interpreted as the pseudoequilibrium modulus of the entanglement network, and therefore the entanglement molecular weight can be evaluated as

$$M_{\mathrm{e}} = 3\rho RT/E_0 \tag{17}$$

where ρ is the density, R is the gas constant, and T is the temperature. The plateau modulus from double reptation was used to obtain the results presented in Table 5. The entanglement molecular weight increased slightly with styrene content from 1300 g mol^{-1} for ES52 to 1760 g mol^{-1} for ES68 and extrapolated to 2290 g mol^{-1} for PES. To compare the polymers on the basis of length, rather than molecular weight which included the phenyl side groups, the number of backbone carbon atoms in the chain segment between entanglements (P_{c}) was calculated from the average monomer molecular weight (M_{a}) as $P_{\mathrm{c}} = 2M_{\mathrm{e}}/M_{\mathrm{a}}$. The entanglement parameters presented in Table 5 followed the results of the previous creep study.[2] The entanglement length increased with styrene content, but the effect was smaller on P_{c} than on M_{e}. Comparisons of P_{c} revealed that the length of the ESI chain segment between entanglements was a factor of 4–5 smaller than the polystyrene chain segment, but only about twice that of polyethylene. It is imagined that the specific chain microstructure of the "pseudorandom" ESIs, with pendant phenyl groups separated by at least two methylene groups, produces chain flexibility that is more like polyethylene than polystyrene.[2] As a consequence of the low entanglement molecular weight, these ESIs are ductile glasses at temperatures 50 °C below the T_{g}.[2]

Table 5. Plateau Modulus and Entanglement Molecular Weight

designation	T (°C)	E_0 (MPa)[a]	M_{e} (g mol^{-1})	M_{a}	P_{c} (mol m^{-3})
PE[b]	25	10.5	480	28	34
	140	7.8	860	28	61
ES52	23	5.5	1300	45	57
ES60-250	23	4.7	1510	50	60
ES68	23	4.0	1760	56	62
PES[c]	23	3.3	2290	66	69
PS[b]	140	0.6	13500	104	260

[a] From des Cloizeaux fit. [b] From ref 32. [c] Alternating ethylene–styrene copolymer, extrapolated values.

In summary, the merit of statistically homogeneous ethylene–styrene interpolymers as a model system for testing contemporary concepts of molecular dynamics on polymers of normal polydispersity, previously demonstrated in creep and nonlinear stress relaxation studies, was confirmed in tests of linear relaxation behavior in the plateau and terminal regions. Relaxation master curves constructed by time–temperature superposition of stress relaxation data in the temperature region T_{g} to $T_{\mathrm{g}} + 30$ °C were the basis for testing various linear relaxation functions for monodisperse polymers and proposed combining rules. Although previously the Doi–Edwards model successfully described the nonlinear strain dependence (damping function) for stress relaxation, the single reptation model did not satisfactorily replicate the distribution of stress relaxation times. However, the combining rule and relaxation function from the des Cloizeaux double reptation approach successfully described the relaxation master curves. In this regard, the study confirmed the small number of previous investigations that sought to test the theories against data for polymers of normal polydispersity. The ESIs were also useful for probing the copolymer composition effect. The plateau modulus followed the additivity rule if the ESIs were viewed as copolymers of ethylene ($E_0 = 10.5$ MPa) and ethylene–styrene dyads ($E_0 = 3.3$ MPa). This assumption was justified by the demonstrated absence of head-to-tail chain insertion of styrene monomer. As a result of the unique chain microstructure, the entanglement molecular weight of ESIs was much closer to that of polyethylene (M_e = 480−860 g mol^{-1}) than to that of polystyrene (M_e = 13 500 g mol^{-1}).

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