Viscoelastic Properties of Poly(ethylene-*co*-styrene) Copolymers

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ABSTRACT: The viscoelastic properties of narrowly distributed linear poly(ethylene-*co*-styrene) copolymers with different mole fractions of styrene ($x_S = 0–20.5$ mol %) and molecular weights ($M_w = 64–214$ kg/mol) were analyzed in the molten state at different temperatures by means of oscillatory rheometry. Analyzing the thermorheological properties of the polymers, we found that the time temperature superposition principle is fulfilled. The corresponding shift factors follow up to 16.5 mol % of styrene units the Arrhenius behavior of neat polyethylene. For a styrene content of about 20 mol %, the polymers no longer crystallize and a transition from Arrhenius to WLF behavior of pure polystyrene was observed. The zero shear viscosity, η_0, of the polymers was derived from the mastercurves. The determination of the plateau modulus by the well-known $\tan \delta$-min criterion is not possible due to the beginning crystallization in the corresponding temperature range. An approximate calculation of this value is based on the characteristic relaxation time $\lambda_x = 1/\omega_x$, corresponding to the crossover of G' and G''. Indeed, the characteristic modulus G_{px} calculated as η_0/λ_x is a good approximation for the plateau modulus G_p. The viscosity–molecular weight and relaxation time–molecular weight scaling relations were established for three copolymers with different molecular weights and nearly the same styrene content. For both material parameters, the scaling exponent is around 3.4, confirming the linear architecture of the investigated polymers. The mixing rules describing the change of such material parameters like zero shear viscosity or plateau modulus independent of styrene content are of logarithmic linear character using the weight fraction of styrene units instead of the mole fraction. The relations found allow the prediction of melt state properties for polymers with arbitrary styrene content. In the future, when catalysts with sufficient activity for the synthesis of high styrene content copolymers are available, these predictions will have to be checked. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **65:** 209–215, 1997

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INTRODUCTION

The rheology of polymer blends and block copolymers has attracted much attention for a couple of years. However, little is known concerning the behavior of random ethene/styrene copolymers. This situation is a consequence of the difficulty residing in the synthesis of poly(ethene-*co*-styrene). The problems occurring in the copolymerizations of olefins with styrene by conventional Ziegler-Natta catalysts have been reported by several authors since 1964.[1–4] Indeed, for a vinyl aro-

matic comonomer such as styrene, only a maximum of about 1 mol % styrene units in the copolymer was reached in the past. The polymers reported often comprise a mixture of homopolymers and copolymers.[2,4]

Recently, as reported in the specific trade and patent literature,[5,6] the synthesis of Mono-Cp-amido-complexes[7–9] was the base for the new metallocene catalyst generation, which produces poly(ethylene-co-styrene) containing over 30 mol % styrene. Up to now, only a few articles[10–12] concerning the characterization of poly(ethylene-co-styrene) were available. The systematic structure/property correlation of this new material has to be established. The influence of polymerization conditions on the copolymerization and the effect of styrene content in the copolymer on its thermal properties have already been published.[11,12] The influence of styrene content on mechanical properties as measured in a tensile experiment was also investigated.[12] It was found that the high styrene copolymers exhibit stress relaxation behavior comparable to that of flexible poly(vinyl chloride), which is known for its unique relaxation response.

Here, we present a study of the rheological properties of these new copolymers. Using dynamic rheology on a series of linear random ethylene/styrene copolymers containing different contents of styrene units and having different molecular weights, the relationship between material parameters like zero shear viscosity and structural characteristics like molecular weight and styrene content is examined.

EXPERIMENTAL

Polymer Synthesis

The copolymers were synthesized with Me$_2$Si-(Me$_4$Cp)(N-*tert*-butyl)TiCl$_2$/MAO (Me, methyl; Cp, cyclopentadienyl; MAO, methylalumoxane); the catalyst was synthesized according to the literature.[11] Copolymerizations were carried out in a 500-mL glass autoclave. The reactor was fed with toluene, styrene, and part of the MAO needed. After thermostating the reactor, argon was removed via vacuum and the reaction mixture was saturated with ethene. The metallocene solution (in 10 wt % MAO solution) was then injected into the reactor. The catalyst concentration was 20 μmol/L, and the Al : Ti ratio was 2,000. Further polymerization conditions were described

earlier.[11] Copolymerizations were stopped by injecting C$_3$H$_7$OH and venting off excess ethene. The copolymers were precipitated by being poured into acidic CH$_3$OH, filtered, and dried under vacuum to constant weight.

Polymer Analysis

To determine the mole percentage of styrene in the copolymers, x_S, nuclear magnetic resonance spectra were recorded on a Bruker ARX 300 spectrometer operating at 300 MHz for ^{1}H and at 75.4 MHz for ^{13}C. Spectra were taken at 100°C with C$_2$D$_2$Cl$_4$ as solvent. The solvent peak (C$_2$HDCl$_4$) was calibrated to 74.06 ppm in the ^{13}C spectra. Molecular weights and molecular weight distributions were determined by gel permeation chromatography versus polyethylene standard. Molecular weight distributions, characterized by the ratio of the weight average to the number average molecular weight, M_w/M_n, were found in the range of 2.3–2.9. All of these data are presented in Table I. From Table I, it can be seen that the styrene content is not uniformly distributed and does not exceed 21 mol %. This is a consequence of the fact that at the moment the synthesis of these new copolymers is difficult and we are far from "tailor-making" these materials. Nevertheless, the investigations allow a first insight in the structure property relationships of these new polymers.

For the discussion of rheological properties, thermal properties like the melting temperature, T_m, and the glass transition temperature, T_g, are also of importance. These data were determined by differential scanning calorimetry and dynamic mechanical analysis and were reported in a previous communication.[11] Here, we present these results for all determined characteristic temperatures in Figure 1 where the weight fraction of styrene in the copolymers, w_S, is used as the abscissa. The polymers to be considered here are indicated in this figure by arrows and the sample name.

For the rheological investigations to be presented here, the polymers are subdivided into three groups. The first group comprises the copolymers S34, S35, and S36, which have nearly the same styrene content of about $x_S \approx 3.5$ mol % and different molecular weights. These polymers are used to establish the viscosity–molecular weight relationship. The second and third groups comprise polymers having molecular weights in the range of polystyrene ($M_w = 71,000$ g/mol: S34,

Table I Molecular and Rheological Data of the Polymers Used

Sample	Styrene Content x_s (mol %)	Styrene Content w_s (weight %)	M_w 10^{-3} (g/mol)	M_w/M_n	η_0 Pas	λ_x sec	10^{-5} G_{px} Pa
PE	0	0	190	2.5	82,000	0.025	32.8
S34	3.4	11.6	64	2.8	3,400	0.002	17.0
S35	3.5	11.9	178	2.3	133,000	0.063	21.1
S36	3.6	12.2	76.5	2.5	9,000	0.004	22.5
S165	16.5	42.3	122	2.6	58,000	0.04	14.5
S203	20.3	48.6	214	2.9	634,000	0.4	15.8
PS	100	100	17	1.05	305,000	1.58	1.9

S36, and S165) or in the range of polyethylene ($M_w = 190,000$ g/mol: S35 and S203), regardless of the styrene content. The molecular weights of the homopolymers serve as reference states, M_w^{ref1} and M_w^{ref2}, respectively.

Sample Preparation and Rheology

To permit the rheological measurements, a stabilizer blend containing 0.2 wt % of a phosphite antioxidant (IRGAFOS 168, Ciba-Geigy AG) and 0.1% of a phenolic antioxidant (IRGANOX 1076,

Ciba-Geigy AG) was used. The stabilizers were solved in 1 mL of acetone and mixed to the copolymer powder. Finally, samples were held under vacuum at 100°C. The stabilized copolymers were then compression molded at 140°C (respectively at 165°C for pure polyethylene) in the form of 1-mm-thick plates having a diameter of 25 mm. The reference polyethylene and polystyrene were also stabilized in order to optimize the comparison with the copolymers.

The rheological properties of the polymers were characterized by dynamic mechanical measurements with a Rheometrics Mechanical Spectrometer RMS 800 operating with parallel plate geometry. The samples were held under nitrogen atmosphere in order to avoid thermooxidative degradation. The shear storage modulus G' and the shear loss modulus G'' were determined over a shear rate range from 0.01 to 100 rad/sec in a temperature interval ranging from 120 to 200°C. The isotherms were shifted to mastercurves at a reference temperature $T_0 = 140°C$ using the program LSSHIFT.[13]
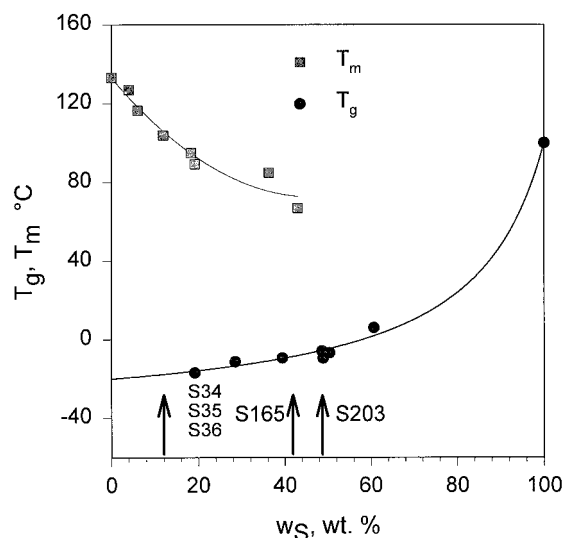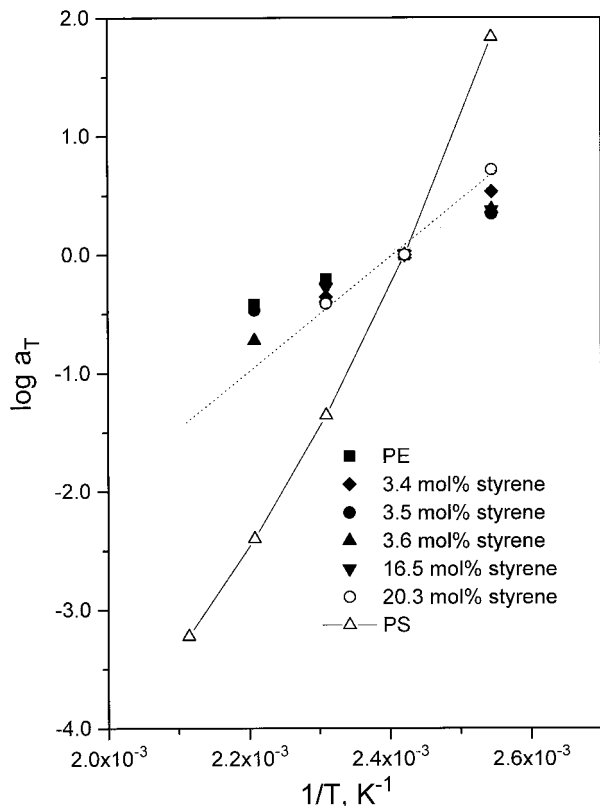

Figure 1 Glass transition temperatures and melting temperatures as a function of the weight content of styrene units in the copolymer. The line through the melting temperatures is to guide the eye, whereas the line in the case of T_g represents a fit using the Gordon-Taylor equation with $K = 0.144$. The arrows indicate the location of the polymers under investigation on the abscissa.

RESULTS AND DISCUSSION

Shift Factors and Mastercurves

The temperature dependence of the horizontal shift factors a_T is presented in Figure 2 for all copolymers as well as for the polyethylene and polystyrene references. Here, the shift factors of the copolymers up to 16.5 mol % styrene are very similar to these of polyethylene and fall within the hatched area presented in this figure. Moreover, the low absolute values for a_T obtained for the copolymers indicate that, in contrast to many homopolymer melts like polystyrene and poly-
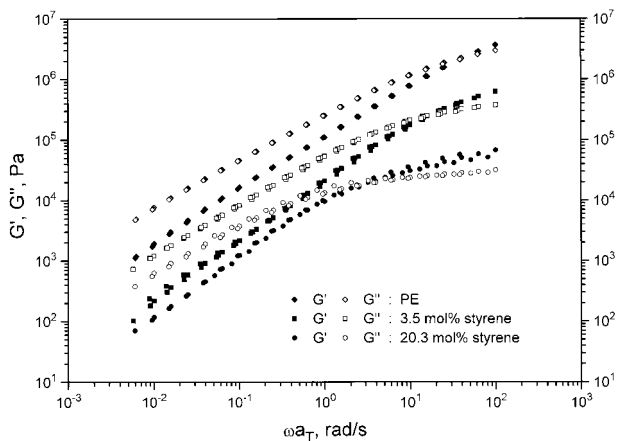
values were cross-checked with η_0 values obtained from the extrapolation procedure known from the Cole-Cole plot.

Because both the plateau and the terminal zones could not be reached, consequently, the determination of the terminal relaxation time λ_0 and the plateau modulus G_p was not possible. However, the cross-point, defined as the point where G' and G'' are equal, can be evaluated. It was shown earlier that the coordinates of this cross-point were related to molecular parameters.[15] The time $\lambda_x = 1/\omega_x$, where ω_x is the abscissa of the cross-point, has been estimated for each sample (see Table I) and can be considered as an approximation for the terminal relaxation time, as Dumoulin and Utracki[17] have already done for polyethylene blends. Furthermore, we will use this characteristic time to determine an approximation of the plateau modulus, G_{px}, using the following formula:

$$G_{px} = \frac{\eta_0}{\lambda_x} \qquad (1)$$

Although λ_x is not the terminal relaxation time, interesting results have been deduced from this approximation, and moreover, the values found for the polyethylene and polystyrene references ($G_{px}^{PE} = 32.8 \ 10^5$ Pa and $G_{px}^{PS} = 1.9 \ 10^5$ Pa) were also consistent with the plateau moduli referred to in the literature.[18,19] The G_{px} values are also given in Table I.

By comparing mastercurves of samples with increasing styrene content, as presented in Figure 4, we notice that the cross-point is regularly shifted to smaller frequencies; this corresponds to increasing relaxation times. This shift is a consequence of the transition of a low T_g flexible polymer that possesses high molecular mobility of chain segments at the reference temperature to a high T_g polymer, which is less flexible and therefore relaxes slower.

Viscosity–Molecular Weight Relationship

Above a critical molecular weight, M_c ($M_c^{PE} \approx 3,800$ g/mol[18], $M_c^{PS} \approx 31,200$ g/mol[18]), the empirical scaling relation for the zero shear viscosity, η_0, is the following:

$$\eta_0 \propto M_w^{\alpha} \qquad (2)$$

An exponent of $\alpha = 3.40$ is usually found for many
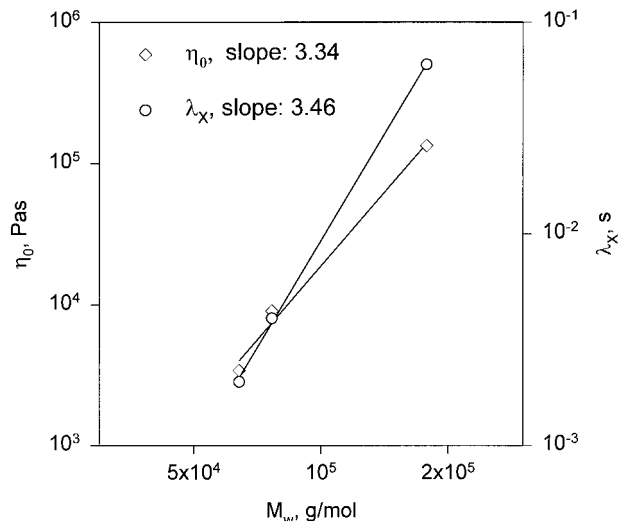
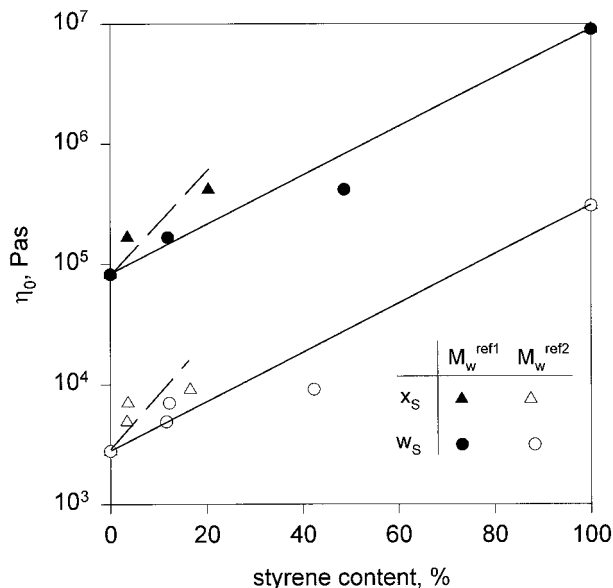**Figure 4** Dependence of the zero shear viscosity, η_0, and the characteristic relaxation time, λ_x, on the weight average molecular weight, M_w, on a logarithmic scale for three copolymers containing about 3.5 mol % styrene units.

monodisperse polymers, but branching of the chains has a great influence on this value and long chain branching polymers exhibit a significant deviation from this scaling relation. To check this relationship for the polymers under investigation, the viscosities of copolymers of the first group are plotted in logarithmic scales versus molecular weight and the result is presented in Figure 4. In our case, the exponent is equal to $\alpha = 3.34$, showing that the copolymers follow the empirical scaling relation usually exhibited by the homopolymers and confirming the fact that these copolymers have a linear structure without any long chain branching known for "substantially linear olefin polymers."[22] Moreover, as will be shown below, this relation will permit us to deduce from a measured zero shear viscosity for fixed styrene content and molecular weight the corresponding η_0 value for the same styrene content but the reference molecular weights M_w^{ref}.

Figure 4 also shows the characteristic times λ_x displaying the same scaling relation as that for the viscosity. In this case, the exponent is $\alpha = 3.46$. This fact supports the idea that the moduli calculated by eq. (1) are good approximations for the molecular weight–independent plateau modulus.

Dependence of Material Parameters on the Styrene Content

Now, we analyze the dependence of material parameters like zero shear viscosity and approxi-

Figure 5 Variation of the zero shear viscosity, η_0, versus the styrene content for two groups of copolymers with, respectively, $M_w^{ref2} \approx 71$ kg/mol and $M_w^{ref1} \approx 190$ kg/mol. The broken lines depict linear regressions using the mole content x_S; the solid lines represent logarithmic linear mixing rules.
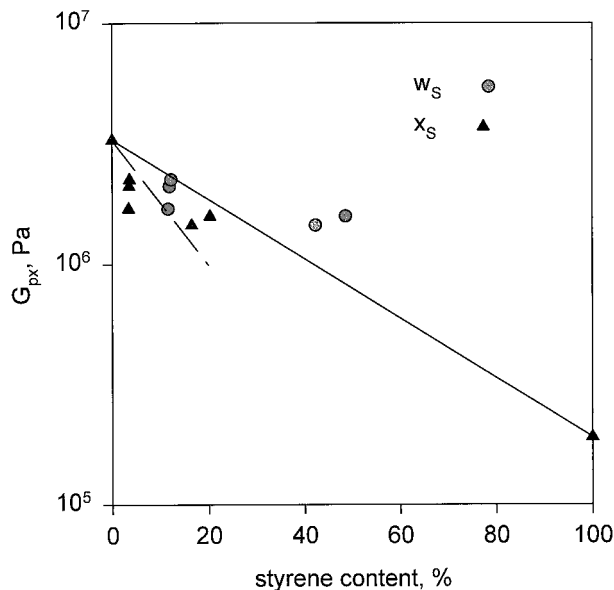
mate plateau modulus, G_{px}, on styrene content. To eliminate the influence of molecular weight, the viscosities of copolymers are corrected to the reference molecular weights of both groups. Additionally, we calculated the viscosities of the homopolymers for molecular weights corresponding to the reference of the other group.

Figure 5 depicts the dependence of the zero shear viscosity versus the styrene content for the two groups of copolymers having $M_w^{ref1} = 71$ kg/mol (open symbols) and $M_w^{ref2} = 190$ kg/mol (closed symbols) reference molecular weights, respectively. The styrene content is given as the weight percentage (w_S, circles) and the mole percentage (x_S, triangles). The lines connecting the viscosities of both homopolymers represent the logarithmic linear mixing rule for the mole content or the weight content of styrene, respectively. The zero shear viscosity regularly increases with increasing styrene content, at least for the styrene content interval studied in this article. As is apparent from Figure 5, for both groups of polymers, we find that the dependence on weight content styrene seems to lie on a straight line, representing the logarithmic linear mixing rule:

$$\log \eta_{0CP} = w_S \log \eta_{0S} + w_E \log \eta_{0E} \qquad (3)$$

η_{0CP} is the zero shear viscosity of the copolymer, and the subscripts indicate the values for pure polystyrene and polyethylene, respectively. The weight percentage of ethylene units is given by w_E. The dependence on x_S is rather nonlinear with a positive deviating tendency, as indicated by the broken lines. These lines represent a linear regression and are drawn to guide the eye. The x_S values are not spread wide enough to establish a nonlinear dependence.

Now, we evaluate the approximate value of the plateau modulus, G_{px}, as determined by eq. (1), on the styrene content for all copolymers, no matter to which group these polymers belong. Besides the fact we mentioned, this is possible because all molecular weights (with the exception of polystyrene) under consideration are above the critical molecular weight M_c' calculated for the copolymers using the linear mixing rule $M_c' = w_S M_c'^{PS} + w_E M_c'^{PE}$, the empirical rule $M_c' \approx 6\, M_e$, and the following values for the entanglement molecular weights of homopolymers: $M_e^{PE} \approx 1{,}300$ g/mol and $M_e^{PS} \approx 18{,}000$ g/mol.[18] Here, M_c' is used instead of M_c because the plateau modulus changes its dependence on molecular weight at higher molecular weights than the viscosity and we are on the safe side. As is apparent from Figure 6, the approximated plateau modulus G_{px} decreases regularly with increasing styrene content, at least

Figure 6 Variation of the approximated plateau modulus G_{px} versus the styrene content. The broken line depicts linear regressions using the mole content x_S; the solid line represents the logarithmic linear mixing rule.

for the styrene content interval studied in this article. The linear mixing rule for the logarithm of the moduli based on the weight percentage of styrene in the copolymer seems to be appropriate for describing the modulus–styrene content relationship quantitatively. The points based on the x_S presentation all lie below the straight line. Such a mixing rule

$$\log G_{pxCP} = w_S \log G_{pxS} + w_E \log G_{pxE} \quad (4)$$

was recently found by Wu and Beckerbauer[20] for other statistical copolymers. They used the volume percentage instead of the weight percentage in their equation. The calculation of the volume percentage by using the atomic volumes of the species, as listed by van Krevelen[21] ($V_{0S} = 99$ cm^3/mol, $V_{0E} = 33$ cm^3/mol), shows that there is no significant difference, and it is hard to decide which presentation is more correct. Nevertheless, it is possible to elucidate the entanglement behavior of the copolymers using eq. (3). The higher the number of styrene units, the fewer the entanglements between the chains. Also, the longer the spacing between entanglements, the greater M_e becomes.

CONCLUSIONS

The investigated copolymers show an interesting thermorheological transition from Arrhenius behavior for copolymers with styrene contents up to 16.5 mol % to WLF behavior for polymers with higher styrene contents. At the transition point, the change of type is associated with the loss of the crystallization ability of the copolymers. Whereas the zero shear viscosities are derived directly from the mastercurves, the plateau moduli are determined by means of the viscosity and the cross-point relaxation time. This method presented for the calculation of the plateau modulus is appropriate for the polymers used. The range of applicability has to be checked for other polymers in the future. The established mixing rules support the idea of logarithmically based linear mixing rules using the weight or volume fractions of styrene. The rheological properties found indicate that the synthesized polymers indeed are linear.

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