

## Estimation of Long-Chain Branching in Ethylene-Propylene Terpolymers from Infinite-Dilution Viscoelastic Properties

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### Synopsis

A method is outlined for estimation of small degrees of long-chain branching in polymers with moderately narrow molecular weight distribution ( $\bar{M}_w/\bar{M}_n < 1.4$ ). The storage and loss shear moduli,  $G'$  and  $G''$ , are measured in dilute solution by the Birnboim-Schrag multiple-lumped resonator and extrapolated to infinite dilution, choosing a suitable solvent viscosity and frequency range such that the data lie in the terminal zone where  $G'$  and  $G''$  are proportional to the second and first powers of frequency, respectively. The intrinsic reduced steady-state shear compliance is determined from these data and corrected for moderate molecular weight heterogeneity (assuming a Gaussian distribution) from knowledge of  $\bar{M}_w/\bar{M}_n$  and the Mark-Houwink exponent  $a$ . The resulting value of  $S_2/S_1^2$  (where  $S_1 = \Sigma \tau_p/\tau_1$ ,  $S_2 = \Sigma (\tau_p/\tau_1)^2$ , the  $\tau_p$ 's being the relaxation times and  $\tau_1$  the longest one) is compared with values calculated by the Zimm-Kilb theory as evaluated by Osaki for comb polymers of regular geometry and different numbers of branch points. The method has been illustrated by measurements on four ethylene-propylene copolymers. One containing no termonomer and one containing a saturated termonomer appeared to be linear; two containing unsaturated termonomers showed small degrees of branching. The method appears to be promising for detecting from one to four branch points per molecule.

### INTRODUCTION

The presence of long-chain branching profoundly affects the physical properties and technological processing of amorphous polymers, although the nature of the effects has not yet been clearly elucidated.<sup>1-4</sup> Interpretation of the role of branching is hampered by the difficulty of knowing whether small extents of branching exist in a given polymer sample unless it has been synthesized in a specific manner to produce a controlled branch geometry. The radius of gyration and intrinsic viscosity are, of course, diminished by the presence of branching,<sup>5,6</sup> but for small numbers of branch points per molecule the changes are not large.

The dynamic viscoelastic properties at infinite dilution, at frequencies near and below the reciprocal of the longest relaxation time, are more sensitive to branching; specifically, the storage modulus of a branched polymer is considerably smaller than that of a linear polymer in this fre-

quency range.<sup>7,8</sup> We have suggested that this feature could be applied to detect and gauge branching,<sup>8</sup> pointing out that molecular weight distribution must be taken into account since it also affects the storage modulus in the opposite direction.<sup>9</sup> We now outline a method for estimating small degrees of random branching from dilute-solution viscoelastic measurements, including a correction for moderate degrees of molecular weight heterogeneity. The method is illustrated by measurements on a series of ethylene-propylene terpolymers.

## THEORY

### Determination of the Reduced Intrinsic Steady-State Compliance

The intrinsic shear storage and loss moduli  $[G']$  and  $[G'']$  are obtained by extrapolating the ratios  $G'/c$  and  $(G'' - \omega\eta_s)/c$  to zero concentration, where  $G'$  and  $G''$  are the storage and loss moduli measured in small oscillating deformations,  $\omega$  is the radian frequency,  $\eta_s$  is the solvent viscosity, and  $c$  is the polymer concentration in g/cc. At low frequencies, all molecular theories predict that  $[G']$  and  $[G'']$  are proportional, respectively, to the second and first powers of  $\omega$ , as follows<sup>10</sup>:

$$[G'] = [A]\omega^2 \equiv (M/RT)([\eta]\eta_s)^2 j_{eR}^0 \omega^2 \quad (1)$$

$$[G''] = [\eta]\eta_s \omega \quad (2)$$

where  $M$  is the molecular weight (uniform in this case),  $[\eta]$  is the intrinsic viscosity, and  $j_{eR}^0$  is the reduced intrinsic steady-state compliance,

$$j_{eR}^0 = (RT/M[\eta]^2) \lim_{c \rightarrow 0} J_e^0/c \quad (3)$$

where  $J_e^0$  is the steady-state shear compliance (in principle measurable from a shear creep experiment).

The dimensionless quantity  $j_{eR}^0$ , which is sensitive to both branching and molecular weight heterogeneity, is the basis of our present analysis. It is determined from experimental data as follows. In a conventional graphic method for comparing experimental viscoelastic data with the predictions of theory,<sup>8,11-13</sup> the reduced intrinsic moduli  $[G']_R = [G']M/RT$  and  $[G'']_R = [G'']M/RT$  are plotted logarithmically against a reduced (dimensionless) frequency  $\omega\eta_s[\eta]M/RT$ . At low frequencies, for  $[G'']_R$ , the ordinate and abscissa are identical; the log  $[G']_R$  line with a slope of 2 intersects the ordinate axis ( $\omega\eta_s[\eta]M/RT = 1$ ) at a point readily apparent from eq. (1) to be  $\log j_{eR}^0$ .

In the theory of Zimm<sup>14</sup> for dilute-solution viscoelastic behavior of linear molecules and that of Zimm and Kilb<sup>15</sup> for branched molecules, which are based on the well-known bead-spring model, when the molecular weight is *uniform*,

$$j_{eR}^0 = S_2/S_1^2 \quad (4)$$

where  $S_1 = \Sigma \tau_p/\tau_1$  and  $S_2 = \Sigma (\tau_p/\tau_1)^2$ ,  $\tau_p$  being the various relaxation times introduced in the theory and  $\tau_1$  the longest relaxation time. (The

summations take into account degeneracy in certain cases where necessary; the definitions of  $S_2$  and  $S_1$  hold only if the modulus contributions associated with all the relaxation times are identical,<sup>16</sup> but that is the case for the theories applied here. An additional subscript 0 sometimes applied to the  $\tau$ 's to denote infinite dilution has been omitted.) If the molecular weight distribution is not uniform, a heterogeneity correction must be applied as described below.

### Estimation of $S_2/S_1^2$ for Randomly Branched Polymers

From the bead-spring theories,<sup>14,15</sup> the entire frequency dependence (exclusive of very high frequencies) of  $[G']_{\mathbf{R}}$  and  $[G'']_{\mathbf{R}}$  can be calculated as functions of the number of beads in the molecular model and a hydrodynamic interaction parameter  $h^*$  which may be regarded roughly as a measure of the ratio of bead size to interbead distance. We restrict the consideration to the single parameter  $S_2/S_1^2$ , however, which is the feature most sensitive to branching. The number of beads should be taken as large as possible because the model is then most realistic and the results are least dependent on the arbitrary number chosen. For linear polymers, numerical evaluations have been made by Lodge and Wu<sup>17</sup>; for star-shaped branched polymers, by Osaki and Schrag<sup>18</sup>; and for comb-shaped polymers with certain geometries, by Osaki et al.<sup>19</sup>

There have been no evaluations for random branching. However, for small numbers of branch points,  $f \leq 5$ , we assume that a regular comb, in which the lengths of the branches and their spacings along the backbone are all equal, is a reasonably appropriate model; an example is shown in Figure 1 with beads on branches ( $N_b$ ) and backbone beads between and outside branches ( $N_s$ ) both equal to 12; here  $f = 3$ . Unfortunately, present computer limitations restrict the Osaki numerical evaluations to a total bead count ( $N = fN_b + (f - 1)N_s - 1$ ) not greater than 111, except for the cases of  $f = 1$  (same as three-arm star<sup>18</sup>) and  $f = 0$  (linear). With increasing  $N_b = N_s$ , the calculated value of  $S_2/S_1^2$  decreases and approaches an asymptotic limit. Values calculated with a UNIVAC 1108 computer are plotted in Figure 2 against  $N_b = N_s$  for several values of  $f$ . For  $f = 0$  and  $f = 1$ , the linear and star calculation methods permit use of large  $N_b$ ,

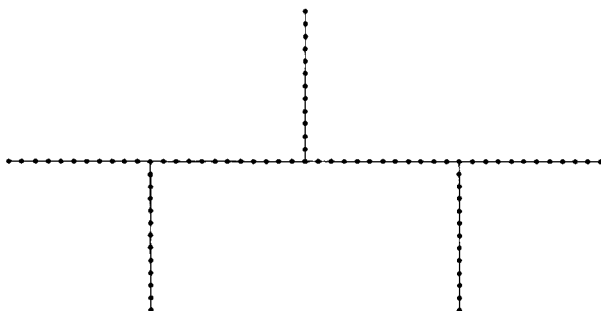


Fig. 1. Example of regular comb model with  $f = 3$  and  $N_b = N_s = 12$ .

TABLE I  
Viscoelastic Coefficients for Regular Combs, Estimated for  
Large  $N_b$  with  $h^* = 0.15$

	$f = 0$	1	2	3	4
$S_2/S_1^2$	0.25	0.17	0.16	0.15	0.14
$g'$	1.00	0.89	0.83	0.79	0.76
$g'$ , random	1.00	0.94	0.90	0.86	0.83

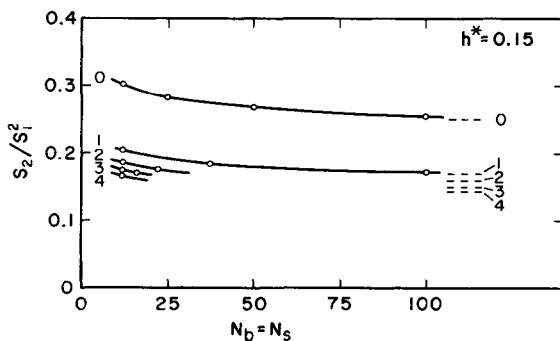


Fig. 2.  $S_2/S_1^2$  calculated for regular combs for  $f = 0$  (linear),  $f = 1$  (equivalent to three-arm star),  $f = 2, 3, 4$ , with different values of  $N_b = N_s$ . Dashed lines denote estimated asymptotic limits.

and essential convergence is achieved. For higher  $f$ , only a rough guess is possible for the asymptotic values of  $S_2/S_1^2$ , as indicated by dashed lines in the figure and listed in Table I. They should be adequate, however, to identify small degrees of branching; in any case, there is a large difference between  $f = 0$  and  $f = 1$ . For  $f$  higher than 5, the theory is probably unsatisfactory.<sup>13</sup> In these calculations, it is necessary to choose a value of  $h^*$ ; 0.15 corresponds to a moderately good solvent, selected here because for practical purposes good solvents are easier to find than theta solvents and they produce larger values of  $G'$  and  $G''$  at comparable polymer concentrations.

An indication of the degree to which a randomly branched molecule can be simulated by a regular comb can be obtained by comparing the intrinsic viscosity ratio,  $g' = [\eta]_f/[\eta]_l$ , calculated for these two models. Here, the subscripts  $f$  and  $l$  refer respectively to a branched molecule with  $f$  branched points and a linear molecule with the same molecular weight (same total number of beads,  $N$ ). The value of  $g'$  for a regular comb is obtained as  $\Phi_f/\Phi_l$ , where the Flory coefficients  $\Phi_f$  and  $\Phi_l$  are calculated as described by Osaki for finite  $N$ <sup>19,20</sup>; it is much less sensitive to  $N_b$  than is  $S_2/S_1^2$ . The value of  $g'$  for a molecule with random trifunctional branches is calculated as proposed by Kurata and collaborators,<sup>21</sup> their eq. (16), based on the theory of Zimm and Stockmayer.<sup>22</sup> These ratios, also listed in Table I, indicate that use of the regular comb model will underestimate somewhat the degree of branching, as might be expected.

### Correction for Molecular Weight Heterogeneity

Presence of molecular weight heterogeneity causes  $j^0_{eR}$  to be larger than  $S_2/S_1^2$ . The problem of resolving simultaneous branching and molecular weight distribution has been treated by Kraus,<sup>23</sup> Ram,<sup>24</sup> and Kurata<sup>25</sup> in terms of combining intrinsic viscosity and gel permeation chromatography data. However, for one or two branches, the intrinsic viscosity is not so different from that of a linear molecule, as seen in Table I. In this range, combination of  $j^0_{eR}$  and GPC might be more useful. At present, we avoid the need for detailed GPC information by treating only the simple case where the molecular weight distribution is sufficiently narrow so that for a given branching index (probability of branching at any monomer residue)  $f$  is the same for all molecular species. Then  $S_2/S_1^2$  is also uniform and the following relation can be derived:

$$j^0_{eR} = \kappa_h S_2/S_1^2 \quad (5)$$

where  $\kappa_h$  is a heterogeneity coefficient. It is now necessary to specify that  $j^0_{eR}$  is determined graphically as described above with  $M$  replaced by the number-average molecular weight in plotting  $[G']M/RT$  against  $\omega\eta_s[\eta]M/RT$ . (The choice of average is arbitrary but must be specified.)

For the ethylene-propylene terpolymers used in the experimental part of this study, the molecular weight distribution is relatively narrow<sup>26</sup> and is expressed by a Gaussian approximation, following the relations:

$$dw(M)/d \ln M = (1/m\sqrt{\pi}) \exp(-y^2) \quad (6)$$

$$y = (1/m) \ln(M/M_0). \quad (7)$$

The parameters  $m$  and  $M_0$  are related to the averages  $\bar{M}_n$  and  $\bar{M}_w$  by the equations

$$m = [2 \ln(\bar{M}_w/\bar{M}_n)]^{1/2} \quad (8)$$

$$M_0 = \bar{M}_n \exp[(m/2)^2]. \quad (9)$$

At infinite dilution, the intrinsic viscosity and the quantity  $[A]$  defined in eq. (1) can be shown to be

$$[A] = \int [A]_M dw \quad (10)$$

$$[\eta] = \int [\eta]_M dw \quad (11)$$

where  $[A]_M$  and  $[\eta]_M$  are functions of molecular weight defined by

$$[A]_M = (M/RT) ([\eta]_M \eta_s)^2 (S_2/S_1^2) \quad (12)$$

$$[\eta]_M = KM^a. \quad (13)$$

Combination of eqs. (1) and (5) to (13) leads to the rather simple expression

$$\kappa_h = (\bar{M}_w/\bar{M}_n)^{(a+1)^2}. \quad (14)$$

If  $\bar{M}_w/\bar{M}_n$  is available and the exponent  $a$  can be estimated, the heterogeneity coefficient in eq. (5) can be easily calculated. The derivation is given in more detail elsewhere<sup>27</sup> for Gaussian and other forms of distribution; the value of  $\kappa_h$  is not very sensitive to the form of the distribution if  $\bar{M}_w/\bar{M}_n$  is below 1.5.

## EXPERIMENTAL

### Materials

Four experimental ethylene-propylene copolymers were generously furnished by Drs. Wendell V. Smith and Ben Ehrlich of Uniroyal, Inc. One contained ethylene and propylene only; the others, small amounts of different termonomers. Their compositions and other characterization data are given in Table II. It was expected that samples A and B would be linear, since they contained no termonomer and a termonomer with a saturated residue respectively, whereas for samples C and D the possibility of branching existed. The number-average molecular weights were quoted by Dr. Ehrlich; the intrinsic viscosities were measured in our laboratory both by conventional capillary viscometry and in the course of the viscoelastic measurements by multiple-lumped resonator (MLR), and the two methods were in quite good agreement.

To provide a good solvent with suitable viscosity and low volatility, it was found necessary to compose a ternary mixture of 46.2% Tetralin (practical, Aldrich), 28.4% O-terphenyl (practical, Eastman), and 25.4% white oil (heavy grade, American Oil Company). The viscosity ( $\eta_s$ ) was 0.0784 poise at 25.00° and 0.0523 poise at 37.78°; the density ( $\rho$ ) was 0.9658 and 0.9564 at these respective temperatures. Solutions were made up by weight with very gentle stirring at room temperature, and the polymer concentration ( $c$ ) in g/ml was calculated assuming additivity of volumes. A very small amount of gel, estimated to be much less than 1% of the polymer, was filtered from solutions of samples C and D. The most concentrated solution was measured first and then sequentially diluted to

TABLE II  
Characterization of Ethylene-Propylene Copolymers

Sample code	A	B	C	D
Termonomer	none	ethyl norbornene	ethylidene norbornene	dicyclo- pentadiene
Moles termonomer/g, $\times 10^3$	0	0.5	0.5	0.6
Ethylene/Propylene weight ratio	50/50	50/50	50/50	65/35
$\bar{M}_n$ (osmotic) $\times 10^{-5}$	2.33	2.29	2.45	2.70
$\bar{M}_w/\bar{M}_n$ (GPC)	1.29	1.19	1.25	1.32
$[\eta]$ in ternary solvent, capillary, ml/g	170	162	155	161
$[\eta]$ in ternary solvent, MLR	160	155	150	155

several lower concentrations, usually a total of five. The concentration range was 0.002 to 0.008 g/ml.

### Method

The storage and loss shear moduli,  $G'$  and  $G''$ , of the solutions were measured with the Birnboim-Schrag multiple-lumped resonator with computerized data acquisition and processing system.<sup>28,29</sup> Only one resonator was used, with five working resonances from 100 to 6000 Hz. However, solutions of samples B and C were measured at two different temperatures to provide additional effective frequencies.

### RESULTS AND DISCUSSION

The quantities  $(G'/c)^{1/2}$  and  $(G'' - \omega\eta_s)/c$  were plotted against  $c$  and extrapolated to zero  $c$  at each frequency as described in previous studies<sup>7,8</sup> to give the corresponding intrinsic quantities  $[G']$  and  $[G'']$ ; an example is shown in Figure 3 for sample D. Complete data are given elsewhere.<sup>27</sup> The initial concentration dependences may be described by the ratios  $\gamma'$  and  $\gamma''$  which are, respectively, the limiting values at low concentrations of the ratio  $(G'/c)^{-1} d(G'/c)/dc$  and the corresponding expression with  $G'' - \omega\eta_s$  substituted for  $G'$ . These ratios decreased with increasing frequency as usually observed.<sup>7,8</sup> At low frequencies, the ratio  $\gamma = \gamma'/\gamma''$

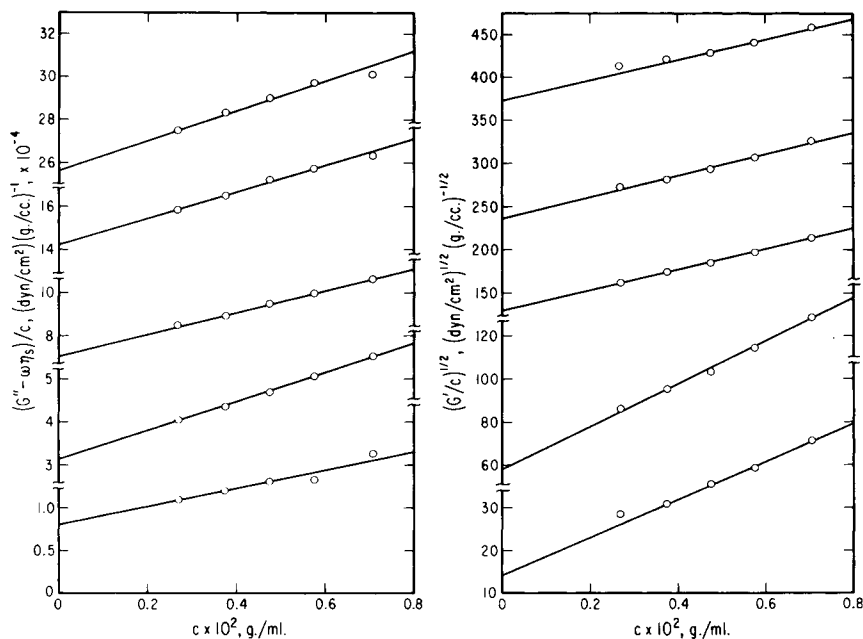


Fig. 3. Plots of  $(G'/c)^{1/2}$  and  $(G'' - \omega\eta_s)/c$  against  $c$  for sample D, each at five frequencies (Hz) as follows, bottom to top: 106, 427, 1039, 2519, and 6060. Note that several different ordinate scales are used.

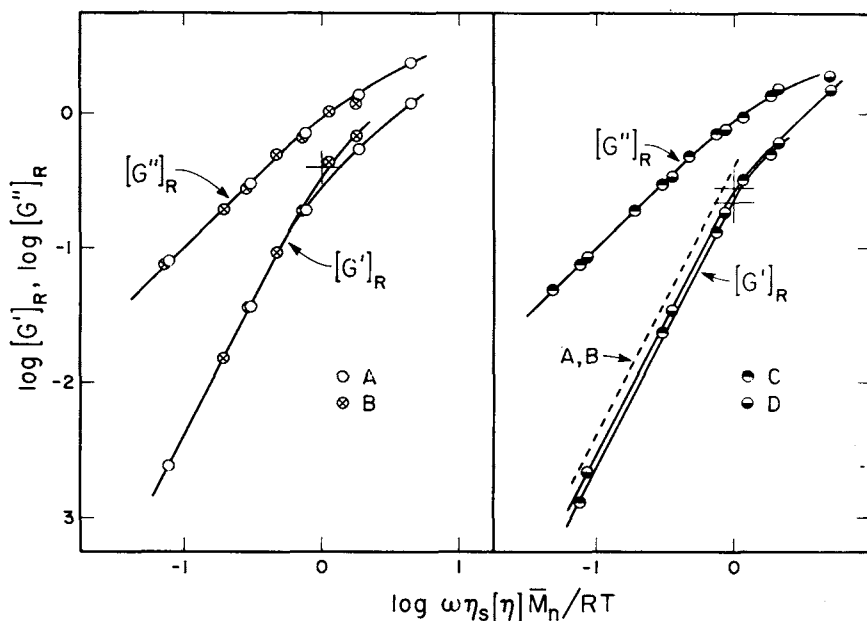


Fig. 4. Logarithmic plots of  $[G']_R$  and  $[G'']_R$  against  $\omega\eta_s[\eta]\bar{M}_n/RT$  for four samples as identified. Crosses denote intersections which specify  $\log j^0_{eR}$ .

appeared to approach a value somewhat above 4, which is consistent with the prediction  $\gamma = 2S_1/S_2$  based on the assumption that the longest relaxation time is the most concentration dependent.

The extrapolated values  $[G']$  and  $[G'']$  were reduced to  $[G']_R = [G'] - \bar{M}_n/RT$  and  $[G'']_R = [G'']\bar{M}_n/RT$  and then plotted logarithmically against  $\omega\eta_s[\eta]\bar{M}_n/RT$  in Figure 4. The choice of solvent viscosity is such as to place the data in the terminal zone where the parameter  $j^0_{eR}$  can be determined by the graphical procedure described above. It is evident that  $j^0_{eR}$  is smaller for samples C and D, as expected if a small degree of branching is present. For more nearly quantitative interpretation, however, it is necessary to apply the heterogeneity correction  $\kappa_h$  which can be obtained from eq. (5) and the data in Table II; then  $S_2/S_1^2 = j^0_{eR}/\kappa_h$ . In this calculation, it is assumed that the Mark-Houwink exponent  $a$  is 0.60 for both linear and branched polymers in this moderately good solvent. Although it should be somewhat smaller with branching, the results are not very sensitive to the choice. The results are listed in Table III, together with the branch numbers  $f$  deduced by comparison with Table I.

According to this analysis, samples A and B are linear; samples C and D have at least three or four branch points per molecule. In spite of the necessity for guessing the values of  $h^* = 0.15$  and  $a = 0.60$  in the calculations, and the asymptotic extrapolations in Figure 2, the relative degrees of branching are probably reliable. In principle, this method should provide a sensitive means of detecting from one to three branches per molecule in



TABLE III  
Experimental  $S_2/S_1^2$  and Estimates of Branch Points

Sample code	$f^0_{eR}$	$\kappa_h$	$S_2/S_1^2$	$f$
A	0.40	1.92	0.21	0
B	0.40	1.56	0.26	0
C	0.22	1.77	0.12 <sub>4</sub>	>4
D	0.28	2.04	0.14	4

samples whose molecular weight distributions are not too broad. Half a gram of sample is sufficient. For higher branching degrees, the method is insensitive to  $f$  and the present theory is probably not reliable; the method of Kurata<sup>25</sup> combining GPC and intrinsic viscosity then becomes preferable.

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