

# Determination of the Entanglement Molecular Weight of Thermoplastic Elastomers by Tensile Retraction Measurements

WILLIAM L. HERGENROTHER and JOHN M. DOSHAK, *Central Research Laboratories, Firestone Tire & Rubber Company, Akron, Ohio 44317*

## Synopsis

The molecular weight between crosslinks was measured as a function of the maximum extension to which samples of solution cast films of ABA triblocks were tested. These measurements were done by applying the kinetic theory of rubber elasticity to the retraction portion of a tensile hysteresis curve. The molecular weight between chain restrictions, as determined by extrapolation to 0% elongation, was found to be identical to the entanglement molecular weight normally associated with the polybutadiene or polyisoprene that was used for the center block. The disentanglement of the small amount of AB diblock present could also be followed by fitting the data collected to what could be pictured kinetically as a simultaneous first- and second-order loss of crosslink density.

## INTRODUCTION

In the first publications describing the use of tensile retraction, it was shown that a constant could be calculated from the retraction portion of a tensile hysteresis loop of an elastomer.<sup>1,2</sup> This constant was shown to be related by rubber elasticity theory to the molecular weight between crosslinks ( $M_c$ ) of the sample at the particular maximum strain at which the test was run. A plot of  $M_c$  as a function of the maximum strain was linear in the range of 10 to over 400% elongation. The intercept was designated as the molecular weight between chain restrictions ( $M_r$ ) and was proposed to be characteristic of all the interactions that hold a particular elastomer together. This includes not only the crosslinks present from chemical reactions but also entanglements and any interactions with fillers.

In this study these measurements were used with solution cast films of thermoplastic elastomers based on polybutadiene and polyisoprene. Since these polymers are not chemically crosslinked, the  $M_r$  determined by this method should represent the entanglement molecular weight ( $M_e$ ) of the rubbery center block. The samples used were the commercially available Kratons obtained from Shell Chemical Co. and were designated D-1102 and D-1107, respectively. The volume fraction of filler ( $v_f$ ) was calculated from the densities of the pure homopolymers and the published styrene contents. The triblock containing polybutadiene has 28% styrene, which corresponds to a  $v_f$  of 0.2483. The D-1107 triblock, which was only 14% styrene, has a  $v_f$  of 0.1230. Equation (1) was previously developed and used to determine the value of  $M_c$ .

$$M_c = \frac{XdRT(\Lambda - \Lambda^{-2})}{\sigma} \quad (1)$$

where  $X = 1 + 2.5v_f + 14.1v_f^2$ ,  $d$  is the density of the stock,  $R$  is the gas constant,  $T$  is the absolute temperature,  $\sigma$  is the stress, and  $\Lambda$  (which is equal to  $1 + X(l - l_0)/l_0$ ) is the strain amplification factor, where  $l_0$  and  $l$  are the initial and test sample lengths.

## EXPERIMENTAL

An Instron 1122 tester controlled by a Hewlett-Packard 9836 computer was used for testing, data acquisition, and calculations. The program was written to allow the same sample to be used by taking 10 evenly spaced maximum elongations in a progressively increasing fashion. Each group of 10 elongations was run at the same crosshead speed. The instrument was automatically rezeroed immediately before each sample was pulled.

The average  $M_c$  was determined on the retraction curve by collecting 25 evenly spaced points in the range of 30–60% of the maximum extension. Then, the set point was determined as the elongation at which the stress returned to zero. The effective strain was then calculated along with the  $M_c$ . The standard deviation associated with this measurement was generally less than 1%.

Best results were obtained by reusing the same 0.25 × 6 in. strip clamped with a 2-in. span. Because of slippage at high extensions, the largest clamping pressure possible was used. Even with the maximum clamping pressure, some slippage did become readily apparent above about 800% elongation. When this did occur, a noticeable increase in the standard deviation of the average  $M_c$  was noted. Since the excellent linearity of the data over a large strain range had been established, values with a standard deviation greater than 3 times the mean were not included in order that the linear least-squared fit would show the best correlation coefficient.

The high clamping pressure caused a buckling of the test strip proportional to the sample thickness. This was accounted for in the test by slowly advancing the cross head until the sample was straight and the negative pressure on the load cell returned to zero. This travel was then added to the initial span and used for all subsequent determinations of maximum elongation. This amounted to about 1% of the original span for a 0.04-in. thick SBR vulcanizates. The ABA solution cast films were sufficiently thin that no such correction was needed.

The range of elongations and the crosshead speeds used are listed in Table I for the thermoplastic elastomers tested.

## Polymers

Films of thermoplastic elastomers were prepared by preparation of a 20% (w/v) solution of the block copolymer in distilled toluene. After degassing, a 5 × 8 in. film was cast onto a clean, level glass plate. After the solvent was allowed to evaporate, the film was removed by soaking the plate in warm water. The typical thickness of the films thus produced was 0.01 in.

TABLE I  
Testing Speed for Different Elongation Ranges of ABA Triblocks

Cross head speed (in./min)	Percent elongation range for	
	SBS	SIS
0.1	—	0.2-2
0.1	—	2.3-5
0.1	—	5.4-9
0.5	1-19	9-18
1	—	18-63
2	25-70	—
5	75-300	63-288
5	325-825	313-538

The sulfur-cured SBR was prepared by mixing 100 phr SBR, 50 phr N-110 carbon black, 3.0 phr zinc oxide, 2.0 phr stearic acid, 1.8 phr sulfur, 1.0 phr antioxidant, and 1.0 phr accelerator. A  $0.04 \times 6 \times 6$  in. plaque was cured at  $300^\circ\text{F}$  for 40 min.

## RESULTS AND DISCUSSION

The use of the computer-controlled Instron now allows a much greater precision in the determination of the  $M_c$ . Previously, standard deviations of 5-10% were measured. Now that at least an eightfold improvement has been made in reducing the error associated with this measurement, a reassessment of any changes that could occur when different test speeds are employed must be made. For this purpose a black-filled sulfur-cured SBR ( $v_f = 0.2347$ ,  $d = 1.149$ ) was tested at a crosshead speed of 0.01-5 in./min (0.5-250%/min) in the elongation range of 25-70%. Figure 1 shows a linear change in a plot of  $M_c$  versus the logarithm of the test speed for each of the maximum elongations utilized. The slopes and linear least-squares sample correlation coefficients ( $r$ ) for these straight lines are summarized in Table II.

Except for the 25% maximum elongation series, all of the slopes are very close to a constant value. The average slope for the samples pulled from 30 to 70% was  $-639 \pm 9$  g/mol, and the average  $r$  was  $-0.985 \pm 0.005$ . The 25% value was probably in error because this was the first elongation pulled after a new sample was clamped in the Instron. It is felt that the compression introduced in this clamping can only be relieved completely by going through one cycle. The procedure utilized to remove the buckling can only, at best, minimize the error obtained on the first elongation measurements. This was verified by running a similar series from 7.5 to 30% elongation. For this extension range, the 5 in./min rate was too fast for the lowest strains utilized and, as a result, this rate was not included in the statistics. However, a reasonable constant value of the slopes was obtained, and the large deviation seen at 25% elongation was established to be an artifact.

Thus, as the test speed increases, the  $M_c$  decreases by a value equal to the slope times the logarithm of the ratio of the new speed to that of the old speed.

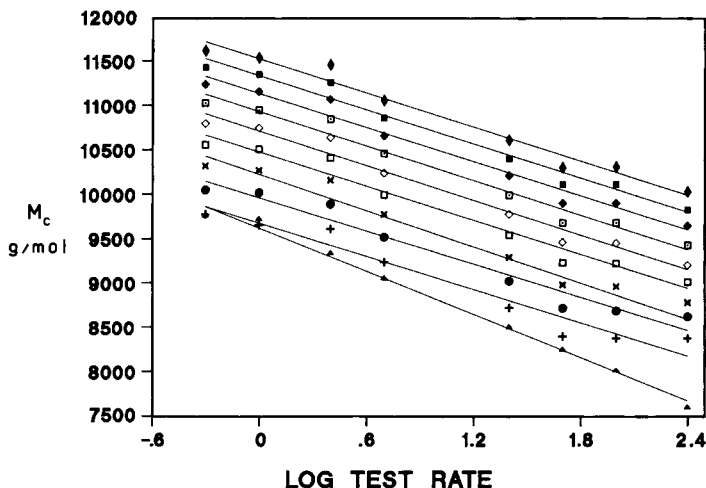


Fig. 1.  $M_c$  vs. logarithm of the test speed for a black loaded sulfur cured SBR taken to a maximum elongation of 25% ( $\blacktriangle$ ), 30% ( $+$ ), 35% ( $\bullet$ ), 40% ( $\times$ ), 45% ( $\square$ ), 50% ( $\diamond$ ), 55% ( $\square$ ), 60% ( $\blacklozenge$ ), 65% ( $\blacksquare$ ), and 70% ( $\blacklozenge$ ).

This difference in  $M_c$  can be accounted for by correcting all the data collected to a constant rate of testing. This correction is needed since the faster test rate produces a rate dependent percent set in the data collected (i.e., the recovery of the sample is slower than the test speed). Although it was previously established that the percent set has been effectively corrected for in the determination of the strain used in Eq. (1), it now appears that a small correction must also be applied to the stress to account for the speed of the test.

Most conveniently, this correction can be applied by repeating the last elongation at the new test speed whenever the test speed was increased. A typical elongation sequence that has been found to be effective can be seen for the SIS test in Table I. With this procedure, the difference in  $M_c$  calculated is added to all the subsequent  $M_c$ 's determined at faster rates of testing. The SBS data

TABLE II  
Statistical Summary of the Data in Figure 1

Maximum percent elongation	Linear least squares	
	Slope (g/mol)	$r$
25	-812	-0.998
30	-625	-0.974
35	-624	-0.980
40	-643	-0.986
45	-642	-0.986
50	-652	-0.987
55	-647	-0.988
60	-644	-0.987
65	-641	-0.988
70	-637	-0.987

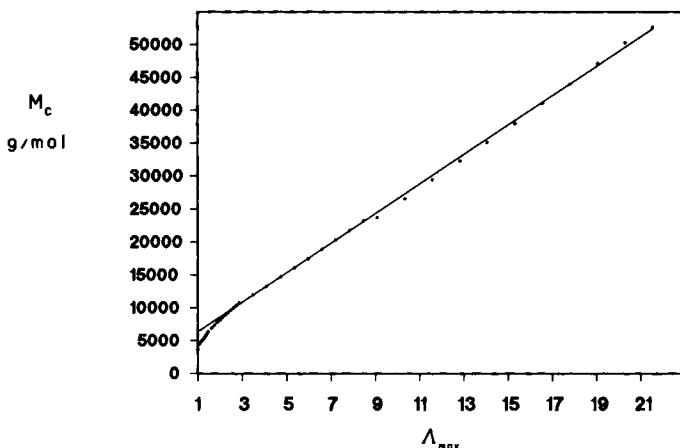


Fig. 2.  $M_c$  vs.  $\lambda_{\max}$  from tensile retraction testing of SBS to 825% elongation, corrected to 25%/min. The solid line was calculated using an  $M_r$  of 6624 g/mol and a slope of 2362 g/mol.

were not collected in this fashion since the shift factor was not noticed in the initial processing. However, upon careful examination of the results, a shift was found to be needed. This was done by extrapolation of the higher speed series to the last maximum extension obtained at a slower rate and then treating the results as discussed here. For the sake of standardization, a test rate of 5%/min was chosen as the reference rate to which all data will be corrected by adding the appropriately determined shift factor to the observed  $M_c$ .

The tensile retraction data collected from the thermoplastic elastomer of SBS can be seen in Figure 2. A good linear plot was obtained with this SBS triblock from 17 to 825% elongation. Similar treatment of the data collected from the SIS triblock also gave a good linear plot in the 2.3–538% elongation range. Table III contains a summary of the shift factors that were used per decade of test speed change along with the slope,  $M_r$ , and  $r$  for these samples.

The plot in Figure 2 was obtained by initially correcting the data to a cross-head speed of 0.5 in./min (25%/min). The value of  $M_r$  listed in Table III, for this polymer, was obtained by a further correction of this number by the addition of 957 g/mol (e.g., the product of the shift factor times the logarithm of 5). None of the other statistical values were changed by converting to a standard rate of 5%/min.

The value of the  $M_r$  determined by this procedure is in good agreement to the  $M_e$  of polyisoprene<sup>3</sup> and polybutadiene<sup>4</sup> that have been reported. These

TABLE III  
Tensile Retraction Summary from Thermoplastic Elastomers Corrected to a Rate of 5%/min

Triblock type	$M_r$ (g/mol)	Slope (g/mol)	$r$	Shift (g/mol)
SIS	16,010	2,440	0.9993	1,529
SBS	7,581	2,362	0.9997	1,369

respective literature values are 14,000 and 5600 g/mol as determined by viscosity measurements on a variety of homopolymers of different molecular weights. If the rate of testing used for these viscosity measurements was assumed to be a factor of 20 times faster than that chosen for the standard tensile retraction test, then an excellent agreement to the literature values could be made. This requires the use of the shift factors to correct the  $M_r$  values listed in Table III to a crosshead speed of 2 in./min (100%/min). Such a correction gave values of 14,040 and 5800 g/mol for the polyisoprene and the polybutadiene, respectively. Thus this close duplication of the known  $M_e$  values of these two different elastomers give considerable credence to the tensile retraction equations that have been developed thus far.

The slope associated with this measurement suggests that, as the polymer coil is perturbed by an outside stress, the number of effective crosslinks is being reduced by this ordering process. More correctly, the relationship being monitored is that of the loss of crosslink density ( $\nu$ ). The  $1/\nu$  plot, that the  $M_c$  represents, can be pictured to be similar to a second-order kinetic expression. This seems particularly appropriate when it is considered that the data has been shifted to a constant test speed and thus the  $\Lambda_{\max}$  can be considered as a function of time. In a second-order kinetic plot, the loss of concentration of the group being followed requires an interaction with itself in the rate determining step to give this type of a straight-line relationship.

At low extensions a deviation was seen from the calculated linear least-squares line for both of these ABA thermoplastics. This can be more readily seen in Figure 3 where the steady departure from this calculated line occurs as lower elongations are considered. This curvature can best be explained by the presence of AB diblock in the thermoplastic elastomer. Such an impurity would only be anchored at one end and thus would show the effects of increasing strain by pulling the loose end out of the effectively crosslinked rubbery network. Such a pull out has been reported by Cohen and Tschoegl<sup>5</sup> in dynamic mechanical measurements on this type of block copolymer. This pull out would

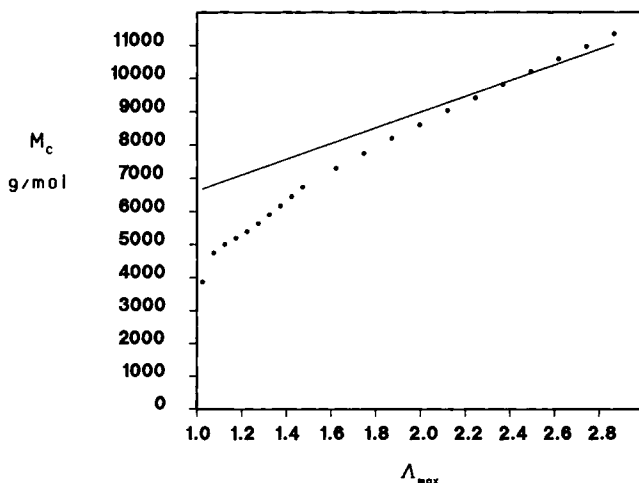


Fig. 3.  $M_c$  vs.  $\Lambda_{\max}$  of Fig. 2 from 0 to 75% elongation.

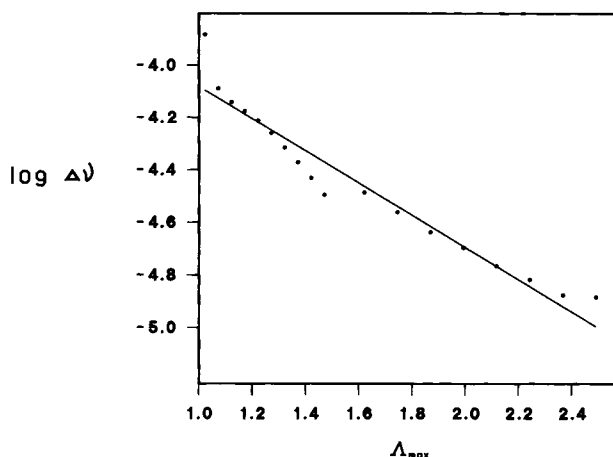


Fig. 4. Logarithm  $\Delta\nu$  vs.  $\Lambda_{\max}$  for SBS. The solid line was calculated using a slope of  $-0.613$  and an intercept of  $-4.078$ .

have the effect of giving a nonlinear portion to the low-strain tensile retraction data. The presence of 14% diblock in the SIS and 5% diblock in the SBS was confirmed by running size exclusion chromatography on these polymers. The same type of deviation was also seen with the SIS triblock.

If the calculated crosslink density ( $\nu_c$ ) was subtracted from the observed crosslink density ( $\nu_0$ ), the difference in crosslink density ( $\Delta\nu$ ) would be the effective crosslinks due to an additional type of interaction [Eq. (2)]. A linear relationship

$$\Delta\nu = \frac{\sigma}{XdRT(\Lambda - \Lambda^{-2})} - \frac{1}{M_r + S(\Lambda_{\max} - 1)} \quad (2)$$

was obtained by plotting the logarithm of this  $\Delta\nu$  as a function of the maximum extension to give the results seen in Figure 4. This sort of relationship, which kinetically is equivalent to a first-order reaction, is what would be predicted from the preceding discussion. The motion of the rubbery portion of the diblock would be dependent on the concentration of the loose ends and in this process should be characterized by a first-order plot. The results of this plot is summarized in Table IV, along with the same type of data generated from the SIS triblock. Here, the slopes and intercepts of the first-order plots are given along

TABLE IV  
Summary of Low-Strain First-Order Tensile Retraction Data from Thermoplastic Elastomers Corrected to 5%/min

Triblock type	$-\log$ slope	$-\log$ intercept	$-r$	$M_0$ (g/mol)
SIS	33.429	4.589	0.997	38,800
SBS	0.613	4.078	0.972	11,970

with the associated molecular weight between crosslinks in the unstrained state ( $M_0$ ) as determined by the intercept.

The relationship of these parameters can be expressed by Eq. (3), where  $s$  is the slope of the semilog plot.

$$\Delta\nu = \frac{1}{M_0} 10^{s(\Lambda_{\max} - 1)} \quad (3)$$

The  $M_0$  of the polybutadiene-based copolymer is significantly lower than that value determined when the center block was replaced with polyisoprene. The  $M_0$  values are approximately twice the measured  $M_e$  values and are probably related to the same physical process. The much lower slope associated with the SBS must reflect the relatively greater difficulty of pulling the entangled loose end of the SB copolymer free of the network as compared to the less tightly entangled polyisoprene analog.

The values for the lower modulus SIS were determined by excluding the first five data points. Such a treatment was necessary because of the scattering encountered while trying to measure the stress on such a weak sample. The correlation obtained using the last eight points was good, considering the factors that are involved in this measurement. These include not only the clamping problem and low stress associated with the first few data point but also the amount of diblock present in the two samples used. The SBS polymer clearly shows that a first-order relationship exists at low maximum elongations. Further information regarding these competitive first- and second-order processes will be presented in subsequent publications.

### References

1. W. L. Hergenrother, *J. Appl. Polym. Sci.*, **32**, 3039 (1986).
2. W. L. Hergenrother, *J. Appl. Polym. Sci.*, **32**, 3683 (1986).
3. G. Holden, E. T. Bishop, and N. R. Legge, *J. Polym. Sci.*, **C26**, 37 (1969).
4. J. T. Gruver and G. Kraus, *J. Polym. Sci.*, **A2**, 797 (1964).
5. R. E. Cohen and N. W. Tschoegl, *Int. J. Polym. Mater.*, **3**, 3 (1974).

Received November 21, 1988

Accepted April 18, 1989