

## **A New Correlation Between Molecular Parameters and Physical Properties of Chlorobutyl Rubbers Grafted with Polystyrene Branches**

**Bela Pukanszky\*, Joseph P. Kennedy and Tibor Kelen\***

Institute of Polymer Science, University of Akron, Akron, Ohio 44325, USA

### Summary

A series of chlorobutyl rubbers grafted with polystyrene branches have been prepared and backbone length, branch density and segment lengths between branches were calculated from the overall graft composition, number average molecular weight, and branch molecular weight. Analysis of the deformation process revealed unexpected correlations between the molecular parameters and tensile properties of the graft: the tensile strength is directly, and the elongation at break inversely proportional to the ratio of branch molecular weight to the molecular weight of segments between the branches. Further, the tensile strength and elongation at break are proportional to the molecular weight of the backbone. A general correlation was found between the backbone molecular weight and the specific breaking energy.

### Introduction

In the course of our ongoing investigations concerning graft and block copolymers we have prepared a series of chlorobutyl rubber-g-polystyrenes (Cl-IIR-g-PSt) having various overall compositions, backbone and branch molecular weights, and branch frequencies, and studied some of their physical-mechanical properties, i.e., yield stress  $\sigma_y$ , Young's modulus  $E$ , elongation  $\epsilon$ , and tensile strength  $\sigma$ . This paper concerns an analysis of these physical properties as a function of graft parameters  $M_B$ ,  $M_C$ , and  $M_b$ , i.e.,  $M_n$  of the backbone,  $M_n$  between branch points, and  $M_n$  of branches, respectively. A new correlation between  $\sigma$  and  $\epsilon$  and the molecular parameters  $M_B$  and  $M_C/M_b$  has been uncovered.

### Experimental

Graft polymerizations and manipulations were carried out in a stainless steel enclosure under nitrogen atmosphere at  $-15^\circ\text{C}$ . A detailed description of the techniques used, starting materials, their sources, purities or purifications has been published (KENNEDY 1977; KENNEDY and CHARLES 1977).

\* Visiting Scientist; permanent address: Central Research Institute for Chemistry, Hungarian Academy of Sciences, P.O. Box 17, 1525 Budapest, Hungary

Overall composition of the grafts was determined by  $^1\text{H}$  NMR spectroscopy (Varian T 60 NMR Spectrometer). Molecular weights were measured by a high speed membrane osmometer (Type HP 503, Hewlett-Packard).

Tensile properties, i.e.,  $\sigma_y$ , E,  $\sigma$  and  $\epsilon$ , were determined from stress versus strain traces obtained on a tensile testing instrument at 50 mm/min crosshead speed (Monsanto Tensiometer 500, Huston Instruments Co.).

### Results and Discussion

Table I is a compilation of composition and select molecular characteristics of chlorobutyl rubber grafted with polystyrene branches Cl-IIR-g-PSt used in our research together with the physical properties obtained. Graft parameters have been calculated from overall composition (wt. fraction of PSt),  $\bar{M}_n$  of the pure (hot acetone-extracted) graft  $\bar{M}_g$ , and  $\bar{M}_n$  of the branch  $\bar{M}_b$ . The  $\bar{M}_b$  has been obtained by determining the  $\bar{M}_n$  of the hot acetone-soluble PSt fraction and assuming that this value is identical to that of the grafted PSt branches. This assumption has been tested and was found to be correct by previous workers (KENNEDY and METZLER 1977; KENNEDY and SMITH 1977; KENNEDY and DAVIDSON 1977; KENNEDY and VIDAL 1975).

The  $\bar{M}_B$ 's shown in Table I are much lower than that of the starting material ( $\bar{M}_n \approx 156,000$  Cl-IIR, HT-1066, Exxon). Degradation may be due to the relatively high grafting temperatures used or manipulation during sample preparation.  $\bar{M}_B$  was calculated by  $\bar{M}_B = \bar{M}_g \cdot (1-w_{\text{PSt}})$ . The average number of branches per graft is  $b = w_{\text{PSt}} \cdot \bar{M}_g / \bar{M}_b$  and the molecular weight of backbone segments between branches is  $\bar{M}_C = \bar{M}_B / (b+1)$ .

A thorough examination of the data in Table I led to the discovery of correlations between graft molecular characteristics and tensile properties. Thus  $\epsilon$  is related to  $\bar{M}_B \cdot \bar{M}_C / \bar{M}_b$  (Figure 1) and  $\sigma$  to  $\bar{M}_B \cdot \bar{M}_b / \bar{M}_C$  (Figure 2). The  $\sigma_y$  and E are related to  $\bar{M}_C / \bar{M}_b$ , however, these values fall into two groups so that a correlation cannot be established (Figure 3). An analysis of the tensile testing process provides an explanation for the observed correlations. At the beginning of the test at small deformations the size and frequency of glassy domains mainly control tensile properties.  $\sigma_y$  and E increase by increasing the number and size of glassy PSt domains (characterized by  $\bar{M}_b$ ) and/or by decreasing the number and size of the rubbery Cl-IIR phase (characterized by  $\bar{M}_C$ ).

The  $\bar{M}_C / \bar{M}_b$  ratio, which characterizes the microstructure of the graft in the Hooke elasticity region, is closely related to the composition of the grafts. As indicated by the data in the first column of Table I, the composition of the grafts fall into two groups

Table I. Composition, molecular characteristics\* and tensile properties of Cl-IIR-g-PSt

| w <sub>PSt</sub> <sup>**</sup> | Graft parameters           |                            |                            |      | Tensile Properties <sup>**</sup> |                                |                       |                              |                |
|--------------------------------|----------------------------|----------------------------|----------------------------|------|----------------------------------|--------------------------------|-----------------------|------------------------------|----------------|
|                                | $\bar{M}_g \times 10^{-3}$ | $\bar{M}_b \times 10^{-3}$ | $\bar{M}_B \times 10^{-3}$ | b    | $\bar{M}_C \times 10^{-3}$       | $\sigma_Y$ (N/m <sup>2</sup> ) | E (N/m <sup>2</sup> ) | $\sigma$ (N/m <sup>2</sup> ) | $\epsilon$ (%) |
| 0.52                           | 132.5                      | 4.6                        | 63.5                       | 14.9 | 4.0                              | 9.5                            | 97.6                  | 13.5                         | 160            |
| 0.52                           | 67.2                       | 4.7                        | 32.6                       | 7.4  | 3.9                              | 9.9                            | 82.3                  | 10.1                         | 85             |
| 0.51                           | 117.6                      | 3.3                        | 57.2                       | 18.3 | 3.0                              | 10.6                           | 100.3                 | 13.1                         | 165            |
| 0.51                           | 120.1                      | 4.9                        | 59.2                       | 12.3 | 4.4                              | 9.3                            | 78.4                  | 11.5                         | 185            |
| 0.50                           | 120.4                      | 3.3                        | 59.9                       | 18.3 | 3.1                              | 9.3                            | 74.6                  | 11.9                         | 180            |
| 0.40                           | 124.9                      | 2.2                        | 75.2                       | 22.2 | 3.2                              | 3.3                            | 22.1                  | 10.6                         | 325            |
| 0.39                           | 129.7                      | 3.4                        | 79.0                       | 14.9 | 5.0                              | 2.9                            | 20.8                  | 11.1                         | 310            |
| 0.38                           | 63.1                       | 2.7                        | 37.1                       | 8.9  | 3.9                              | 4.4                            | 28.9                  | 5.2                          | 140            |

\*Molecular weights are number averages

\*\*Weight fraction of PSt in the graft

\*\*\*Averages from triplicates

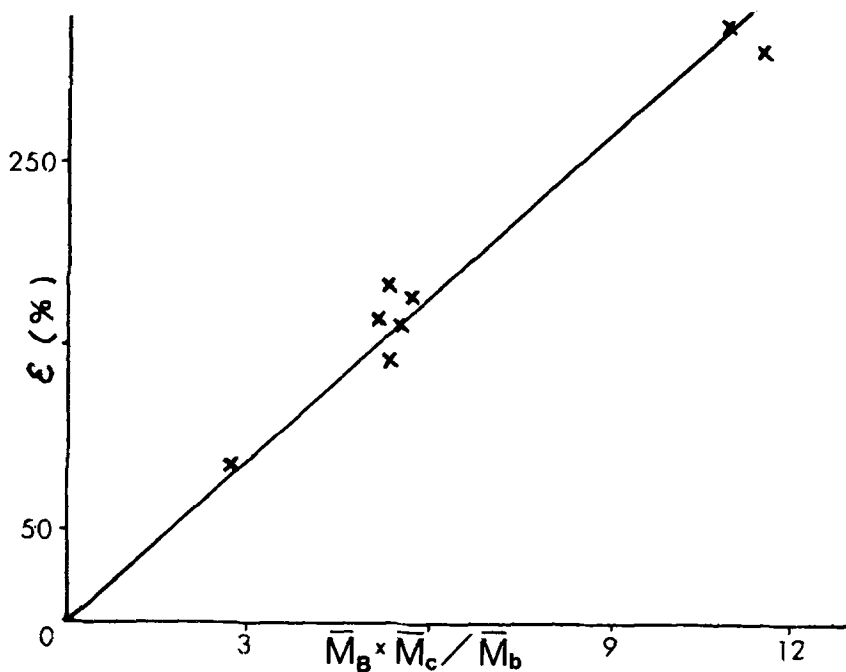


Figure 1. Elongation at break as a function of  $\bar{M}_B \cdot \bar{M}_C / \bar{M}_b$  of Cl-IIR-g-PSt

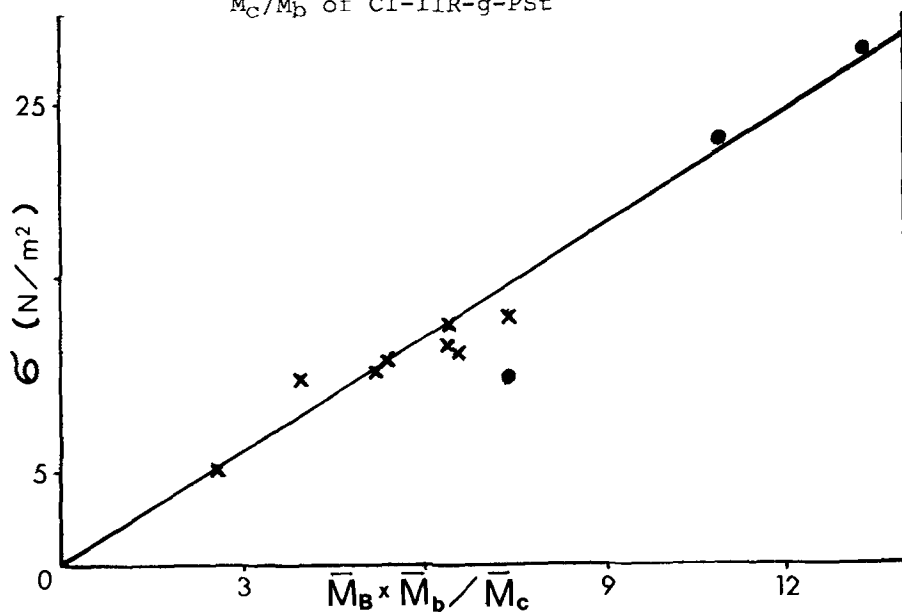


Figure 2. Tensile strength as a function of molecular characteristics (x:Cl-IIR-g-PSt, •: EPDM-g-PSt)

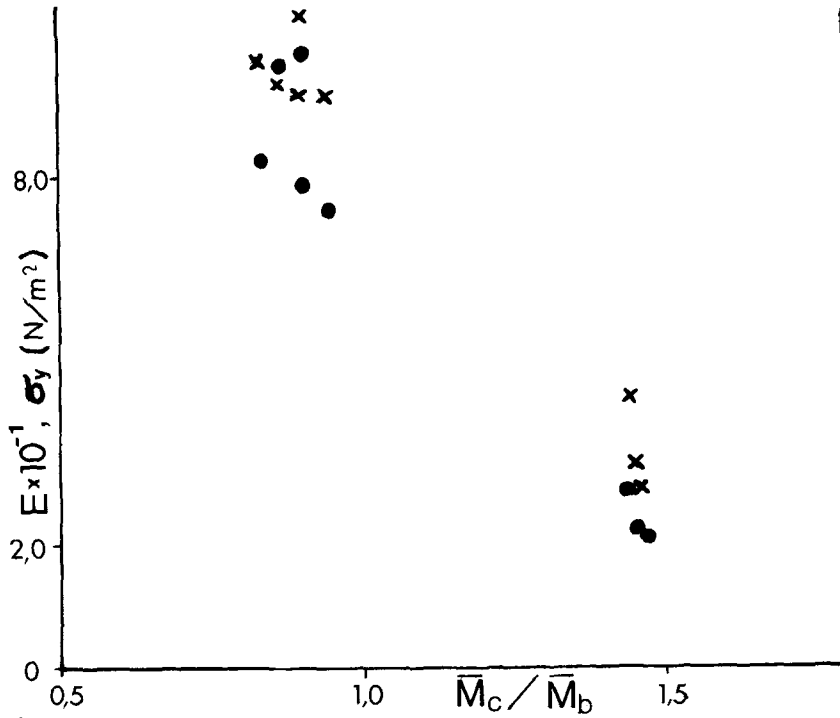


Figure 3. Yield stress and Young's modulus of Cl-IIR-g-PSt as a function of  $\bar{M}_c/\bar{M}_b$  ( $\times = \sigma_y$ ,  $\bullet = E$ )

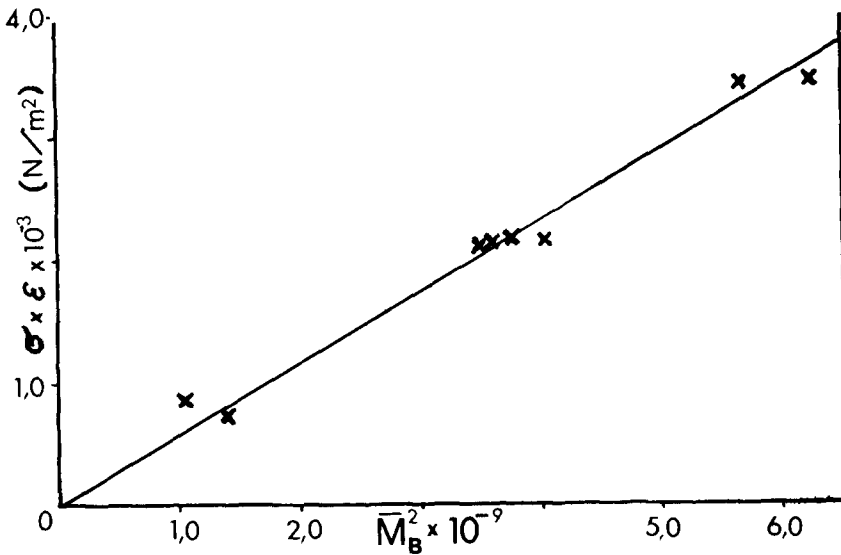


Figure 4. Correlation between the specific breaking energy and the square of backbone molecular weight of Cl-IIR-g-PSt

(~51 and ~39% PSt); thus it is not too surprising that two strongly segregated groups of data appear in the  $\sigma_Y$  or E versus  $\bar{M}_C/\bar{M}_b$  plots also (Figure 3).

At break the specimens undergo high deformations: the molecules are stretched and the original domains break up. Larger molecules undergo higher deformations than smaller ones and  $\epsilon$  is a function of the length of the backbone. In contrast, the branches resist and hinder deformation.  $\epsilon$  should increase with decreasing branch density (increasing  $\bar{M}_C$ ) and decreasing PSt branch length. These expectations are expressed by the correlation  $\epsilon = f(\bar{M}_B \cdot \bar{M}_C/\bar{M}_b)$  and are borne out by the data shown in Figure 1.

In contrast to  $\epsilon$ , the  $\sigma$  increases with increasing branch density and branch length. The length of the backbone is important here too, because it augments intermolecular secondary forces and reduces plastic deformation, and thus increases the strength of the material. A combination of these considerations led to the correlation  $\sigma = f(\bar{M}_B \cdot \bar{M}_b/\bar{M}_C)$  corroborated by the data shown in Figure 2. We included in this figure some earlier data of Cl-EPDM-g-PSt (KENNEDY and SMITH 1974). The similarity in the characteristics between the rubbery Cl-IIR and Cl-EPDM components and the good fit to these data justifies their inclusion.

An examination of the correlations shown in Figures 1 and 2,  $\epsilon = f(\bar{M}_B \cdot \bar{M}_C/\bar{M}_b)$  and  $\sigma = f(\bar{M}_B \cdot \bar{M}_b/\bar{M}_C)$ , led to the discovery of a general relationship between molecular parameters of polymers and their physical performance:

$$\sigma \cdot \epsilon = \bar{M}_B^2$$

Figure 4 shows the corresponding plot using the available data. The validity of this expression is not restricted to grafts and investigations to prove the general validity of this relationship for homopolymers are under way.

#### Acknowledgements

Financial assistance by the Institute of Cultural Relations, Hungary, and the NSF (INT-78-27245) is gratefully acknowledged.

#### References

- KENNEDY, J. P. and DAVIDSON, D.L., J. Appl. Polym. Sci., Appl. Polym. Symp., 30, 13 (1977)  
 KENNEDY, J. P.: Cationic Graft Copolymerization. J. Appl. Polymer Sci., Appl. Polym. Symp., 30 (1977)  
 KENNEDY, J. P., CHARLES, J.J., J. Appl. Polym. Sci., Appl. Polym., 30, 119 (1977)  
 KENNEDY, J. P. and METZLER, D.K.: J. Appl. Polym. Sci., Appl. Polym. Symp. 30, 141 (1977)

KENNEDY, J. P., SMITH, R.R.: Polymer Blends, Grafts and Blocks, SPERLING, L. H., ed., Plenum Press, New York, London 1974, p. 303  
KENNEDY, J.P. and VIDAL, A., J. Polym. Sci., Polym. Chem. Ed. 13, 1765 (1975)

*Received March 18, 1981*