Properties of Random and Block Copolymers of Butadiene and Styrene. I. Dynamic Properties and Glassy Transition Temperatures

G. KRAUS, C. W. CHILDERS, and J. T. GRUVER, *Research and Development Department, Phillips Petroleum Company, Bartlesville, Oklahoma 74003*

Synopsis

The effect of monomer sequence on physical properties was investigated for butadiene–styrene solution copolymers made by organolithium initiation. The polymers varied from random copolymers of uniform composition along the polymer chain to ideal block polymers of specific block sequence arrangement and included rubbers of intermediate degrees of randomness. Uniform composition random copolymers exhibit a single glass transition temperature and a very narrow dynamic loss peak corresponding to this transition. The glass transition can be predicted from the styrene content and the microstructure of the butadiene portion of the rubber. Random copolymers in which composition varies along the polymer chain, and to some extent between molecules, exhibit a single glass transition, but the dynamic loss peak is broadened. The extent of this broadening is shown to be compatible with the sequence distribution, polymer segments of various compositions losing mobility at different temperatures. This indicates a tendency for association between segments of different temperatures. This indicates a tendency for association between segments of different chains which are similar in composition. Block copolymers display two transitions, corresponding to T_g for each type of block. The position and width of the dynamic loss peaks are related to block length and compositional purity of the blocks.

INTRODUCTION

The two-phase nature of butadiene–styrene block copolymers has been described by Angelo, Ikeda, and Wallach.[1] The present investigation is concerned with both random and block copolymers, as well as with polymers of intermediate degrees of randomness.

To facilitate interpretation of results it will be convenient to classify the polymers with respect to monomer sequence as follows:

Uniformly Random Copolymers. The comonomers follow each other in statistically random fashion all along the chain. Composition does not vary along the chain and all molecules have the same composition. In such polymers composition is necessarily also constant with conversion.

Random Copolymers. In these polymers composition changes continuously along the polymer chain and with conversion, without giving rise to a detectable block structure.

Block Copolymers. These polymers consist of two or more block sequences, at least one of which is not a homopolymer or uniformly random copolymer sequence.

Ideal Block Copolymers. All block sequences are uniform in composition, which changes discontinuously at the junction points of the blocks.

EXPERIMENTAL

Polymers. The polymers were synthesized by methods described in the patent literature.[2] Ideal block copolymers were prepared by incremental monomer addition, other block copolymers by charging the monomers simultaneously. Ethers and amines were used as additives to prepare random copolymers.

Chemical Analysis for Block Polystyrene. The method of Kolthoff, Lee, and Carr[3] was used to determine the weight fraction of styrene contained in block structures. It is based on the degradation of the butadiene portion of the molecule by *tert*-butylhydroperoxide in *p*-dichlorobenzene, catalyzed by osmium tetroxide. The resulting small molecular fragments (low molecular weight aldehydes) are soluble in ethanol whereas the unattacked polystyrene is not. The polystyrene is isolated by pouring the digested reaction mixture into ethanol and filtering out the polymer.

Infrared Analysis. Schnell[4] has suggested an approximate analysis of "blockiness" in butadiene–styrene copolymers based on two conformational absorption bands in the far infrared spectrum. A polystyrene absorption band at 542 cm.$^{-1}$ (18.5 μ) is shifted to 560 cm.$^{-1}$ (17.9 μ) in random butadiene–styrene copolymers. The ratio of optical densities (β) at these two wavelengths thus furnishes an index of block structure. In the present study the spectra were obtained on solid films cast from benzene solution. Figure 1 shows spectra for two extreme cases of 75:25 butadiene–styrene copolymers—a uniformly random polymer and an ideal block copolymer. The values of the block index β are 0.88 and 1.92, respectively. Analysis of the microstructure of the butadiene portion of the polymers was carried out by the method of Silas et al.[5]

Glass Transition Temperatures. Glass transitions were determined dilatometrically using an ethanol–water (92.5:7.5) mixture as the displacement fluid for low-temperature work. The upper transitions in block polymers were determined using mercury as displacement fluid.

Dynamic Measurements. A Nonius (N. V. Nederlandsche Instrumentenfabriek Nonius, Delft, Holland) torsion pendulum was used to measure the dynamic shear moduli and loss tangents of cured and uncured polymers as a function of temperature between −140 and 100°C. Results were calculated in the manner described by Ferry.[6] Interpolation to constant frequency in the temperature range between T_g and $(T_g + 100)$ was made by calculating a temperature correction using the Williams, Landel, and Ferry (WLF) equation[6] with universal constants. The magnitude of this correction did not exceed 4°C. No correction was made below T_g or above $(T_g + 100)$ since this is outside the range for which the WLF equation is applicable.
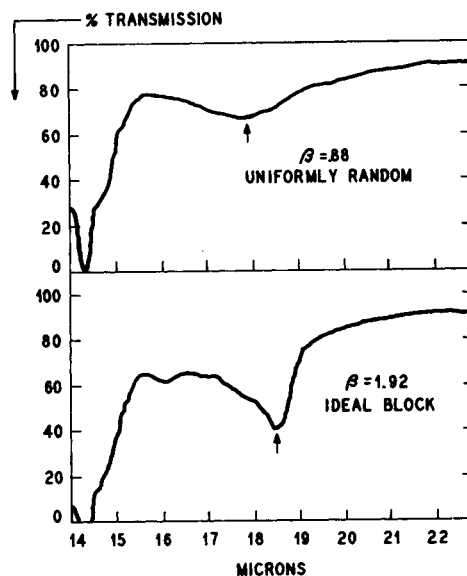
Fig. 1. Far-infrared spectra of copolymers of butadiene (75%) and styrene (25%).

Compounding Recipes.   Random copolymers were cured in recipe A and block copolymers in recipe B (Table I).

TABLE I

	Recipe A	Recipe B
Polymer	100 (random)	100 (block)
Zinc oxide	3	3
Stearic acid	2	2
Resin 731	—	3
Flexamine	1	1
Sulfur	1	1.5
Santocure	1	—
Methyl tuads	—	0.9
Captax	—	0.4
Cure time, min.	45	45
Cure temperature, °C.	153	153

RESULTS AND DISCUSSION

Characterization of Chain Architecture

Knowledge of monomer sequence along the polymer chain may be derived from polymerization data (initiation and propagation rates, incremental vs. simultaneous monomer addition, catalyst functionality, composition vs. conversion curves, etc.), chemical analyses for block polystyrene and infrared analyses.   Table II shows examples of the principal polymer types investigated in the present study, all containing 25% total styrene by weight.   Several points are worth noting.   The vinyl content of the

butadiene portion of the polymer molecules is higher in the random co-polymers as a result of the effects of the chemical randomizers.   Because of the influence of microstructure on the glass transition temperature this has some pronounced effects on physical properties, which are quite divorced from the effects of monomer sequence, and must be considered in the inter-pretation of results.

TABLE II
Polymer Descriptive Data

Identi-fi-cation	Polymer type	No. of styrene block se-quences (termi-nal)	Styrene, % Charged	Anal.	Block styrene, % Anal.	Polybutadiene microstructure, % cis	trans	Vinyl	IR block index
A	Uniformly Random	—	25	24.9	0	21.0	50.2	28.8	0.88
B	Random	—	25	24.5	0	31.6	42.0	26.4	0.92
C	Block	1	25	24.8	16.4	31.9	58.1	10.0	1.18
D	Ideal Block	1	25	24.1	24.8	33.5	54.8	11.7	1.92
E	Block	2	25	24.7	11.5	27.1	59.1	13.8	1.29
F	Ideal Block	2	25	24.4	23.9	35.8	54.8	9.4	1.68
H	Block	1	25	24.2	11.7	35.2	54.9	9.9	1.52

In ideal block copolymers of butadiene and styrene the analyses for total and block polystyrene are substantially identical.   This is not the case in block copolymers made by adding all monomers initially, where a portion of the styrene ends up in the rubbery block.   The average composition of the rubbery block is easily calculated, but it should be realized that the sequence of styrene in the rubbery block is nonrandom.   Figure 2 shows a
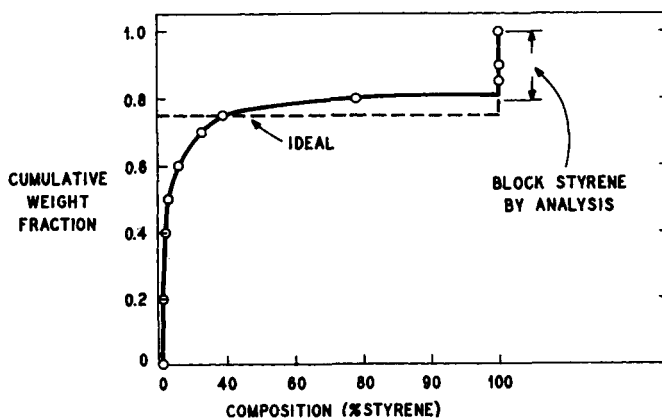

Fig. 2. Composition distribution in a 25% styrene block copolymer.

composition distribution of such a polymer calculated from conversion data. If initiation were instantaneous and in absence of termination reactions, this would also be the cumulative distribution of styrene along the polymer chain. Since initiation was not instantaneous in this example the curve is only an approximation of the latter.

The infrared method furnishes similar information as the chemical polystyrene determination, but also takes into account short sequences of styrene which may be lost in the chemical determination (due to the low molecular weight of the fragments). Figure 3 shows a comparison of the two methods applied to random and block copolymers varying in monomer (Bd:S) ratio from 90:10 to 60:40. The deviations shown at zero and small (chemical) block styrene analyses are due to the shortness of blocks. Uniformly random copolymers can be distinguished from non-uniform, random ones by the infrared method, the degree of discrimination being, of course, dependent on the degree of deviation from a purely statistical sequence. The small difference between polymers A and B in Table II may well be within experimental variations.

The Glass Transition

For an amorphous polymer at a given temperature, the proximity of this temperature to the glass transition (T_g) is one of the most important factors in determining physical properties. The T_g of butadiene–styrene copolymers is primarily a function of butadiene microstructure and the amount and distribution of styrene in the polymer. Block polymers exhibit two glass transitions, characteristic of each type of block. Molecular weight has the usual effect on T_g, which carries through to block length in block copolymers.
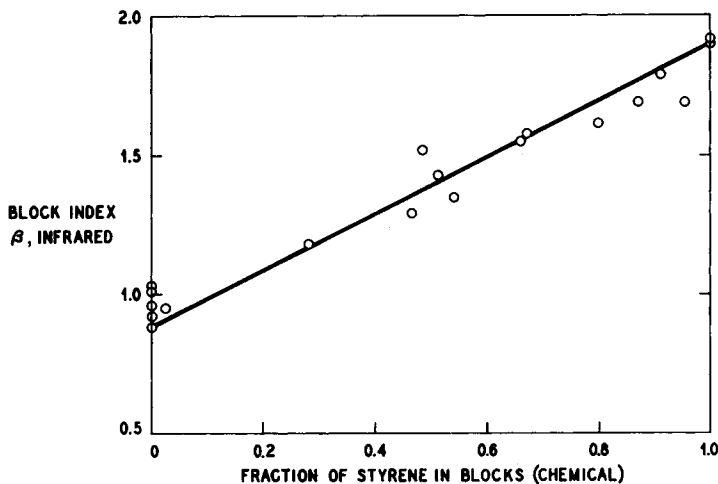

Fig. 3. Comparison of block styrene analyses.

Polybutadiene itself is a random, configurational terpolymer of *cis*-1,4, *trans*-1,4, and 1,2 addition (vinyl) units. We have found that T_g of polybutadiene can be expressed by an extension of the Gordon-Taylor[7] equation to a higher number of components

$$T_g = \sum C_i \Delta\beta_i \cdot T_{gi} / \sum C_i \Delta\beta_i \tag{1}$$

where C_i is the weight fraction of the ith component, T_{gi} the glass transition of the pure homopolymer of monomer i, and $\Delta\beta_i$ the difference in coefficient of volume expansion of liquid and glass for the homopolymer. For polybutadiene we have, approximately, the values given in Table III.

TABLE III

	T_g, °C.	$\Delta\beta \times 10^4$
cis	−114	4.9
trans	−102	2.9
Vinyl (atactic)	−7	4.3

The values listed for *trans* are estimates only, because rapid crystallization makes measurements of T_g near 100% *trans* impossible. They do, however, produce a good fit to experimental data when used in eq. (1), as is illustrated in Figure 4.

The use of eq. (1) can be extended to random copolymers of butadiene and styrene by adding a fourth component with $T_g = 100$, $\Delta\beta = 1.5 \times 10^{-4}$. The T_g is the accepted value for polystyrene, but $\Delta\beta$ is only one-half of the value observed in the homopolymer. Our results, therefore, indicate that the styrene copolymers do not follow the simple Gordon-Taylor theory.
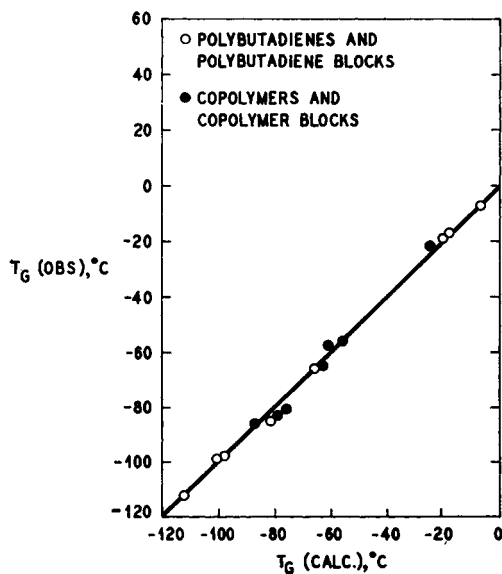

Fig. 4. Observed vs. calculated glass transitions.

(The significance of this, according to a recent theory of Kanig,[8] is that the interaction energy between unlike units cannot be expressed as the arithmetic mean of the interactions between like units.) Shown as solid circles in Figure 4 are values for random copolymers and random copolymer sequences of block polymers.

The upper (styrene) glass transition temperature of seven block polymers examined fell between 78 and 83.5°C., substantially lower than T_g of polystyrene of high molecular weight. Estimates from kinetic number-average molecular weights and block styrene contents indicate block lengths of the order of 20,000 molecular weight units or less. This alone could not account for the lower T_g, but the presence of antioxidant might further lower the transition temperature. We have found no evidence that the arrangement of styrene block sequences (e.g., terminal vs. simple) in any way affects T_g.

Dynamic Properties

Far more discriminating than the glass transition temperatures are the dynamic storage and loss moduli or loss tangents. Figure 5 shows the storage moduli (measured at 0.1 cps) for gum vulcanizates of copolymers containing 25% styrene and varying in monomer sequence from uniformly random to ideal block. Figure 6 shows the loss tangents. The principal transitions are clearly recognizable. The dilatometrically determined T_g's are also indicated on Figure 5.
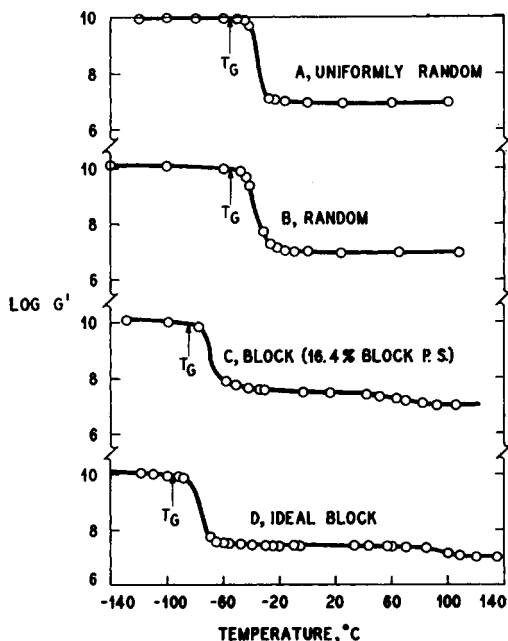

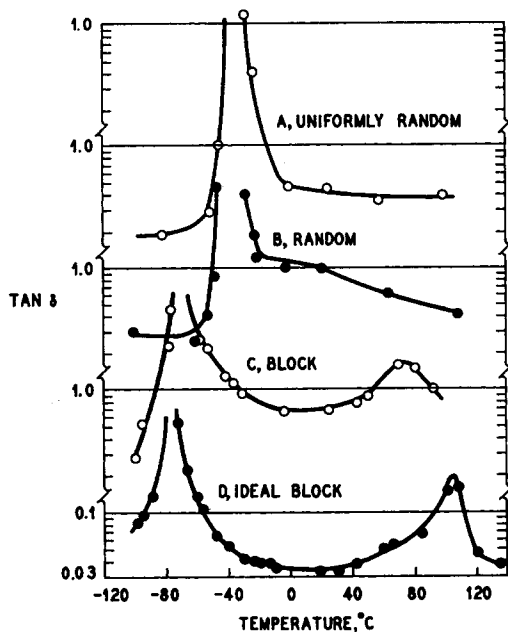Fig. 5. Storage moduli of random and block copolymers (25% styrene).

Fig. 6. Loss tangents of random and block copolymers (25% styrene).

Of particular interest is the fact that the degree of randomness in a co-
polymer is clearly reflected in these data, particularly in the loss tangents.
This is evident in narrower loss peaks for transitions involving sequences of
homogeneous composition. For block sequences (or whole molecules)
varying in composition there is broadening of the loss peaks with occasional
development of pronounced "shoulders." This is ascribed to chain seg-
ments of various compositions passing through their glass transitions, each
at its characteristic temperature. Quantitatively, if for any homogeneous
composition C, loss tangent is a function ϵ of $[T - T_g(C)]$, that is

$$\tan \delta = \epsilon [T - T_g(C)] \qquad (2)$$

and if the distribution in compositions is $g(C)$, we have for a copolymer of
inhomogeneous composition

$$\tan \delta = \int g(C) \, \epsilon [T - T_g(C)] dC \qquad (3)$$

provided that the shape of the loss peak is independent of C. The result
of such computation is shown as the dotted line in Figure 7. The distri-
bution function $g(C)$ was determined from the composition vs. conversion
curve and the integrations carried out graphically. $T_g(C)$ was obtained
from eq. (1). It appears that the calculated loss tangent are in substantial
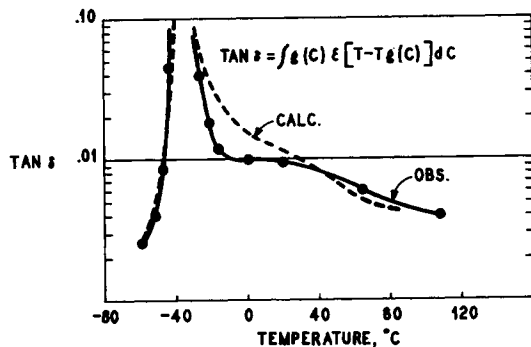agreement with experiment.

Fig. 7. Calculated vs. observed loss tangents for compositionally heterogeneous random copolymer.

The introduction of a second styrene block to form an $S_xB_yS_x$ type structure causes no major change in the loss tangent–temperature curves (Fig. 8). There is a consistent shift toward lower temperatures of the styrene transition in the terminal block polymers, which appears to be associated with shorter block lengths. (At constant molecular weight, but equal block styrene contents the block length would be halved.) The comparisons shown in Figure 8 are for 25% styrene copolymers of ideal block structure (top) and for block polymers of approximately 12% block polystyrene (bottom). Supporting evidence for the position of the styrene loss peak being a function of block length is obtained from comparison of all four curves (Table IV). This comparison presupposes equal total molecular weight. While molecular weights were not measured, estimates based on initiator levels indicate that the molecular weight varied by considerably less than a factor of two.
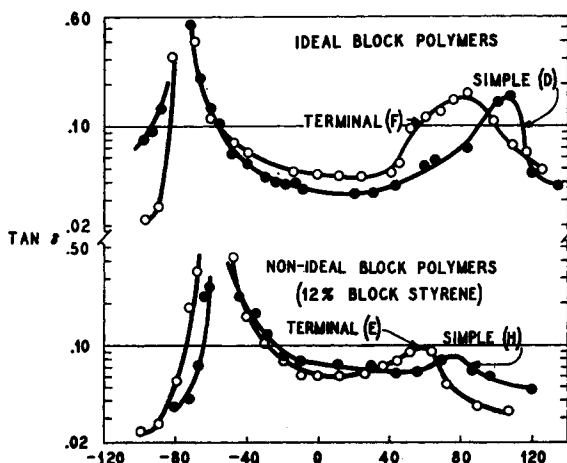

Fig. 8. Loss tangents of simple and terminal styrene block copolymers (25% styrene)

TABLE IV

Approx. block length (% block styrene)	Position of loss peak, °C.
24.8	104
23.9/2	84
11.7	76
11.5/2	60

Because of the dimensional stability of terminal block copolymers at temperatures between the two transitions (to be discussed in detail in a later paper) it is possible to obtain torsional hysteresis measurements on the unvulcanized polymers. The data allow one to just barely detect the styrene loss peak. These polymers form stable networks between transitions, but above the styrene transition the networks disintegrate and the loss rises in the manner expected for a viscous polymer melt. The top of Figure 9 shows three such block polymers of approximately 12% block styrene (25% total styrene) and varying in molecular weight as indicated by Mooney viscosity. The effect of block length on the upper transition is once more apparent. The bottom of Figure 9 shows a terminal block polymer of ideal block structure (23.9% block styrene). Consistent with the interpretation given above, this polymer shows the transition of the rubbery block at the lower temperature characteristic of pure polybutadiene, the butadiene loss peak is narrower and the styrene peak occurs at the highest temperature of the four polymers shown. The nature of the flat loss maximum at 0°C. in this polymer is not clear.
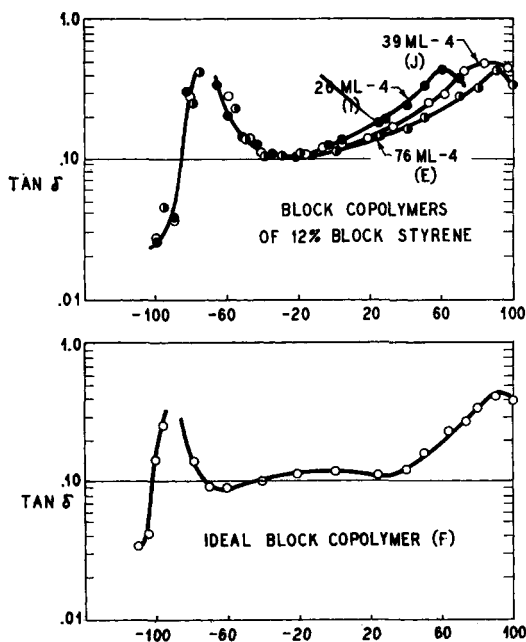

Fig. 9. Loss tangents of unvulcanized terminal styrene block copolymer (25% styrene)

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Résumé

L'effet de la séquence des monomères sur les propriétés physiques a été étudié pour les copolymères de butadiène et styrène obtenus en solution par initiation aux organolithiens. Les polymères variaient depuis des copolymères statistiques de composition uniforme le long de la chaîne polymérique jusqu'à des polymères séquencés en bloc avec arrangement de séquences spécifiques et incluaient des caoutchoucs de degrés intermédiaires de composition statistique. Des copolymères de composition statistique uniforme montraient une seule température de transition vitreuse et un pic de perte dynamique très étroit correspondant à cette transition. La transition vitreuse peut être prédite au départ de la teneur en styrène et de la microstructure de la partie butadiénique du caoutchouc. Des copolymères statistiques dans lesquels la composition varie le long de la chaîne polymérique, et, à un certain degré, entre les molécules manifestaient une seule transition vitreuse, mais des pics de perte dynamique élargis. Le degré de cit élargissement est compatible avec la distribution de séquences, les segments polymériques de composition variable perdant leur mobilité à des températures différentes. Ceci indique une tendance à l'association entre les segments de différentes chaînes qui sont de compositions similaires. Les polymères séquencés montraient deux transitions correspondant àu T_g de chaque type de séquence. La position et la largeur des pics de perte dynamique sont liés à la longueur du bloc et à la pureté du point de vue composition de ces séquences.

Zusammenfassung

Der Einfluss der Monomersequenz auf die physikalischen Eigenschaften wurde an lithium-organisch-gestarteten Lösungscopolymeren von Butadien und Styrol untersucht. Die Polymeren lagen im Bereich von statistischen Copolymeren mit einheitlicher Zusammensetzung entlang der Polymerkette bis zu idealen Blockpolymeren mit spezifischer Blocksequenzanordnung und schlossen Kautschuk von mittlerem Unordnungsgrad ein. Statistische Copolymere mit einheitlicher Zusammensetzung zeigen eine einzige Glasumwandlungstemperatur und ein sehr enges, dieser Umwandlung entsprechendes dynamisches Verlustmaximum. Die Lage der Glasumwandlung kann aus dem Styrolgehalt und der Mikrostruktur der Butadienanteils des Kautschuk vorhergesagt werden. Statistische Copolymere, deren Zusammensetzung sich längs der Polymerkette, und in einem gewissen Ausmass von Molekül zu Molekül, ändert, zeigen eine einzige Glasumwandlung, das dynamische Verlustmaximum ist aber verbreitert. Das Ausmass dieser Verbreiterung ist mit der Sequenzverteilung vereinbar; Polymersegmente mit verscheidener Zusammensetzung verlieren ihre Beweglichkeit bei verschiedenen Temperaturen. Das spricht für eine Assoziationstendenz zwischen ähnlich zusammengesetzten Segmenten verschiedener Ketten. Blockcopolymere weisen zwei, dem T_g jedes Blocktyps entsprechende Umwandlungen auf. Lage und Breite der dynamischen Verlustmaxima hängen von Blocklänge und Reinheit der Zusammensetzung der Blöcke ab.