Properties of Random and Block Copolymers of Butadiene and Styrene.   II.   Melt Flow

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Synopsis

Flow curves, log (rate of shear) versus log (shear stress), as functions of temperature were obtained for several butadiene–styrene copolymers of fixed (25%) styrene content, differing in monomer sequence distribution.   A random copolymer of constant composition along the polymer chain and narrow molecular weight distribution (MWD) exhibited behavior similar to linear, narrow MWD polybutadienes;   the flow was Newtonian at low shear stresses, and the flow curves for various temperatures were accurately superimposable by a shift along the log (shear rate) axis.   In a random copolymer varying in composition along the polymer chain, non-Newtonian behavior was more pronounced, and temperature–shear rate superposition did not succeed, a trend further perpetuated in copolymers of a single long styrene block sequence.   The latter resemble branched polymers, as would be expected from association of the styrene blocks.   With two styrene blocks, association produces network structures below the glass transition of polystyrene with consequent loss of flow.   Disruption of these associations above T_g (styrene) imparts the greatest thermoplasticity to these elastomers.   There is evidence, however, that some of the associations persist at temperatures well in excess of T_g (styrene).

INTRODUCTION

In Part I of this series of papers,[1] dealing with the glass transitions and dynamic behavior of butadiene–styrene random and block copolymers, we have shown that when the length of block sequences becomes sufficiently large, the blocks segregate to form a two-phase system.   In the present paper we examine the consequences of this phenomenon on the melt flow of these polymers.

Melt viscosities of random and block copolymers are of obvious interest from the practical standpoint of polymer processing;   they also give considerable insight into the structure of the melts.   Previous studies at these laboratories[2–4] have demonstrated the principal effects of molecular weight, molecular weight distribution, and long-chain branching on the Newtonian and non-Newtonian viscosities of polybutadienes.   In general, Newtonian flow is favored by low molecular weight, narrow distribution, freedom from long-chain branching, and a high temperature relative to T_g. At fixed weight-average molecular weight, broad molecular weight distri-

SIMPLE BLOCK (ONE STYRENE SEQUENCE)

TERMINAL STYRENE BLOCKS

TERMINAL BUTADIENE BLOCKS
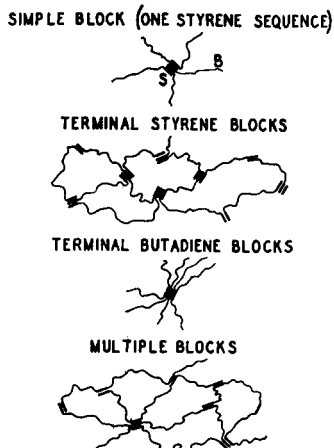
MULTIPLE BLOCKS

Fig. 1. Structures in block copolymers (schematic).

bution leads to shear thinning (non-Newtonian flow) at lower rates of shear and hence also to lower viscosity at practical shear rates. Long-chain branching, in *high molecular weight* polymers produces large low shear viscosities with very pronounced shear thinning (high "shear response").

In the following we shall adhere to the classification scheme of the preceding paper[1] in designating polymers as *uniformly random* if the monomer units follow each other in strictly statistical fashion, *random* if the polymers vary in composition along the chain and between chains without giving rise to long block sequences, *block* if one or more long block sequences are present, and *ideal block* if all block sequences are uniform in composition.

It is apparent from the above that any block polymer containing at least two long sequences of styrene can form a network-like structure between the glassy transition temperatures of the rubbery and styrene blocks and that polymers with only a single long styrene sequence will resemble branched rubbers in behavior between these transitions (Fig. 1). It is the intent of this work to examine how closely these analogies can be applied to the melt flow behavior.

If they can, the next logical question is how far above T_g (styrene) the association of styrene blocks and its effects persist. A related question concerns the effects of nonrandomness in monomer sequence in the absence of pure blocks. None of these effects appear to have been investigated for any copolymer system.

EXPERIMENTAL

The polymers used in this study were similar, if not identical, to the organolithium-initiated solution polymers described in Part I;[1] some of their structural characteristics are set forth in Table I.

TABLE I
Polymer Descriptive Data

Identification	Polymer type	η_{inh}[a]	No. of styrene block sequences	Styrene, %[b]	Block styrene, %[c]	Polybutadiene microstructure, %[c]			Infrared block index[c]
						cis	trans	Vinyl	
A	Uniformly random	1.82	None	25.3[d]	0	19.3	46.7	34.0	0.88
B	Random	1.56	None	25.1[d]	0	26.6	52.2	21.2	0.92
C	Block	0.94	1	24.8[d]	16.4	31.9	58.1	10.0	1.18
D	Ideal block	0.88	1	24.4[d]	24.5	33.5	56.9	9.6	1.74
E	Ideal block	0.97	2	24.4[d]	23.9	35.8	54.8	9.4	1.68
F-1	Random	0.87	None	25	0	41.0	13.2	45.8	—
F-2	Block	0.78	1	25	8.1	42.5	30.5	27.0	—
F-3	Block	0.86	1	25	9.6	44.5	32.0	23.5	—
F-4	Block	0.84	1	25	11.3	45.4	35.5	19.1	—
F-5	Block	0.81	1	25	19.7	51.8	41.7	6.5	—

[a] In toluene at 25°C.
[b] 25% styrene charged to all polymerizations.
[c] Determined by methods described in reference 1.
[d] Anal.

Viscosity

All melt viscosities were determined by the capillary extrusion technique as described in an earlier paper from this laboratory.[2] Viscosities were calculated from the data by using the treatment of Philippoff and Gaskins,[5] i.e., corrections were applied for both pressure losses at the capillary entrance and for nonparabolic flow profile (Rabinowitch correction) to obtain the shear rate at the capillary wall.

Molecular Weights

Absolute values of the molecular weight averages were not determined on any of the polymers. However, for the purpose of interpretation of the data it is useful to obtain approximate estimates of $\bar{M}_w$ for polymers A and F-1. These are provided by an inherent viscosity versus $\bar{M}_w$ correlation on solution-polymerized 75:25 butadiene–styrene rubbers (toluene, 25°C.).

$$\eta_{inh} = 3.22 \times 10^{-4}\bar{M}_w^{0.67} \qquad (14\% \text{ vinyl})$$

Because of differences in vinyl content and molecular weight distribution between the various polymers these are rough estimates only.

RESULTS AND DISCUSSION

Figure 2 shows flow curves for a uniformly random copolymer (25% styrene) of approximately 400,000 weight-average molecular weight (polymer A, Table I). The flow curves are shown at four temperatures; additionally all experimental points have been superimposed onto the 100°C. curve by a shift along the ordinate. The significant features of these results are the Newtonian behavior up to a shear stress of 10⁶ dyne/ cm.[2] and the success of the shear rate–temperature superposition. This general behavior is also typical of linear polybutadienes prepared by alkyllithium catalysts.[2]

Figure 3 shows similar data for a linear random copolymer of nonuniform composition (polymer B, Table I). The curves are very similar in the low-shear, Newtonian range, but are not strictly equidistant along the ordinate. Therefore, temperature superposition does not quite succeed. There is also a growing trend toward non-Newtonian behavior, which is continued in the block (polymer C, Fig. 4) and ideal block polymers (polymer D, Fig. 5). The failure of the temperature shift becomes increasingly apparent in the block copolymers. This is substantially the result expected for a multichain structure which tends to disintegrate at high temperature. At 80°C. the multichain structure is most pronounced, giving rise to high viscosity at low shear rates and high shear response. The trend persists to higher temperatures, but to a smaller degree. The result is a fanning out of the flow curves toward lower shear stresses and shear rates. It also appears that remnants of the "star" structure persist to quite high temperatures.

With terminal block copolymers the response at 80°C. is still mainly elastic, and no meaningful melt viscosities can be obtained.   At 100°C. or above, the disintegration of the physical network leads to a very large temperature coefficient of viscosity (polymer E, Fig. 6).
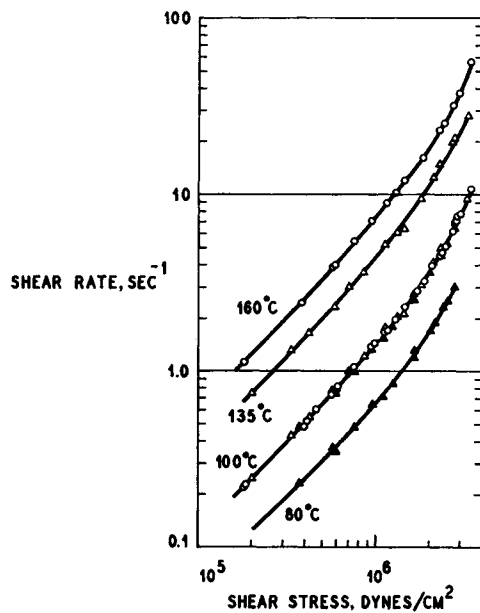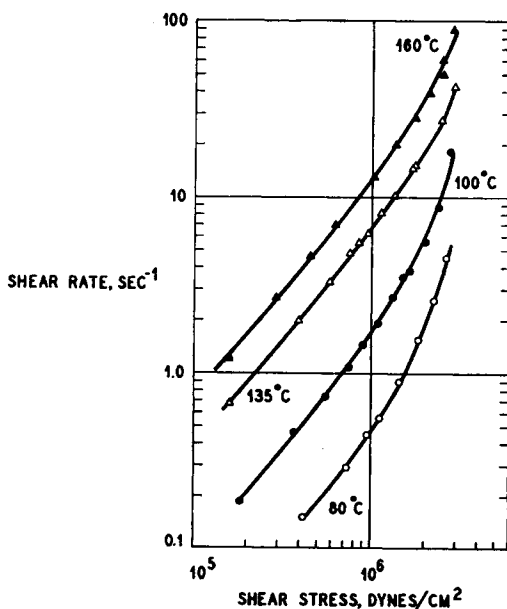

Fig. 2. Flow curves for polymer A.

Fig. 3. Flow curves for polymer B.

The effects of random versus block structure on the temperature coefficient of viscosity are summarized in Figure 7. The data are shown for a shear stress of 5×10^5 dyne/cm.². At a higher shear stress the slopes of the
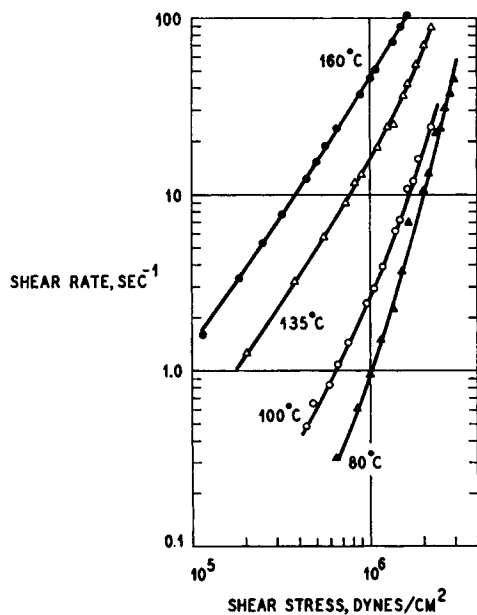

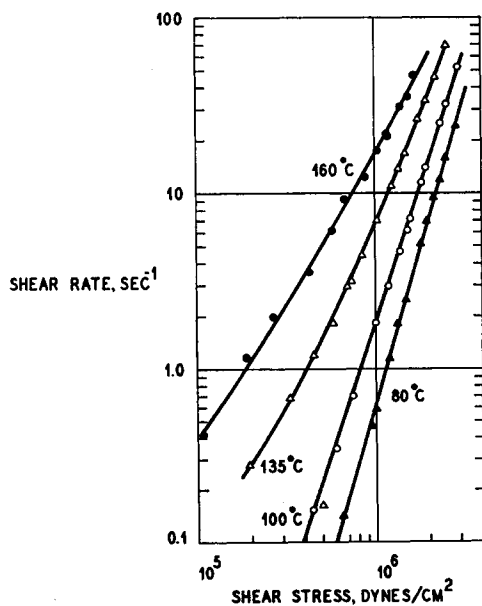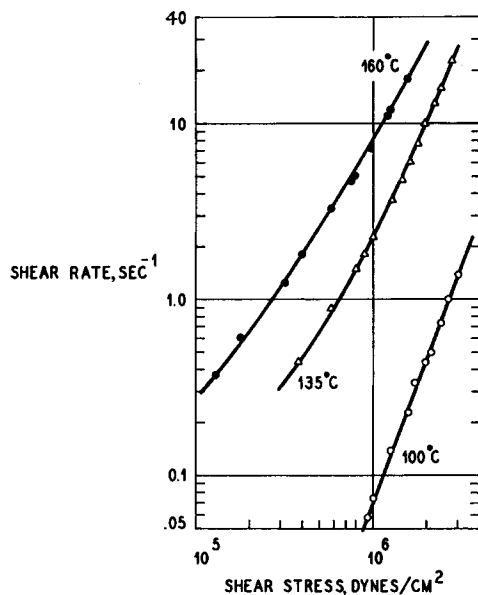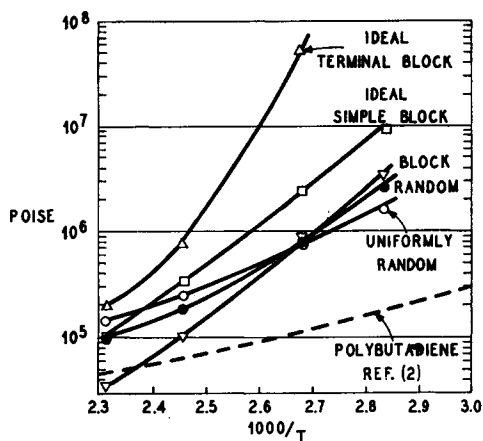Fig. 4. Flow curves for polymer C.

Fig. 5. Flow curves for polymer D.

Fig. 6. Flow curves for polymer E.

Fig. 7. Temperature coefficient of viscosity. Shear stress $= 5 \times 10^5$ dyne/cm.²; all copolymers 75:25 butadiene–styrene.

curves for the random polymers would be unchanged, but those of the block polymers would be smaller. It is readily seen how increasing block character induces thermoplasticity by raising the temperature coefficient of the viscosity.

Figures 2–7 do not permit comparisons of absolute magnitudes of the viscosity since the polymers differ in molecular weight. Weight-average molecular weights of copolymers of non-uniform monomer sequence and molecular composition are difficult to determine, but an attempt at a
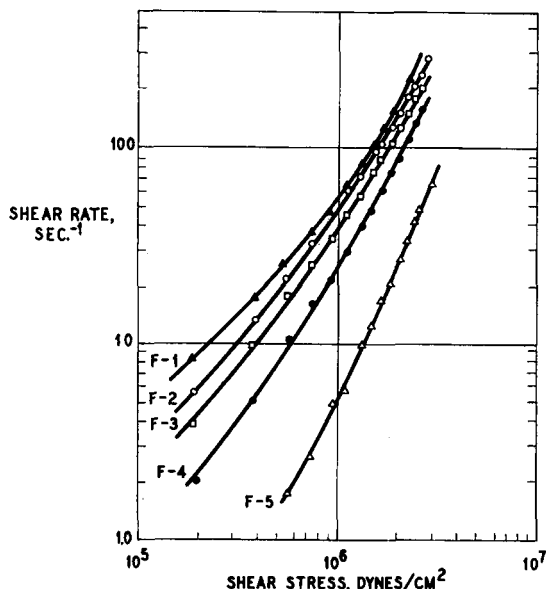
Fig. 8. Effect of increasing block content on flow of 25% styrene copolymers (polymers F-1 to F-5).

constant molecular weight series has been made.   The results are shown in Figure 8.   In this series of polymerizations initiator (n-butyllithium) was held constant and the level of randomizing agent (di-n-butyl carbitol) was varied from 0 to 1 phm (polymers F-1 to F-5).   From the effective initiator level the number-average molecular weight of these polymers is estimated to be in the vicinity of 70,000.   The weight-average molecular weight is approximately 130,000 for the most random copolymer and probably decreases somewhat with increasing block content.   Because of the effects of randomizer on vinyl content, the latter increases with the degree of randomization.   It has been found[6] that increasing vinyl content in polybutadienes raises the melt viscosity due to enhancement of segmental friction (T_g rises), even though the number of skeletal carbon atoms at constant molecular weight would decrease.   Since both molecular weight and microstructure effects would tend to increase the viscosity with degree of randomness, the observed opposite effect must be due to an inherent increase in viscosity due to block structure.   This is consistent with the hypothesis that the polymers flow very much like multichain polymers. The increased shear response is also apparent in the data of Figure 8.

References

1. G. Kraus, C. W. Childers, and J. T. Gruver, J. Appl. Polymer Sci., 11, 1581 (1967).
2. J. T. Gruver and G. Kraus, J. Polymer Sci. A, 2, 797 (1964).
3. G. Kraus and J. T. Gruver, J. Polymer Sci. A, 3, 105 (1965).

4. G. Kraus and J. T. Gruver, *J. Appl. Polymer Sci.*, **9,** 739 (1965).

5. W. Philippoff and F. H. Gaskins, *Trans. Soc. Rheol.*, **2,** 263 (1958).

6. G. Kraus and J. T. Gruver, *Advances in Polymer Science and Technology*, Soc. Chem. Ind. Monograph No. 26, London, 1967, p. 37.

Résumé

Des courbes d'écoulement, log (vitesse de cisaillement) en fonction du log (tension de cisaillement), pour diverses températures ont été obtenues pour de nombreux copolymères butadiène–styrène à teneur en styrène fixe (25%) mais différent par la distribution des séquences monomériques. Un copolymère statistique de composition constante tout au long de la chaîne polymérique et ayant une distribution étroite des poids moléculaires (MWD), présente un copolymère similaire à celui des polybutadiènes linéaires à distribution étroite des poids moléculaires; l'écoulement est Newtonien aux tensions de cisaillement faibles et les courbes d'écoulement à diverses températures sont superposables avec précision par un glissement le long de l'axe du logarithme des vitesses de cisaillement. Dans un copolymère statistique variant en composition le long de la chaîne polymérique le comportement non-Newtonien est plus prononcé et la superposition température-vitesse de cisaillement ne peut pas se faire; cette tendance s'accentue encore dans les copolymères contenant une seule longue séquence d'unités styréniques. Ces derniers ressemblent à des polymères branchés et cela doit résulter de l'association des blocs styréniques. Avec deux blocs styréniques, l'association produit une structure réticulaire en-dessous de la transition vitreuse du polystyrène avec, comme conséquence, une diminution d'écoulement. La rupture de ces associations au-dessus du T_g (styrène) produit une très grande thermoplasticité dans ces élastomères. Il est toutefois évident que certaines associations persistent à des températures nettement plus élevées que la température T_g du polystyrène.

Zusammenfassung

Fliesskurven, nämlich log (Schergeschwindigkeit) vs. log (Scherspannung), wurden für einige Butadien–Styrol-Copolymere mit festgehaltenem (25%) Styrolgehalt aber verschiedener Monomersequenzverteilung in Abhängigkeit von der Temperatur erhalten. Ein statistisches Copolymeres mit konstanter Zusammensetzung längs der Polymerkette und enger Molekulargewichtsverteilung (MWD) zeigte ein ähnliches Verhalten wie lineare Polybutadiene mit enger Molekulargewichtsverteilung; bei niedriger Schubspannung trat Newton'sches Fliessen auf und die Fliesskurven für verschiedene Temperaturen konnten dirch Verschiebung längs der log (Schergeschwindigkeits)-Achse genau superponiert werden. Bei einem statistischen Copolymeren mit variierender Zusammensetzung längs der Polymerkette trat das nicht-Newton'sche Verhalten stärker hervor und eine Temperatur–Schergeschwindigkeits-Superponierung führte nicht zum Erfolg: dieser Zug setzte sich weiters in Copolymeren mit einer einzigen langen Styrol-Blocksequenz fort. Letztere ähneln verzweigten Polymeren, wie nach der Assoziation der Styrolblöcke zu erwarten ist. Mit zwei Styrolblöcken führt die Assoziation unterhalb der Glasumwandlung von Polystyrol zu Netzwerkstrukturen mit Verlust des Fliessens. Die Zerstörung dieser Assoziationen oberhalb T_g (Styrol) erteilt diesen Elastomeren die grösste Thermoplastizität. Es bestehen aber Hinweise dafür, dass ein Teil der Assoziationen noch bei Temperaturen weit oberhalf T_g (Styrol) vorhanden ist.