Structural Changes in Melts of Butadiene–Styrene and Isoprene–Styrene Block Polymer-Based Pressure-Sensitive Adhesives

GERARD KRAUS, *Research and Development, Phillips Petroleum Co., Bartlesville, Oklahoma 74003* and TAKEJI HASHIMOTO, *Department of Polymer Chemistry, Kyoto University, Kyoto, Japan*

Synopsis

Rheological and small angle x-ray scattering (SAXS) measurements show that typical pressure-sensitive adhesives prepared from block polymers of butadiene or isoprene with styrene maintain the domain structure of the block polymer well beyond the polystyrene domain T_g, but form homogeneous melts above a critical temperature, T_c. For the examples investigated, T_c lies some 20°C below the usual hot melt processing temperature. The extremely high resistance to creep of the adhesives at service temperatures is explained as being the result of viscous flow with the domain structure in a state of dynamic equilibrium, in which polystyrene blocks are detached from domains and reattached to others. A transition between nonequilibrium and equilibrium domain structures is revealed clearly by SAXS for one of the block polymers used in this work.

INTRODUCTION

It is now well established that the domain structure of butadiene–styrene and isoprene–styrene block polymers survives heating beyond the upper (polystyrene) glass transition temperature $(T_g{}^s)$ and that there exists a temperature (T_c), usually well above $T_g{}^s$, at which these polymers become homogeneous melts. Evidence for this transition from a microheterogeneous state to a homogeneous one has been adduced from rheological measurements[1–6] and confirmed unequivocally by small angle x-ray scattering (SAXS) studies.[6–10]

This phenomenon has important practical implications whenever block polymers of this type are used to formulate pressure-sensitive adhesive compositions. Adhesives based on SBS, SIS, SEBS (hydrogenated SBS), or their star-branched versions (SB$\rightarrow{}_x$, (SI$\rightarrow{}_x$, (SEB$\rightarrow{}_x$, are outstanding in their resistance to shear creep (a property also referred to as holding power) because the domain structure is preserved at service temperatures. Suitable tackifying resins and plasticizers are selectively soluble in the rubbery phase of the block polymers, leaving the polystyrene domains to act as physical crosslink sites.[11–13] On the other hand, as long as these domains persist beyond $T_g{}^s$ their effect will be to raise the melt viscosity,[2] clearly an undesirable feature in the processing of the adhesives as hot melts. A logical objective would be, therefore, to formulate adhesives with the lowest possible T_c, without adversely affecting adhesive properties such as tack, peel strength, or holding power.

The existence of T_c in practical block polymer-based adhesives has been suggested,[13] but not proven. The present article provides the desired experimental proof for representative compositions prepared from isoprene–styrene and butadiene–styrene block polymers.

TABLE I
Polymer Characterization Data

	Polymer I	Polymer B
Styrene, %	16	30
Comonomer, %	Isoprene (84)	Butadiene (70)
Inherent viscosity (THF, 25°C)	1.44	0.90
$\overline{M}_w$	149,000	131,000
$\overline{M}_n$	103,000	118,000
M_s (styrene block length)	10,000	11,000
Free polystyrene, %	<1	2
Uncoupled diblock polymer, %	26	3
Mean functionality of branching (x)	3.1	3.5

EXPERIMENTAL

Materials

Polymers selected for this study were star-branched multichain block polymers, $(SB)_x$ and $(SI)_x$, of composition and molecular weight suitable for use in pressure-sensitive adhesives. Characterization data are supplied in Table I. Molecular weights and related information were obtained by GPC. Adhesive formulations, for short identified as IA and BA, are given in Table II.

Adhesive BA was mixed in a Brabender Plasticorder at 177°C for 30 min. Adhesive IA was solution mixed in toluene at ambient temperature. Adhesive tapes were prepared by solution coating the adhesive (30% solids in toluene) onto 0.05 mm thick Mylar backing using a Byrd applicator and drying the adhesive 16 h at 50°C *in vacuo*. Thickness of the dry adhesive layer was 0.04–0.05 mm.

To establish possible changes in polymer molecular weight during processing, the adhesive layer was removed from a portion of each tape and examined by GPC. The results showed no difference whatever in the molecular weight distribution of polymer I before and after compounding and processing. Polymer B showed an increase of 14% in peak molecular weight in the finished adhesive and an accentuated high-molecular-weight tail in the distribution, indicating further branching by oxidative or shear-induced crosslinking. Such changes or the reverse (decreases in molecular weight by chain scission) are not at all uncommon in hot melting processing of unsaturated polymers.

Samples for SAXS measurements were cut from 1 mm thick sheets, compression molded between release paper. Mold temperature was 150°C for pure block polymers, 105°C for adhesive compositions. Molding time was 90 s.

TABLE II
Adhesive Compositions

	IA	BA
Block polymer used	I	B
Parts: Polymer	100	100
Tackifying Resin	75[a]	88[b]
Stabilizer	1[c]	1[c]

[a] Wingtack 95, polyterpene (Goodyear Chemical Co.).
[b] Picco Alpha 115, poly(α-pinene) (Hercules, Inc.).
[c] Irganox 1010 (Ciba-Geigy).

Rheological Measurements

Steady flow melt viscosities were determined by capillary rheometry using dies of L/R ratio 2.717, 17.829, and 38.660. Both entrance effect and Rabinowitsch corrections were applied to all data.[14] Dynamic viscoelastic measurements were carried out with a Rheometrics Inc. Dynamic Spectrometer. Holding power of adhesive films was determined by Pressure Sensitive Tape Council Standard Method PTSC-7.

SAXS Measurements

SAXS measurements were performed with a linear position sensitive x-ray detector and 12 KW rotating anode x-ray generator[15–17] (Cu-Kα radiation). Sample-to-detector distance was 1154 mm, each channel corresponding to 0.2 mrad angle. X-ray exposure time for the measurements of each scattering curve shown in Figures 8–12 was 1000 s. In the oscilloscope displays of scattered intensity versus angle (Fig. 8–12), the origin of each curve is shifted diagonally to avoid overlap. The samples were sealed into nitrogen-filled cells to minimize oxidation during measurement.

Electron Microscopy

Ultrathin sections of Polymer B were prepared by cryomicrotomy, stained by the OsO_4 method of Kato,[18] and examined under a Philips EM300 electron microscope.

RESULTS

Steady Flow Viscosity

Figures 1 and 2 show the steady flow viscosities at several temperatures for adhesives IA and BA. At low temperatures flow is highly non-Newtonian over the entire range of shear rates examined, while at high temperatures the curves exhibit a well-defined low shear Newtonian regime. Although this fact alone is sometimes taken as evidence of a transition from a two-phase to a homogeneous melt structure, it is not sufficient to establish such a change. In homogeneous, thermorheologically simple polymer melts, lowering the temperature causes the doubly logarithmic viscosity–shear rate curve to shift diagonally upward along lines of constant shear stress, i.e., in a "northwesterly" direction. The result is that over a fixed range of shear rates the curves become increasingly non-Newtonian the lower the temperature, even in simple melts. A structural change would demand evidence of thermorheological complexity. Figure 3 shows an attempted temperature reduction of the data of Figure 1. Unexpectedly, the reduction is highly successful, probably because there is not sufficient overlap in experimental points from different temperatures to reveal deviations from time–temperature superposition. Similar results (not shown) were obtained with adhesive BA. Therefore, the steady flow viscosities of Figures 1 and 2 permit no conclusions regarding a transition to a homogeneous system.
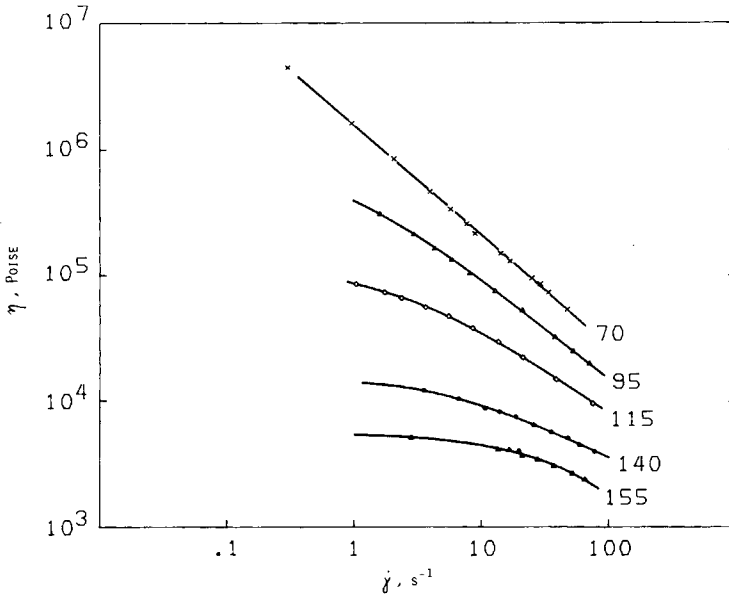
Fig. 1. Steady flow viscosity of adhesive IA; temperatures in °C.

Shear Creep (Holding Power)

In the shear creep experiment one observes the slippage of a tape adhering to a smooth, substantially vertical substrate under a constant load. If the compliance of the tape backing is negligible, compared to that of the adhesive layer, the situation is that of a parallel plate translational viscometer. For a
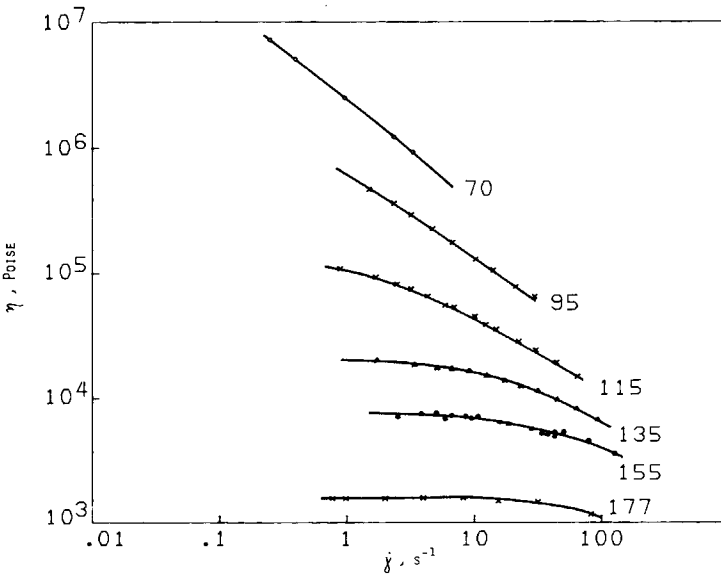

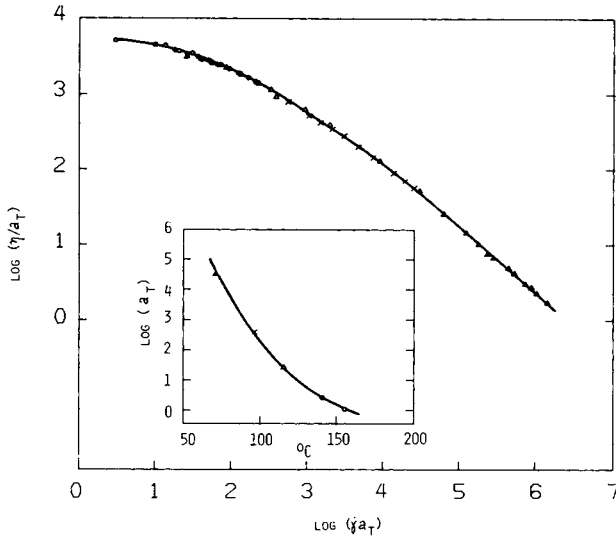Fig. 2. Steady flow viscosity of adhesive BA; temperatures in °C.

Fig. 3. Temperature-reduced steady flow viscosity of adhesive IA-155°C.

Newtonian liquid the solution for this geometry is[19]

$$t = \eta(H_0{}^2 - H^2)/2H_0 a \tau_0 \tag{1}$$

where t is the time for the overlap of tape and substrate to decrease from an initial value H_0 to H, η is the viscosity, a the thickness, and τ_0 the shear stress referred to the initial overlap area. In the standard test for holding power of adhesives, H_0 is 2.54 cm and the time to $H_0 - H = 0.16$ cm is taken as the result, $t_{0.16}$. Consequently

$$\eta = 0.155 \, a\tau_0 t_{0.16} \tag{2}$$

Equation (2) is a reasonably good approximation also for a non-Newtonian adhesive because the shear stress changes only 6.3% during the test. A solution exists also for a power law fluid,[13,20] but this is still only an approximation and is much more difficult to use. Figure 4 compares viscosities calculated from holding power tests at 70°C with those measured by capillary rheometry. Although the two sets of data do not overlap, they extrapolate smoothly into a single curve. (Since the adhesives are viscoelastic one might expect part of the displacement ΔH to be recoverable. For the condition of the test, however, the effect will be small for plausible values of the steady state compliance. Indeed, no significant recovery was detected experimentally. It also may be noted that our results give no indication of a yield stress prior to onset of non-Newtonian flow. This does not deny the possible existence of such a critical stress; the data of Figure 4 merely indicate that its value cannot exceed ca. 10^5 dyn/cm^2 in the examples at hand.)

The fact that holding power in block polymer-based adhesives is basically a viscosity effect appears firmly established; results such as those of Figure 4 have been obtained by us with many adhesives of the present type.
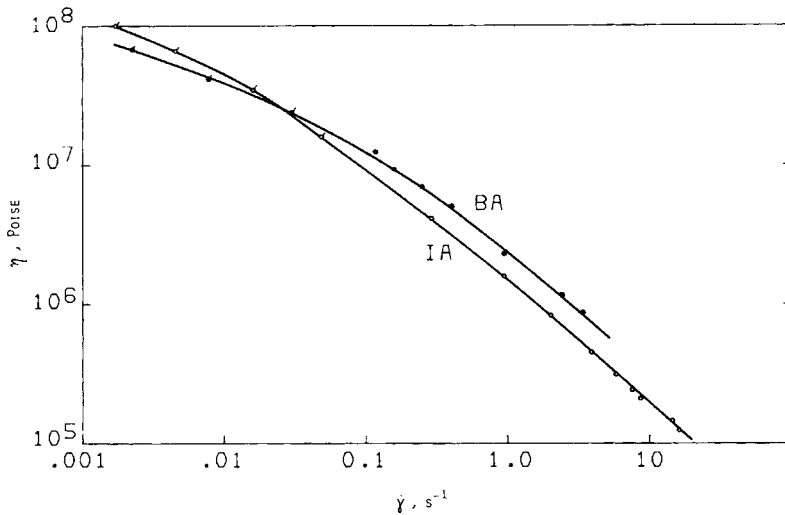
Fig. 4. Viscosities from creep (flagged symbols) and from capillary rheometry at 70°C.

Dynamic Viscosity

Figure 5 displays the dynamic viscosity of adhesive IA, reduced to 155°C with the same shift factors used in superposition of the steady flow viscosity data. Comparison with Figure 3 shows $|\eta^*|$ to lie slightly below η when $\omega = \dot{\gamma}$. Thus, the rule of Cox and Merz[21]

$$|\eta^*|(\omega) = \eta(\dot{\gamma}), \qquad \omega = \dot{\gamma} \tag{3}$$

is not strictly obeyed, but the deviation is surprisingly small for a block polymer system. Similar behavior was observed for adhesive BA. Again, as in the case of η, the temperature dependence of $|\eta^*|$ gives no indication of an abrupt transition from a microheterogeneous to a homogeneous system.
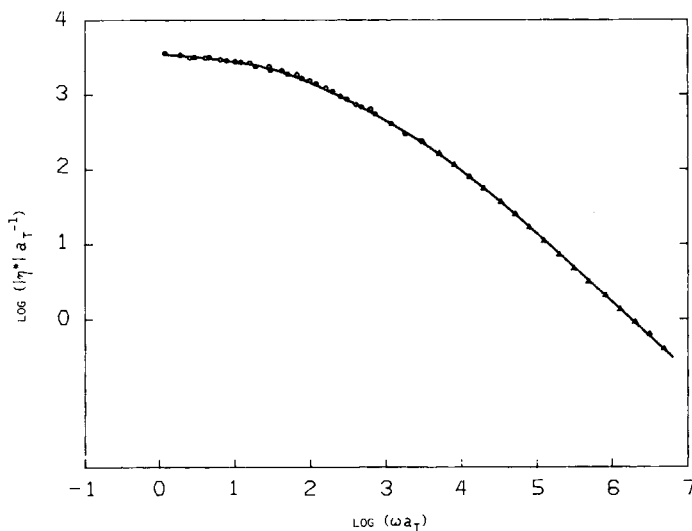
Fig. 5. Dynamic viscosity of adhesive IA reduced to 155°C.

Isochronal temperature scans (heating rate $= 2°C/min$) of the dynamic storage and loss moduli of IA and BA are given in Figures 6 and 7. The curves show first of all the T_g of the polystyrene domains (maximum in G'') at about 85°C. Beyond T_g, there is a noticeable increase in the slope $-d \log G'/dT$, occurring at 129° and 119°C for IA and BA, respectively. This break in G' is more distinct for IA, but in neither case is the effect as pronounced as in pure block polymers,[6] where its appearance has been interpreted as the transition to a homogeneous melt. The derivative $-d \log G'/dT$ reaches maximum values at 139° (IA) and 134°C (BA), and we regard these temperatures as marking the center of the transition from the well-formed domain structure to the homogeneous state through a series of successive states of increased interdomain mixing. The fact that the isochronal data permit observation of the transition, while our isothermal data taken at various temperatures do not, is evidently the consequence of the greater number of closely spaced measurement temperatures employed in the isochronal experiment.

Small Angle X-Ray Scattering (SAXS)

SAXS curves for the undiluted polymers, I and B, are shown in Figures 8 and 9. They represent scattered intensity, in counts, versus scattering angle (see Experimental section). Curves taken at different temperatures are displaced along both axes to avoid overlap. Referring first to the data for polymer I (Fig.
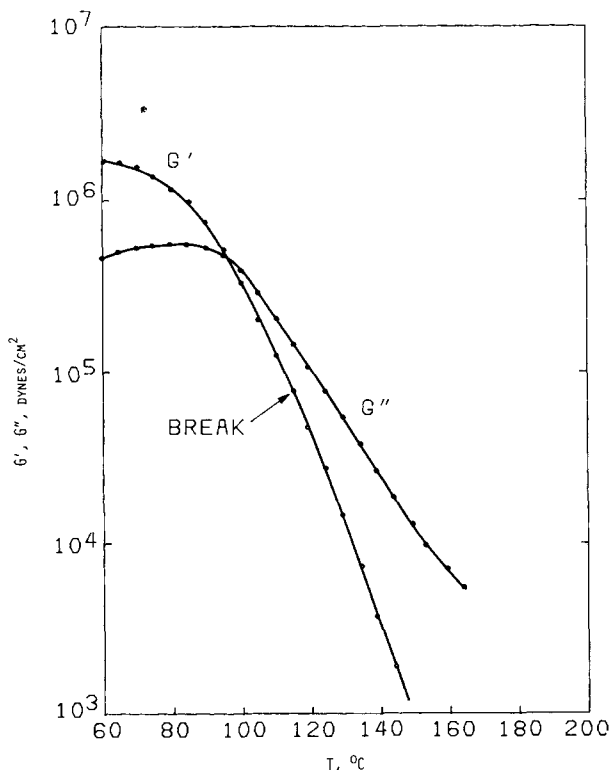

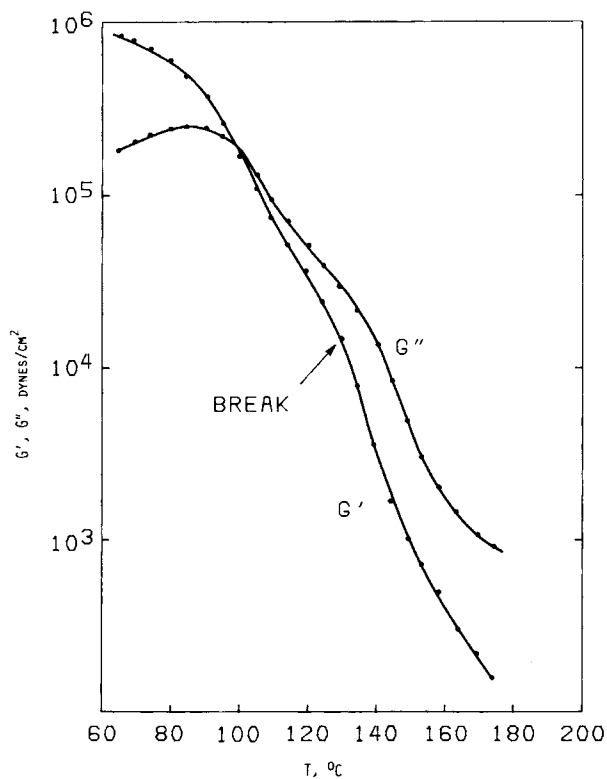Fig. 6. Dynamic moduli of adhesive IA, 0.1 Hz.

Fig. 7. Dynamic moduli of adhesive BA, 0.1 Hz.

8), we note that the SAXS maximum present at room temperature persists well above T_gs, but disappears somewhere between 200°C and 230°C. This behavior is characteristic of this kind of block polymer.[7-10] In the example of polymer B (Fig. 9) the behavior is more complicated. The original scattering maximum tends to disappear with heating, but a new maximum appears near 180°C which is then stable to temperatures at least as high as 230°C. As shown in Table III, the Bragg spacings for the two maxima are different—42 and 28 nm. The ap-
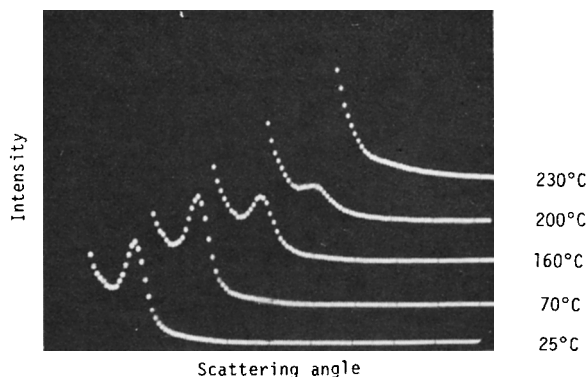
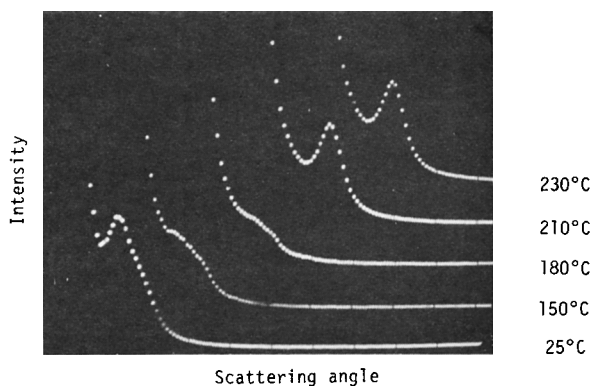Fig. 8. Temperature dependence of SAXS curves for polymer I.

Fig. 9. Temperature dependence of SAXS curves for polymer B.

parent change in morphology is irreversible; on cooling the specimen from 230°C to 25°C the maximum persists through the intermediate range of temperatures and the spacing remains 23 nm. On reheating, the new peak is maintained and, although some decrease in maximum intensity is observed at 230°C, "melting" is far from complete at this temperature (Fig. 10).

The morphological change in sample B has no counterpart in the adhesive formulation BA, and both adhesives (Figs. 11 and 12) show similar behavior. The SAXS maximum resulting from the domain structure is evident at room temperature and, with undiminished intensity, at 70°C, the temperature of the holding power tests. Melting of the domain structure occurs well above T_g

TABLE III
SAXS Bragg Spacings and Critical Temperatures for Disappearance of Domain Structure

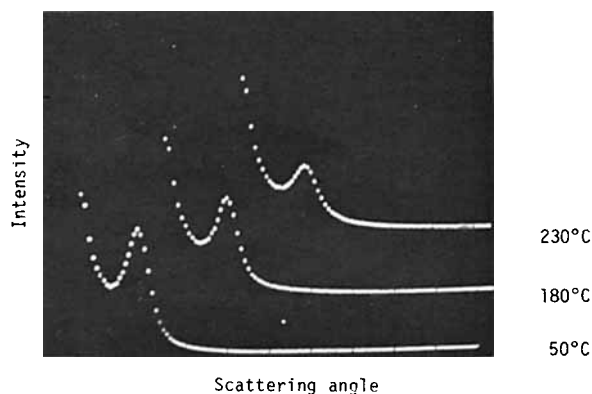| Polymer (Adhesive)	Bragg Spacing, nm	T_c, °C
I	30.3	230
B	42.0	—
	28.0	>230
IA	28.0–29.1	180
BA	26.1–28.0	170

Fig. 10. Temperature dependence of SAXS curves of sample B subjected to preheating at 230°C.
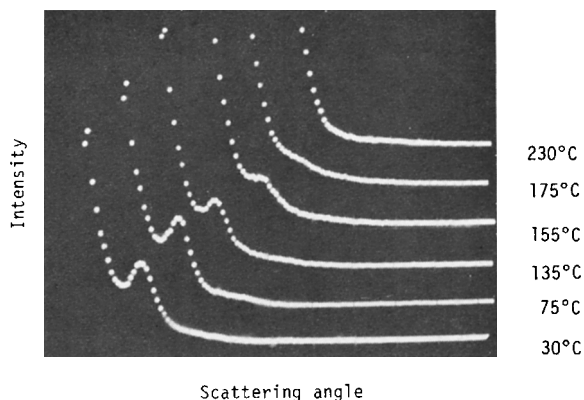
Fig. 11. Temperature dependence of SAXS curves for IA.

(polystyrene) and appears to be complete near 180°C (IA) and 170°C (BA). Small increase in Bragg spacing accompany heating (Table III), but this appears to be of no particular consequence. The determination of the critical temperatures, T_c, of Table III was made by plotting the maximum intensity against temperature (Fig. 13).

DISCUSSION

The above results demonstrate, for pressure-sensitive adhesive (PSA) formulations, phenomena observed earlier on pure block polymers but only surmised to apply to adhesive compositions. These are the survival of the block polymer domain structure in presence of large amounts of diluent (tackifier) *well above* normal service temperature and even above $T_g{}^s$, and the transition to a homogeneous melt at a T_c lying somewhat below the recommended processing temperature for hot melt adhesives containing unsaturated block polymers (ca. 190°C).

The T_c transition is revealed much more clearly in the SAXS curves than in the rheological data, but the results are consistent. The "center" of the transition from dynamic mechanical data was estimated as 139°C for IA and 134°C for BA.
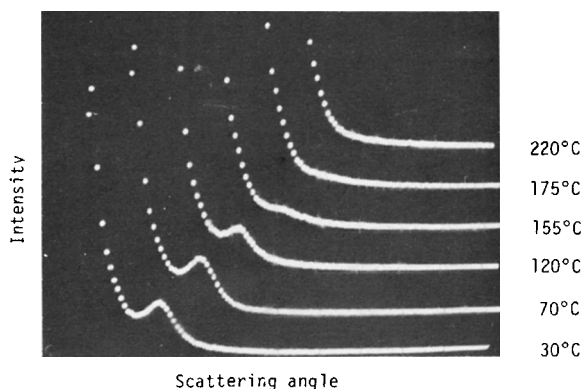

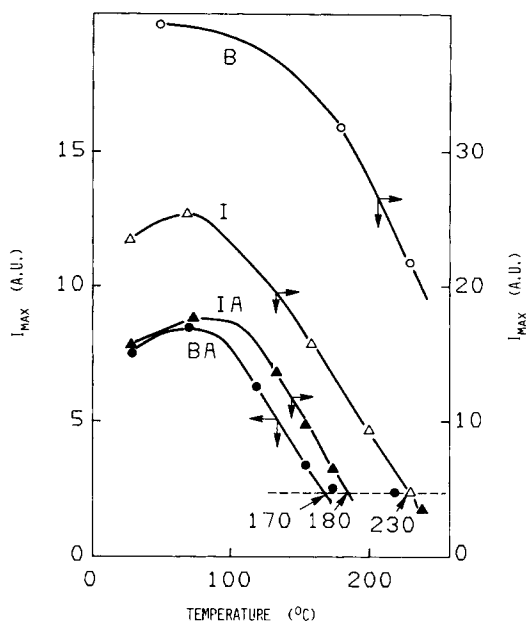Fig. 12. Temperature dependence of SAXS curves for BA.

Fig. 13. Summary of SAXS data.

The corresponding estimates from Figure 13 would be roughly 150°C and 130°C. Exact correspondence would not be expected in view of different heating rates employed in the two experiments.

There appears to be little doubt that the mechanism by which the superior "holding power" of these adhesives below $T_g{}^s$ is achieved is (non-Newtonian) flow with the domain structure intact to an extent sufficient to maintain an infinite network, as envisaged by earlier workers[22,23] for the flow of pure block polymers at low shear rates (but above $T_g{}^s$). In this mechanism, flow is thought to occur by detachment of individual or clusters of polystyrene blocks from polystyrene domains and reattachment to others. The result is a shear-biased state of dynamic quilibrium. At low shear stresses and below $T_g{}^s$ this equilibrium is so far on the network side that flow is exceedingly small.

There is much interesting information contained in the SAXS data. The change in polymer B from one domain morphology to another between $T_g{}^s$ and T_c is confirmed by electron micrographs. In the original morphology (Fig. 14), the polystyrene domains are more nearly cylindrical and are oriented to a significant degree; the domain boundaries appear somewhat diffuse. After heating to 230°C and cooling, the orientation disappears and the morphology is much more clearly developed (Fig. 15). The polystyrene domains are essentially spherical, although not without some connectivity. This is evidently the equilibrium morphology in the melt and is set on cooling the polymer below the polystyrene domain T_g. The SAXS data are consistent with these observations. The equilibrium morphology gives a well-formed scattering maximum, while the SAXS pattern for the original sample shows considerable broadening. In view of the orientation of the original sample it is difficult to interpret the apparently larger Bragg spacing.

In general, T_c increases with increasing block polymer molecular weight, but
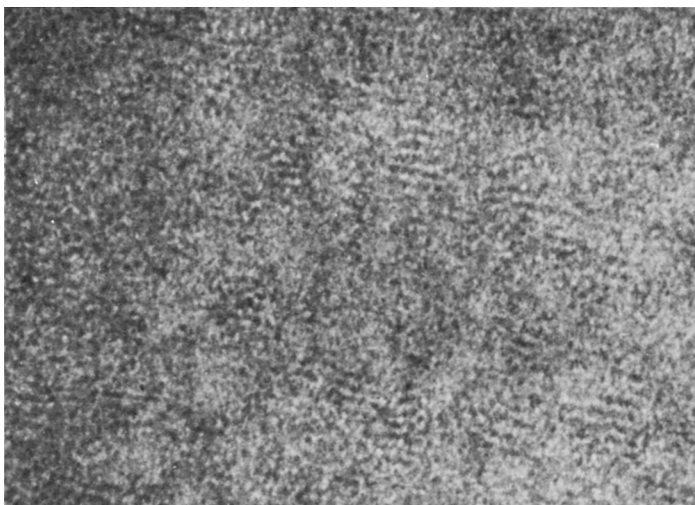
Fig. 14. Electron micrograph of polymer B in original condition; 80,000×.

polymer I is seen to have a much lower T_c in spite of its higher $\overline{M}_w$. The explanation must be sought in compositional differences.[7,9] The enthalpy of demixing is $\chi k T \phi (1 - \phi)$, which is largest when the volume fractions ϕ and $(1 - \phi)$ are equal. In the present examples $\phi(1 - \phi)$ is 0.197 and 0.122 for B and I, respectively, which favors the demixed state for B more strongly than for I. This argument presumes no large difference in the interaction parameter χ, which appears to be true here.

The expected effect of low-molecular-weight additives is a lowering of T_c, as observed here. From Table III the depressions in T_c are 50°C for IA and >60°C for BA. The latter adhesive has the higher diluent content, but solubility effects must also play a role here. The data are obviously too limited to permit detailed interpretation of compositional and solubility effects. This was not the objective of this study.
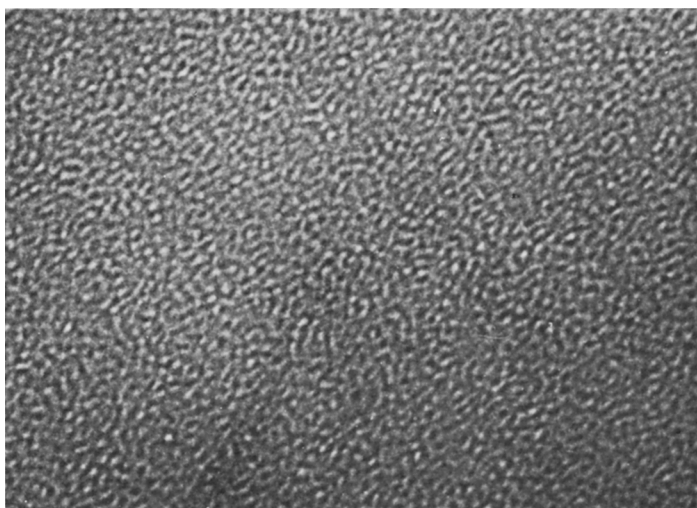

Fig. 15. Electron micrograph of polymer B after heating to 230°C and cooling; 80,000×.

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