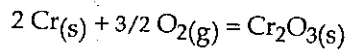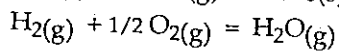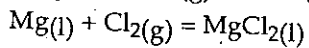1. For a simple eutectic system of $L \longrightarrow \alpha + \beta$,
   (a) draw the phase diagram of this system and then draw schematically the free energy curves from high to low temperatures.
   (b) Based on the Gibbs phase rule, determine the degree of freedom at eutectic point, in the L phase and in the two phase region of $\alpha + \beta$. (20%)

2. For a binary system the solubility of A in β phase is 0.08 and B in α phase is 0.12. Both α and β phases obey the Henry's law and no intermediate phase is present.
   (a) Calculate the Henry's law constants for both solutions.
   (b) Draw the activities curves for both A and B. (20%)

3. Two β phase particles of radius r_1 and r_2 ($r_1 > r_2$)are present in a matrix of α phase. No other phase is present. Assume local equilibrium is reached near the α/β interface. Determine the composition of α phase near the two β particles by drawing the free energy curves. Assume the temperature is high enough for diffusion to occur, determine which particle will grow at the expense of the other and how the growth will occur. (20%)

3. Determine the maximum pressure of water vapor in wet hydrogen at 1 atm pressure in which chromium can be heated without oxidation occurring at 1500 K. Is the oxidation of Cr by water vapor exothermic or endothermic? (20%)

4. Magnesium can be removed from Mg–Al liquid solutions by selectively forming the chloride $MgCl_2$. Calculate the activity of Mg in the liquid Mg–Al system which can be achieved at 800°C by reacting the solution with an H_2–HCl gas mixture containing hydrogen at essentially 1 atm pressure and $P_{HCl} = 10^{-5}$ atm to form pure liquid $MgCl_2$. (20%)

$$2\,Cr_{(s)} + 3/2\,O_{2(g)} = Cr_2O_{3(s)} \qquad \Delta G° = -1120300 + 260\,T \quad \text{Joules}$$

$$H_{2(g)} + 1/2\,O_{2(g)} = H_2O_{(g)} \qquad \Delta G° = -246000 + 54.8\,T \quad \text{Joules}$$

$$Mg_{(l)} + Cl_{2(g)} = MgCl_{2(l)} \qquad \Delta G° = -605000 + 125.4\,T \quad \text{Joules}$$
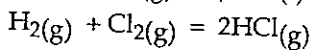
$$H_{2(g)} + Cl_{2(g)} = 2HCl_{(g)} \qquad \Delta G° = -182200 + 3.60\,T\ln T - 43.68\,T \quad \text{Joules}$$

Physical Metallurgy

(1) Give five planes which belong to [$\bar{1}01$] zone axis.　　　　　　10%

(2) Explain the difference between elastic scattering and inelastic scattering.　　10%

(3) How to define the Burgers vector of a dislocation.　　　　　　10%

(4) Explain the term" slip system", give three slip systems of a body-cubic crystal.

　　　　　　　　　　　　　　　　　　　　　　　　　10%

(5) Discuss the effect of grain boundaries on the mechanical properties of ductile materials.

　　　　　　　　　　　　　　　　　　　　　　　　　10%

(6) What is the driving force for recovery, recrystallization, grain growth and secondary recrystallization respectively.　　　　　　　　　　10%

(7) Give a schematic phase diagram of a binary system which has peritectic transformation reaction.　　　　　　　　　　　　　　　　　10%

(8) In terms of atomic processes, explain the activation energy of diffusion.　　10%

(9) Explain the following terms:　　　　　　　　　　　　　20%
　　(a) fatigue　　　　(b) creep　　　(c) superplasticity　　(d) superalloy
　　(e) superconductivity　　　(f)martensite　　　(e) composite

POLYMER PROCESSING (1998)

note: remember to define all the symbols used.

1. Answer briefly the following extrusion-related questions,

   (a) why a short L/D die is preferred when using a profile die in the extrusion process, where L is the equivalent length and D the equivalent diameter of a die. The profile die is used for extruding polymer products of irregular shape.

   (b) why a long L/D die is preferred when using a circular die in the extrusion process. The circular die is used for extruding, among many examples, the polymer tubes and rods.

   (c) what are the "lubrication approximations," frequently used in the flow analysis of polymer processing?

   (d) Without using any mathematical equations, describe the flow phenomenon in the coathanger die used for extruding a sheet or flat film in the extruder.

   (e) What are the elastic effects in the capillary flows?

   [25%, 5%/ea]

2. During the mold filling, in an injection molding process, of an end gated rectangular mold whose width is much greater than its thickness,

   (a) describe how and why the fountain flow is formed.

   (b) sketch the flow pattern (including the velocity profile and the velocity gradient profile, along the thickness direction) in the advancing front between the two parallel plates.

   (c) describe the skin-core morphology of a crystallizable polymer injection molded by the above rectangular mold.

   (d) same as (c) but for an amorphous polymer.

   (e) describe how the "weld line" is formed.

   [25%, 5%/ea]

Polymerization reaction and mechanism

1) Compare the difference between emulsion polymerization and normal radical polymerization from the aspects of polymerization rate and molecular weight. (20 %)

2) What are the characteristic features of "living" polymerization ? (15 %)

3) Cationic polymerization generally has a stronger dependence of its final properties (such as molecular weight, configuration... et al.) on the reaction solvent used in the synthesis step as compared with radical polymerization, why? (15 %)

Styrene(ST)-butadiene(BD) block copolymers were synthesized by the 'living polymer' technique using n-butyl lithium catalyst in benzene at room temperature. ST/BD mole ratios in SBS were changed from 80/20 to 40/60, and the samples expressed as SBS-1 to -5 as shown in Table 1. For a comparison, an ionic copolymer (IC) was synthesized by polymerizing a mixture of the two monomers with a charged ST/BD mole ratio of 60/40. All the samples used were prepared so as to attain the attempted molecular weight of $M_n=1.55 \times 10^5$. The number average molecular weights measured by the osmotic method are greater than the expected values. Temperature dependences of the dynamic modulus (E') and the dynamic loss (E") were measured by a direct-reading dynamic viscoelastometer. Despite the changes in sequence length, each sample showed two E" peaks, as shown in Figure 1. In the ionic copolymer, however, the low temperature peak shifted up to -60°C and high temperature peak down to 95°C. Stress/strain behavior was observed by using a tensile tester at a strain rate of 0.5 cm/min at 25°C, under 65 per cent relative humidity. The elongation at break and yield stress are shown in Figure 2 and Table 1.

Stress relaxation behavior was measured using SBS, BSB, IC and for a comparison, mono-dispersed PS as well as polyblend by means of an Instron type tensile tester as shown in Figure 3. Measurements using BSB were not successful. Differences are noted in the longer time region rather than in the shorter time region. Impact strength values of the copolymers are summarized in Table 1. The ST-BD block copolymers gave a sheet of complete transparency or translucency, despite the presence of two-phase system. Light transmittances exceed 50 per cent for all samples, a very high value compared with that of polyblend (Table 1). The fine structures of the block copolymers were observed under the electron microscope by using the osmium tetraoxide staining and hardening procedure developed by Kato. An electron micrograph of an ultrathin section of compression-molded sheet of SBS (ST/BD mole ratio 60/40) is shown in Figure 4. The dimension of the particles (stained black) seemed to vary from 300 to 350 Å, although they are not always separated from each other. Dimensions of the particles decrease with decreasing BD sequence length in SBS block copolymers as shown in Figure 5. [M. Matsuo, T. Ueno, H. Horino, S. Chujya, and H. Asai, *Polymer, 9*, 425 (1968)]
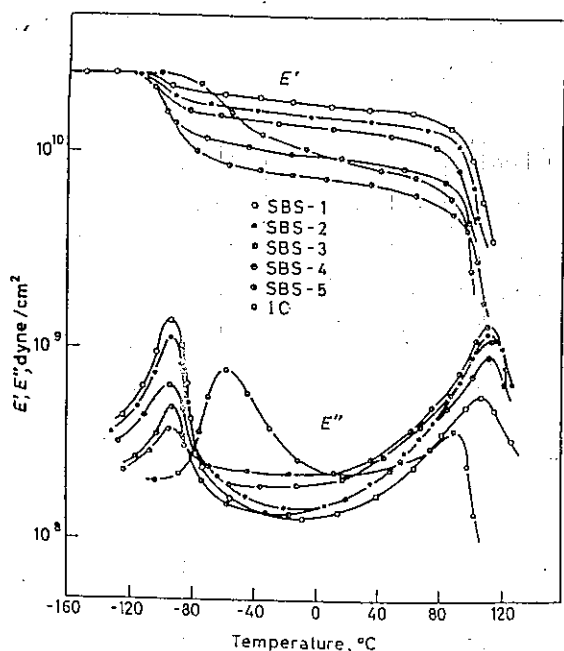
Figure 1—Temperature dependences of dynamic modulus (E') and dynamic loss (E") for the SBS type block copolymers with varying BD sequence length and IC. Measured frequency 110 c/s
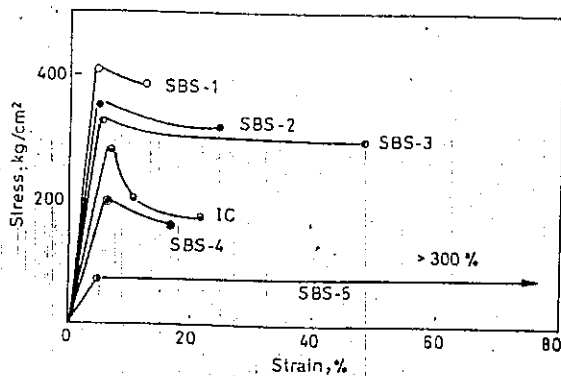
Figure 2—Stress/strain relationships for the SBS type block copolymers with varying BD sequence length

Table 1. Properties of ST-BD block copolymers

Samples	ST/BD mole ratios (charged)	Elongn at break	Light transmittance‡	Impact strength	Heat distort. temperature§
		%	%		°C
SBS-1	80/20	12	75	0·5†	100
SBS-2	70/30	25	81	0·4†	87
SBS-3	60/40	49	72	0·8†	66
SBS-4	50/50	17	68	>2·9†	54
SBS-5	40/60	>300	66	>2·9†	5
IC	60/40	22	57	1·6†	82
Commercial HI-PS	--	30	0	7·0*	75
Polyblend	60/40	2	0	0·5†	--

Charpy impact strength (kg cm/cm³).
Dynstrat impact value (kg cm).
Average values of the light transmittances of 1 mm thick plates measured at the wavelengths of 400, 500, 600 and 700 mμ.

1. Explain why the measured M_n is greater than the attempted M_n. What is the principle of the osmotic pressure method? Can we use other methods to measure the molecular weight of these block copolymers? Why? (15%)

2. SBS DP sequences are 720-350-720, 790-685-790, 1840-2450-1840, 1300-2580-1300, and 740-2240-740, respectively. Identify their chemical composition in ST/BD mole ratios. (10%)

3. Interpret the dynamic mechanical properties (Figure 1) in detail, such as: The heights of E" peaks and E' varied with the compositions. Is it changed as expected? The peaks' position of the ionic copolymer shifted with respect to SBS copolymers. (15%)

4. Discuss the stress/strain relationships with varying BD sequence length in Figure 2. Is there any relationship between Figures 1 and 2? (15%)

5. From the stress relaxation spectra in Figure 3, explain the relaxation time difference in the longer time. (10%)

6. Interpret the micrographs in Figures 4 and 5. (15%)

7. From the mole ratios, elongation at break, and impact strength in Table 1, discuss their relationships and heterogeneous two-phase systems. (20%)
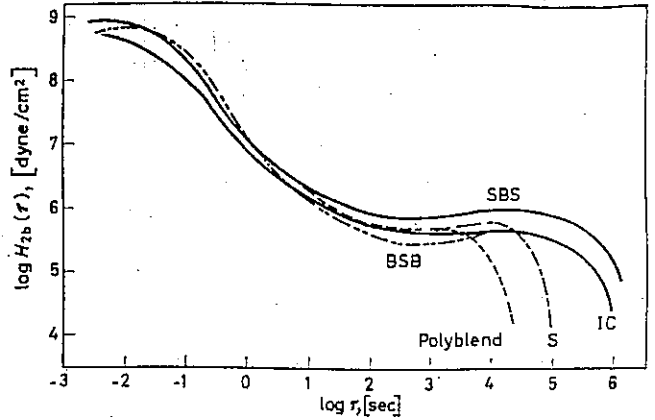

Figure 3—Stress relaxation spectra of the ST–BD block copolymers as compared with the blend of PC and PBD, and its component PS
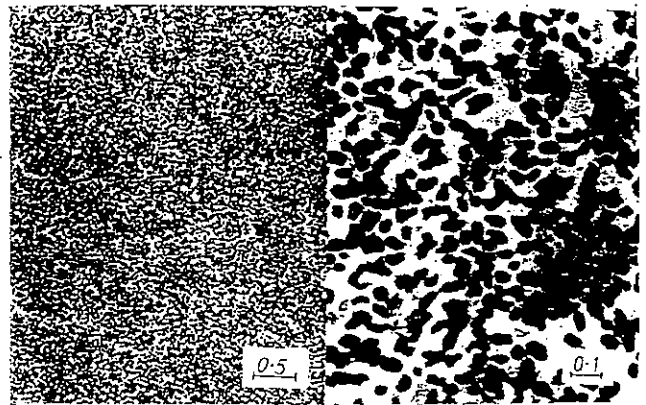

Figure 4. —Electron micrograph of an ultrathin section of a compression-moulded sheet of SBS type block copolymer, showing spherical shapes of BD sequences. (ST/BD mole ratio=60/40)
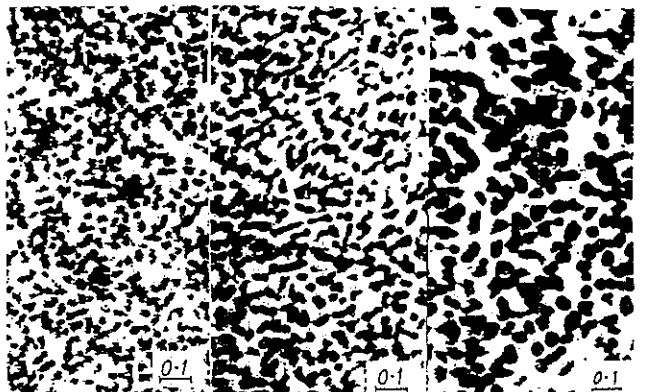

Figure 5 —Electron micrographs of ultrathin sections of compression-moulded sheet of SBS type block copolymers. Effect of BD sequence length under a given total molecular weight. ST/BD mole ratios: left=80/20, middle=70/30, right=60/40