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Compression Molded Polyurethane Block Copolymers
III Evaluation of Microphase Compositions

by

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This paper presents methods to estimate the microphase compositions in polyurethane segmented block copolymers based upon combined analyses by small-angle x-ray scattering and differential scanning calorimetry. The methods are applied to a system of polyurethanes prepared from 4,4'-diphenylmethane diisocyanate, 1,4-butanediol, and a 2000 MW ethylene glycol capped polypropylene oxide prepolymer. The resultant microphase compositions predict microphase transition temperatures that compare well with observed values.

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"Compression Molded Polyurethane Block Copolymers III Evaluation of Microphase Compositions"

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Introduction

The versatile mechanical properties of segmented polyurethane elastomers are generally attributed to the formation of a microphase separated structure due to incompatibility of the glassy hard segment and rubbery soft segment sequences. In most investigations, the degree of microphase separation has been found to be incomplete. That is, microdomains are not pure as a result of intersegmental mixing. Mixing within the soft microphase is reflected by an elevation in its glass transition temperature as compared to the pure component value[1,2]. The dissolution of hard segments within the soft microphase is associated with the broad distribution of hard segment sequence lengths inherent from the polymerization reaction[3]. Shorter hard segments have a lower driving force for microphase separation and might be expected to dissolve preferentially. Preferential solvation of shorter sequences provided the basis for the model for polyurethane morphology developed by Koberstein and Stein[4]. This model predicts that the hard microdomain thickness is controlled by the compatibility, being related to the shortest phase-separated hard segment sequence length. A recent small angle x-ray scattering (SAXS) investigation[1] provided strong evidence in favor of this model by demonstrating a qualitative correlation between hard microdomain structure and the soft microphase glass transition temperature. The soft microphase composition and associated glass transition temperature is an important parameter to be controlled since it has a direct influence on the low-temperature extensibility and modulus of the material.

The composition and glass transition temperature of the hard microphase is equally important due to its influence on the heat distortion or deflection temperature and plateau modulus. Hard segment glass transition temperatures estimated from differential scanning calorimetry (DSC)[2,5] or thermomechanical analysis[2,6,7] are found to be lower than that of the pure hard segment[8], suggesting the presence of "dissolved" soft segment units. These "dissolved" units most probably result from non-equilibrium entrapment of soft segment sequences of the multiblock chain.

The importance of microphase separation in controlling polyurethane properties provides strong motivation for the development of methods to characterize the degree of microphase separation. A number of such methods have consequently appeared. Camberlin and Pascault proposed a method based solely on the results of DSC measurements[9]. In their treatment, dissolved hard segments were assumed to have a negligeable contribution to the change in heat capacity at the soft microphase glass transition. This assumption is inconsistent with use of the Fox equation[10], since this equation is based upon the assumption that heat capacity contributions are equivalent for both constituents as has been emphasized by Couchman[11]. A similar DSC annealing-quenching method was employed to construct an apparent microphase composition-temperature diagram for a segmented polyurethane block copolymer[5]. Analysis of the experimental data also suggested that the heat capacity contribution from dissolved hard segments was negligeable as assumed by Camberlin and Pascault, but did not resolve the apparent discrepancy with theory. Methods for the determination of microphase compositions from the results of scattering experiments have also appeared[1]. In general, these methods require either an additional experiment, fitting a model, or making restrictive assumptions in order to arrive at a solution.

In this communication, we present methods for the determination of microphase compositions in two-phase systems that are based upon a combined analysis of DSC and SAXS experiments. The methods are applied to the experimental data for the series of polyurethane elastomers described in the preceding two articles, but are generally applicable for all two-phase materials.

Theory

DSC Analysis of Glass Transition Temperatures

Thermal Analysis has been applied widely to study miscibility in polymer blends. The goal of these investigations is generally to relate glass transition temperatures (Tg) to the overall blend compostion and characteristic thermal properties of the blend constituents. A number of equations that express this relationship have appeared[10,11,15-17] both of empirical and thermodynamic origin. Equations of similar form have been developed to describe the glass transition behavior of copolymers[18,19]. The most general of these theories are those of Couchman[11,17,18]. The Couchman equations have been shown to reduce to the more familiar empirical relations given appropriate assumptions. The basis of the Couchman theory for random copolymers is the consideration of individual contributions associated with the various dyad species that comprise the chain. Each dyad ij (e.g. monomers i and j) makes a contribution Tg_{ij} to the glass transition temperature(Tg), and ΔCp_{ij} to the change in heat capacity (ΔCp) at Tg. In the original development, the equations predicting the overall Tg and ΔCp for a copolymer containing m species i and j take the form

$$\ln Tg = \frac{\sum_{i}^{m}\sum_{j}^{m} w_{ij}\, \Delta Cp_{ij} \ln Tg_{ij}}{\sum_{i}^{m}\sum_{j}^{m} w_{ij}\, \Delta Cp_{ij}} \qquad (1)$$

and

$$\Delta Cp = \frac{\sum_{i}^{m}\sum_{j}^{m} w_{ij}\, \Delta Cp_{ij}}{\sum_{i}^{m}\sum_{j}^{m} w_{ij}} \qquad (2)$$

The w_{ij} terms refer to the weight fractions of ij dyads. They may be determined from the chemical composition of the copolymer and the reactivity ratios.

In the particular case of segmented polyurethane elastomers, these equations can be applied to characterize the glass transition process of the soft microphase. The soft microphase consists of soft segments connected by covalent bonds to dissolved hard segment units. This "mixed" soft microphase can thus be treated as a single phase copolymer system comprised of three component species. These species are the soft segment(s), the diisocyanate residue(d), and the chain extender residue(c). If the soft segment prepolymer is treated as a single species(ds), the polyurethane chain "dissolved" within the soft microphase presents the structure of an alternating copolymer represented by $-[(dc)_n ds]-$, where n is the average number of diisocyanate residues per dissolved hard segment. Furthermore, this copolymer chain contains no like dyads, and only unlike dyads of the type soft segment/diisocyanate (type sd) or diisocyanate/chain extender (type dc). The Couchman equations for the polyurethane soft microphase may therefore be written

$$\ell n\, Tg = \frac{w_{sd}\, \Delta Cp_{sd}\, \ell n\, Tg_{sd} + w_{dc}\, \Delta Cp_{dc}\, \ell n\, Tg_{dc}}{w_{sd}\, \Delta Cp_{sd} + w_{dc}\, \Delta Cp_{dc}} \qquad (3)$$

and

$$\frac{\Delta Cp}{W_1} = \frac{w_{sd}\, \Delta Cp_{sd} + w_{dc}\, \Delta Cp_{dc}}{w_{sd} + w_{dc}} \qquad (4)$$

Here ΔCp is the heat capacity change per gram of total polymer at the soft microphase glass transition temperature and W_1 is the overall weight fraction of the soft ("mixed") microphase. Further simplification of the equation may be accomplished by approximating terms of the type $\ell n\, Tg_{ij}$ by $1/Tg_{ij}$.

If the dissolved copolymer may be considered random, that is if the polymerization reaction proceeds statistically, definition of the dyad fractions is straightforward. The weight fraction of each dyad is simply related to the product of the probabilities of finding each species

$$w_{ij} = \frac{f_i\, f_j\, M_{ij}}{M} \qquad (5)$$

where M is the average molecular weight of the dissolved chains, M_{ij} is the dyad molecular weight, and f_i is the mer fraction of species i. Regardless of the length distribution of "dissolved" hard segments, the mer fractions are dictated by stoichiometry to have the values

$$f_s = \frac{1}{2n+2}, \quad f_d = \frac{n+1}{2n+2} \text{ and } f_c = \frac{n}{2n+2} \qquad (6)$$

where n is the average number of diisocyanate residues per dissolved hard segment. With these substitutions, the Couchman equations for a segmented polyurethane block copolymer can be rearranged to give:

$$\Delta Cp_{dc} = \frac{M_{sd}\ \Delta Cp_{sd}\ (Tg - Tg_{sd})\ Tg_{dc}}{M_{dc}\ n\ (Tg_{dc} - Tg)\ Tg_{sd}} \qquad (7)$$

and

$$W_1 = \frac{\Delta Cp\ (M_{sd} + n\ M_{dc})}{M_{sd}\ \Delta Cp_{sd} + n\ M_{dc}\ \Delta Cp_{dc}} \qquad (8)$$

The principle unknowns in these equations are W_1, ΔCp_{dc} and n. In general, they may be determined from the results of the DSC analysis alone. In the case of MDI - based polyurethanes however, ΔCp_{dc} is also an unknown because of the difficulty in observing a well defined hard segment glass transition process. The two equations (7 & 8) thus contain three unkowns, n, ΔCp_{dc}, and W_1; two knowns, M_{sd} and M_{dc}; and five measurable quantities, Tg, ΔCp, Tg_{dc}, Tg_{sd} and ΔCp_{sd}. The quantities Tg and ΔCp are those values measured for the soft microphase of the copolymer of interest; Tg_{dc} is measured from a pure hard segment copolymer; and Tg_{sd} and ΔCp_{sd} are measured from a diisocyanate end-capped prepolymer or alternating diisocyanate/soft segment copolymer. It is apparent that in addition to Eqns. 7 and 8, a third relationship is needed to solve for the three unknowns (i.e., n, ΔCp_{dc}, and W_1). This additional equation is furnished by relations obtained from small-angle x-ray scattering analysis described in the preceding paper. From this analysis the compositions and overall fractions of both the soft and hard microphases may be evaluated. (See Appendix for a complete description of the method.)

A semi-empirical approach can be developed as an alternative to the Couchman equations as has been described in a previous publication[5]. The basis of the approach are two equations relating heat capacity changes, microphase compositions, and glass transition temperatures. For a homogeneous single phase copolymer the total ΔCp_{mix} is taken as the linear weighted combination of the two pure constituent values (i.e. soft segment denoted by 1, hard segment by 2)[17]

$$\Delta Cp_{mix} = w_1 \, \Delta Cp_1 + (1-w_1) \, \Delta Cp_2 \qquad (9)$$

where w_i is the weight fraction of constituent i with heat capacity change ΔCp_i. The Tg behavior for the mixture is represented by a generalized Fox equation[15]

$$\frac{w_1 + (1-w_1)k}{Tg_{mix}} = \frac{w_1}{Tg_1} + k\,\frac{(1-w_1)}{Tg_2} \qquad (10)$$

The parameters in (9) and (10) were obtained previously by experimental determination of ΔCp_{mix} and Tg_{mix} on quench-mixed specimens of various known compositions[5]. The previous analysis furnished values of ΔCp_1=0.194 cal/g, ΔCp_2=0, k=1.18, Tg_1=-69°C, and Tg_2=109°C. In practice, the specimens are two-phase in nature; therefore (9) and (10) are applied to characterize the composition of the soft microphase. That is, the fraction of soft segment in the soft microphase, $w_{1,S}$, is estimated by solving (10) for $w_1 = w_{1,S}$ with Tg_{mix} replaced by the experimental soft microphase Tg and the additional parameters k, Tg_1, and Tg_2 as given above. In principal, the soft segment content of the hard microphase, $w_{2,S}$, could be determined by application of (10) to the hard microphase Tg. It is more consistent however to employ the lever rule, from which it follows that

$$w_{2,S} = \frac{W_{SS} - W_1 w_{1,S}}{(1-W_1)} \qquad (11)$$

where W_{SS} is the overall soft segment weight fraction of the specimen. The overall weight fraction of the soft-segment-rich microphase is calculated from

$$W_1 = \frac{\Delta Cp_S}{\Delta Cp_1\, W_{1,S} + \Delta Cp_2\, (1-W_{1,S})} \qquad (12)$$

where ΔCp_S is the measured heat capacity change at the soft microphase Tg. The previously determined pure component ΔCp values are employed in (12) for this purpose.

Small-Angle X-Ray Scattering Analysis

Small-angle x-ray scattering originates from spatial fluctuations in electron density within a material. Analysis of the SAXS intensity then can be used to estimate microphase compositions. The degree of microphase separation is characterized by the mean square variance in electron density, $\Delta\rho^2$, which may be estimated by determination of the scattering invariant. Experimental invariants may be calculated following the method of Bonart et al.[20]. The first invariant includes the effects of interfacial mixing and is given by

$$\overline{\Delta\rho^2}' = C \int_0^\infty [\tilde{I}(s) - I_b(s)]s\, ds \qquad (13)$$

The second invariant corrects for the presence of diffuse microphase boundaries and is calculated from

$$\overline{\Delta\rho^2}'' = C\, \frac{\int_0^\infty [\tilde{I}(s) - \tilde{I}_b(s)]s\, ds}{\exp[-38\, (\sigma s)^{1.81}]} \qquad (14)$$

The origins of these relations have already been discussed in detail[1,4,20]. C is a known constant; $\tilde{I}_b(s)$ is a background intensity arising from thermal density and concentration fluctuations within the microphases; and σ is a parameter related to the diffuse microphase boundary thickness. The latter two terms are determined from regression to a modified Porod relation, which for infinite-slit-height collimation, takes the form[21,22]

$$\lim\,[\tilde{I}(s)] = \frac{K}{s^3}\exp\,[-38(\sigma s)^{1.81}] + \tilde{I}_b\,(s) \qquad (15)$$

The term $\tilde{I}_b(s)$ is assumed to be independent of s, and is equal to the limiting slope of a plot of $\tilde{I}_b(s)s^3$ vs. s^3 following Bonart et al.[20]. The Porod constant K and the diffuse boundary parameter σ are calculated from a plot of

$$\ell n\;\{[\tilde{I}(s) - \tilde{I}_b(s)]\;s\}^3 \text{vs. } s^{1.81},$$

as discussed elsewhere[1,4,21,22]. An effective dimension E of the interphase gradient is given by $E=\sigma\sqrt{12}$[22]. The Porod constant may be used further to calculate the surface to volume ratio from[23]

$$S/V = [K\; 16\pi^2\; \phi_1\; (1-\phi_1)\; /\overline{\Delta\rho^2}''\;]\; K_{abs} \qquad (16)$$

where K_{abs} is an absolute intensity calibration factor and ϕ_1 is the overall volume fraction of the soft microphase.

The relationship between the SAXS variances (Eqns. 13 and 14) and phase compositions follows from the general definition of a second moment of the electron density distribution for a two phase system

$$\overline{\Delta\rho^2} = \phi_1\;(\rho_1-\bar{\rho})^2 + (1-\phi_1)\;(\rho_2-\bar{\rho})^2 \qquad (17)$$

The material average electron density is defined as

$$\bar{\rho} = \phi_1\;\rho_1 + (1-\phi_1)\rho_2 \qquad (18)$$

where ρ_1 and ρ_2 are the average electron densities of the soft and hard microphases respectively.

The material average electron density may be evaluated from the known chemical composition of the material and an experimental measurement of its mass density[24]. The system of SAXS relations effectively consists of two equations with two measurable quantities, $\overline{\Delta\rho^2}$ and $\bar{\rho}$, and three unknowns. The additional information needed to solve the complete system of equations is furnished by the DSC analysis described in the preceding section. The complete set of equations is quite cumbersome due to the involvement of volume fractions, mass fractions, mass densities and electron densities and is described in detail in the Appendix. Solution of these equations yields a complete specificaion of the amounts and compositions of each microphase.

Experimental

Materials

A series of segmented polyurethane block copolymers with varying hard segment content are studied. The hard segments consist of 4,4'-diphenylmethane diisocyanate (MDI) chain extended with butanediol (BD). The soft segment is polyoxpropylene ($\bar{M}_n$=2000, functionality=1.94) end capped with 30.4 weight percent oxyethylene. The polymers are prepared by a one-step bulk polymerization process with four percent excess MDI to ensure complete reaction[13]. The notation used for this series of polymers is PU-XX, where XX represents the weight fraction of hard segment. The chemical compositions of the materials studied are presented in Table 1 along with some associated physical characteristics. The polymers used in this study[1,2,5,13] are reprecipitated from dimethyl formamide solutions of the as received polymers and then molded into 2mm thick, 1.5 inch diameter disks at 180°C and 3000 psi for 5 minutes under vacuum. Elemental analysis of a few selected samples confirms that the as molded polymers have the same chemical content as the original samples. These molding conditions were selected since they produced materials that present only a single melting endotherm in high rate DSC tests (see first paper in this series). The materials should therefore possess morphologies which are uniform across an entire specimen.

The pure alternating block copolymer of MDI and soft segment (denoted PU-MDI) is prepared by solution polymerization in tetrahydrofuran (THF). The THF is dried under calcium hydride and distilled over sodium wire and benzophenone prior to usage. The MDI (Eastman Kodak) is filtered through a fritted glass filter at 80°C in order to remove dimers and impurities. The MDI monomers are added slowly to the reacting solution (five percent solution in THF) at 10 percent in excess of the stoichiometric ratio. Less than one percent of dibutyl tin dilaurate (DBTL) is used as a catalyst for the reaction. The reaction is carried out at 60°C and rigorously stirred for two days to complete the reaction. The polymer is then reprecipitated from solution with dried methanol.

Small-Angle X-Ray Scattering

Small-angle x-ray sacttering experiments are performed on a step scanning Kratky camera equipped with a proportional counter (CuKα source with Ni fiter, wavelength λ=1.5418 Å). The sample to detector distance (SDD) is 214mm and the step size between each measurement is 50 microns. A Lupolen standard is used for the purpose of absolute intensity calibration. The raw intensity curves are then smoothed[1], corrected for parasitic slit scattering and sample attenuation, and desmeared according to Vonk's routine[14]. A more complete description of the analysis procedure is given in the preceding article.

TABLE 1

Materials	Hard Segment wt. % (MDI + BD)	Density (gm/cc)	Average MW* of Hard Seg. (gm/mole HS)	# MDI per* Hard Segment
PU-20	20	1.142	500	1.7
PU-30	30	1.165	900	2.8
PU-40	40	1.192	1400	4.2
PU-50	50	1.218	2000	6.2
PU-60	60	1.235	3100	9.2
PU-70	70	1.270	4800	14.1
PU-80	80	1.292	8100	24.0

*Calculated from Peeble's most probable distribution for one-step polymerization[3].

Microphase Composition Calculations

Extension of Couchman's Theory

Calculation of the microphase composition by coupling the SAXS invariant data with the modified Couchman relations for the case of segmented polyurethanes is described fully in the Appendix. In order to solve these equations, a number of parameters need to be determined experimentally. The specific volume of the pure soft segment is measured pycnometrically, and that of the pure hard segment is obtained from the total polymer density (measured by the buoyancy method) by assuming volume additivity[1]. ΔCp and Tg of the soft microphase were measured by DSC in the first paper of this series as were ΔCp_{sd} and Tg_{sd} (from the end-capped prepolymer) (see Table 2). The other parameters in the relations are fixed except for Tg_{dc} and ΔCp_{dc}, for the pure hard segment. Fixing either of these parameters is sufficient to solve the equations. In order to simplify the equations, we assume a value of Tg_{dc} = 110°C, as has been reported in the literature[8]. We also assume that Tg_{dc} is a constant, independent of the sequence length distribution (i.e. molecular weight of the dissolved hard segments), although there is some evidence that it is influenced by molecular weight[26]. Finally, we neglect crystallinity of the hard microdomain, which has been estimated as less than 23% for all materials (see first article in series). The parameters which we will solve for are n, the average length of hard segment dissolved within the soft microphase, ΔCp_{dc}, and W_1, the overall weight fraction of the soft microphase. From these parameters, all other parameters may then be calculated. An iterative procedure is adopted for the solution of these relations. First a value of n is assumed, whereupon a value for the theoretical x-ray invariant $\overline{\Delta\rho_T^2}''$ is calculated (see A.13)

Table 2

Results of Experimental Characterization

Material	ΔC_{p_S} ($^{cal}/_{g\ K}$) at Soft Microphase Tg	T_{g_S}(K) of Soft Microphase	T_{g_H}(K) of Hard Microphase	Electron Density Variances (mole e^-/cc)^{2}x10^3	
				$\overline{\Delta\rho^2}'$	$\overline{\Delta\rho^2}''$
Polyol	0.198	204	-	-	-
Prepolymer	0.168	215	-	-	-
PU-30	0.132	233	364	0.525	0.625
PU-40	0.119	230	356	0.625	0.792
PU-50	0.092	230	353	0.972	1.080
PU-60	0.0635	232	351	1.030	1.170
PU-70	0.038	239	346	0.974	1.110

The value of n is then adjusted in iterative fashion until the theoretical invariant is equal to one of the two experimental invariants $\overline{\Delta\rho^2}''$ and $\overline{\Delta\rho^2}''$ (see Table 2).

The two experimental invariants lead to different results because they treat the interphase material differently. Which value is appropriate depends upon whether or not the interfacial material contributes to the soft microphase glass transition process. In the first model (lower part of Figure 1), it is apparent that $\overline{\Delta\rho^2}'$ incorporates mixing both at the interphase and within the microphase proper. Calculations based upon this invariant therefore include the interphase material in the Tg modelling, and will give an upper bound on the degree of mixing. The invariant $\overline{\Delta\rho^2}''$ corresponding to the model in the upper half of Figure 1 is corrected for the interphase material. The Tg modelling does not consider interfacial material and thus represents a lower bound on the degree of mixing.

The results of calculations based upon the two invariant models are given in Tables 3 and 4 respectively. Neither model produces satisfying results. The value of n for example does not exhibit behavior consistent with our previous SAXS modelling[1,4] and the results of the preceding paper. In this model, we propose the existence of a critical hard segment length. All segments below this critical length would dissolve in the soft microphase. The value of n obtained, however, is not approximately constant as would be expected from this reasoning. In addition, the ΔCp_{dc}. values are not reasonable, especially for the results based upon $\overline{\Delta\rho^2}'$. In this case, ΔCp_{dc} exceeds that of the pure soft segment (0.1976 cal/gm°C) for all cases. The best estimate of ΔCp_{dc} determined from the reported Tg_{dc} and the Simha-Boyer rule[27] is only 0.07 cal/gm°C. The ΔCp_{dc} results based upon $\overline{\Delta\rho^2}''$ (Table 3) show a minimum value of 0.13 cal/gm°C for PU-50

Table 3

Microphase Composition Calculations Based upon $\overline{\Delta\rho^2}'$, Including Interphase Material

Sample	Average No. of BD n	ΔCp_{dc}	Weight Fraction Soft Phase W_1	Volume Fraction Soft Phase ϕ_1	Weight Fraction H.S. in Soft Phase $W_{1,H}$	S.S. in Soft Phase $\phi_{1,S}$	H.S. in Hard Phase $\phi_{2,H}$
PU-30	0.20	0.6712	0.6712	0.6920	0.1373	0.8854	0.5561
PU-40	1.51	0.7458	0.7458	0.7658	0.2760	0.7634	0.7705
PU-50	1.63	0.5895	0.5895	0.6173	0.2882	0.7539	0.8188
PU-60	0.64	0.3516	0.3516	0.3804	0.1891	0.8406	0.7491
PU-70	0.44	0.1959	0.1959	0.2190	0.1667	0.8601	0.8214

Note: The invariants used are corrected for thermal density fluctuations and employ the following parameters, Tg_{dc} = 110°C; Tg_{sd} = -57.6°C; ΔCp_{sd} = .1679 cal/gm°C; hard segment density = 1.354 gm/cc; soft segment density = 1.01 gm/cc.

Table 4

Microphase Composition Calculations Based upon $\overline{\Delta\rho^2}''$, Excluding Interphase Material

Sample	Average No. of BD n	ΔCp_{dc}	Weight Fraction Soft Phase W_1	Volume Fraction Soft Phase ϕ_1	Weight Fraction H.S. in Soft Phase $W_{1,H}$	S.S. in Soft Phase $\phi_{1,S}$	H.S. in Hard Phase $\phi_{2,H}$
PU-30	0.05	4.97	0.6560	0.6789	0.1173	0.9025	0.5750
PU-40	1.35	0.14	0.7312	0.7529	0.2614	0.7765	0.7821
PU-50	0.38	0.13	0.5721	0.6016	0.2648	0.7735	0.8259
PU-60	0.26	0.82	0.3335	0.3639	0.1451	0.8787	0.7563
PU-70	(0.00)	5.00	0.1837	0.2075	0.1112	0.9077	0.8241

Note: The invariants used are corrected for thermal density fluctuations and diffuse boundary thickness and employ the following parameters, Tg_{dc} = 110°C; Tg_{sd} = -57.6°C; ΔCp_{sd} = .1679 cal/gm°C; hard segment density = 1.354 gm/cc; soft segment density = 1.01 gm/cc.

in reasonable agreement with the prediction of the Simha-Boyer rule. Unreasonably high values are seen for compositions at the two limits however. As a consequence of the ΔCp_{dc} behavior, the predicted soft segment contents for both models show a minimum for PU-50. This is contrary to the overall trend observed in the experimental Tg data for the soft phase (Table 2). In addition, the predicted hard segment fractions of the hard phase show a miximum as a function of hard segment content, whereas the experimental apparent hard microdomain glass transition temperatures (Table 2) decrease monotonically with increase in hard segment content.

It is evident from these calculations that the Couchman theory can not account for the glass transition behavior in polyurethane elastomers. This in part can be attributed to the observation that the heat capacity change of the dissolved hard segments at the soft microphase Tg is effectively zero[2,5,9]. In addition, other physico-chemical phenomena may occur that can effect the Tg process. It is probable, for example, that the dissolved hard segments participate in hydrogen bonds either with other dissolved hard segments or with the ether oxygen of the soft segment[28]. Sung and Schneider[29] have postulated that hydrogen bonds can influence the Tg process through their role as physical crosslinks. In addition, as was mentioned previously, we have assumed that Tg_{dc} is independent of sequence length, whereas there is some indication[26] that the chemical junctions between blocks act in much the same fashion as endgroups to impart a sequence length dependence to Tg_{dc}. Finally, there is some ambiguity as to how to treat the material in the interphase region. We have no clear idea of how much of the interfacial material takes part in the soft microphase glass transition process. Since our estimates indicate that the interphase in polyurethanes may account for as much as 20% of the material[30], this ambiguity can lead to substantial error. At present, it appears unlikely that a rigorous approach including all of the factors which influence the Tg's of these polyurethanes can be developed. The approach developed herein, or a similar one may be useful in examining the behavior of less complicated segmented copolymers.

A Self Consistent Phenomonalogical Approach

In view of the deficiency of the straightforward thermodynamic approach to modelling polyurethanes, there is considerable motivation to develop a more empirical approach to the problem of determining microphase compositions. Such an approach readily presents itself as a result of the accessability of the homogeneous (i.e. disordered) state for polyurethanes. It has been previously demonstrated that at temperatures of ca. 240°C, microphase separation is not manifest. Furthermore, the disordered mixed state may be frozen in by rapidly quenching these materials. The Tg and ΔCp behavior of these quenched samples can save as a calibration for the effect of mixture composition on the Tg and ΔCp of either the hard or soft phase. This calibration would presumably account for all effects, such as molecular length, mixing and hydrogen bonding, which influence the glass transition temperature. Previously, we found that the ΔCp behavior of our materials quenched from the disordered state followed relation (9), yield regression parameter of $\Delta Cp_1 = 0.194$, equivalent to that measured for the pure soft segment (i.e. 0.198), and $\Delta Cp_2 \simeq 0$.

The behavior of the single Tg observed for the disordered quenched specimens was found to be well described by the modified Fox equation (Equation 10), with $Tg_1 = -60°C$ measured from the pure soft segment; $Tg_2 = 383°K$ and $K = 1.18$ determined by regression of (10) upon the experimental Tg vs. W_1 data.

Equations (9) and (10) then serve as semi-empirical calibration relations which may be applied to characterize either the hard or soft microphase compositions through analysis of the respective ΔCp and Tg for that microphase. The use of this phenomenological approach allows one to take into account the actual Tg behavior even though the fundamental principles underlying this behavior may not be clearly understood. The self-consistency of the approach may be examined in two ways: by calculation of a theoretical invariant and comparison to experimental results; and by calculation of the hard microphase Tg's and comparing them with experimental results.

The self-consistant calculation begins by application of (10) to the experimental soft microphase Tg data. This leads to the composition of the soft microphase. The overall weight fraction of the soft microphase is determined by application of (9) to the Δp data for the soft microphase glass transition. At this point the compositions and volume fractions of both microphases are known. A theoretical estimate of the invariant may then be obtained through relations A.11-A.14 and appropriate transformations between weight and volume fractions. A theoretical estimate of the hard microphase Tg is then provided by application of (10) to the hard-segment-rich mixture.

The results of the self-consistent empirical model calculations are given in Table 5. Qualitatively, the results are pleasing.

Table 5

Microphase Composition Calculations Based Upon
Modified Fox Empirical Model

Sample	ϕ_1, Volume Fraction Soft Phase	S.S. in Soft Phase, $W_{1,S}$	H.S. in Hard Phase, $W_{2,H}$	Fraction of H.S. Dissolved in Soft Phase	Tg(K) Hard Phase	Electron Density Variance (mole e^-/cc)^{2}x10^3
PU-30	0.893	0.764	0.836	0.703	340	0.43
PU-40	0.779	0.786	(1.06) 1.00*	0.416	(400) 382*	1.54
PU-50	0.599	0.790	0.934	0.251	364	1.58
PU-60	0.424	0.771	0.874	0.162	349	1.27
PU-70	0.270	0.720	0.856	0.108	344	0.82

*Assuming pure hard phase

The purity of the phases, reflected in the values of the third and fourth columns of Table 5 is lowest for low and high contents of hard segment, and go through a maximum at intermediate hard segment contents. A similar trend in "intraphase mixing" was observed by x-ray analysis in the preceeding paper.

A more quantitative comparison of the model with experimental data is presented in Figures 2 and 3. The calculated electron density variances (Figure 2) reflect the same qualitative trend as both of the experimentally determined variances (see equations 13 and 14). The agreement is good for low and high hard segment contents, however the calculation overestimates the variance at intermediate compositions. A similar trend is observed when comparing the apparent hard phase glass transition temperatures in Figure 3. The Tg is overestimated at intermediate compositions corresponding to an overestimate in hard phase purity.. This result is consistent with the overestimate in the electron density variance for the same compositions.

In light of the many assumptions that have gone into the empirical model, the qualitative agreement with experiment is promising. Several of these assumptions bear further examination. First of all, the effects of crystallization have been neglected. While the materials have been processed to give low crystallinities (i.e. less than 23%) the presence of crystallinity is a complicating factor and leads to several important questions. Would it be more appropriate to employ a three phase model consisting of a crystalline hard segment, a mixed hard phase, and a mixed soft phase? Where is the mixed hard phase located; is it truly a separate phase? How will crystallinity affect the apparent hard phase Tg? In fact, the variance data in Figure 2 are consistent with the degree of crystallinity data discussed in the first paper of this series. These data showed a gradual increase in crystallinity up to a miximum of ca .22% for PU-70.

Secondly, the hard segment glass transition temperature has been assumed to be independent of molecular weight. A limited amount of experimental data suggest the contrary is true (26). Incorporation of a molecular weight dependent Tg into the theory would be an involved task due to the intrinsic distribution in molecular weight of the hard segment. In practice, two molecular weight distributions would be required, one for the "dissolved" hard segments and another for the segregated hard segments. Each population would have a distinct Tg. The calibration of Tg based upon specimens frozen in the disordered state by quenching, only gives information regarding Tg of the entire hard segment length distribution.

It is clear that to better test the models we have developed, it would be appropriate to apply them to a simpler polyurethane system which is incapable of crystallization. Our initial attemps at this approach have failed due to the strong tendency for these urethanes to absorb water and consequently degrade during processing. Efforts to circumvent this problem are ongoing, and should result in a better test of these equations for the determination of microphase compositions in polyurethanes and other block copolymers.

Comparison with the Koberstein-Stein Model of Polyurethane Microdomain Structure

The Koberstein-Stein model of microdomain structure (4) is based upon the concept of a critical hard segment sequence length. Hard segment sequences shorter than this length are thought to dissolve within the soft microphase. Sequences longer than the critical length segregate into hard microdomains with a more or less lamellar structure and a thickness roughly equivalent to the critical sequence length. If the hard segment sequence length follows a most probable distribution as expected (3), the partitioning of hard segment species between the soft and hard microphases would most likely occur as depicted schematically in Figure 4. Since polyurethanes of varying hard segment content will have intrinsically different hard segment distributions, they will also contain different amounts of intersegmental mixing. The critical hard segment sequence length however should depend primarily on the soft segment type and length, and be relatively independent of hard segment content.

The preceeding paper in this series, and earlier papers from our laboratory have examined many of the features of this model, and found them to be consistent with a variety of experimental data. A further comparison can be made through examination of the mcirophase composition data from the present analysis. Since all microphase compositions are known (within the assumptions and validity limits of the analysis), the fraction of hard segments dissolved within the soft microphase can be determined by:

$$W_{H,DISSOLVED} = \frac{W_1 W_{1,H}}{W_1 W_{1,H} + (1-W_1)w_{2,H}} \qquad (19)$$

The critical sequence length can be evaluated by integrating the sequence length distribution untl $W_{H,DISSOLVED}$ equals the fraction of sequences below the critical length.

The estimated fractions of hard segments dissolved within the soft microphase are given in Table 5 based upon the empirical model calculation. The critical hard segment sequence lengths calculated from this data (using distributions derived by Peebles (3)) are given in Table 6. The critical lengths are sensitive to the degree of reaction conversion assumed in the calculation of the hard segment seqeunce length distribution. The critical length increases with increase in conversion.

An estimate of the conversion may be obtained by consideration of the overall molecular weight of the polymers. The number average molecular weight of PU-60 (estimated from gel permeation chromatography relative to polystyrene standards) is about 50,000 Daltons. This corresponds to a conversion of about 95%.

Table 6

Estimated Critical Hard Segment Sequence Lengths*

Material	N_c (100% conversion)	N_c (100% conversion)	N_c (100% conversion)
PU-30	7.0	5.5	5.0
PU-40	5.8	4.9	4.3
PU-50	6.0	4.7	4.0
PU-60	5.7	4.8	3.8
PU-70	8.0	5.0	3.6

*Hard segments with N_c or more diisocyanate residues per sequence length are assumed to reside within the hard microdomain.

Table 7

Calculated Hard Microdomain and Repeat Unit Thickness

	Volume Fraction Hard Microdomain ϕ_2	SAXS Interdomain Spacing d_{1p}(nm)	Hard Microdomain Thickness THS(nm)	Repeat Unit Thickness (nm) T_{HS}/NC (95% Conversion)
PU-30	.299	15.2	4.5	0.82
PU-40	.584	21.9	12.8	2.6
PU-50	.743	13.7	10.2	2.2
PU-60	.838	13.3	11.1	2.3
PU-70	.891	11.7	10.4	2.1

Assuming 95% conversion, the calculated critical lengths are all approximately equal to 5, indicating that hard segment sequences containing 5 or more diisocyanate residues are segregated to form the hard microdomain. This result is consistent with the idea of a critical length as embodied in the Koberstin-Stein model, although it is difficult to ascertain an absolute value without direct knowledge of the hard segment sequence length distribution.

The thickness of the hard microdomain, assuming a lamellar morphology can be calculated from

$$T_{HS} = \phi_2 \, d_{1D} \qquad (19)$$

where ϕ is the volume fraction of the hard microphase (determined from the modified Fox model), and d_{1D} is the one-dimensional interdomain period determined by small angle x-ray scattering (see preceeding paper in series). These values are presented in Table 7. Except for PU-30, for which the lamellar assumption in (19) is probably inappropriate, the hard segment thickness is roughly constant, falling in the range of 10-13nm. These data are also consistent with the Koberstin-Stein model (4) of polyurethane morphology which predicts that the critical hard segment length controls the thickness of the hard microdomain. Our estimated value of N_c was ca. 5 for all specimens of hard segment contents of 40% and higher, consistent with a constant microdomain thickness in these materials.

These findings are clearly contrary to the behavior reported for monodisperse hard segment model compounds (31), where the crystal thickness is linearly dependent on the sequence length. It is interesting to note however that our estimated repeat unit length (i.e. the microdomain thickness divided by N_c) is 2.1-2.6 nm (see Table 7), which compares well to the value of ca 1.9-2.0 nm reported for the d_{001}-spacing of the hard segment model compounds.

From these results, it appears that the morphological behavior of polyurethanes is strongly dependent on polydispersity. In monodisperse model compounds, extend chains are predominant while in normal segmented polyurethanes, the evidence supports the occurence of some type of hard segment chain folding or reentry into the hard microdomain. This need not be tight folds with adjacent reentry as considered in the model compound studies, and would probably result in a highly disordered structure commensurate with the poorly defined diffraction patterns observed for bulk polyurethanes.

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Appendix A

Calculation of Microphase Compositions Using Couchman's Theory Combined with SAXS Analysis

The small angle x-ray scattering invariant calculation (Eqns. 13 and 14) provides an estimate of the mean square fluctuation in electron density or electron density variance. By definition, for a two phase system, the variance is related to the volume fraction ϕ_i and electron densities ρ_i of the microphases

$$\overline{\Delta\rho^2} = \phi_1(\rho_1-\bar{\rho})^2 + (1-\phi_1)\ (\rho_2-\bar{\rho})^2 \qquad (A.1)$$

1 and 2 refer to the soft and hard microphases respectively. The material average density is defined as

$$\bar{\rho} = \phi_1\rho_1 + (1-\phi_1)\rho_2 \qquad (A.2)$$

If the two microphases are each mixtures of hard and soft segments, their electron densities may be written

$$\rho_1 = \phi_{1,s}\rho_s + (1-\phi_{1,s})\rho_H \qquad (A.3)$$

and

$$\rho_2 = \phi_{2,s}\rho_s + (1-\phi_{2,s})\rho_H \qquad (A.4)$$

where the subscript s and H refer to soft and hard segment respectively. The term $\phi_{1,s}$, for example, is the volume fraction of soft segment in phase 1, that is the soft microphase.

The set of SAXS equations contains five unknowns: ϕ_1, ρ_1, ρ_2, $\phi_{1,s}$, $\phi_{2,s}$. The variance $\overline{\Delta\rho^2}$ is measured experimentally; ρ_s is determined from the measured mass density and known chemical composition of the pure soft segment; $\bar{\rho}$ is calculated from the measured mass density and known chemical composition of the block copolymer; ρ_H is calculated from the known overall hard segment content, ϕ_H, with the assumption of volume additivity

$$\rho_H = \frac{\bar{\rho} - (1-\phi_H)\rho_s}{\phi_H} \qquad (A.5)$$

In order to solve the four equations in five unknowns, additional equations are obtained from the DSC analysis of the soft microphase. In constructing these equations, the equations of Couchman are modified[11,17,18] to accomodate the polyurethane structure. This structure may be represented as $-[(dc)_n ds]$ for all hard segment sequences which are dissolved within the soft microphase where n is the average length of a dissolved hard segment, s is a soft segment, d a diisocyanate residue, and c a chain extender residue. It follows that the number fraction of the species are

$$f_s = \frac{1}{2n+2} \qquad f_d = \frac{n+1}{2n+2} \qquad f_c = \frac{n}{2n+2} \tag{A.6}$$

As a result of the alternating structure of the chain, only two dyads are possible, a hard/soft segment moiety (sd), and a hard segment/chain extender dyad (dc). From the known molecular weights (s=2000, d=250, and c=90) the dyad weight fractions following 5 become

$$f_{sd} = \frac{(n+1)2250}{M} \quad \text{and} \quad f_{dc} = \frac{n(n+1)340}{M} \tag{A.7}$$

substitution into (7) and (8) gives

$$Cp_{cd} = \frac{2250\ \Delta Cp_{sd}(Tg-Tg_{sd})Tg_{dc}}{340n\ (Tg_{dc}-Tg)Tg_{sd}} \tag{A.8}$$

and

$$W_1 = \frac{\Delta Cp\ (2250+340n)}{2250\ \Delta Cp_{sd} + 340n\ \Delta Cp_{cd}} \tag{A.9}$$

The unknowns in these two equations are ΔCp_{cd}, W_1, and n. Tg_{dc} is taken from the literature as 110°C[8]; and ΔCp_{sd} and Tg_{sd} are the measured values for PU-MDI; and Tg and ΔCp are experimental values determined for the copolymer of interest. In order to solve for the three unknowns in Equations A.8 and A.9, additional equations are required that relate to the SAXS equations (A.1-A.4).

A solution is determined by iteration. After assuming a value for n, ΔCp_{cd} is calculated from (A.8), and subsequently W_1 may be determined from (A.9.) With ΔCp_{cd} and W_1 known and n assumed, a theoretical SAXS invariant can be evaluated from the following relations. The volume fraction of soft segment in the soft microphase is

$$\phi_{1,s} = \frac{f_s M_s \nu_s}{f_s M_s \nu_s + (f_d M_d + f_c M_c)\nu_H} = \frac{2000\nu_s}{2000\nu_s + (340n + 250)\nu_H} \qquad (A.10)$$

where the f_i terms are defined in Equation (6) and ν_i is the specific volume; ν_s for the pure soft segment is measured, and ν_H for the pure hard segment is estimated from ν_s and the specific volume of the copolymer of interest, ν_T, by assuming volume additivity.

The overall volume fraction of the soft-segment-rich microphase or soft microphase is then calculated from

$$\phi_1 = W_1/\{\nu_T[\phi_{1,S}/\nu_S + (1-\phi_{1,S})/\nu_H]\} \qquad (A.11)$$

The electron density of the soft microphase is calculated from

$$\rho_1 = \phi_{1,s}\, \rho_s + (1-\phi_{1,s})\rho_H$$

where ρ_s and ρ_H are the electron densities of the pure soft segment and pure hard segment respectively. ρ_s is measured from the pure soft segment and ρ_H is estimated from the measured material average electron density, $\bar{\rho}$, assuming volume additivity. The hard microphase electron density is determined by rearranging Eqn. 18 to give

$$\rho_2 = \frac{\bar{\rho} - \phi_1\, \rho_1}{(1-\phi_1)} \qquad (A.12)$$

The material average electron density is dictated by the reaction stoichiometry to be

$$\bar{\rho} = [W_{ss}\nu_s\ o + {}_s\ (1-W_{ss})\ \nu_H\rho_H]/\nu_T \qquad (A.13)$$

where W_{ss} is the overall weight fraction of soft segment in the copolymer formulation.

A theoretical SAXS invariant is then calculated from

$$\overline{\Delta\rho_T^{2}}'' = \phi_1(1-\phi_1)(\rho_1-\rho_2)^2 \qquad (A.14)$$

The theoretical invariant thus calculated is then compared to the experimental invariants $\overline{\Delta\rho^2}'$ and $\overline{\Delta\rho^2}''$. The assumed value of n is then adjusted iteratively until the theoretical and experimental invariants agree. Attainment of this convergence furnishes complete specification of the microphase compositions and amounts.

Appendix B

Calculation of Microphase Composites and Properties Using the Modified Fox Analysis

The overall weight fraction of the soft microphase (following equation 12) is given by

$$W_1 = \frac{\Delta Cp_s}{W_{1,s}\, \Delta Cp_1 + \Delta Cp_2\, (1-W_{1,s})} \qquad (B.1)$$

A previous calibration of the polyurethanes used in this study yielded $\Delta Cp_1 = 0.194$ and $\Delta Cp_2 \simeq 0$. Thus the experimental measurement of the heat capacity change at the soft microphase Tg, ΔCp_s, is sufficient to calculate W_1. The composition of the soft microphase is determined by application of (10) to experimental measurements of Tg_s, the soft microphase Tg. The weight function of soft segment in the soft microphase, $W_{1,s}$ is determined from

$$W_{i,s} = \frac{K\, Tg_1\, (Tg_2 - Tg_s)}{Tg_2\, (Tg_s - Tg_1) + kTg_1\, (Tg_2 - Tg_s)} \qquad (B.2)$$

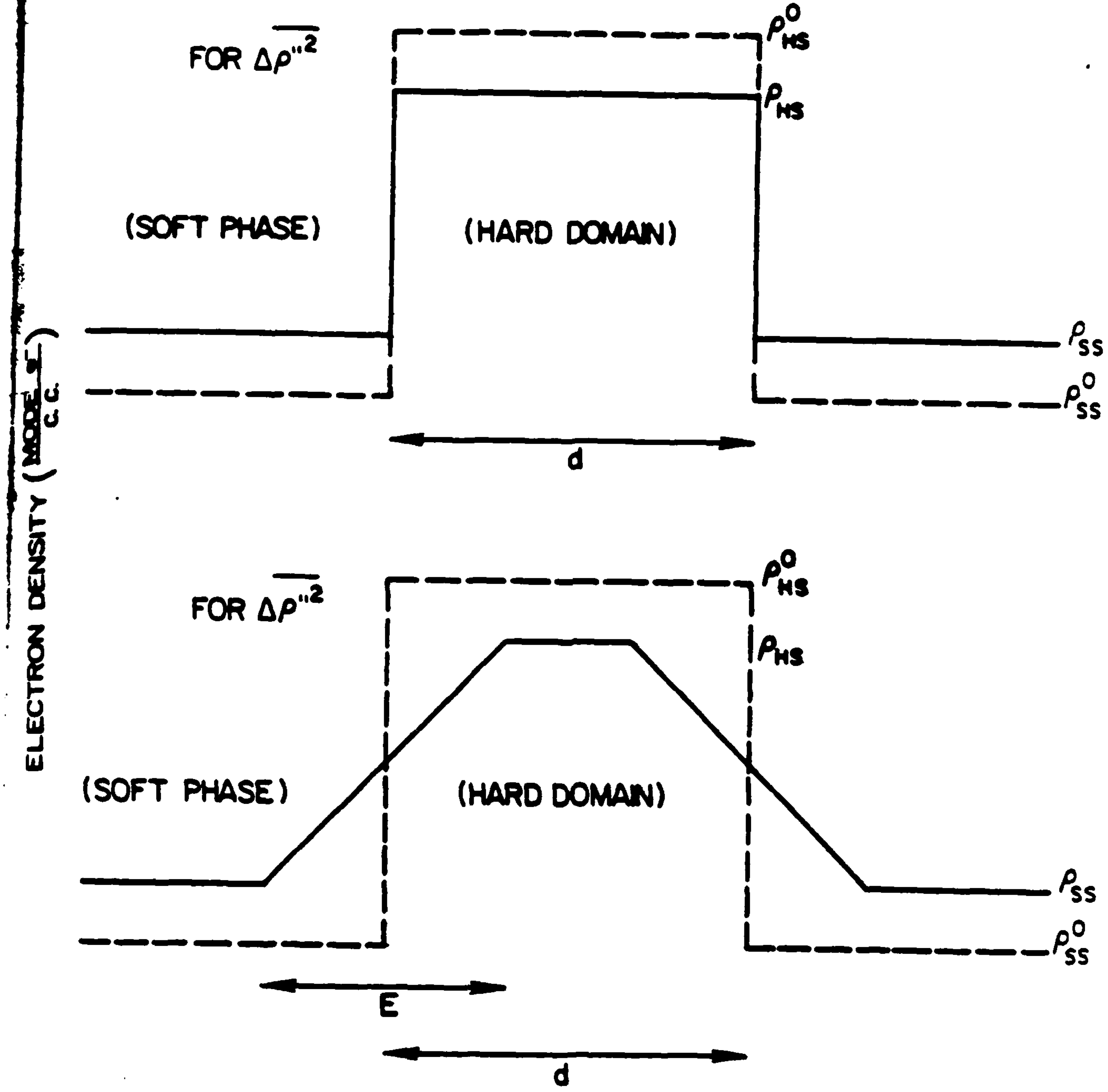
The previous analysis furnished values of $K = 1.18$, $Tg_1 = -69$°C and $Tg_2 = 109$°C. The composition of the hard microphase is then given by the lever rule

$$W_{2,s} = \frac{W_{ss} - W_1\, w_{1,s}}{(1-W_1)} \qquad (B.3)$$

where W_{ss} is the known overall weight fraction of soft segment in the material. The Tg of the mixed hard microphase can then be calculated by rearrangement of (10) to give

$$Tg_H = \frac{[w_{2,s} + (1-w_{2,s})k]\, Tg_1\, Tg_2}{w_{2,s}\, Tg_2 + K\, (1-w_{2,s})\, Tg_1} \qquad (B.4)$$

Once the phase compositions are known, the electron variances are calculated by application of A.11-A.14.



~~FIGURE III.~~8 Fig 1.

Fig 2

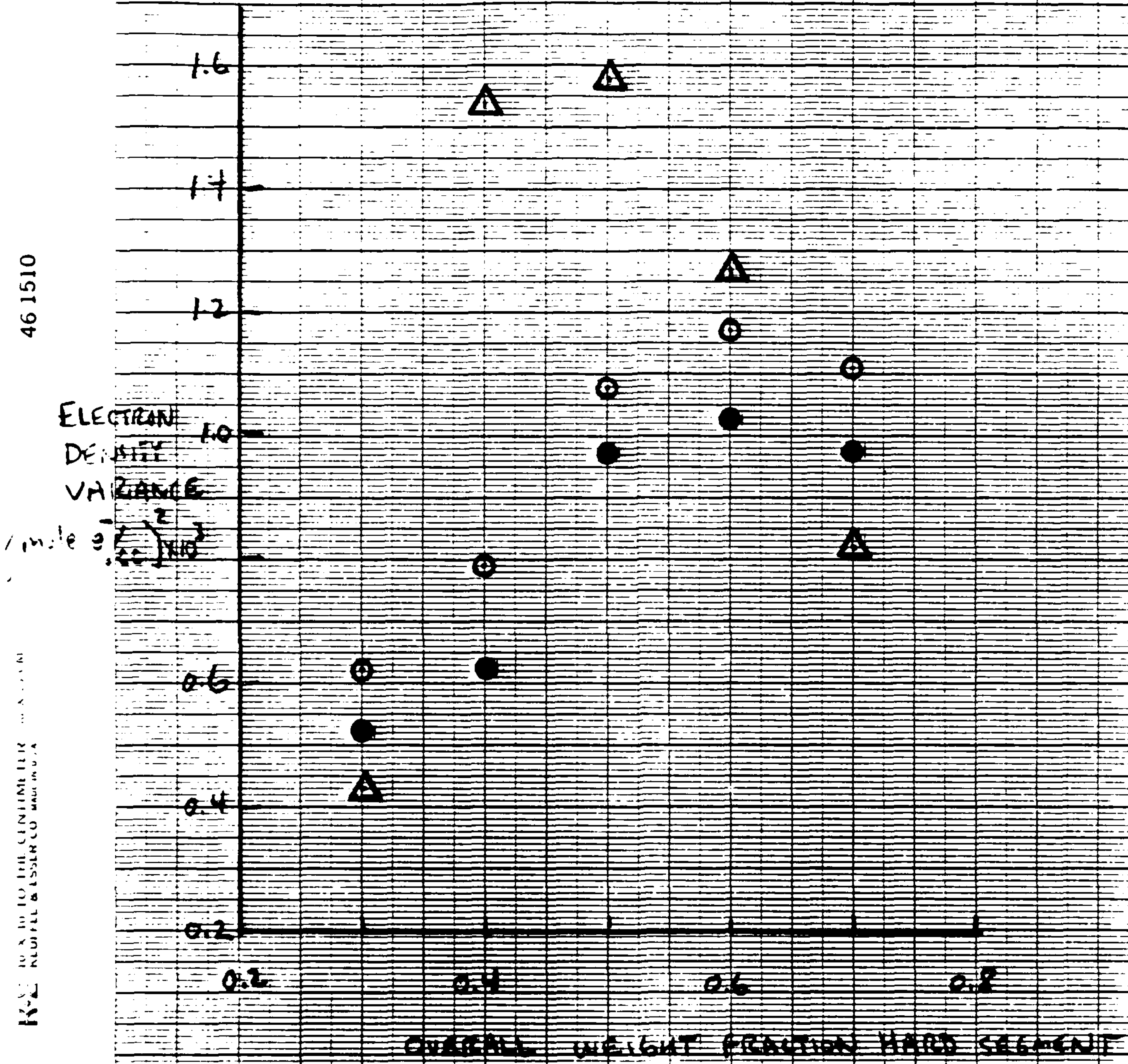
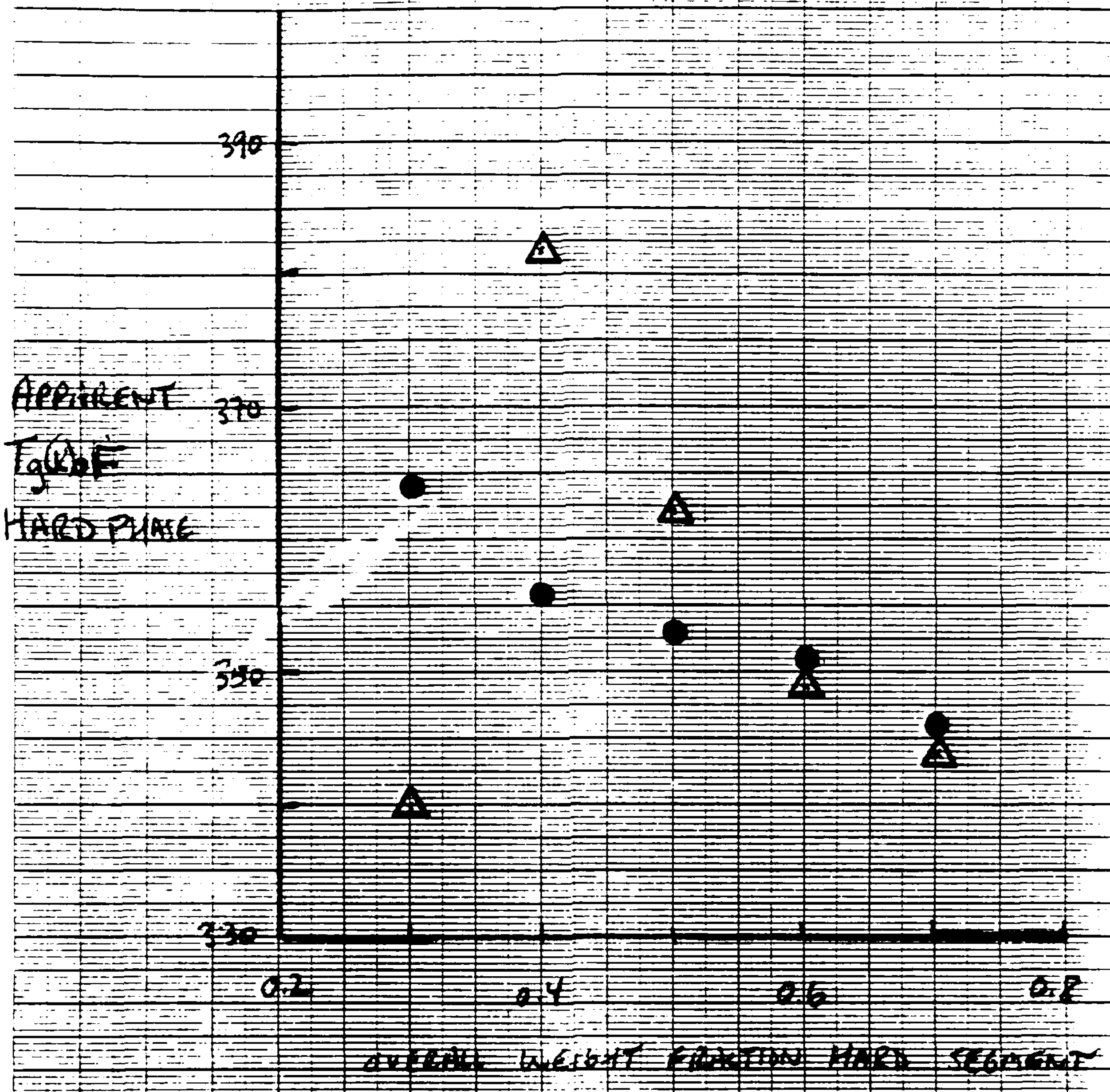
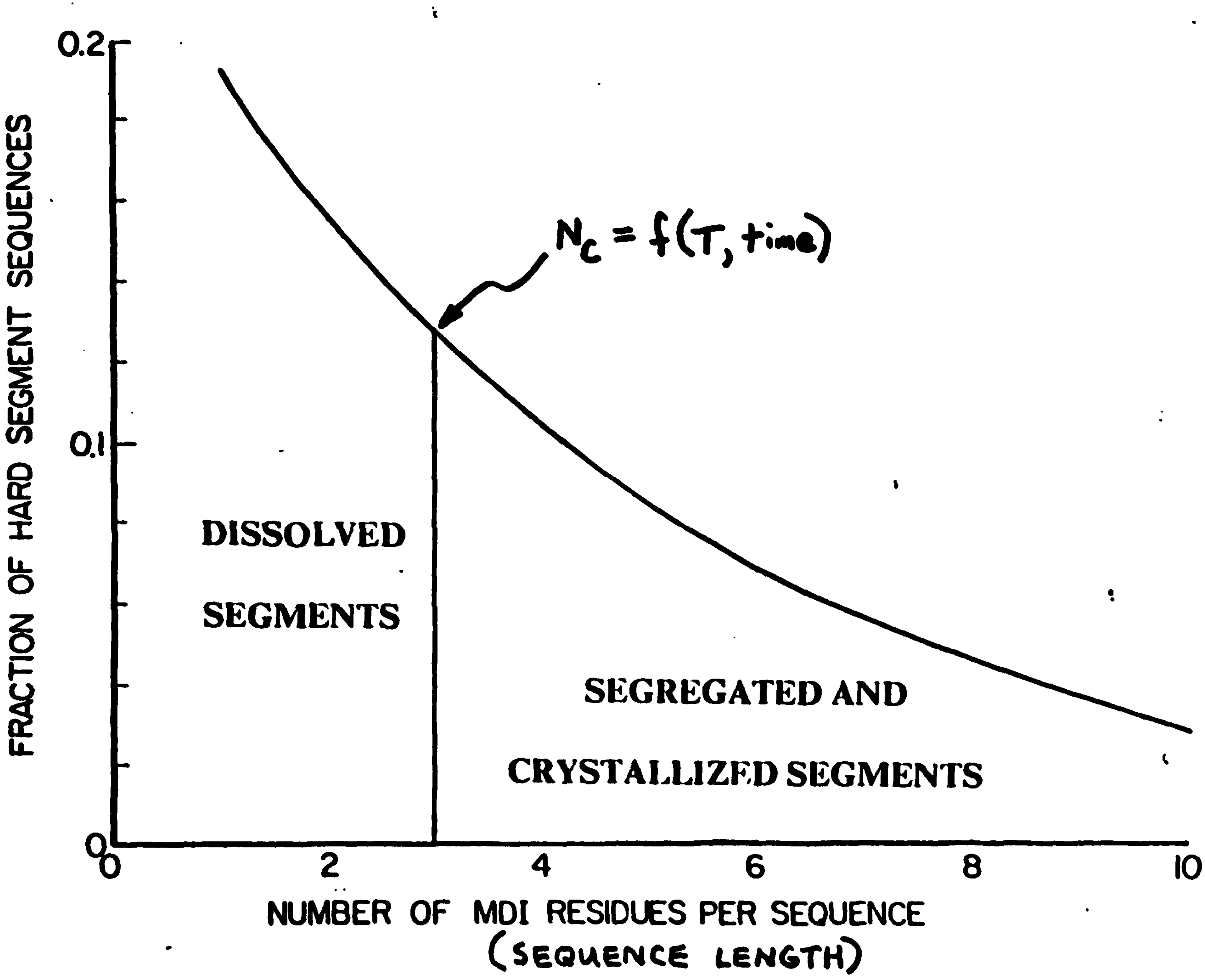

ELECTRON DENSITY VARIANCE
(mole e⁻/cc)² x10³
1.6
1.4
1.2
1.0
0.6
0.4
0.2
0.2
0.4
0.6
0.8
OVERALL WEIGHT FRACTION HARD SEGMENT

Fig 3


APPARENT
Tg(K) OF
HARD PHASE
390
370
350
330
0.2
0.4
0.6
0.8
OVERALL WEIGHT FRACTION HARD SEGMENT


0.2
0.1
0
FRACTION OF HARD SEGMENT SEQUENCES
0
2
4
6
8
10
NUMBER OF MDI RESIDUES PER SEQUENCE
(SEQUENCE LENGTH)
$N_c = f(T, time)$
DISSOLVED SEGMENTS
SEGREGATED AND CRYSTALLIZED SEGMENTS

4